2017

H2 Chemistry

1.	Anderson Serangoon Junior College	
2.	Anglo Chinese Junior College	
3.	Catholic Junior College	
4.	Dunman High School	
5.	Hwa Chong Institution	
6.	Innova Junior College	
7.	Jurong Pioneer Junior College	
8.	Meridian Junior College	
9.	Millennia Institute	
10.	Nanyang Junior College	
11.	National Junior College	
12.	Pioneer Junior College	
13.	Raffles Institution	
14.	River Valley High School	
15.	Serangoon Junior College	
16.	St. Andrew's Junior College	
17.	Temasek Junior College	
18.	Victoria Junior College	
19.	Yishun Innova Junior College	

ANDERSON JUNIOR COLLEGE

2017 JC 2 PRELIMINARY EXAMINATIONS

CHEMISTRY **9729/01**

Paper 1 Multiple Choice

18 September 2017

1 hour

Additional Materials: Multiple Choice Answer Sheet
Data Booklet

READ THESE INSTRUCTIONS FIRST

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

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

Each correct answer will score one mark. A mark will not be deducted for a wrong answer.
Any rough working should be done in this booklet.
The use of an approved scientific calculator is expected, where appropriate.

Multiple Choice Answer Sheet

Write your name, PDG and NRIC / FIN number, **including** the reference letter.

Shade the NRIC / FIN number.

Exam Title: JC2 PRELIM

Exam Details: H2 Chemistry / Paper 1

Date: 18/09/2017

This document consists of **16** printed pages.

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

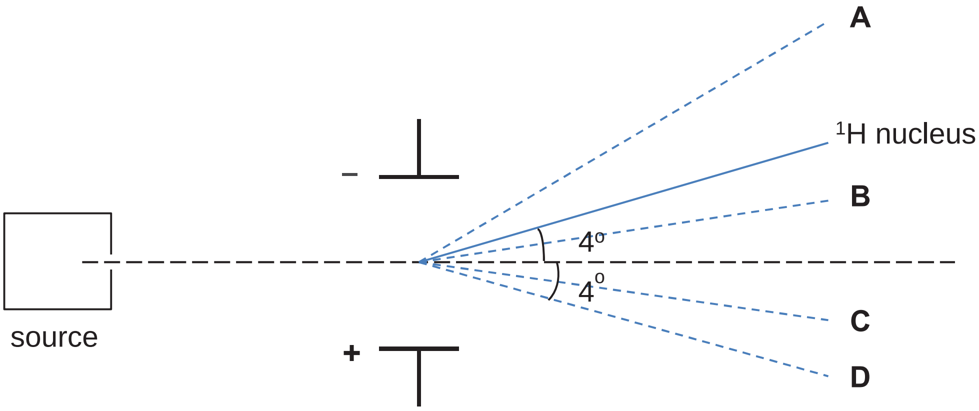
Tritium, ${}^{3}_{1}H$, a radioactive isotope of hydrogen, slowly turns into a helium isotope ${}^{3}_{2}He$.

Which statements about the two isotopes are **incorrect**?

1 Both isotopes have more neutrons than electrons.
2 Both isotopes have the same number of protons in their nuclei.
3 Both isotopes have the same number of charged sub–atomic particles.

A 2 only
B 1 and 3 only
C 2 and 3 only
D 1, 2 and 3

2 When passed through an electric field, the ^{1}H nucleus is deflected as shown below.

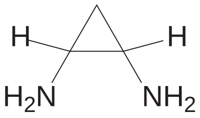


Which of the above beams represents the deflection for an ion $^{2}X^{2-}$?

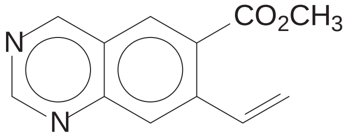
3 Which of the following molecules / ions has the smallest bond angle?

A SF_2 **B** XeF_2 **C** SO_3^{2-} **D** AlH_4^{-}

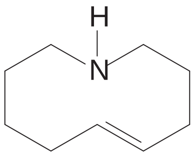
4 Compounds **F, G** and **H** are cyclic compounds.



F



G



H

Which bond is **not** present in the compounds above?

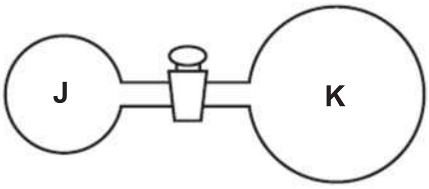
A a σ bond formed by sp^3–sp^3 overlap between two C atoms in **F**

B a σ bond formed by sp^2–sp^2 overlap between C and N atoms in **G**

C a σ bond formed by sp^3–sp^2 overlap between two C atoms in **H**

D a σ bond formed by sp^2–sp^2 overlap between C and N atoms in **H**

5 Two glass vessels **J** and **K** are connected by a closed valve.



J contains helium gas at 20 °C and a pressure of 1 x 10^5 Pa. **K** has been evacuated, and has three times the volume of **J**. 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?

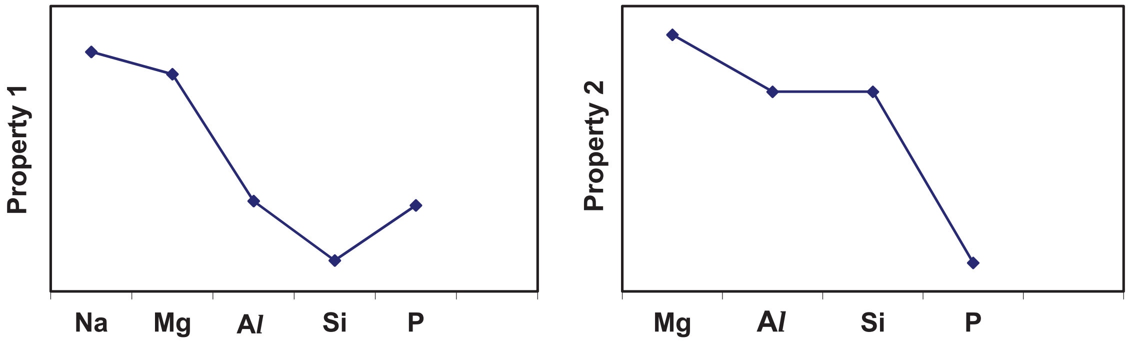
A 3.18×10^4 Pa

B 4.24×10^4 Pa

C 1.25×10^5 Pa

D 5.09×10^5 Pa

6 The graphs below show the variation of two properties of some period 3 elements and/or their compounds.



Which of the following correctly describes properties 1 and 2?

	Property 1	Property 2
A	atomic radius of the elements	electrical conductivity of the elements
B	melting point of the chlorides	pH of oxides when added to water
C	melting point of the elements	first ionisation energies of the elements
D	electrical conductivity of elements	pH of chlorides when added to water

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

If iron is heated separately with chlorine, bromine and iodine, what are the likely products?

	chlorine	bromine	iodine
A	$FeCl_2$	$FeBr_2$	FeI_2
B	$FeCl_3$	$FeBr_2$	FeI_2
C	$FeCl_3$	$FeBr_3$	FeI_2
D	$FeCl_3$	$FeBr_3$	FeI_3

8 When 10 cm^3 of a hydrocarbon was burnt in 100 cm^3 of excess oxygen, the volume of the residual gas mixture contracted by 20 cm^3 after passing through a solution of aqueous sodium hydroxide. The remaining volume of gas was just sufficient to completely burn exactly 30 cm^3 of the same hydrocarbon. All volumes were measured at room temperature and pressure conditions.

What is the formula of the hydrocarbon?

A C_2H_2 **B** C_2H_3 **C** C_2H_4 **D** C_2H_6

9 Sulfuric acid, one of the most important industrial chemicals, can carry out several functions in chemical reactions.

Three examples of industrial reactions in which sulfuric acid is used are shown below.

reaction 1 $Al_2O_3 + 3H_2SO_4 \longrightarrow Al_2(SO_4)_3 + 3H_2O$

reaction 2 $Cu + H_2SO_4 \longrightarrow CuO + SO_2 + H_2O$

reaction 3 $(CH_3)_3COH + H_2SO_4 \longrightarrow (CH_3)_2C{=}CH_2 + H_2SO_4 + H_2O$

What is the function of sulfuric acid in each reaction?

	reaction 1	reaction 2	reaction 3
A	acidic	oxidising	dehydrating
B	acidic	acidic	dehydrating
C	dehydrating	oxidising	catalytic
D	dehydrating	acidic	catalytic

10 *Some of these data are also relevant to question 14*.

Given the following enthalpy change

$$N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g) \qquad \Delta H^\ominus = -92\ \text{kJ mol}^{-1}$$
$$N_2(g) + 4H_2(g) + Cl_2(g) \longrightarrow 2NH_4Cl(s) \qquad \Delta H^\ominus = -629\ \text{kJ mol}^{-1}$$
$$NH_3(g) + HCl(g) \longrightarrow NH_4Cl(s) \qquad \Delta H^\ominus = -176\ \text{kJ mol}^{-1}$$

What is the standard enthalpy change of formation of gaseous hydrogen chloride?

A -361 kJ mol^{-1}

B -185 kJ mol^{-1}

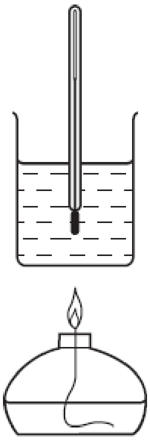
C -92.5 kJ mol^{-1}

D -46.3 kJ mol^{-1}

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

A student carried out an experiment to determine the enthalpy change of combustion of ethanol.

The following results were obtained by the student.



initial temperature of the water	25 °C
final temperature of the water	68 °C
mass of alcohol burner before burning	260.65 g
mass of alcohol burner after burning	259.65 g
mass of glass beaker plus water	160.00 g
mass of glass beaker	60.00 g

Given that the enthalpy change of combustion of ethanol is −1370 kJ mol^{-1}, what is the efficiency of heat transferred to the water?

A 46% **B** 60% **C** 81% **D** 97%

12 An example of a three–way honeycomb type catalytic converter is shown below.

The catalytic converter involves three simultaneous reactions. In the first, NO_x gases get reduced; in the second and third, unburnt hydrocarbon and carbon monoxide are completely oxidised.

Which of the following equations does **not** represent the reactions that took place in the catalytic converter?

A $C(g) + O_2(g) \longrightarrow CO_2(g)$

B $2CO(g) + O_2(g) \longrightarrow 2CO_2(g)$

C $2NO(g) + 2CO(g) \longrightarrow N_2(g) + 2CO_2(g)$

D $2C_8H_{18}(g) + 25O_2(g) \longrightarrow 16CO_2(g) + 18H_2O(g)$

13 A radioactive element has two isotopes, **L** and **M**, with half–lives of 3 min and 9 min respectively.

An experiment starts with *n* times as many atoms of **L** as of **M**. After 9 min, the number of atoms of **L** and **M** are both equal.

Given that radioactive decay is a first order reaction, what is the value of *n*?

A 0.5 **B** 2 **C** 4 **D** 8

14 *Use of the data in question 10 is relevant to this question.*

Which of the following statement is true about the Haber process for the manufacture of ammonia?

A Adding a catalyst increases the equilibrium yield of ammonia but the rate of production of ammonia is faster.

B Adding neon gas at constant pressure increases the equilibrium yield of ammonia but the rate of production of ammonia is slower.

C Decreasing the temperature increases the equilibrium yield of ammonia but the rate of production of ammonia is slower.

D Removing nitrogen gas at constant volume increase the equilibrium yield of ammonia but the rate of production of ammonia is slower.

15 The Gibbs free energy change of reaction, $\Delta G^{\ominus}$, for the contact process is shown below.

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) \qquad \Delta G^{\ominus} = -142\ \text{kJ mol}^{-1}$$

Which statement about the equilibrium constant, K_p at 25 °C is true?

A K_p is less than 1.

B K_p is greater than 1.

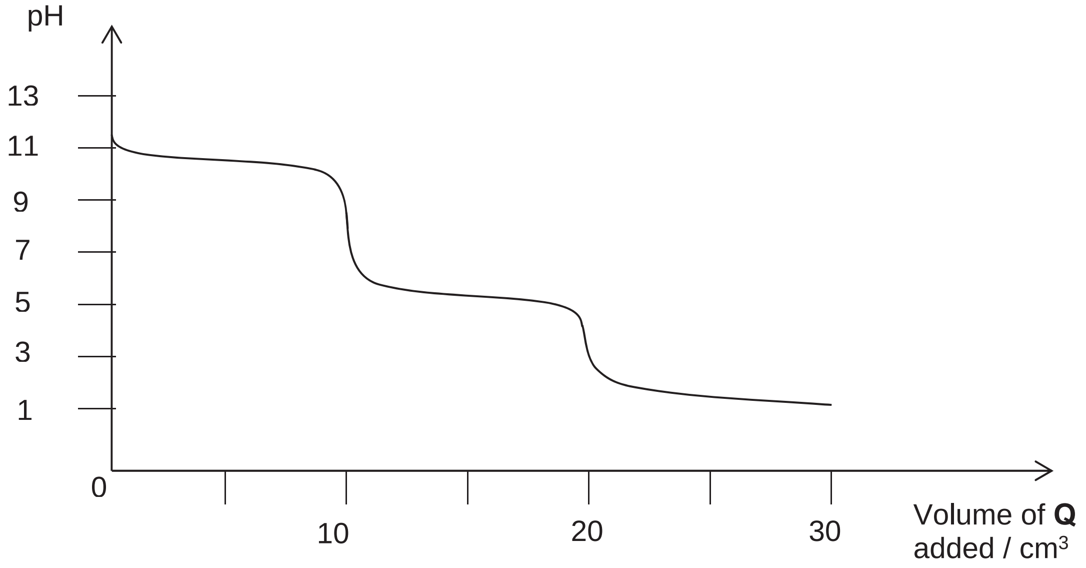
C K_p is equal to 1.

D No conclusion can be drawn about K_p.

16 What is the pH of the final solution formed when 30 cm^3 of 0.10 mol dm^{-3} HNO_3 is added to 20 cm^3 of 0.20 mol dm^{-3} ammonia?
[K_b of ammonia = 1.8×10^{-5} mol dm^{-3}]

A 4.3 **B** 5.2 **C** 8.8 **D** 10.8

17 The diagram below shows the change of pH produced by gradually adding aqueous **Q** to a certain volume of aqueous **P**. The concentration of each constituent of the aqueous solutions **P** and **Q** is 0.1 mol dm^{-3}.



What could **P** and **Q** be?

	P	Q
A	NaOH + KOH	HC*l*
B	$H_2NCH_2CH_2NH_2$	HC*l*
C	Na_2CO_3	$CH_2(COOH)_2$
D	KOH	CH_3COOH

18 When heated with chlorine, the hydrocarbon 2–methylbutane, $CH_3CH_2CH(CH_3)_2$, undergoes free radical substitution.

In a propagation step, which free radical will be formed most readily?

A $\overset{\bullet}{C}H_2CH_2CH(CH_3)_2$

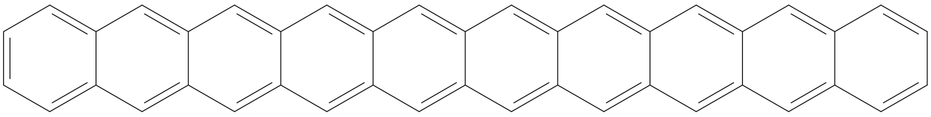
B $CH_3\overset{\bullet}{C}HCH(CH_3)_2$

C $CH_3CH_2\overset{\bullet}{C}(CH_3)_2$

D $CH_3CH_2CH(\overset{\bullet}{C}H_2)CH_3$

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

The longest acene, decacene, comprising of 10 linearly fused benzene ring, has been made for the first time in 2017.



Which statements about the molecule are correct?

1 Each of the C–C–C bond angle is 120º.

2 The π electrons are delocalised.

3 The bond energy of each carbon–carbon bond in the molecule is equal to 350 kJ mol^{-1}.

4 Each C atom has a valency of 3.

A 1, 3 and 4 only

B 2, 3 and 4 only

C 1 and 2 only

D 1 and 3 only

20 Ozone depletion potential (ODP) is a measure of the effectiveness of chlorofluoroalkanes in destroying stratospheric ozone.

In which sequence are compounds listed in increasing order of their ODPs?

A $CHClF_2 < CH_3CCl_2F < CCl_2FCClF_2$

B $CHClF_2 < CCl_2FCClF_2 < CH_3CCl_2F$

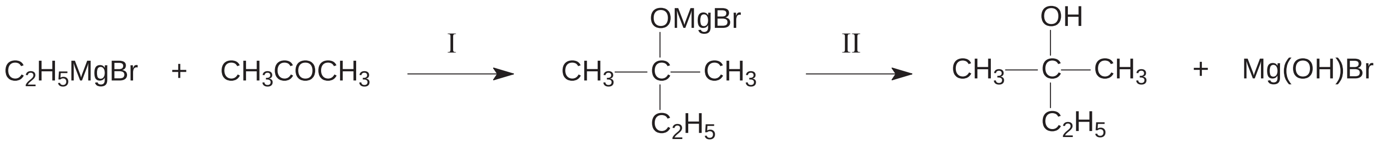
C $CCl_2FCClF_2 < CHClF_2 < CH_3CCl_2F$

D $CH_3CCl_2F < CCl_2FCClF_2 < CHClF_2$

The following information is relevant to questions **21** and **22**.

Most of the chemistry of magnesium relates to its ionic compounds. However, magnesium does form an important group of covalent compounds which are known as Grignard reagents. Many Grignard reagents, with different alkyl or aryl groups, are widely used in organic syntheses.

The following reaction scheme shows a typical example of the use of a Grignard reagent.

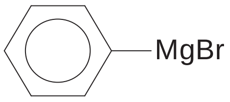
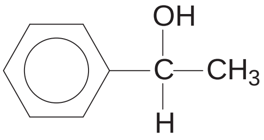
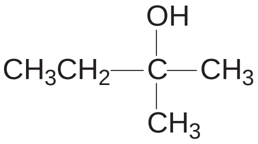
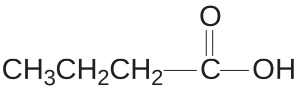


$$C_2H_5MgBr + CH_3COCH_3 \xrightarrow{I} CH_3C(OMgBr)(C_2H_5)CH_3 \xrightarrow{II} CH_3C(OH)(C_2H_5)CH_3 + Mg(OH)Br$$

21 What are the types of reaction shown in this reaction scheme?

	I	II
A	electrophilic addition	acid–base
B	nucleophilic substitution	elimination
C	nucleophilic addition	acid–base
D	nucleophilic addition	hydrolysis

22 Which of the following sets show the correct reactants and products obtained upon undergoing the same reaction scheme?

	reactants	products
1	 + CH_3CHO	 + Mg(OH)Br
2	$CH_3CH_2CH_2MgBr$ + CH_3COCH_3	 $CH_3CH_2C(OH)(CH_3)CH_3$ + Mg(OH)Br
3	$CH_3CH_2CH_2MgBr$ + CO_2	 $CH_3CH_2CH_2COOH$ + Mg(OH)Br

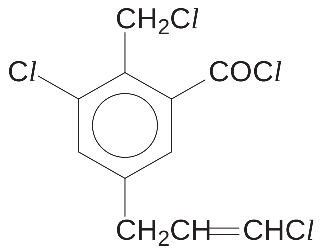
A 2 only

B 3 only

C 1 and 2 only

D 1 and 3 only

23 Compound **T** has the structure as shown below.

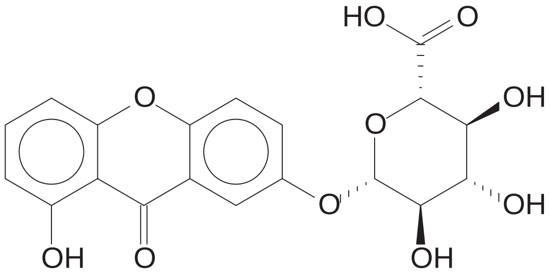


1 mol of compound **T** is warmed with aqueous sodium hydroxide. The resulting solution is cooled and acidified with dilute nitric acid. Excess aqueous silver nitrate is then added to it.

How many moles of silver chloride is precipitated out?

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

24 The pigment *Indian Yellow*, which first appeared in the 14th century and then vanished at the end of the Victorian era, was made famous by artist Joseph Mallord William Turner.



Indian Yellow

In the following reactions, R–O–R remains unaltered.

Which of the following observation is correct?

A It reacts with hot, alkaline aqueous iodine to give a yellow solid.

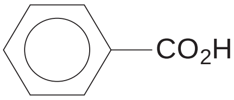
B It reacts with hot, acidified $K_2Cr_2O_7$ to give a compound with 3 carbonyl groups.

C It reacts with aqueous bromine to incorporate up to 6 atoms of bromine in each molecule.

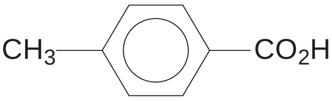
D It reacts with excess sodium metal to produce 2.5 mol of hydrogen gas for each mole of the molecule.

25 Consider the following four carboxylic acids.

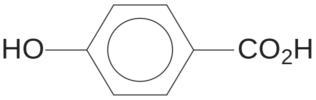
1



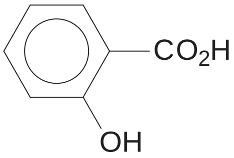
2



3



4

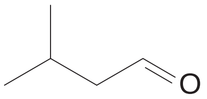


What is the relative order of **decreasing** pK_a?

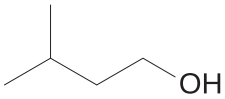
A	3	2	1	4
B	1	2	3	4
C	4	1	2	3
D	2	1	4	3

26 The following compounds are responsible for the smell of tequila.

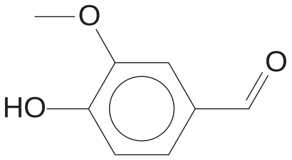
1



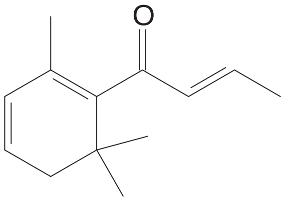
2



3



4



Which of the compounds can be oxidised by acidified potassium dichromate(VI) and can be reduced by sodium borohydride?

A 2 only

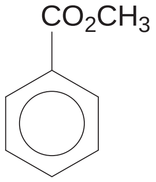
B 1 and 3 only

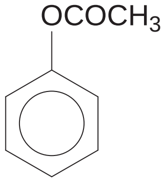
C 2 and 4 only

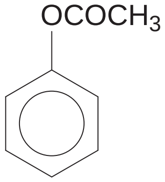
D 1, 3 and 4 only

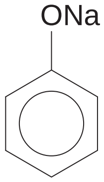
27 Deuterium, D, is an isotope of hydrogen.

Which compounds will react to produce deuterophenol, C_6H_5OD, in good yield?

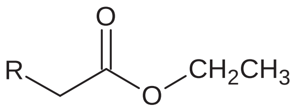
A  + NaOD in D_2O, with heat

B  + NaOD in D_2O, with heat

C  + DC*l* in D_2O, with heat

D  + D_2O

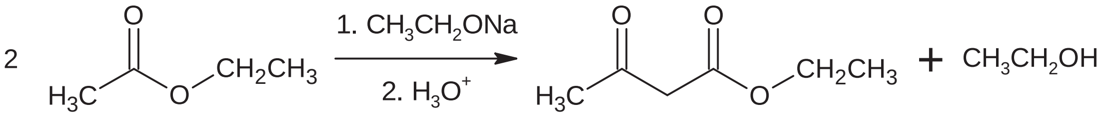
28 Members of an ethyl ester homologous series have the general formula



where R = C_nH_{2n+1}, and n = 0, 1, 2 …

Each member undergoes Claisen condensation with either itself or another member of the series to form a β–keto ester.

For example, the first member of the series, ethyl ethanoate, combines with itself in the presence of sodium ethanoate, followed by acidification, to form ethyl 3–oxobutanoate. Ethanol is eliminated in the process.

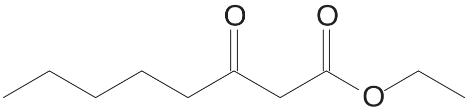


ethyl ethanoate

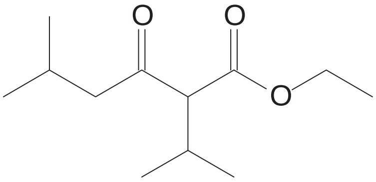
ethyl 3-oxobutanoate
(β-keto ester)

Which of the following is a possible product of the Claisen condensation between ethyl ethanoate and the **fourth** member of the series?

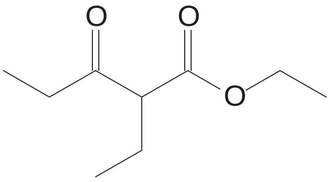
A



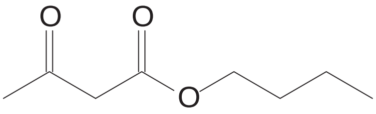
B



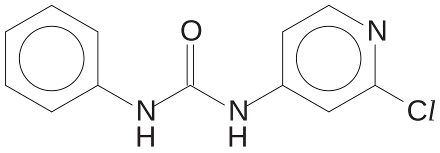
C



D



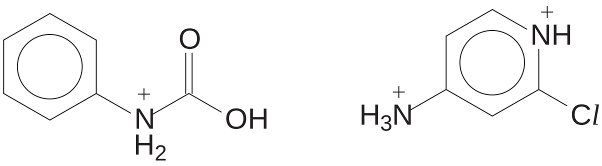
29 In 2011, farmers in Eastern China were hit by a spate of exploding watermelons. This was a result of the overuse of *forchlorfenuron*, a plant growth regulator.



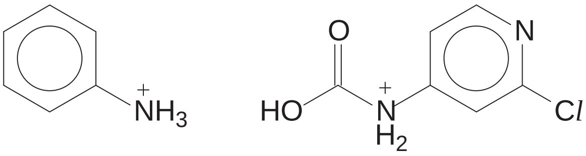
forchlorfenuron

What are the organic products formed when forchlorfenuron is heated with dilute acid?

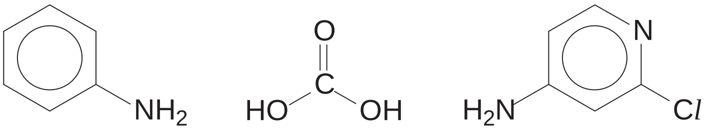
A



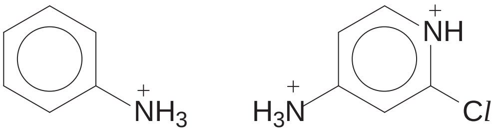
B



C



D



30 When excess of NaOH(aq) are added to $Fe(NO_3)_2(aq)$, a dirty green precipitate is formed. On standing in air, the precipitate turns reddish brown.

Which process does **not** occur in this sequence?

A Acid–base

B Ligand exchange

C Oxidation

D Precipitation

ANDERSON JUNIOR COLLEGE

2017 JC 2 PRELIMINARY EXAMINATIONS

NAME:____________________________ **PDG:**_____ /16

CHEMISTRY **9729/02**

Paper 2 Structured Questions **13 September 2017**

2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name, PDG and register number on all the work you hand in.
Write in dark blue or black pen.
You may use a pencil for any diagrams, graphs or rough working.
Do not use staples, paper clips, highlighters, glue or correction fluid.

Answer **all** questions in the spaces provided on the Question Paper.
The use of an approved scientific calculator is expected, where appropriate.
A Data Booklet is provided.

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	/ 15
	2	/ 13
	3	/ 16
	4	/ 14
	5	/ 17
Total		/ 75

This document consists of **20** printed pages.

Answer **all** the questions.

1 **(a)** *Use of the Data Booklet will be relevant to this question.*

Iron ore from different mines will contain different percentages by mass of iron. The percentage of iron in a sample of ore can be estimated by converting all of the iron present into Fe^{2+}(aq) ions and then using a redox titration.

The sample of ore is crushed, weighed and then dissolved in aqueous acid. The Fe^{3+}(aq) ions are then reduced to Fe^{2+}(aq) ions by reaction with an excess of aqueous tin(II) chloride, $SnCl_2$.

(i) Construct an ionic equation for the reduction of Fe^{3+}(aq) ions with aqueous tin(II) chloride solution.

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

(ii) Calculate the standard cell potential, $E^{\ominus}_{cell}$, for this reaction.

[1]

(iii) Explain why tin(II) chloride will reduce Fe^{3+}(aq) ions to Fe^{2+}(aq) ions, but will **not** reduce Fe^{2+}(aq) ions to metallic iron.

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

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

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

A sample of iron ore weighing 11.05 g was converted to Fe^{2+}(aq) ions using the method described above. The resultant solution was then made up to a volume of 250 cm^3 in a volumetric flask.

25.0 cm^3 portions of this solution were then titrated with 0.100 mol dm^{-3} of aqueous potassium dichromate(VI) using a suitable indicator. The results are shown below.

titration number	1	2	3
initial burette reading / cm^3	0.00	19.95	2.10
final burette reading / cm^3	19.95	40.05	22.15
titre / cm^3	19.95		

(iv) Complete the table on page **2** and use the results to determine the number of moles of potassium dichromate(VI) required to react with the Fe^{2+} ions in 25.0 cm^3 of the solution.

[2]

(v) Write an ionic equation for the reaction of Fe^{2+} ions with acidified $Cr_2O_7^{2-}$ ions.

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

(vi) Calculate the total number of moles of Fe^{2+} in the original solution made up from the iron ore, and hence calculate the percentage by mass of iron in the sample of iron ore.

[2]

(b) Iron and magnesium form iodate(V) compounds as shown, $Fe(IO_3)_2$ 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) Draw a dot–and–cross diagram to show the bonding in iodate(V) ion, IO_3^-. In your diagram use the symbols '•' and 'x' to distinguish electrons from iodine and oxygen atoms, and the symbol '□' for any additional electrons responsible for the overall negative charge.

[1]

(ii) Write a balanced equation for the thermal decomposition of $Mg(IO_3)_2$.

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

(iii) $Mg(IO_3)_2$ is found to decompose at 900 K.

By quoting suitable data from the *Data Booklet*, suggest and explain if $Fe(IO_3)_2$ will decompose at a higher or lower temperature than $Mg(IO_3)_2$.

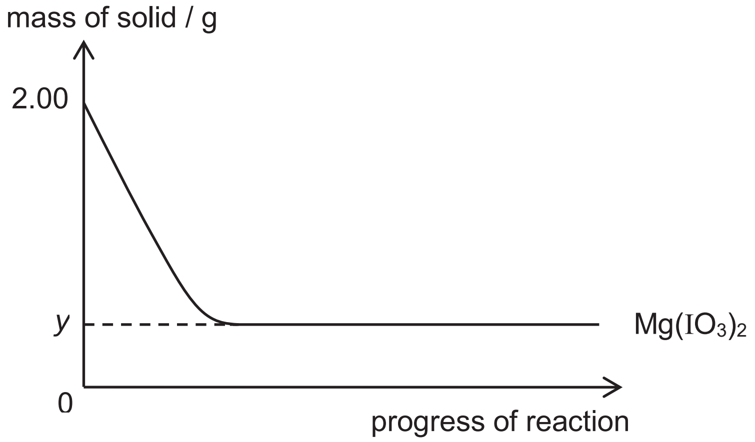
……………………………………………………………………………………………………..

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

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

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

The graph below shows the change in mass when 2.00 g of $Mg(IO_3)_2$ is heated at temperature, T °C.



(iv) Determine the value of *y*.

[1]

(v) On the same axes, show clearly the sketch for the decomposition of 2.00 g of $Fe(IO_3)_2$ at the same temperature. [1]

[Total: 15]

2 **(a)** Explain the meaning of the term *homogenous catalyst* and illustrate your answer by using one specific reaction involving a transition metal or its compound behaving as one.

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

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

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

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

(b) *Use of the Data Booklet is relevant to this question.*

Aqueous hydrogen peroxide is fairly stable but when a mixture of cobalt(II) salt and tartaric acid $HO_2CCH(OH)CH(OH)CO_2H$ is added to aqueous hydrogen peroxide, the following changes take place.

The initial pink solution *slowly* turns into a green solution containing cobalt(III) species and then oxygen is *vigorously* evolved. Finally the solution turns pink again. Tartaric acid and the cobalt(II) salt can be recovered from the solution at the end.

(i) Write an equation for the overall reaction.

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

(ii) State the role of cobalt(II) salt in this reaction and give evidence to support your answer.

………………………………………………………………………………………………

………………………………………………………………………………………………

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

(iii) With the aid of relevant data in the *Data Booklet*, show that $Co^{3+}(aq)$ is not stable in aqueous solution and hence comment on the role of tartaric acid in this reaction.

………………………………………………………………………………………………

………………………………………………………………………………………………

………………………………………………………………………………………………

………………………………………………………………………………………………

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

(c) The decomposition of hydrogen peroxide follows a first order kinetics.

A 100 cm^3 of hydrogen peroxide undergoes complete decomposition to liberate 96 cm^3 of oxygen gas. It is found that 48 cm^3 of oxygen gas was collected in 35 minutes. All gaseous volumes were measured at room temperature and pressure.

(i) Calculate the initial concentration of hydrogen peroxide.

[1]

(ii) Estimate the time taken for 88 cm^3 of oxygen gas to be collected.

[1]

(iii) Calculate the rate constant *k*, including the units for the reaction.

[2]

(iv) What percentage of the hydrogen peroxide in a solution of concentration 0.20 mol dm^{-3} would decompose in 35 minutes at the same temperature?

[1]

(v) Outline a suitable method, other than the gas collection method, to find the order of reaction for the decomposition of hydrogen peroxide.

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

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

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

[Total: 13]

3 The Pollutant Standards Index (PSI) is an air quality indicator. It is based on five pollutants: particulate matter (PM10), sulfur dioxide, carbon monoxide, ozone and nitrogen dioxide.

To calculate the overall PSI, the PSI value is first determined, using the following table, for **each** of the five pollutants.

i	**PSI value, P_i**	**Concentration, C_i**				
		PM10 (μg m^{-3})	**SO_2 (μg m^{-3})**	**CO (mg m^{-3})**	**Ozone (μg m^{-3})**	**NO_2 (μg m^{-3})**
1	50	50	80	5.0	118	–
2	100	150	365	10.0	157	–
3	200	350	800	17.0	235	1130
4	300	420	1600	34.0	785	2260
5	400	500	2100	46.0	980	3000
6	500	600	2620	57.5	1180	3750

[1 μg = 10^{-6} g; 1 mg = 10^{-3} g]

Given the concentration of a pollutant (with units as stated in the table above), where C_{i+1} > concentration of pollutant > C_i ,

$$\text{PSI of pollutant} = \left[\left(\frac{P_{i+1} - P_i}{C_{i+1} - C_i}\right)\left(\text{concentration of pollutant} - C_i\right)\right] + P_i$$

The overall PSI is then based on the maximum value out of the five calculated PSI pollutant values.

In Singapore, the 24–hr PSI is used by the National Environment Agency (NEA) to provide health advisory.

24−hr PSI	**Healthy Persons**	**Elderly, Pregnant women, Children**	**Persons with chronic lung disease, heart disease, stroke**
< 100	Normal activities		
101–200	Minimise prolonged or strenuous outdoor physical exertion.	Minimise prolonged outdoor activity.	Avoid all outdoor activities. If outdoor activity is unavoidable, wear N95 mask.
201–300	Avoid prolonged or strenuous outdoor physical exertion. If outdoor activity is unavoidable, wear N95 mask.	Avoid all outdoor activities. If outdoor activity is unavoidable, wear N95 mask (for adults).	
>300	Minimise all outdoor exposure. If outdoor activity is unavoidable, wear N95 mask.		

(a) **(i)** In a 1 m^3 sample of air, the mass of PM10 and carbon monoxide were found to be 320 μg and 20 mg respectively. Calculate the PSI values for each of the above pollutants, leaving your answers to **3 significant figures**.

[2]

(ii) Given that the PSI value of sulfur dioxide, ozone and nitrogen dioxide are 150, 112 and 133 respectively for the same sample of gas, use these values and your answers to **(a)(i)** to determine the overall PSI.

[1]

(iii) Assuming that the current overall PSI level is your answer in **(a)(ii)**, what advice would you give to a Physical Education (PE) teacher in Anderson Junior College who will be conducting a PE lesson soon?

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

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

(b) The amount of sulfur dioxide in a sample of air can be determined by first reacting it with sodium iodate, $NaIO_3$. Iodine is one of the products in this reaction.

(i) Write an ionic equation for the reaction between sulfur dioxide and sodium iodate.

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

(ii) When a 1 m^3 sample of air was bubbled through a solution of sodium iodate, the resulting solution was neutralised by 10.0 cm^3 of 0.005 mol dm^{-3} sodium hydroxide solution.

Calculate the concentration of sulfur dioxide, in $\mu g\ m^{-3}$, in the sample of air.

[2]

(c) Some countries have set limits for particulates in the air. For example, the European Union has a daily average (24–hour) limit of 180 μg m^{-3} for PM10. Cities that violate this daily limit face a hefty financial penalty that is calculated with consideration of many factors such as the severity the violation has on the ecosystem, duration of the non–compliance and country's GDP etc.

(i) A collected sample of air from the German city of Leipzig contains 2 x 10^{-5} % by mass of PM10. Given that the density of air is 1 kg m^{-3}, calculate the concentration of PM10 in the sample collected.

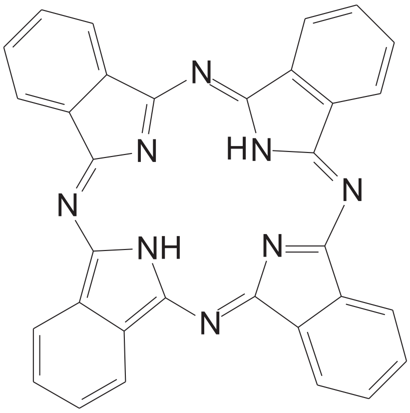
[1]

(ii) Hence, deduce whether the German city of Leipzig will be faced with any financial penalty.

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

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

(d) A team of researchers at the National University of Singapore has come up with an eco–friendly and cost–effective solution to keep out the harmful PM2.5 particles found in haze. They created a nanofibre liquid solution by modifying phthalocyanine, a blue–green coloured aromatic compound commonly used in dyes for clothes. The solution can be applied to non–woven mesh to become thin, see–through air filters that block out up to 90% of PM2.5 particles.



phthalocyanine

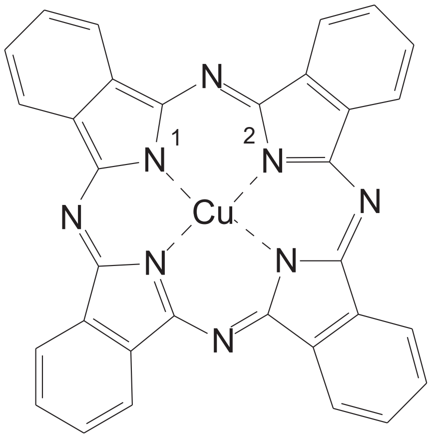
(i) Give the molecular formula of phthalocyanine.

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

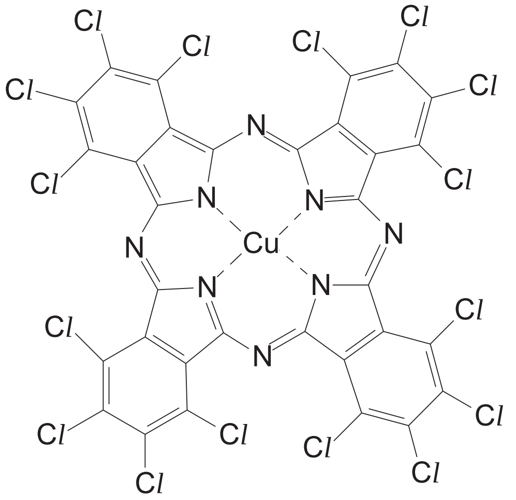
(ii) Suggest why phthalocyanine can be described as aromatic.

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

(e) Copper phthalocyanine dyes are artificial organic pigments derived from phthalocyanine. They are produced by introducing solubilising groups, such as methanesulfonic acid, CH_3SO_3H.



phthalocyanine blue



phthalocyanine green

(i) Name the type of bonds formed between copper and the nitrogen atoms numbered 1 and 2 in phthalocyanine blue.

N1 ……………………………………………

N2 …………………………………………… [2]

(ii) Give the electronic configuration of the copper in phthalocyanine blue.

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

(iii) Deduce the number of electrons around the N1 nitrogen atom.

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

(iv) Account for the difference in the colour of the two copper phthalocyanine dyes given above.

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

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

[Total: 16]

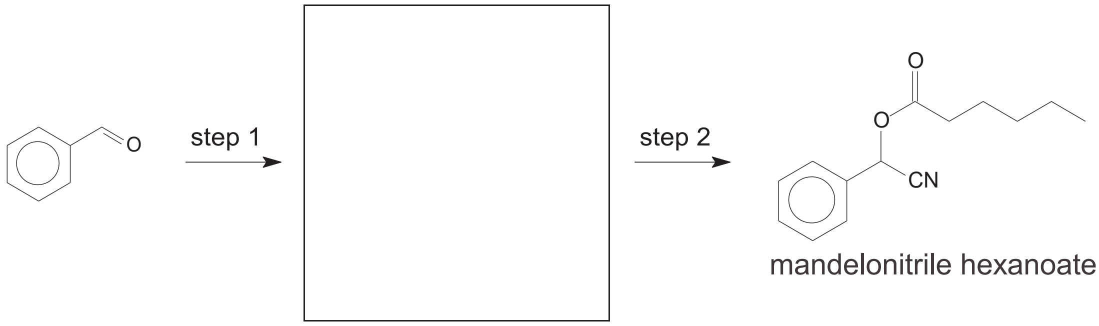
4 The *Oribatula tibialis* mite uses hydrogen cyanide, HCN, a highly volatile and toxic substance, to poison its predators.

The HCN is stored in the form of mandelonitrile hexanoate, $C_{14}H_{17}NO_2$, in the mite's oil glands, to avoid poisoning itself.

(a) In order to confirm the identity of mandelonitrile hexanoate in mite's oil glands, synthetic mandelonitrile hexanoate was made in the laboratory and dissolved in hexane.

Both synthetic mandelonitrile hexanoate and the extracted oil gland from *Oribatula tibialis* mite were then sent for analysis using various analytical techniques.

(i) Suggest the reagents that can be used to prepare mandelonitrile hexanoate from benzaldehyde at **low** temperature conditions. Show the structure of the intermediate organic compound in the box below.



step 1 ……………………………………………………………………………………………

step 2 ……………………………………………………………………………………………
[3]

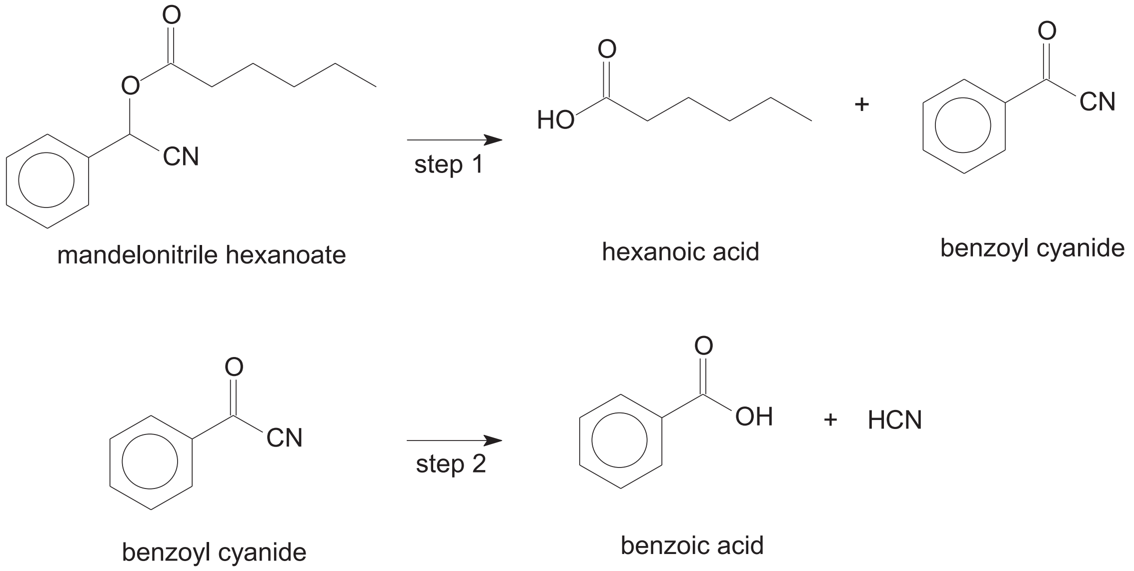
(ii) Suggest, in terms of the intermolecular forces involved, a reason why mandelonitrile hexanoate can dissolve in hexane.

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

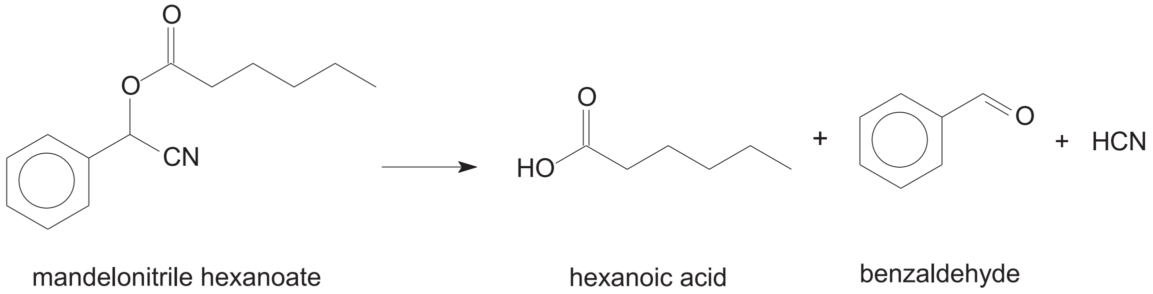
……………………………………………………………………………………………………[1]

When attacked by predators, the *Oribatula tibialis* mite secretes mandelonitrile hexanoate, which then release HCN, when in contact with the moisture, for example, from the predators' saliva. The HCN can be released via two different chemical pathways.

Pathway **I** illustrates a two–step process.



In pathway **II**, benzaldehyde is produced instead of benzoic acid.



(b) **(i)** By considering the change in structural formula shown in pathway **I**, suggest **two** types of reaction that could have occurred in step 1.

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

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

(ii) In step 2 of pathway **I**, the intermediate benzoyl cyanide breaks down into benzoic acid and HCN.

It was reported that benzoyl cyanide is less reactive than benzoyl chloride when it is in contact with water. Suggest a possible reason for this.

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

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

(iii) Suggest a simple chemical test that could be carried out to confirm which chemical pathway has occurred.

You may assume that HCN has vapourised completely from the product mixture.

…………………………………………………………………………………………………

…………………………………………………………………………………………………

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

(c) Benzaldehyde can be oxidised by peroxybenzoic acid, without consumption of oxygen, to give benzoic acid.

The standard enthalpy change of the reaction below is –316 kJ mol^{-1}.

$$C_6H_5CHO(l) + C_6H_5CO_3H(s) \longrightarrow 2C_6H_5CO_2H(s)$$

The standard enthalpy change of formation of peroxybenzoic acid and benzaldehyde are given in the table below.

Name	Formula	$\Delta H_f^\ominus$ / kJ mol^{-1}
peroxybenzoic acid	$C_6H_5CO_3H(s)$	–367
benzaldehyde	$C_6H_5CHO(l)$	–87

(i) Define the term *standard enthalpy change of formation*, $\Delta H_f^\ominus$ of a compound.

…………………………………………………………………………………………………

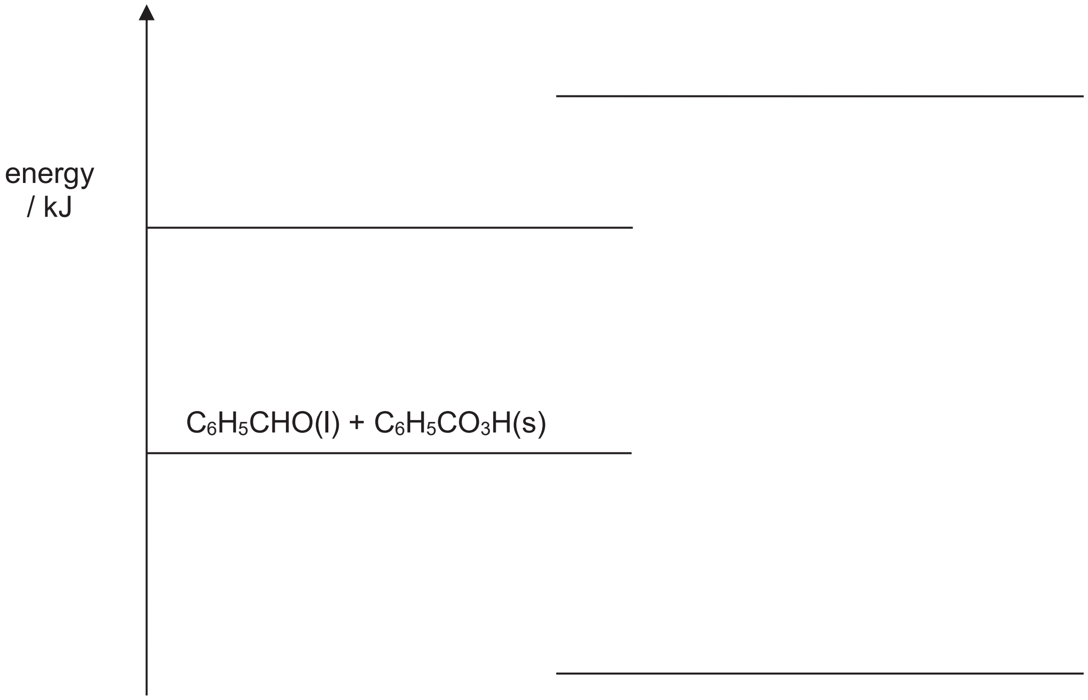
………………………………………………………………………………………………[1]

(ii) Use the data given above to calculate the enthalpy change of formation of benzoic acid.

[1]

(iii) Draw arrows on the energy diagram below to show each of the energy terms involved in the steps you have used in your calculation in **(c)(ii)**.

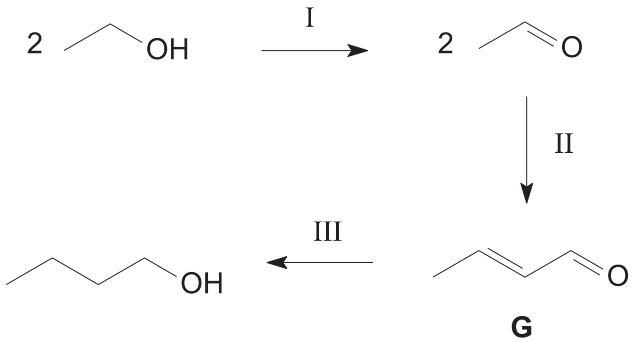
Label each level with the appropriate formulae.



[3]

[Total: 14]

5 Scientists in the United States of America have come up with a simple 3–stage process to convert ethanol into butan–1–ol, in what could be an important step forward for renewable energy.



(a) **(i)** State the reagents and conditions required for stages I and III.

stage I ………………………………………………………………………………………......

stage III ……………………………………………………………………………………....
[2]

(ii) Write an equation for the incomplete combustion of butan–1–ol, giving CO_2 and CO in a 3 : 1 ratio.

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

(iii) Describe the type(s) of stereoisomerism shown by compound **G**.
Draw the displayed formula of the stereoisomers of **G**.

Type of isomerism ………………………………………………..

[2]

(iv) **G** reacts with a suitable reducing agent to give compound **H**.

H effervesces with sodium metal but does not react with 2,4–dinitrophenylhydrazine. **H** also decolourises aqueous bromine.

Suggest the structure of **H** and explain these observations.

…………………………………………………………………………………………………

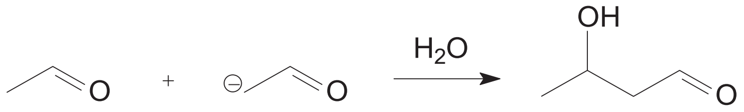
…………………………………………………………………………………………………

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

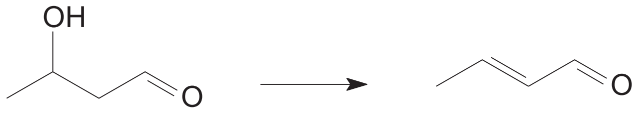
(b) The mechanism for stage II of the process in forming the α,β–unsaturated aldehyde **G** is thought to involve three steps.

Step 1 The first step involves an acid–base reaction.

Step 2 This is followed by a nucleophilic addition reaction to form the intermediate 3–hydroxybutanal.

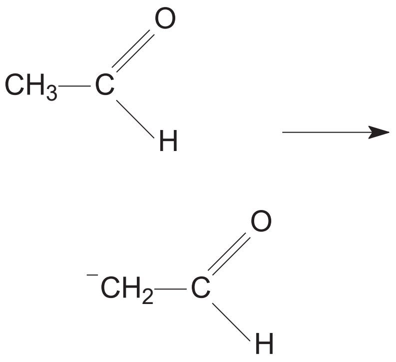


Step 3 Elimination of water is involved in the last step.



G

(i) Complete the diagram to suggest a mechanism to show how 3–hydroxybutanal intermediate is formed. Show all charges and relevant lone pairs and show the movement of electron pairs by using curly arrows.



[2]

(ii) A different product can be formed together with **G**, in step 3, albeit in lower yield. Suggest a reason for this.

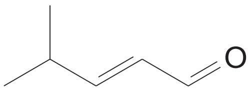
....

....

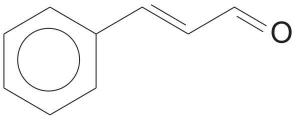
....[1]

(iii) Deduce the structures of suitable carbonyl compounds to synthesise each of the following α,β–unsaturated aldehyde.

(I)



(II)



[3]

(c) Butan–1–ol has a number of constitutional isomers.

(i) Draw the structural formula of the other three alcohols with the same molecular formula as butan–1–ol. Label your structures **J**, **K** and **L**. Classify these alcohols as primary, secondary or tertiary.

[2]

(ii) Identify which alcohol reacts with alkaline aqueous iodine and write a balanced equation for the reaction, showing the structural formula of the products.

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

[2]

[Total: 17]

ANDERSON JUNIOR COLLEGE

2017 JC 2 PRELIMINARY EXAMINATIONS

CHEMISTRY **9729/03**

Paper 3 Free Response **15 September 2017**

2 hours

Candidates answer on separate paper.

Additional Materials: Answer Paper
Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name, PDG and register number on all the work you hand in.
Write in dark blue or black pen.
You may use a pencil for any diagrams, graphs or rough working.
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.

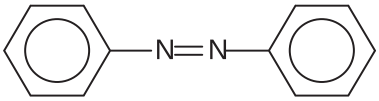
This document consists of **13** printed pages.

Section A

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

1 **(a)** Scientists in Germany have developed a liquid crystal elastomers (LCE)–based adhesive that uses UV light to switch and control its level of stickiness within seconds.

To control adhesion, the team used azobenzene, $C_{12}H_{10}N_2$ in the LCE as the light responsive molecule, which isomerises quickly from one state to another and changes size under UV light. This effect flexes the material enough to cause the microstructures to peel away from a surface and unstick, akin to how a gecko loses adhesion by moving its feet. When the light is removed, the material quickly recovers to its flat, sticky state.



azobenzene

(i) State the type of hybridisation that is present on the nitrogen atom and draw the shape of the hybrid orbitals around one of the nitrogen atom in azobenzene. Suggest the bond angle around this nitrogen atom. [3]

(ii) State the type of isomerism that is present in azobenzene and draw the two structures that illustrate the isomerism. [2]

(iii) Suggest, with a reason, the isomer that is responsible for the peeling of microstructures away from a surface. [1]

(b) *Use of the Data Booklet is relevant to this question.*

Compound **U,** $C_{17}H_{17}N_3O_3$ is not soluble in NaOH(aq) and HC*l*(aq). It gives 2 products when heated under reflux with acidified potassium dichromate. Orange potassium dichromate turns green during the process. Upon careful neutralisation of the resultant mixture, compounds **V** and **W** are formed.

V, $C_{13}H_{10}N_2O_2$ is a derivative of azobenzene, and has a proton (^{1}H) chemical shift value of 13.0 ppm.

W gives an orange precipitate when treated with 2,4–dinitrophenylhydrazine but it has no reaction with Tollens' reagent. It gives a yellow precipitate and compound **X** when warmed with aqueous mixture of sodium hydroxide and iodine. Effervescence was observed when **W** was treated with aqueous sodium hydrogencarbonate.

When **W** is heated with excess CH_3Cl, it gives compound **Y,** $C_7H_{14}NO_3Cl$, as the major product.

Suggest structures for **U** – **Y** and explain the reactions described above.
(The –N=N– structure remains unaltered in this question) [9]

[Total: 15]

2 Silver forms a series of halides of general formula Ag*X*. The chloride, bromide and iodide of silver are sparingly soluble in water at room temperature.

Data about the solubilities in water and the solubility products of the chloride, bromide and iodide of silver at 298 K are given below.

Salt	Solubility / mol dm^{-3}	Solubility product / $mol^2\ dm^{-6}$
$AgCl$	1.4×10^{-5}	2.0×10^{-10}
$AgBr$	7.1×10^{-7}	5.0×10^{-13}
AgI	8.9×10^{-9}	to be calculated

In this question, give **each** of your numerical answers to **one** decimal place.

(a) **(i)** Write an expression for the solubility product, K_{sp} of silver iodide. [1]

(ii) From the data above, calculate a value for K_{sp} of silver iodide. [1]

(iii) To a 2.0 dm^3 of saturated solution of AgI, 0.025 g of $AgNO_3(s)$ was added. Calculate the mass of precipitate formed. [2]

(b) When a precipitate is formed, $\Delta G^{\ominus}_{ppt}$ is given by the following expression.

$$\Delta G^{\ominus}_{ppt} = 2.303\ RT\ \log_{10} K_{sp}$$

(i) Use the data above to calculate $\Delta G^{\ominus}_{ppt}$, for silver chloride. [1]

(ii) When silver nitrate is added to solution containing chloride ions, a white precipitate is observed. The white precipitate dissolves when aqueous ammonia was added. Upon adding of aqueous sodium bromide to the resultant mixture, a cream precipitate is obtained.

With the aid of suitable equations, explain the chemistry that is occurring during these reactions. [3]

(c) For silver fluoride, AgF, $K_{sp} = 1.006\ mol^2\ dm^{-6}$ at 298 K.
Use the expression given in **(b)** to determine whether silver fluoride is soluble in water at 298 K.

Explain your answer. [2]

[Total: 10]

3 **(a)** Great research efforts have been put into the production of sustainable fuels, such as hydrogen and synthetic hydrocarbons. One of particular interest is a solar–driven thermochemical process which utilises a metal oxide catalyst to produce carbon monoxide from carbon dioxide.

In the first stage, the metal oxide (MO_2) is reduced to release oxygen gas. In the second stage, carbon dioxide then oxidises the reduced metal oxide to generate carbon monoxide.

The 2–stage process is as shown below.

Stage 1: $MO_2(s) \rightleftharpoons MO_{2-x}(s) + \frac{x}{2}O_2(g)$ $\Delta H_1 > 0$

Stage 2: $MO_{2-x}(s) + xCO_2(g) \rightleftharpoons MO_2(s) + xCO(g)$

(i) Stage 1 is carried out at a high temperature of 1500 ^{o}C.

State *Le Chatelier's Principle* and use it to explain why such a high temperature is necessary. [2]

(ii) Give the equation, with state symbols, for the overall equilibrium reaction. [1]

(iii) The $\Delta H^{\ominus}$ of the reaction in **(a)(ii)** is +283 kJ mol^{-1} when $x = 1$.

Using relevant data from the *Data Booklet*, calculate the carbon–oxygen bond energy in carbon monoxide. [2]

(iv) Given that the standard Gibbs free energy change, $\Delta G^{\ominus}$, of the reaction in **(a)(ii)** is +237 kJ mol^{-1} at 298 K, calculate the $\Delta S^{\ominus}$ for this reaction and comment on its sign with respect to the reaction. [2]

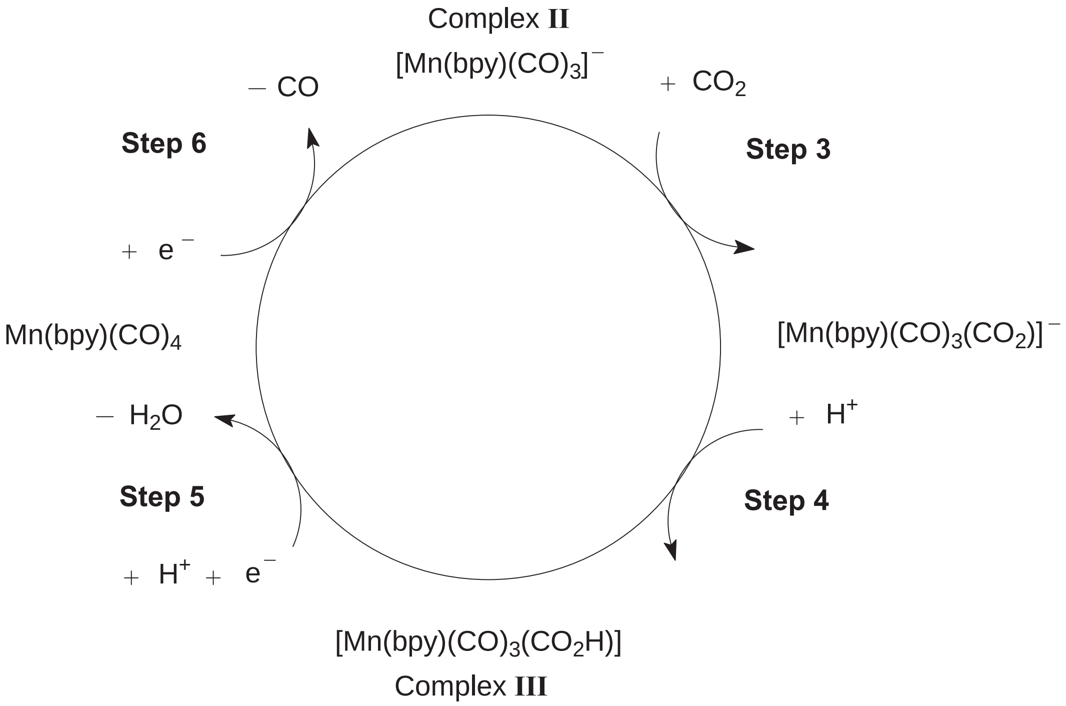
(b) The conversion of carbon dioxide to carbon monoxide is also important in helping to slow down global warming. Another method that was developed by scientists involves the use of metal complexes as catalysts to capture carbon dioxide and reduce it to carbon monoxide using visible light.

The starting reagent for the method involves the conversion of Complex **I**, $Mn(bpy)(CO)_3(Br)$ to the catalyst for the process, Complex **II**, $[Mn(bpy)(CO)_3]^-$.

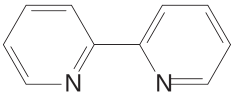
Step 1: $Mn(bpy)(CO)_3(Br) + e^- \longrightarrow [Mn(bpy)(CO)_3(Br)]^-$

Step 2: $[Mn(bpy)(CO)_3(Br)]^- + e^- \longrightarrow [Mn(bpy)(CO)_3]^- + Br^-$

Complex **II** then undergoes a catalytic reduction process with carbon dioxide as seen below.



where bpy =



(i) Using N⌒N to represent the bpy ligand, draw the structure of Complex **I** and state its shape. [2]

(ii) State which of the six steps involve a **decrease** in the number of ligands bonded to the manganese ion. [1]

(iii) Suggest the type of reaction which takes place in steps 1 and 4. [1]

(iv) A solution containing Complex **III** is orange in colour.

Explain how such a colour could arise. [3]

(c) The CarbFix project in Iceland is also targeted at alleviating the global problem of increasing industrial carbon dioxide (CO_2) emissions and climate change. All waters in contact with the atmosphere absorb CO_2, but this method speeds up the process by injecting waters containing CO_2 into basaltic rocks which are rich in divalent cations such as calcium and magnesium. The method is called "stoning" as the CO_2 is captured and stored in the rocks as insoluble carbonates.

Water containing CO_2 reacts with the divalent cations present in basaltic rocks according to the following equilibrium.

$$M^{2+} + CO_2 + H_2O \rightleftharpoons MCO_3 + 2H^+ \qquad \text{———— (1)}$$

(i) Explain why the precipitation of the metal carbonate takes place at high pH. [1]

(ii) Water containing CO_2 also reacts with Group 2 carbonates to form the corresponding soluble hydrogencarbonates in the following equilibrium.

$$CO_2(g) + H_2O(l) + MCO_3(s) \rightleftharpoons M(HCO_3)_2(aq) \qquad \text{———— (2)}$$

These soluble compounds are then washed away by rainwater that percolates through rocks on hills and mountains and emerges as springs in the hillside. These are known as mineral waters and they often contain chlorides and hydrogencarbonates of Group 2 metals.

One such mineral water has the following composition.

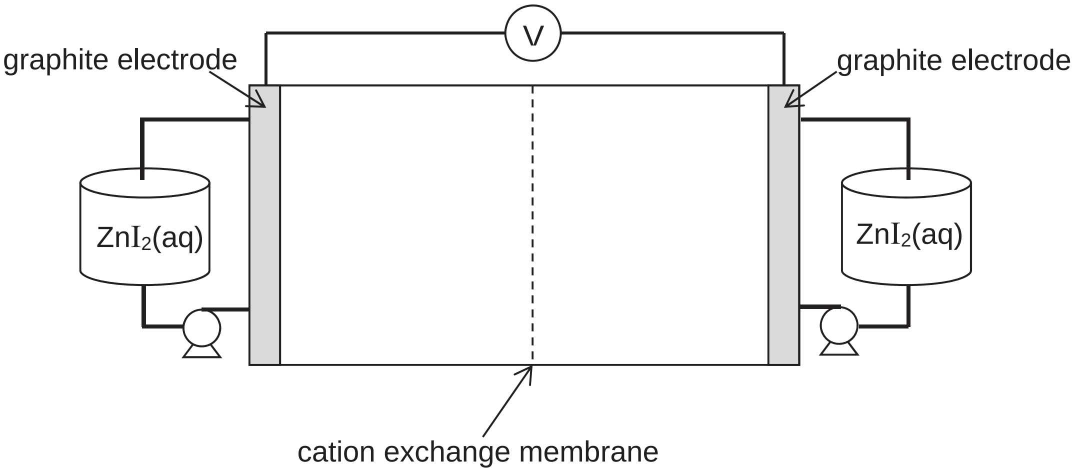
ion	**concentration / g dm^{-3}**
Ca^{2+}	0.0120
Mg^{2+}	0.0073
Cl^-	0.0284
HCO_3^-	0.0244

Calculate the concentrations of these ions in mol dm^{-3} and hence suggest the formulae of the salts that could exist in the solution, and their relative amounts. [3]

(iii) Suggest the composition of the rock through which the rainwater had percolated and use equation (2) to explain how the mineral water had been formed. [2]

[Total: 20]

4 Redox flow batteries are rechargeable batteries that have received growing attention as a cost–effective energy storage solution. Compounds with iodine can be used to generate electrical energy in redox flow batteries. One such battery is the zinc–iodide battery shown below.



In the zinc–iodide flow cell, graphite is used as the electrodes and the two half–cells are separated by a cation exchange membrane which allows cations to flow through. The electrolyte, $ZnI_2(aq)$, is stored in two external tanks. When required, the electrolyte is pumped into both half–cells.

During charging, metallic zinc is deposited on the negative electrode and iodine is formed at the positive electrode. When a light bulb is connected across the two electrodes, the bulb lights up as the battery discharges.

(a) **(i)** By reference to the *Data Booklet*, choose two half–equations to construct the balanced equation for the reaction that occurs during the discharging process. [2]

(ii) Calculate the value for $E^{\ominus}_{cell}$ for this zinc–iodide battery. [1]

(iii) Hence calculate the $\Delta G^{\ominus}$ for this cell. [1]

(iv) Suggest why there is a need for a cation exchange membrane in the battery. [1]

(b) The iodine formed during charging can complex with the iodide ions in the electrolyte to form triiodide ions, I_3^-. This reduces the efficiency of the battery, as formation of triiodide ions reduces the amount of I^- available for redox reaction.

Recent research has shown that addition of bromide, Br^-, to the zinc–iodide battery frees up the iodide ions, as bromide can form a similar complex with iodine.

Draw a dot and cross diagram of the complex formed between iodine and bromide ion and state its shape. [2]

(c) Compounds with a halogen and an alcohol group are known as halohydrins. Halohydrins are useful intermediates in organic synthesis as they contain two reactive functional groups.

(i) Halohydrins can be synthesised from the reaction of alkenes with aqueous bromine.

Describe the mechanism of the reaction between 1–methylcyclohexene and aqueous bromine to form bromohydrin. In your answer, show any relevant charges, lone pairs of electrons and movement of electrons. [4]

(ii) The bromohydrin formed in **(c)(i)** exists as a mixture of stereoisomers. Draw the structure of each stereoisomers of the bromohydrin formed. [2]

(iii) Suggest one simple test–tube reaction, other than aqueous bromine, to distinguish 1–methylcyclohexene and the bromohydrin formed in **(c)(i)**, stating clearly the reagents and conditions required and the observations you would see. [2]

[Total: 15]

Section B

Answer **one** question from this section.

5 The oxygen family, also called the chalcogens, consists of the elements found in Group 16 of the Periodic Table and is considered among the main group elements. It consists of the elements oxygen, sulfur, selenium, tellurium and polonium.

(a) State and explain the trend in the first ionisation energy of the Group 16 elements down the group. [2]

(b) **(i)** State two assumptions of the kinetic theory of gases. [2]

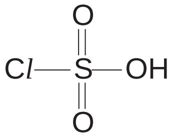
(ii) Sketch the expected variations of *p*V with *p* for a given amount of an ideal gas at constant temperature. [1]

In an experiment conducted at constant temperature, the volumes of separate samples containing equal amounts of gases **D** and **E** were measured at different pressures and the results are tabulated below. The two unknown gases **D** and **E** could be hydrogen or oxygen.

Experiment No.	**Gas D**		**Gas E**	
	***p* / Pa**	**V / m³**	***p* / Pa**	**V / m³**
1	3.5×10^5	6.50×10^{-3}	4.0×10^5	5.80×10^{-3}
2	7.0×10^5	3.14×10^{-3}	8.0×10^5	2.85×10^{-3}
3	14.0×10^5	1.50×10^{-3}	15.0×10^5	1.46×10^{-3}
4	21.0×10^5	9.30×10^{-4}	20.0×10^5	1.07×10^{-3}

(iii) Compute the *p*V values for each of the above experiments and use them to identify gases **D** and **E**. Explain your reasoning. [3]

(c) The diagram below shows the structure of chlorosulfuric acid, HSO_3Cl, which is a Lewis base.



chlorosulfuric acid

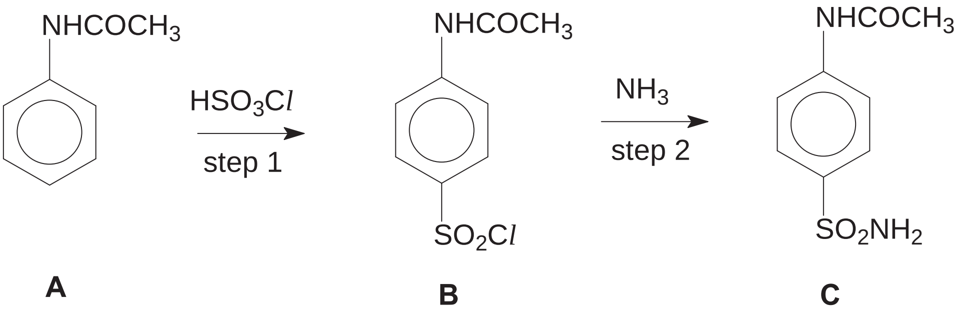
(i) What do you understand by the term *Lewis base*? [1]

(ii) Chlorosulfuric acid is made by reacting sulfuric acid with phosphorus pentachloride, PCl_5. Acidic white fumes are evolved during the reaction.

Write a balanced equation for the reaction between sulfuric acid and phosphorus pentachloride. [1]

(iii) By comparing the structure of chlorosulfuric acid with that of sulfuric acid, explain why sulfuric acid is expected to be a stronger acid than chlorosulfuric acid. [1]

(d) The following reaction scheme shows the synthesis of **C**, a precursor to the sulfonamide antibacterial drugs.



(i) Explain why compound **A** is neutral. [1]

(ii) $C_6H_5CONHCH_3$ is an isomer of **A**. Describe a simple chemical test to distinguish between the two isomers, stating clearly how each compound behaves in the test. [2]

Step 1 is catalysed by concentrated sulfuric acid.

(iii) Write an equation to illustrate the reaction between concentrated sulfuric acid and chlorosulfuric acid, HSO_3Cl. [1]

(iv) Hence, name and describe the mechanism for the reaction involved in the preparation of **B**, including curly arrows to show the movement of electrons, and all charges. [3]

Step 2 is carried out under anhydrous condition.

(v) What type of reaction is step 2? [1]

(vi) Suggest why step 2 has to be carried out under anhydrous condition. [1]

[Total: 20]

6 **(a)** In acidic solution, bromate(V) ions, BrO_3^-, slowly oxidise bromide ions to bromine. The progress of the reaction may be followed by adding a fixed amount of phenol together with some methyl red indicator.

The bromine produced during the reaction reacts very rapidly with phenol. When all the phenol is consumed, any further bromine bleaches the indicator immediately. The initial rate of formation of Br_2 is indicated by the time for the bromine to bleach the indicator.

The total volume of the reaction mixture is the same in all four experiments and the following kinetic data are obtained at 25 °C.

Experiment	**$[BrO_3^-]$ / mol dm^{-3}**	**$[Br^-]$ / mol dm^{-3}**	**pH**	**Initial rate of formation of Br_2 / mol dm^{-3} s^{-1}**
1	0.10	0.10	1.00	8×10^{-2}
2	0.10	0.05	1.00	4×10^{-2}
3	0.05	0.05	1.00	2×10^{-2}
4	0.05	0.10	1.30	1×10^{-2}

(i) Write a balanced equation for the reaction between bromide ion and bromate(V) ion. [1]

(ii) Determine the order of the reaction with respect to each of the following reactants

- BrO_3^-
- Br^-
- H^+. [2]

(iii) Write the rate equation for this reaction. [1]

(iv) Calculate the rate constant of the reaction at this temperature, stating its units. [1]

(b) Describe, and explain in molecular terms, how the rate of reaction is affected by an increase in temperature. You should include a reference to the Boltzmann distribution in your answer. [3]

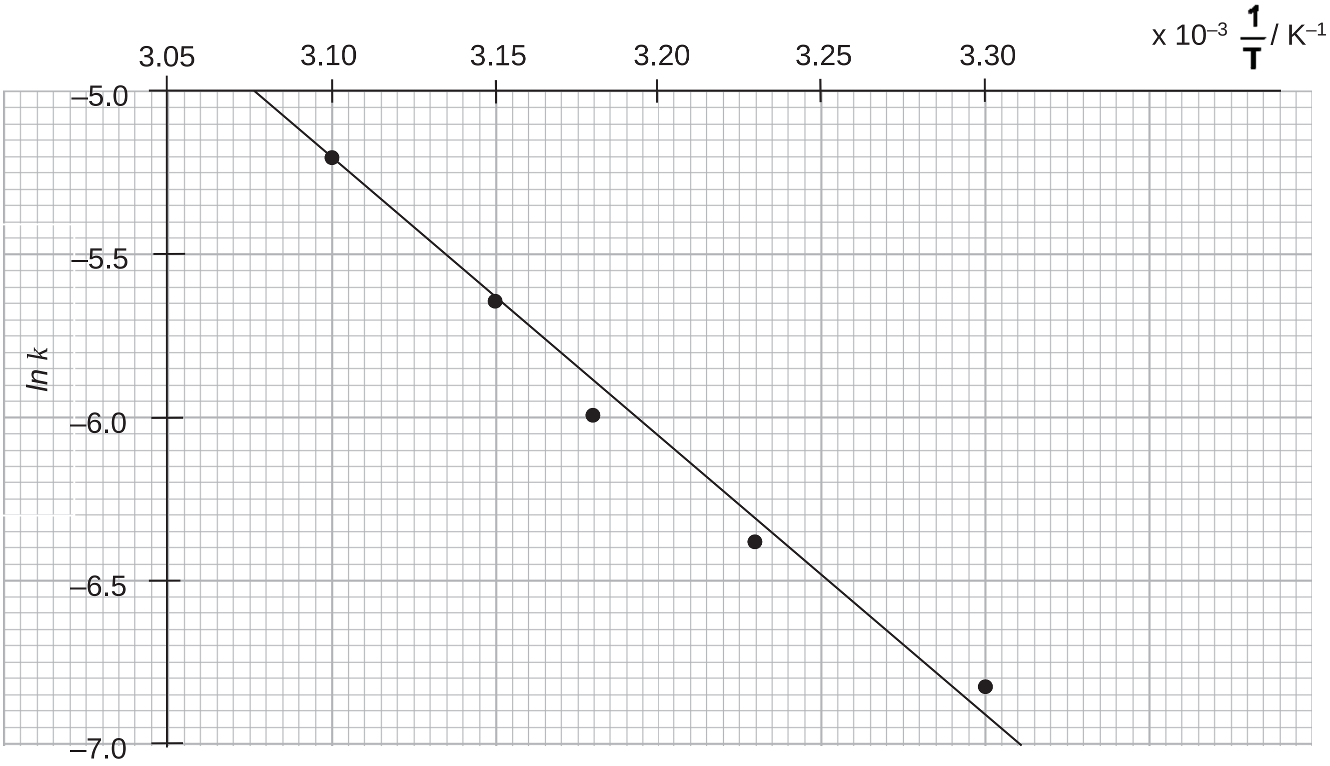
(c) The effect of temperature on the rate constant, *k*, can be expressed by the following equation.

$$\ln k = \ln A - \frac{E_a}{R}\left(\frac{1}{T}\right)$$

A is a constant;
E_a is the activation energy;
R is the molar gas constant (8.31 J K^{-1} mol^{-1}) and
T is the absolute temperature.

In a separate experiment to investigate the effect of temperature on the rate constant of the reaction between bromide ion and bromate(V) ion, the graph below was obtained.

Graph of *ln k* against $\frac{1}{T}$



(i) Calculate the activation energy, E_a, of the reaction. [1]

(ii) Suggest why the activation energy of the reaction is high. [1]

(iii) Make a sketch of the graph shown above onto your writing paper. On the same axes, sketch the graph of *ln k* versus $\frac{1}{T}$ when the reaction proceeds in the presence of a catalyst. Label your graphs clearly. Explain your answer. [1]

(d) This question is about compound **K**, C_6H_7ON, which is formed when phenylhydroxylamine, C_6H_5NHOH, is warmed with dilute sulphuric acid.

- Compound **K** is not very soluble in water, but dissolves in HC*l*(aq).
- It also dissolves in NaOH(aq), but not in Na_2CO_3(aq).
- On reaction with 1 mol of ethanoyl chloride, CH_3COCl, **K** forms compound **L**, $C_8H_9O_2N$.

On reaction with Br_2 (aq), **L** produces compound **M**, $C_8H_7O_2NBr_2$. When **K** is reacted with 2 mol of ethanoyl chloride, it produces compound **N**, $C_{10}H_{11}O_3N$, which is not soluble in either HC*l*(aq) or NaOH(aq).

Compound **K** can be synthesised by treating phenol with dilute nitric acid, followed by reaction with tin metal and hydrochloric acid.

(i) Deduce the structures of compounds **K**, **L**, **M** and **N**. Explain the chemistry of the reactions described, writing equations where appropriate. [There is no need to comment on the chemistry of the formation of **K** from phenylhydroxylamine.] [7]

(ii) The reaction of **K** to form **L** produces a minor product **P**, which is a constitutional isomer of **L**. Suggest the structure of **P** and explain this observation. [2]

[Total: 20]

H2 Chemistry 9729 **AJC 2017 JC2 PRELIM** **Paper 1 – 30 marks**

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

A	**7**
B	**8**
C	**8**
D	**7**

Anderson Junior College
H2 Chemistry 9729 **2017 JC2 PRELIM Paper 1 Suggested Solutions**

1 $^{3}_{1}H$ contains 1 proton, 1 electron and 2 (3 – 1) neutrons. **D**

$^{3}_{2}He$ contains 2 protons, 2 electrons and 1 (3 – 2) neutron.

1 ^{3}He has less neutrons than electrons.
2 ^{3}H has one proton while ^{3}He has two protons.
3 ^{3}H has two charged sub–atomic particles while ^{3}He has four charged sub–atomic particles.

2 angle of deflection $\alpha \ \frac{\text{charge size}}{\text{mass}}$ **D**

for $^{1}H^{+}$, $\frac{z}{m}=+\frac{1}{1}$
for $^{2}X^{2-}$, $\frac{z}{m}=-\frac{2}{2}$
Hence, angle of deflection for $^{2}X^{2-}$ = –4°

3 **A**

		shape / angle
A	SF_2	bent / ~104.5°
B	XeF_2	linear / 180°
C	SO_3^{2-}	trigonal pyramidal / ~107°
D	AlH_4^-	tetrahedral / 109.5°

4 The hybridisation state of N atom can be determined using similar approach as that for C atoms, except the *lone pair of electrons on N* can sometimes be occupying a *sp*^{2} *(norm)* or *sp*^{3} *hybrid orbital*. The question will likely provide information on the shape of the molecule with respect to N atom to link it to the hybridisation state – planar (sp^2) and tetrahedral (sp^3). **D**

A is correct. All C atoms in **F** are sp^3 hybridised. Hence, each C–C bond is a σ bond formed by a sp^3–sp^3 overlap between two C atoms.

B is correct. The N atoms in **G** has the same hybridisation state as carbon in benzene (i.e. sp^2) except that in place of a C–H bond pair, a lone pair now occupies the sp^2 hybrid orbital. The unhybridised p orbital of each N atom overlap with the adjacent p orbitals of C atoms to form a delocalised ring of π electron cloud.

C is correct. There are two sp^2 hybridised C atoms and both are bonded to sp^3 hybridised C atoms.

D **is incorrect**. From option **C**, the two sp^2 hybridised C atoms are not bonded to any N atom. And the N atom in **H** is likely to be sp^3 hybridised.

5 $pV = nRT$ **A**

for the same amount of He gas, n and R remain constant throughout. He gas will diffuse to occupy both vessels **J** and **K** when the valve is opened, i.e. volume of space occupied by gas = (v + 3v)

$p_i = 1 \times 10^5$ Pa	p_f = ? Pa
$T_i = (20 + 273)$ K	$T_f = (100 + 273)$ K
V_i = v	V_f = 4v (sum of vessels **J** and **K**)

$$(\frac{pV}{T})_i = (\frac{pV}{T})_f$$

$$p_f = \frac{(1x10^5)(v)}{(20+273)} x \frac{(100+273)}{4v}$$

= 3.18 x 105 Pa

6 Property 1: melting point of chlorides **B**

Chlorides of Mg form giant ionic lattice structures, have much higher melting point than simple molecular chlorides of A*l*, Si and P

Property 2: pH of oxides

oxides	MgO	Al_2O_3	SiO_2	P_4O_{10}
Structure	giant ionic lattice		giant molecular	simple molecular
Reaction with water	weakly alkaline solution (pH ≈ 9)	insoluble (pH = 7)		acidic solution (pH = 1)

The most obvious clue to identifying the property would be the plateau from A*l* to Si, which is due to the insoluble oxides of the two elements.

7 On heating with Cl_2, Br_2 and I_2, the respective iron(II) halides will be formed, since their reduction potential are more positive than that of Fe^{2+}/Fe. **C**

$Fe^{2+} + e^- \rightleftharpoons Fe$ –0.44 V

$Cl_2 + 2e^- \rightleftharpoons 2Cl^-$ +1.36 V

$Br_2 + 2e^- \rightleftharpoons 2Br^-$ +1.07 V

$I_2 + 2e^- \rightleftharpoons 2I^-$ +0.54 V

Due to the oxidising nature of the halogens, Cl_2 and Br_2 can further oxidise the iron(II) to iron(III) since their reduction potential are more positive than that of Fe^{3+}/Fe^{2+}.

$Fe^{3+} + e \rightleftharpoons Fe^{2+}$ +0.77 V

(Note: Fe is not oxidised to Fe^{3+} in a single reaction because the reduction potential of Fe^{3+}/Fe (–0.04 V) is less negative than that of Fe^{2+}/Fe (–0.44 V). Fe will more likely be oxidised to Fe^{2+}.)

8 Given that molar ratio of carbon dioxide : hydrocarbon is 2 : 1, there are <u>two carbon atoms</u>. ∴ let formula of hydrocarbon be C_2H_x **A**

$$\Rightarrow C_2H_x(g) + (2 + \frac{x}{4})O_2(g) \longrightarrow 2CO_2(g) + \frac{x}{2}H_2O(l)$$

Since the <u>remaining O_2</u> can <u>burn</u> up <u>exactly 30 cm^3 of the same hydrocarbon</u>, this means that <u>100 cm^3 of O_2</u> can burn <u>40 cm^3 of the hydrocarbon</u>.

$\Rightarrow$ Molar ratio of hydrocarbon : O_2 = 40 : 100 = 1 : $\frac{5}{2}$

$\Rightarrow 2 + \frac{x}{4} = 2.5$

$\Rightarrow x = 2$

Formula of hydrocarbon is $\underline{C_2H_2}$.

9 **A**

reaction 1 $Al_2O_3 + 3H_2SO_4 \longrightarrow Al_2(SO_4)_3 + 3H_2O$

reaction 2 $Cu + H_2SO_4 \longrightarrow CuO + SO_2 + H_2O$

reaction 3 $(CH_3)_3COH + H_2SO_4 \longrightarrow (CH_3)_2C{=}CH_2 + H_2SO_4 + H_2O$

Reaction 1 is an <u>acid–base reaction</u> (clue: O.N. of the elements remain).
Reaction 2 is a <u>redox reaction</u> (most obvious clue: O.N. of Cu increases; S decreases).
Reaction 3 is an <u>elimination reaction</u>; H_2SO_4 is a <u>catalyst</u> here (clue: H_2SO_4 remains unchanged after the reaction).

10 **C**

$$N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g) \qquad \Delta H^\ominus = -92\text{ kJ mol}^{-1}$$

$$N_2(g) + 4H_2(g) + Cl_2(g) \longrightarrow 2NH_4Cl(s) \qquad \Delta H^\ominus = -629\text{ kJ mol}^{-1}$$

$$NH_3(g) + HCl(g) \longrightarrow NH_4Cl(s) \qquad \Delta H^\ominus = -176\text{ kJ mol}^{-1}$$

$$\tfrac{1}{2}H_2(g) + \tfrac{1}{2}Cl_2(g) \longrightarrow HCl(g) \qquad \Delta H_f^\ominus(HCl)$$

$$\begin{tikzcd}
N_2(g) + 4H_2(g) + Cl_2(g) \arrow[r, "-629"] \arrow[d, "-92"'] & 2NH_4Cl(s) \\
2NH_3(g) + H_2(g) + Cl_2(g) \arrow[r, "2\Delta H_f^\ominus(HCl)"'] & 2NH_3(g) + 2HCl(g) \arrow[u, "2(-176)"']
\end{tikzcd}$$

$2\Delta H_f^\ominus(HCl) = -(-92) + (-629) - 2(-176)$

$\Delta H_f^\ominus(HCl) = \underline{-92.5\text{ kJ mol}^{-1}}$

11 Info from *Data Booklet*, c = 4.18 J g^{-1} K^{-1} **B**

Heat absorbed by water = (160 – 60) x 4.18 x (68 – 25)
= 17974 J

Heat released by ethanol = 1370 x 1000 x $\frac{1.0}{2(12.0)+6(1.0)+16.0}$
= 29783 J

The difference in the heat transferred is due to heat loss. Hence in this case, efficiency can be calculated by taking the ratio $\frac{\text{heat absorbed}}{\text{heat released}}$.

% efficiency = $\frac{17974}{29783}$ x 100%
= 60 %

12 The reactions taking place in the catalytic converter include simultaneous reduction of NO_x and oxidation of CO (option **C**), oxidation of unburnt hydrocarbons (option **D**) and oxidation of CO (option **B**). **A**

Hydrocarbons contain C and H atoms. Carbon is not a hydrocarbon.

13 The easiest approach to answering this question is to start from the *equimolar quantities of* ***L*** *and* ***M*** *after 9 min* and work backwards. Let the amount be. **C**

Since **L** has undergone 3 half–lives, its initial concentrations will be 8**L**.
Initial concentration of **M** will be 2**M** as it has undergone 1 half–lives.

$$\begin{tikzcd}
8x\,\mathbf{L} \arrow[r] & 4x\,\mathbf{L} \arrow[r] & 2x\,\mathbf{L} \arrow[r] & x\,\mathbf{L} \\
2x\,\mathbf{M} \arrow[rrr] & & & x\,\mathbf{M}
\end{tikzcd}$$

∴ value of n = $\frac{8x}{2x}$
= 4

14 $N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$ $\Delta H^\ominus = -92$ kJ mol^{-1} **C**

A is incorrect. Adding a catalyst does not affect the equilibrium yield; it only increases the rate of achieving equilibrium because the rates of both forward and backward reaction increase by the same extent.

B is incorrect. Adding neon at constant pressure will decrease the partial pressures of the particles present (both reactants and products)*. Since the reaction results in a decrease in no. of moles of gaseous particles, position of equilibrium (P.O.E.) shifts to the left to increase the pressure, resulting in a decrease in equilibrium yield.

*[$p_a = \frac{n_a}{n_{total}} p_{total}$, n_{total} increases while n_a and and p_{total} remain]

Addition of an inert gas at constant volume will have no impact on the P.O.E. because the partial pressure of the reactants and products are not affected.

[$p_a = \frac{n_a}{n_{total}} p_{total}$, n_{total} and p_{total} increase to the same extent while n_a remains]

C **is correct**. Decreasing the temperature favours the forward exothermic reaction and P.O.E. shifts to the right (equilibrium yield increase) and the rate of production of ammonia is slower as the average kinetic energy of the particles decrease.

D is incorrect. Removing N_2 at constant volume ($\Rightarrow$ partial pressure of N_2 decreases) will cause the P.O.E. to shift to the left (decrease in yield) and rate of production of ammonia is slower due to a decrease in concentration of reactants.

15 Since $\Delta G^\ominus < 0$ **B**

$\Rightarrow$ the forward reaction is spontaneous and
$\Rightarrow$ position of equilibrium lies to the right.
$\Rightarrow$ the amount of products at equilibrium is more than that of the reactants.
i.e. K_p is greater than 1

Alternatively, using $\Delta G^\ominus = -RT \ln K$
$\Rightarrow K > 1$

16 By inspection, ammonia is in excess. An alkaline buffer (excess unreacted NH_3 and NH_4^+) is obtained. **C**

$[NH_4^+]$ = nHC*l* ÷ total volume
= (30 x 0.1) ÷ 50
= 0.06 mol dm^{-3}

$[NH_3]$ = (20 x 0.2 – 30 x 0.1) ÷ 50
= 0.02 mol dm^{-3}

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]}$$

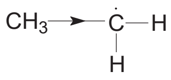
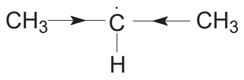
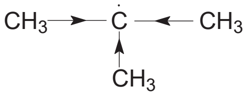
$[OH^-] = 6 \times 10^{-6}$
pOH =5.2
pH = 8.8

or use

$$pOH = pK_b + \lg\frac{[NH_4^+]}{[NH_3]}$$

17 By inspection, the base is diprotic (2 equivalence points) and likely to be a weak one (low initial pH). And since the final pH is approximately 1, the acid added is likely a strong acid. **C**

18 Due to the inductive electron-donating effect of alkyl groups, the stability of the radicals are in increasing order of: **C**

a primary radical < a secondary radical < a tertiary radical

Thus, the tertiary radical being the most stable will be formed most readily.

19 The following hint "… *comprising of 10 linearly fused benzene ring* …" is useful in solving the question. **C**

1 **is correct**. Each C atom is sp^2 hybridised. The sp^2 hybridised orbitals are arranged in a trigonal planar manner about each C atom, giving a bond angle of 120°.

2 **is correct**. The delocalised ring of π electrons is formed by the overlapping of p orbitals on adjacent C atoms.

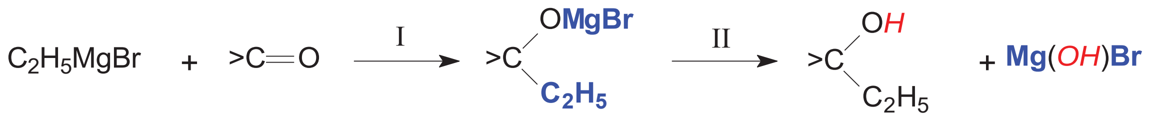
3 is incorrect. The carbon–carbon bond energies should be intermediate between that of the bond energy of a C–C bond in alkane and the C=C bond in alkene.

[refer to the *Data Booklet* – bond energy of C=C (benzene) is 520 kJ mol^{-1}, between 350 kJ mol^{-1} (C–C) and 610 kJ mol^{-1} (C=C)]

4 is incorrect. The valency of each C is still 4. In each C, 3 valence electrons are used in the formation of three σ bonds, and 1 electron is delocalised into the 42 π–electron system.

20 Chlorofluoroalkanes generate C*l*• radicals which destroy stratospheric ozone. The more C*l* atoms that is present in the molecule, the more C*l*• radicals can be generated, and the higher the ODP. **A**

21 **D**



Step I involves the addition of $-\mathbf{C_2H_5}$ and –**MgBr** across the carbonyl group (in bold). As the reactive carbon is electron deficient, it is susceptible to nucleophilic attack.

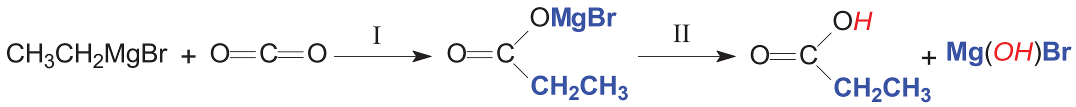
Step II involves the hydrolysis of O–Mg bond (observe the *H* and *OH* added – in italics). This reaction is dependent on the polarity across the O(δ–) – Mg(δ+) bond.

22 **D**

1 **is correct**. Similar to the above steps, $-\mathbf{C_6H_5}$ and –**MgBr** are added to the carbonyl group of CH_3CHO, followed by hydrolysis of the O–Mg bond to form $\mathbf{C_6H_5}CH(O\mathit{H})CH_3$ and **Mg**(*OH*)**Br**.

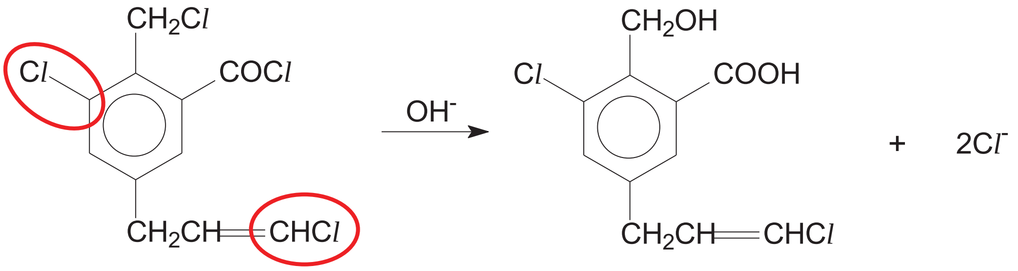
2 is incorrect. The reactant has a longer carbon chain (additional $-CH_2-$).

3 **is correct**. By observation, a carboxylic acid will be formed when CO_2 reacts with a Grignard reagent.



(To visualize, replace the 2 R group substituents on the reactive carbon (>C) with an oxygen doubly bonded (=O) to the carbon in CO_2.)

23 **B**



Nucleophilic substitution does not occur due to the delocalisation of the lone pair of electrons on the C*l* atom into the benzene ring (or adjacent C=C double bond), creating a partial double bond character in the C–C*l* bond (circled). The polarity of the C–C*l* bond is also decreased due to the delocalisation and hence the C atom of the C–C*l* bond is less electron deficient and less susceptible to attack by the OH^- nucleophile.
Steric hindrance due to repulsion of the nucleophile by the π electron cloud could also be used as a reason.

24 **D**

1 is incorrect. Absence of CH_3COR or $CH_3CH(OH)R$. Hence, it does not react with $I_2/OH^-(aq)$.

2 is incorrect. All three 2° alcohol present in *Indian Yellow* will be oxidised by $Cr_2O_7^{2-}/H^+$ to give a compound with four carbonyl groups.

3 is incorrect. Only 2 atoms of Br will be substituted on the benzene ring at the 2nd and 4th position with respect to phenol group. Even if you had use the concept that ether (R–O–R group) has similar reactivity as phenol, still the number of Br atom incorporated will be less than 6 Br atoms. However, do note that reactivity of ether is not in the syllabus. Hence, you have to follow the clue given in the question to decide when it is reactive and when it is assumed to be inert. (refer to N2008/III/5d, N2013/II/3aiv, N2009/I/24 etc)

4 **is correct.** Each mole of –OH group reacts with Na metal to form ½mol of $H_2(g)$. Since there are 5 mol of –OH group per mol of *Indian Yellow*, 2.5 mol of $H_2(g)$ is formed.

25 **A**

decreasing $pK_a \Rightarrow$ increasing K_a and increasing strength of acid
Observe that all four compounds are carboxylic acids, hence the order of strength is dependent on the substituent present and its position relative to –COOH group.

Recall: Strength of an acid depends on the stability of its conjugate base.
(Why? $pK_a + pK_b = 14$ at 298 K, so the bigger the pK_b is, the smaller the pK_a will be. A stable base will mean it is unreactive/weak base $\Rightarrow$ greater K_a for its conjugate acid.)

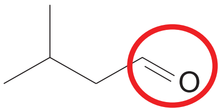
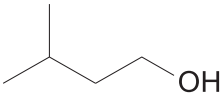
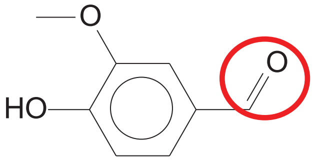
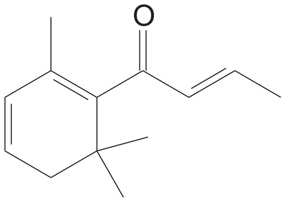
Compare carboxylate ions: **H**–$C_6H_4COO^-$ and **CH_3**–$C_6H_4COO^-$

- Presence of electron donating alkyl group in $CH_3C_6H_4CO_2H$ reduces the dispersal of the –ve charge to a smaller extent and thus stabilises the conjugate base to a smaller extent.
- Hence $CH_3C_6H_4CO_2H$ has a larger pK_a than $C_6H_5CO_2H$. (narrow down to options **A** and **D**)

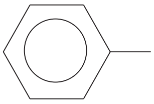
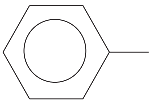
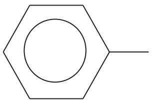
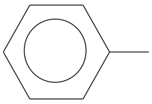
Compare: 4–hydroxybenzoic acid and 2–hydroxybenzoic acid**.**

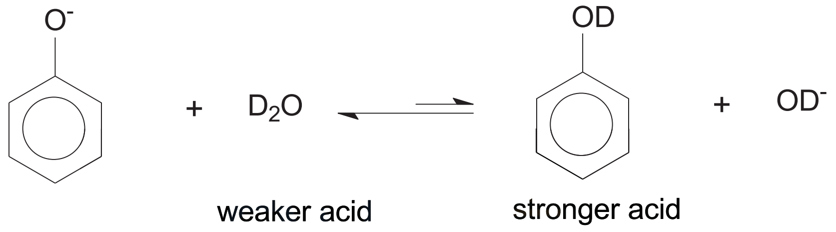
- Close proximity of the phenol group to carboxylic acid group in 2–hydroxybenzoic acid enables it to form intramolecular hydrogen bonding which helps to stabilise the conjugate base to a greater extent.
- Hence 2–hydroxybenzoic acid has a lower pK_a than 4–hydroxybenzoic acid. (option **A**)

26 $Cr_2O_7^{2-}/H^+$ is able to oxidise 1°, 2° alcohols and <u>aldehyde</u>.
NaBH$_4$ is able to reduce <u>aldehyde</u> and ketones. **B**

		$Cr_2O_7^{2-}/H^+$	$NaBH_4$
1		√	√
2		√	X
3		√	√
4		√	X

27 **C**

	Type of reaction	**Products**
A	base–catalysed hydrolysis	 $CO_2^-Na^+$ + CH_3OD
B	base–catalysed hydrolysis	 O^-Na^+ + $CH_3CO_2^-Na^+$
C	acid–catalysed hydrolysis	 OD + CH_3CO_2D
D	no reaction	 O^-Na^+

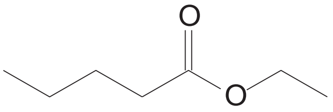


Since C_6H_5OD is a stronger acid than D_2O, the position of equilibrium lies to the left as C_6H_5OD is a better proton donor. $C_6H_5O^-$ will not react with D_2O to give a good yield of C_6H_5OD.

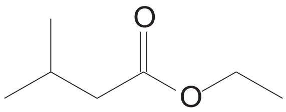
28 Given that the first member of the series is ethyl ethanoate **B**

⇒ n = 0

∴ the fourth member of the series (<u>n = 3</u>) will be either

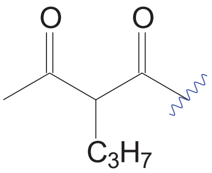


or

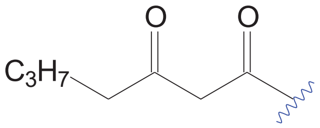


(branched isomer)

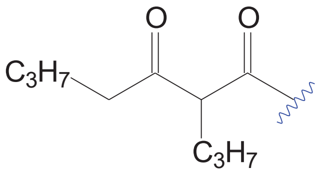
By observation, a possible product must have one of the following structures.



or



or



Hence,

A is incorrect. One of its reactants is the <u>fifth member</u> of the series (i.e. n = 4).

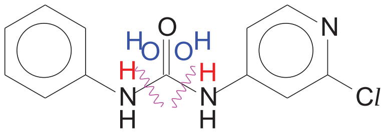
B **is correct**. It is formed between <u>two fourth members</u> of the series.

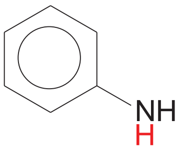
C is incorrect. It is formed between a <u>second</u> and a <u>third member</u> of the series.

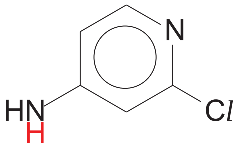
D is incorrect. It is not part of the ethyl ester series. It is a <u>butyl ester</u>.

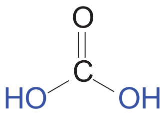
29 **D**

When forchlorfenuron undergoes hydrolysis







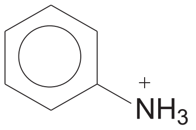


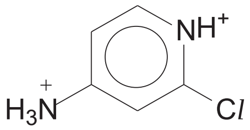
non organic product

are formed.

However as the reaction was carried out in <u>acidic medium</u>,

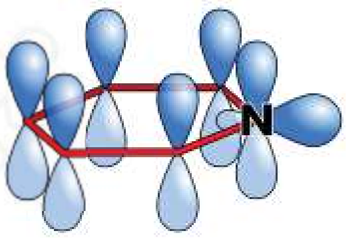
the basic groups will be protonated (e.g. –NH_2)





<u>FYI</u>

The N atom in the pyridine is basic as its lone pair is not delocalised in the ring but occupies the sp^2 hybrid orbital. Instead, it is the unhybridised p orbital (with an electron) overlap with the p orbitals of the adjacent C atoms to form an aromatic ring as illustrated in the diagram on the right.



30 When excess of NaOH (aq) are added to $Fe(NO_3)_2(aq)$, a dirty green precipitate of $Fe(OH)_2(s)$ is formed. **B**

$$[Fe(H_2O)_6]^{2+}(aq) + 2OH^-(aq) \longrightarrow [Fe(OH)_2(H_2O)_4](s) + 2HOH(l)$$

OH^- accepts a proton from the hydrated iron(II) complex (<u>acid–base reaction</u>), resulting in the <u>precipitation</u> of $Fe(OH)_2(s)$.
On standing in air, $Fe(OH)_2(s)$ is <u>oxidised</u> to $Fe(OH)_3(s)$, reddish brown precipitate.

Anderson Junior College
H2 Chemistry 9729 **2017 JC2 Prelim Paper 2 Suggested Solutions**

1 (a) (i) $2Fe^{3+}(aq) + Sn^{2+}(aq) \longrightarrow 2Fe^{2+}(aq) + Sn^{4+}(aq)$ [1]

ignore state symbols

(ii) $E^\ominus (Fe^{3+}/Fe^{2+}) = +0.77$ V [1]
$E^\ominus (Sn^{4+}/Sn^{2+}) = +0.15$ V

$E^\ominus_{cell} = E^\ominus_{reduction} - E^\ominus_{oxidation}$
$= +0.77 - (+0.15)$
$= \underline{+0.62 \text{ V}}$

(iii) Reduction of Fe^{3+} to Fe^{2+} by $SnCl_2$ is <u>spontaneous</u> since the $E^\ominus_{cell}$ calculated in **(ii)** is <u>positive</u>. [2]

$E^\ominus (Fe^{2+}/Fe) = -0.44$ V
$E^\ominus (Sn^{4+}/Sn^{2+}) = +0.15$ V

$E^\ominus_{cell} = -0.44 - (+0.15)$
$= \underline{-0.59 \text{ V}} < 0$ (not spontaneous)

However, the reduction of Fe^{2+} to Fe by $SnCl_2$ is <u>not spontaneous</u> since the $E^\ominus_{cell}$ is <u>negative</u>.

[1]: determine $E^\ominus_{cell}$ for reduction of Fe^{2+}
[1]: conclusion based on both $E^\ominus_{cell}$

(iv) [2]

titration number	1	2	3
initial burette reading / cm^3	0.00	19.95	2.10
final burette reading / cm^3	19.95	40.05	22.15
titre / cm^3	19.95	<u>20.10</u>	<u>20.05</u>

average volume of KI used = ½(20.10 + 20.05)
= <u>20.08 cm^3</u>

$$n(K_2Cr_2O_7) \text{ required} = \frac{20.08}{1000} \times 0.100$$
$= 0.002008$ mol
$= \underline{0.00201 \text{ mol}}$

[1]: correctly determine the titre for run 2 and 3 and used it to find the average titre based on hierarchy rule (i.e. within 0.05 cm^3 in this case)
[1]: $n(K_2Cr_2O_7)$

(v) $6Fe^{2+}(aq) + Cr_2O_7^{2-}(aq) + 14H^+(aq) \longrightarrow 6Fe^{3+}(aq) + 2Cr^{3+}(aq) + 7H_2O(l)$ [1]

ignore state symbols

(vi) n(Fe^{2+}) in 25.0 cm^3 of solution = 6 x 0.00201 [2]

= 0.01206 mol

n(Fe^{2+}) in 250 cm^3 of solution = 0.01206 x 10

= <u>0.1206 mol</u>

mass of Fe present = 0.1206 x 55.8

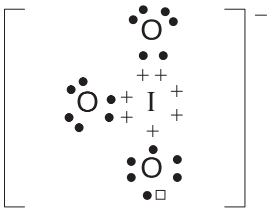
= 6.729 g

% by mass of iron in the sample of iron ore = $\frac{6.729}{11.05}$ x 100%

= <u>60.9 %</u>

[1]: n(Fe^{2+}) originally present in 250 cm^3 (scaling)
[1]: % by mass of iron in iron ore (ecf)

(b) **(i)** [1]



□ e from metal
\+ e from I
• e from O

[1]: correct dot–and–cross

(ii) [1]

$$\mathbf{Mg(IO_3)_2 \longrightarrow MgO + I_2 + \frac{5}{2}O_2}$$

(iii) [2]

- size of cations : <u>Mg^{2+}(0.065nm) > Fe^{2+}(0.061nm)</u>
- charge of the cations is the same
- <u>charge density</u> of M^{2+}: Mg^{2+} < Fe^{2+}
- <u>polarising power</u> of M^{2+}: Mg^{2+} < Fe^{2+}
- Fe^{2+} ion is able to <u>distort</u> electron cloud of IO_3^- anion to a <u>greater extent</u>. Hence, I–O covalent bond within the IO_3^- anion is <u>more weakened</u> in $Fe(IO_3)_2$.
- $Fe(IO_3)_2$ will need to be heated to a <u>lower temperature</u> for decomposition.

[1]: charge density / polarsising power (based on ionic radius quoted)
[1]: extent of distortion / weakening of I–O bond and lower temperature required

(accept comparable / similar temperature)

(iv) [1]

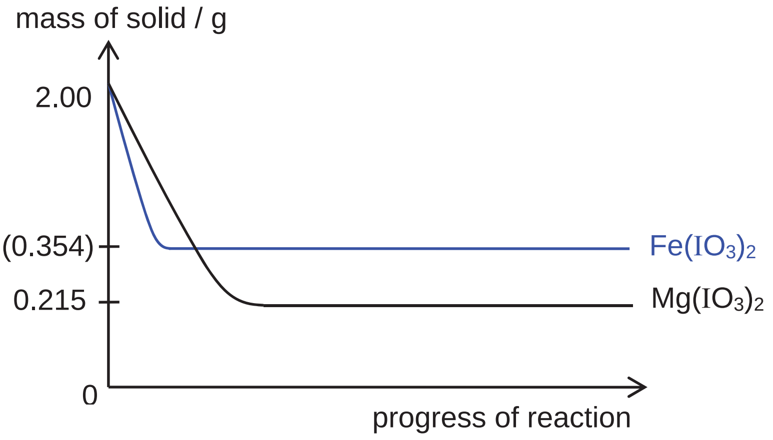
n($Mg(IO_3)_2$) reacted = $\frac{2.00}{24.3+2[126.9+3(16.0)]}$ (or $\frac{2.00}{374.1}$)

= 5.35 x 10^{-3} mol

mass of MgO left, *y* = 5.35 x 10^{-3} x (24.3 + 16.0)

= <u>0.215 g</u>

(v) [1]



[1]: steeper gradient and larger mass of residue

$$n(Fe(IO_3)_2) \text{ reacted} = \frac{2.00}{55.8 + 2[126.9 + 3(16.0)]} \quad \left(\text{or } \frac{2.00}{405.6}\right)$$

$= 4.93 \times 10^{-3}$ mol

mass of FeO left, y = $4.93 \times 10^{-3} \times (55.8 + 16.0)$

= $\underline{0.354 \text{ g}}$

2 (a) Homogenous catalyst increases the rate of a reaction where the reactant(s) and the catalyst exist in the same phase. For example, Fe^{2+}(aq) catalyses the reaction between I^-(aq) and $S_2O_8^{2-}$(aq). [2]

[1]: definition
[1]: example (accept other homogeneous system e.g. H_2O_2/Mn^{2+})

(b) (i) $H_2O_2 \longrightarrow H_2O + \frac{1}{2}O_2$ [1]

(ii) (homogeneous) catalyst [2]

Rate of reaction is slow without cobalt(II) but becomes vigorous in its presence. Cobalt(II) forms an intermediate (cobalt(III)) and is regenerated at the end of the reaction.

[1]: role
[1]: evidence (either one)

(iii) $E^\ominus$ (Co^{3+}/Co^{2+}) = +1.89 V [2]
$E^\ominus$ (O_2/H_2O) = +1.23 V

$E^\ominus_{cell}$ = +1.89 – (+1.23)
= +0.66 V > 0 (spontaneous)

Co^{3+}(aq) readily reduces to Co^{2+}(aq) in aqueous solution but yet Co(III) is formed in this reaction (green solution).

Tartaric acid acts as a ligand which stabilises Co(III).

[1]: shows unstability of Co^{3+}(aq)
[1]: role of tartaric acid

(c) (i) [1]

$$n(O_2) = \frac{96}{24000}$$
$$= 4.00 \times 10^{-3} \text{ mol}$$
$$n(H_2O_2) = 2 \times 4.00 \times 10^{-3}$$
$$= 8.00 \times 10^{-3} \text{ mol}$$
$$[H_2O_2] = \frac{8.00\times10^{-3}}{0.100}$$
$$= 0.0800 \text{ mol dm}^{-3}$$

(ii) When volume of O_2(g) collected reaches 88 cm³, 8 cm³ of O_2 is left to be collected ($\frac{8}{96} = \frac{1}{12}$). [1]

$$1 \longrightarrow \frac{1}{2} \longrightarrow \frac{1}{4} \longrightarrow \frac{1}{8} \longrightarrow \longrightarrow \frac{1}{12}\ [(\frac{1}{2})^n]$$

$\frac{C}{C_o} = (\frac{1}{2})^n$, where n = no. of half–life undergone

$$\frac{1}{12} = (\frac{1}{2})^n$$

$$n = \ln(\frac{1}{12}) \div \ln(\frac{1}{2})$$
$$= 3.58$$

estimated time taken for 88 cm^3 of O_2 collected = 3.58 x 35
= 125 min

(accept 4 x 35 = 140 min because $\frac{8}{96} \approx (\frac{1}{2})^4$ / 3.5 x 35 = 122.5 min because $\frac{1}{12}$ is between $\frac{1}{8}$ and $\frac{1}{16}$, i.e. 3rd and 4th half–life)

(iii) $k = \frac{\ln 2}{t_{½}} = \frac{\ln 2}{35}$ [2]

$= \underline{0.0198\ \text{min}^{-1}}$

(iv) time taken for H_2O_2 to decrease to the same extent (i.e. 50% in this case) will be the same regardless $[H_2O_2]$ is 0.08 mol dm^{-3} or 0.2 mol dm^{-3} because "*half–life is independent of the initial concentration*". [1]

Alternatively,
rate = $k\ [H_2O_2]$ (1st order reaction)
If $[H_2O_2]$ x 2.5 times, rate x 2.5 times.

Hence,

for 0.08 M H_2O_2	0.04 mol dm^{-3} decomposed in 35 min
for 0.2M H_2O_2	0.1 mol dm^{-3} decomposed in 35 min (as rate x 2.5) i.e. $\frac{0.1}{0.2}$ x 100% = 50% decomposed

(v) Titrate the $[H_2O_2]$ remaining at regular time intervals against a standard solution of $KMnO_4$. [1]
Monitor the decrease in mass of the H_2O_2 solution at regular time intervals.

[1] either one

3 **(a)** **(i)** [2]

PSI of PM10 = $\frac{200-100}{350-150}(320-150)+100$ = $\underline{185}$

PSI of CO = $\frac{300-200}{34-17}(20-17)+200$ = $\underline{218}$

[1] each

(ii) overall PSI is the maximum value out of 185, 218, 112, 133 and 150.
Hence overall PSI is $\underline{218}$. [1] ecf

(iii) I would advise the PE teacher to <u>avoid strenuous physical exertion</u> / <u>conduct the lesson indoor</u> (words to the effect based on valid reasoning). [1] ecf

(b) **(i)** [1]

$SO_2 + 2H_2O \longrightarrow SO_4^{2-} + 4H^+ + 2e^-$ (x 5)
$2IO_3^- + 12H^+ + 10e^- \longrightarrow I_2 + 6H_2O$

overall: $\mathbf{5SO_2 + 4H_2O + 2IO_3^- \longrightarrow 5SO_4^{2-} + 8H^+ + I_2}$

(ii) $H^+ + OH^- \longrightarrow H_2O$ [2]

n(NaOH) reacted = 0.01 x 0.005
= 5×10^{-5} mol
n(H^+) reacted with NaOH = 5×10^{-5}

n(SO_2) in 1 m^3 sample of air = $5 \times 10^{-5} \times \frac{5}{8}$
= $\underline{3.125 \times 10^{-5}\text{ mol}}$
mass of SO_2 in 1 m^3 sample of air = 3.125×10^{-5} x [32.1 + 2(16.0)] (or 64.1)
= 0.00200 g
= 2000 μg
concentration of SO_2 = <u>2000</u> μg m^{-3}

[1]: [SO_2] in mol m^{-3}
[1]: [SO_2] in μg m^{-3}

(c) **(i)** In 1 m^3, [1]

mass of air is 1 kg

mass of PM10 is $\frac{2\text{x}10^{-5}}{100}$ x 1 = 2×10^{-7} kg = 0.0002 g = 200 μg

Hence concentration of PM10 is <u>200</u> μg m^{-3}

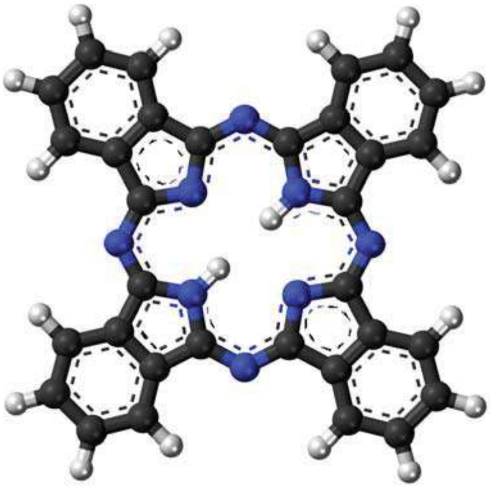
(ii) Since concentration calculated in **(c)(i)** is <u>more than 180</u>, the sample of air has exceeded the limit. [1] ecf

The German city of Leipzig <u>will be fined</u>.

(d) **(i)** $\mathbf{C_{32}H_{18}N_8}$ [1]

(ii) It contains a <u>ring of delocalised pi electron clouds</u> / the p orbitals of the N and C atoms can overlap sideways to form <u>conjugated ring system of pi bonds</u>. [1]

FYI



ball and stick diagram

(e) **(i)** copper and N1: ionic [2]
copper and N2: dative

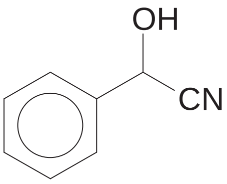
[1] each

(ii) electronic configuration of Cu is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^1$ [1]
electronic configuration of Cu^{2+} is $\mathbf{1s^2 2s^2 2p^6 3s^2 3p^6 3d^9}$

(iii) **8** [1]

(iv) presence of C*l* atoms alters the extent of d–orbital splitting by the ligands and hence energy absorbed by electron (d–d transition) and colour observed will be different [1]

4 **(a)** **(i)** [3]



step 1: HCN in the presence of NaCN (or trace of NaOH)

step 2: $CH_3CH_2CH_2CH_2CH_2COCl$ (do not accept its carboxylic acid)

[1]: structure
[1] each reagent

(ii) The instananeous dipole–induced dipole attractions between the non–polar benzene ring / pentyl ($–(CH_2)_4CH_3$) group in mandelonitrile hexanoate molecule and the non–polar hexane molecule are comparable in strength to that between mandelonitrile hexanoate molecules and between hexane molecules. [1]

(b) **(i)** Hydrolysis (or nucleophilic acyl substitution) of ester and oxidation of 2^o alcohol [2]

[1] each

(ii) the C–C bond in COCN is stronger than the C–C*l* bond in COC*l* [1]
or $CN^–$ in COCN is poorer leaving group than $Cl^–$ in COC*l*
or the carbonyl C in COCN is less electron deficient than in COC*l*

[1] either one

(iii) Add Tollens' reagent and warm, if a silver mirror (or grey ppt) is formed, benzaldehyde is present. Hence, pathway II has occurred. Otherwise, pathway I has occurred. [2]

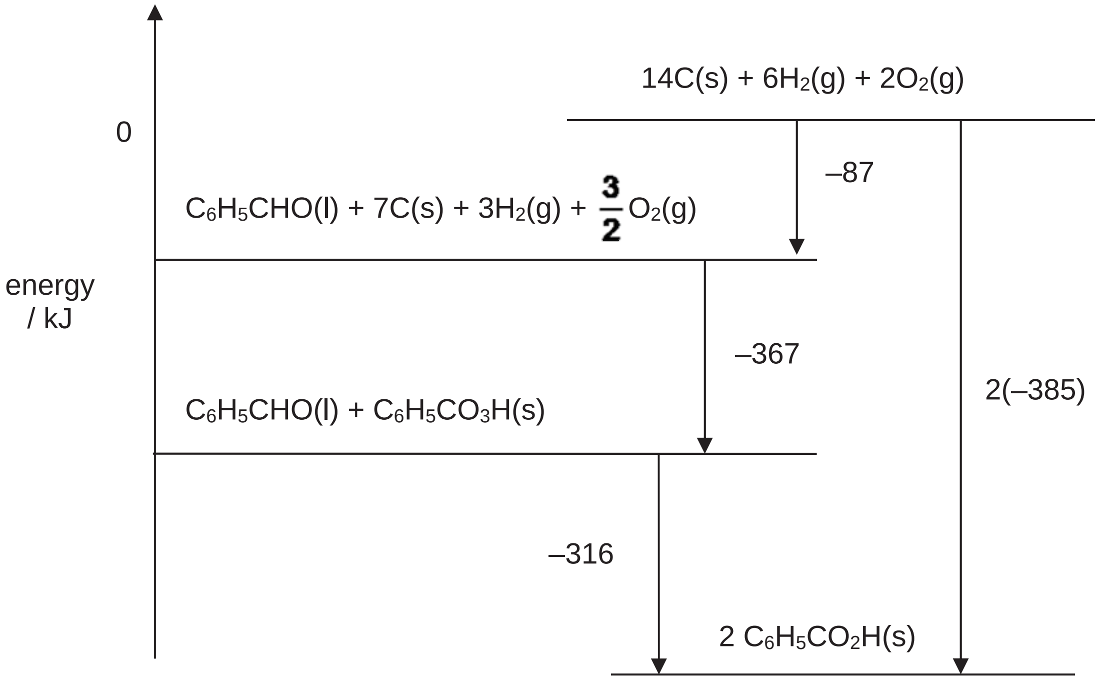
(accept 2,4–dinitrophenylhydrazine, $Cr_2O_7^{2–}/H^+$, $MnO_4^–/H^+$ / yellow (orange) ppt, orange solution turned green, purple solution decolourised due to benzaldehyde)

(c) **(i)** The amount of heat absorbed or evolved when one mole of substance is formed from its constituent elements in their standard states *at* 298 K and 1 bar. [1]

(ii) $–316 = 2\Delta H_f^\ominus(C_6H_5CO_2H) – [(–367) + (–87)]$ [1]
$\Delta H_f^\ominus (C_6H_5CO_2H) = \underline{–385 \text{ kJ mol}^{–1}}$

Need a home tutor? Visit smiletutor.sg

(iii) [3]



[1]: constituent elements at the highest energy level (assigned 0)
[1]: corresponding compounds at the 3 other energy levels
[1]: correct stoichiometry, state symbols and arrow directions

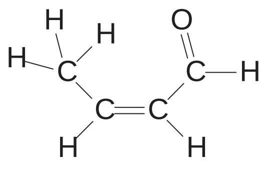
5 **(a)** **(i)** stage I: $K_2Cr_2O_7$, dilute H_2SO_4, warm with immediate distillation [2]

stage III: H_2, Pt / Pd, room temperature (accept Ni, with or w/o warm/heat)

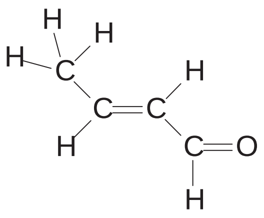
[1] each

(ii) $$\mathbf{C_4H_{10}O + \frac{11}{2}O_2 \longrightarrow 3CO_2 + CO + 5H_2O}$$ [1]

(iii) cis–trans isomerism [2]



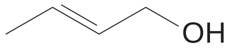
cis



trans

[1]: type of isomerism with correct label
[1]: displayed structure

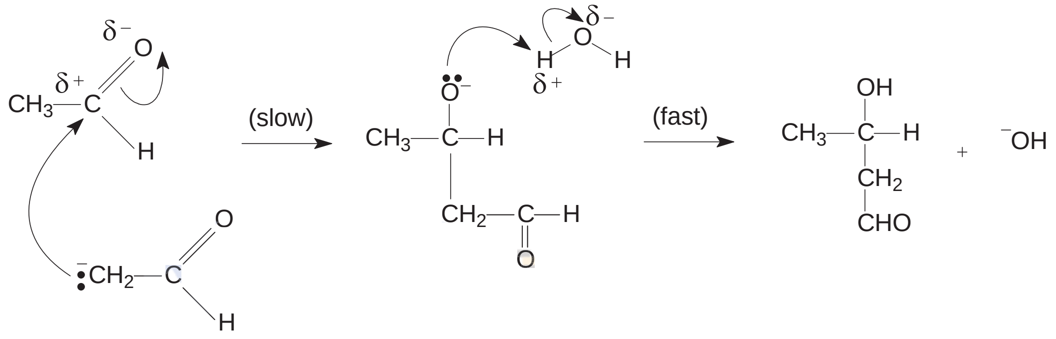
(iv) [2]



G is reduced to **H** (an alcohol) which reacts with sodium metal to give effervescence of H_2. **H** does not react with 2,4–DNPH due to absence of aldehyde/ketone. It reacts with aqueous Br_2 because of the C=C bond present.

[1]: structure of **H**
[1]: explanation (alcohol and C=C essential; do not accept hydroxyl or –OH group in place of alcohol)

(b) **(i)** [2]



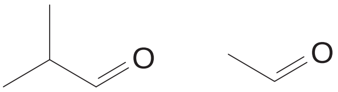
[1]: dipoles (BOD if missing on H_2O), charges and lone pairs
[1]: curly arrows and intermediate

(ii) Able to lose H and OH on adjacent C atoms in 2 different ways, giving rise a different product formed. [1]
Absence of resonance stabilised / delocalised structure / less substituted alkene compared to **G**, resulting in lower yield.

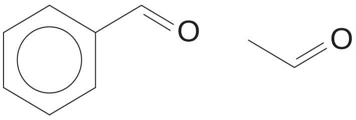
The other product is $CH_2{=}CHCH_2CHO$.

(iii) [3]

I

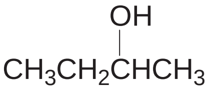


II



[1]: ethanal (CH_3CHO) for both
[1] each for the other 2

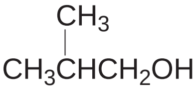
(c) **(i)** [2]



$CH_3CH_2CH(OH)CH_3$

J

2^o



$CH_3CH(CH_3)CH_2OH$

K

1^o

$(CH_3)_3COH$

L

3^o

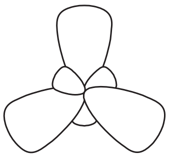
[1]: all 3 structural isomers correctly identified and labelled (in any order)
[1]: corresponding classification of 3 alcohols

(ii) **J** reacts with alkaline aqueous iodine [2]

$$CH_3CH_2CH(OH)CH_3 + 4I_2 + 6OH^- \longrightarrow CH_3CH_2CO_2^- + CHI_3 + 5I^- + 5H_2O$$

[1]: correctly identified the alcohol with positive reaction with I_2/OH^-
[1]: balanced equation

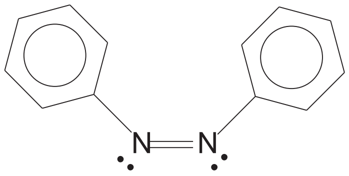
1 **(a)** **(i)** Hybridisation: sp^2 [3]



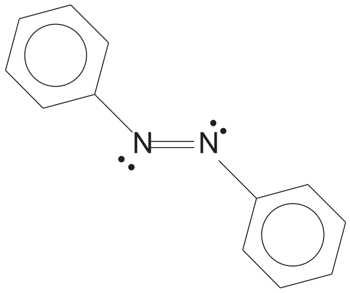
bond angle = 117^o (accept 110^o < angle < 120^o)

[1]: hybridisation
[1]: hybrid orbitals (allow ecf if hybridisation was wrongly determined)
[1]: bond angle (ecf)

(ii) cis–trans isomerism [1]



cis



trans

[1]: type of isomerism
[1]: structure with correct label (ignore if lp are missing)

(iii) cis–isomer [2]

For the cis–isomer, bending / flexing occurred which allows the microstructure to peel away from the surface.

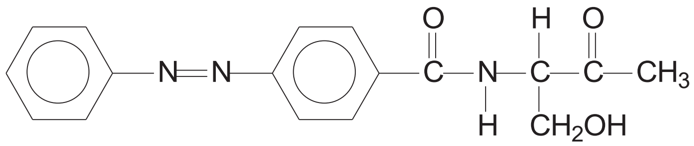
(b) [2]

Observation	Type of reaction	Deduction
Compound **U,** $C_{17}H_{19}N_3O_3$ is not soluble in NaOH(aq) and HC*l*(aq).	(absence of acid–base reaction)	**U** likely to contain amide.
U gives 2 products when heated under reflux with $Cr_2O_7^{2-}/H^+$.	hydrolysis	**U** contains amide or ester group.
Orange $Cr_2O_7^{2-}/H^+$ changes from orange to green during the process.	oxidation	**U** or its hydrolysed products contain 1^o / 2^o alcohol or aldehyde group.
V, $C_{13}H_{10}N_2O_2$ has a proton chemical shift of 13.0 ppm.		**V** contains –COOH. **W** contains 4 C atoms and 1 N atom.

W gives an orange precipitate when treated with 2,4–DNPH but it has no reaction with Tollens' reagent.	condensation / addition–elimination	**W** contains ketone group.
W gives a yellow precipitate and **X** when warmed with I_2/NaOH.	oxidation	**W** contains $RCOCH_3$. **X** is a sodium salt
Effervescence was observed when **W** was treated with $NaHCO_3(aq)$.	acid–base	**W** contains –COOH
When **W** is heated with excess CH_3Cl, it gives **Y**, $C_7H_{14}NO_3Cl$, as the major product.	nucleophilic substitution	**W** contains 1° amine **Y** is a quaternary salt.

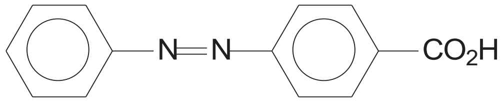
[4]: 14–18 points
[3]: 10–13 points
[2]: 7–9 points
[1]: 3–6 points

U



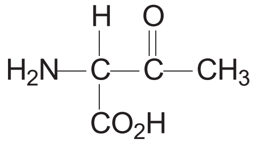
(ecf from **V** and **W**)

V



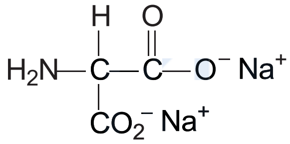
(allow –COOH group to be in other positions)

W



$\mathrm{H_2N{-}CH(CO_2H){-}C(=O){-}CH_3}$

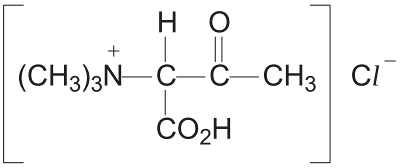
X



$\mathrm{H_2N{-}CH(CO_2^-\,Na^+){-}C(=O){-}O^-\,Na^+}$

(ecf from **W**)

Y



$\mathrm{[(CH_3)_3\overset{+}{N}{-}CH(CO_2H){-}C(=O){-}CH_3]\;Cl^-}$

(ecf from **W**)

[1] each correct structure

(overall only penalised once if final answers are not given to 1 dp for this question)

2 **(a)** **(i)** $K_{sp} = [Ag^+]\,[I^-]$ [1]

(ii) $[Ag^+] = [I^-] = [AgI(aq)]$ [1]

$K_{sp} = (8.9 \times 10^{-9})^2$

$= \underline{7.9 \times 10^{-17}}\ mol^2\ dm^{-6}$

[1]: answer given to 1 dp

(iii) $[Ag^+] = \frac{1}{2}\left(\frac{0.025}{[107.9 + 14.0 + 3(16.0)]}\right)$ [2]

$= \underline{7.4 \times 10^{-5}}\ mol\ dm^{-3}$

Let the solubility of AgI, after addition of $AgNO_3$, be *s*.

$K_{sp} = [Ag^+]\,[I^-]$

$7.92 \times 10^{-17} = (7.36 \times 10^{-5} + s)(s)$

Since solubility of AgI in water is << 10^{-5}, $(7.36 \times 10^{-5} + s) \approx 7.36 \times 10^{-5}$

$s = 1.08 \times 10^{-12}\ mol\ dm^{-3}$

Mass of AgI ppted $= (8.9 \times 10^{-9} - 1.08 \times 10^{-12}) \times 2 \times (107.9 + 126.9)$

$= \underline{4.2 \times 10^{-6}\ g}$

[1]: $[Ag^+]$ added to 2 dm^3 saturated solution

[1]: mass of AgC*l* ppted

(b) **(i)** $\Delta G^{\ominus}_{ppt} = 2.303\ RT \log_{10} K_{sp}$ [1]

$= 2.303(8.31)(298)(\log 2.0 \times 10^{-10})\ J\ mol^{-1}$

$= \underline{-5.5 \times 10^4\ J\ mol^{-1}}$

(ii) $Ag^+ + Cl^- \longrightarrow AgCl(s)$ [3]

White ppt is formed due to the <u>formation of insoluble AgC*l*</u>.

$AgCl + 2NH_3 \longrightarrow [Ag(NH_3)_2]^+ + Cl^-$

White ppt <u>dissolves</u> due to the <u>formation of a complex ion</u>.

$Ag+ + Br^- \longrightarrow AgBr(s)$

Cream ppt is obtained when NaBr is added to the resultant mixture because $\underline{K_{sp}\text{ of AgBr} < K_{sp}\text{ of AgC}l}$

[1] each equation and explanation

(c) $\Delta G^{\ominus}_{ppt} = 2.303\ RT \log_{10} K_{sp}$ [2]

$= 2.303(8.31)(298)(\log_{10} 1.006)$

$= \underline{+14.8\ J\ mol^{-1}}$

Since $\Delta G^{\ominus}_{ppt}$ is +ve, precipitation will <u>not occur</u>

i.e. AgF is soluble

[1]: $\Delta G^{\ominus}_{ppt}$ calculated

[1]: conclusion (ecf)

3 **(a)** **(i)** *Le Chatelier's Principle* states that if a change is made to a reversible reaction in dynamic equilibrium, the position of equilibrium shifts so as to minimise that change and to re–establish equilibrium. [2]

A high temperature favours the forward endothermic reaction which helps to absorb the excess heat. Position of equilibrium lies to the right for stage 1.

[1]: stating Le Chatelier's Principle
[1]: explanation

(ii) $x\text{CO}_2\text{(g)} \rightleftharpoons x\text{CO(g)} + \frac{x}{2}\text{O}_2\text{(g)}$ [1]

(iii) $\Delta H_f^\ominus = \Sigma\text{BE(bonds broken)} - \Sigma\text{BE(bonds formed)}$ [2]
$283 = 2\text{BE(C=O)} - [\text{BE(C}\equiv\text{O)} + \frac{1}{2}\text{BE(O=O)}]$
$\text{BE(C}\equiv\text{O)} = 2(805) - 283 - \frac{1}{2}(496)$
$= \underline{+1079\ \text{kJ mol}^{-1}}$

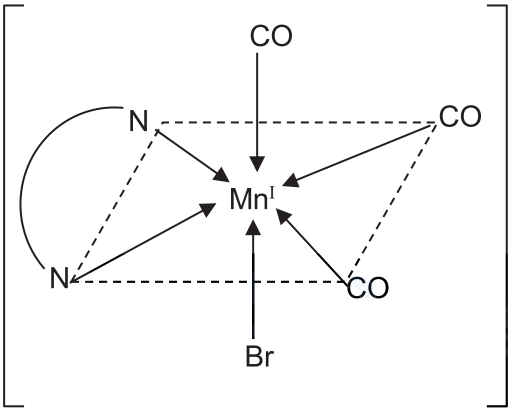
[1]: correct identification of bonds broken and bonds formed
[1]: BE(C≡O) (ecf if 740 is used as BE(C=O); i.e. $+949\ \text{kJ mol}^{-1}$)

(iv) $\Delta G^\ominus = \Delta H^\ominus - T\Delta S^\ominus$ [2]
$237 = 283 - (298)(\Delta S^\ominus)$
$\Delta S^\ominus = \underline{+0.154\ \text{kJ K}^{-1}\text{mol}^{-1}}$
$= \underline{+154\ \text{J K}^{-1}\ \text{mol}^{-1}}$

Entropy change for the reaction is positive, indicating an increase in disorder of system / ways of distributing energy as seen from the equation in **(ii)** where there is an increase in number of moles of gaseous particles.

[1]: $\Delta S^\ominus$, include units
[1]: explaining link between entropy change and disorder of reaction

(b) **(i)** [2]



shape: octahedral

[1]: structure (dative bonds of bidentate ligand cannot be both on axial position)
[1]: shape

(ii) steps 2 and 6 [1]

(iii) step 1: reduction [1]
step 4: acid base reaction

(iv) In the presence of ligands, the partially filled 3d orbitals of Mn are split into two levels (non–degenerate) with a small energy gap (d orbital splitting). [3]
When light passes through, energy corresponding to the blue light is absorbed and an electron in a lower energy d–orbital is promoted to a higher energy d–orbital. (d–d transition).
The orange colour of the solution is the complementary colour of the blue light absorbed.

[1]: partially filled 3d–orbital; small energy gap
[1]: d–d transition
[1]: absorption of blue (complementary to orange)

(c) **(i)** When pH is high, $[H^+]$ is low, position of equilibrium shifts to the right and hence more metal carbonate will be precipitated. [1]

(ii) [3]

$$[Ca^{2+}] = \frac{0.0120}{40.1} = \underline{2.99 \times 10^{-4}\ \text{mol dm}^{-3}}$$

$$[Mg^{2+}] = \frac{0.0073}{24.3} = \underline{3.00 \times 10^{-4}\ \text{mol dm}^{-3}}$$

$$[Cl^-] = \frac{0.0284}{35.5} = \underline{8.00 \times 10^{-4}\ \text{mol dm}^{-3}}$$

$$[HCO_3^-] = \frac{0.0244}{[1.0 + 12.0 + 3(16.0)]} = \underline{4.00 \times 10^{-4}\ \text{mol dm}^{-3}}$$

$CaCl_2 : MgCl_2 : Ca(HCO_3)_2 : Mg(HCO_3)_2 = \underline{2 : 2 : 1 : 1}$

[2]: all concentrations; [1]: any two correct
[1]: correct ratio

(iii) The rock is made up of calcium carbonate, magnesium carbonate, (calcium chloride and magnesium chloride). [2]

Rainwater containing dissolved atmospheric carbon dioxide shifts the equilibrium position of (2) to the right.

$$CO_2(g) + H_2O(l) + MCO_3(s) \rightleftharpoons M(HCO_3)_2(aq)$$

Group 2 bicarbonates are soluble, hence it accounts for the presence of HCO_3^- in mineral water.

Calcium chloride and magnesium chloride present in the rock also can dissolve in the rainwater, causing Ca^{2+}, Mg^{2+} and Cl^- to be present in mineral water.

[1]: composition of rock
[1]: explanation using equation (2) to account for presence of bicarbonate

4 **(a)** **(i)** anode: Zn $\longrightarrow$ Zn^{2+} + $2e^-$ [2]

cathode: I_2 + $2e^-$ $\longrightarrow$ $2I^-$

Zn + I_2 $\longrightarrow$ $2I^-$ + Zn^{2+}

[1]: 2 correct half–equations
[1]: balanced equation

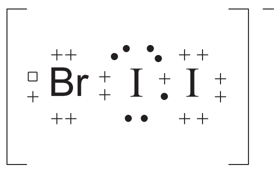
(ii) $E^\ominus_{cell}$ = 0.54 – (– 0.76) [1]
= <u>+1.30 V</u>

(iii) $\Delta G^\ominus$ = –nF$E^\ominus_{cell}$ [1]
= –2 x 96500 x 1.30
= <u>–2.50 x 10^5 J mol^{-1}</u>

(value of n depends on balanced equation in (i))

(iv) To allow Zn^{2+} ions to move from the anode to the cathode during discharging to <u>prevent built up of charges</u> / to <u>maintain electrical neutrality</u>. [1]

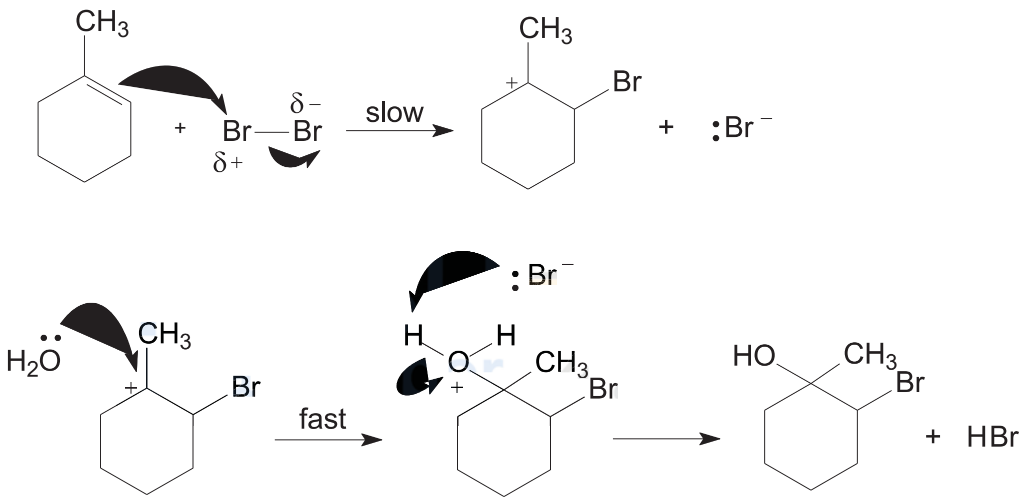
(b) [2]



shape: <u>linear</u>

[1]: dot–and–cross
[1]: shape

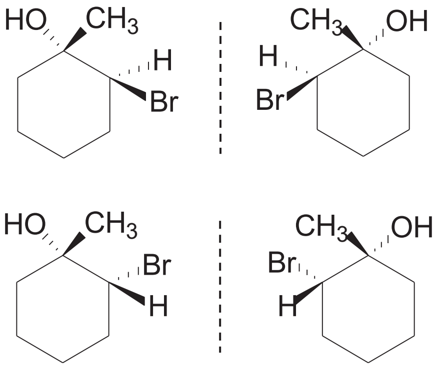
(c) **(i)** electrophilic addition [4]



(accept if deprotonation by Br^- is shown over 2 steps)

[1]: name of mechanism
[1]: dipoles and charges
[1]: lone pairs and curly arrows
[1]: intermediates and product

(ii) [2]



[2]: all 4
[1]: any 2

(iii) Reagents and condition: Na metal, room temperature [2]
Observation: effervescence observed with bromohydrin but no effervescence observed with cyclohexene.

OR
Reagents and condition: anhydrous PCl_5 / $SOCl_2$, room temperature
Observation: white fumes observed with bromohydrin but no white fumes observed with cyclohexene.
OR
Reagents and condition: $KMnO_4$, dilute H_2SO_4, cold/heat
Observation: purple $KMnO_4$ decolourises for cyclohexene but purple $KMnO_4$ remains for bromohydrin.

Alternative (less preferred)
Reagents and condition: NaOH(aq) and heat, cool and add HNO_3 then $AgNO_3$.
Observation: cream ppt observed with bromohydrin but no ppt observed with cyclohexene.

[1]: reagents and condition (do not accept aq. Br_2)
[1]: corresponding observations

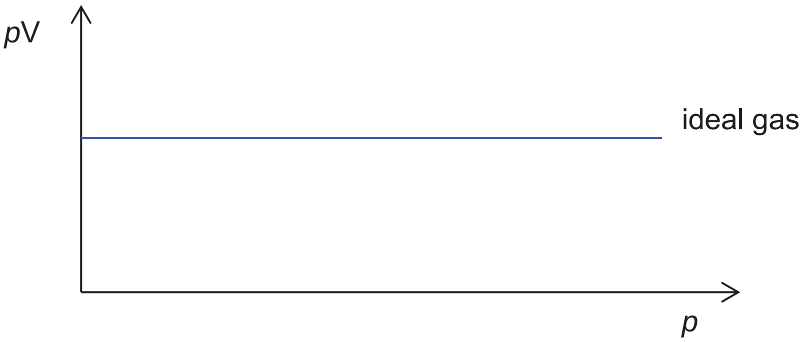
5 **(a)** First I.E. decreases down the group [2]
nuclear charge increase
but electrons are added to next electron/quantum shell
attraction between the nucleus and the valence electron decreases
less energy required to remove the valence electron.

[1]: trend
[1]: explanation in terms of increased nuclear charge but weaker attraction due to valence electron being further from nucleus / at a higher energy level

(b) **(i)** Gas particles occupies negligible space [2]
Negligible forces of attraction between gas particles

[1] each

(ii)



[1]: sketch complete with ideal gas line and axes labelled

(iii) [3]

Experiment No.	pV for gas **D**	pV for gas **E**
1	2275	2320
2	2198	2280
3	2100	2190
4	1953	2140

The pV values of Gas **D** deviates more from a constant value than Gas **E**. Hence, Gas **D** behaves less like an ideal gas than Gas **E**.

Gas **E** is H_2, which is smaller in size and also has weaker instantaneous dipole–induced dipole interactions between molecules and deviate less from ideality while gas **D** is O_2 which is a larger molecule with relatively stronger instantaneous dipole–induced dipole interactions.

[1]: all pV values
[1]: identify gases **D** and **E**
[1]: explanation

(c) **(i)** *Lewis base* is defined as an electron pair donor. [1]

(ii) $PCl_5 + SO_2(OH)_2 \longrightarrow ClSO_3H + POCl_3 + HCl$ [1]

(iii) $H_2SO_4 + H_2O \rightleftharpoons HSO_4^- + H_3O^+$ [1]
$ClSO_3H + H_2O \rightleftharpoons ClSO_3^- + H_3O^+$

The HSO_4^- conjugate base is more stable because there will be greater charge dispersal as it has an additional and more electronegative O. Thus the P.O.E. of H_2SO_4 acid ionisation lie more to the right.

(d) **(i)** The lone pair of electrons on N is delocalised to the carbonyl carbon and hence it is not available in accepting a proton, making **A** a neutral compound. [1]

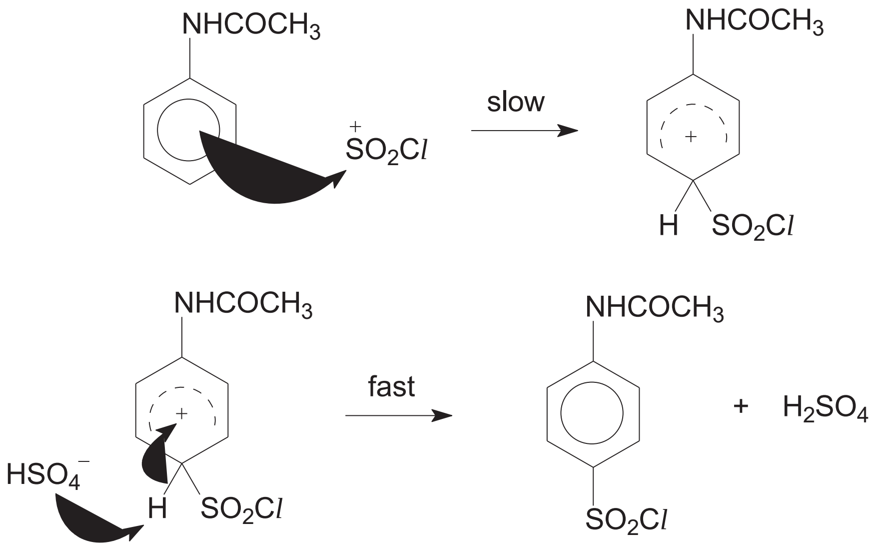
(ii) Boil/heat with NaOH(aq), followed by adding $Br_2(aq)$ to the resultant hydrolysed products. [2]
The product of **A** (phenylamine) will decolorise the orange $Br_2(aq)$ together with a white ppt but not the other isomer.

[1]: reagents and condition (accept HCl, if followed by excess NaOH)
[1]: corresponding observations

(iii) $ClSO_3H + 2H_2SO_4 \longrightarrow ClSO_2^+ + 2HSO_4^- + H_3O^+$ [1]

(accept $ClSO_3H + H_2SO_4 \longrightarrow ClSO_2^+ + HSO_4^- + H_2O$)

(iv) electrophilic substitution [3]



[1]: name of mechanism
[1]: dipoles, charges and lone pairs
[1]: curly arrows, intermediate and regeneration of catalyst

(v) nucleophilic substitution [1]

(vi) H_2O nucleophile competes with NH_3 nucleophile for the electron deficient S to displace Cl^-, affecting the yield of **C**. [1]

6 **(a)** **(i)** [R] $BrO_3^- + 6H^+ + 5e^- \longrightarrow \frac{1}{2}Br_2 + 3H_2O$ [1]

[O] $Br^- \longrightarrow \frac{1}{2}Br_2 + e^-$

$\mathbf{5Br^- + BrO_3^- + 6H^+ \longrightarrow 3Br_2 + 3H_2O}$

(ii) Comparing Expt 1 & 2, [2]

when $[Br^-]$ increases by 2 times, rate increases by 2 times $\left(\frac{8\text{x}10^{-2}}{4\text{x}10^{-2}}\right)$.

$\Rightarrow$ rate is directly proportional to $[Br^-]$
$\Rightarrow$ reaction is <u>1st order with respect to Br^-</u>

Comparing Expt 2 & 3,

when $[BrO_3^-]$ increases by 2 times, rate increases by 2 times $\left(\frac{4\text{x}10^{-2}}{2\text{x}10^{-2}}\right)$.

$\Rightarrow$ rate is directly proportional to $[BrO_3^-]$
$\Rightarrow$ reaction is <u>1st order with respect to BrO_3^-</u>

$[H^+]$ at pH 1.00 = 0.100 mol dm^{-3}
$[H^+]$ at pH 1.30 = 0.0501 mol dm^{-3}

Comparing Expt 1 & 4 and let order of reaction with respect to H^+ be x

$$\frac{8 \text{ x } 10^{-2}}{1 \text{ x } 10^{-2}} = \frac{(0.10)(0.10)(0.1)^x}{(0.05)(0.10)(0.05)^x}$$

x = 2
$\Rightarrow$ reaction is <u>2nd order with respect to H^+</u>

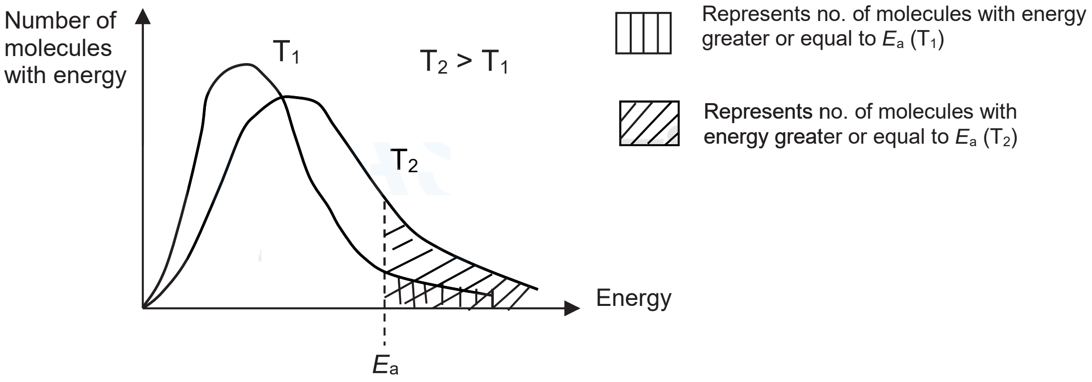
[1] each

(iii) $\mathbf{rate = k\,[BrO_3^-]\,[Br^-]\,[H^+]^2}$ [1]

(iv) Using values from Expt 1, [1]

$8 \text{ x } 10^{-2} = k\,(0.10)\,(0.10)\,(0.10)^2$
k = <u>800 $mol^{-3}\,dm^9\,s^{-1}$</u>

(b) [2]



When temperature increases, the <u>(average) kinetic energies of the reactant molecules increase</u>.
As shown on the diagram, the <u>number of reactant molecules with energy greater or equal to the activation energy</u> will <u>increase</u>.
This results in an increase in the <u>frequency of effective collisions</u>. Hence, the <u>rate of reaction increases</u>.

[1]: correct axes, shape of graph (including beginning from origin) and correct shift of graph and shading when T increase
[1]: correct explanation (in terms of ave KE increase and frequency of effective collision increase)
[1]: correct conclusion

(c) **(i)** As seen in the equation, $\ln k = \ln A - \frac{E_a}{R}(\frac{1}{T})$ [1]

gradient = $-\frac{E_a}{R}$

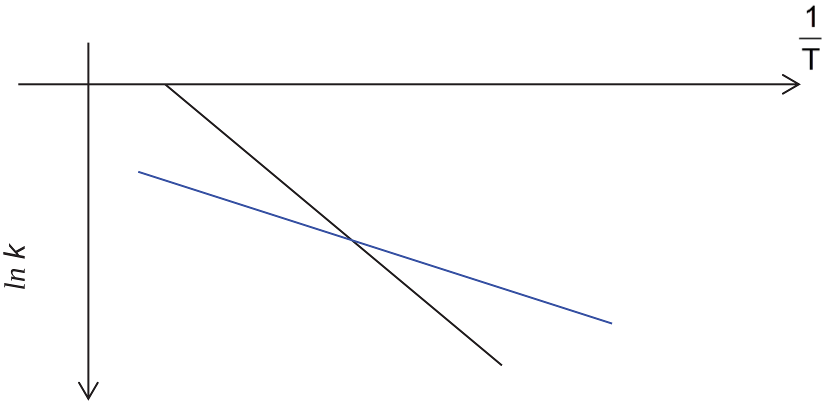
Taking points from the graph, gradient = $\frac{-5.20 - (-6.90)}{(3.10 - 3.30) \times 10^{-3}} = -8500$

$-8500 = -\frac{E_a}{R}$

E_a = <u>+70600 J mol^{-1}</u>

(ii) Both BrO_3^- and Br^- are <u>negatively charged</u> and they experience <u>inter–electronic repulsion</u> and hence E_a of the reaction is high. [1]

(iii) [1]



Since the reaction will have a <u>lower activation energy</u> in the presence of a catalyst, the slope will be <u>less steep.</u>

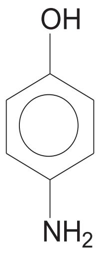
(d) **(i)** [7]

Observation	**Type of reaction**	**Deduction**
K, C_6H_7ON, is not very soluble in water, but dissolves in $HCl(aq)$.	acid–base	**K** contains basic <u>amine</u> group.
K also dissolves in $NaOH(aq)$, but not in $Na_2CO_3(aq)$.	acid–base	**K** contains acidic <u>phenol</u> group Absence of $-CO_2H$.
On reaction with 1 mol of CH_3COCl, **K** forms compound **L**, $C_8H_9O_2N$.	nucleophilic (acyl) substitution / condensation	**L** contains an <u>amide</u> group or <u>ester</u> group.
On reaction with $Br_2(aq)$, **L** produces compound **M**, $C_8H_7O_2NBr_2$.	electrophilic substitution	2 x Br substituted suggests that <u>one of the 2, 4 or 6 position</u> of L is occupied.

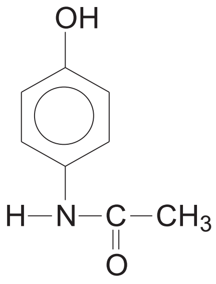
When **K** is reacted with 2 mol of ethanoyl chloride, it produces compound **N**, $C_{10}H_{11}O_3N$.	nucleophilic (acyl) substitution / condensation	**N** contains an amide group and an ester group.
N is not soluble in either HC*l*(aq) or NaOH(aq).	–	absence of basic amine and acidic phenol group
K can be synthesised by treating phenol with dil. HNO_3.	electrophilic substitution	4–nitrophenol (or 2–nitrophenol) is formed.
Followed by reaction with Sn metal and HC*l*.	reduction	4–nitrophenol is reduced to form **K** which contains an amine group.

[3]: 14–18 points
[2]: 9–13 points
[1]: 4–8 points

K

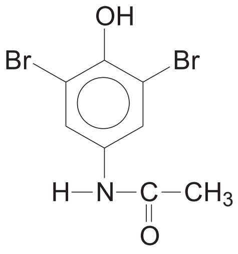


L

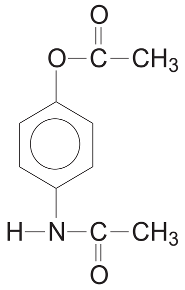


Accepts 2–aminophenol.
Likewise for **L**, **M**, **N**.

M



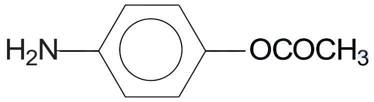
N



(ecf from **L**, i.e. give **P** instead)

[1] each correct structure

(ii) [2]



P is

Presence of nucleophilic $-NH_2$ and–OH groups in **K** allows the 1 mol of CH_3COCl to react with the more nucleophilic $-NH_2$ group to form **L** or to react with the less nucleophilic –OH group to form minor product **P**.

[1]: structure of **P**
[1]: explanation why there 2 possible products and which is major/minor

AJC 2017 JC2 Preliminary Examinations

H2 Chemistry (9729/04) Science Practical Preparation List

Apparatus List

No.	**Apparatus**	**Quantity per student**
1	10 cm^3 measuring cylinder	2
2	50 cm^3 measuring cylinder	1
3	250 cm^3 conical flask	2
4	250 cm^3 volumetric flask	1
5	250 cm^3 beaker	1
6	burette with clip – one labelled as **FA 1**	2
7	25.0 cm^3 pipette with pipette filler	1
8	filter funnel	2
9	weighing bottle	2
10	styrofoam cup with lids	2
11	thermometer (-5 °C to +50 °C at 0.2 °C)	1
12	test tube rack	1
13	test tube (big)	6
14	test tube (small)	6
15	test tube holder	1
16	plastic bag of – litmus papers, plastic teat droppers x 3, tissue, splinter, filter paper strip	1
17	white tile	1
18	retort stand	1
19	safety goggles	1
20	deionised water bottle	1
21	access to weighing balance	communal
22	lighter	1 per bench

Chemicals Required

No.	Label	Identity and concentration	Quantity per student
1	**FA 1**	20 g dm^{-3} $KMnO_4$	80 cm^3
2	**FA 2**	0.100 mol dm^{-3} $Na_2S_2O_3$(aq)	150 cm^3
3	**FA 3**	100 g dm^{-3} KI(aq)	50 cm^3
4	**FA 4**	1 mol dm^{-3} H_2SO_4	50 cm^3
5	**FA 6**	1 mol dm^{-3} of HC*l*	200 cm^3
6	**FA 7**	Na_2CO_3(s)	~ 6g
7	**FA 8**	$NaHCO_3$(s)	~ 5g
8	**FA 9**	50 g dm^{-3} hydrated $Cu(NO_3)_2$(aq)	20 cm^3
9	**FA 10**	50 g dm^{-3} $FeSO_4$ (aq)	20 cm^3

Bench Reagents (shared by 2 students)

No.	Label	Concentration
1	aqueous NaOH	2.0 mol dm^{-3}
2	dilute H_2SO_4	1.0 mol dm^{-3}
3	aqueous NH_3	2.0 mol dm^{-3}
4	KI(aq)	0.1 mol dm^{-3}
5	aluminum powder	-
6	K_2CrO_4(aq)	50 g dm^{-3}
7	starch solution	1%
8	$Na_2S_2O_3$	200 g dm^{-3}
9	concentrated HC*l*	36%
10	limewater	-

Anderson Junior College
H2 Chemistry 9729 **2017 JC2 Prelim Paper 4 Suggested Solutions**

<table>
<tr><th>Qn</th><th>Suggested Mark Scheme</th><th>Mark</th></tr>
<tr><td>1(a)(i), (ii)</td><td>Correctly calculates the volume of FA 1 used and volume of FA 1 used is within 40.00 to 45.00 cm^3, both inclusive.</td><td>1</td></tr>
<tr><td></td><td>Tabulates initial and final burette readings for table and volume of FA 2 used in (a)(ii).

Table has appropriate headers and units.
Tabulation may be vertical or horizontal; lines are not essential but there should be no absences of headers.
Where units have not been included in the header, there should be the appropriate unit for each entry in the table.

Do NOT award this mark if any final and initial burette readings in either table are inverted or 50 is used as the initial burette reading in either table.</td><td>1</td></tr>
<tr><td></td><td>All the final/initial burette readings for all accurate titres in BOTH tables are recorded to the nearest 0.05 cm^3.

<i>Treat all titres as “accurate” unless labelled rough or 1st titre is of lower precision than subsequent titres</i></td><td>1</td></tr>
<tr><td></td><td>Has at least TWO uncorrected titires for end–point within 0.10 cm^3

* refers to uncorrected titres i.e. ignore arithmetical errors made when calculating the titre values</td><td>1</td></tr>
<tr><td></td><td>Check and correct, if necessary, subtractions in the titre table.

Examiner then selects the “best” titre using the hierarchy:
two identical; titres within 0.05 cm^3; titres within 0.1 cm^3, etc

$\text{Calculate student titre x } \dfrac{\text{student volume of FA 1 added}}{\text{teacher volume of FA 1 added}}$

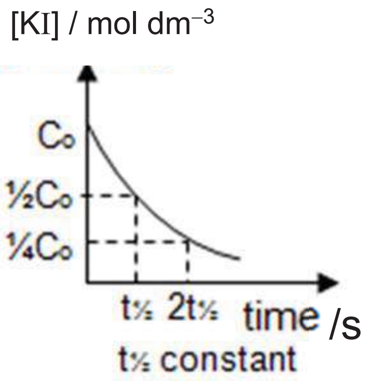
<i>Teacher’s results</i>
<table>
<tr><th>Shift</th><th>volume of FA 1 added / cm^3</th><th>average titre volume / cm^3</th></tr>
<tr><td>1</td><td>40.90</td><td>25.78</td></tr>
<tr><td>3</td><td></td><td>25.85</td></tr>
</table>

Calculate difference in teacher and student scaled values (Δ <i>titre</i>) and award “quality” marks as below.

Give 3 marks if this difference is within 0.20 cm^3
Give 2 marks if this difference is > 0.20 cm^3 but $\leq$ 0.40 cm^3
Give 1 mark if this difference is > 0.40 cm^3 but $\leq$ 0.60 cm^3
Give 0 marks for a difference that is > 0.60 cm^3.</td><td>3</td></tr>
<tr><td></td><td></td><td></td></tr>
</table>

(a)(iii)	Obtains appropriate 'average', to 2 d.p., from any experiments with uncorrected end–point values within 0.10 cm^3. *Do not award this mark if the titres used are not identified either in the table (by, for examples, a tick) or in a calculation.* *Do **not** award this mark if there are arithmetic errors in the table.*	1
(b)(i)	Let the volume of **FA 1** used for dilution be V_{FA1} cm^3. n(MnO_4^-) in **FA 1** used = $\frac{V_{FA1}}{1000} \times 0.100 = V_{FA1} \times 10^{-4}$ mol n(MnO_4^-) in 25.0 cm^3 of **FA 5** = $\frac{V_{FA1} \times 10^{-4}}{10} = V_{FA1} \times 10^{-5}$ mol	1 1
(b)(ii)	n($S_2O_3^{2-}$) = 5 x n(MnO_4^-) in 25.0 cm^3 of **FA 5** = $V_{FA1} \times 10^{-5} \times 5$ mol	1
(b)(iii)	Let the average volume of **FA 2** used = V_m cm^3. [$S_2O_3^{2-}$] in **FA 2** = $V_{FA1} \times 10^{-5} \times 5 \times \frac{1000}{V_m}$ mol dm^{-3}	1
(c)	No, using burettes to measure the volume of **FA 3** and **FA 4** will not improve the accuracy of the titration data as <u>both **FA 3** and **FA 4** are used in excess</u> OR the <u>amount of I_2 formed</u> only <u>depends on the amount of $KMnO_4$ used</u>, which was already accurately measured.	1
(d)	% error in volumetric flask $= \frac{0.15 \times 100}{250} = 0.06\%$ % error in pipette = $\frac{0.1 \times 100}{25.0} = 0.4\%$ % error in burette = $\frac{2(0.05) \times 100}{25.65} = 0.390\%$ Total error = <u>0.850%</u> Also accept if the error for measuring 40.00 cm^3 and 45.00 cm^3 of **FA 1** with burette is included, then the total error = 1.07 – 1.1%	1
(e)(i)	Order of reaction = 1	1
(e)(ii)	Since total volume of reaction mixture is kept constant, • [KI] $\propto V_{KI}$ used Also since rate $\alpha \frac{1}{t}$ (as the volume of $Na_2S_2O_3$ is kept constant) AND • when the volume of KI is doubled, the time taken for the iodine to appear is halved. Rate of reaction is directly proportional to [KI]. OR • $V_{KI} \times t$ = constant	1 1

(e)(iii)



1

(e)(iv)

1. Using a 50 cm^3 measuring cylinder, measure 40 cm^3 of KI and pour the solution into a 250 cm^3 conical flask.
2. Using a 10 cm^3 measuring cylinder, measure 10 cm^3 of $Na_2S_2O_3$ and add this into the same conical flask.
3. Using a 25 cm^3 measuring cylinder, measure 25 cm^3 of H_2O and pour into the conical flask.
4. Measure 25 cm^3 of X using another 25 cm^3 measuring cylinder.
5. Rapidly pour X into the conical flask and start the stop–watch at the same time.
6. Swirl the reaction mixture.
7. Note the time taken for brown colour of iodine to first appear.

Marks	Requirements	Key Marking Points
[2]	Appropriate quantities of substances used	1. vol of $Na_2S_2O_3$ = 10 cm^3 2. vol of KI = 40 cm^3 or 20 cm^3 3. vol of X = 25 cm^3 (or other volume except 50 cm^3) 4. vol of water added to maintain total volume at 100 cm^3 (1 mark for any 2 points, 2 marks for all 4 points)
[1]	Appropriate apparatus and their capacities	1. $Na_2S_2O_3$: 10 cm^3 measuring cylinder or 50 cm^3 burette or 10 cm^3 pipette 2. KI / X /H_2O : 50 cm^3 / 25 cm^3 measuring cylinder or 50 cm^3 burette or 25 cm^3 pipette 3. 250 cm^3 conical flask
[2]	Essential experimental details to ensure reliable results	1. Start reaction by adding X last and rapidly 2. Simultaneously start reaction with starting stopwatch 3. Swirl the reaction mixture 4. Stop stopwatch when brown colour of iodine appears (1 mark for any 2 points, 2 marks for all 4 points)

5

<table>
<tr><th>Qn</th><th>Suggested Mark Scheme</th><th>Mark</th></tr>
<tr><td>2</td><td>
<table>
<tr><td>Mass of empty weighing bottle / g</td><td></td></tr>
<tr><td>Mass of weighing bottle and FA 7/8 / g</td><td></td></tr>
<tr><td>Mass of weighing bottle and <u>residual</u> FA 7/8 / g</td><td></td></tr>
<tr><td>Mass of FA 7/8 used / g</td><td></td></tr>
</table>
<table>
<tr><td>Highest / Lowest temperature reached / ^{o}C</td><td></td></tr>
<tr><td>Initial temperature of FA 6 / ^{o}C</td><td></td></tr>
<tr><td>Temperature rise / drop / ^{o}C
Or Change in temperature / ^{o}C</td><td></td></tr>
</table>
• Tabulates <u>weighings / temperature</u> in appropriate manner. Tabulation may be vertical or horizontal; lines are not essential but there should be no absence of headers.
• Correct use of <u>highest</u> and <u>lowest</u> temperature.
• Correct use of <u>rise/ drop</u>.
• Tables have correct <u>headers</u> and units. Where <u>units</u> have not been included in the header, there should be the appropriate unit for <u>each entry</u> in the tables.
• For students who record “Change” in temperature, the corresponding sign must be included.
• <i>Ignore the absence of a calculated mass for FA 7/8.</i>
</td><td>1</td></tr>
<tr><td></td><td>Complete set of masses (refer to table above)
<i>Do not award mark if Tare function is used.</i>

The mass of FA 7/8 weighed is within specified limits.
4.45 g ≤ FA 7 ≤ 5.05 g
3.45 g ≤ FA 8 ≤ 4.05 g

Correctly calculate the mass of FA 7/8.</td><td>1</td></tr>
<tr><td></td><td>All the mass readings are recorded to 3 d.p.
All temperatures are recorded to 0.1 ^{o}C</td><td>1</td></tr>
<tr><td></td><td><u>Accuracy mark.</u>

If $\frac{\Delta T}{\text{mass of FA} 7/8}$ for both experiments +/– 0.05 from Teacher’s result

If $\frac{\Delta T}{\text{mass of FA} 7/8}$ for both experiments +/– 0.2 from Teacher’s result

<i>Teacher’s results</i>
<table>
<tr><th>Shift</th><th>ΔT / m for FA 7</th><th>ΔT / m for FA 8</th></tr>
<tr><td>1</td><td>6.2 / 4.523 = 1.371</td><td>5.4 / 3.620 = 1.492</td></tr>
<tr><td>3</td><td>6.4 / 4.831 = 1.325</td><td>5.6 / 3.674 = 1.524</td></tr>
</table>
</td><td>2
(max)

1</td></tr>
<tr><td></td><td></td><td></td></tr>
<tr><td>(a)</td><td>Correctly calculates q = $V_{\textbf{FA 6}}c\Delta T$ = 50 x 4.2 x ΔT
Ignore if q has sign or has a wrong unit.
Ignore if ΔT was calculated wrongly.</td><td>1</td></tr>
</table>

(b)	Correctly calculates no of moles of HC*l* = 1 x $\frac{50}{1000}$ = 0.0500 mol	1
(c)	Correctly calculates number of moles of Na_2CO_3 used = $\frac{\text{mass of FA 7 used}}{106.0}$	1
(d)	Since 0.0500 moles of HC*l* requires only 0.0250 moles of Na_2CO_3 for complete reaction, Na_2CO_3 is in excess.	1
(e)	Correctly calculates $\Delta H_1 = -\frac{q}{nHCl} = -\frac{q}{0.0500} \times 2 = -a$ kJ mol^{-1} Correct sign for ΔH_1 = –ve	1
(f)	Correctly calculates q = $V_{FA\,6}c\Delta T$ = 50 x 4.2 x ΔT Ignore if q has sign or has a wrong unit. Ignore if ΔT was calculated wrongly.	1
(g)	Correctly calculates number of moles of $NaHCO_3$ used = $\frac{\text{mass of FA 8 used}}{84.0}$	1
(h)	Recognises that the limiting reagent is $NaHCO_3$ and uses the number of moles of $NaHCO_3$ to determine ΔH. Correctly calculates $\Delta H_2 = +\frac{q}{nNaHCO_3} = +b$ kJ mol^{-1} Correct sign for ΔH_2 = +ve	1
(i)	Correctly calculates $\Delta H_3 = 2\Delta H_2 - \Delta H_1 = 2b - (-a)$ kJ mol^{-1}	1
	Shows working in all calculations in **1(a)(iii)**, **1(b)**, **2(a) – (c) and 2(e) – (i)**. All calculations must be relevant although they may not be complete or correct. *Any calculations not attempted loses this mark.*	1
	Shows appropriate significant figures (3 s.f.) in all final answers in **1(b)**, **2(a) – (c) and 2(e) – (i)**. Shows appropriate units in **1(a)(iii)**, **1(b)**, **2(a) – (c) and 2(e) – (i)**. *Any calculations not attempted loses this mark.*	1
(j)	No effect. This is because HC*l* was already used in excess, hence ΔH_2 calculated is independent of the number of moles of HC*l*. Therefore, ΔH_3 will not be affected.	1

Qn	Suggested Mark Scheme
3(a)	

	observations for FA 9	observations for FA 10
Add NaOH(aq), followed by a spatula load of aluminium powder.	blue ppt (1), insoluble in excess NaOH (1). pungent gas evolved turned moist red litmus blue (1) – NH_3 (1)	
Add concentrated HCl dropwise.	blue solution turns (green) then yellowish green/yellow (1) no effervescence observed (1). no NO_2 gas evolved (1).	
To the **FA 9** and concentrated HCl mixture, add deionised water.	yellowish–green/yellow solution turns (green) then blue (1)	
Add KI(aq).	(white/cream) ppt in brown solution (1)	
To the resulting solution, add $Na_2S_2O_3$(aq).	brown colour discharged (1) white/cream ppt observed (1)	
Add 1 cm^3 dilute H_2SO_4 followed by 1 cm^3 of K_2CrO_4(aq). Divide into 2 portions.		pale blue green solution turns (green) then yellowish–brown (1)
To one portion, add KI(aq) followed by 1 cm^3 of starch solution.		brown solution formed (1) turns dark blue / blue–black on addition of starch. (1)
To the other portion, add NaOH(aq).		brown ppt (1) insoluble in excess NaOH.

Scoring for **QA** of **FA 9** and **FA 10:**	
Number of correct observations	Award (max 4)
11 and more	4
7 – 10	3
4 – 6	2
at least 3	1

<table>
<tr><th>Qn</th><th>Suggested Mark Scheme</th><th>Mark</th></tr>
<tr><td></td><td>**SUMMARY**

FA 9: Cu^{2+}, NO_3^- (do not accept NH_4^+, NO_2^-)
FA 10: Fe^{2+}
Correctly identifies both cations

Correctly identifies anion and supports answer with evidence that NH_3 evolved with NaOH and A*l* powder (either NO_3^- or NO_2^-) but no NO_2 gas evolved on addition of acid (so can only be NO_3^-).</td><td>1

1</td></tr>
<tr><td></td><td></td><td></td></tr>
<tr><td>**(b)(i)**

(ii)</td><td>ligand exchange

redox</td><td>1

1</td></tr>
<tr><td></td><td></td><td></td></tr>
<tr><td>**(c)(i)**</td><td>
<table>
<tr><th></th><th>dilute HC*l*</th><th>NaOH(aq)</th></tr>
<tr><td>MgO</td><td>soluble</td><td>insoluble</td></tr>
<tr><td>Al_2O_3</td><td>soluble</td><td>soluble</td></tr>
<tr><td>SiO_2</td><td>insoluble</td><td>insoluble</td></tr>
<tr><td>ZnO</td><td>soluble</td><td>soluble</td></tr>
</table>

All correct
At least 2 correct</td><td>2(max)
1</td></tr>
<tr><td></td><td></td><td></td></tr>
<tr><td>**(ii)**</td><td>Outline a logical sequence of testing that
• successfully identifies **FA 11**
• reduces the possibility to 2
• reduces the possibility to 3

(Broad workable outline, not on details)

Deduction with:
• correct formula of species present (or balanced equations)
• correct observations
• explanations

8 out of 10 given (≥ 80%)

5 – 7 (≥ 50%)

At least 3 (30%)</td><td>2(max)
1
0

3(max)

2

1</td></tr>
</table>

Suggested Plan

Test	Observation	Deduction	Explanation
1. Add excess aq NaOH to a portion of **FA 11**.	Dissolves (1)	Al_2O_3 or ZnO	Both are amphoteric oxides, react with aq NaOH forming soluble salts: (1) $Al_2O_3(s) + 2OH^-(aq) + H_2O(l) \longrightarrow \underline{2Al(OH)_4^-(aq)}$ $ZnO(s) + 2OH^-(aq) + H_2O(l) \longrightarrow \underline{Zn(OH)_4^{2-}(aq)}$
	Does not dissolve (1)	SiO_2 or MgO.	MgO is a basic oxide and has no reaction with a base/an alkali. (1) SiO_2 an acidic oxide with giant molecular structure, no reaction with aqueous alkali nor soluble in aqueous solution. (1) (SiO_2 would only react with hot conc. NaOH)
2. If oxide not soluble in step 1, add aq HC*l* to a portion of **FA 11**	Oxide insoluble (1)	SiO_2	An acidic oxide which does not react nor dissolve in aq acid.
	Dissolves (1)	MgO	MgO is a basic oxide that reacts and dissolve in dil. HC*l*. $MgO(s) + 2H^+(aq) \longrightarrow \underline{Mg^{2+}(aq)} + H_2O(l)$
3. If oxide soluble in step 1, dissolve a portion of **FA 11** in dil. HC*l*.			The amphoteric oxides react and dissolve in dil. HC*l*. $ZnO(s) + 2H^+(aq) \longrightarrow Zn^{2+}(aq) + H_2O(l)$ $Al_2O_3(s) + 6H^+(aq) \longrightarrow 2Al^{3+}(aq) + 3H_2O$
To the solution, add aq NH_3 till excess	white ppt, soluble in excess aq NH_3 (1)	ZnO	$Zn^{2+}(aq) + 2OH^-(aq) \longrightarrow Zn(OH)_2(s)$ $Zn(OH)_2(s) + 4NH_3(aq) \longrightarrow \underline{Zn(NH_3)_4^{2+}(aq)} + 2OH^-(aq)$ (1)
	white ppt, insoluble in excess aq NH_3 (1)	Al_2O_3	$\underline{Al(OH)_3(s)}$

ANDERSON JUNIOR COLLEGE

2017 JC 2 PRELIMINARY EXAMINATIONS

NAME:___________________________ **PDG:**_____ /16

CHEMISTRY **9729/04**

Paper 4 Practical

23 August 2017

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, PDG and register number on all the work you hand in.
Give details of the practical shift and laboratory where appropriate, in the boxes provided.
Write in dark blue or black pen.
You may use a pencil for any diagrams, graphs or rough working.
Do not use staples, paper clips, glue or correction fluid.

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

The use of an approved scientific calculator is expected, where appropriate.
You may lose marks if you do not show your working or if you do not use appropriate units.
Quantitative Analysis Notes are printed on pages 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 thiosulfate ions

Potassium manganate(VII), $KMnO_4$, is an oxidising agent that can be used to determine the concentration of a solution of sodium thiosulfate.

To do this, aqueous potassium manganate(VII) is used to react with excess aqueous potassium iodide, KI to produce iodine solution. In this reaction, iodide ions are oxidised to iodine by manganate(VII) ions in acidic solution.

$$2MnO_4^-(aq) + 10I^-(aq) + 16H^+(aq) \longrightarrow 2Mn^{2+}(aq) + 5I_2(aq) + 8H_2O(l)$$

The iodine produced is then titrated with aqueous thiosulfate ions.

$$2S_2O_3^{2-}(aq) + I_2(aq) \longrightarrow S_4O_6^{2-}(aq) + 2I^-(aq)$$

You are provided with the following.
FA 1 is 0.100 mol dm^{-3} of potassium manganate(VII), $KMnO_4$.
FA 2 is an aqueous solution of sodium thiosulfate, $Na_2S_2O_3$.
FA 3 is an aqueous solution of potassium iodide, KI.
FA 4 is dilute sulfuric acid, H_2SO_4.

In this question, you are to perform a dilution of the $KMnO_4$ provided before carrying out a titration. The data from this titration will be used to determine the concentration of $S_2O_3^{2-}$ in **FA 2**.

(a) (i) Dilution of FA 1

1. Fill a burette with **FA 1**.
2. Run between 40.00 cm^3 and 45.00 cm^3 of **FA 1** into 250 cm^3 volumetric flask.
3. Make up to the mark with deionised water.
4. Shake the volumetric flask to obtain a homogeneous solution and label this solution **FA 5**.
5. Record all burette readings and the volume of **FA 1** that you used for dilution in the space provided in Table 1.1 below.

Table 1.1

Final burette reading / cm^3	
Initial burette reading / cm^3	
Volume of **FA 1** used / cm^3	

[1]

(ii) Titration of iodine liberated by FA 5 with FA 2

1. Fill a second burette with **FA 2**.
2. Using a pipette, transfer 25.0 cm^3 of **FA 5** into the conical flask.
3. Using appropriate measuring cylinders, add about 10 cm^3 of **FA 3** and about 10 cm^3 of **FA 4** to the conical flask.
4. Run **FA 2** from the burette into this flask until the colour of the solution just turns colourless.
5. Record your titration results in the space provided below. Make certain that your recorded results show the precision of your working.
6. Repeat points **1** to **5** as necessary until consistent results are obtained.

Results

[6]

(iii) 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]

(b) **(i)** Calculate the amount of manganate(VII) ions, MnO_4^-, in 25.0 cm^3 of **FA 5**.

amount of MnO_4^- in 25.0 cm^3 of **FA 5** = ……………………………………….. [2]

(ii) Given that one mole of manganate(VII) ions liberates sufficient iodine from potassium iodide to react with five moles of thiosulfate ions, $S_2O_3^{2-}$, calculate the number of moles of thiosulfate ions present in the volume of **FA 5** that you found necessary in the titration.

amount of $S_2O_3^{2-}$ ions needed = ……………………………………….. [1]

(iii) Determine the concentration, in mol dm^{-3}, of $S_2O_3^{2-}$ in **FA 2**.

concentration of $S_2O_3^{2-}$ in **FA 2** = ……………………………………….. [1]

(c) A student suggests that the volumes of **FA 3** and **FA 4** should be measured using a burette instead of measuring cylinders, so as to improve the accuracy of the titration data.

Do you agree with the student? Explain your answer.

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

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

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

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

(d) A teacher performs this same experiment, using the quantities described earlier, and obtains a mean titre volume of 25.65 cm^3.

The errors (uncertainties) associated with each reading using a volumetric flask, pipette and burette are ± 0.15 cm^3, ± 0.1 cm^3 and ± 0.05 cm^3 respectively.

Calculate the maximum total percentage error (uncertainty) of this mean titre value.

[1]

(e) **Planning**

X is another oxidising agent that can react with potassium iodide, KI, to give iodine, I_2.

The rate equation for this reaction is rate = k $[KI]^a$ $[X]^b$, where a and b are the orders of reaction with respect to KI and X respectively.

An investigation was carried out to determine the order of reaction with respect to KI. This is done by mixing different volumes of the X and KI, together with a fixed volume of sodium thiosulfate, $Na_2S_2O_3$. The I_2 produced from the reaction between X and KI will react with the $Na_2S_2O_3$ added and be reduced back to iodide, I^-. When all the $Na_2S_2O_3$ is used up, the colour of I_2 will appear.

The kinetics of this reaction can be determined by measuring the time taken for the colour of I_2 to first appear.

The following experiments were carried out to determine the order of reaction with respect to KI.

Experiment	volume of X / cm^3	volume of KI / cm^3	volume of H_2O / cm^3	volume of $Na_2S_2O_3$ / cm^3	time / s
1	50	40	0	10	40
2	50	20	20	10	82

(i) From the data given above, state the order of reaction with respect to KI.

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

(ii) Explain clearly how the above results support your answer in **(e)(i)**.

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

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

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

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

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

(iii) Sketch the graph of concentration of KI against time based on the order you have determined in **(e)(i).**

[1]

(iv) You are to plan an investigation for **one further experiment**, which together with those above, will allow you to determine the order of reaction with respect to X.

In your plan, you should include details of

- the volumes of the solutions you would use
- the apparatus and their capacities that you would use
- the procedure that you would follow, including details on how you would obtain reliable results.

…………………………………………………………………………………………………… [5]

[Total: 23]

2 Determination of the enthalpy change of a reaction, ΔH_r

You are required to obtain values of ΔH for two chemical reactions and use them to calculate ΔH for a third reaction.

FA 6 is 1 mol dm^{-3} hydrochloric acid, HCl.
FA 7 is solid sodium carbonate, Na_2CO_3.
FA 8 is solid sodium hydrogencarbonate, $NaHCO_3$.

Experiment 1

1. Weigh an empty weighing bottle.
2. Place between 4.50 g and 5.00 g of **FA 7** in the weighing bottle.
3. Place a dry Styrofoam cup inside a 250 cm^3 beaker.
4. Using a measuring cylinder, place 50 cm^3 of **FA 6** into the Styrofoam cup.
5. Place the lid onto the cup through the thermometer from the top. Stir the liquid in the cup with the thermometer and measure its temperature when it reaches a steady temperature. Read and record this temperature in your table.
6. Tip **cautiously** the contents of the weighing bottle into the acid in the Styrofoam cup, stir gently with the thermometer and record the **highest** temperature obtained in your table.
7. Calculate the change in temperature.
8. Reweigh the empty weighing bottle.

In an appropriate format in the space provided below, record all measurements of mass and temperature. Calculate the mass of **FA 7** used.

Results

(a) If 4.2 J are required to raise the temperature of 1 cm^3 of solution by 1 ^{o}C, calculate the amount of heat absorbed in **Experiment 1**.

[1]

(b) Calculate the number of moles of HC*l* added to the cup.

[1]

(c) Calculate the number of moles of Na_2CO_3 added to the cup.
[M_r (Na_2CO_3) = 106.0]

[1]

(d) Explain which reagent was added in excess.

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

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

(e) Calculate the enthalpy change ΔH_1 for the following reaction.

$$Na_2CO_3(s) + 2HCl(aq) \longrightarrow 2NaCl(aq) + H_2O(l) + CO_2(g) \qquad \text{---}\ \Delta H_1$$

[1]

Experiment 2

1. Weigh an empty weighing bottle.
2. Place between 3.50 g and 4.00 g of **FA 8** in the weighing bottle.
3. Place a dry Styrofoam cup inside a 250 cm^3 beaker.
4. Using a measuring cylinder, place 50 cm^3 of **FA 6** into the Styrofoam cup.
5. Place the lid onto the cup through the thermometer from the top. Stir the liquid in the cup with the thermometer and measure its temperature when it reaches a steady temperature. Read and record this temperature in your table.
6. Tip **cautiously** the contents of the weighing bottle into the acid in the Styrofoam cup, stir gently with the thermometer and record the **lowest** temperature obtained in your table.
7. Calculate the change in temperature.
8. Reweigh the empty weighing bottle.

In an appropriate format in the space provided below, record all measurements of mass and temperature. Calculate the mass of **FA 8** used.

Results

[5]

(f) If 4.2 J are required to raise the temperature of 1 cm^3 of solution by 1 ^oC, calculate the amount of heat absorbed in **Experiment 2**.

[1]

(g) Calculate the number of moles of $NaHCO_3$ added to the cup.
[M_r ($NaHCO_3$) = 84.0]

[1]

(h) Calculate the enthalpy change ΔH_2 for the following reaction.

$$NaHCO_3(s) + HCl(aq) \longrightarrow NaCl(aq) + H_2O(l) + CO_2(g) \quad \text{---} \ \Delta H_2$$

[1]

(i) Use your answers in **(e)** and **(h)** to calculate ΔH_3 for the following reaction.

$$2NaHCO_3(s) \longrightarrow Na_2CO_3(s) + H_2O(l) + CO_2(g) \quad \text{---} \ \Delta H_3$$

[3]

(j) A student decides to repeat the experiment with 2.0 mol dm^{-3} HC*l* in **Experiment 2** instead of the given concentration of 1.0 mol dm^{-3} as specified in the instructions.

This mistake may lead to differences in heat exchange and reaction rate.

Is there any other effect this mistake would have on the value of ΔH_3 that she has calculated?

effect on ΔH_3 ....

explanation ....

....

.... [1]

[Total: 17]

3 Inorganic Qualitative Analysis

(a) Carry out the following tests on **FA 9** and **FA 10** which contain cations and anions 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^-.

Record your observations in the space provided in Table 3.1.

Your answers should include
- details of colour changes and precipitates formed.
- the names of gases evolved and details of the test used to identify each one.

Use a fresh 1 cm^3 sample of each solution for each test.

In all tests, the reagent should be added gradually until no further change is observed, with shaking after each addition.

Table 3.1

test	observations with **FA 9**	observations with **FA 10**
Add NaOH(aq), followed by a spatula load of aluminium powder.		
Add concentrated HC*l* dropwise. To the **FA 9** and concentrated HC*l* mixture, add deionised water.		

test	observations with **FA 9**	observations with **FA 10**
Add KI(aq). To the resulting solution, add $Na_2S_2O_3$(aq).		
Add 1 cm^3 dilute H_2SO_4 followed by 1 cm^3 of K_2CrO_4(aq). Divide into 2 portions. To one portion, add KI(aq) followed by 1 cm^3 of starch solution. To the other portion, add NaOH(aq).		

[4]

Summary

Use your observations to identify the following ions

FA 9 contains the cation …………………………… and anion ……………………………

FA 10 contains the cation ……………………………

State and explain all the evidence for your identification of the anion in **FA 9**.

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

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

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

(b) State the type of reaction that occurs when

(i) concentrated HC*l* is added to **FA 9**.

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

(ii) K_2CrO_4(aq) is added to **FA 10**.

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

(c) **Planning**

FA 11 is a sample of white powder which contains **one** of the four oxides:

magnesium oxide (MgO), aluminium oxide (Al_2O_3), zinc oxide (ZnO), silicon dioxide (SiO_2)

(i) Fill in the spaces in Table 3.2 the expected solubility for each of the oxides, when mixed separately, in dilute HC*l* and aqueous NaOH.

Table 3.2

	dilute HC*l*	NaOH(aq)
MgO		
Al_2O_3		
SiO_2		
ZnO		

[2]

(ii) Using your expected observation in **(c)(i)**, suggest a plan using test tube reactions to identify the oxide present in **FA 11**.

In planning your tests you may use **only** the following reagents and no others.

Dilute hydrochloric acid, HCl
Aqueous sodium hydroxide, $NaOH$(aq)
Aqueous ammonia, NH_3(aq)

You may use a flow scheme or a table to chart the sequence of reactions to establish the identity of **FA 11**.

Your completed plan should include expected observations, deductions with explanation and/or formula of species present at **each** stage. Definite deductions may be made from tests where there appears to be no reaction.

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

…………………………………………………………………………………………… [5]

[Total: 15]

Qualitative Analysis Notes
[ppt. = precipitate]

(a) Reactions of aqueous cations

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

(b) Reactions of anions

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

(c) Tests for gases

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

(d) Colour of halogens

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

ANGLO-CHINESE JUNIOR COLLEGE
DEPARTMENT OF CHEMISTRY
Preliminary Examination

CHEMISTRY **9729/01**
Higher 2

Paper 1 Multiple Choice

24 August 2017
1 hour

Additional Materials: Optical Answer Sheet
Data Booklet

READ THESE INSTRUCTIONS FIRST

Write in soft pencil.
Do not use staples, paper clips, glue or correction fluids.
Write your name, index number and tutorial class on the Optical 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 Optical Answer Sheet.

Read the instructions on the Optical Answer Sheet very carefully.

Each correct answer will score one mark. A mark will not be deducted for a wrong answer.

Any rough working should be done in this booklet.

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

This document consists of **14** printed pages, including this cover page.

[Turn over

For each question there are four possible answers, **A**, **B**, **C**, and **D**. Choose the **one** you consider to be correct.

1 Carbon disulfide is a colourless volatile liquid with the formula CS_2. The compound is used frequently as a building block in organic chemistry as well as an industrial solvent.

It reacts with nitrogen monoxide, NO, to form a yellow solid and two gases. These two gases are formed in equal amounts.

What are these two gases?

A CO_2, NO_2
B CO_2, N_2
C CO, N_2
D CO_2, N_2O

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

Which of the following ions will be deflected the **most** in an electric field?

A S^{2-}
B Br^{-}
C F^{-}
D O^{2-}

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

Nuclear magnetic resonance (NMR) spectroscopy is an analytical technique that uses the magnetic properties of certain atomic nuclei in order to elucidate the structure of an organic molecule.

Atomic nuclei with an even number of protons and an odd number of neutrons (or vice versa) are most suitable for NMR spectroscopy.

Which of the following nuclei is **least** suitable for NMR spectroscopy?

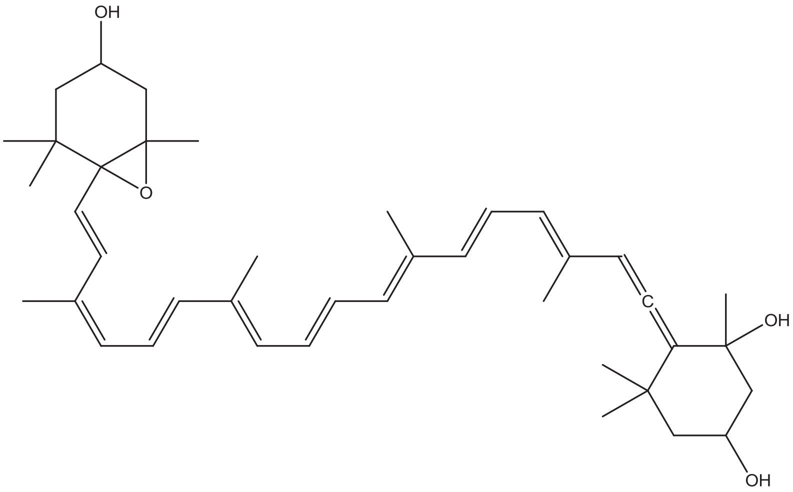
A ^{28}Si
B ^{31}P
C ^{103}Rh
D ^{19}F

4 A 25.00 cm^3 sample of a solution of 0.150 mol dm^{-3} MoO_x^{2-} was passed through a Jones reductor (a column of zinc powder). It was reduced to Mo^{3+}. The filtrate required 22.50 cm^3 of 0.100 mol dm^{-3} acidified $KMnO_4$ (aq) to obtain back the original amount of MoO_x^{2-}.

What is the value of x?

A 4
B 3
C 2
D 1

5 Neoxanthin is a major xanthophyll found in green leafy vegetables such as spinach.



Which of the following σ bonds are present in neoxanthin?

1 A σ bond formed by sp^2–sp^3 overlap.
2 A σ bond formed by s–p overlap.
3 A σ bond formed by sp–sp^2 overlap.

A 1 and 2 only
B 1 and 3 only
C 2 and 3 only
D 1, 2 and 3

6 The enthalpy changes for the following reactions were measured experimentally:

$CH_3CH_2CH_3(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(l)$ $\Delta H = -2202$ kJ mol^{-1}
$H_2(g) + \frac{1}{2} O_2(g) \rightarrow H_2O(l)$ $\Delta H = -286$ kJ mol^{-1}
$CH_3–C{\equiv}C–H(g) + 2H_2(g) \rightarrow CH_3CH_2CH_3(g)$ $\Delta H = -310$ kJ mol^{-1}

What is the enthalpy change of combustion of propyne, $CH_3–C{\equiv}C–H$, in terms of kJ mol^{-1}?

A -2226 **B** -1940 **C** -1606 **D** -1320

7 35 cm^3 of 0.001 mol dm^{-3} nitric acid solution was added to 35 cm^3 of sulfuric acid solution of the same concentration. What is the resulting pH of the combined solution?

A 1.5 **B** 2.5 **C** 2.8 **D** 3.0

8 In which of the following pairs is the bond angle in the first species smaller than that in the second species?

1 PBr_3, PBr_4^+

2 H_2Se, H_2O

3 SF_2, SCl_2

A 1 and 2 only

B 1 and 3 only

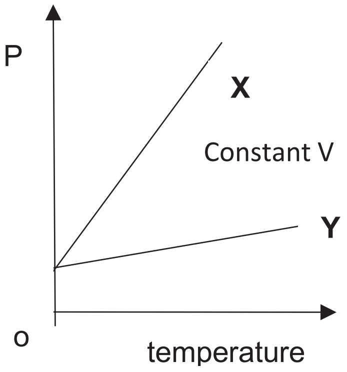
C 2 and 3 only

D 1, 2 and 3

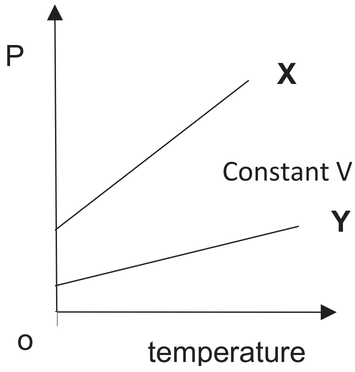
9 **X** and **Y** are both ideal gases. **X** has the smaller molecular mass.

Which of the following diagrams correctly describe the behaviour of equal masses of these gases? All temperatures are measured in °C.

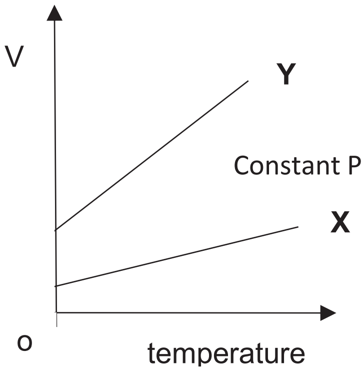
A



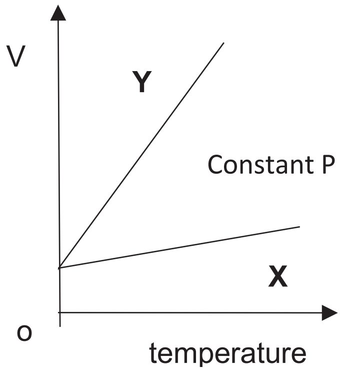
B



C



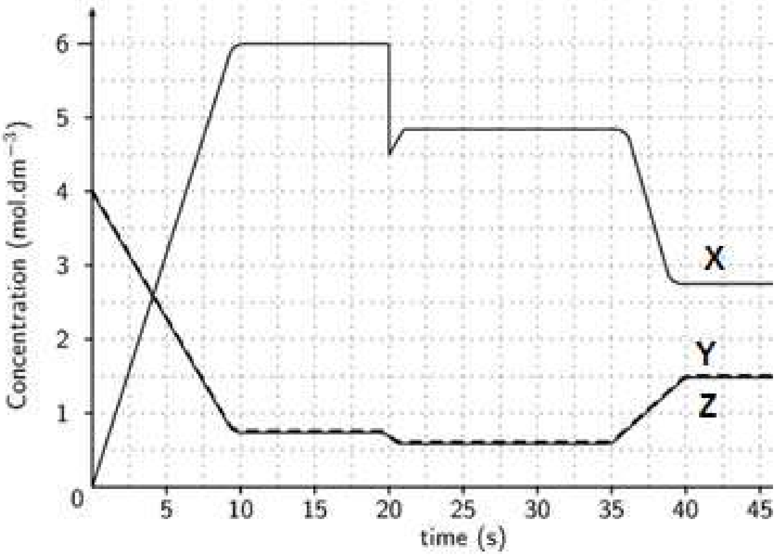
D



10 **X** exists in equilibrium with **Y** and **Z**.

$$2X\,(g) \rightleftharpoons Y\,(g) + Z\,(g)$$

The concentrations of **X**, **Y** and **Z** varies across time as shown below. Note that the dotted line refers to both concentrations of **Y** and **Z**.



Which of the following statements is **false**?

A The equilibrium constant is dimensionless.

B **X**(g) was taken out of the system at 20 s.

C Given that the temperature was decreased at 35 s, it can be concluded that the forward reaction is endothermic.

D Temperature has no effect on the spontaneity of this reaction.

11 The stepwise dissociation equations of phosphoric acid and the corresponding equilibrium constants are shown below.

$H_3PO_4 \rightleftharpoons H_2PO_4^- + H^+$ $K_a = 7.50 \times 10^{-3}$ mol dm^{-3}

$H_2PO_4^- \rightleftharpoons HPO_4^{2-} + H^+$ $K_a = 6.20 \times 10^{-8}$ mol dm^{-3}

$HPO_4^{2-} \rightleftharpoons PO_4^{3-} + H^+$ $K_a = 2.20 \times 10^{-13}$ mol dm^{-3}

A phosphate buffer with pH 7 needs to be prepared.

Which is the best way to prepare such a solution?

A Dissolving Na_3PO_4 alone in water.

B Dissolving H_3PO_4 and NaH_2PO_4 in water.

C Dissolving Na_2HPO_4 and Na_3PO_4 in water.

D Dissolving Na_2HPO_4 and NaH_2PO_4 in water.

12 An equilibrium can be represented by the equation below.

$$\mathbf{W}\,(aq) + \mathbf{X}\,(aq) \rightleftharpoons \mathbf{Y}\,(aq) + \mathbf{Z}\,(aq)$$

In 0.50 dm^3 of a certain mixture, the concentrations of these substances at equilibrium were as shown:

Species	**W**	**X**	**Y**	**Z**
Concentration / mol dm^{-3}	1.00	2.00	2.00	1.00

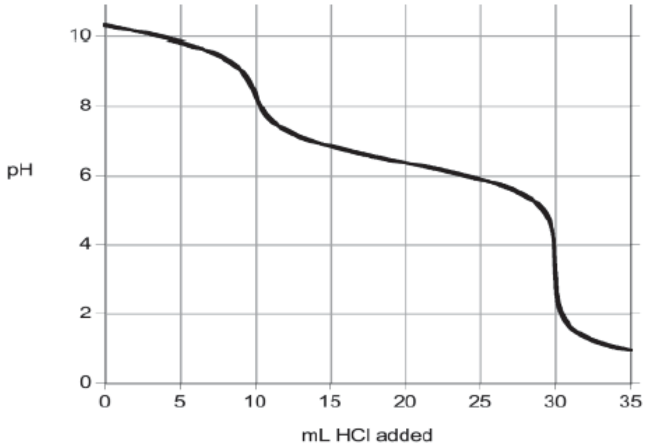
A certain amount of **Y** was added to this equilibrium mixture.

What is the number of moles of **Y** added such that the new equilibrium [**W**] is 1.20 mol dm^{-3}?

Assume that the temperature remained constant throughout.

A 0.10 **B** 0.20 **C** 0.75 **D** 1.50

13 A sample of washing powder which contains a mixture of Na_2CO_3 and $NaHCO_3$ was titrated with aqueous hydrochloric acid and the following titration curve was obtained.



What is the mole ratio of HCO_3^- to CO_3^{2-} in the washing powder?

A 1:1 **B** 1:2 **C** 2:1 **D** 3:1

14 The table below contains the standard reduction potential values for some cobalt and mercury species.

half-equation	**E^o/ V**
$Co^{3+}(aq) + e \rightleftharpoons Co^{2+}(aq)$	+1.82
$Co^{2+}(aq) + 2e \rightleftharpoons Co(s)$	-0.28
$Hg^{2+}(aq) + e \rightleftharpoons Hg^{+}(aq)$	+0.91
$Hg^{+}(aq) + e \rightleftharpoons Hg(l)$	+0.80

Which one of the following predictions is correct?

A Both Co^{2+} and Hg^{+} will disproportionate.

B Neither Co^{2+} nor Hg^{+} will disproportionate.

C Only Co^{2+} will disproportionate.

D Only Hg^{+} will disproportionate.

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

The reaction between iodide and peroxydisulfate ($S_2O_8^{2-}$) is slow due to its high activation energy.

Which of the following cannot function as a catalyst for the above mentioned reaction?

A V^{2+} **B** Mn^{2+} **C** Mn^{3+} **D** Co^{3+}

16 The decomposition of hydrogen peroxide is a first order reaction.

It takes 20 minutes for a 0.140 mol dm^{-3} solution of hydrogen peroxide to halve its concentration.

How much time (in minutes) does it take for a 0.280 mol dm^{-3} solution of hydrogen peroxide to halve its concentration?

A 80 **B** 40 **C** 20 **D** 10

17 The reaction mechanism between O_2 and HBr is as proposed:

$HBr + O_2 \rightarrow HO_2Br$ (slow)

$HO_2Br + HBr \rightarrow 2HOBr$

$HOBr + HBr \rightarrow Br_2 + H_2O$

Which of the following statements is true?

A The bromine in HO_2Br is oxidised in the second step.

B The overall equation is $O_2 + 4HBr \rightarrow 2Br_2 + 2H_2O$.

C The half-life of this reaction is constant.

D HO_2Br is the only intermediate.

18 The numerical values of the solubility products at 25 °C for $PbCl_2$ and PbI_2 are 1.70×10^{-5} and 9.80×10^{-9} respectively.

What is the value of the equilibrium constant for the reaction below?

$$PbI_2 (s) + 2Cl^- (aq) \rightleftharpoons PbCl_2 (s) + 2I^- (aq)$$

A 3.01×10^{6}

B 1.73×10^{3}

C 5.76×10^{-4}

D 3.32×10^{-7}

19 Mohr's salt is named after the German chemist Karl Friedrich Mohr, who made many important advances in the methodology of titration in the nineteenth century.

It is a double salt because it contains two cations and an anion.

Heating solid Mohr's salt with sodium hydroxide liberated a colourless gas. A green precipitate is also formed. It was insoluble in excess sodium hydroxide. On standing in air the solid turned brown.

What is the formula of Mohr's salt?

A $AgCr(CO_3)_2$

B $Ag_2Fe(CO_3)_2$

C $Fe(NH_4)(SO_4)_2$

D $Fe(NH_4)_2(SO_4)_2$

20 Photographic film contains silver halides, which absorb light to form silver metal and halogens are formed. Different silver halides have different sensitivity to light and will undergo this process to a different extent.

During the development of the film, a solution of aqueous ammonia or sodium thiosulfate is used to dissolve the unreacted silver halides. However, sodium thiosulfate is preferred, as some silver halides are not soluble in aqueous ammonia.

Which statements concerning the above processes are correct?

1 Metallic silver forms a very stable complex with thiosulfate, hence silver halides are soluble.

2 The decomposition of the silver halide to metallic silver and the respective halogen is easier for AgBr than for AgC*l* because bromide is more reducing than chloride.

3 AgBr is less soluble than AgC*l* in aqueous ammonia, as solubility product of AgC*l* is of a higher value.

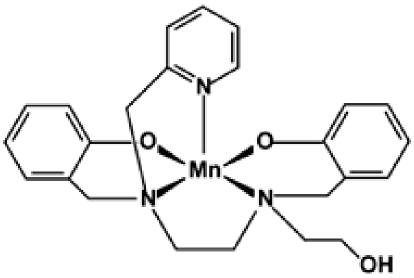
A 1 and 2 only

B 1 and 3 only

C 2 and 3 only

D 1, 2 and 3

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



Which of the following statements about the above complex is **false**?

A There are no 4s electrons in manganese in this complex.

B This complex contains five ligands.

C The coordination number of this complex is 5.

D The oxidation number of manganese in this complex is +2.

22 Cobalt forms many coloured complexes with ligands such as H_2O and $SCN^–$.

A 100 cm^3 solution of $Co^{2+}(aq)$ turns from pink to bright blue when 10 cm^3 of NaSCN(aq) is added to the solution.

$$\underset{\text{pale pink}}{[Co(H_2O)_6]^{2+}(aq)} + 4SCN^–(aq) \rightleftharpoons \underset{\text{bright blue}}{[Co(SCN)_4]^{2–}(aq)} + 6H_2O(l)$$

At equilibrium, $[Co(H_2O)_6]^{2+}$ and $[Co(SCN)_4]^{2–}$ are found to be present in a mole ratio of 1:10.

Given that lg K_c for the equilibrium is 3.00, which of the following statements is **false**?

A At equilibrium, $[SCN^–] = 3.16 \times 10^{–1}$ mol $dm^{–3}$.

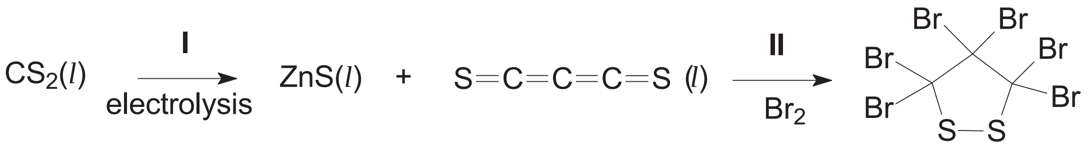
B $[Co(SCN)_4]^{2–}$ is more stable than $[Co(H_2O)_6]^{2+}$.

C The units of K_c is $mol^{–4}\ dm^{12}$.

D Dilution of the reaction mixture decreases the ratio of $[Co(H_2O)_6]^{2+}$ to $[Co(SCN)_4]^{2-}$ at equilibrium.

23 Carbon disulfide, CS_2, can be electrolysed into carbon subsulfide, C_3S_2, an unusual compound.

The boiling points of these two compounds are 46.2 °C and 90.0 °C respectively.



Which of the following statements are **false**?

1 Bromine is acting as a reducing agent in **II**.

2 C_3S_2 has the higher boiling point because there are more covalent bonds to be broken than in CS_2.

3 The carbon atoms in C_3S_2 do not share a common oxidation state.

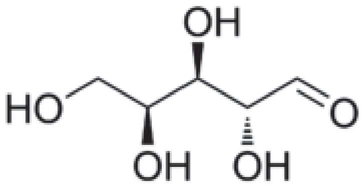
A 2 and 3 only

B 1 and 3 only

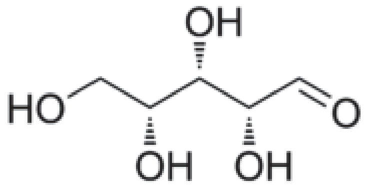
C 1 and 2 only

D 1, 2 and 3

24 L-lyxose and D-xylose are monosaccharides.



L-lyxose



D-xylose

Which of the following statements are true?

1 They have the same melting point.

2 The same volume of hydrogen gas is produced when excess sodium is added to equal amounts of each of them under the same conditions.

3 Both compounds undergo intramolecular nucleophilic substitution to form cyclic esters.

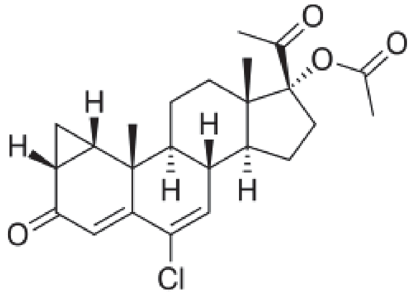
A 1 and 2 only

B 1 and 3 only

C 2 and 3 only

D 2 only

25 Cyproterone acetate (abbreviated as CPA) is a drug that is used in the treatment of androgen-related conditions like acne and prostate cancer.



Which of the following statements about CPA are correct?

1 One mole of CPA undergoes condensation with three moles of 2,4-dinitrophenylhydrazine.

2 Two moles of yellow precipitate is formed when one mole of CPA is warmed with alkaline iodine solution.

3 CPA does not cause a colour change in hot acidified potassium dichromate(VI).

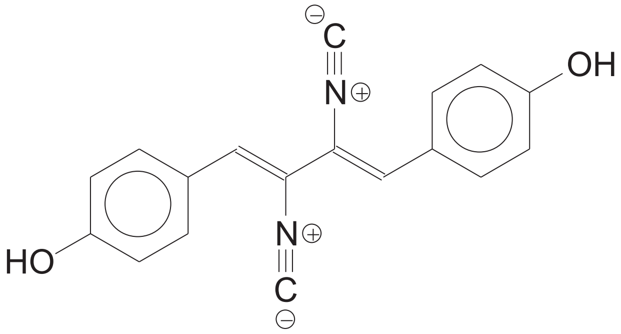
A 1 and 3 only

B 1 and 2 only

C 2 and 3 only

D 3 only

26 Xantocillin was first isolated from *Penicillium notatum* in the 1950s. It is used as an antibiotic.



xantocillin

Which of the following statements about xantocillin is **false**?

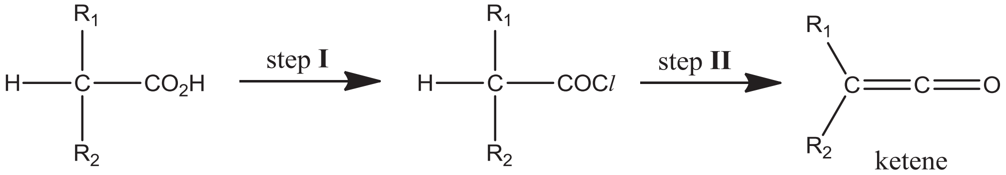
A It is a nitrile.

B It exists as three cis-trans isomers.

C There are four sp hybridised atoms.

D It gives a violet colouration on adding neutral iron(III) chloride.

27 Ketenes are important reagents in organic synthesis. They can be formed from carboxylic acids via the synthetic route below.



Z

Which of the following statements about the above reaction are correct?

1 The ketene will always be non-chiral, no matter which **Z** is used as the starting reactant.

2 Hydrochloric acid can be used as the reagent in step **I**.

3 The ketene can be converted back into **Z** by using water under suitable conditions.

A 1 and 2 only

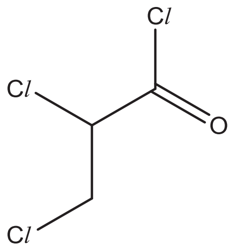
B 1 and 3 only

C 2 and 3 only

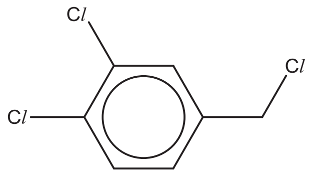
D 1, 2 and 3

28 Aqueous silver nitrate can be used to test for the presence of halogens in organic compounds. Which of the following compounds produces a precipitate most readily when aqueous silver nitrate is added?

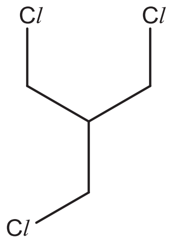
A



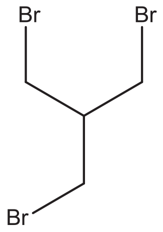
B



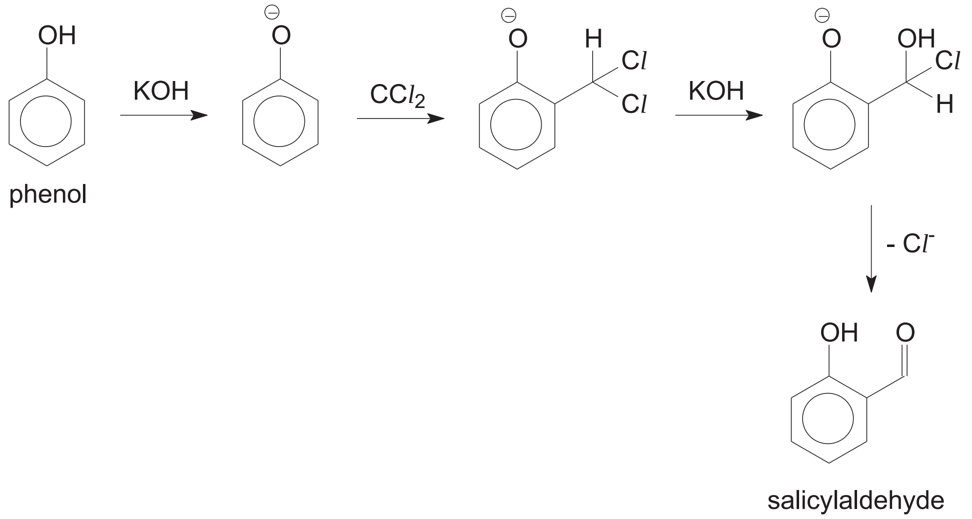
C



D



29 The Reimer–Tiemann reaction is a chemical reaction used for the ortho-formylation of phenols, with the simplest example being the conversion of phenol to salicylaldehyde.



Which of the following types of reaction are involved in the above reaction scheme?

1 Nucleophilic substitution

2 Electrophilic substitution

3 Elimination

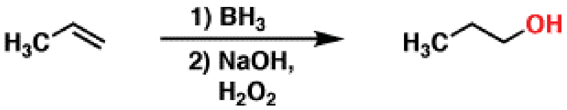
A 1 and 2 only

B 1 and 3 only

C 2 and 3 only

D 1, 2 and 3

30 Hydroboration is one of the many methods to hydrate alkenes to alcohols. An example is shown below.



Which of the following alcohols cannot be formed via hydroboration?

A Butan-2-ol from but-1-ene

B 2-methylpropan-1-ol from 2-methylpropene

C 3-methylpentan-2-ol from 3-methylpent-2-ene

D 4-methylhexan-3-ol from 3-methylhex-3-ene

END OF PAPER

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 **15 August 2017**
2 hours

Candidates answer on the Question Paper
Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name, index number, form class, tutorial class and subject tutor's name on all the work you hand in.
Write in dark blue or black pen.
You may use a soft pencil for any diagrams, graphs or rough working.
Do not use staples, paper clips, glue or correction fluid.

Answer **all** questions.
A Data Booklet is provided.

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

For Examiner's Use	
Question no.	**Marks**
1	**/ 7**
2	**/ 13**
3	**/ 9**
4	**/ 11**
5	**/ 5**
6	**/ 9**
7	**/ 14**
8	**/ 7**
TOTAL	**/ 75**

This document consists of **21** printed pages, including this cover page.

For more than two millenia human ingenuity has turned natural and synthetic poisons into weapons of war. World War I was especially hailed by historians as the “Chemists’ War” because it was the first war in which chemical weapons were used on such an enormous scale, even on civilians. Chemicals were used to bring widespread destruction and death. It set the precedence for World War II. On the bright side, chemicals were used to save millions of soldiers’ lives in World War II.

Question 1 examines how chemical weapons were used to kill in World War I, while Question 2 examines the use of chemicals as medicine in the battlefields of World War II.

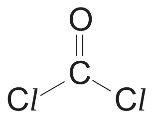
1 A range of different chemicals - chlorine, phosgene and mustard “gas” - were used as weapons throughout World War I.

Their melting and boiling points are tabulated below.

Gas	**Melting point / ^{0}C**	**Boiling point / ^{0}C**
chlorine	-101.5	-34.0
phosgene	-118	8.3
mustard “gas”	14.4	217.0

Chlorine was first used on a large scale by the German forces at Ypres in April 1915. It reacts with water in the lungs to form hydrochloric acid, which can quickly lead to death. At lower concentrations, it can cause coughing, vomiting, and irritation to the eyes.

(a) Phosgene is a colourless gas, with an odour likened to that of ‘musty hay’.



phosgene

Phosgene is known to react violently with water to give hydrochloric acid and carbonic acid. Give the equation of the reaction between phosgene and water.

[1]

(b) The Germans introduced another chemical weapon – mustard “gas”. It was fired into enemy positions by cannons.

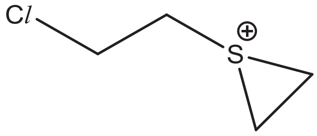
(i) How is the name mustard “gas” misleading?

[1]

1 **(b)** The structural formula of mustard “gas” is $ClCH_2CH_2SCH_2CH_2Cl$.

Unlike alkyl halides, mustard “gas” reacts instantly with water to form hemi-mustard, $ClCH_2CH_2SCH_2CH_2OH$.

(ii) The following intermediate is thought to be formed by mustard “gas” itself via an intramolecular nucleophilic substitution before the attack of water.



How does this intermediate make the hydrolysis of mustard “gas” easier than that of alkyl halides?

[1]

(iii) The conversion of the intermediate in **b(ii)** to hemi-mustard involves two steps, the first involving the attack by water and the second involving deprotonation.

Use curly arrows to show how the intermediate in **b(ii)** is converted into hemi-mustard.

[2]

1 (b) (iv) Hemi-mustard can be further attacked by water to form **J**, $C_4H_{10}SO_2$.

Draw the structure of **J**.

[1]

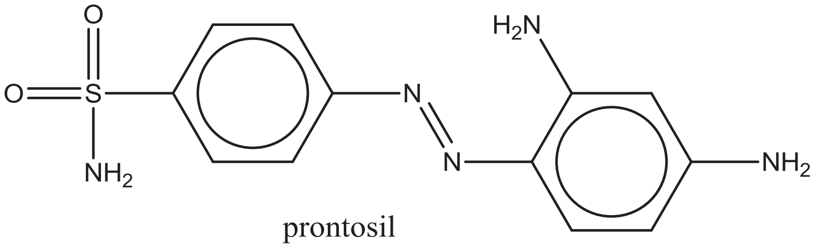
(v) On reaction with concentrated sulfuric acid at 140 ^{0}C, hemi-mustard can be converted into **K**, C_4H_8SO, which does not decolourise bromine.

Draw the structure of **K**.

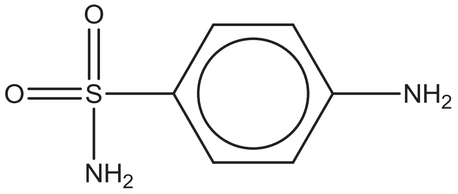
[1]

[Total: 7 marks]

2 **(a)** Prontosil and sulfanilamide are anti-bacterial drugs.



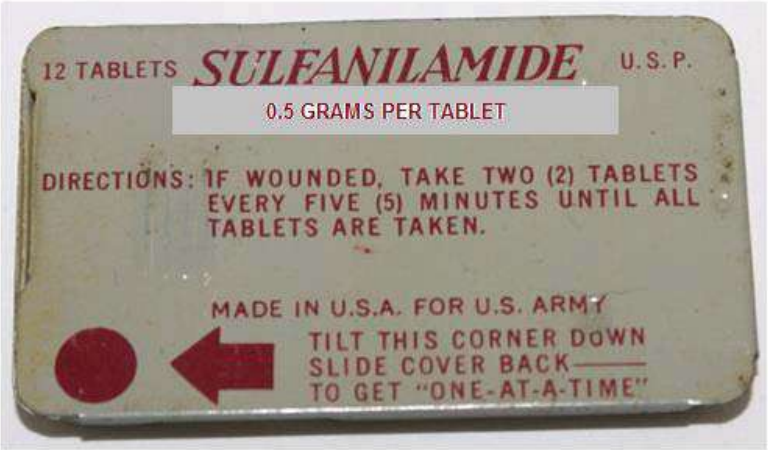
prontosil



sulfanilamide

These two drugs saved many soldiers in World War II.

The photo below is that of a **sulfanilamide kit** issued by the United States Army to its soldiers during World War II.



12 TABLETS SULFANILAMIDE U.S.P.

0.5 GRAMS PER TABLET

DIRECTIONS: IF WOUNDED, TAKE TWO (2) TABLETS EVERY FIVE (5) MINUTES UNTIL ALL TABLETS ARE TAKEN.

MADE IN U.S.A. FOR U.S. ARMY

TILT THIS CORNER DOWN
SLIDE COVER BACK——
TO GET "ONE-AT-A-TIME"

One source states that the maximum daily dosage of sulfanilamide is 6.5 g per kg of patient. An average US army soldier may be assumed to weigh about 70 kg.

Sulfanilamide has many side-effects – itching, headache, diarrhoea, pale skin, vomiting, dizziness, fatigue.

Is it safe for a wounded US army soldier to consume as many as 30 **kits** worth of tablets in a single day? Justify with calculations.

[1]

2 (b) Prontosil was found to be active in *vivo* (in human bodies) while sulfanilamide was found to be active both in *vivo* and in *vitro* (in bacterial cultures grown in petri dishes).

It was later proven that intestinal enzymes break down prontosil to sulfanilamide in the human intestine – in this reaction, the oxidation states of certain nitrogen atoms are altered.

There are a few classes of enzymes as listed below.

Transferases catalyse group transfer reactions.

Hydrolases catalyse reactions that involve hydrolysis.

Ligases are used in catalysis where two substrates are litigated and the formation of carbon-carbon, carbon-sulfide, carbon-nitrogen, and carbon-oxygen bonds due to condensation reactions.

Reductases catalyse reduction reactions.

Oxidases catalyse oxidation reactions.

(i) Suggest the type of intestinal enzyme which catalyses the conversion of prontosil to sulfanilamide.

[1]

(ii) Name the side-product in the conversion of prontosil to sulfanilamide.

[1]

To analyse the sulfanilamide content in a pill, it was dissolved in HC*l* (aq).

(c) Sulfanilamide is not very soluble in water. Explain why sulfanilamide is not soluble in water but is soluble in HC*l* (aq).

[2]

2 A 0.350 g sample of an antibiotic powder containing sulfanilamide was dissolved to form an aqueous solution.

The solution was diluted and made up to the mark in a 100 cm^3 graduated flask. A 25.0 cm^3 aliquot was transferred into a conical flask, in which 25.0 cm^3 of 0.0200 mol dm^{-3} $KBrO_3$ was added. About 10 g of solid KBr was then added.

BrO_3^- reacts with bromide according to the equation:

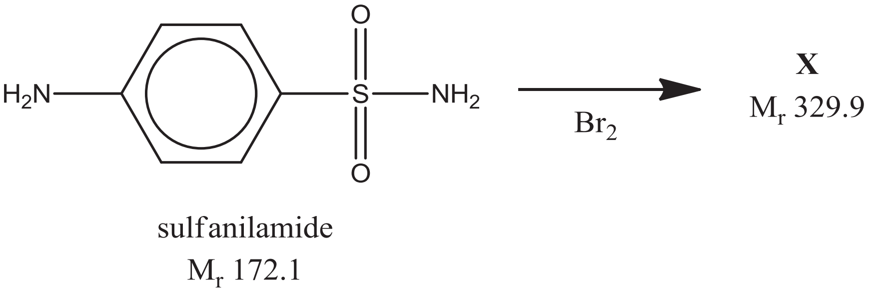
$$BrO_3^- + 5Br^- + 6H^+ \rightarrow 3Br_2 + 3H_2O$$

(d) **(i)** Calculate the amount of Br_2 formed.

[1]

The bromine formed then reacts with the sulfanilamide to form **X**.

Note that the following equation is not balanced.



(ii) By comparing the M_r of sulfanilamide and **X**, show that **X** is a dibrominated compound.

[1]

(iii) Draw the structure of **X**, ignoring the directing effects of the $–SO_2NH_2$ group.

[1]

2 **(e)** After ten minutes, an excess of KI was added.

$$Br_2 + 2I^- \rightarrow 2Br^- + I_2$$

The liberated iodine was then titrated with 18.00 cm^3 of 0.0900 mol dm^{-3} $Na_2S_2O_3$.

$$I_2 + 2S_2O_3^{2-} \rightarrow S_4O_6^{2-} + 2I^-$$

Calculate the amount of bromine which reacted with the KI.

[1]

(f) Using your answers to **(d)** and **(e)**, calculate the amount of sulfanilamide which reacted with the bromine.

[2]

(g) Hence, calculate the percentage mass of sulfanilamide in the sample.

[2]

[Total: 13 marks]

3 Hydrazine (N_2H_4) was first used as rocket fuel in World War II, and has since been used as a propellent for maneuvering spacecraft, as it decomposes rapidly and exothermically into hydrogen gas and nitrogen gas.

Hydrazine may be produced industrially by the Olin-Rashig process from NH_2Cl and ammonia.

$$NH_2Cl\ (g) + NH_3\ (g) \rightleftharpoons HCl\ (g) + N_2H_4\ (g)$$

The values of K_c are tabulated below with the corresponding temperatures.

T / K	298	304	503
K_c	1.525×10^6	1.230×10^5	2.201×10^4

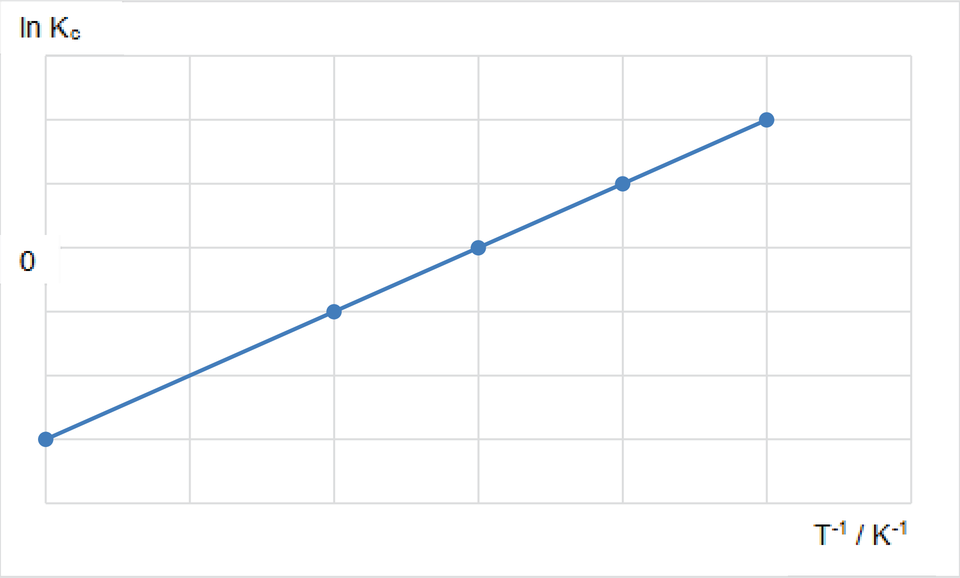
(a) State the value of K_p at 304 K. Justify your answer.

[2]

(b) By manipulating the relationship of $K_c = e^{\frac{-\Delta G}{RT}}$, we obtain

$$R \ln K_c = \frac{1}{T}(-\Delta H) + \Delta S.$$

The graph below was plotted with ln K_c as the y-axis and $\frac{1}{T}$.as the x-axis.



(i) Describe how you would obtain the value of ΔS from the above graph.

[1]

3 **(b)** **(ii)** Another way to find the standard entropy change of a reaction is to consider the standard molar entropies of the species involved.

Species	HC*l* (g)	N_2H_4 (g)	NH_2Cl (g)	NH_3 (g)
Standard molar entropy / J mol^{-1} K^{-1}	187	239	201	193

Calculate the standard entropy change of the Olin-Rashig process.

[1]

(iii) Hence, using your answer to **b(ii)** and the equation in **(b)**, calculate the standard enthalpy change of the Olin-Rashig reaction, including its units.

[1]

(c) The pK_a and pK_b values of the two reactants – monochloramine (NH_2Cl) and ammonia - are tabulated below.

Product	NH_2Cl	NH_3
pK_a	14	32.5
pK_b	15	4.75

Explain these differences as much as you can.

[2]

3 **(d)** Monochloramine is an oxidising agent.

$$NH_2Cl + 2H^+ + 2e \rightarrow NH_4Cl$$

The reduction potentials of the above half-reaction is +1.45 V.

However, in alkaline medium, the reduction potential is + 0.74 V.

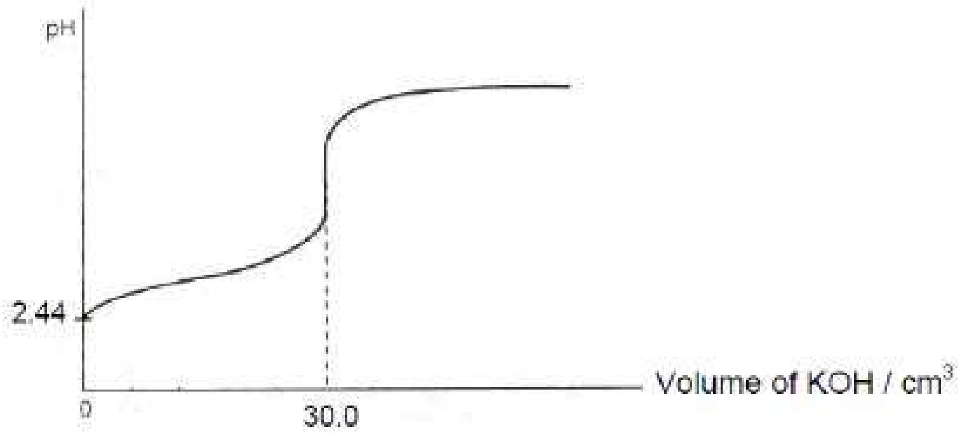
Explain the difference between these two reduction potentials.

[2]

[Total: 9 marks]

4 **(a)** Ethanoic acid, a weak monobasic acid, is the main component in vinegar.

When a 20.0 cm^3 sample of vinegar was titrated against 0.05 mol dm^{-3} aqueous potassium hydroxide using a pH meter, the following graph was obtained.



(i) Show that the concentration of the ethanoic acid solution is 0.0750 mol dm^{-3}.

[1]

(ii) Hence use your answer and the initial pH to show that ethanoic acid is a weak acid.

[2]

4 (a) (iii) Show that the acid dissociation constant of ethanoic acid has a numerical value of 1.85×10^{-4}.

[2]

(iv) Calculate the value of the pH after 15.00 cm^3 of aqueous potassium hydroxide has been added.

[1]

(v) Write a suitable chemical equation, with state symbols, to explain why the equivalence pH is above 7.

[1]

(b) (i) Solution **A** was prepared by adding 10.00 cm^3 of the potassium hydroxide solution to 25.0 cm^3 of the ethanoic acid solution.

Calculate the pH of solution **A**.

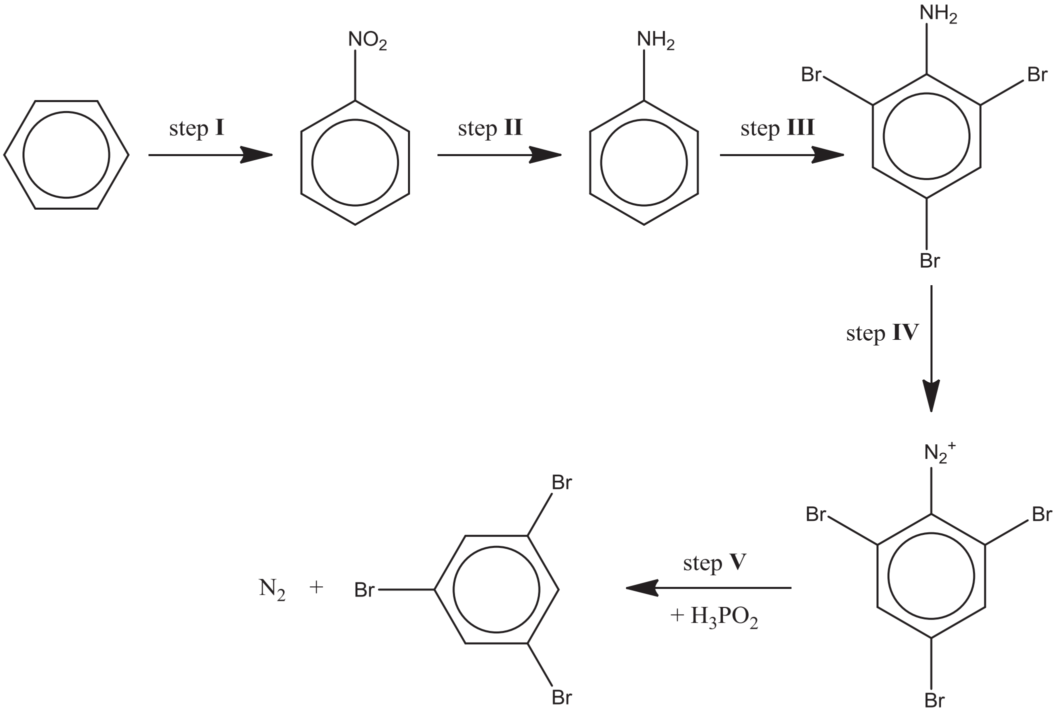
[2]

(ii) When a small amount of acid or base is added to solution **A**, its pH remained relatively constant. Explain, with the aid of equations, why this is so.

[2]

[Total: 11 marks]

5 Study the synthetic route from benzene to 1,3,5-tribromobenzene, shown below.



(a) State the reagents and conditions used in steps **I** and **II.**

[2]

(b) By examining the positions of the bromine atoms, suggest why 1,3,5-tribromobenzene cannot be made directly from benzene with bromine.

[1]

(c) Phosphinic acid, H_3PO_2, is used in step **V**. Only one out of its three hydrogen atoms is acidic. A non-acidic hydrogen substituted on the benzene to liberate nitrogen gas.

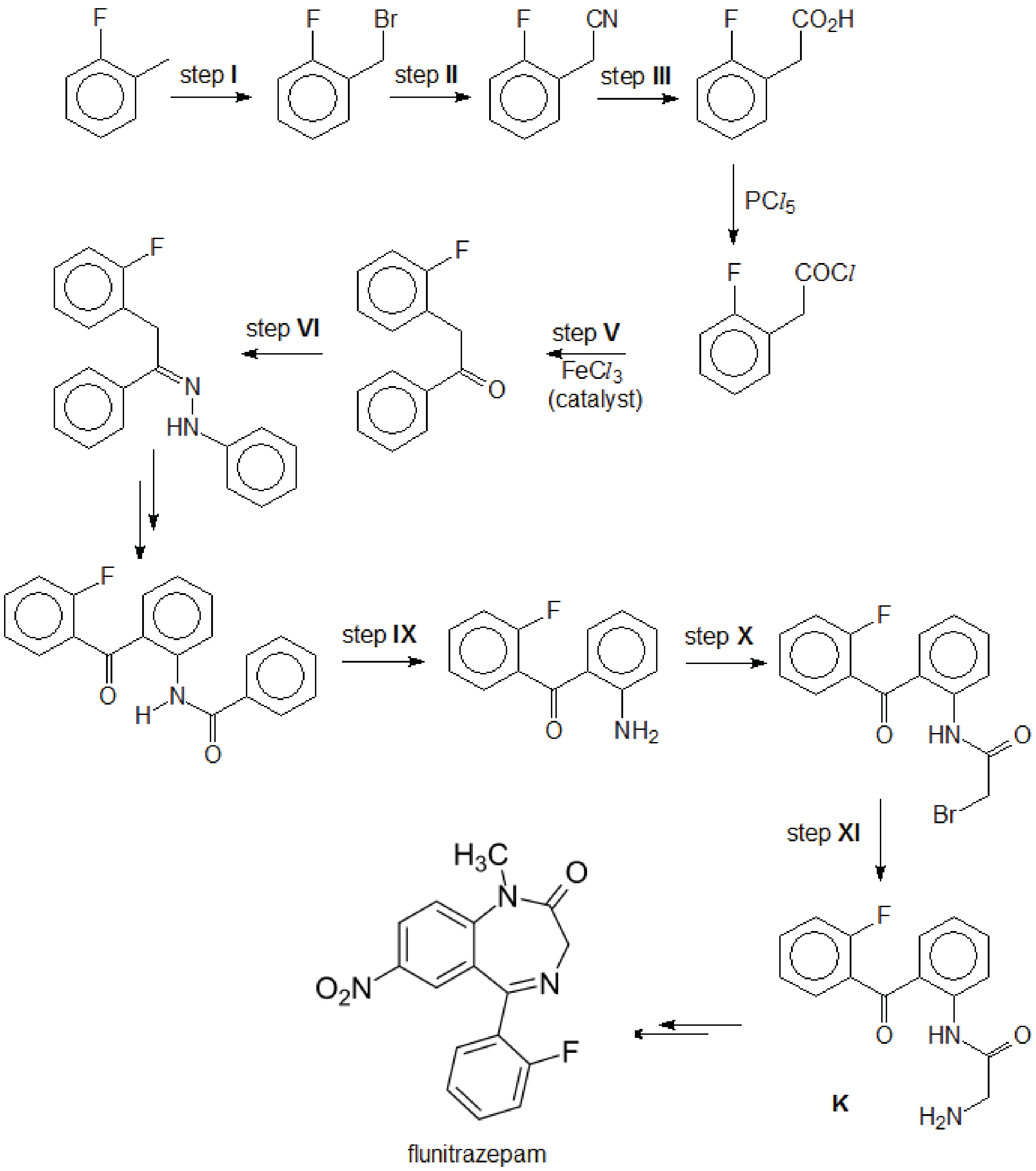
Draw the structure of phosphinic acid and circle the hydrogen atom which substitutes on the benzene.

[2]

[Total: 5 marks]

6 (a) Flunitrazepam is a drug used in the short-term treatment of insomnia and as a pre-medication in surgical procedures and for inducing anaesthesia.

Study the synthetic route to flunitrazepam shown below.

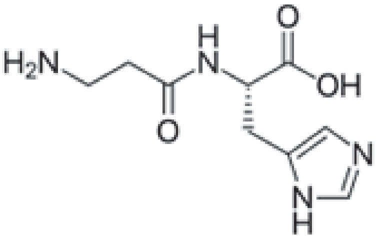


6 **(a)** Fill in the table below with the appropriate reagents and conditions.

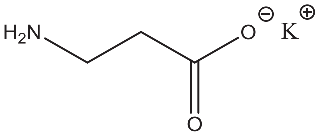
Step	Reagents and conditions
I	
II	
III	
V	
VI	
XI	

[6]

6 (b) Carnosine is a dipeptide health supplement. It first appeared in the mainstream health community around a decade ago in the form of supplements, eye-drops and skin creams.



(i) One of the products is β–alanine (structure shown below) when carnosine is hydrolysed with hot KOH (aq).



Draw the structural formula of the other product.

(ii) α-alanine is one of the twenty essential amino acids. It is a constitutional isomer of β–alanine. Unlike β–alanine, it is chiral. Draw the skeletal formula of α-alanine.

(iii) Sarcosine is another constitutional isomer of β–alanine. It is an α-amino acid, just like α-alanine. Draw the structural formula of sarcosine.

[3]

[Total: 9 marks]

7 Sulfur forms many cyclic allotropes with different ring sizes. In the solid state, the most stable allotrope of sulfur is the form of S_8. In the gas phase, all ring sizes from S_3 to S_{12} have been detected.

(a) In the gas phase, the different ring sizes are in equilibrium. The equation for the equilibrium between S_7(g) and S_8(g) is given below:

$$7S_8\,(g) \rightleftharpoons 8S_7\,(g)$$

(i) Give the expression for the equilibrium constant, K_c, for the reaction between S_7 and S_8 as written above.

[1]

When dissolved in an organic solvent, S_6, S_7 and S_8 were all detected in equilibrium in the following proportions by mass:

Allotrope	S_6	S_7	S_8
% by mass	1.5	0.5	98.0

(ii) Calculate the amount of S_7 and S_8 at equilibrium when 1.00 g of sulfur is dissolved in 1.00 dm^3 of solvent.

[2]

(iii) Calculate the value of the equilibrium constant in **(i)**.

[1]

(b) In the solid phase, S_8 crystallises in two well-known allotropic forms: orthorhombic and monoclinic. Both combust in excess oxygen to form liquid SO_3. The standard enthalpy changes of combustion of these two forms are as follows:

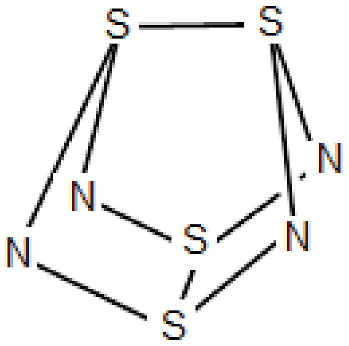
$$\Delta H_c\ (S_8\text{, orthorhombic}) = -296.8\ kJ\ mol^{-1}$$
$$\Delta H_c\ (S_8\text{, monoclinic}) = -297.1\ kJ\ mol^{-1}$$

Draw an energy level diagram to conclude which is the more stable form.

[2]

7 **(c)** Sulfur also forms an interesting cage-like compound with nitrogen, S_4N_4.

(i) There are π bonds in S_4N_4 which are alternating.



The π bonds are omitted in the structural formula shown above.

Fill in the missing π bonds onto the structural formula above.

[1]

S_4N_4 reacts with hot NaOH(aq) to give thiosulfate ($S_2O_3^{2-}$)and trithionate ($S_3O_6^{2-}$) in 1:2 ratio. Ammonia is the gaseous side-product.

(ii) Suggest what makes this reaction spontaneous.

[1]

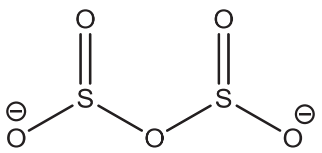
(iii) The skeletal equation is as such:

$$S_4N_4 + OH^- + H_2O \rightarrow S_2O_3^{2-} + S_3O_6^{2-} + NH_3$$

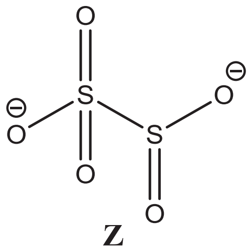
Balance the ionic equation.

[1]

7 **(d)** There are two possible structures of the metabisulfite ion ($S_2O_5^{2-}$), as shown below.



Y



Z

(i) Using appropriate values from the Data Booklet, calculate the enthalpy changes of atomisation of **Y** and **Z**. Hence deduce which is more stable.

[2]

(ii) Metabisulfite (structure **Z**) decomposes to SO_2 and sulfite (SO_3^{2-}) in a single step. Draw curly arrows to show the electron movement in this decomposition.

[1]

7 (d) (iii) Potassium metabisulfite, $K_2S_2O_5$, is a white crystalline powder.

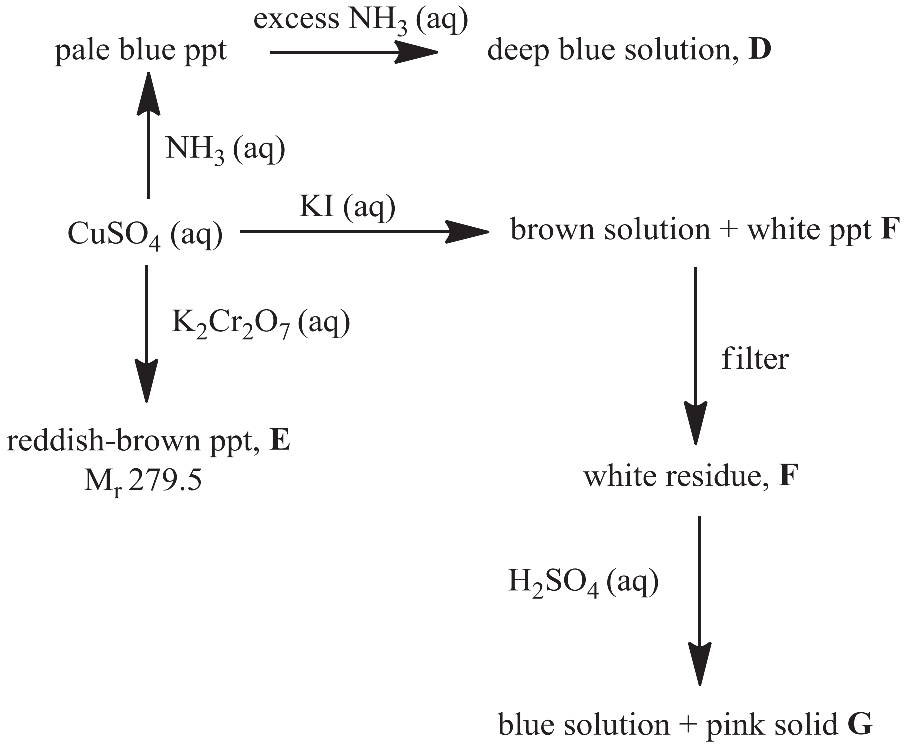
It is chemically very similar to sodium metabisulfite, $Na_2S_2O_5$, with which it is sometimes used interchangeably. Potassium metabisulfite is generally preferred out of the two as a food preservative as it does not contribute sodium to the diet.

Explain why potassium metabisulfite decomposes at a higher temperature on heating than sodium metabisulfite.

[2]

[Total: 14 marks]

8 **(a)** Copper(II) sulfate can undergo a series of reactions as shown in the reaction scheme below.



Identify **D**, **E**, **F** and **G**.

D:

F:

E:

G:

[4]

(b) Ionisation isomerism is a special type of constitutional isomerism in which the isomers form different ions in solution.

There is a pair of cobalt(III) ionisation isomers, **K** and **L**. They have molecular formula $CoBrSO_4(NH_3)_4$. **K** is red while **L** is dark violet.

On addition of aqueous barium nitrate, only **K** gave a white precipitate.
On addition of aqueous silver nitrate, only **L** gave an off-white precipitate.

(i) Give the structural formulae of the cations in **K** and **L**.

K:

L:

[2]

(ii) Explain briefly why **K** and **L** exhibit different colours.

[1]

[Total: 7 marks]

END OF PAPER

ANGLO-CHINESE JUNIOR COLLEGE
DEPARTMENT OF CHEMISTRY
Preliminary Examination

CHEMISTRY
Higher 2

9729/03

Paper 3

18 August 2017
2 hours

Additional Materials: Writing Paper
Data Booklet
Cover Page

READ THESE INSTRUCTIONS FIRST

Write your index number and name, form class and tutorial class on all the work you hand in.
Write in dark blue or black pen.
You may use a pencil for any diagrams, graphs or rough working.
Do not use staples, paper clips, glue or correction fluid.

Answer **all** questions in Section **A**.
Answer **either** question 4 or 5 in Section **B**.
Start each question on a new sheet of writing paper.

A Data Booklet is provided.
The use of an approved calculator is expected, where appropriate.
You are reminded of the need for good English and clear presentation in your answers.

At the end of the examination, fasten all your work securely behind a cover sheet.
The number of marks is given in brackets [ ] at the end of each question or part question.

This document consists of **17** printed pages, including this cover page.

Section A – Answer **ALL** questions. Begin each question on a fresh piece of writing paper.

1 This question is about Period 3 and Group 2 elements.

(a) Phosphorus sulfide, P_4S_3, is used in small amounts in the tip of a matchstick. On striking a matchstick, this compound burns to form sulfur dioxide and phosphorus pentoxide.

(i) Write the equation for this reaction. [1]

(ii) The melting points of the two oxides formed in **(a)(i)** differ significantly from that of silicon(IV) oxide (SiO_2). Account for this difference in terms of structure and bonding of each oxide. [2]

(iii) The solid oxide formed in **(a)(i)** dissolves in water to give an acidic solution.

Write the equation for this reaction and give an approximate pH of the solution formed. [2]

(b) A Group 2 nitrate exists as a hydrate $\mathbf{M}(NO_3)_2.xH_2O$. On heating, 1.80 g of this hydrate lost 0.55 g in the form of steam, as it was converted into the anhydrous nitrate, $\mathbf{M}(NO_3)_2$. Subsequent heating to constant mass produced a white residue and mixture of two gases. The gases produced were passed through aqueous sodium hydroxide. The remaining gas occupied 95 cm^3 at 101 kPa and 30 °C.

(i) Write an equation, with state symbols, representing the thermal decomposition of Group 2 nitrates, $\mathbf{M}(NO_3)_2$. [1]

(ii) Assuming that the gas behaves ideally, calculate the amount of remaining gas formed. [1]

(iii) Hence, calculate the value of x and deduce the identity of metal **M**. [3]

(c) Calcium oxide is the key ingredient for the process of making cement.

When 1.50 g calcium is burned in air, calcium oxide is formed together with a red brown solid.

The red brown solid has the following composition by mass: Ca, 81.1%; N, 18.9%. Adding water to the red brown solid produces calcium hydroxide and 19.2 cm^3 of ammonia gas at room temperature and pressure.

(i) Deduce the formula of the red brown solid. [2]

(ii) Write the chemical equation for the reaction between the red brown solid with water. [1]

(iii) Write the chemical equation for the reaction of calcium with O_2 and hence calculate the mass of CaO formed when 1.5 g of calcium is burnt in O_2. [2]

1 **(d)** A diagonal relationship is said to exist between certain pairs of diagonally adjacent elements in the second and third Periods of the Periodic Table.

For instance, lithium shows similar chemical properties to magnesium.

(i) Write the equation for the thermal decomposition of lithium carbonate. [1]

(ii) Explain why this is unlike that of the other Group 1 carbonates. [1]

(e) Lithium nitride, Li_3N, is a red solid. It is the only stable Group 1 nitride. The nitrides of all the Group 2 elements are known.

Li_3N is currently investigated as a storage medium for hydrogen gas.

$$Li_3N + 2H_2 \rightleftharpoons 2LiH + LiNH_2$$

State the role of hydrogen. [1]

(f) A diagonal relationship also exists between boron and silicon.

B_2O_3 is acidic, like SiO_2 but unlike the oxides of the other Group 13 elements.

(i) Write a balanced chemical equation, with state symbols, that illustrates the acidic nature of SiO_2. [1]

(ii) Write a balanced chemical equation, with state symbols, that illustrates the acidic nature of B_2O_3, given that it forms a similar anion as in **(i)**. [1]

[Total: 20]

2 **(a)** Divalent metal cations like tin and cadmium form insoluble precipitates with NaOH (aq).

The K_{sp} of $Sn(OH)_2$ is 5.45×10^{-27} $mol^3\ dm^{-9}$.

(i) If the concentration of $Cd(OH)_2$ in a saturated solution is 1.217×10^{-5} mol dm^{-3}, determine the solubility product of $Cd(OH)_2$. [1]

(ii) Calculate the molar solubility of $Sn(OH)_2$ in a solution of pH 8. [2]

(iii) A certain solution has 0.002 mol dm^{-3} each of Cd^{2+} and Sn^{2+}.

Calculate the pH range over which the two cations can be effectively separated. [2]

(b) Propanone, also known as "acetone", is one of the most important solvents in organic chemistry – it can be used to dissolve many things from fats and waxes to airplane glue and nail polish.

It decomposes to **H** and ketene ($H_2C{=}C{=}O$). At 600 °C, the decomposition rate constant is 8.7×10^{-3} s^{-1}.

(i) Suggest the identity of **H**. [1]

(ii) Determine the half-life of the reaction at 600 °C. [1]

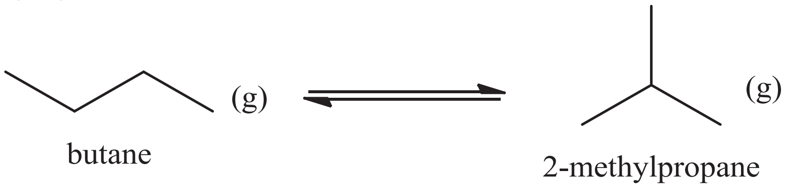
(iii) How much time is required for 75% of a sample of propanone to decompose at 600 °C? [1]

(iv) The Arrhenius equation links different parameters (its activation energy, the absolute temperature, and its rate constant at that temperature) of a reaction together.

$$\mathrm{k} = \mathrm{A}e^{-\frac{\mathrm{E_a}}{\mathrm{RT}}}$$

Given that the half-life of the reaction at 500 °C is 8700 s and using your answer to **(ii)**, calculate the activation energy (including its units) of this reaction. [2]

2 **(c)** Under appropriate conditions, butane can be made to isomerise reversibly to 2-methylpropane at 298K.



	butane	**2-methylpropane**
S^o / J K^{-1} mol^{-1}	310	295
ΔH_f^o / kJ mol^{-1}	-127.2	-135.6

(i) Calculate the ΔG^o for the forward isomerisation reaction. [2]

(ii) Given that $\Delta G^o = -RT \ln K_p$, calculate the equilibrium constant, K_p, for the isomerisation reaction. [1]

(iii) Write the K_p expression for the isomerisation equilibrium. [1]

(iv) Determine the mole fractions of the two gases at equilibrium. [3]

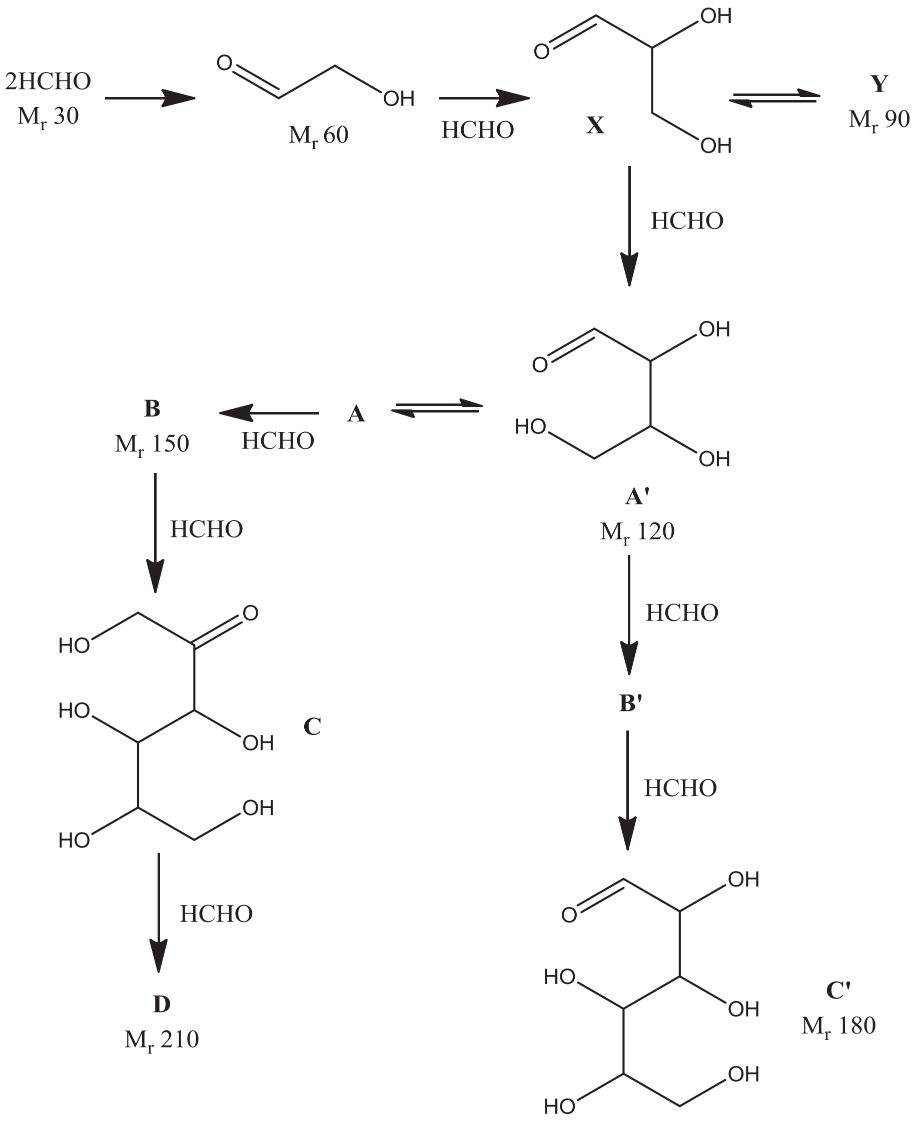
(v) In the industry, 2-methylpropane is used to make compound **Y**, C_8H_{18}.

Y has the whole range of carbon atoms; it contains primary, secondary, tertiary and quaternary carbon atoms.

Draw the structural formula of **Y**, assuming that the original carbon skeleton did not rearrange. [1]

2 **(d)** Life in the universe is widely thought to have originated from methanal, HCHO, through the Formose reaction.

In this reaction, methanal is converted into a vast range of sugars like ribose and from there to RNA, an important hereditary material.



(i) **X** and **Y** are functional group isomers.

Y does not rotate the plane of plane-polarised light. Fehling's and Tollens' tests are the only tests which can differentiate between **X** and **Y**.

Draw the structural formula of **Y**. [1]

(ii) Suggest a reason why the interconversion of **C** to **C'** cannot be done in a single step. [1]

(iii) Draw the structural formula of **D**. [1]

[Total: 21]

3 This question is on Group 17, the halogens.

Chlorate(V), ClO_3^-, reacts with chloride according to the equation:

$$2ClO_3^- (aq) + 2Cl^- (aq) + 4H^+ (aq) \rightarrow Cl_2 (g) + 2ClO_2 (aq) + 2H_2O (l)$$

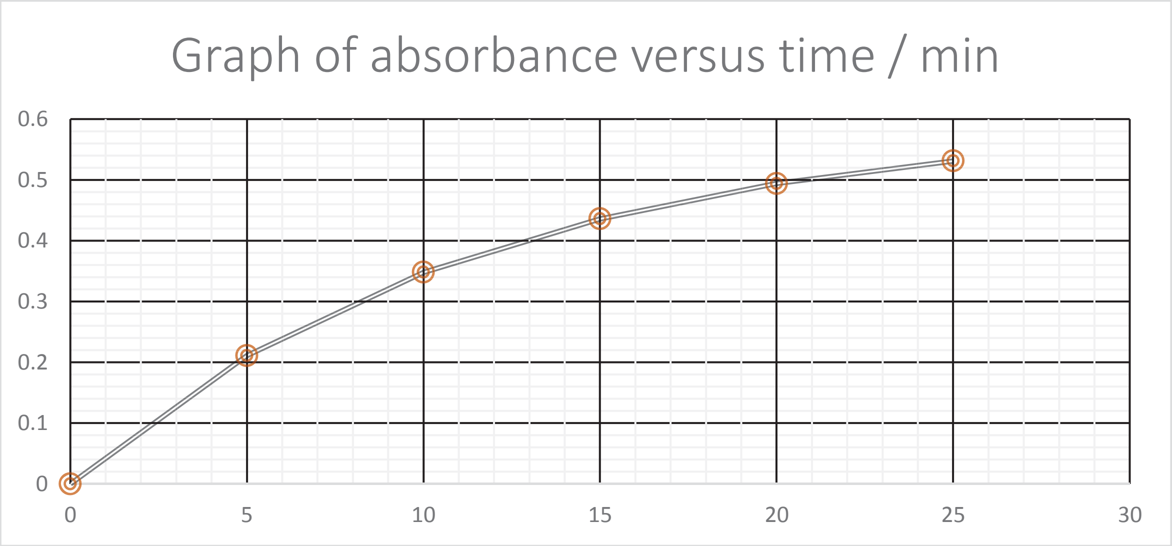
(a) To study the kinetics of chlorate(V)-chloride reaction, an experiment was conducted using a mixture in which the concentrations of the reactants are as follows: 0.000480 mol dm^{-3} of ClO_3^-, 0.1 mol dm^{-3} of Cl^- and 0.4 mol dm^{-3} of H^+.

At five-minute intervals, small samples of the reaction mixture were withdrawn, quenched and placed into the UV-vis spectrometer to record its absorbance value. The absorbance value corresponds to the concentration of the product ClO_2.

The results of the above experiment are shown below.

Time/min	0	5	10	15	20	25
Absorbance/A	0.000	0.211	0.348	0.436	0.494	0.531

The graph of absorbance/A against time/min is plotted below.



3 **(a)** **(i)** Beer-Lambert's Law states that the absorbance values, A, is directly proportional to the concentration of absorbing species, c, as shown below.

$$A = \varepsilon c l$$

where ε is the molar extinction coefficient and l is the path length, which is usually 1.0 cm.

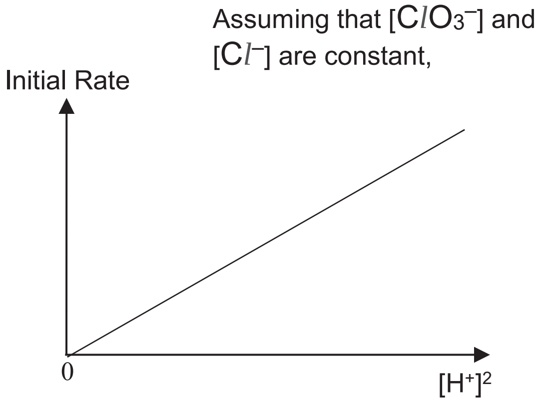
This equation can be used to calculate the absorbance value when maximum amount of ClO_2 was formed.

Show that the maximum absorbance value in the above experiment is 0.600, given that ε of ClO_2 is 1250 mol^{-1} dm^3 cm^{-1}. [2]

(ii) From the graph provided on the previous page and the information given in **(a)(i)**, determine the half-life with respect to ClO_3^- and hence the order of reaction with respect to ClO_3^-. [2]

To obtain the full rate law, a further experiment was conducted.

The following graph was obtained.



(iii) Using the above data, determine the order of the reaction with respect to H^+. [1]

(iv) Given that the units of k is mol^{-3} dm^9 s^{-1}, write the rate equation of the chlorate(V)-chloride reaction. [1]

(v) State a physical property that can be monitored as the reaction progresses. [1]

3 **(b)** Heating solid halides with concentrated H_2SO_4 is one of the ways to obtain hydrogen halides.

However, the halides have different reactivities with concentrated H_2SO_4.

(i) Write an equation to show the reaction of KCl with concentrated H_2SO_4. [1]

(ii) However, when KI is treated with concentrated sulfuric acid, HI will be contaminated with other gaseous products. Identify these gaseous products. [2]

(iii) Suggest another reagent that can be reacted with potassium iodide to obtain pure hydrogen iodide. [1]

The interhalogens are compounds that are made up of two or more different halogens.

ICl and IBr are two such examples.

(c) Even though ICl is more polar than IBr, IBr has a higher boiling point than ICl. Explain this dilemma as clearly as you can. [2]

(d) ICl reacts with water in which water is acting as the nucleophile.

The equation for the reaction is as follows.

$$ICl + H_2O \rightarrow H\mathbf{X} + HO\mathbf{Y}$$

(i) By comparing relative electronegativities, identify **X** and **Y**. [1]

(ii) Hence propose a two-step mechanism for this reaction. Include curly arrows and partial charges. [2]

(e) ICl_3 exists as a planar dimer I_2Cl_6 in solid state. The two iodine atoms are the central atoms.

(i) Draw the structure of the dimer. [1]

(ii) The molten form of ICl_3 is able to conduct electricity because it undergoes auto-ionisation.

One species is square planar and the other is bent with respect to the central iodine atom.

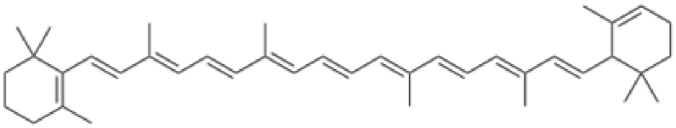
Deduce the formulae of the cation and the anion. [2]

[Total: 19]

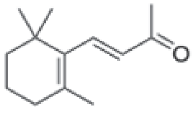
Section B - Choose <u>either</u> question **4** or **5**. Begin it on a fresh piece of writing paper.

4 α-carotene is a red-orange pigment found in plants and fruits. It is the yellow/orange pigment that gives vegetables and fruits their rich colors. The name "carotene" came about when it was first discovered in carrot roots in 1831.

(a) α-carotene is metabolised to form α-ionone and β-ionone, which share the same molecular formula, $C_{13}H_{20}O$.



α-carotene



β-ionone

(i) Explain why hot acidified $KMnO_4$ cannot be used in the conversion of α-carotene to β-ionone. [1]

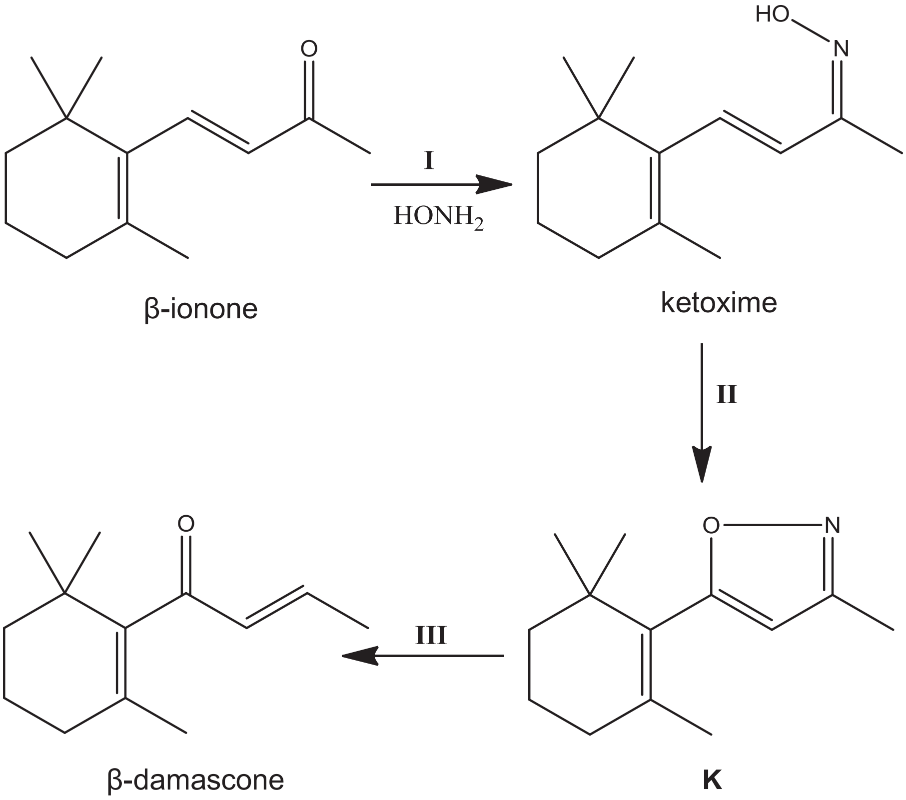
(ii) Based on the structure of α–carotene, draw the structural formula of α-ionone. [1]

(iii) Specify what type of constitutional isomerism is shown between α-ionone and β-ionone. [1]

(iv) Give the structural formula of a constitutional isomer of β-ionone, where neutral iron(III) chloride solution is the <u>only</u> chemical test that can distinguish between itself and β-ionone. [1]

(v) Give the structural formula of a constitutional isomer of β-ionone, which can be distinguished from β-ionone by warm alkaline iodine. [1]

4 **(b)** β-ionone forms β-damascone via an electrochemical route.



It involved the formation of ketoxime in step **I**, followed by an anodic oxidation in step **II**. In the last step, the oxygen-nitrogen bond was cleaved to give β-damascone.

(i) Name the type of reaction in step **I**. [1]

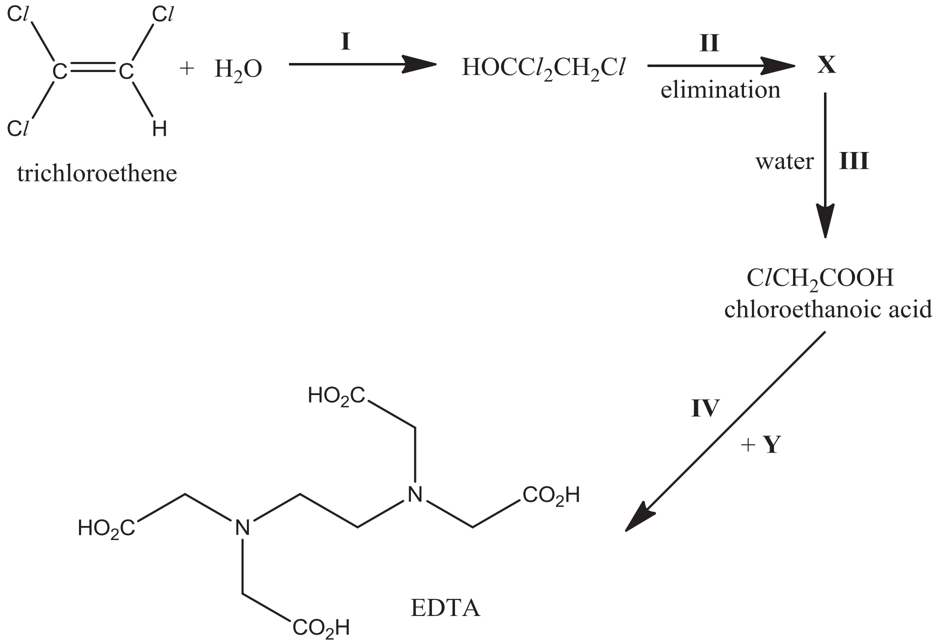
(ii) Construct a balanced half-equation for the oxidation of ketoxime in step **II** under acidic conditions.

You are to use “ketoxime” and “**K**” in your half-equation. [1]

(iii) β-damascone exists as a pair of cis-trans isomers. Draw the cis isomer. [1]

4 **(c)** Ethylenediaminetetraacetic acid (EDTA) is a colourless, water-soluble solid. It is on the World Health Organization's List of Essential Medicines.

EDTA can be synthesised via the following reaction route.



(i) **X** gave a white precipitate when aqueous silver nitrate was added to it. Give the structural formula of **X**. [1]

(ii) Give the structural formula of **Y**. Hence, state a potential problem that might happen when it reacts with chloroethanoic acid. [2]

(d) Chloroethanoic acid can be synthesised from methanal via a three-step route. State the reagents and conditions used in each step and the intermediates involved. [4]

(e) The Kolbe electrolysis involves conversion of carboxylate salts into alkanes. It can be represented by the following half-equation.

$$3\ R_1COO^- + 3\ R_2COO^- \rightarrow R_1{-}R_1 + R_1{-}R_2 + R_2{-}R_2 + 6CO_2 + 6e^-$$

where R_1 and R_2 may not represent the same alkyl group.

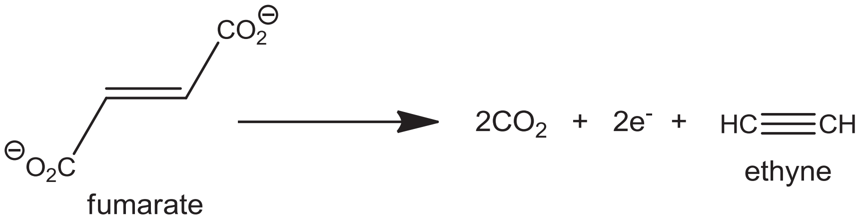
In a certain electrolysis, two carboxylate salts were electrolysed, forming three alkanes.

The relative molecular masses are 58.0, 86.0 and 114.0. The alkane with M_r 58.0 is non-chiral. The alkane with M_r 114.0 exists as three stereoisomers - two of which are chiral and the third is non-chiral.

(i) Identify the two carboxylate salts used. [2]

(ii) Draw the stereochemical formula of any of the two chiral stereoisomers. [1]

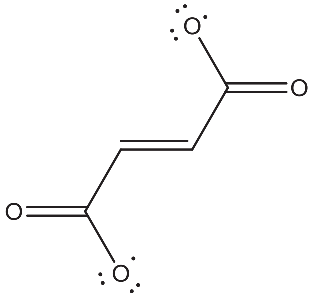
4 **(e)** In a special application of the Kolbe electrolysis, fumarate was electrolysed into ethyne.



(iii) Kolbe electrolysis proceeds via radical intermediates, which are formed and reacted via homolytic fission and fusion.

Explain the term *homolytic fission*. [1]

(iv) The decomposition of fumarate into ethyne and carbon dioxide happens through two steps – the first of which forms the neutral diradical species below as the intermediate.



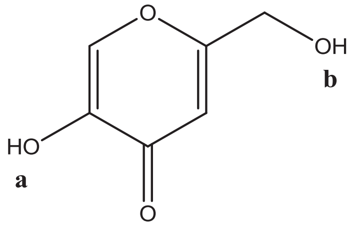
Use curly arrows to show how the intermediate decomposes to ethyne and carbon dioxide. [1]

[Total: 20]

5 Melanin is a naturally-occurring organic compound that is responsible for the colour of the skin. The higher the melanin content, the darker the skin is. In the Asian market, skin-lightening lotions have grown to be the most on-demand skin care cosmetic products.

One common ingredient of such lotions is kojic acid, which works by slowing down the rate of formation of melanin. It is obtained from the fermentation of rice malt.

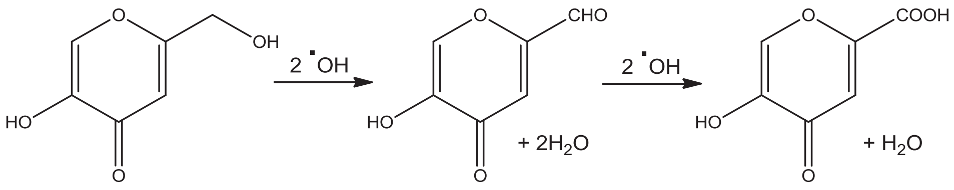
The structure of kojic acid is shown below with the two hydroxyl groups labelled **a** and **b**.



kojic acid

(a) For each of the hydroxyl groups **a** and **b**, explain if it will be substituted with a chlorine atom when one mole of kojic acid is reacted with two moles of PCl_5 at room temperature. [2]

(b) Kojic acid also functions as an antioxidant, scavenging hydroxyl radicals ($^{\bullet}OH$) that are responsible for ageing. One mole of kojic acid can react with a total of four moles of the radicals to form comenic acid via an intermediate **Z** as shown in the scheme below.



kojic acid compound **Z** comenic acid

(i) Given the following information, use curly arrows to draw the mechanism for the formation of comenic acid from compound **Z** in two separate steps.

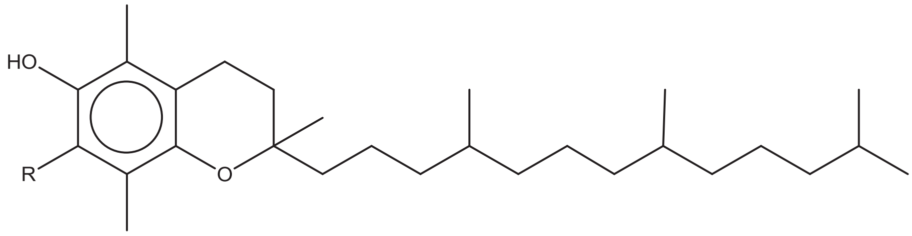
Step 1:
An •OH radical reacts with compound **Z** to form an organic radical intermediate with H_2O being formed as a by-product.

Step 2:
Another •OH radical react with the intermediate formed from the first step. [2]

(ii) Draw another possible organic by-product in the formation of comenic acid from compound **Z**. [1]

5 **(c)** Besides kojic acid, vitamin E is also an essential ingredient that acts as an antioxidant in skin-lightening lotions.

One class of vitamin E is tocopherol, the general structure of which is shown below.



tocopherol

The table below shows the substituent R of two different types of tocopherol, namely α- and β-tocopherol.

	–R
α-tocopherol	$-CH_3$
β-tocopherol	–H

Arrange phenol, α-tocopherol and β-tocopherol in an increasing order of pK_a values. Hence, explain the difference in acidity among the three compounds. [3]

(d) To increase the effectiveness and marketability of skin-lightening lotions, titanium dioxide, TiO_2, is often added as a sunscreen agent due to its reflective property.

Solid titanium dioxide reacts with hydrofluoric acid, HF, to form a coordination compound, $H_2[TiF_6]$, and water.

(i) Write a balanced chemical equation, with state symbols, for the above reaction. [1]

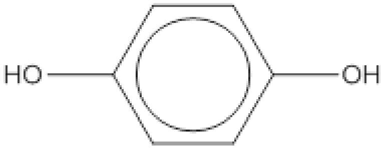
(ii) Explain whether the above reaction is a redox reaction. [1]

(iii) State the electronic configuration of titanium in $H_2[TiF_6]$. Hence, explain whether the complex ion is coloured. [3]

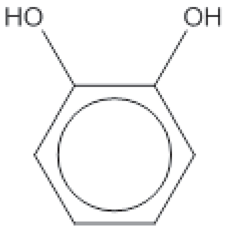
5 **(e)** Hydroquinone and catechol are isomers.

Hydroquinone has been used for more than half a century in the formulation of skin lotions to help fade uneven skin tone and dark spots. Catechol, on the other hand, is an important synthetic precursor to pesticides, flavours, and fragrances.

The structures of both compounds, together with their boiling points, are shown below.



hydroquinone
(boiling point: 287 °C)



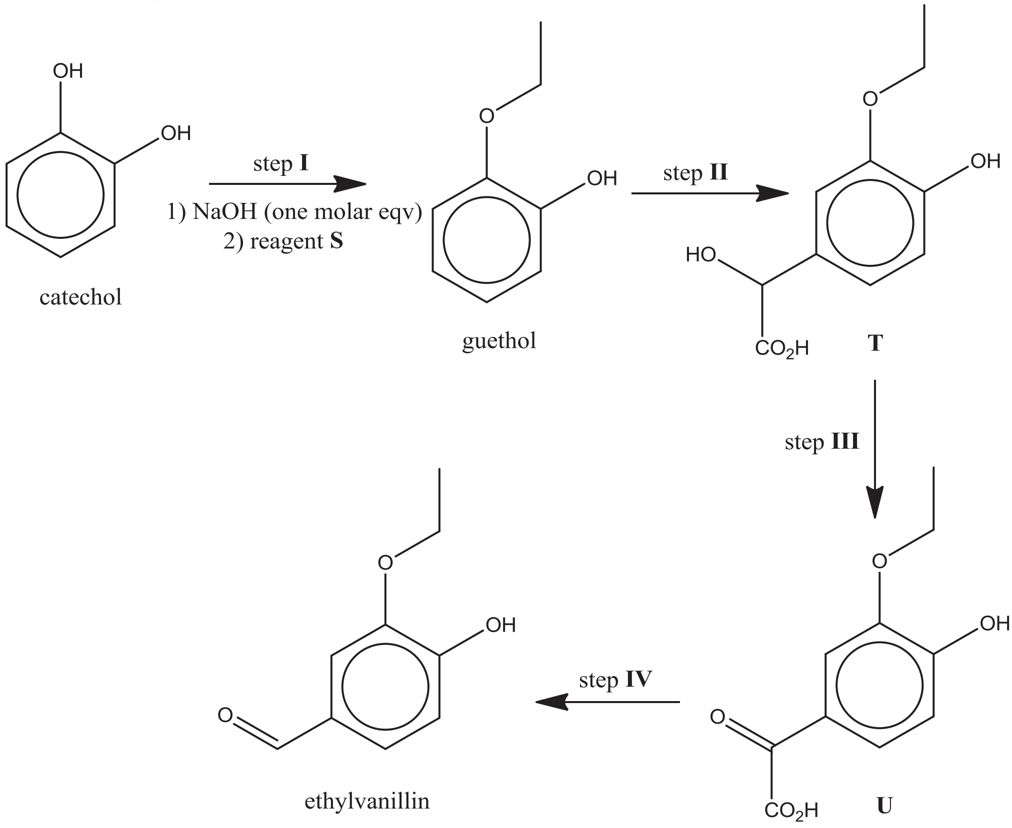
catechol
(boiling point: 246 °C)

(i) Explain why catechol has the lower boiling point. [1]

(ii) Catechol is able to function as a bidentate ligand, but not hydroquinone.

Explain why hydroquinone cannot function as a bidentate ligand. [1]

5 **(f)** Catechol is used industrially to make ethylvanillin, a flavourant reputedly three times more potent than vanillin itself.



Assume that the ether functional group (R–O–R') is inert.

(i) Explain the purpose of adding NaOH in step **I**. [1]

(ii) Name reagent **S** in step **I**. [1]

(iii) Outline the synthetic pathway to convert ethylvanillin back to compound **T**. Draw the intermediate formed. [3]

[Total: 20]

END OF PAPER

ANGLO-CHINESE JUNIOR COLLEGE
DEPARTMENT OF CHEMISTRY
Preliminary Examination

CHEMISTRY **9729/01**
Higher 2

Paper 1 Multiple Choice

24 August 2017
1 hour

Additional Materials: Optical Answer Sheet
Data Booklet

READ THESE INSTRUCTIONS FIRST

Write in soft pencil.
Do not use staples, paper clips, glue or correction fluids.
Write your name, index number and tutorial class on the Optical 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 Optical Answer Sheet.

Read the instructions on the Optical Answer Sheet very carefully.

Each correct answer will score one mark. A mark will not be deducted for a wrong answer.

Any rough working should be done in this booklet.

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

This document consists of **14** printed pages, including this cover page.

For each question there are four possible answers, **A**, **B**, **C**, and **D**. Choose the **one** you consider to be correct.

1 Carbon disulfide is a colourless volatile liquid with the formula CS_2. The compound is used frequently as a building block in organic chemistry as well as an industrial solvent.

It reacts with nitrogen monoxide, NO, to form a yellow solid and two gases. These two gases are formed in equal amounts.

What are these two gases?

A CO_2, NO_2 **B** CO_2, N_2 **C** CO, N_2 **D** CO_2, N_2O

The yellow solid is sulfur.

You cannot balance the equation (with the two product gases in equal amounts) with the three other options.

Balanced equation:

$$CS_2 + 2NO \rightarrow CO_2 + N_2 + 2S$$

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

Which of the following ions will be deflected the **most** in an electric field?

A S^{2-} **B** Br^{-} **C** F^{-} **D** O^{2-}

You are to refer to the Data Booklet for the ionic radii (although it is not absolutely necessarily to do so; you can use the Group trend for ionic sizes).

The charge density of the oxide ion is the highest amongst the four.

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

Nuclear magnetic resonance (NMR) spectroscopy is an analytical technique that uses the magnetic properties of certain atomic nuclei in order to elucidate the structure of an organic molecule.

Atomic nuclei with an even number of protons and an odd number of neutrons (or vice versa) are most suitable for NMR spectroscopy.

Which of the following nuclei is **least** suitable for NMR spectroscopy?

A ^{28}Si **B** ^{31}P **C** ^{103}Rh **D** ^{19}F

A: no. of protons 14 no. of neutrons = 28 – 14 = 14

B: no. of protons 15 no. of neutrons = 31 – 15 = 16

C: no. of protons 45 no. of neutrons = 103 – 45 = 58

D: no. of protons 9 no. of neutrons = 19 – 9 = 10

4 A 25.00 cm^3 sample of a solution of 0.150 mol dm^{-3} MoO_x^{2-} was passed through a Jones reductor (a column of zinc powder). It was reduced to Mo^{3+}. The filtrate required 22.50 cm^3 of 0.100 mol dm^{-3} acidified $KMnO_4$ (aq) to obtain back the original amount of MoO_x^{2-}.

What is the value of x?

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

Amt of electrons involved = (22.50 X 0.100 / 1000) X 5 = 0.01125

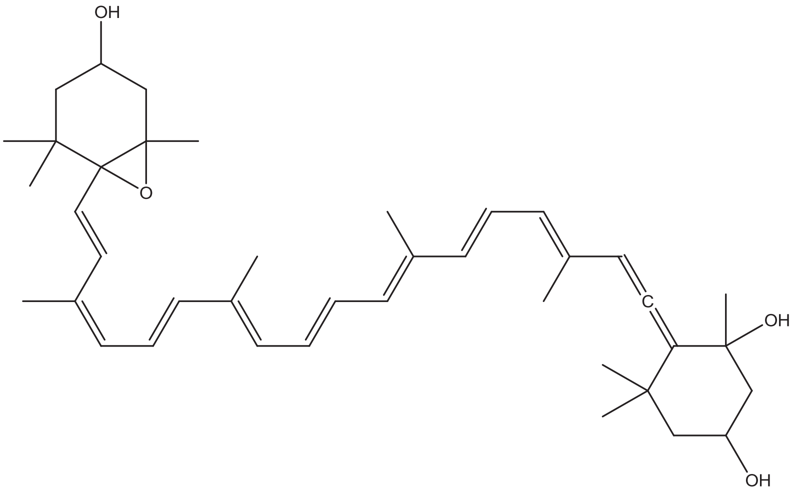
Change in oxidation state in Mo = 0.01125 / (25.00 X 0.150 / 1000) = 3

Original oxidation state of Mo = 3 + 3 = 6

Hence x = 4.

For each question there are four possible answers, **A**, **B**, **C**, and **D**. Choose the **one** you consider to be correct.

5 Neoxanthin is a major xanthophyll found in green leafy vegetables such as spinach.



Which of the following σ bonds are present in neoxanthin?

1 A σ bond formed by sp^2–sp^3 overlap.

2 A σ bond formed by s–p overlap.

3 A σ bond formed by sp–sp^2 overlap.

A 1 and 2 only

B 1 and 3 only

C 2 and 3 only

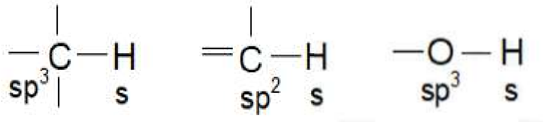
D 1, 2 and 3

Recall:

Linear Carbon: sp (eg. =C= or —C≡)
Trigonal Planar Carbon: sp^2
Tetrahedral Carbon: sp^3

Bent Oxygen (or Tetrahedral in terms of electron pair geometry) in C-O-C and C-O-H: sp^3

Option 2 is wrong. For s-p overlap, it means that the s orbital belongs to hydrogen, whereas the p orbital (unhybridised) belong to carbon. But the overlaps in the following cases are:



6 The enthalpy changes for the following reactions were measured experimentally:

$CH_3CH_2CH_3(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(l)$ $\Delta H = -2202$ kJ mol^{-1}
$H_2(g) + \frac{1}{2} O_2(g) \rightarrow H_2O(l)$ $\Delta H = -286$ kJ mol^{-1}
$CH_3{-}C{\equiv}C{-}H(g) + 2H_2(g) \rightarrow CH_3CH_2CH_3(g)$ $\Delta H = -310$ kJ mol^{-1}

What is the enthalpy change of combustion of propyne, $CH_3{-}C{\equiv}C{-}H$, in terms of kJ mol^{-1}?

A -2226 **B** -1940 **C** -1606 **D** -1320

$$\begin{tikzcd}
CH_3{-}C{\equiv}C{-}H(g) + 4O_2(g) + 2H_2(g) + O_2(g) \arrow[r, "\Delta Hc(\text{propyne})"] \arrow[d, "-310"'] & 3CO_2(g) + 2H_2O(l) + 2H_2(g) + O_2(g) \arrow[ddl, "(2)(-286)"] \\
CH_3CH_2CH_3(g) + 4O_2(g) + O_2(g) \arrow[d, "-2202"'] & \\
3CO_2(g) + 4H_2O(l) &
\end{tikzcd}$$

By Hess' Law,

$\Delta Hc(\text{propyne}) = -310 - 2202 - (2)(-286) = -1940$ kJ mol^{-1}

7 35 cm^3 of 0.001 mol dm^{-3} nitric acid solution was added to 35 cm^3 of sulfuric acid solution of the same concentration. What is the resulting pH of the combined solution?

A 1.5 **B** 2.5 **C** 2.8 **D** 3.0

Amount of H^+ from HNO_3 = (0.035)(0.001) = 0.000035 mol

Amount of H^+ from H_2SO_4 = (2)(0.035)(0.001) = 0.000070 mol

$[H^+]$ = (0.000035 + 0.000070) ÷ (0.035 + 0.035) = 0.0015 mol dm^{-3}

pH = $-\log [H^+]$ = 2.82

8 In which of the following pairs is the bond angle in the first species smaller than that in the second species?

1 PBr_3, PBr_4^+

2 H_2Se, H_2O

3 SF_2, SCl_2

A 1 and 2 only

B 1 and 3 only

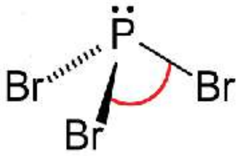
C 2 and 3 only

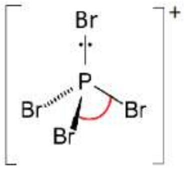
D 1, 2 and 3

Recall: VSEPR model dictates that

"Lone Pair – Lone Pair repulsion > Lone Pair – Bond Pair repulsion > Bond Pair – Bond Pair repulsion"

Option 1

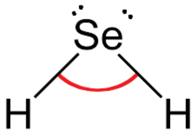




Lone pair on P in PBr_3 is closer to nucleus of P, compared to the Bond Pair in PBr_4^+.

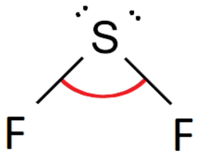
There is stronger repulsion between lone pair and bond pair in PBr_3. Hence the bond angle will be smaller than that in PBr_4^+.

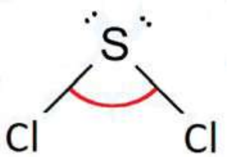
Option 2



Selenium is larger atom than Oxygen. Selenium is also less electronegative than Oxygen.
Electron density in Se–H bond is further away from Se, compared to electron density in O–H bond.
There is weaker repulsion between bond pairs in H_2Se. Hence the bond angle will be smaller than that in H_2O.

Option 3



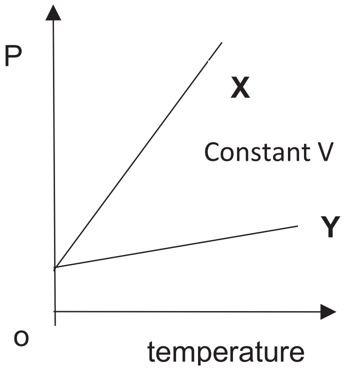


Fluorine is more electronegative than chlorine.
Electron density in S–F bond is further away from S, compared to electron density in S–Cl bond.
There is weaker repulsion between bond pairs in SF_2. Hence the bond angle will be smaller than that in SCl_2.

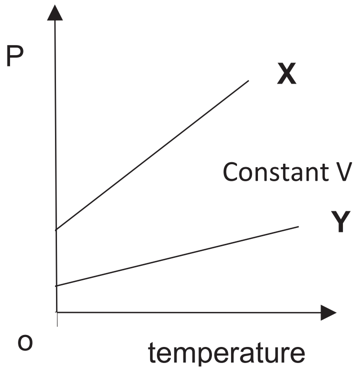
9 **X** and **Y** are both ideal gases. **X** has the smaller molecular mass.

Which of the following diagrams correctly describe the behaviour of equal masses of these gases? All temperatures are measured in °C.

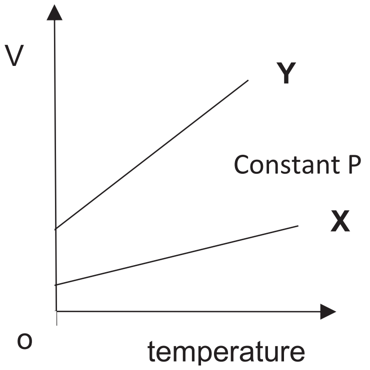
A



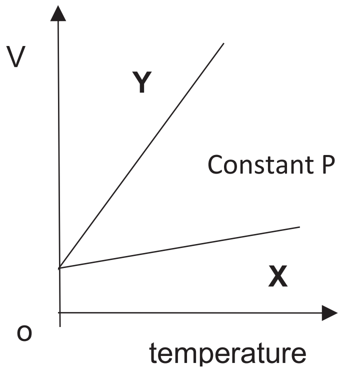
B



C



D



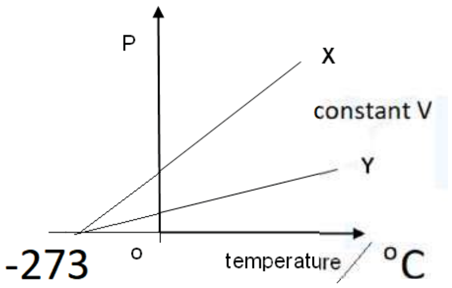
For Ideal Gas, PV = nRT

PV = (m / M_r) RT

At constant Volume, P = (m R / VM_r) T

where Gradient of Line = (m R / VM_r)

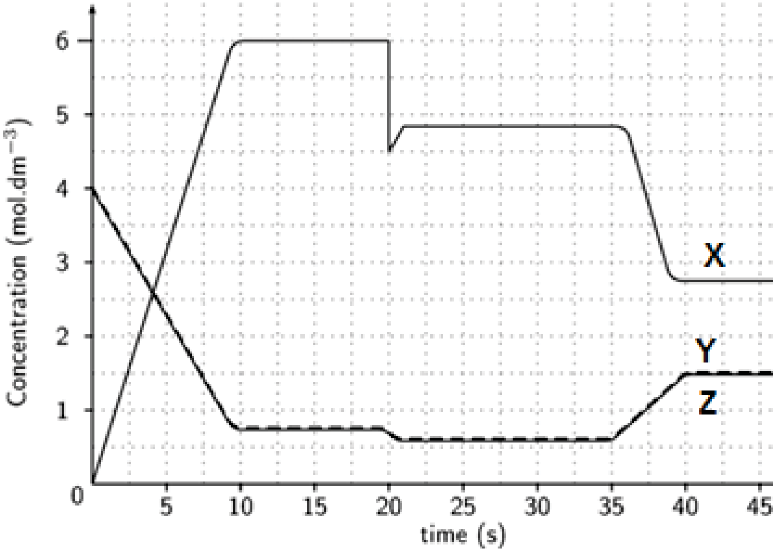
X has smaller M_r than Y. Hence the line for X has a steeper gradient than Y.



10 **X** exists in equilibrium with **Y** and **Z**.

$$2\mathbf{X}\,(g) \rightleftharpoons \mathbf{Y}\,(g) + \mathbf{Z}\,(g)$$

The concentrations of **X**, **Y** and **Z** varies across time as shown below. Note that the dotted line refers to both concentrations of **Y** and **Z**.



Which of the following statements is **false**?

A The equilibrium constant is dimensionless.

B **X**(g) was taken out of the system at 20 s.

C Given that the temperature was decreased at 35 s, it can be concluded that the forward reaction is endothermic.

D Temperature has no effect on the spontaneity of this reaction.

Option A

$K_p = (P_y P_z) / P_x^2$ atm . atm / atm^2

Hence Kp is dimensionless.

Option B

Sudden decrease in [X], but [Y] and [Z] both decrease over time at t = 20s.

This implies that X(g) is taken out of the system at t = 20s.

Option C

If $\Delta H_{forward}$ = +ve, temperature must increase for the POE to shift right.

Option D

$\Delta G = \Delta H - T\Delta S$

$\Delta S = 0$ because there is no change in total amount of gaseous particles in the system, regardless of the system shifting left or right.
Assumption: Temperature is not low enough for liquefaction of gases to occur.

11 The stepwise dissociation equations of phosphoric acid and the corresponding equilibrium constants are shown below.

$$H_3PO_4 \rightleftharpoons H_2PO_4^- + H^+ \qquad K_a = 7.50 \times 10^{-3}\ \text{mol dm}^{-3}$$
$$H_2PO_4^- \rightleftharpoons HPO_4^{2-} + H^+ \qquad K_a = 6.20 \times 10^{-8}\ \text{mol dm}^{-3}$$
$$HPO_4^{2-} \rightleftharpoons PO_4^{3-} + H^+ \qquad K_a = 2.20 \times 10^{-13}\ \text{mol dm}^{-3}$$

A phosphate buffer with pH 7 needs to be prepared.

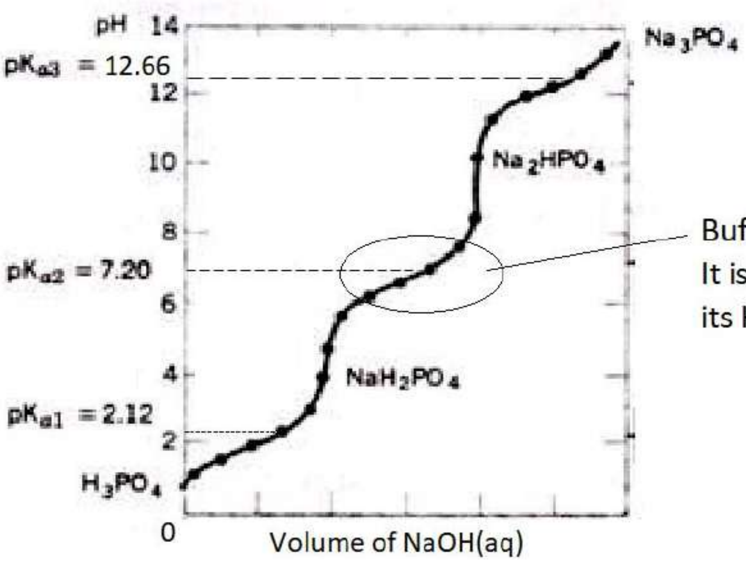
Which is the best way to prepare such a solution?

A Dissolving Na_3PO_4 alone in water.

B Dissolving H_3PO_4 and NaH_2PO_4 in water.

C Dissolving Na_2HPO_4 and Na_3PO_4 in water.

D Dissolving Na_2HPO_4 and NaH_2PO_4 in water.



Buffer with pH = 7 lies within this region. It is made up of $H_2PO_4^-$ (weak acid) and its HPO_4^{2-} (conjugate base).

12 An equilibrium can be represented by the equation below.

$$\mathbf{W}\,(aq) + \mathbf{X}\,(aq) \rightleftharpoons \mathbf{Y}\,(aq) + \mathbf{Z}\,(aq)$$

In 0.50 dm^3 of a certain mixture, the concentrations of these substances at equilibrium were as shown:

Species	**W**	**X**	**Y**	**Z**
Concentration / mol dm^{-3}	1.00	2.00	2.00	1.00

A certain amount of **Y** was added to this equilibrium mixture.

What is the number of moles of **Y** added such that the new equilibrium [**W**] is 1.20 mol dm^{-3}?

Assume that the temperature remained constant throughout.

A 0.10 **B** 0.20 **C** 0.75 **D** 1.50

At initial equilibrium, Kc = [Y(aq)] [Z(aq)] ÷ [W(aq)] [X(aq)]

Kc = (2.00)(1.00) ÷ (1.00)(2.00)

Kc = 1

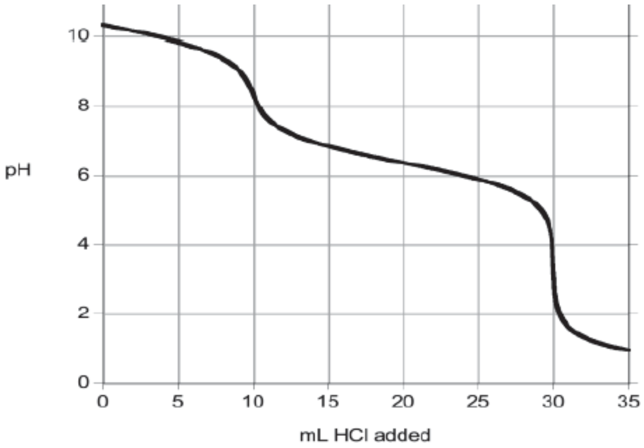
	W (aq) +	**X** (aq) ⇌	**Y** (aq) +	**Z** (aq)
Initial Conc	1.00	2.00	2.00 + a	1.00
Change	+0.20	+0.20	–0.20	–0.20
Eqm Conc	1.20	2.20	1.80 + a	0.80

For the new equilibrium, Kc = (1.80 + a)(0.80) ÷ (1.20)(2.20) = 1

Upon solving, a = 1.5 mol dm^{-3}

Since it is 0.5 dm^3 solution, therefore the amount added = (1.5)(0.5) = 0.75 mol

13 A sample of washing powder which contains a mixture of Na_2CO_3 and $NaHCO_3$ was titrated with aqueous hydrochloric acid and the following titration curve was obtained.



What is the mole ratio of HCO_3^- to CO_3^{2-} in the washing powder?

A 1:1 **B** 1:2 **C** 2:1 **D** 3:1

The first 10 cm^3 of HCl is used for: $H^+(aq) + CO_3^{2-}(aq) \rightarrow HCO_3^-(aq)$

The next (30 – 10) = 20 cm^3 of HCl is used for: $H^+(aq) + HCO_3^-(aq) \rightarrow H_2CO_3(aq)$

But this $HCO_3^-(aq)$ comes from the original sample, and from the first reaction.

Hence the $HCO_3^-(aq)$ from original sample should correspond to (20 – 10) = 10 cm^3 of HCl.

Amount of $HCO_3^-(aq)$: Amount of $CO_3^{2-}(aq)$

≡ Volume of HCl reacting with $HCO_3^-(aq)$ in original sample : Volume of HCl reacting with $CO_3^{2-}(aq)$ in sample

= 10 cm^3 : 10 cm^3

= 1 : 1

14 The table below contains the standard reduction potential values for some cobalt and mercury species.

half-equation	**E^{o}/ V**
Co^{3+} (aq) + e $\rightleftharpoons$ Co^{2+} (aq)	+1.82
Co^{2+} (aq) + 2e $\rightleftharpoons$ Co (s)	-0.28
Hg^{2+}(aq) + e $\rightleftharpoons$ Hg^{+}(aq)	+0.91
Hg^{+}(aq) + e $\rightleftharpoons$ Hg(*l*)	+0.80

Which one of the following predictions is correct?

A Both Co^{2+} and Hg^{+} will disproportionate.

B Neither Co^{2+} nor Hg^{+} will disproportionate.

C Only Co^{2+} will disproportionate.

D Only Hg^{+} will disproportionate.

For $Co^{2+} \rightarrow Co^{3+} + Co$

$E^{\ominus}_{cell} = E^{\ominus}_{red} + E^{\ominus}_{ox} = (-0.28) + (-1.82) = -2.10$ V

Since $E^{\ominus}_{cell} < 0$, the reaction is NOT spontaneous.

For $Hg^{+} \rightarrow Hg^{2+} + Hg$

$E^{\ominus}_{cell} = E^{\ominus}_{red} + E^{\ominus}_{ox} = (+0.80) + (-0.91) = -0.11$ V

Since $E^{\ominus}_{cell} < 0$, the reaction is NOT spontaneous.

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

The reaction between iodide and peroxydisulfate ($S_2O_8^{2-}$) is slow due to its high activation energy.

Which of the following cannot function as a catalyst for the above mentioned reaction?

A V^{2+} **B** Mn^{2+} **C** Mn^{3+} **D** Co^{3+}

From Data Booklet, $V^{2+} + 2e \rightleftharpoons V$ -1.20 V

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

$I_2 + 2e \rightleftharpoons 2I^-$ $+0.54$ V

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

Case 1: $S_2O_8^{2-}$ react first with V^{2+}.

$S_2O_8^{2-} + 2V^{2+} \rightarrow 2SO_4^{2-} + 2V^{3+}$
$E^{\ominus}_{cell} = E^{\ominus}_{red} + E^{\ominus}_{ox} = (+2.01) + (+0.26) = +2.27$ V
Since $E^{\ominus}_{cell} > 0$, the reaction is spontaneous.

Subsequently, V^{3+} must react to form V^{2+} again, for V^{2+} to function as a catalyst.
$2I^- + 2V^{3+} \rightarrow I_2 + 2V^{2+}$
$E^{\ominus}_{cell} = E^{\ominus}_{red} + E^{\ominus}_{ox} = (-0.26) + (-0.54) = -0.80$ V
Since $E^{\ominus}_{cell} < 0$, the reaction is NOT spontaneous.

Hence V^{2+} cannot function as a catalyst in this reaction.

Case 2: I^- react first with V^{2+}.

$2I^- + V^{2+} \rightarrow I_2 + V$
$E^{\ominus}_{cell} = E^{\ominus}_{red} + E^{\ominus}_{ox} = (-1.20) + (-0.54) = -1.76$ V
Since $E^{\ominus}_{cell} < 0$, the reaction is NOT spontaneous.

16 The decomposition of hydrogen peroxide is a first order reaction.

It takes 20 minutes for a 0.140 mol dm^{-3} solution of hydrogen peroxide to halve its concentration.

How much time (in minutes) does it take for a 0.280 mol dm^{-3} solution of hydrogen peroxide to halve its concentration?

A 80 **B** 40 **C** 20 **D** 10

Half-life is the time required for a quantity to reduce to half its initial value.

"Half its initial value" means that it is 50% of its initial value. It is about percentage or ratio, not about the absolute amount.

For 1st order reaction, $k\ t_{½} = \ln 2$. Since temperature is constant, the rate constant (k) will be constant, and hence the half-life ($t_{½}$) will be constant.

17 The reaction mechanism between O_2 and HBr is as proposed:

$HBr + O_2 \rightarrow HO_2Br$ (slow)

$HO_2Br + HBr \rightarrow 2HOBr$

$HOBr + HBr \rightarrow Br_2 + H_2O$

Which of the following statements is true?

A The bromine in HO_2Br is oxidised in the second step.

B The overall equation is $O_2 + 4HBr \rightarrow 2Br_2 + 2H_2O$.

C The half-life of this reaction is constant.

D HO_2Br is the only intermediate.

Option A

$$H{-}O{-}O{-}\underset{+1}{Br} + H{-}Br \rightarrow 2H{-}O{-}\underset{+1}{Br}$$

Option B: Add up all the elementary steps to get the overall equation.

$HBr + O_2 \rightarrow HO_2Br$

$+ HO_2Br + HBr \quad + 2HOBr$

$+ HOBr + HBr \quad + Br_2 + H_2O$

$+ HOBr + HBr \quad + Br_2 + H_2O$

Note: Add Step 3 TWO times in order to cancel out the 2HOBr in Step 2.

Option C

Rate = k $[HBr]^1 [O_2]^1$

This is not a first-order reaction.

Note: We need to assume that the HBr is NOT in large excess. Otherwise, Rate = k” $[O_2]^1$

This is a pseudo first-order reaction. Then the half-life will be constant.

Similarly, we assume that O_2 is NOT in large excess.

Option D

HOBr is another intermediate.

18 The numerical values of the solubility products at 25 °C for $PbCl_2$ and PbI_2 are 1.70×10^{-5} and 9.80×10^{-9} respectively.

What is the value of the equilibrium constant for the reaction below?

$$PbI_2\,(s) + 2Cl^-\,(aq) \rightleftharpoons PbCl_2\,(s) + 2I^-\,(aq)$$

A 3.01×10^{6}

B 1.73×10^{3}

C 5.76×10^{-4}

D 3.32×10^{-7}

K_{sp} of $PbCl_2 = [Pb^{2+}][Cl^-]^2 = 1.70 \times 10^{-5} \rightarrow [Cl^-]^2 = 1.70 \times 10^{-5} / [Pb^{2+}]$

K_{sp} of $PbI_2 = [Pb^{2+}][I^-]^2 = 9.80 \times 10^{-9} \rightarrow [I^-]^2 = 9.80 \times 10^{-9} / [Pb^{2+}]$

$K_c = [I^-]^2 / [Cl^-]^2 = (9.80 \times 10^{-9}) / (1.70 \times 10^{-5}) = \underline{\mathbf{5.76 \times 10^{-4}}}$

19 Mohr's salt is named after the German chemist Karl Friedrich Mohr, who made many important advances in the methodology of titration in the nineteenth century.

It is a double salt because it contains two cations and an anion.

Heating solid Mohr's salt with sodium hydroxide liberated a colourless gas. A green precipitate is also formed. It was insoluble in excess sodium hydroxide. On standing in air the solid turned brown.

What is the formula of Mohr's salt?

A $AgCr(CO_3)_2$

B $Ag_2Fe(CO_3)_2$

C $Fe(NH_4)(SO_4)_2$

D $Fe(NH_4)_2(SO_4)_2$

Heating the solid with NaOH liberated a colourless gas of ammonia, thus NH_4^+ is present.

The green precipitate of $Fe(OH)_2$ was formed, which was insoluble in excess sodium hydroxide and turned brown due to oxidation by air to $Fe(OH)_3$, thus Fe^{2+} is present.

Given the above deduction, the answer can be narrowed down to options C or D. To ensure that the overall compound is electrically neutral, there must be one mole of Fe^{2+}, two moles of NH_4^+ and two moles of SO_4^{2-} per mole of the salt. Hence, $\underline{\mathbf{Fe(NH_4)_2(SO_4)_2}}$ must be the salt.

20 Photographic film contains silver halides, which absorb light to form silver metal and halogens are formed. Different silver halides have different sensitivity to light and will undergo this process to a different extent.

During the development of the film, a solution of aqueous ammonia or sodium thiosulfate is used to dissolve the unreacted silver halides. However, sodium thiosulfate is preferred, as some silver halides are not soluble in aqueous ammonia.

Which statements concerning the above processes are correct?

1 Metallic silver forms a very stable complex with thiosulfate, hence silver halides are soluble.

2 The decomposition of the silver halide to metallic silver and the respective halogen is easier for AgBr than for AgC*l* because bromide is more reducing than chloride.

3 AgBr is less soluble than AgC*l* in aqueous ammonia, as solubility product of AgC*l* is of a higher value.

A 1 and 2 only

B 1 and 3 only

C 2 and 3 only

D 1, 2 and 3

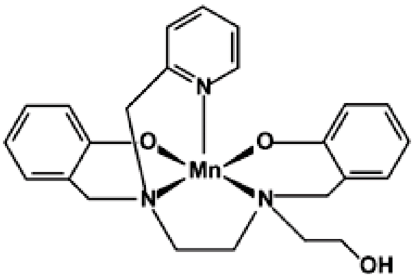
1: False. It is silver ion (Ag^+), not metallic silver, that complexes with thiosulfate.

2: True. Going down Group 17, the reducing power of the halides increases. It is true that bromide is more reducing than chloride.

3: True. Given that both AgC*l* and AgBr are binary salts, their K_{sp} values can be compared directly to determine which is more soluble. Since AgBr is less soluble than AgC*l* in aqueous ammonia, its K_{sp} value must be lower than that of AgC*l*.

Hence, statements **2 and 3 only are correct**.

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



Which of the following statements about the above complex is **false**?

A There are no 4s electrons in manganese in this complex.

B This complex contains five ligands.

C The coordination number of this complex is 5.

D The oxidation number of manganese in this complex is +2.

A: True. Mn^{2+}: [Ar]$3d^5$. The two 4s electrons have been removed in the formation of Mn^{2+} from Mn.

B: False. The complex **does not contain five ligands**. There is only one polydentate ligand.

C: True. As there are five dative covalent bonds formed into the Mn^{2+} ion, the coordination number is 5.

D: True. As the complex is electrically neutral overall, the central metal ion must be Mn^{2+} as it is bonded to two O^-.

22 Cobalt forms many coloured complexes with ligands such as H_2O and SCN^-.

A 100 cm^3 solution of $Co^{2+}(aq)$ turns from pink to bright blue when 10 cm^3 of NaSCN(aq) is added to the solution.

$$[Co(H_2O)_6]^{2+}(aq) + 4SCN^-(aq) \rightleftharpoons [Co(SCN)_4]^{2-}(aq) + 6H_2O(l)$$

pale pink bright blue

At equilibrium, $[Co(H_2O)_6]^{2+}$ and $[Co(SCN)_4]^{2-}$ are found to be present in a mole ratio of 1:10.

Given that lg K_c for the equilibrium is 3.00, which of the following statements is **false**?

A At equilibrium, $[SCN^-] = 3.16 \times 10^{-1}$ mol dm^{-3}.

B $[Co(SCN)_4]^{2-}$ is more stable than $[Co(H_2O)_6]^{2+}$.

C The units of K_c is mol^{-4} dm^{12}.

D Dilution of the reaction mixture decreases the ratio of $[Co(H_2O)_6]^{2+}$ to $[Co(SCN)_4]^{2-}$ at equilibrium.

A: True.

$$K_c = 1000 = \frac{[[Co(SCN)_4]^{2-}]}{[[Co(H_2O)_6]^{2+}][SCN^-]^4} = \frac{(10 / 0.11)}{(1 / 0.11)[SCN^-]^4}$$

$\therefore [SCN^-] = 0.316$ mol dm^{-3}

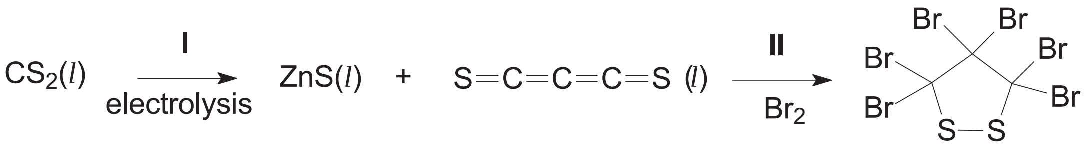
B: True. SCN^- is a stronger ligand than H_2O, thus $[Co(SCN)_4]^{2-}$ is more stable than $[Co(H_2O)_6]^{2+}$. This can also be concluded from the fact that at equilibrium, the mole ratio $[Co(SCN)_4]^{2-} : [Co(H_2O)_6]^{2+} = 10 : 1$.

C: True. $K_c = \frac{[[Co(SCN)_4]^{2-}]}{[[Co(H_2O)_6]^{2+}][SCN^-]^4}$ $(mol\ dm^{-3})^{-4} \rightarrow mol^{-4}\ dm^{12}$

D: False. By Le Chatelier's Principle, dilution of the reaction mixture causes the position of equilibrium to shift to the left, resulting in an **increase in the ratio of $[Co(H_2O)_6]^{2+}$ to $[Co(SCN)_4]^{2-}$ at equilibrium**.

23 Carbon disulfide, CS_2, can be electrolysed into carbon subsulfide, C_3S_2, an unusual compound.

The boiling points of these two compounds are 46.2 °C and 90.0 °C respectively.



Which of the following statements are **false**?

1 Bromine is acting as a reducing agent in **II**.

2 C_3S_2 has the higher boiling point because there are more covalent bonds to be broken than in CS_2.

3 The carbon atoms in C_3S_2 do not share a common oxidation state.

A 2 and 3 only

B 1 and 3 only

C 1 and 2 only

D 1, 2 and 3

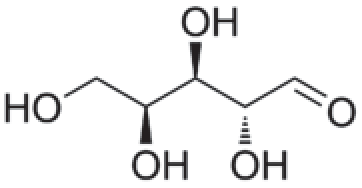
1: False. Bromine is acting as an oxidising agent in **II**.

2: False. The boiling point of a simple covalent molecule depends on the intermolecular forces of attraction, not the number or strength of the covalent bonds.

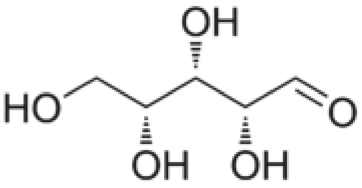
3: True. Each of the carbon atoms directly bonded to sulfur is +3, while the other carbon not directly bonded to sulfur is +2.

Hence, statements **1 and 2 only are false**.

24 L-lyxose and D-xylose are monosaccharides.



L-xylose



D-xylose

Which of the following statements are true?

1 They have the same melting point.

2 The same volume of hydrogen gas is produced when excess sodium is added to equal amounts of each of them under the same conditions.

3 Both compounds undergo intramolecular nucleophilic substitution to form cyclic esters.

A 1 and 2 only

B 1 and 3 only

C 2 and 3 only

D 2 only

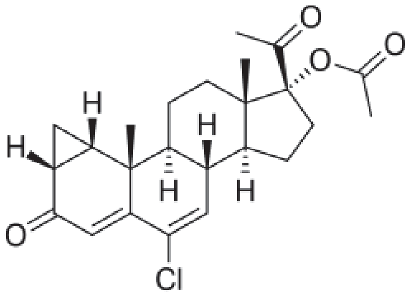
1: False. L-xylose and D-xylose are not enantiomers (they are diastereomers), thus they have different physical properties, such as melting point.

2: True. Both L-xylose and D-xylose have four hydroxyl groups each. One mole of the monosaccharide produces two moles of hydrogen gas when reacted with sodium.

3: False. Ester is formed from the reaction between a carboxylic acid (or acyl halide) and an alcohol functional group. There is no carboxylic acid functional group in either monosaccharides.

Hence, statement **2 only is correct**.

25 Cyproterone acetate (abbreviated as CPA) is a drug that is used in the treatment of androgen-related conditions like acne and prostate cancer.



Which of the following statements about CPA are correct?

1 One mole of CPA undergoes condensation with three moles of 2,4-dinitrophenylhydrazine.

2 Two moles of yellow precipitate is formed when one mole of CPA is warmed with alkaline iodine solution.

3 CPA does not cause a colour change in hot acidified potassium dichromate(VI).

A 1 and 3 only

B 1 and 2 only

C 2 and 3 only

D 3 only

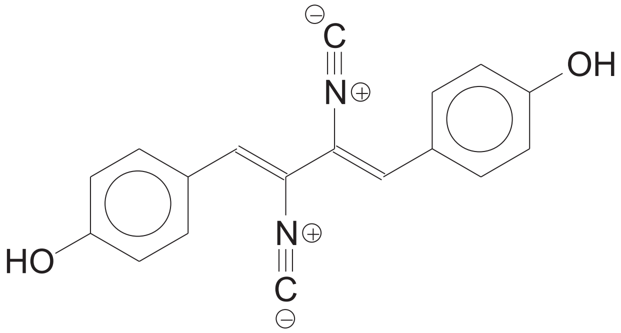
1: False. One mole of CPA undergoes condensation with only two moles of 2,4-DNPH.

2: False. Only one mole of yellow precipitate is formed when one mole of CPA is subjected to iodoform test.

3: True. Alkenes can only be oxidised by hot acidified potassium manganate(VII), while the alcohol formed from the cleavage of the ester bond is a tertiary alcohol and thus cannot be oxidised.

Hence, statement **3 only is correct**.

26 Xantocillin was first isolated from *Penicillium notatum* in the 1950s. It is used as an antibiotic.



xantocillin

Which of the following statements about xantocillin is **false**?

A It is a nitrile.

B It exists as three cis-trans isomers.

C There are four sp hybridised atoms.

D It gives a violet colouration on adding neutral iron(III) chloride.

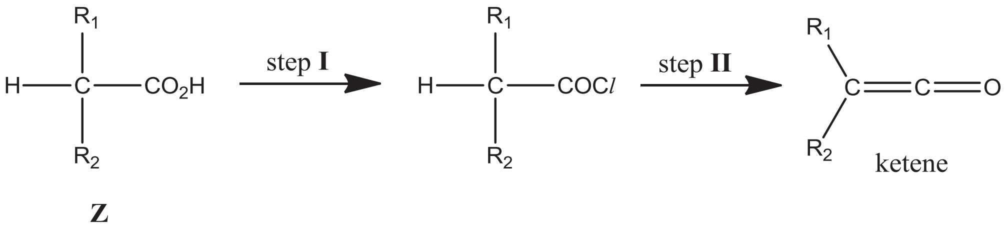
A: False. It is **not a nitrile** (–CN), but rather contains isocyanide (–NC) functional groups.

B: True. As xantocillin is symmetrical and there are two C=C double bonds, there are the cis-cis, cis-trans (or trans-cis) and trans-trans isomers.

C: True. Each of the two isocyanide (–NC) functional groups contains one sp carbon atom and one sp nitrogen atoms. Hence, there are four sp hybridised atoms in total.

D: True. Phenol reacts with neutral iron(III) chloride to give a violet colouration.

27 Ketenes are important reagents in organic synthesis. They can be formed from carboxylic acids via the synthetic route below.



Which of the following statements about the above reaction are correct?

1 The ketene will always be non-chiral, no matter which **Z** is used as the starting reactant.

2 Hydrochloric acid can be used as the reagent in step **I**.

3 The ketene can be converted back into **Z** by using water under suitable conditions.

A 1 and 2 only

B 1 and 3 only

C 2 and 3 only

D 1, 2 and 3

1: True. There is no chiral carbon in the ketene (C=C=O) functional group.

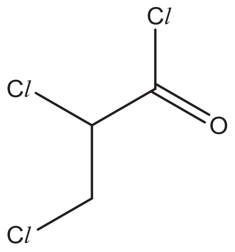
2: False. Such conversion can be achieved through the use of PCl_3, PCl_5 or $SOCl_2$ instead of HCl.

3: True. Water acts as a nucleophile to convert ketene back into **Z**.

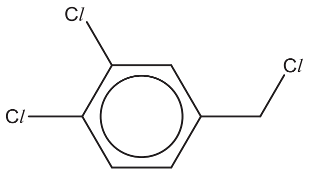
Hence, statements **1 and 3 only are correct**.

28 Aqueous silver nitrate can be used to test for the presence of halogens in organic compounds. Which of the following compounds produces a precipitate most readily when aqueous silver nitrate is added?

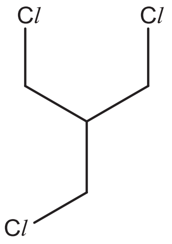
A



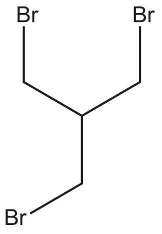
B



C

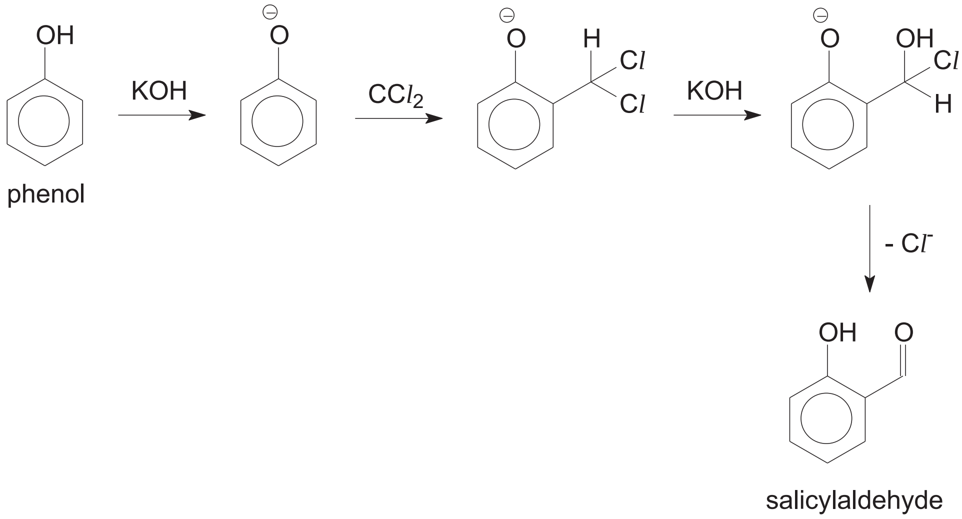


D



As acyl chloride is the easiest to hydrolyse, the compound in option **A** will produce a precipitate most readily upon the addition of aqueous silver nitrate.

29 The Reimer–Tiemann reaction is a chemical reaction used for the ortho-formylation of phenols, with the simplest example being the conversion of phenol to salicylaldehyde.



Which of the following types of reaction are involved in the above reaction scheme?

1 Nucleophilic substitution

2 Electrophilic substitution

3 Elimination

A 1 and 2 only

B 1 and 3 only

C 2 and 3 only

D 1, 2 and 3

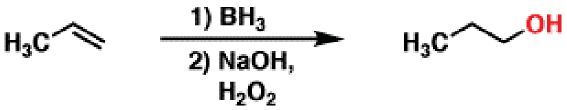
1: True. Step 3 involves nucleophilic substitution of –C*l* to –OH.

2: True. Step 2 involves electrophilic substitution on the 2-position of the phenyl ring.

3: True. Step 4 involves elimination of C*l*⁻.

Hence, statements **1, 2 and 3 are correct**.

30 Hydroboration is one of the many methods to hydrate alkenes to alcohols. An example is shown below.



Which of the following alcohols cannot be formed via hydroboration?

A Butan-2-ol from but-1-ene

B 2-methylpropan-1-ol from 2-methylpropene

C 3-methylpentan-2-ol from 3-methylpent-2-ene

D 4-methylhexan-3-ol from 3-methylhex-3-ene

As seen from the example, hydroboration is an anti-Markovnikov electrophilic addition reaction. It means a hydrogen atom is added to the more substituted carbon atom instead of the less substituted carbon atom.

As such, subjecting but-1-ene to hydroboration should result in the formation of butan-1-ol instead of butan-2-ol.

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 **15 August 2017**
2 hours

Candidates answer on the Question Paper
Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name, index number, form class, tutorial class and subject tutor's name on all the work you hand in.
Write in dark blue or black pen.
You may use a soft pencil for any diagrams, graphs or rough working.
Do not use staples, paper clips, glue or correction fluid.

Answer **all** questions.
A Data Booklet is provided.

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

For Examiner's Use	
Question no.	**Marks**
1	**/ 7**
2	**/ 13**
3	**/ 9**
4	**/ 11**
5	**/ 5**
6	**/ 9**
7	**/ 14**
8	**/ 7**
TOTAL	**/ 75**

This document consists of **21** printed pages, including this cover page.

For more than two millenia human ingenuity has turned natural and synthetic poisons into weapons of war. World War I was especially hailed by historians as the “Chemists’ War” because it was the first war in which chemical weapons were used on such an enormous scale, even on civilians. Chemicals were used to bring widespread destruction and death. It set the precedence for World War II. On the bright side, chemicals were used to save millions of soldiers’ lives in World War II.

Question 1 examines how chemical weapons were used to kill in World War I, while Question 2 examines the use of chemicals as medicine in the battlefields of World War II.

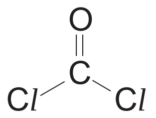
1 A range of different chemicals - chlorine, phosgene and mustard “gas” - were used as weapons throughout World War I.

Their melting and boiling points are tabulated below.

Gas	**Melting point / ^{0}C**	**Boiling point / ^{0}C**
chlorine	-101.5	-34.0
phosgene	-118	8.3
mustard “gas”	14.4	217.0

Chlorine was first used on a large scale by the German forces at Ypres in April 1915. It reacts with water in the lungs to form hydrochloric acid, which can quickly lead to death. At lower concentrations, it can cause coughing, vomiting, and irritation to the eyes.

(a) Phosgene is a colourless gas, with an odour likened to that of ‘musty hay’.



phosgene

Phosgene is known to react violently with water to give hydrochloric acid and carbonic acid. Give the equation of the reaction between phosgene and water.

$$COCl_2 + 2H_2O \rightarrow H_2CO_3 + 2HCl$$

[1]

(b) The Germans introduced another chemical weapon – mustard “gas”. It was fired into enemy positions by cannons.

(i) How is the name mustard “gas” misleading?

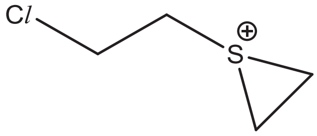
It is actually a liquid at room temperature because its melting point is lower than room temperature and its boiling point is higher than room temperature.

[1]

1 **(b)** The structural formula of mustard "gas" is $ClCH_2CH_2SCH_2CH_2Cl$.

Unlike alkyl halides, mustard "gas" reacts instantly with water to form hemi-mustard, $ClCH_2CH_2SCH_2CH_2OH$.

(ii) The following intermediate is thought to be formed by mustard "gas" itself via an intramolecular nucleophilic substitution before the attack of water.



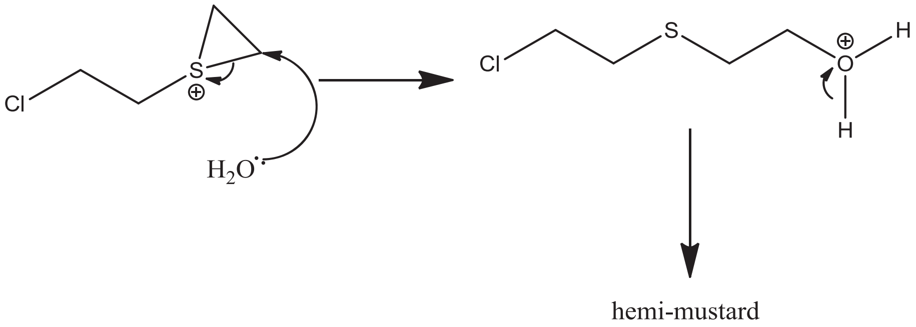
How does this intermediate make the hydrolysis of mustard "gas" easier than that of alkyl halides?

The presence of angle/ring strain in this intermediate makes it more susceptible to nucleophilic attack than the mustard gas molecule itself.

[1]

(iii) The conversion of the intermediate in **b(ii)** to hemi-mustard involves two steps, the first involving the attack by water and the second involving deprotonation.

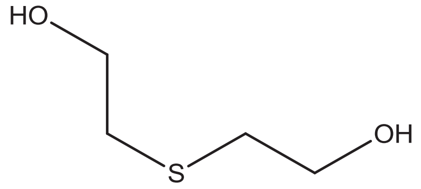
Use electron arrows to show how the intermediate in **b(ii)** is converted into hemi-mustard.



[2]

1 (b) (iv) Hemi-mustard can be further attacked by water to form **J**, $C_4H_{10}SO_2$.

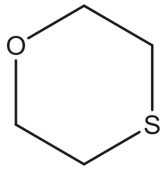
Draw the structure of **J**.



[1]

(v) On reaction with concentrated sulfuric acid at 140 °C, hemi-mustard can be converted into **K**, C_4H_8SO, which does not decolourise bromine.

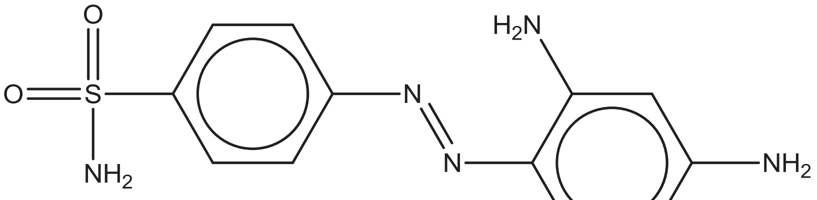
Draw the structure of **K**.



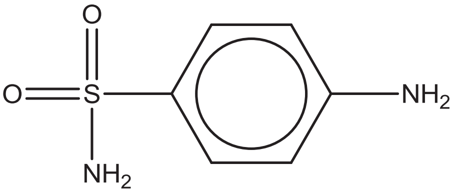
[1]

[Total: 7 marks]

2 **(a)** Prontosil and sulfanilamide are anti-bacterial drugs.



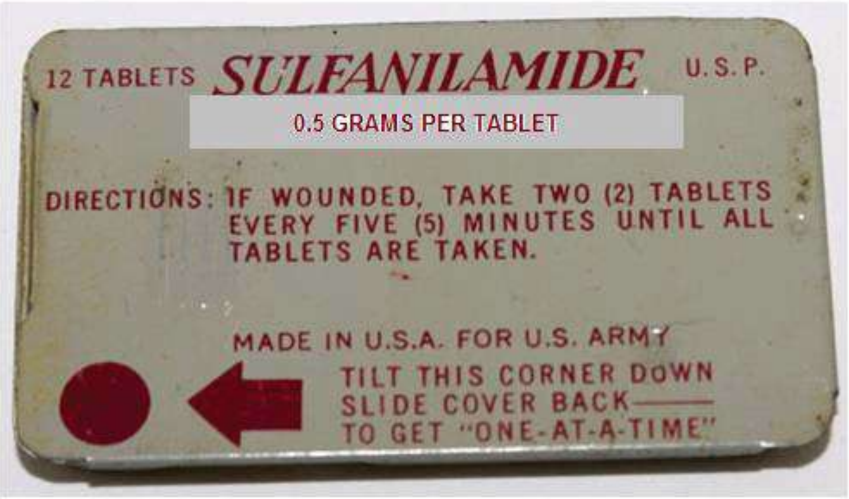
prontosil



sulfanilamide

These two drugs saved many soldiers in World War II.

The photo below is that of a **sulfanilamide kit** issued by the United States Army to its soldiers during World War II.



One source states that the maximum daily dosage of sulfanilamide is 6.5 g per kg of patient. An average US army soldier may be assumed to weigh about 70 kg.

Sulfanilamide has many side-effects – itching, headache, diarrhoea, pale skin, vomiting, dizziness, fatigue.

Is it safe for a wounded US army soldier to consume as many as 30 **kits** worth of tablets in a single day? Justify with calculations.

Yes.
Mass of drug in 30 kits = 30(12)0.5 g < 6.5(70) g

[1]

2 **(b)** Prontosil was found to be active in *vivo* (in human bodies) while sulfanilamide was found to be active both in *vivo* and in *vitro* (in bacterial cultures grown in petri dishes).

It was later proven that intestinal enzymes break down prontosil to sulfanilamide in the human intestine – in this reaction, the oxidation states of certain nitrogen atoms are altered.

There are a few classes of enzymes as listed below.

Transferases catalyse group transfer reactions.

Hydrolases catalyse reactions that involve hydrolysis.

Ligases are used in catalysis where two substrates are litigated and the formation of carbon-carbon, carbon-sulfide, carbon-nitrogen, and carbon-oxygen bonds due to condensation reactions.

Reductases catalyse reduction reactions.

Oxidases catalyse oxidation reactions.

(i) Suggest the type of intestinal enzyme which catalyses the conversion of prontosil to sulfanilamide.

Reductase

[1]

(ii) Name the side-product in the conversion of prontosil to sulfanilamide.

1,2,4-triaminobenzene or benzene-1,2,4-triamine

[1]

To analyse the sulfanilamide content in a pill, it was dissolved in HC*l* (aq).

(c) Sulfanilamide is not very soluble in water. Explain why sulfanilamide is not soluble in water but is soluble in HC*l* (aq).

Sulfanilamide is not very soluble in water due to limited hydrogen bonding due to the presence of benzene / hydrophobic nature of benzene.

However, in acid, sulfanilamide is a base / will be protonated by acid / becomes ionic, so interactions with water change from hydrogen bonding to the more favorable / stronger ion-dipole interactions.

[2]

2 A 0.350 g sample of an antibiotic powder containing sulfanilamide was dissolved to form an aqueous solution.

The solution was diluted and made up to the mark in a 100 cm^3 graduated flask. A 25.0 cm^3 aliquot was transferred into a conical flask, in which 25.0 cm^3 of 0.0200 mol dm^{-3} $KBrO_3$ was added. About 10 g of solid KBr was then added.

BrO_3^- reacts with bromide according to the equation:

$$BrO_3^- + 5Br^- + 6H^+ \rightarrow 3Br_2 + 3H_2O$$

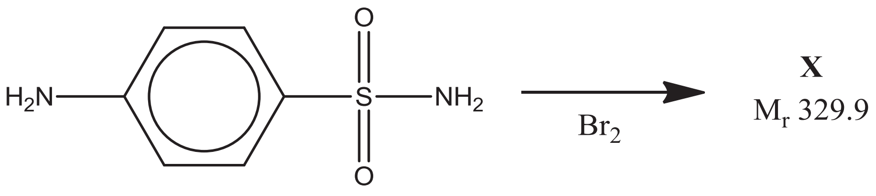
(d) **(i)** Calculate the amount of Br_2 formed.

Amount of Br_2 = 3 * (25.0 * 0.0200 / 1000) = 0.00150 mol

[1]

The bromine formed then reacts with the sulfanilamide to form **X**.

Note that the following equation is not balanced.



sulfanilamide
M_r 172.1

(ii) By comparing the M_r of sulfanilamide and **X**, show that **X** is a dibrominated compound.

The A_r of bromine is 79.9 to the nearest 1 dp.

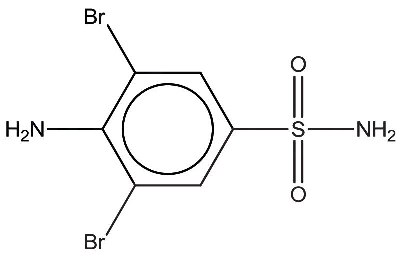
Observing the 0.9 in the M_r of **X**, we can conclude there are two bromine atoms in **X**.

Or

329.9 + 2 – (172.1) = 159.8 = 2(79.9)

[1]

(iii) Draw the structure of **X**, ignoring the directing effects of the $–SO_2NH_2$ group.



[1]

2 (e) After ten minutes, an excess of KI was added.

$$Br_2 + 2I^- \rightarrow 2Br^- + I_2$$

The liberated iodine was then titrated with 18.00 cm^3 of 0.0900 mol dm^{-3} $Na_2S_2O_3$.

$$I_2 + 2S_2O_3^{2-} \rightarrow S_4O_6^{2-} + 2I^-$$

Calculate the amount of bromine which reacted with the KI.

Amt of iodine = 0.5 * (18.00 * 0.0900 / 1000) = 8.10×10^{-4} mol = amount of bromine reacted with KI.

[1]

(f) Using your answers to **(d)** and **(e)**, calculate the amount of sulfanilamide which reacted with the bromine.

Amt of bromine reacted with sulfanilamide
$= (1.50 \times 10^{-3}) - (8.10 \times 10^{-4}) = 6.90 \times 10^{-4}$ mol

amt of sulfanilamide which reacted with the bromine $= 3.45 \times 10^{-4}$ mol

[2]

(g) Hence, calculate the percentage mass of sulfanilamide in the sample.

Mass of sulfanilamide in sample = $3.45 \times 10^{-4} \times 4 \times 172 = 0.2374$ g

Percentage mass of sulfanilamide in sample = $\frac{0.2374\,g}{0.350g} \times 100\% = 67.8\%$

[2]

[Total: 13 marks]

3 Hydrazine (N_2H_4) was first used as rocket fuel in World War II, and has since been used as a propellent for maneuvering spacecraft, as it decomposes rapidly and exothermically into hydrogen gas and nitrogen gas.

Hydrazine may be produced industrially by the Olin-Rashig process from NH_2Cl and ammonia.

$$NH_2Cl\ (g) + NH_3\ (g) \rightleftharpoons HCl\ (g) + N_2H_4\ (g)$$

The values of K_c are tabulated below with the corresponding temperatures.

T / K	298	304	503
K_c	1.525×10^6	1.230×10^5	2.201×10^4

(a) State the value of K_p at 304 K. Justify your answer.

1.230×10^5

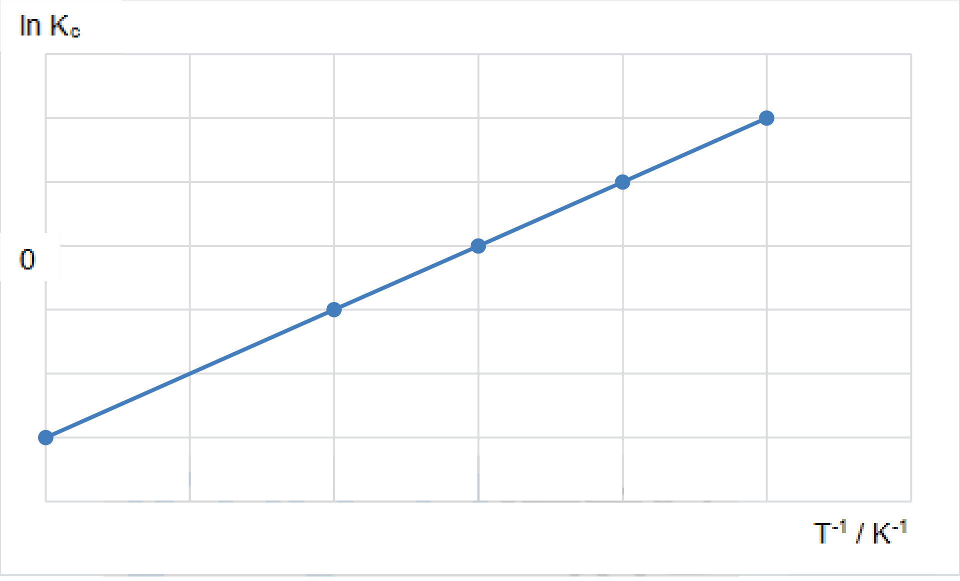
As the unit of K_c is dimensionless OR there are equal amounts of gaseous reactants and products in the equation, the value of K_c is the same as the value of K_p.

[2]

(b) By manipulating the relationship of $K_c = e^{\frac{-\Delta G}{RT}}$, we obtain

$$R \ln K_c = \frac{1}{T}(-\Delta H) + \Delta S.$$

The graph below was plotted with ln K_c as the y-axis and $\frac{1}{T}$.as the x-axis.



(i) Describe how you would obtain the value of ΔS from the above graph.

Read off the y-intercept and then multiply it by R

[1]

3 **(b)** **(ii)** Another way to find the standard entropy change of a reaction is to consider the standard molar entropies of the species involved.

Species	HCl (g)	N_2H_4 (g)	NH_2Cl (g)	NH_3 (g)
Standard molar entropy / J mol^{-1} K^{-1}	187	239	201	193

Calculate the standard entropy change of the Olin-Rashig process.

Standard entropy change

$= \sum S\,(products) - \sum S\,(reactants)$

$= 187 + 239 - (201+193)$

$= +32$ J mol^{-1} K^{-1}

[1]

(iii) Hence, using your answer to **b(ii)** and the equation in **(b)**, calculate the standard enthalpy change of the Olin-Rashig reaction, including its units.

$$\mathrm{R} \ln \mathrm{K_c} = \frac{1}{\mathrm{T}}(-\Delta\mathrm{H}) + \Delta\mathrm{S}$$

$8.31 \ln (1.525 * 10^6) = (1/298)(-\Delta H) + 32$

$\Delta H = -25.7$ kJ mol^{-1}

[1]

(c) The pK_a and pK_b values of the two reactants – monochloramine (NH_2Cl) and ammonia - are tabulated below.

Product	NH_2Cl	NH_3
pK_a	14	32.5
pK_b	15	4.75

Explain these differences as much as you can.

NH_2Cl has an Cl atom which is more electronegative than H in NH_3.

The presence of the more electronegative chlorine atom in NH_2Cl compared to hydrogen in NH_3 causes the lone pair on the nitrogen in monochloramine to be less available than the lone pair in ammonia. Hence, monochloramine is the weaker base as shown by the bigger pK_b.

The presence of the more electronegative chlorine atom in NH_2Cl compared to hydrogen in NH_3 causes the conjugate base of monochloramine to be more stable than the conjugate base of ammonia. Hence monochloramine is the stronger acid as shown by the bigger pK_a.

[2]

3 **(d)** Monochloramine is an oxidising agent.

$$NH_2Cl + 2H^+ + 2e \rightarrow NH_4Cl$$

The reduction potentials of the above half-reaction is +1.45 V.

However, in alkaline medium, the reduction potential is + 0.74 V.

Explain the difference between these two reduction potentials.

In alkaline medium, concentration of H^+ will be lower, thus backward reaction is favoured.

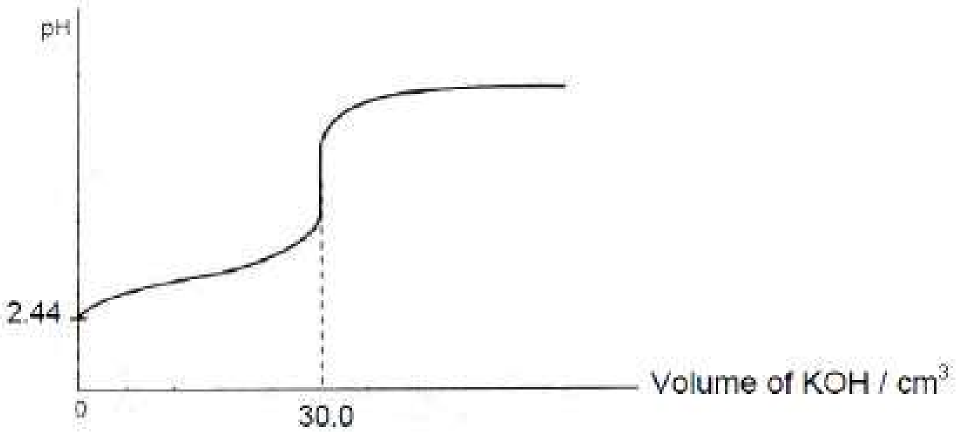
The tendency of monochloramine to be reduced decreases, and hence the reduction potential decreases.

[2]

[Total: 9 marks]

4 **(a)** Ethanoic acid, a weak monobasic acid, is the main component in vinegar.

When a 20.0 cm^3 sample of vinegar was titrated against 0.05 mol dm^{-3} aqueous potassium hydroxide using a pH meter, the following graph was obtained.



(i) Show that the concentration of the ethanoic acid solution is 0.0750 mol dm^{-3}.

Amount of KOH
= 30.0/1000 * 0.05

Concentration of ethanoic acid solution
= (30.0/1000 * 0.05) / (20.0/1000) = 0.0750 M (shown)

[1]

(ii) Hence use your answer and the initial pH to show that ethanoic acid is a weak acid.

If ethanoic acid were a strong acid where dissociation is complete (100%), $[H^+] = 0.0750$ M, pH = – log (0.0750) = 1.12

However, it is a weak acid where dissociation is partial, the $[H^+]$ dissociated is low, the actual pH would be higher than 1.12.
OR

$[H^+] = 10^{-2.44} = 0.003631$ M < 0.0750M, dissociation of acid is not complete, it is a weak acid.

[2]

4 **(a)** **(iii)** Show that the acid dissociation constant of ethanoic acid has a numerical value of 1.85 x 10^{-4}.

$[H^+]$ = 0.003631 M
$K_a = (0.003631)^2 / (0.0750 – 0.003631) = 1.85 \times 10^{-4}$ M

[2]

(iv) Calculate the value of the pH after 15.00 cm^3 of aqueous potassium hydroxide has been added.

When 15.00 cm^3 of KOH is added, half of the weak acid would have reacted. It is a maximum buffering capacity.

$pH = pK_a = 3.73$

[1]

(v) Write a suitable chemical equation, with state symbols, to explain why the equivalence pH is above 7.

Hydrolysis of conjugate base:

$$CH_3CO_2^- (aq) + H_2O (l) \rightleftharpoons CH_3CO_2H (aq) + HO^- (aq)$$

[1]

(b) **(i)** Solution **A** was prepared by adding 10.00 cm^3 of the potassium hydroxide solution to 25.0 cm^3 of the ethanoic acid solution.

Calculate the pH of solution **A**.

Amt of ethanoic acid remaining = $\frac{25\times0.0750}{1000} - \frac{10\times0.0500}{1000}$ = 0.001375 mol
Amt of ethanoate = 0.0005
$pH = pK_a + \lg (\frac{[salt]}{[acid]})$
$= -\lg (1.85 \times 10^{-4}) + \lg (0.0005/0.001375) = 3.29$

[2]

(ii) When a small amount of acid or base is added to solution **A**, its pH remained relatively constant. Explain, with the aid of equations, why this is so.

Solution **A** is buffer as there are large reservoirs of ethanoic acid (weak acid) and ethanoate ions (conjugate base).

When a small amount of acid is added,

$$CH_3CO_2^- + H^+ \rightarrow CH_3CO_2H$$

The formation of CH_3CO_2H is insignificant compared to the large reservoir of CH_3CO_2H. Hence, the pH does not decrease significantly.

When a small amount of base is added,

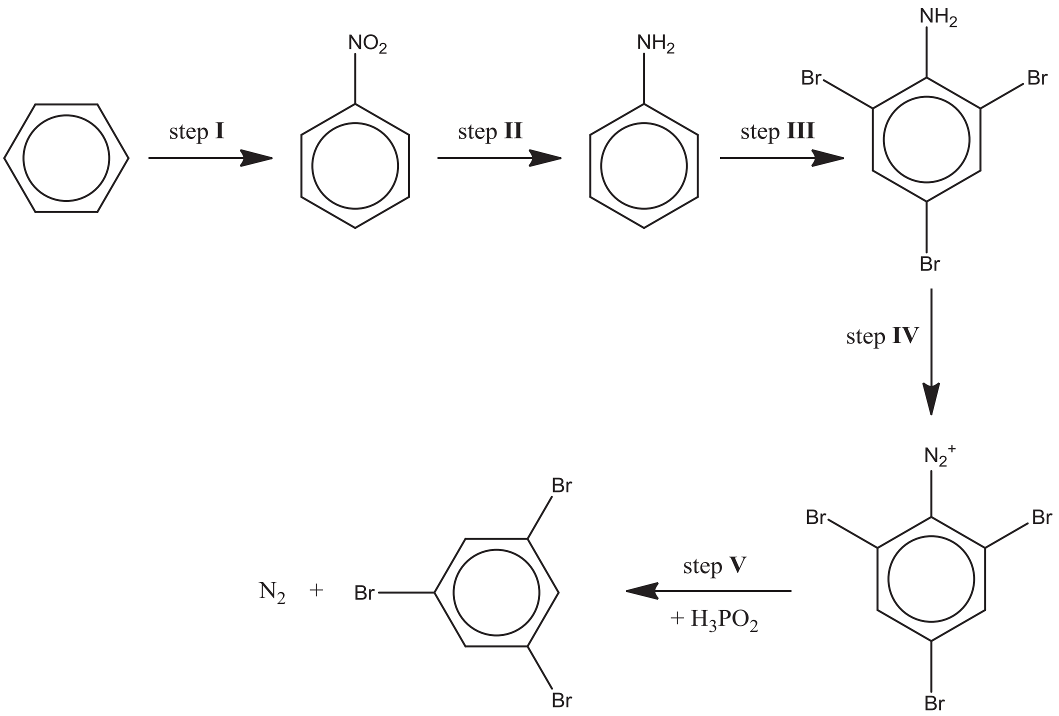
$$CH_3CO_2H + OH^- \rightarrow CH_3CO_2^- + H_2O$$

The formation of $CH_3CO_2^-$ is insignificant compared to the large reservoir of $CH_3CO_2^-$. Hence, the pH does not increase significantly.

[2]

[Total: 11 marks]

5 Study the synthetic route from benzene to 1,3,5-tribromobenzene, shown below.



(a) State the reagents and conditions used in steps **I** and **II.**

step **I** : Conc. HNO_3, conc. H_2SO_4, 55 -60 ^{0}C
step **II** : Sn, conc HC*l* , heat under reflux

[2]

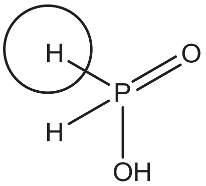
(b) By examining the positions of the bromine atoms, suggest why 1,3,5-tribromobenzene cannot be made directly from benzene with bromine.

Bromine is a 2,4-director.

[1]

(c) Phosphinic acid, H_3PO_2, is used in step **V**. Only one out of its three hydrogen atoms is acidic. A non-acidic hydrogen substituted on the benzene to liberate nitrogen gas.

Draw the structure of phosphinic acid and circle the hydrogen atom which substitutes on the benzene.

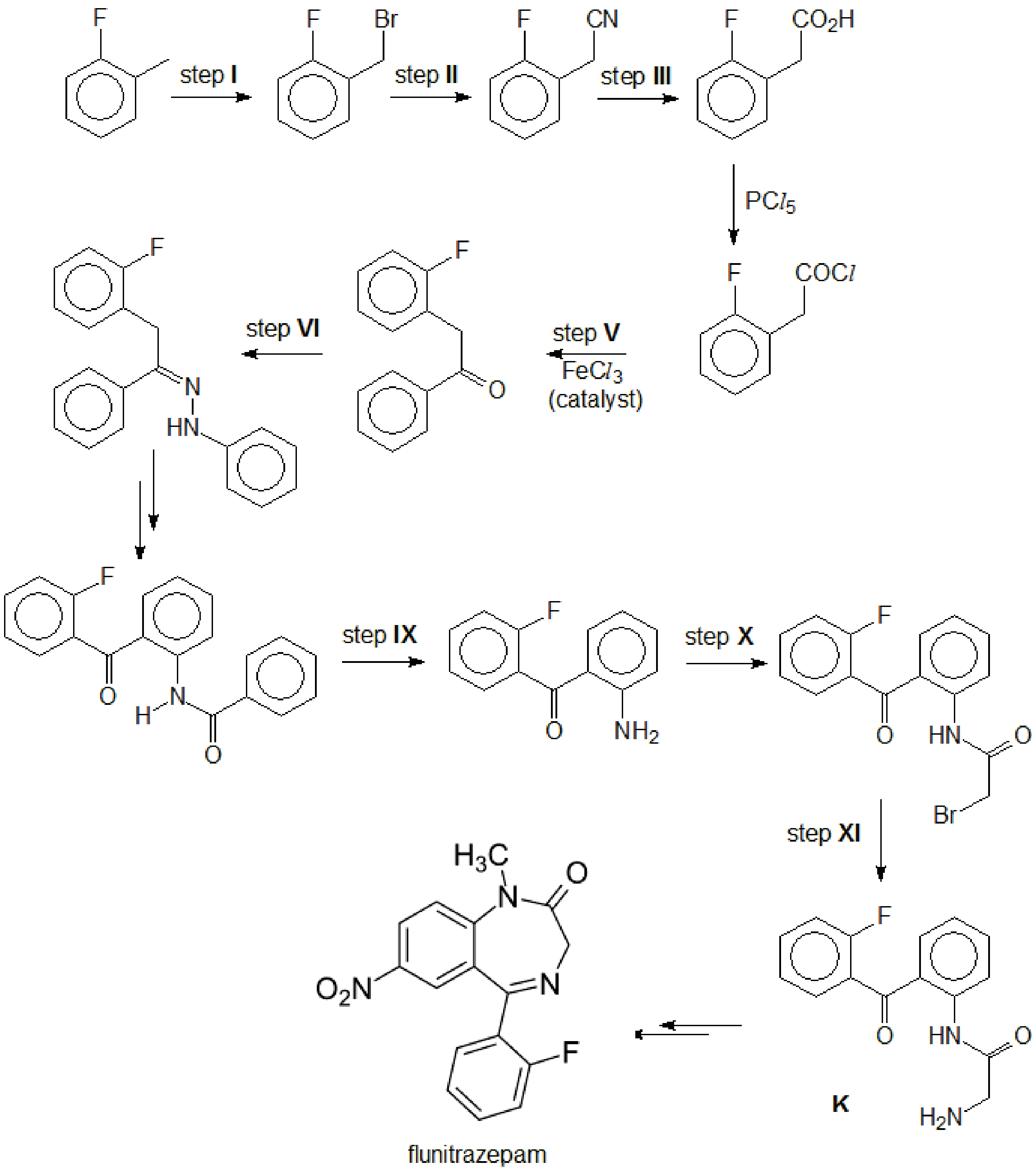


[2]

[Total: 5 marks]

6 **(a)** Flunitrazepam is a drug used in the short-term treatment of insomnia and as a pre-medication in surgical procedures and for inducing anaesthesia.

Study the synthetic route to flunitrazepam shown below.

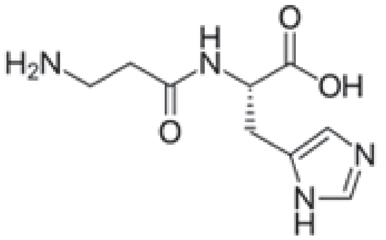


6 **(a)** Fill in the table below with the appropriate reagents and conditions.

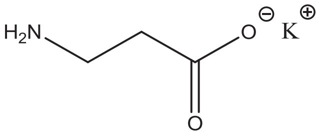
Step	**Reagents and conditions**
I	Limited Br_2, UV or high temp
II	KCN, ethanol, heat under reflux
III	H_2SO_4 (aq) (or HCl), heat under reflux
V	Benzene
VI	Phenylhydrazine ($C_6H_5NHNH_2$)
XI	excess ammonia, ethanol, heat in sealed tube. Or concentrated ammonia, heat at high pressure

[6]

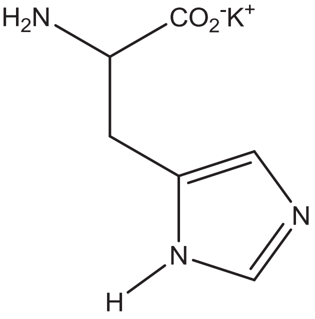
6 (b) Carnosine is a dipeptide health supplement. It first appeared in the mainstream health community around a decade ago in the form of supplements, eye-drops and skin creams.


carnosine

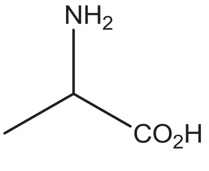
(i) One of the products is β–alanine (structure shown below) when carnosine is hydrolysed with hot KOH (aq).



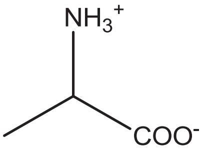
Draw the structural formula of the other product.



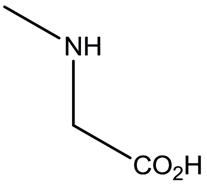
(ii) α-alanine is one of the twenty essential amino acids. It is a constitutional isomer of β–alanine. Unlike β–alanine, it is chiral. Draw the skeletal formula of α-alanine.



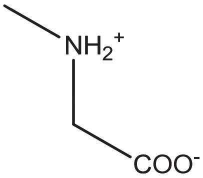
OR



(iii) Sarcosine is another constitutional isomer of β–alanine. It is an α-amino acid, just like α-alanine. Draw the structural formula of sarcosine.



OR



[3]
[Total: 9 marks]

7 Sulfur forms many cyclic allotropes with different ring sizes. In the solid state, the most stable allotrope of sulfur is the form of S_8. In the gas phase, all ring sizes from S_3 to S_{12} have been detected.

(a) In the gas phase, the different ring sizes are in equilibrium. The equation for the equilibrium between S_7(g) and S_8(g) is given below:

$$7S_8\,(g) \rightleftharpoons 8S_7\,(g)$$

(i) Give the expression for the equilibrium constant, K_c, for the reaction between S_7 and S_8 as written above.

$K_c = [S_7]^8 / [S_8]^7$

[1]

When dissolved in an organic solvent, S_6, S_7 and S_8 were all detected in equilibrium in the following proportions by mass:

Allotrope	S_6	S_7	S_8
% by mass	1.5	0.5	98.0

(ii) Calculate the amount of S_7 and S_8 at equilibrium when 1.00 g of sulfur is dissolved in 1.00 dm^3 of solvent.

Amount of S_7 = 0.005 / (7 X 32.1) = 2.23 X 10^{-5} mol
Amount of S_8 = 0.98 / (8 X 32.1) = 3.82 X 10^{-3} mol

[2]

(iii) Calculate the value of the equilibrium constant in **(i)**.

$$K_c = \frac{(2.23\times10^{-5})^8}{(3.82\times10^{-3})^7} = 5.15 \text{ X } 10^{-21} \text{ mol dm}^{-3}$$

[1]

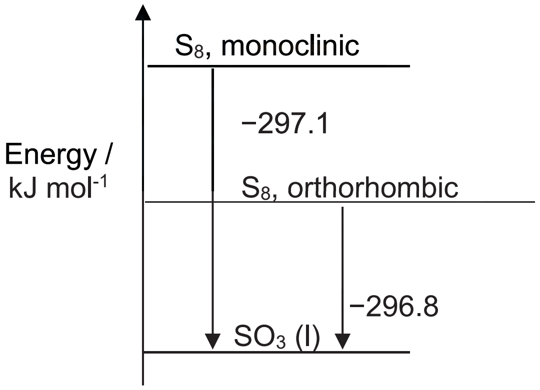
(b) In the solid phase, S_8 crystallises in two well-known allotropic forms: orthorhombic and monoclinic.

Both combust in excess oxygen to form liquid SO_3. The standard enthalpy changes of combustion of these two forms are as follows:

$$\Delta H_c\ (S_8\text{, orthorhombic}) = -296.8 \text{ kJ mol}^{-1}$$
$$\Delta H_c\ (S_8\text{, monoclinic}) = -297.1 \text{ kJ mol}^{-1}$$

Draw an energy level diagram to conclude which is the more stable form.

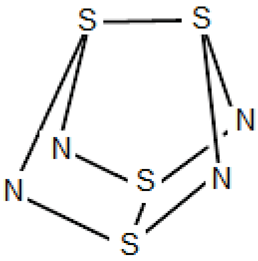
Orthorhombic [1]



[2]

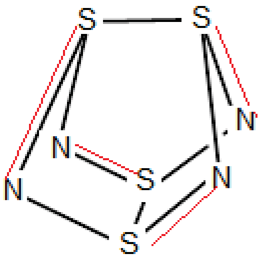
7 **(c)** Sulfur also forms an interesting cage-like compound with nitrogen, S_4N_4.

(i) There are π bonds in S_4N_4 which are alternating.



The π bonds are omitted in the structural formula shown above.

Fill in the missing π bonds onto the structural formula above.



[1]

S_4N_4 reacts with hot NaOH(aq) to give thiosulfate ($S_2O_3^{2-}$)and trithionate ($S_3O_6^{2-}$) in 1:2 ratio. Ammonia is the gaseous side-product.

(ii) Suggest what makes this reaction spontaneous.

An increase in entropy with the formation of gas.

[1]

(iii) The skeletal equation is as such:

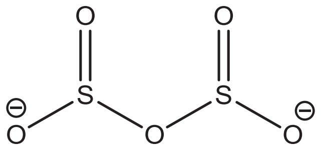
$$S_4N_4 + OH^- + H_2O \rightarrow S_2O_3^{2-} + S_3O_6^{2-} + NH_3$$

Balance the ionic equation.

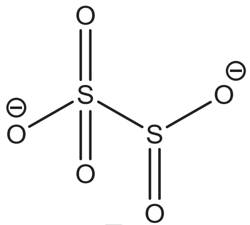
$$2S_4N_4 + 6OH^- + 9H_2O \rightarrow S_2O_3^{2-} + 2S_3O_6^{2-} + 8NH_3$$

[1]

7 **(d)** There are two possible structures of the metabisulfite ion ($S_2O_5^{2-}$), as shown below.



Y



Z

(i) Using appropriate values from the Data Booklet, calculate the enthalpy changes of atomisation of **Y** and **Z**. Hence deduce which is more stable.

ΔH_{atom}**Y** = 4(S-O) + 2(S=O) = 4(360) + 2(500) = + 2440 kJ mol^{-1}

ΔH_{atom} **Z =** 2(S-O) + 2(S=O) + (S-S) = 2(360) + 3(500) + 264
= + 2484 kJ mol^{-1}

Z is the more stable one.

[2]

(ii) Metabisulfite (structure **Z**) decomposes to SO_2 and sulfite (SO_3^{2-}) in a single step. Draw curly arrows to show the electron movement in this decomposition.

[1]

7 **(d)** **(iii)** Potassium metabisulfite, $K_2S_2O_5$, is a white crystalline powder.

It is chemically very similar to sodium metabisulfite, $Na_2S_2O_5$, with which it is sometimes used interchangeably. Potassium metabisulfite is generally preferred out of the two as a food preservative as it does not contribute sodium to the diet.

Explain why potassium metabisulfite decomposes at a higher temperature on heating than sodium metabisulfite.

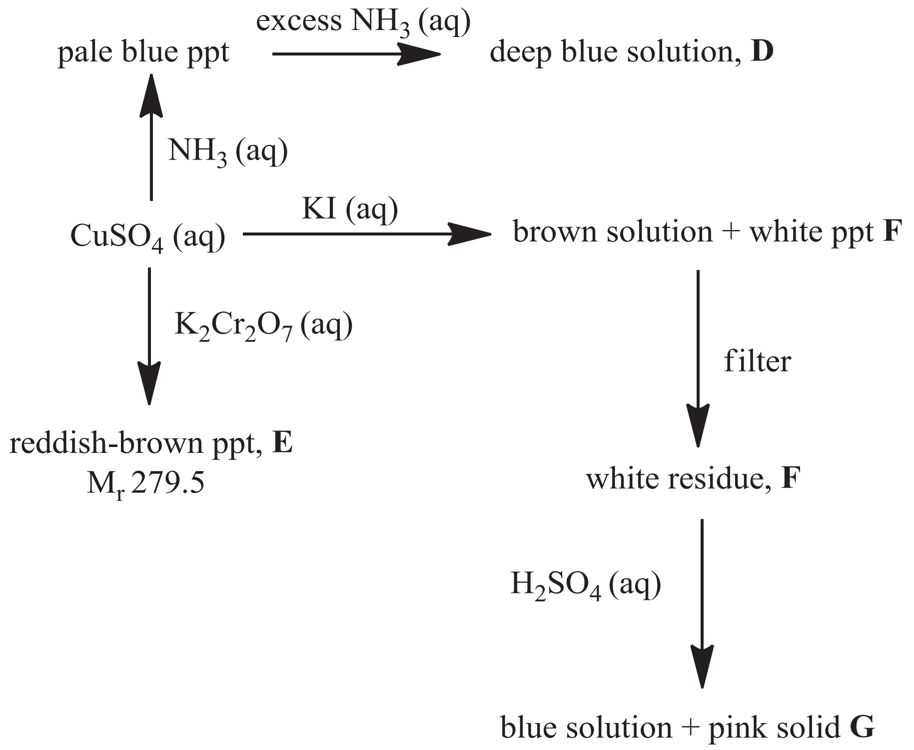
K^+ has the lower polarising power due to its lower charge density as compared to Na^+.

Hence, the covalent bonds in the metabisulfite ion in $K_2S_2O_5$ is weakened to the lesser extent. [1]

[2]

[Total: 14 marks]

8 **(a)** Copper(II) sulfate can undergo a series of reactions as shown in the reaction scheme below.



Identify **D**, **E**, **F** and **G**.

D: $Cu(NH_3)_4(H_2O)_2^{2+}$ or $Cu(NH_3)_4^{2+}$

F: CuI or Cu_2I_2

E: $CuCr_2O_7$

G: Cu

[4]

(b) Ionisation isomerism is a special type of constitutional isomerism in which the isomers form different ions in solution.

There is a pair of cobalt(III) ionisation isomers, **K** and **L**. They have molecular formula $CoBrSO_4(NH_3)_4$. **K** is red while **L** is dark violet.

On addition of aqueous barium nitrate, only **K** gave a white precipitate.
On addition of aqueous silver nitrate, only **L** gave an off-white precipitate.

(i) Give the structural formulae of the cations in **K** and **L**.

K: $[CoBr(NH_3)_4]^{2+}$ or $[Co(H_2O)Br(NH_3)_4]^{2+}$
L: $[CoSO_4(NH_3)_4]^{+}$ or $[Co(H_2O)SO_4(NH_3)_4]^{+}$

[2]

(ii) Explain briefly why **K** and **L** exhibit different colours.

Different ligands will split the energy of the d orbitals by different extents, hence visible light of different wavelengths will be absorbed, leading to different colours.

[1]

[Total: 7 marks]

END OF PAPER

ANGLO-CHINESE JUNIOR COLLEGE
DEPARTMENT OF CHEMISTRY
Preliminary Examination

CHEMISTRY **9729/03**
Higher 2

Paper 3 18 August 2017
2 hours

Additional Materials: Writing Paper
Data Booklet
Cover Page

READ THESE INSTRUCTIONS FIRST

Write your index number and name, form class and tutorial class on all the work you hand in.
Write in dark blue or black pen.
You may use a pencil for any diagrams, graphs or rough working.
Do not use staples, paper clips, glue or correction fluid.

Answer **all** questions in Section **A**.
Answer **either** question 4 or 5 in Section **B**.
Start each question on a new sheet of writing paper.

A Data Booklet is provided.
The use of an approved calculator is expected, where appropriate.
You are reminded of the need for good English and clear presentation in your answers.

At the end of the examination, fasten all your work securely behind a cover sheet.
The number of marks is given in brackets [ ] at the end of each question or part question.

This document consists of **17** printed pages, including this cover page.

Section A – Answer **ALL** questions. Begin each question on a fresh piece of writing paper.

1 This question is about Period 3 and Group 2 elements.

(a) Phosphorus sulfide, P_4S_3, is used in small amounts in the tip of a matchstick. On striking a matchstick, this compound burns to form sulfur dioxide and phosphorus pentoxide.

(i) Write the equation for this reaction. [1]

$$P_4S_3 + 8O_2 \rightarrow 3SO_2 + P_4O_{10}$$

(ii) The melting points of the two oxides formed in **(a)(i)** differ significantly from that of silicon(IV) oxide (SiO_2). Account for this difference in terms of structure and bonding of each oxide. [2]

The two above-mentioned oxides are simple covalent molecules while SiO_2 has a giant covalent structure. Overcoming weak IMF between P_4O_{10} and SO_2 molecules versus strong covalent bonds between Si and O atoms. SiO_2 has the highest melting point.

(iii) The solid oxide formed in **(a)(i)** dissolves in water to give an acidic solution.

Write the equation for this reaction and give an approximate pH of the solution formed. [2]

$$P_4O_{10} + 6H_2O \rightarrow 4H_3PO_4 \qquad \text{pH 2 or 3}$$

(b) A Group 2 nitrate exists as a hydrate $\mathbf{M}(NO_3)_2.xH_2O$. On heating, 1.80 g of this hydrate lost 0.55 g in the form of steam, as it was converted into the anhydrous nitrate, $\mathbf{M}(NO_3)_2$. Subsequent heating to constant mass produced a white residue and mixture of two gases. The gases produced were passed through aqueous sodium hydroxide. The remaining gas occupied 95 cm^3 at 101 kPa and 30 °C.

(i) Write an equation, with state symbols, representing the thermal decomposition of Group 2 nitrates, $\mathbf{M}(NO_3)_2$. [1]

$$M(NO_3)_2\,(s) \rightarrow MO\,(s) + 2NO_2\,(g) + \tfrac{1}{2}\,O_2\,(g)$$

(ii) Assuming that the gas behaves ideally, calculate the amount of remaining gas formed. [1]

3.81×10^{-3}

(iii) Hence, calculate the value of x and deduce the identity of metal **M**. [3]

No. of moles of nitrate present = (ii) × 2 = 7.621×10^{-3}
No. of moles of water = 0.55 / 18.0 = 3.056×10^{-2}

$x = \frac{3.056 \times 10^{-2}}{7.621 \times 10^{-3}} = 4$

A_r of **M** = 40.0

Calcium

(c) Calcium oxide is the key ingredient for the process of making cement.

When 1.50 g calcium is burned in air, calcium oxide is formed together with a red brown solid.

The red brown solid has the following composition by mass: Ca, 81.1%; N, 18.9%.

Adding water to the red brown solid produces calcium hydroxide and 19.2 cm^3 of ammonia gas at room temperature and pressure.

(i) Deduce the formula of the red brown solid. [2]

	Mass percentage / A_r	Simplest ratio
Ca	2.0275	3
N	1.35	2

Ca_3N_2

(ii) Write the chemical equation for the reaction between the red brown solid with water. [1]

$$Ca_3N_2 + 6H_2O \rightarrow 3Ca(OH)_2 + 2NH_3$$

(iii) Write the chemical equation for the reaction of calcium with O_2 and hence calculate the mass of CaO formed when 1.5 g of calcium is burnt in O_2. [2]

$$2Ca\ (s) + O_2\ (g) \rightarrow 2CaO\ (s)$$

n(calcium) = 0.0374
n(calcium oxide) = 0.0374
m(calcium oxide) = 0.0374 x (40 + 16) = 2.10 g

1 **(d)** A diagonal relationship is said to exist between certain pairs of diagonally adjacent elements in the second and third Periods of the Periodic Table.

For instance, lithium shows similar chemical properties to magnesium.

(i) Write the equation for the thermal decomposition of lithium carbonate. [1]

Li_2CO_3 (s) → CO_2 (g) + Li_2O (s)

(ii) Explain why this is unlike that of the other Group 1 carbonates. [1]

The charge densities (or polarising power) of Li^+ and Mg^{2+} are similar.
or
The electronegativities of lithium and magnesium are similar.

(e) Lithium nitride, Li_3N, is a red solid. It is the only stable Group 1 nitride. The nitrides of all the Group 2 elements are known.

Li_3N is currently investigated as a storage medium for hydrogen gas.

$$Li_3N + 2H_2 \rightleftharpoons 2LiH + LiNH_2$$

State the role of hydrogen. [1]

Electrophile / Proton donor / Acid / Bronsted acid / Lewis acid

(f) A diagonal relationship also exists between boron and silicon.

B_2O_3 is acidic, like SiO_2 but unlike the oxides of the other Group 13 elements.

(i) Write a balanced chemical equation, with state symbols, that illustrates the acidic nature of SiO_2. [1]

SiO_2 (s) + 2NaOH (l) / (aq) → Na_2SiO_3 (l) / (aq) + H_2O (l)

(ii) Write a balanced chemical equation, with state symbols, that illustrates the acidic nature of B_2O_3, given that it forms a similar anion as in **(i)**. [1]

B_2O_3 (s) + 6NaOH (l) / (aq) → $2Na_3BO_3$ (l) / (aq) + $3H_2O$ (l)

[Total: 20]

2 **(a)** Divalent metal cations like tin and cadmium form insoluble precipitates with NaOH (aq).

The K_{sp} of $Sn(OH)_2$ is 5.45×10^{-27} mol^3 dm^{-9}.

(i) If the concentration of $Cd(OH)_2$ in a saturated solution is 1.217×10^{-5} mol dm^{-3}, determine the solubility product of $Cd(OH)_2$. [1]

$4(1.217 \times 10^{-5})^3 = 7.21 \times 10^{-15}$ mol^3 dm^{-9}

(ii) Calculate the molar solubility of $Sn(OH)_2$ in a solution of pH 8. [2]

$[OH^-] = 10^{-6}$ mol dm^{-3}

No. of moles of $Sn(OH)_2$ that can dissolve in 1 dm^3 water

$= \frac{5.45 \times 10^{-27}}{10^{-12}} = 5.45 \times 10^{-15}$ mol

(iii) A certain solution has 0.002 mol dm^{-3} each of Cd^{2+} and Sn^{2+}.

Calculate the pH range over which the two cations can be effectively separated. [2]

$$\frac{5.45 \times 10^{-27}}{0.002} < [OH^-]^2 < \frac{7.21 \times 10^{-15}}{0.002}$$
$$1.651 \times 10^{-12} < [OH^-] < 1.899 \times 10^{-6}$$

Lower pH = 14 + log (1.651×10^{-6}) = 2.22

Higher pH = 14 + log (1.899×10^{-6}) = 8.28

$2.22 < pH < 8.28$

(b) Propanone, also known as "acetone", is one of the most important solvents in organic chemistry – it can be used to dissolve many things from fats and waxes to airplane glue and nail polish.

It decomposes to **H** and ketene ($H_2C{=}C{=}O$). At 600 °C, the decomposition rate constant is 8.7×10^{-3} s^{-1}.

(i) Suggest the identity of **H**. methane or CH_4 [1]

(ii) Determine the half-life of the reaction at 600 °C. 79.7 s [1]

(iii) How much time is required for 75% of a sample of propanone to decompose at 600 °C? [1]

2 X 79.7 = 159 seconds

(iv) The Arrhenius equation links different parameters (its activation energy, the absolute temperature, and its rate constant at that temperature) of a reaction together.

$$k = Ae^{-\frac{E_a}{RT}}$$

Given that the half-life of the reaction at 500 °C is 8700 s and using your answer to **(ii)**, calculate the activation energy (including its units) of this reaction. [2]

Rate constant at 500 °C = 7.97 X 10^{-5} s^{-1}

Converts both temperatures to Kelvins

$$k_{873K} = 8.70 \times 10^{-3} = Ae^{-\frac{Ea}{873R}} \quad \text{------ (1)}$$

$$k_{773K} = 7.97 \times 10^{-5} = Ae^{-\frac{Ea}{773R}} \quad \text{------ (2)}$$

(1) Divided by (2):

$$109.1593476 = e^{\frac{Ea}{R}(\frac{1}{773}-\frac{1}{873})}$$

$$\frac{Ea}{R}\left(\frac{1}{773}-\frac{1}{873}\right) = \ln(109.1593476)$$

E_a = 8.31 x ln (109.1593476) / (1.48186 X 10^{-4}) = + 263165 J mol^{-1}

E_a = + 264 kJ mol^{-1}

2 **(c)** Under appropriate conditions, butane can be made to isomerise reversibly to 2-methylpropane at 298K.

	butane	2-methylpropane
S° / J K^{-1} mol^{-1}	310	295
ΔH$_f$° / kJ mol^{-1}	-127.2	-135.6

(i) Calculate the ΔG° for the forward isomerisation reaction. [2]

ΔH_{rxn}^{o} = -8.40 kJ mol^{-1} ΔS_{rxn}^{o} = -15 J K^{-1} mol^{-1}
ΔG_{rxn}^{o} = -8.40 – 298(-0.015) = -3.93 kJ mol^{-1}

2 **(c)** **(ii)** Given that ΔG^o = -RT ln K_p, calculate the equilibrium constant, K_p, for the isomerisation reaction. [1]

$K_p = e^{\frac{3930}{8.31(298)}} = 4.89$

(iii) Write the K_p expression for the isomerisation equilibrium. [1]

$K_p = P_{(2\text{-methylpropane})} / P_{(\text{butane})}$

(iv) Determine the mole fractions of the two gases at equilibrium. [3]

Let the mole fraction of butane be x.

Mole fraction of 2-methylpropane = 1 – x

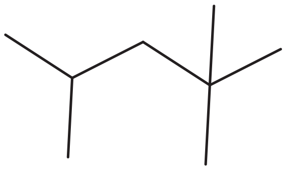
K_p = (1-x)/x

X ($CH(CH_3)_3$) = 0.830

(v) In the industry, 2-methylpropane is used to make compound **Y**, C_8H_{18}.

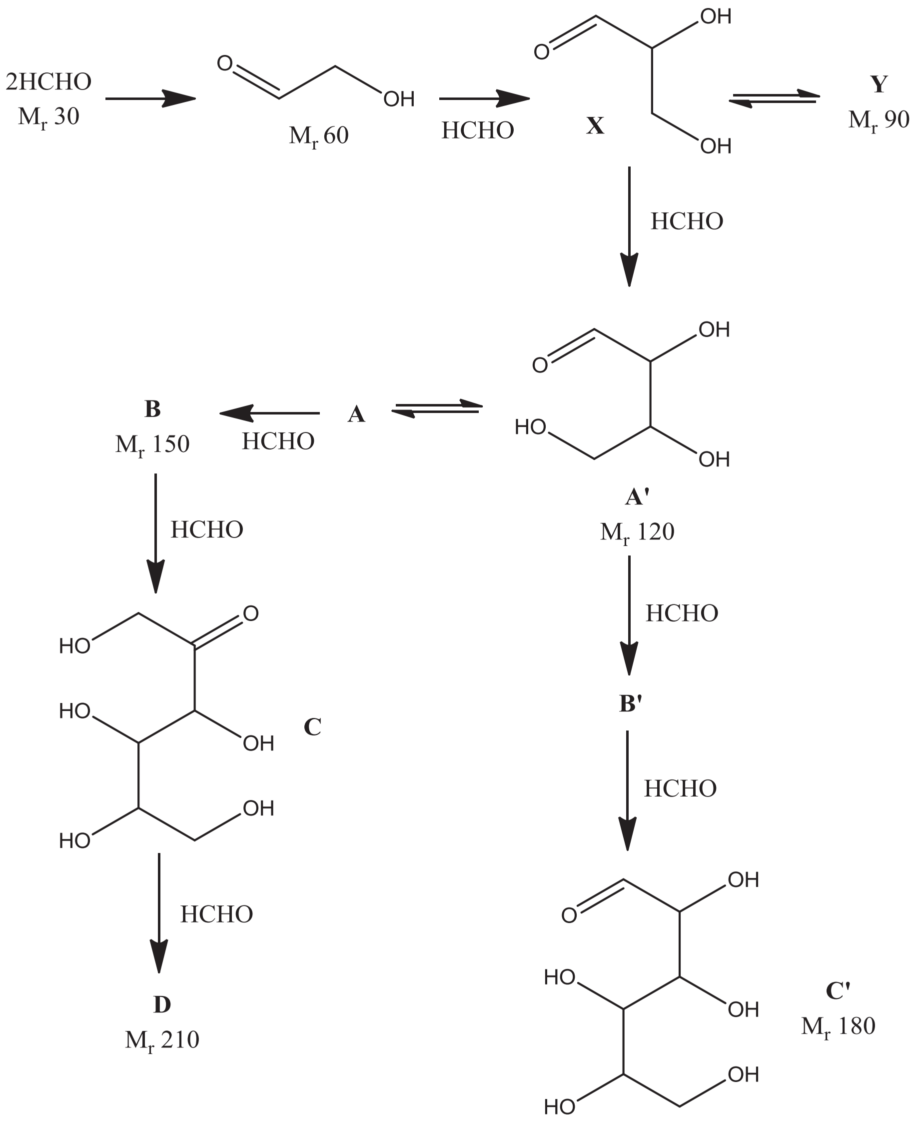
Y has the whole range of carbon atoms; it contains primary, secondary, tertiary and quaternary carbon atoms.

Draw the structural formula of **Y**, assuming that the original carbon skeleton did not rearrange. [1]



2 **(d)** Life in the universe is widely thought to have originated from methanal, HCHO, through the Formose reaction.

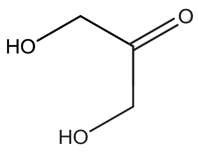
In this reaction, methanal is converted into a vast range of sugars like ribose and from there to RNA, an important hereditary material.



(i) **X** and **Y** are functional group isomers.

Y does not rotate the plane of plane-polarised light. Fehling's and Tollens' tests are the only tests which can differentiate between **X** and **Y**.

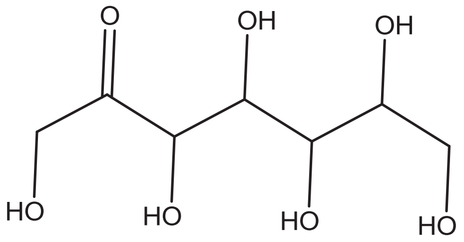
Draw the structural formula of **Y**. [1]



2 **(d)** **(ii)** Suggest a reason why the interconversion of **C** to **C'** cannot be done in a single step. [1]

- You cannot simultaneously reduce the aldehyde and oxidise the secondary alcohol in C'.
- You cannot simultaneously reduce the ketone and oxidise the primary alcohol in C.

(iii) Draw the structural formula of **D**. [1]



[Total: 21]

3 This question is on Group 17, the halogens.

Chlorate(V), ClO_3^-, reacts with chloride according to the equation:

$$2ClO_3^- (aq) + 2Cl^- (aq) + 4H^+ (aq) \rightarrow Cl_2 (g) + 2ClO_2 (aq) + 2H_2O (l)$$

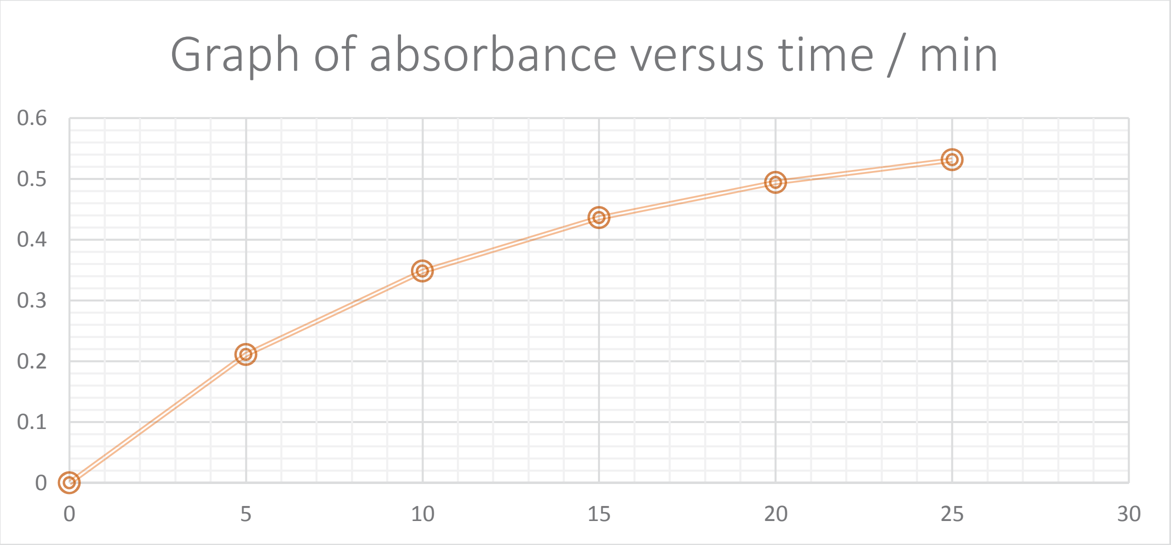
(a) To study the kinetics of chlorate(V)-chloride reaction, an experiment was conducted using a mixture in which the concentrations of the reactants are as follows: 0.000480 mol dm^{-3} of ClO_3^-, 0.1 mol dm^{-3} of Cl^- and 0.4 mol dm^{-3} of H^+.

At five-minute intervals, small samples of the reaction mixture were withdrawn, quenched and placed into the UV-vis spectrometer to record its absorbance value. The absorbance value corresponds to the concentration of the product ClO_2.

The results of the above experiment are shown below.

Time/min	0	5	10	15	20	25
Absorbance/A	0.000	0.211	0.348	0.436	0.494	0.531

The graph of absorbance/A against time/min is plotted below.



3 **(a)** **(i)** Beer-Lambert's Law states that the absorbance values, A, is directly proportional to the concentration of absorbing species, c, as shown below.

$$A = \varepsilon c l$$

where ε is the molar extinction coefficient and l is the path length, which is usually 1.0 cm.

This equation can be used to calculate the absorbance value when maximum amount of ClO_2 was formed.

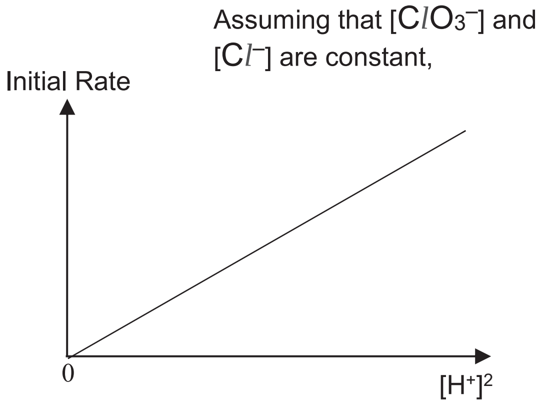
Show that the maximum absorbance value in the above experiment is 0.600, given that ε of ClO_2 is 1250 $mol^{-1}\,dm^{3}\,cm^{-1}$. [2]

Recognises that chlorate(V) is the limiting reagent.
A = 1250(1.0)(0.000480) = 0.600

3 **(a)** **(ii)** From the graph provided on the previous page and the information given in **(a)(i)**, determine the half-life with respect to ClO_3^- and hence the order of reaction with respect to ClO_3^-. [2]

Half-lives roughly constant at x min (acceptable range from 7 to 9 min)
1st order wrt ClO_3^-

To obtain the full rate law, a further experiment was conducted.
The following graph was obtained.



(iii) Using the above data, determine the order of the reaction with respect to H^+. [1]
2nd order

(iv) Given that the units of k is $mol^{-3}\,dm^{9}\,s^{-1}$, write the rate equation of the chlorate(V)-chloride reaction. [1]

Rate = k[chloride][chlorate(V)]$[H^+]^2$

(v) State a physical property that can be monitored as the reaction progresses. [1]

Change in <u>pH</u> or change in <u>Electrical conductivity</u> or change in <u>mass</u>
Change in <u>pressure</u> (constant volume) or
Change in <u>volume</u> (constant pressure)

3 **(b)** Heating solid halides with concentrated H_2SO_4 is one of the ways to obtain hydrogen halides.

However, the halides have different reactivities with concentrated H_2SO_4.

(i) Write an equation to show the reaction of KC*l* with concentrated H_2SO_4. [1]

$KCl + H_2SO_4 \rightarrow KHSO_4 + HCl$

(ii) However, when KI is treated with concentrated sulfuric acid, HI will be contaminated with other gaseous products. Identify these gaseous products. [2]

SO_2 and H_2S

(iii) Suggest another reagent that can be reacted with potassium iodide to obtain pure hydrogen iodide. Conc. phosphoric acid or conc. H_3PO_4 [1]

The interhalogens are compounds that are made up of two or more different halogens.

IC*l* and IBr are two such examples.

(c) Even though IC*l* is more polar than IBr, IBr has a higher boiling point than IC*l*. Explain this dilemma as clearly as you can. [2]

Based on the relative strengths of pdpd alone, IBr should have the lower boiling point. However, the electron cloud size of the IBr is big enough such that its idid is stronger than the IMF present between IC*l* molecules.

(d) IC*l* reacts with water in which water is acting as the nucleophile.

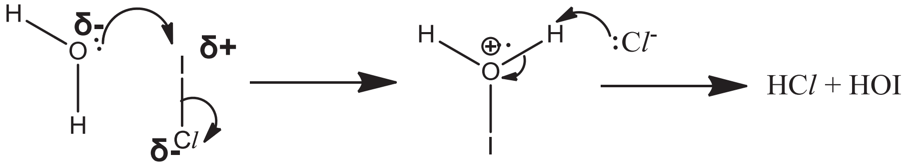
The equation for the reaction is as follows.

$$ICl + H_2O \rightarrow H\mathbf{X} + HO\mathbf{Y}$$

(i) By comparing relative electronegativities, identify **X** and **Y**. [1]

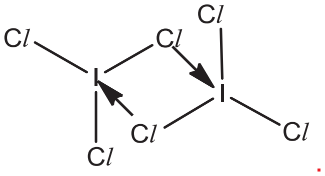
X is chlorine while **Y** is iodine.

3 **(d)** **(ii)** Hence propose a two-step mechanism for this reaction. Include curly arrows and partial charges. [2]



(e) ICl_3 exists as a planar dimer I_2Cl_6 in solid state. The two iodine atoms are the central atoms.

(i) Draw the structure of the dimer. [1]



(ii) The molten form of ICl_3 is able to conduct electricity because it undergoes auto-ionisation.

One species is square planar and the other is bent with respect to the central iodine atom.

Deduce the formulae of the cation and the anion. [2]

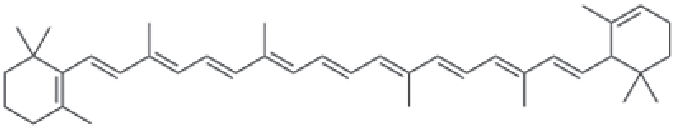
ICl_4^- and ICl_2^+

[Total: 19]

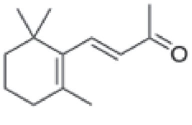
Section B - Choose <u>either</u> question **4** or **5**. Begin it on a fresh piece of writing paper.

4 α-carotene is a red-orange pigment found in plants and fruits. It is the yellow/orange pigment that gives vegetables and fruits their rich colors. The name "carotene" came about when it was first discovered in carrot roots in 1831.

(a) α-carotene is metabolised to form α-ionone and β-ionone, which share the same molecular formula, $C_{13}H_{20}O$.



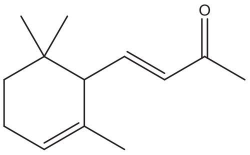
α-carotene



β-ionone

(i) Explain why hot acidified $KMnO_4$ cannot be used in the conversion of α-carotene to β-ionone. The alkenes will be oxidised too. [1]

(ii) Based on the structure of α–carotene, draw the structural formula of α-ionone. [1]



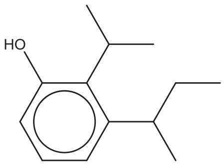
(iii) Specify what type of constitutional isomerism is shown between α-ionone and β-ionone. [1]

Positional isomers.

(iv) Give the structural formula of a constitutional isomer of β-ionone, where neutral iron(III) chloride solution is the <u>only</u> chemical test that can distinguish between itself and β-ionone. [1]

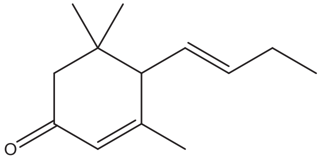
Proposed structure has to be a phenol and seven carbons outside the benzene, without rings and π bonds.

Example:

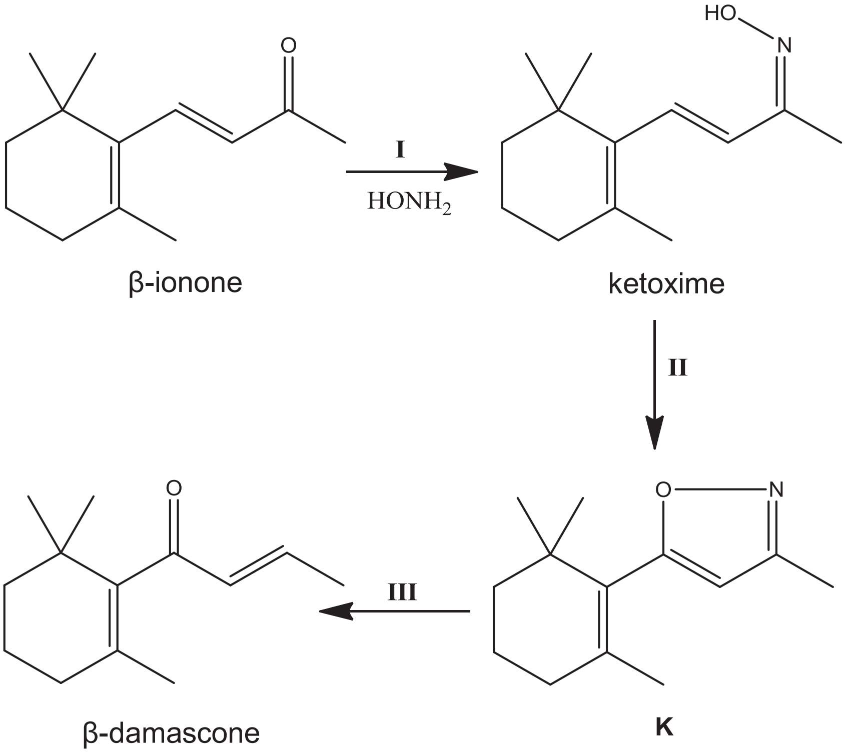


4 **(a)** **(v)** Give the structural formula of a constitutional isomer of β-ionone, which can be distinguished from β-ionone by warm alkaline iodine. [1]

Proposed structure need not necessarily be a ketone.
If it is a ketone, it is **not** a methyl ketone.

Example: 

(b) β-ionone forms β-damascone via an electrochemical route.



It involved the formation of ketoxime in step **I**, followed by an anodic oxidation in step **II**. In the last step, the oxygen-nitrogen bond was cleaved to give β-damascone.

(i) Name the type of reaction in step **I**. [1]

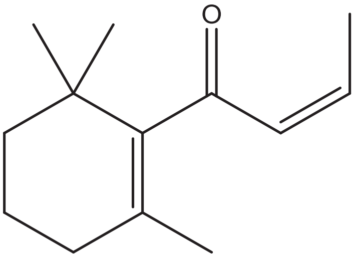
condensation or addition elimination

(ii) Construct a balanced half-equation for the oxidation of ketoxime in step **II** under acidic conditions.

You are to use “ketoxime” and “**K**” in your half-equation. [1]

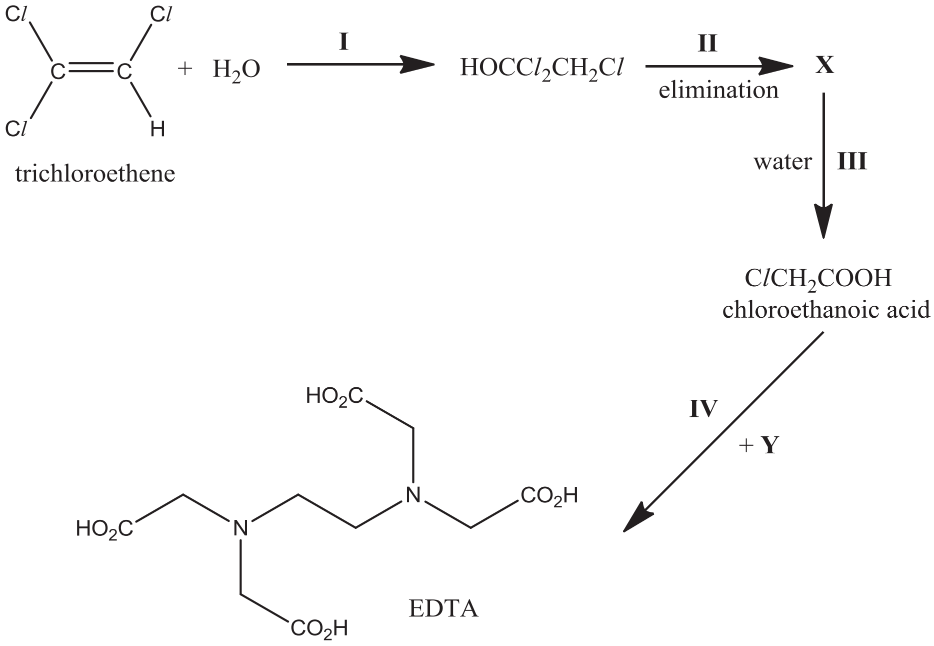
ketoxime → K + $2H^+ + 2e$

4 **(b)** **(iii)** β-damascone exists as a pair of cis-trans isomers. Draw the cis isomer. [1]



(c) Ethylenediaminetetraacetic acid (EDTA) is a colourless, water-soluble solid. It is on the World Health Organisation's List of Essential Medicines.

EDTA can be synthesised via the following reaction route.



(i) **X** gave a white precipitate when aqueous silver nitrate was added to it. Give the structural formula of **X**. [1]

$ClCH_2COCl$

(ii) Give the structural formula of **Y**. Hence, state a potential problem that might happen when it reacts with chloroethanoic acid. [2]

$H_2N(CH_2)_2NH_2$

Form the salt / acid-base reaction rather than nucleophilic (acyl) substitution / condensation

4 **(d)** Chloroethanoic acid can be synthesised from methanal via a three-step route. State the reagents and conditions used in each step and the intermediates involved. [4]

$HCHO \rightarrow HOCH_2CN \rightarrow ClCH_2CN \rightarrow ClCH_2CO_2H$
Step I: HCN, trace amt of NaCN, 10 to 20 ^{0}C
Step II: $SOCl_2$ / PCl_5 / PCl_3
Step III: heat with aqueous acid

(e) The Kolbe electrolysis involves conversion of carboxylate salts into alkanes. It can be represented by the following half-equation.

$$3\ R_1COO^- + 3\ R_2COO^- \rightarrow R_1{-}R_1 + R_1{-}R_2 + R_2{-}R_2 + 6CO_2 + 6e^-$$

where R_1 and R_2 may not represent the same alkyl group.

In a certain electrolysis, two carboxylate salts were electrolysed, forming three alkanes.

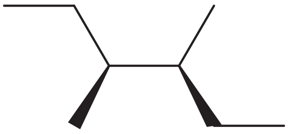
The relative molecular masses are 58.0, 86.0 and 114.0.

The alkane with M_r 58.0 is non-chiral.

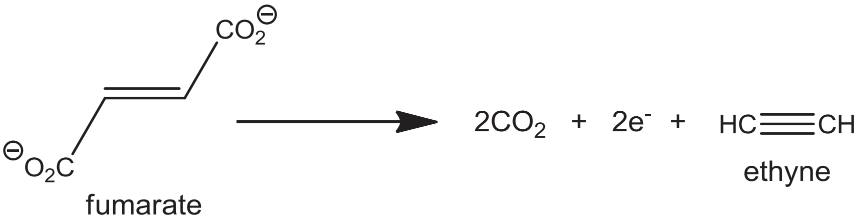
The alkane with M_r 114.0 exists as three stereoisomers - two of which are chiral and the third is non-chiral.

(i) Identify the two carboxylate salts used. [2]
Propanoate and 2-methylbutanoate

(ii) Draw the stereochemical formula of any of the two chiral stereoisomers. [1]



In a special application of the Kolbe electrolysis, fumarate was electrolysed into ethyne.



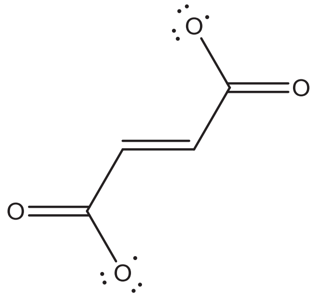
$^{\ominus}O_2C$–CH=CH–$CO_2^{\ominus}$ $\longrightarrow$ $2CO_2$ + $2e^-$ + HC≡CH

4 **(e)** **(iii)** Kolbe electrolysis proceeds via radical intermediates, which are formed and reacted via homolytic fission and fusion.

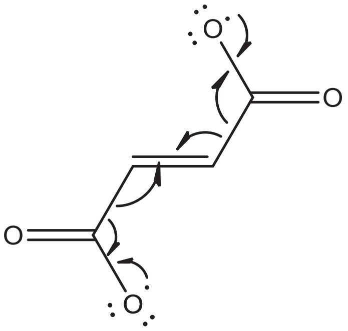
Explain the term *homolytic fission*. [1]

Homolytic fission is the process in which the two electrons in a covalent bond are divided equally between the two atoms when the bond breaks.

(iv) The decomposition of fumarate into ethyne and carbon dioxide happens through two steps – the first of which forms the neutral diradical species below as the intermediate.



Use curly arrows to show how the intermediate decomposes to ethyne and carbon dioxide. [1]

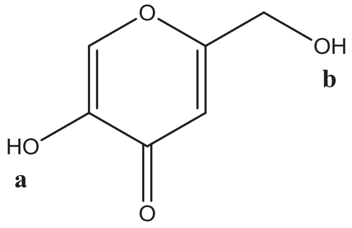


[Total: 20]

5 Melanin is a naturally-occurring organic compound that is responsible for the colour of the skin. The higher the melanin content, the darker the skin is. In the Asian market, skin-lightening lotions have grown to be the most on-demand skin care cosmetic products.

One common ingredient of such lotions is kojic acid, which works by slowing down the rate of formation of melanin. It is obtained from the fermentation of rice malt.

The structure of kojic acid is shown below with the two hydroxyl groups labelled **a** and **b**.



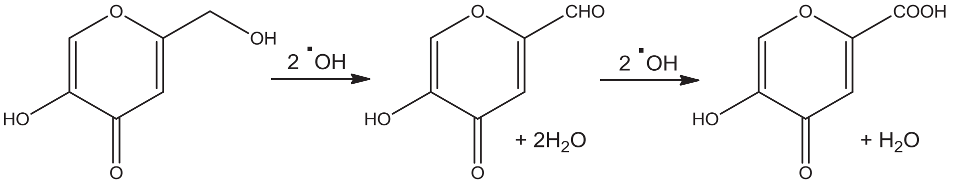
kojic acid

(a) For each of the hydroxyl groups **a** and **b**, explain if it will be substituted with a chlorine atom when one mole of kojic acid is reacted with two moles of PCl_5 at room temperature. [2]

For **a**, the C-O bond possesses a partial double bond character due to the overlap of the p orbital of the oxygen with that of the sp^2 carbon. As such, the bond is not easily broken, disallowing the substitution of ‘a’.

For **b**, the C-O bond is not as strong, thus the nucleophilic substitution will take place more readily.

(b) *Kojic acid* also functions as an antioxidant, scavenging hydroxyl radicals ($^{\bullet}$OH) that are responsible for ageing. One mole of *kojic acid* can react with a total of four moles of the radicals to form *comenic acid* via an intermediate **Z** as shown in the scheme below.



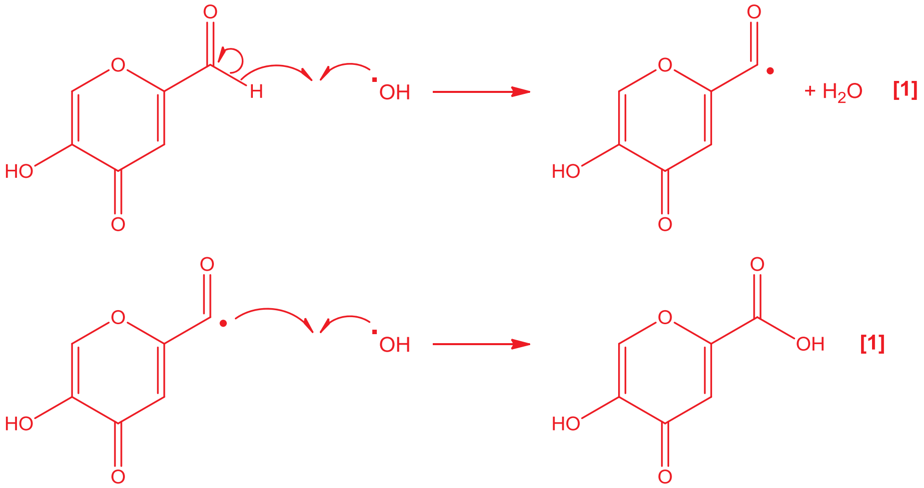
kojic acid compound **Z** comenic acid

(i) Given the following information, use curly arrows to draw the mechanism for the formation of comenic acid from compound **Z** in two separate steps.

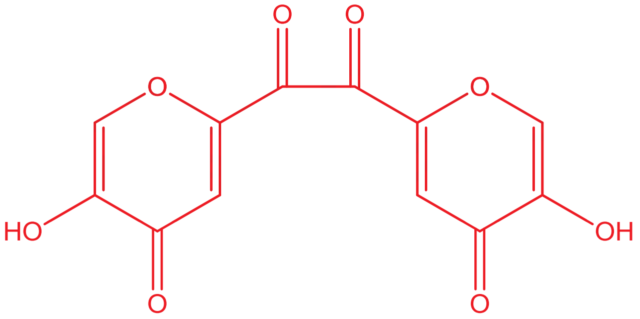
Step 1:
An •OH radical reacts with compound **Z** to form an organic radical intermediate with H_2O being formed as a by-product.

Step 2:
Another •OH radical react with the intermediate formed from the first step.

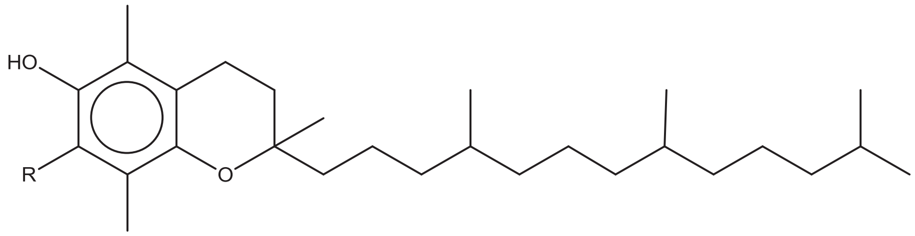
[2]



5 **(b)** **(ii)** Draw another possible organic by-product in the formation of comenic acid from compound **Z**. [1]



5 **(c)** Besides kojic acid, vitamin E is also an essential ingredient that acts as an antioxidant in skin-lightening lotions. One class of vitamin E is tocopherol, the general structure of which is shown below.



tocopherol

The table below shows the substituent R of two different types of tocopherol, namely α- and β-tocopherol.

	–R
α-tocopherol	$–CH_3$
β-tocopherol	–H

Arrange phenol, α-tocopherol and β-tocopherol in an increasing order of pK_a values. Hence, explain the difference in acidity among the three compounds. [3]

pK_a of phenol < β-tocopherol < α-tocopherol

Phenol is the strongest acid as its conjugate base is the most stable due to the fact that there are no electron-donating groups attached to the benzene ring to intensify the negative charge on the oxygen atom.

α-tocopherol is a weaker acid compared to β-tocopherol as the former has one additional electron-donating alkyl / methyl group that destabilises its conjugate base.

(d) To increase the effectiveness and marketability of skin-lightening lotions, titanium dioxide, TiO_2, is often added as a sunscreen agent due to its reflective property.

Solid titanium dioxide reacts with hydrofluoric acid, HF, to form a coordination compound, $H_2[TiF_6]$, and water.

(i) Write a balanced chemical equation, with state symbols, for the above reaction. [1]

$$TiO_2\,(s) + 6HF\,(aq) \rightarrow H_2[TiF_6]\,(aq) + 2H_2O\,(l)$$

(ii) Explain whether the above reaction is a redox reaction. [1]

It is not a redox reaction since the oxidation state of titanium remains the same at +4 in TiO_2 and $H_2[TiF_6]$.

5 **(d)** **(iii)** State the electronic configuration of titanium in $H_2[TiF_6]$. Hence, explain whether the complex ion is coloured. [3]

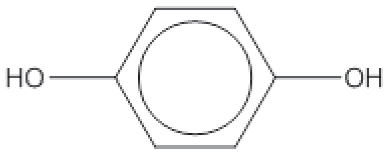
Ti^{4+} : $1s^22s^22p^63s^23p^6$

As there are no electrons in the 3d subshell of Ti^{4+}, there is no d-d transition to promote an electron from a lower energy d orbital to a higher energy d orbital. As such, the complex ion is colourless.

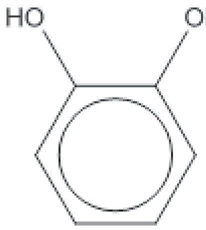
(e) Hydroquinone and catechol are isomers.

Hydroquinone has been used for more than half a century in the formulation of skin lotions to help fade uneven skin tone and dark spots. Catechol, on the other hand, is an important synthetic precursor to pesticides, flavours, and fragrances.

The structures of both compounds, together with their boiling points, are shown below.



hydroquinone
(boiling point: 287 °C)



catechol
(boiling point: 246 °C)

(i) Explain why catechol has the lower boiling point. [1]

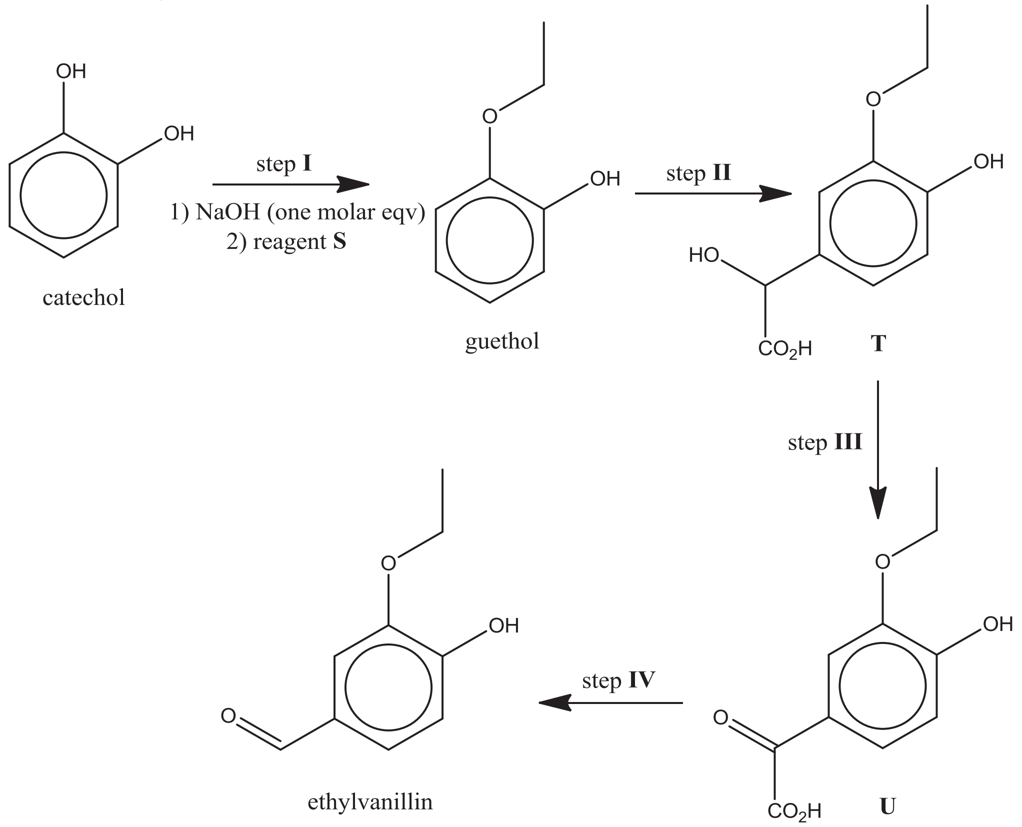
The presence of intramolecular hydrogen bonding between the two phenolic / -OH groups in catechol makes its intermolecular hydrogen bonding less extensive than that between hydroquinone molecules, thus catechol requires less heat energy to overcome the intermolecular hydrogen bonding.

(ii) Catechol is able to function as a bidentate ligand, but not hydroquinone.

Explain why hydroquinone cannot function as a bidentate ligand. [1]

The oxygen atoms / phenolic / -OH groups in hydroquinone point to opposite directions, thus they cannot form dative bonds to the same central metal species.

5 **(f)** Catechol is used industrially to make ethylvanillin, a flavourant reputedly three times more potent than vanillin itself.



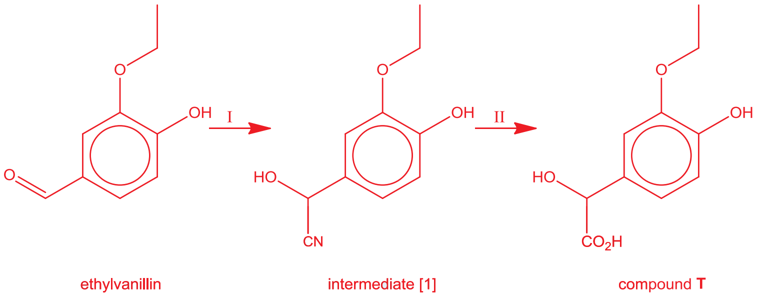
Assume that the ether functional group (R–O–R') is inert.

(i) Explain the purpose of adding NaOH in step **I**. [1]

To deprotonate the phenol functional group to make it a **better** nucleophile.

(ii) Name reagent **S** in step **I**. Chloroethane / bromoethane / iodoethane [1]

(iii) Outline the synthetic pathway to convert ethylvanillin back to compound **T**. Draw the intermediate formed. [3]



Step I: HCN, trace amount of KCN / NaCN, 10-20 °C

Step II: dilute HC*l* / H_2SO_4, heat

[Total: 20]

END OF PAPER

Question 1

In this experiment, you are required to find the concentration in mol dm^{-3} of sodium thiosulfate, $Na_2S_2O_3$, in solution **FA 1**.

You are provided with:
FA 1 contains sodium thiosulfate, $Na_2S_2O_3$.
FA 2 is potassium manganate (VII) containing 1.83 g dm^{-3} $KMnO_4$.
FA 3 is 1 mol dm^{-3} sulfuric acid, H_2SO_4.
FA 4 is 10% potassium iodide containing 4 g dm^{-3} KI.

You are also provided with starch indicator.

Dilution of FA 2

(a) By using a burette measure between 41.00 cm^3 and 42.00 cm^3 of **FA 2** into the 250 cm^3 graduated flask.

Record your burette readings and the volume of **FA 2** added to the flask in the space below.

Final burette reading / cm^3	41.50
Initial burette reading / cm^3	0.00
Volume of **FA2** used / cm^3	41.50

[2]

Make up the contents of the flask to the 250 cm^3 mark with distilled water. Stopper and mix the contents thoroughly by slowly inverting the flask a number of times. Label this solution **FA5**.

Titration

Filll a second burette with **FA 1**, the solution containing sodium thiosulfate.

Use a measuring cylinder to transfer 10 cm^3 of **FA 3** and 10 cm^3 of **FA 4** into a conical flask. Pipette 25.0 cm^3 of **FA 5** into the conical flask containing the mixture of **FA 3** and **FA 4**. The potassium manganate (VII) oxidises potassium iodide to iodine, I_2.

Titrate the liberated iodine with **FA 1** as follows. Run the solution from the burette into the conical flask until the initial brown colour of the iodine becomes pale yellow. Then add 1 cm^3 of the starch indicator and continue to add **FA 1** drop by drop until the blue-black colour of the starch-iodine complex disappears, leaving a colourless solution. This is the end-point of the titration.

Record your titration results in the space below. Make certain that your recorded results show the precision of your working. Repeat your experiment to obtain consistent results.

	1	2
Final burette reading / cm^3	24.20	24.20
Initial burette reading / cm^3	0.00	0.00
Volume of **FA1** used / cm^3	24.20	24.20

[6]

(b) From your titration results obtain a suitable volume of **FA 1** to be used in your calculations. Show clearly how you obtained this volume.

Average titre = (24.20 + 24.20) / 2 = 24.20 cm^3

Volume of **FA1** = ………………… [1]

Calculations

Show your working and appropriate significant figures in all of your calculations.

(c) Calculate how many moles of $KMnO_4$ are contained in the **FA 2** run into the graduated flask. [A_r: K, 39.1; O, 16.0; Mn, 54.9]

No. of moles of $KMnO_4$ added into the graduated flask $= \frac{41.50}{1000} \times \frac{1.83}{158.0}$

$= \underline{4.81 \times 10^{-4}}$

No. of moles of $KMnO_4$ added into the graduated flask = ……………………… [1]

(d) Calculate how many moles of $KMnO_4$ are then pipetted from the 250 cm^3 graduated flask into the titration flask.

No. of moles of $KMnO_4$ pipetted into the titration flask $= 4.81 \times 10^{-4} \times \frac{25.0}{250}$

$= \underline{4.81 \times 10^{-5}}$

No. of moles of $KMnO_4$ pipetted into the titration flask = ……………………… [1]

(e) Use this answer to calculate how many moles of iodine molecules, I_2 are formed when the manganate (VII) ions react with an excess of iodide ions in the titration flask.

$$MnO_4^- + 8H^+ + 5e \rightarrow Mn^{2+} + 4H_2O$$
$$I^- \rightarrow \frac{1}{2} I_2 + e$$

No. of moles of I_2 formed $= 4.81 \times 10^{-5} \times 2.5 = \underline{1.20 \times 10^{-4}}$

No. of moles of iodine molecules, I_2 formed = ……………………… [1]

(f) Use this answer to calculate how many moles of sodium thiosulfate, $Na_2S_2O_3$ react with the iodine molecules formed.

$$2S_2O_3^{2-} \rightarrow S_4O_6^{2-} + 2e$$
$$\tfrac{1}{2} I_2 + e \rightarrow I^-$$

No. of moles of $Na_2S_2O_3$ reacted = $1.20 \times 10^{-4} \times 2$ = $\underline{2.40 \times 10^{-4}}$

No. of moles of thiosulfate ions reacted = ……………………… [1]

(g) Calculate the concentration in mol dm^{-3} of the sodium thiosulfate, $Na_2S_2O_3$, in **FA 1**.

Concentration of $Na_2S_2O_3$ in FA1 = $2.40 \times 10^{-4} \times \frac{1000}{24.20}$ = 9.93×10^{-3} mol dm^{-3}

Concentration of sodium thiosulfate = ……………………… [1]

[Total: 14 marks]

Question 2

The derivation of rate equations is an important part of the process of discovering a reaction mechanism.

The experiment detailed in this question is part of an investigation into the mechanism of the iodination of propanone:

$$CH_3COCH_3(aq) + I_2(aq) \rightarrow CH_3COCH_2I(aq) + H^+(aq) + I^-(aq)$$

The reaction is catalysed by hydrogen ions and hence the rate equation can be expressed as

$$\text{Rate} = k\,[CH_3COCH_3]^a\,[H^+]^b\,[I_2]^c$$

where a, b and c are the orders with respect to the species shown in the rate equation.

FA 1 contains sodium thiosulfate, $Na_2S_2O_3$ (from Question 1)
FA 3 is 1 mol dm^{-3} sulfuric acid, H_2SO_4 (from Question 1)
FA 6 is 1 mol dm^{-3} aqueous propanone
FA 7 is 0.02 mol dm^{-3} I_2 in KI solution (5 g of I_2 and 33 g of KI in 1 dm^3 solution)
FA 8 is 1 mol dm^{-3} $NaHCO_3$

Procedure

1. Pipette 25.0 cm^3 of **FA 3** into a conical flask.
2. Using the same pipette deliver 25.0 cm^3 of **FA 6** into the same conical flask.
3. Using a measuring cylinder, collect 50 cm^3 of **FA 7**.
4. Transfer the **FA 7** into the conical flask containing the mixture of **FA 3** and **FA 6** as quickly as possible and at the same time start the stop watch. Swirl the mixture in the conical flask to ensure complete mixing.
5. When the reaction has been going on for 3 minutes, pipette 10.0 cm^3 of the reaction mixture into another conical flask containing 10 cm^3 of **FA 8**, noting the exact time at which this was done.
6. Mix the solution thoroughly and titrate the mixture against **FA 1** from a burette until the solution turns yellow. Using the plastic dropper add 1 cm^3 of starch and continue titration until the solution becomes colourless.
7. Repeat **steps 5 – 6**, at times of 6, 9, 12 and 15 minutes.
8. Record yours results in the table below:

Results

Time when reaction mixture was added to $NaHCO_3$					
Final Volume / cm^3					
Initial Volume / cm^3					
Vol. of **FA1** used / cm^3					

[6]

For Examiner's Use

(a) Plot a graph of the volume of **FA 1** used against time.

- ***Labelled axes of appropriate scale***
- ***Straight line (best fit)***

[2]

(b) What is the purpose of adding the reaction mixture to **FA 8** in Step 5. Explain.

$NaHCO_3$ neutralises the acid and hence stops the reaction so that the amount of iodine remaining at that instant can be determined

[1]

For Examiner's Use

(c) The acid **(FA 3)** and the propanone **(FA 6)** are used in large excess in the reaction. Explain why this is necessary.

To ensure that the concentration of propanone and H^+ remains approximately constant during the duration of the reaction

[1]

(d) Based on your graph, what conclusion can your draw about how the rate of reaction depends on the reactant of interest in this investigation?

Whilst iodine concentration is decreasing with time, the graph is a straight line and hence rate is constant throughout the reaction [1]. Reaction is independent of iodine concentration [1].

[2]

In another similar experiment at the same temperature, the volume of propanone used was halved but the total volume was kept constant by adding water to the reaction mixture. When a similar graph was plotted, the gradient at each point was half that obtained from the first graph.

(e) Why must water be added to the reaction mixture to keep total volume constant in the second experiment?

To ensure that the concentration of propanone varies directly with its volume

[1]

(f) What conclusion can you draw from the above information?

1st order with respect to propanone as halving the concentration cause the rate of reaction to halve as well.

[1]

Planning

The **method of initial rates** allows the values of these orders to be found by running the reaction multiple times under controlled conditions and measuring the rate of the reaction in each case. All variables are held constant from one run to the next, except for the concentration of one reactant. The order of that reactant concentration in the rate law can be determined by observing how the reaction rate varies as the concentration of that one reactant is varied. This method is repeated for each reactant until all the orders are determined. The initial rate experiment involves measuring the time taken for some easily recognisable event to happen very early on in a reaction. In using the initial rate method, time interval for the reaction to proceed to a given point must be kept short, otherwise the rate will become more of an average rate rather than the initial (instantaneous rate).

For the reaction investigated in Question 2, you are to design a plan that will allow you to determine the rate equation by the **initial rate method**.

In your plan, you should include details of
- Step-wise procedure that must be followed
- Details of type of apparatus used
- Results to be tabulated
- Processing of results
- Interpretation of results

[10]

Considerations

Using the initial rate method
- In using the initial rate method, time interval for the reaction to proceed to a given point must be kept reasonably short. Since the time taken for the iodine colour to be discharged is used as a measure of the reaction rate, the amount of iodine used in the reaction must be small.
- Hence, set up reaction mixtures with different amount of the reactant of interest keeping the rest constant, will allow for the concentration of the reactant that we are interested in to be varied and hence understand how the rate varies with it.

Procedure

- Into a clean dry conical flask, place 5 cm^3 of sulfuric acid, 4cm^3 of iodine solution and 11 cm^3 of deionized water. All volumes can be measured using different measuring cylinders of appropriate capacity.
- Instill 3 drops of starch solution into the conical flask.
- Using another measuring cylinder, collect 5 cm^3 of the propanone.
- Pour the propanone into the conical flask and start the stop watch immediately.
- Swirl the reaction mixture and place it on a white tile.
- Record the time taken for the dark blue colour of the reaction mixture to disappear.
- Repeat the experiment for the other mixtures as shown in the table below.

Expt	Vol of propanone / cm^3	Vol of H_2SO_4 / cm^3	Vol of iodine / cm^3	Vol of water / cm^3	Time taken / s
1	5	5	4	11	
2	10	5	4	6	
3	5	10	4	6	
4	5	5	2	13	

Processing of Results

- Rate of reaction α (Vol of I_2 used / time taken)
- Compute the rate for each of the four experiments
- Comparing Expt 1 & 2, deduce order w.r.t. propanone
- Comparing Expt 1 & 3, deduce order w.r.t H^+
- Comparing Expt 1 & 4, deduce order w.r.t I_2

Interpretation of Results

- If rate remains unchanged when the concentration of the reactant under investigation is changed, then reaction is 0 order with respect to that reactant
- If rate is doubled when concentration of reactant of interest is doubled, then reaction is 1st order with respect to that reactant
- If rate is quadruples when concentration of reactant of interest is doubled, then reaction is 2nd order with respect to that reactant

[Total: 24 marks]

Question 3

You are to perform the tests given in the following table on each of **FA 9**, **FA 10** and **FA 11** to identify, where possible, the cation and anion present in each solution.

Record details of colour changes observed, formation of any precipitate and the solubility of any such precipitate in an excess of the reagent added.

Where gases are released, they should identified by a test, described in the appropriate place in your table. You should indicate clearly at what stage in a test a change occurs.

Marks are **not** given for chemical equations. **No additional tests for ions present should also be attempted**.

Test	Observations [7]		
	FA 9	**FA 10**	**FA11**
(a) To 1 cm depth of solution in a test-tube, add aqueous sodium hydroxide drop-by-drop, until it is in excess.	White precipitate is formed, soluble in excess of NaOH	No precipitate is formed, hence no observable change	White precipitate is formed, soluble in excess of NaOH
(b) To 1 cm depth of solution in a test-tube, add aqueous ammonia drop-by-drop, until it is in excess.	White precipitate is formed, soluble in excess of aqueous NH_3	No precipitate is formed, hence no observable change	White precipitate is formed, insoluble in excess of aqueous NH_3
(c) To 1 cm depth of solution in a test-tube, add aqueous barium chloride, then	No precipitate is formed, hence no observable change	No precipitate is formed, hence no observable change	White precipitate is formed
add dilute hydrochloric acid.			White precipitate is insoluble in dilute HC*l*
(d) To 1 cm depth of solution in a test-tube, add 2 cm depth of water and 1 cm depth of aqueous silver nitrate, then divide the resultant solution into 2 parts.	No precipitate is formed, hence no observable change	Yellow precipitate is formed	No precipitate is formed, hence no observable change

To 1 part of solution, add dilute nitric acid.		Yellow precipitate is insoluble in dilute HNO_3	No precipitate is formed, hence no observable change
To 1 part of solution, add aqueous ammonia.		Yellow precipitate is insoluble in aqueous NH_3	White precipitate is formed, insoluble in excess of aqueous NH_3

For Examiner's Use

(e) For each of the solutions **FA 9**, **FA 10** and **FA 11**, summarise the evidence from the tests performed to identify the cations and/or anions present.

FA 9 contains **Zn^{2+}**

Supporting evidence

White precipitate is formed when **FA 9** is added to NaOH & aqueous NH_3. White precipitate is observed to be soluble in excess of both NaOH & aqueous NH_3.

FA 10 contains **I^-**

Supporting evidence

Yellow precipitate of AgI is formed when **FA 10** is added to a solution of $AgNO_3$. AgI remains insoluble in dilute HNO_3 & aqueous NH_3.

FA 11 contains **Al^{3+}** and **SO_4^{2-}**

Supporting evidence

When NaOH & aqueous NH_3 are added to sample of **FA 11**, a white precipitate is formed, but white precipitate is soluble in excess NaOH & but insoluble in excess aqueous NH_3.

White precipitate of $BaSO_4$ is formed when $BaCl_2$ is added to sample of **FA 11**, and white precipitate is insoluble in dilute HCl.

[4]

(f) **Do not perform the tests for the following ions.**

It is believed that when testing a solution containing both NH_4^+ ions and NO_3^- ions, students should identify the NH_4^+ ion before attempting to identify the NO_3^- ion. Suggest a reason for the experimental procedure to be as such.

To test for the presence of NO_3^-, NaOH, Al strip/foil and heat are required for the liberation of NH_3 gas. Similarly, NaOH & heat are required to test for the presence of NH_4^+.

Hence it is necessary for students to identify the NH_4^+ ion before identifying NO_3^-, since test for NO_3^- will also yield similar experimental observations.

[1]

Planning

You are given aqueous solutions of the following acids:

$CH_3CH_2COCOOH$; CH_3COCH_2COOH; $CH_3CH(OH)CH_2COOH$ and $CH_3CH_2CH(OH)COOH$

Outline a sequence of simple chemical tests, by which you could identify each of the above acids.

[5]

EITHER

- Iodoform reaction on all four
  - Positive for CH_3COCH_2COOH and $CH_3CH(OH)CH_2COOH$
- Oxidation with H^+/MnO_4^- or $H^+/Cr_2O_7^{2-}$
  - Positive for $CH_3CH(OH)CH_2COOH$ and $CH_3CH_2CH(OH)COOH$

	Iodoform	**Oxidation**
$CH_3CH_2COCOOH$	-	-
CH_3COCH_2COOH	+	-
$CH_3CH(OH)CH_2COOH$	+	+
$CH_3CH_2CH(OH)COOH$	-	+

OR

- Brady's test on all four
  - Positive for CH_3COCH_2COOH and $CH_3CH_2COCOOH$
- Iodoform reaction on all four
  - Positive for $CH_3CH(OH)CH_2COOH$ and CH_3COCH_2COOH

	Brady's test	**Iodoform**
$CH_3CH_2COCOOH$	+	-
CH_3COCH_2COOH	+	+
$CH_3CH(OH)CH_2COOH$	-	+
$CH_3CH_2CH(OH)COOH$	-	-

Procedure

To each of the 4 acids in a test tube, add a few drops of 2,4 dinitrophenylhydrazine.

- The ones that give a yellow ppt contain carbonyl functional groups whilst those that do not probably contain the alcohol functional groups

To a second sample of the 4 acids in separate test tubes add a mixture of iodine in aqueous sodium hydroxide and warm.

- The one that gives a pale yellow ppt will be CH_3COCH_2COOH or $CH_3CH(OH)CH_2COOH$

Tabulate the results to deduce their identity:

	TEST 1	**TEST 2**
A		
B		
C		
D		

[Total: 17 marks]

~ END OF PAPER~

Catholic Junior College

JC 2 Preliminary Examinations

Higher 2

CHEMISTRY

9729/01

Paper 1 Multiple Choice

29 August 2017

Additional Materials: Multiple Choice Answer Sheet
Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name, HT group and NRIC/FIN number on the Answer Sheet in the spaces provided.
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.

Read the instructions on the Answer Sheet very carefully.

Each correct answer will score one mark. A mark will not be deducted for a wrong answer.
Any rough working should be done in this booklet.
The use of an approved scientific calculator is expected, where appropriate.

This document consists of **14** printed pages and **0** blank page.

For each question there are ***four*** possible answers, ***A***, ***B***, ***C*** and ***D***. Choose the **one** you consider to be correct.

1 When an unknown organic compound is burned completely in excess oxygen, 90 cm^3 of gaseous products is collected. When cooled to room temperature, the gaseous volume decreased to 50 cm^3. A further decrease of 40 cm^3 in the gaseous volume was observed when the gaseous mixture is passed through aqueous potassium hydroxide.

What is the possible identity of the organic compound?

1 CH_2CH_2
2 CH_3CO_2H
3 $CH_3CH_2CH_3$
4 CH_2CHCH_2OH

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

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

A vanadium salt of unknown oxidation state was dissolved in water to form a solution of 0.500 mol dm^{-3}. It was found that 20.4 cm^3 of this solution will react with 1.00 g of zinc powder to form vanadium(II) solution.

What is the possible identity of the vanadium salt used?

A V^{2+} **B** V^{3+} **C** VO^{2+} **D** VO_2^+

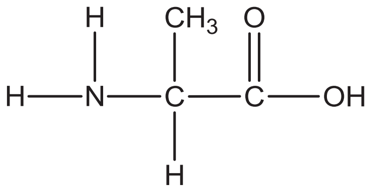
3 The table below gives some data about four ions.

ions	number of neutrons	number of nucleons
Q$^-$	16	33
R$^+$	19	39
S^{2-}	17	33
T^{2+}	18	35

Which of the following pairs consists of ions that are isoelectronic?

A **Q**$^-$ and **S**$^{2-}$
B **R**$^+$ and **S**$^{2-}$
C **S**$^{2-}$ and **T**$^{2+}$
D **Q**$^-$ and **T**$^{2+}$

4 Which bond angle is present in a molecule of alanine, $H_2NCH(CH_3)CO_2H$, but is **not** present in its zwitterion?



alanine

A 90° **B** 107° **C** 109° **D** 120°

5 What are the types of chemical bonds present in solid phenylammonium chloride, $C_6H_5NH_3Cl$?

1 dative covalent bonds
2 ionic bonds
3 hydrogen bonds

A 2 only
B 1 and 2 only
C 2 and 3 only
D 1, 2 and 3

6 Which one of the following shows the standard enthalpy change of formation of carbon monoxide?

A $C(s) + \frac{1}{2}O_2(g) \rightarrow CO(g)$
B $C(s) + CO_2(g) \rightarrow 2CO(g)$
C $C(g) + \frac{1}{2}O_2(g) \rightarrow CO(g)$
D $C(g) + CO_2(g) \rightarrow 2CO(g)$

7 Nitrogen dioxide, NO_2, has an unpaired electron and dimerises to form N_2O_4.

$$2NO_2(g) \rightarrow N_2O_4(g)$$

Which of the following statements about the spontaneity of the reaction is true?

A The reaction is only spontaneous at low temperatures.

B The reaction is only spontaneous at high temperatures.

C The reaction is spontaneous at all temperatures.

D The reaction is non-spontaneous at all temperatures.

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

Gas canisters used in camping stoves contain partially liquefied hydrocarbon. A canister was connected to a gas syringe and the valve opened slightly to allow some gas into the syringe. 0.200 g of the gas occupied a volume of 96.0 cm^3 at a temperature of 30.0 °C and a pressure of 101 kPa.

What is the average M_r of the gas mixture?

A 31 **B** 52 **C** 479 **D** 519

9 At a certain temperature, three gases N_2, O_2 and HC*l* were mixed and the following reaction occurred:

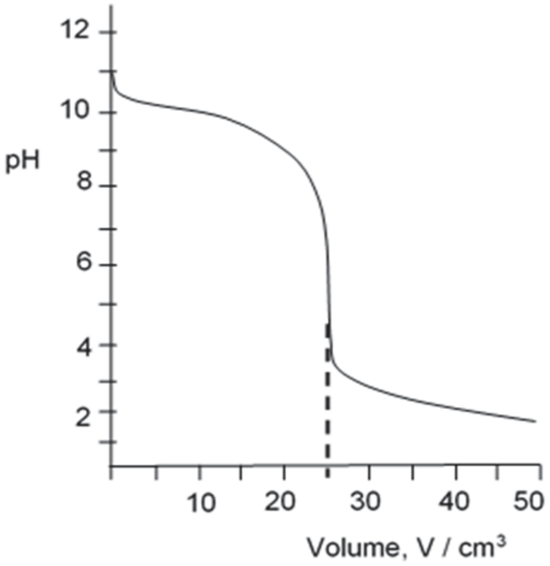
$$2N_2(g) + 3O_2(g) + 4HCl(g) \rightleftharpoons 4NOCl(g) + 2H_2O(g)$$

The initial partial pressures of N_2, O_2 and HC*l* are 0.800 atm, 0.800 atm and 0.400 atm respectively. After equilibrium has been established, it is found that the partial pressure of steam is 0.15 atm.
What is the numerical value of K_p for this reaction at this temperature?

A 1.20 **B** 22.7 **C** 0.0217 **D** 0.0251

10 In an acid-base titration, a 0.10 mol dm^{-3} solution of an acid is added to a 25 cm^3 of a 0.10 mol dm^{-3} solution of a base.

The pH value of the solution is plotted against the volume, V, of acid added as shown in the diagram.



Which of the following statements is **incorrect**?

A The titration involved a strong acid and a weak base.

B The pair of solutions could have been HC*l*(aq) and CH_3NH_2(aq).

C Methyl orange is a suitable indicator for the above titration.

D When concentration of acid is doubled, the end point volume of the titration would be halved while the pH at equivalence point would remain unchanged.

11 The following two reactions are examples of acid-base reactions.

Reaction 1: $HNO_3 + H_2SO_4 \rightleftharpoons H_2NO_3^+ + HSO_4^-$

Reaction 2: $NH_3 + BF_3 \rightarrow NH_3BF_3$

Which of the following correctly describes the behaviour of each species?

	Brønsted acid	Brønsted base	Lewis acid	Lewis base
A	HNO_3	NH_3	H_2SO_4	HSO_4^-
B	H_2SO_4	HNO_3	BF_3	NH_3
C	HSO_4^-	NH_3	BF_3	$H_2NO_3^+$
D	$H_2NO_3^+$	HSO_4^-	NH_3BF_3	NH_3

12 The decomposition of hydrogen peroxide is known to be a first order reaction.

$$2H_2O_2 \rightarrow 2H_2O + O_2$$

The rate constant is found to be 4.95×10^{-2} min^{-1}. If the initial concentration of H_2O_2 is 4.00 mol dm^{-3}, what will be the concentration of H_2O_2 after 64 min?

A 0.50 mol dm^{-3}

B 0.20 mol dm^{-3}

C 0.17 mol dm^{-3}

D 0.13 mol dm^{-3}

13 The rate equation for the reaction 2**W** + **X** → **Y** + **Z** is given as rate = k[**W**][**X**]. In an experiment to study the kinetics of the reaction, the initial concentration of **W** used is 0.20 mol dm^{-3} and the initial concentration of **X** used is 0.001 mol dm^{-3}.

Which of the following statements regarding the experiment is correct?

A The half-life for the [**X**] against time curve is approximately constant.

B The mechanism for the above reaction involves one step.

C The units of the rate constant is $mol^{-2}dm^{6}s^{-1}$.

D Doubling the initial concentration of **W** to 0.40 mol dm^{-3} will not affect the half-life of **X**.

14 The oxide and chloride of an element **E** are mixed separately with water. The two resulting solutions have the same effect on litmus.
What is element **E**?

A Mg **B** A*l* **C** Si **D** P

15 Which of the following statements about iodine or its compounds are correct?

1 A crystal of iodine contains covalent bonds and instantaneous dipole-induced dipole forces of attraction.

2 When aqueous chlorine is added to potassium iodide and the aqueous mixture shaken with tetrachloromethane, a purple organic layer is obtained.

3 The first ionisation energy of iodine is less than that of bromine.

4 The thermal stability of hydrogen iodide is higher than that of hydrogen bromide.

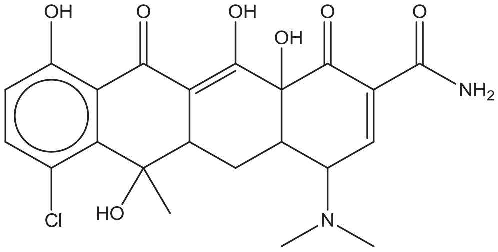
A 1 and 3 only

B 1, 2 and 3 only

C 3 and 4 only

D 2, 3 and 4 only

16 *Aureomycin* is a powerful oral antibiotics that is effective against a wide range of infections.

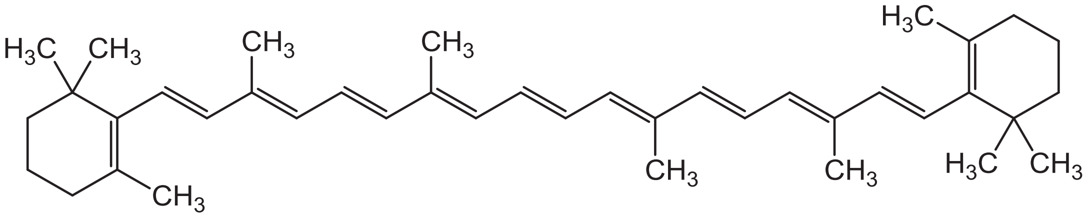


Aureomycin

Which row correctly indicates the number of chiral centres and sp^2 hybridised carbon in a molecule of *aureomycin*?

	Number of chiral centres	Number of sp^2 hybridised C
A	4	10
B	4	13
C	5	10
D	5	13

17 β-carotene is responsible for the orange colour of carrots.



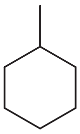
β–carotene

β-carotene is oxidised by hot, concentrated, acidified $KMnO_4$.

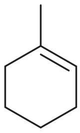
How many different products formed from the above reaction contain the ketone functional group?

A 2 **B** 4 **C** 6 **D** 8

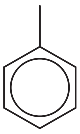
18 Which of the statements are true regarding the three compounds below?



I



II

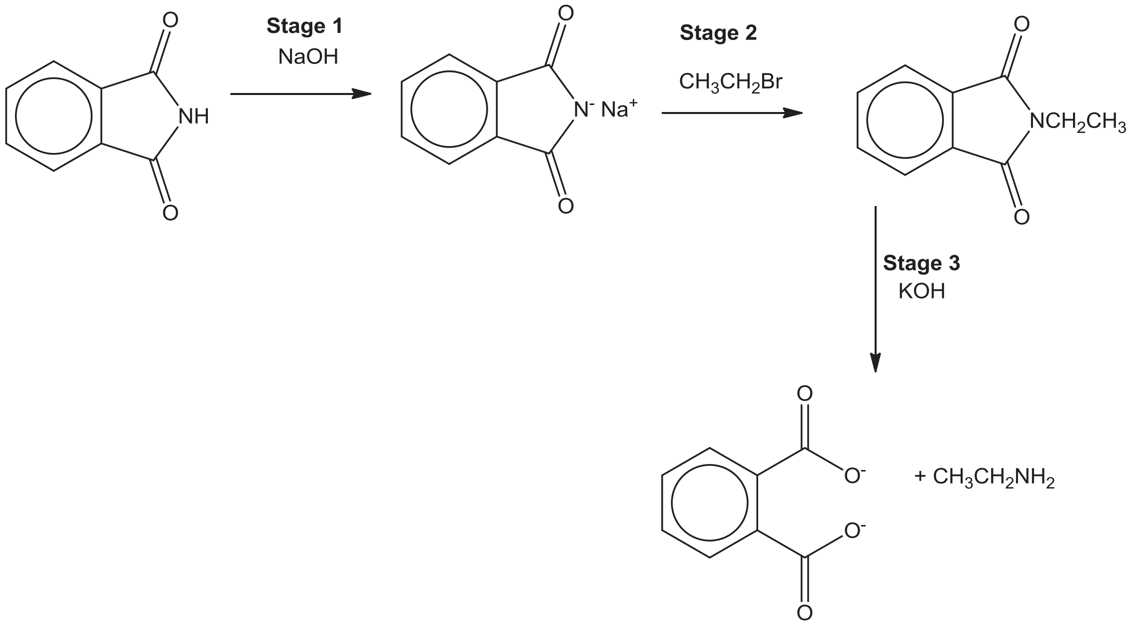


III

1 Compounds **I** and **III** will not decolourise Br_2 in CCl_4.
2 Compounds **I** and **II** will decolourise acidified $KMnO_4$ at 298 K.
3 Compound **III** will not react with chlorine in the presence of uv light.
4 Compound **III** will react with bromine in the presence of a homogeneous catalyst.

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

19 A sequence of reactions is shown below.

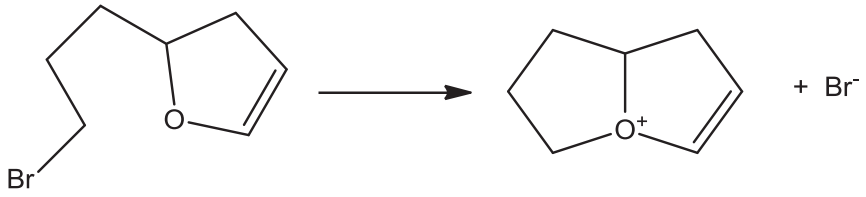


Which of the following correctly describes the type of reactions for Stages **1** to **3**?

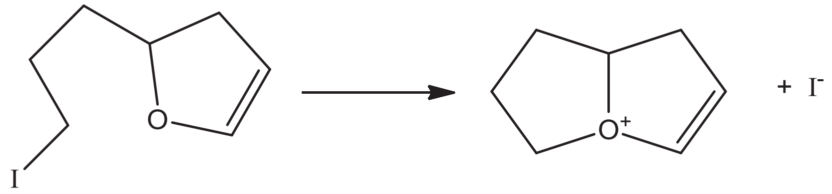
	Stage 1	Stage 2	Stage 3
A	neutralisation	electrophilic substitution	nucleophilic substitution
B	hydrolysis	nucleophilic substitution	hydrolysis
C	redox	nucleophilic addition	nucleophilic substitution
D	neutralisation	nucleophilic substitution	hydrolysis

20 The intramolecular reactions below occur via nucleophilic substitution mechanism.

Reaction 1



Reaction 2



Reaction 2 is faster than reaction 1 under identical conditions.

Which statement explains this difference?

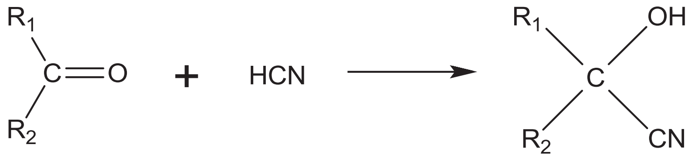
A Br is more electronegative than I.

B The I^- ion is a stronger nucleophile than Br^-.

C The C–Br bond is more polar than the C–I bond.

D The C–Br bond is stronger than the C–I bond.

21 Cyanohydrins can be made from carbonyl compounds by generating CN^- ions from HCN in the presence of a weak base.



In a similar reaction, $^-CH_2COOCH_3$ ions are generated from CH_3COOCH_3 by strong bases.

Which compound can be made from an aldehyde and CH_3COOCH_3?

A $CH_3CH(OH)COOCH_3$

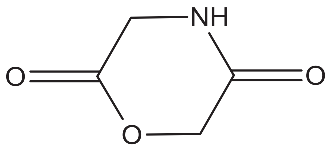
B $CH_3COOCH_2CH(OH)CH_3$

C $CH_3CH_2CH(OH)CH_2COOCH_3$

D $(CH_3)_2C(OH)CH_2COOCH_3$

[Turn over

22 The cyclic compound **X** is heated with acidified $KMnO_4$.

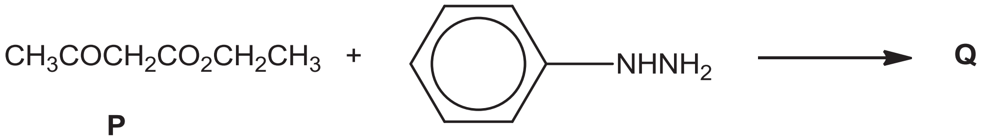


Compound **X**

What are the final organic products of the reaction?

- **A** $HOCH_2CO_2H$ and $HO_2CCH_2NH_3^+$
- **B** $HO_2CCH_2NH_3^+$
- **C** $HOCH_2CHO$ and $H_2NCH_2CO_2H$
- **D** H_2NCOCH_2OH and $HOCH_2CHO$

23 The first stage in the synthesis of *Antipyrine,* a fever medication, is the reaction between compound **P** and phenylhydrazine.

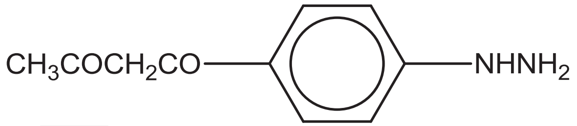


P

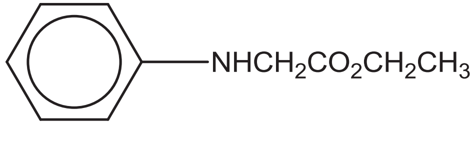
phenylhydrazine

Which of the following correctly represents the structure of product **Q**?

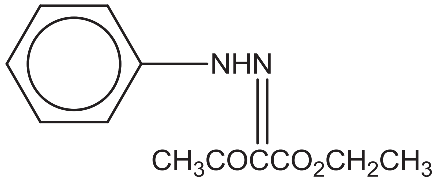
A

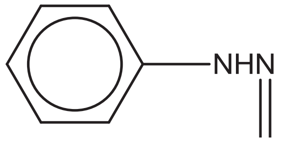


B



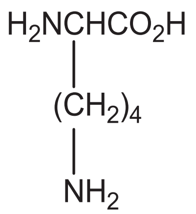
C





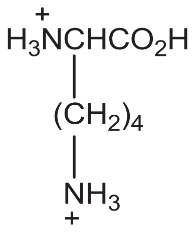
D

24 Lysine is an α-amino acid.



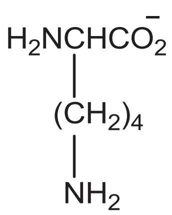
$$\begin{array}{c}\mathrm{H_2NCHCO_2H}\\ |\\ \mathrm{(CH_2)_4}\\ |\\ \mathrm{NH_2}\end{array}$$

Which structure is predominant when lysine is in an aqueous solution of pH 9.5, given that lysine has three pK_a values of 2.2, 8.9 and 10.5?



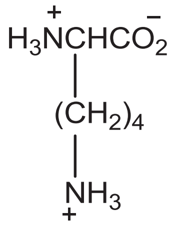
$$\begin{array}{c}\mathrm{H_3\overset{+}{N}CHCO_2H}\\ |\\ \mathrm{(CH_2)_4}\\ |\\ \mathrm{\underset{+}{N}H_3}\end{array}$$

A



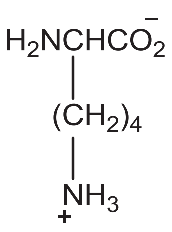
$$\begin{array}{c}\mathrm{H_2NCHC\overset{-}{O_2}}\\ |\\ \mathrm{(CH_2)_4}\\ |\\ \mathrm{NH_2}\end{array}$$

B



$$\begin{array}{c}\mathrm{H_3\overset{+}{N}CHC\overset{-}{O_2}}\\ |\\ \mathrm{(CH_2)_4}\\ |\\ \mathrm{\underset{+}{N}H_3}\end{array}$$

C

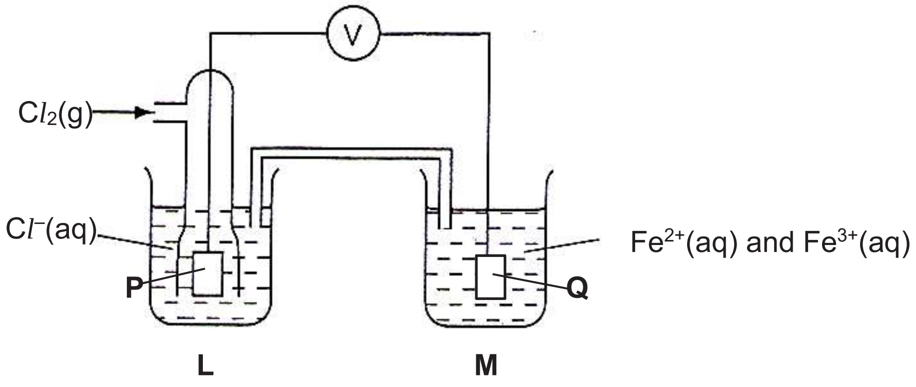


$$\begin{array}{c}\mathrm{H_2NCHC\overset{-}{O_2}}\\ |\\ \mathrm{(CH_2)_4}\\ |\\ \mathrm{\underset{+}{N}H_3}\end{array}$$

D

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

The cell shown below is set up under standard conditions where **P** and **Q** are platinum electrodes.



Which of the following statements is correct?

A Addition of KCN to half-cell **M** will not affect $E_{cell}^{\ominus}$.

B The voltmeter will show a reading of about 2.13 V.

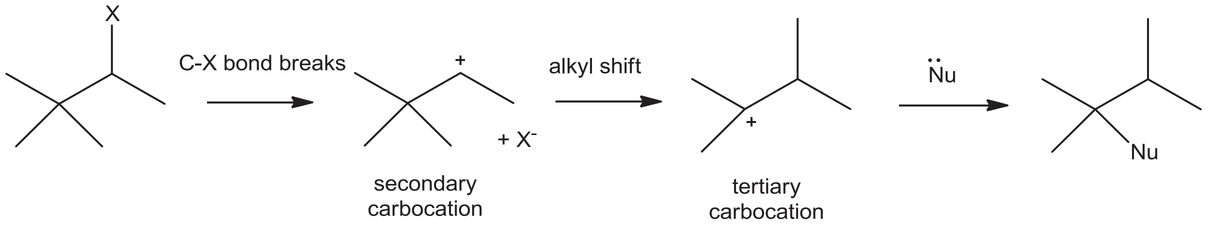
C The electrons will flow from **Q** to **P** through the voltmeter.

D **P** will be the negative electrode.

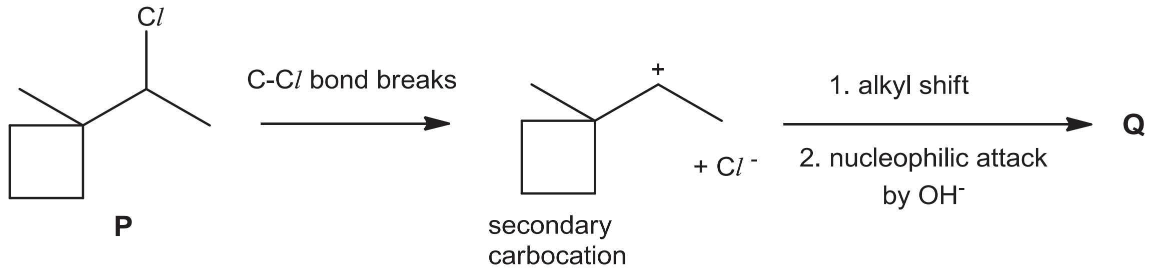
26 During electroplating, a current is passed through a cell containing aqueous silver nitrate using inert electrodes. After some time, 1.35 g of silver was deposited at one electrode. What volume of gas would be produced at the other electrode at r.t.p.?

A 70 cm^3 **B** 75 cm^3 **C** 140 cm^3 **D** 150 cm^3

27 In S_N1 reactions involving secondary halogenoalkanes, alkyl shift can sometimes occur after the breaking of C–X bond to form a more stable tertiary carbocation.

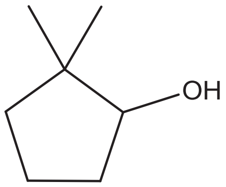


Rearrangements need not always involve methyl groups. In situation when the carbocation is formed adjacent to a strained ring, such as a cyclobutane, it is more favourable for one of the alkyl groups in the ring, rather than the methyl group, to shift so as to cause **ring expansion** and the formation of a less strained ring.

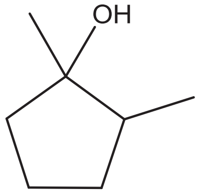


Which of the following is a possible identity of **Q**?

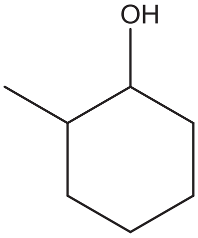
A



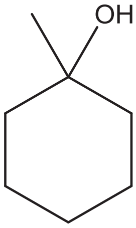
B



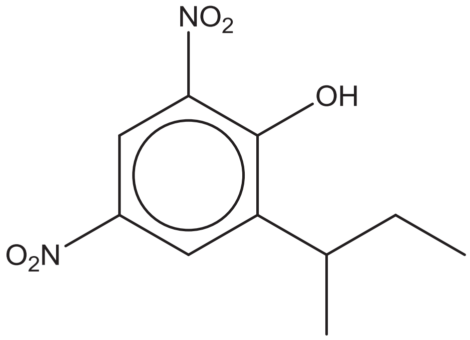
C



D



28 *Binapacryl* is used as a fungicide.



Binapacryl

Which of the following statements about *Binapacryl* are correct?

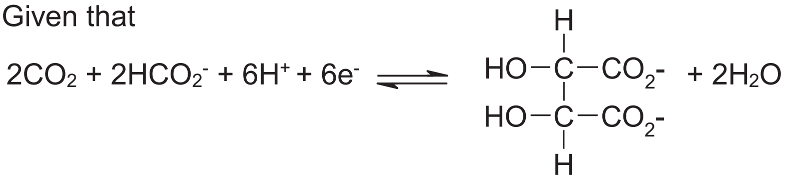
1 It dissolves in water to give a neutral solution.
2 It is inert towards acidified potassium dichromate(VI) solution.
3 It decolourises aqueous bromine to form a white precipitate.
4 It reacts with ethanoic acid in the presence of concentrated sulfuric acid to form an ester.

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

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

The reaction between peroxodisulfate(VI) ion, $S_2O_8^{2-}$, and tartrate ion, $[CH(OH)CO_2^-]_2$, is slow due to a high activation energy.

The reaction can be catalysed by a homogeneous catalyst.
Given that



$$2CO_2 + 2HCO_2^- + 6H^+ + 6e^- \rightleftharpoons \begin{array}{c} H \\ | \\ HO-C-CO_2^- \\ | \\ HO-C-CO_2^- \\ | \\ H \end{array} + 2H_2O \qquad E^\ominus = +0.56\text{ V}$$

Which metal ion is **not** a suitable catalyst for this reaction?

A Co^{2+} **B** Cr^{2+} **C** Mn^{3+} **D** Fe^{3+}

30 Chromium forms a series of compounds with the general formula $CrCl_3 \bullet 6H_2O$. One of these compounds, **X** is violet and produces an aqueous solution from which all the chlorine can be precipitated as $AgCl$ upon addition of aqueous silver nitrate.
Another compound **Y** is green and produces an aqueous solution from which only one third of the chlorine can be precipitated with silver nitrate.

Which of the following statements about **X** and **Y** is **incorrect**?

A **X** is an ionic compound consisting of $[Cr(H_2O)_6]^{3+}$ and Cl^- ions.

B **Y** is an ionic compound consisting of $[Cr(Cl)_2(H_2O)_4]^+$ and Cl^- ions.

C Oxidation number of Cr in **X** is +3 while the oxidation number of Cr in **Y** is +1.

D Oxidation number of Cr in **X** and **Y** remains unchanged during precipitation of $AgCl$.

Catholic Junior College
JC2 Preliminary Examinations
Higher 2

CANDIDATE NAME	
CLASS	2T

CHEMISTRY 9729/02

Paper 2 Structured Questions

18 August 2017

2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name and class on all the work you hand in.
Write in dark blue or black pen.
You may use an HB pencil for any diagrams or graphs.
Do **not** use staples, paper clips, glue or correction fluid.

Answer **all** questions in the spaces provided on the Question Paper.
The use of an approved scientific calculator is expected, where appropriate.
A Data Booklet is provided.

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

For Examiner's Use			
Paper 1			30
Paper 2	**Q 1**	12	
	Q 2	19	
	Q 3	18	
	Q 4	9	
	Q 5	10	
	Q 6	7	75
Paper 3	**Q 1**	22	
	Q 2	20	
	Q 3	18	
	Q 4	20	
	Q 5	20	80
Total			185

This document consists of **14** printed pages and **0** blank page.

Answer **all** the questions.

1 Sedimentary rocks formed at the earth's surface by the accumulation of particulate matter are usually transported to the place of deposition by water, wind, or mass movement of glaciers. Dolostone, a sedimentary rock, consists of a mixture of minerals such as calcium and magnesium carbonates.

Table 1.1 below shows some properties of calcium carbonate and magnesium carbonate.

Table 1.1

	Numerical values of K_{sp} at 25 °C	Decomposition temperature / ˚C
calcium carbonate	5.0×10^{-9}	900
magnesium carbonate	1.0×10^{-5}	540

(a) **(i)** Write an expression for the solubility product, K_{sp}, of calcium carbonate.

....[1]

(ii) Calculate the solubility, in mol dm^{-3}, of calcium carbonate in water at 25 °C.

[1]

(iii) A saturated solution **X** containing calcium hydroxide and calcium carbonate has a pH of 13 at 25 °C.

Given that the K_{sp} of calcium hydroxide is 5.5×10^{-6} mol^3 dm^{-9} and using your answer in **(a)(i)**, calculate the solubility of calcium carbonate in solution **X**.

[2]

(iv) Comment on, and explain, the difference in the solubilities of calcium carbonate in water and in solution **X**.

....

....

....[2]

(v) When rainwater runs over dolostone, a chemical reaction occurs as shown below:

$$\mathbf{M}CO_3(s) + CO_2(aq) + H_2O(l) \rightleftharpoons 2HCO_3^-(aq) + \mathbf{M}^{2+}(aq)$$

where **M** is a group 2 metal

I. Suggest the source of CO_2 (aq) for the reaction.

....[1]

II. When a sample of saturated solution of $Ca(HCO_3)_2$ is heated, a reaction occurs and a precipitate is formed. Using the equation above, suggest why this happens.

....

....

....[2]

(b) Calcium carbonate can be decomposed by heating at high temperatures.

(i) Write an equation for the thermal decomposition of calcium carbonate.

....[1]

(ii) Calcium carbonate decomposes at a higher temperature than magnesium carbonate. Explain why this is so.

....

....

....

....

....[2]

[Total: 12]

2 **(a)** Table 2.1 gives data about some physical properties of the elements calcium and copper.

Table 2.1

physical property	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
melting point / °C	839	1085
boiling point / °C	1484	2562

(i) Explain why the atomic radius of copper is smaller than that of calcium.

....

....

....[2]

(ii) Explain why copper has a higher melting point than calcium.

....

....

....[2]

(iii) Apart from the properties given in Table 2.1, state clearly the difference in one other physical property between copper and calcium.

....

....[1]

(b) Copper, scandium and zinc are d-block elements. However, copper is a transition element while scandium and zinc are not.

(i) Define the term *transition element*.

....

....[1]

(ii) Explain why scandium is not classified as a transition element.

....

....[1]

(c) Manganese is also a transition element and shows great tendency to form stable coloured complexes with ligands.

(i) Define the term *ligand*.

....

....[1]

(ii) Draw the shape of the complex ion, $[Mn(CN)_6]^{4-}$.

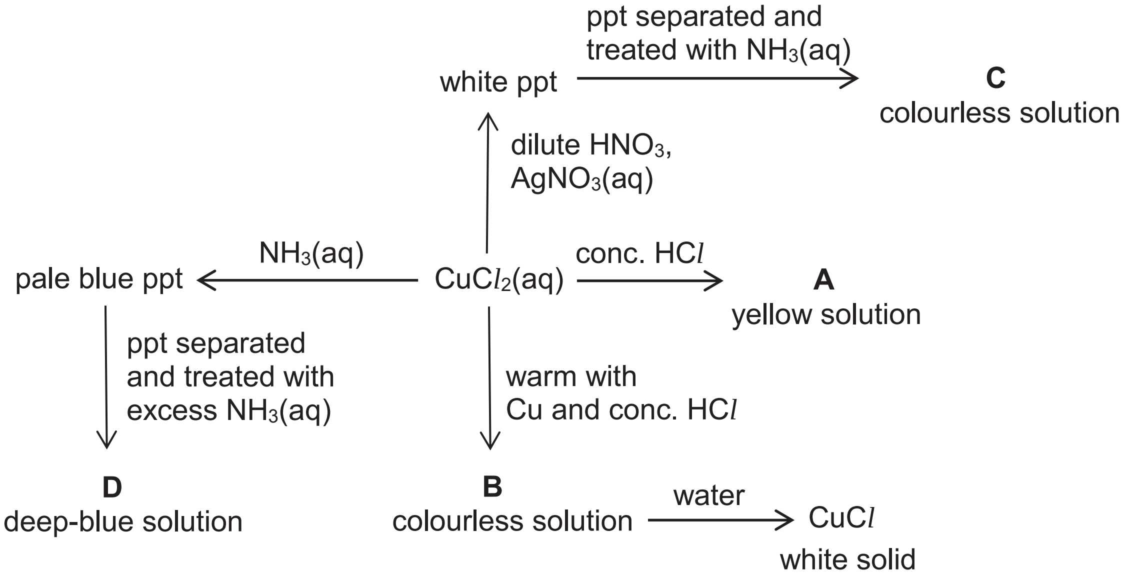
[2]

(d) Copper has more than one oxidation state and many of its compounds have colours in the blue-green-yellow part of the visible spectrum.

Write the *spdf* electronic configuration of copper(II) ions.

Cu^{2+} .... [1]

(e) Aqueous copper(II) chloride, $CuCl_2$, is a blue solution which gives the following reactions.



Both **A** and **B** contain complex ions of copper and chlorine.

(i) State the formula of compound **C**.

....[1]

(ii) Suggest the formula and shape of the complex ion present in **D**.

Formula .... [1]

Shape .... [1]

(iii) What type of reaction occurs when **A** is formed from $CuCl_2(aq)$?

.... [1]

(iv) Explain why **A** is yellow in colour.

....

....

....

....

....

....[3]

(v) Explain why **B** is colourless.

....

....

....[1]

[Total: 19]

3 Industrially, ethanol, CH_3CH_2OH, is manufactured by reacting ethene with steam in the presence of a catalyst. The reaction is reversible and the equation is as follows:

$$CH_2{=}CH_2(g) + H_2O(g) \rightleftharpoons CH_3CH_2OH(g)$$

At equilibrium, only 5 % of the ethene is converted into ethanol. To increase the overall yield of ethanol, ethanol is regularly removed from the equilibrium mixture as it is formed and more ethene is added into the reaction mixture. The volume of steam is not increased as this may disable the catalyst.

(a) Apart from the methods mentioned above, suggest one other method which will increase the conversion of ethene into ethanol. Explain your answer briefly.

....

....[2]

Alcoholic beverages can contain up to 40 % of ethanol. Excessive consumption of ethanol depresses the activity of the central nervous system. The blood alcohol concentration (BAC) is a good measure of the extent to which the activity of the central nervous system is depressed. It is usually defined as follows

$$\text{BAC} = \text{mg of ethanol per 100 cm}^3 \text{ of blood}$$

Ethanol is sufficiently volatile to pass from the blood into the air in the lungs and the following equilibrium is set up:

$$CH_3CH_2OH(\text{blood}) \rightleftharpoons CH_3CH_2OH(g)$$

(b) **(i)** Suggest an expression for K_c for the equilibrium of ethanol between the blood and the air in the lungs.

[1]

(ii) Using your answer to **(b)(i)** and given that the equilibrium constant, K_c, for this process is 4.35×10^{-4}, calculate the breath alcohol concentration (in mg of ethanol / 100 cm^3 of air) which corresponds to the 80 mg / 100 cm^3 of blood legal limit for BAC.

[1]

(iii) Hence determine the legal limit of breath alcohol concentration in mol dm^{-3}.

[2]

(c) The handheld breathalyser contains an electrochemical cell in which ethanol is oxidised. At one electrode, atmospheric oxygen is reduced to water and the other electrode ethanol is oxidised to ethanoic acid. The electric current produced gives an approximation of the overall blood alcohol concentration (BAC).

Give the half–equation for each electrode reaction and hence give the overall equation showing the oxidation of ethanol.

....

....

....

....

....

....[2]

(d) Ethanol can be burned in excess oxygen as fuel. Complete combustion of ethanol releases 1367 kJ mol^{-1} of heat energy.

(i) Write an equation to show the standard enthalpy change of combustion of ethanol.

....[1]

(ii) Use the bond energies given in the *Data Booklet* to calculate another value for the standard enthalpy change of combustion of ethanol.

[3]

(iii) Suggest a reason for the discrepancy between this value and that quoted in **(d)**.

....

....[1]

(e) **(i)** The complete combustion of ethanoic acid, CH_3CO_2H, releases 873 kJ mol^{-1} of energy. Use this value and the enthalpy change of combustion of ethanol given in **(d)** to construct an energy cycle to calculate the enthalpy change when 1.0 mol of ethanol in the body is oxidised to ethanoic acid and water only.

[3]

(ii) The metabolism of ethanol in the human body leads to partial oxidation which releases 770 kJ mol^{-1} of energy. Assuming that ethanol is oxidised to ethanoic acid and carbon dioxide only, use your answer to **(e)(i)** and any other relevant data to calculate the proportion of ethanol metabolised to ethanoic acid and to carbon dioxide respectively.

[2]

[Total: 18]

4 **(a)** Aerosol spray is a type of dispensing system which creates an aerosol mist of liquid particles. This is used with a can that contains a product and propellant under pressure. Hair spray is a common example of an aerosol spray where butane is often used as the propellant.

(i) A typical can of hair spray has a volume of 300 ml and 70 % of which is the hair product. Given that the can has an internal pressure of 100 psi, at 27 °C, calculate the maximum amount of butane present in the can. (1 psi = 6894.76 Pa)

[2]

(ii) The can of hair spray is used such that only the propellant, butane gas, remained and the internal pressure of the can decreased to 20 psi. If the can is left in a car that reaches 50 °C on a hot afternoon, what is the new pressure in the can?

[1]

(iii) As a safety precaution, the propellant has to be completely expelled from the can prior to disposal and subsequent incineration. Using concepts from the Ideal Gas Law, explain qualitatively, why this precaution is necessary.

....

....

....

....[1]

(b) In 1873, Johannes D. van der Waals, a physicist proposed a modification to the ideal gas equation to better model real gas behaviour. The new equation, usually referred to as the van der Waals equation, has the following expression.

$$\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT$$

P is the observed pressure exerted by the gas.
V is the volume of the container in which the gas is contained.
The constants a and b have positive values and are characteristic of a gas.

Suggest why the term $\frac{an^2}{V^2}$ is **added** to P and the term nb is **subtracted** from V respectively.

$P + \frac{an^2}{V^2}$: ....

....

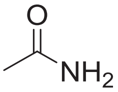
....[1]

$V - nb$: ....

....

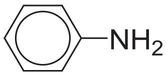
....[1]

(c) Arrange the following three compounds in increasing order of basicity.



ethanamide

ethylamine



phenylamine

Order of basicity:

Explain your answer.

....

....

....

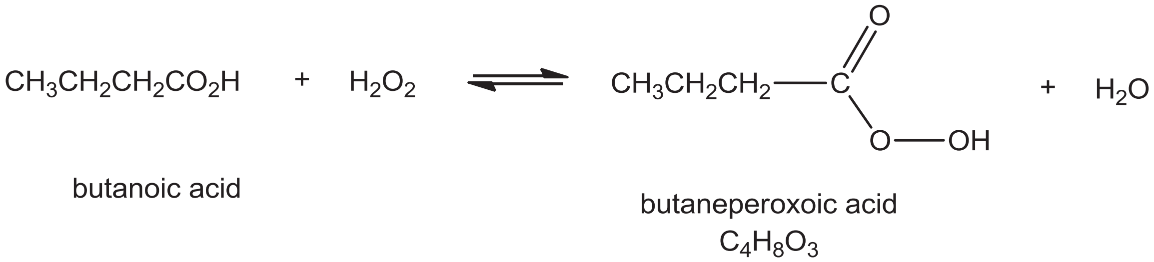
....

....

....[3]

[Total: 9]

5 **(a)** Butaneperoxoic acid, a type of peroxyacid, is produced when butanoic acid reacts with hydrogen peroxide.



(i) Identify the type of hybridisation involved for the C atom of O=C-O in butaneperoxoic acid and hence state its bond angle.

Hybridisation of C ……………………………………..

Bond angle …………………………………….. [2]

(ii) Non-cyclic compounds **A** and **B** are functional group isomers of butaneperoxoic acid. 1 mole of hydrogen gas is produced when 1 mole of **A** and 1 mole of **B** are reacted with Na metal separately. **A** produces yellow precipitate when reacted with aqueous alkaline iodine while **B** does not. When reacted with hot acidified $K_2Cr_2O_7$, orange $K_2Cr_2O_7$ turns green in the presence of **A** but not **B**.

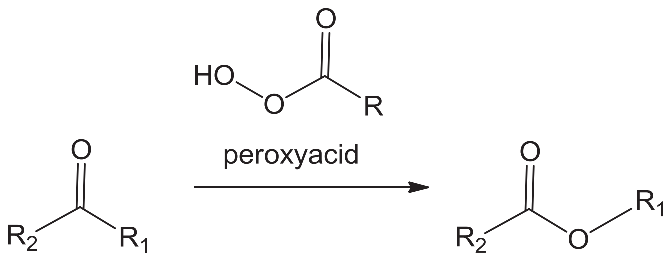
Draw the displayed formula of **A** and **B**, hence state the specific type of isomerism between **A** and **B**.

Compound **A**	Compound **B**

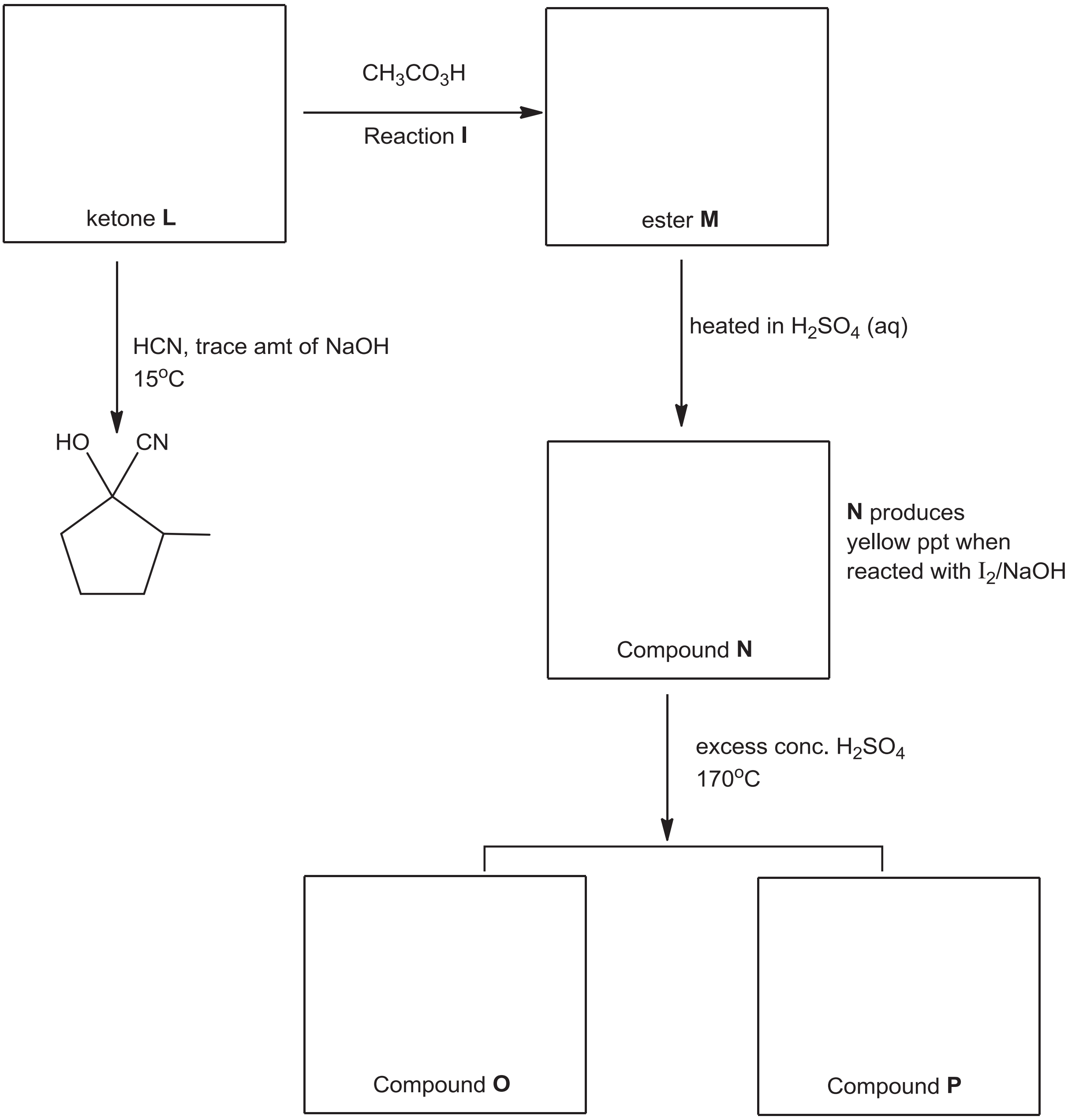
[2]

Type of isomerism between **A** and **B** ……………………………………… [1]

(b) The Baeyer-Villiger oxidation is an organic reaction that converts ketones into esters using peroxyacids.



In the following reaction scheme, reaction **I** is a Baeyer-Villiger oxidation. Give the structural formulae of compounds **L**, **M**, **N**, **O** and **P**. [5]



Both Compounds **O** and **P** decolourise aqueous bromine

[Total: 10]

6 2-methylbut-2-ene is reacted with bromine in an inert solvent in the absence of light.

(a) Describe the mechanism for the above reaction.

[3]

(b) **(i)** State the type of isomerism exhibited by the organic product(s) formed in the above reaction, and hence, draw the structures of the isomers.

type of isomerism ……………………………………………………………………...[1]

Structures of isomers:

[1]

(ii) It was found that the product(s) formed from **(a)** do not rotate plane of polarised light. Using the mechanism drawn in **(a)**, suggest why this is so.

....

....

....

....[2]

[Total: 7]

Catholic Junior College

JC2 Preliminary Examinations
Higher 2

CHEMISTRY 9729/03

Paper 3 Free Response

25 August 2017

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.

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 and **0** blank page.

[Turn over

Section A

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

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

(a) Under acidic conditions, ethanol reacts with dichromate(VI) ions quantitatively to give ethanoic acid and chromium(III) ions.

$$3CH_3CH_2OH + 2Cr_2O_7^{2-} + 16H^+ \rightarrow 3CH_3CO_2H + 4Cr^{3+} + 11H_2O$$

A student carried out the following experiment to determine the concentration of ethanol in a brand of wine.

A 10.0 cm^3 sample of the wine was diluted to 250 cm^3. He then added 25.0 cm^3 of 0.156 mol dm^{-3} $K_2Cr_2O_7$(aq) and excess dilute H_2SO_4 to a 25.0 cm^3 portion of the diluted solution. After allowing the mixture to stand for about an hour at room temperature, the excess $K_2Cr_2O_7$ in the mixture was then titrated with 0.118 mol dm^{-3} $(NH_4)_2Fe(SO_4)_2$(aq) using an appropriate indicator. At the end-point of the titration, he used 12.25 cm^3 of the Fe^{2+}(aq) solution.

(i) Write an ionic equation for the reaction that occurs during titration. [1]

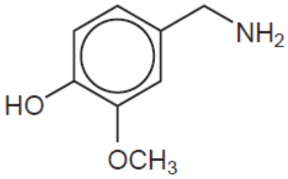
(ii) Calculate the concentration, in mol dm^{-3}, of ethanol in this brand of wine. [4]

(b) The relatively high alcohol content in wine makes it difficult to pair wine with spicy food because the combination can create a painful burning sensation on the lips and tongue that cannot be wiped or rinsed away.

Capsaicin, $C_{18}H_{27}NO_3$, is the active ingredient in spicy food that gives the hot taste of chilli peppers. The structure of capsaicin can be deduced from the following reactions.

When capsaicin is boiled with dilute sulfuric acid, compound **A**, $C_{10}H_{18}O_2$, and the salt of compound **B**, are produced. Compound **B**, $C_8H_{11}NO_2$, has the structure shown, where the CH_3O– group can be regarded as inert.

compound **B**



When **A** is heated with concentrated acidified $KMnO_4$, compound **C**, $C_6H_{10}O_4$, and compound **D**, $C_4H_8O_2$, are produced. **C** can be prepared from $Br(CH_2)_4Br$ in two steps whereas **D** can be prepared directly from $(CH_3)_2CHCH_2OH$.

Compounds **A**, **C** and **D** all react with aqueous sodium carbonate.

(i) What observations and deductions could be made from the reaction of **A**, **C** and **D** with aqueous sodium carbonate? [2]

(ii) Draw the structural formula of **D** and state the reagents and conditions required for its preparation from $(CH_3)_2CHCH_2OH$. [2]

(iii) Show how compound **C** can be prepared from $Br(CH_2)_4Br$, stating clearly the reagents and conditions required for each step, and give the structural formulae of **C** and the intermediate formed. [4]

(iv) Hence suggest the structure for **A** and two possible structures for capsaicin. [3]

(c) Methanol, CH_3OH, is the simplest alcohol that could be used to power a fuel cell in an electric car.

Figure 1.1 shows a preliminary design of a methanol fuel cell. The fuel and oxygen are fed continuously to the two electrodes which are made of platinum. Methanol is oxidised when the fuel cell is operated.

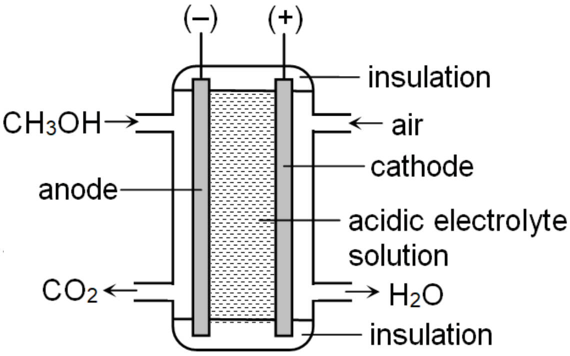


Fig. 1.1

(i) Write balanced equations for the half reactions at each electrode and for the overall cell reaction. [2]

(ii) Write a cell representation, indicating clearly on the cell representation the direction of electron flow in the external circuit. [1]

(iii) Use appropriate data from the *Data Booklet* to explain why an acidic electrolyte is often preferred to an alkaline electrolyte. [1]

(iv) The design of the above fuel cell could be improved by replacing the acidic electrolyte solution with a film of solid H^+ ion-conducting polymer.

Suggest a reason for doing so. [1]

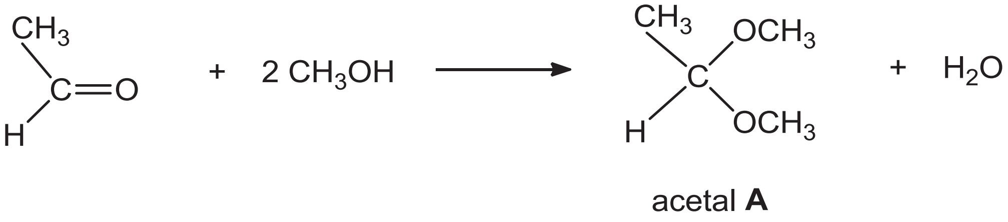
(v) Methanol could also be used as fuel in an internal combustion engine.

Suggest one advantage of the methanol fuel cell over such an internal combustion engine that uses methanol. [1]

[Total: 22]

[Turn over

2 Acetals are molecules that contain 2 –OR groups bonded to the same carbon and are formed when aldehydes are reacted with an alcohol in the presence of an acid. The reaction between ethanal and methanol in the presence of acid, to produce acetal **A** was studied.



(a) When the initial rate of this reaction was measured at various starting concentrations of ethanal, methanol and H^+, the following results were obtained:

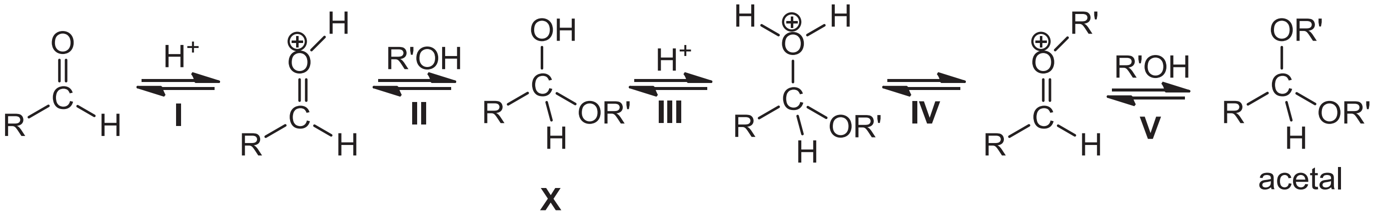
Experiment number	**[CH_3CHO] / mol dm^{-3}**	**[CH_3OH] / mol dm^{-3}**	**[H^+] / mol dm^{-3}**	**relative rate**
1	0.20	0.10	0.05	1.00
2	0.25	0.10	0.05	1.25
3	0.25	0.32	0.05	4.00
4	0.10	0.16	0.10	1.60

(i) Use the data in the table to determine the order with respect to
I ethanal
II methanol and
III H^+.
[3]

(ii) Use your results from **(a)(i)** to write the rate equation for the reaction. [1]

(iii) Calculate the relative rate of reaction for a mixture in which the starting concentrations of all three reactants are 0.20 mol dm^{-3}. [1]

(b) The mechanism of acetal formation is proposed to proceed through the following steps.

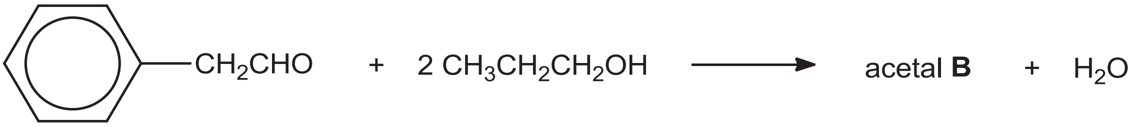


(i) The protonation of the carbonyl group in step **I** is necessary for step **II** to take place. Suggest a reason for this. [1]

(ii) Using your answer to **(a)(ii)**, state with reasons, which one is the rate-determining step of the reaction mechanism. [2]

(iii) The species in the mechanism have various roles. They can be reactants, products, catalysts or intermediates. Suggest, with a reason in each case, the roles of H^+ and **X**. [2]

(c) Draw the structure of the acetal **B** formed from the reaction between phenylethanal and propan-1-ol.

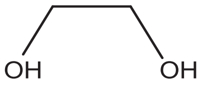


[1]

(d) Acetal formation is useful in organic synthesis. When an aldehyde or ketone is converted to an acetal, the carbonyl group is protected from attack by reagents such as bases and reducing agents. The acetal can later be hydrolysed by a strong acid to form the original aldehyde or ketone since the formation of acetals is a reversible reaction.

Suggest a suitable synthesis route for the following conversion

which involves the initial formation of an acetal group using ethane-1,2-diol,



. [2]

(e) Methanol is currently studied as a potential green fuel that greatly reduces the pollution to the environment.

$$CH_3OH(l) + \frac{3}{2}O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$$

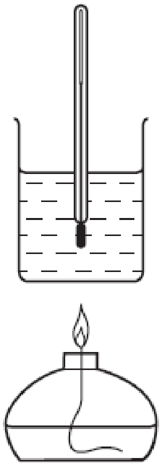
(i) The standard molar entropy, $S^\ominus$ is the entropy content of one mole of substance under standard conditions. Given the following standard molar entropy values, calculate the standard entropy change of combustion of methanol. [1]

	$S^\ominus$ /J K^{-1} mol^{-1}
$CH_3OH(l)$	126.8
$O_2(g)$	205.0
$CO_2(g)$	213.6
$H_2O(l)$	69.9

(ii) Hence, explain the significance of the sign of the standard entropy change of combustion of methanol. [1]

[Turn over

(iii) A student carried out an experiment to determine the enthalpy change for the combustion of methanol. A sample of methanol was burnt under laboratory conditions and the following results were obtained by the student.



initial temperature of the water	25.0 °C
final temperature of the water	48.2°C
mass of alcohol burner before burning	259.65 g
mass of alcohol burner after burning	259.15 g
mass of glass beaker and water	150.00 g
mass of glass beaker	50.00 g

Given that the theoretical enthalpy change of combustion of methanol is –726 kJ mol^{-1}, calculate the percentage of heat evolved used to heat up the water.

[2]

(iv) Using the theoretical enthalpy change of combustion and other relevant information given above, calculate the change in standard Gibbs free energy for the combustion reaction. [1]

(v) Predict and explain the effect on the spontaneity of this reaction of increasing the temperature. [2]

[Total: 20]

3 **(a)** Water pollution is any chemical, physical or biological change in the quality of water that has a harmful effect on any living thing that consumes it. In 2008, a cholera outbreak in Zimbabwe occurred due to a lack of proper water treatment. It is possible to stop the spread of cholera by treating water with chlorine or solid calcium chlorate(I). Calcium chlorate(I), $Ca(ClO)_2$, reacts with water to form chloric(I) acid, $HClO$, which acts as a general biocide.

(i) Write an ionic equation for the reaction of calcium chlorate(I) with water. [1]

(ii) Chloric(I) acid, $HClO$, can also be formed by adding chlorine dioxide gas, ClO_2, to water as shown in the equation below:

$$4ClO_2 + 2H_2O \rightarrow HClO + HClO_3$$

Identify the specific type of reaction that chlorine has undergone by stating the oxidation states of chlorine in the relevant species. [2]

(iii) An environmental scientist decides to analyse a sample of treated water to find out the amount of chlorine it contains. A 250 cm^3 sample of the chlorine–containing water was treated with an excess of potassium iodide solution.

$$Cl_2(aq) + 2I^-(aq) \rightarrow I_2(aq) + 2Cl^-(aq)$$

The sample was subsequently titrated with 12.30 cm^3 of 0.001 mol dm^{-3} sodium thiosulfate solution to find out how much iodine had been formed.

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

Calculate the concentration of Cl_2, in mol dm^{-3}, in the original sample of treated water. [2]

(iv) Suggest a reason why it may be preferable to use calcium chlorate(I) rather than chlorine for treating drinking water. [1]

(b) The extraction of aluminium from its ore is highly energy intensive and often results in pollution of the environment. Phosphorus, however, poses a threat to biodiversity in aquatic ecosystems through the depletion of oxygen via the excessive growth and decomposition of aquatic plants and algae.

When heated in chlorine, both aluminium and phosphorus form chlorides.

(i) Describe the observations when a **limited** amount of water is added to the chlorides of aluminium and phosphorus respectively and write equations for any reactions that occur. [2]

(ii) Write equations for any reactions that might occur when an **excess** amount of water is added to the chlorides of aluminium and phosphorus respectively and suggest the pH of each solution formed. [2]

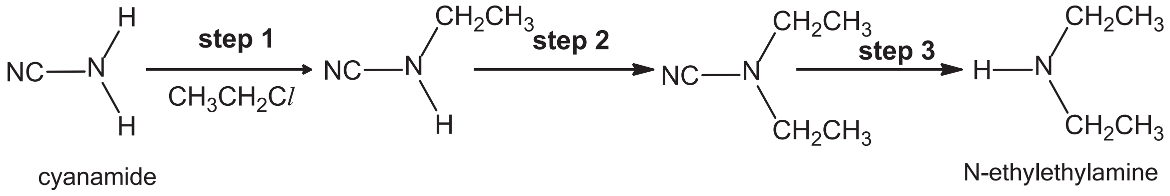
[Turn over

(c) Cyanamide, CH_2N_2, is a compound commonly used in fertilisers that could also cause eutrophication, which deplete the water's oxygen supply through excessive growth and decomposition of algae and water plants.

$$N{\equiv}C{-}NH_2$$

cyanamide

Cyanamide is a useful precursor for the synthesis of secondary amines with a relatively high yield. Below is the sequence of steps for the synthesis of N-ethylethylamine.

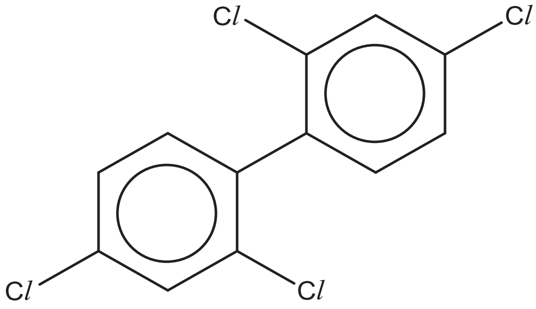


(i) Describe the mechanism for the reaction in **step 1**. In your answer, show any relevant charges, lone pairs of electrons and movement of electrons. [4]

(ii) Identify the two roles of cyanamide in your mechanism. [1]

(iii) Besides using a specific catalyst and heating under reflux for **steps 1** and **2**, suggest another condition which would give a high yield of the intermediate formed in **step 2**. [1]

(d) 2,2',4,4'-tetrachlorobiphenyl is a common organic pollutant that is immiscible in water.



2,2',4,4'-tetrachlorobiphenyl

Suggest two reasons why 2,2',4,4'-tetrachlorobiphenyl is typically inert and chemically unreactive to nucleophilic reagents. [2]

[Total: 18]

Section B

Answer **one** question from this section.

4 Transition elements show unique properties that distinguish them from s-block elements, such as calcium. These include variable oxidation states in their compounds, and the formation of coloured complex ions.

(a) Chromium, a transition element, forms two common series of compounds. One containing chromium in the +3 oxidation state while the other containing chromium in +6 oxidation state.

The complex ion $[Cr(OH)_6]^{3-}$ is green whereas the complex ion $[Cr(NH_3)_6]^{3+}$ is purple. Both of these complexes are octahedral.

In an octahedral complex, the d subshell of a transition metal ion is split into two energy levels.

(i) Using the Cartesian axes, like those shown in Fig 4.1, draw fully-labelled diagrams of the following.

- One of the d orbitals at the lower energy level in an octahedral complex. Label this diagram 'lower'.
- One of the d orbitals at the upper energy level in an octahedral complex. Label this diagram upper.

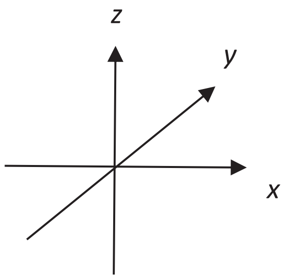


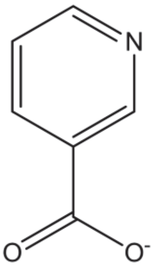
Fig. 4.1

[2]

(ii) Explain why splitting of the d-subshell occurs in an octahedral complex, using your d orbital diagrams in **(a)(i)**. [2]

(iii) By considering your answer to **(a)(ii)**, suggest why $[Cr(OH)_6]^{3-}$ and $[Cr(NH_3)_6]^{3+}$ have different colours. [1]

(b) Chromium(III) nicotinate is commonly used as chromium supplementation for medical conditions associated with diabetes mellitus type 2. This octahedral complex contains three nicotinate ions per chromium ion. The nicotinate ion has the structure shown below.



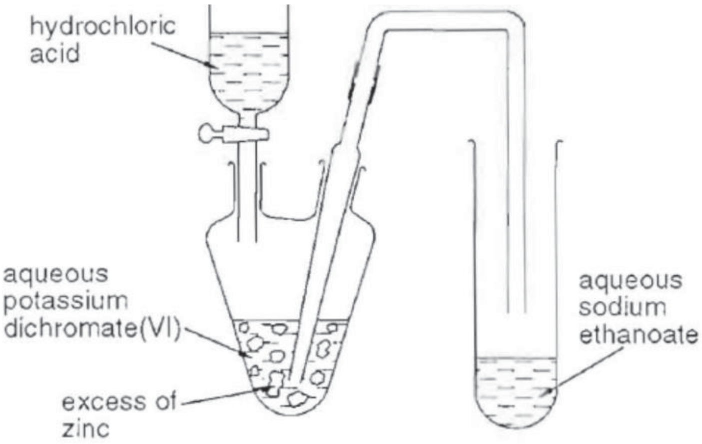
nicotinate ion

(i) Copy the structure of nicotinate ion and circle the atoms that are bonded to chromium(III) ion. Explain your choice of atoms. [2]

(ii) What is the overall charge of this complex? [1]

(c) Chromium-containing compounds are useful reagents in the laboratory.

The apparatus and reagents shown in the diagram are used to prepare chromium(II) ethanoate, which is a reducing agent.



All the acid is added to the dichromate solution and the zinc in the flask. The tap funnel is left open. The flask is shaken and chromium soon reaches the Cr^{3+} state.

(i) Write balanced equations for the **two** reactions involving zinc which take place initially in the flask. [2]

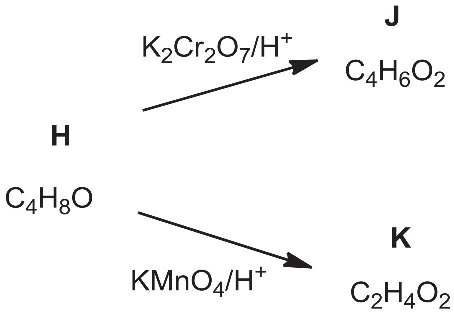
The colour of the solution in the flask subsequently changes as Cr^{2+}(aq) is produced.

(ii) Using relevant redox potential values in the *Data Booklet*, show why the reduction of Cr^{3+} to Cr^{2+} is likely to proceed. [2]

The tap funnel is subsequently closed and the liquid in the flask forced over into the tube containing the aqueous sodium ethanoate to form chromium(II) ethanoate.

(iii) By considering your answers to **(c)(i)**, suggest what causes the liquid to be forced over into the tube. [1]

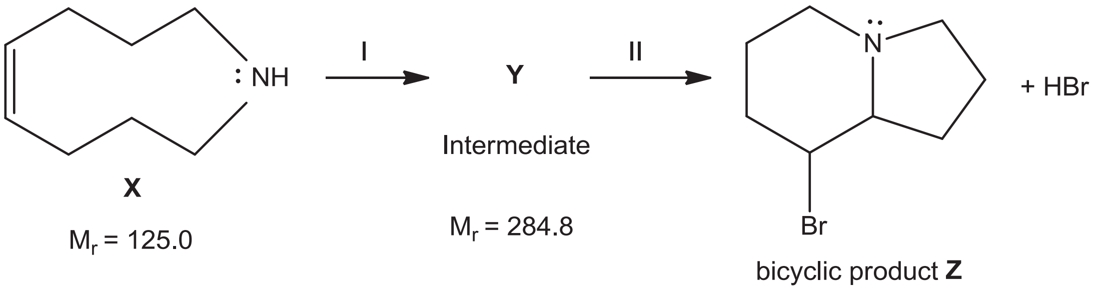
(d) Another chromium-containing compound, $K_2Cr_2O_7$, together with $KMnO_4$ are common oxidising agents used in organic synthesis. $KMnO_4$ is the more powerful of the two, as shown by the following scheme.



All three compounds, **H**, **J** and **K** react with sodium metal. **J** and **K** react with Na_2CO_3, but **H** does not. **H** and **J** decolourise aqueous bromine.

Suggest structures for **H**, **J** and **K**. [3]

(e) The bicyclic product **Z** shown below can be formed from **X** in the following scheme:



(i) Suggest reagents and conditions for Step I and the structure of **Y**. [2]

(ii) Given that Step II is an intramolecular reaction, explain the conversion of **Y** into **Z**, drawing curly arrows to show the movement of electron pair where necessary. State the type of reaction in Step II. [2]

[Total: 20]

[Turn over

5 Hydroformylation is used commercially for producing aldehydes from alkenes. The aldehyde produced is then converted into other organic compounds.

Butanal is synthesised from propene from the following hydroformylation reaction at 500 K.

$$CH_3CH{=}CH_2(g) + CO(g) + H_2(g) \rightleftharpoons CH_3CH_2CH_2CHO(g) \qquad \Delta H < 0$$

(a) An equimolar mixture of $CH_3CH{=}CH_2$, CO and H_2 at an initial total pressure of 150 atm is allowed to reach dynamic equilibrium. Figure 5.1 below shows the graphs of partial pressure of $CH_3CH{=}CH_2$ and $CH_3CH_2CH_2CHO$ against time.

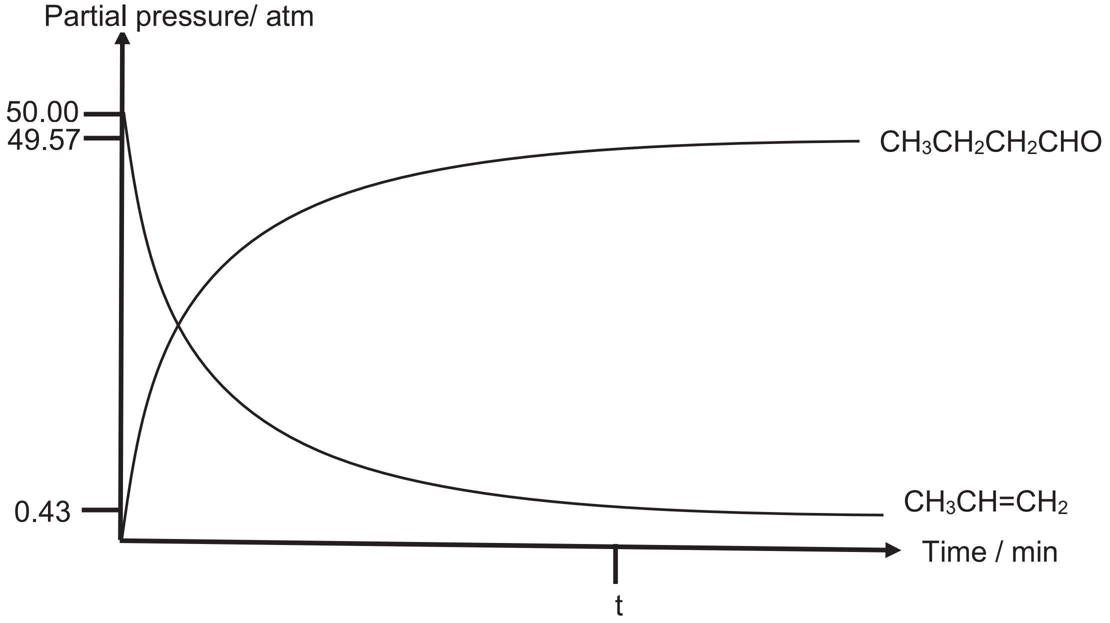


Figure 5.1

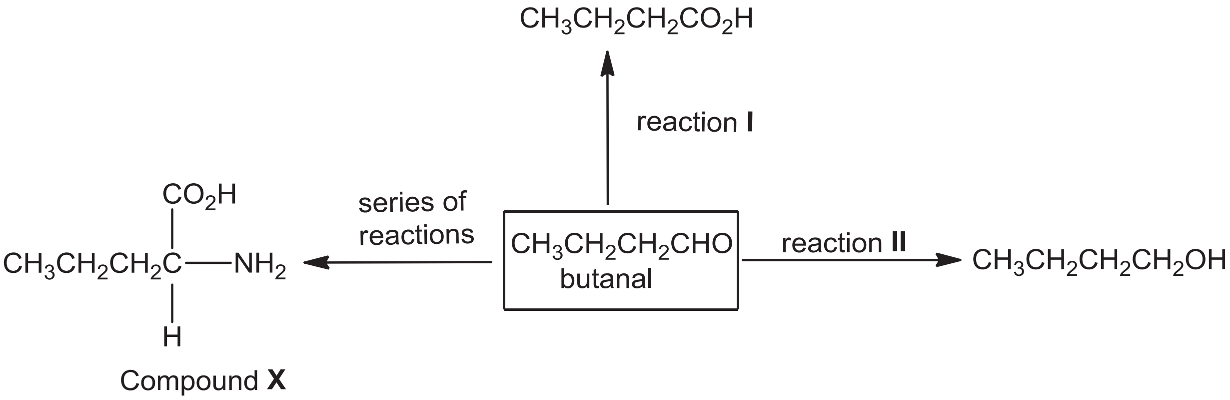
(i) Define the term *dynamic equilibrium*. [1]

(ii) Write an expression for K_p for the above reaction. [1]

(iii) Using Figure 5.1 above, calculate K_p for the hydroformylation reaction at 500 K, stating its units. [3]

(iv) Suggest how the graphs of partial pressure against time for $CH_3CH{=}CH_2$ and $CH_3CH_2CH_2CHO$ would differ from that shown in Figure 5.1 when the experiment is repeated at a higher temperature. [2]

Butanal, synthesised from hydroformylation reaction, can undergo further reactions as shown in the reaction scheme below.



(b) From reaction **I** above, butanoic acid is produced. Comment on the difference in the solubility of butanal and butanoic acid in water. [2]

(c) In reaction **II**, butanal is reduced to give butan-1-ol. One of the commonly used reducing agents is lithium aluminium hydride, $LiAlH_4$, which is usually dissolved in dry ether.

(i) Given that $LiAlH_4$ exist as $Li^+[AlH_4]^-$, draw the dot-and-cross diagram for $LiAlH_4$. [1]

(ii) The reaction between $LiAlH_4$ and butanal to form butan-1-ol happens in two-steps.

The first step involves a nucleophilic addition reaction between the hydride ion, H^-, from $LiAlH_4$ and butanal to form an anion.
The second step involves the protonation of the anion to form butan-1-ol.

Using the information above, show how the anion in the first step is formed with the use of curly arrows, showing the movement of electrons and charges. [2]

(iii) Other than $LiAlH_4$, $NaBH_4$ can also be used to convert butanal to butan-1-ol. By considering the chemical bonds in $LiAlH_4$ and $NaBH_4$, suggest why $LiAlH_4$ is a more powerful reducing agent $NaBH_4$. [1]

(iv) State a reason why $LiAlH_4$ cannot be used to reduce alkenes even though it is a powerful reducing agent. [1]

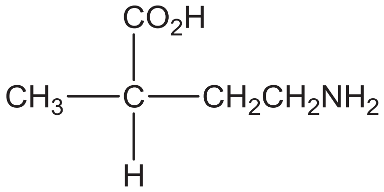
(v) Expain how the rate of the reaction in **(c)(ii)** would differ if butanone is used in place of butanal. [2]

(d) Draw the structure of the predominant form produced when compound **X** is in an aqueous solution of pH 7. [1]

(e) Write two equations to show how the solution in **(d)** is able to resist the change in pH upon addition of small amounts of acid and base. [2]

[Turn over

(f) Compound **Y** is an isomer of compound **X**. Draw the structural formula of the **final** product when compound **Y** reacts with PCl_5. [1]



$$\mathrm{CH_3}-\overset{\displaystyle \mathrm{CO_2H}}{\underset{\displaystyle \mathrm{H}}{\mathrm{C}}}-\mathrm{CH_2CH_2NH_2}$$

Compound **Y**

[Total: 20]

Catholic Junior College

JC2 Preliminary Examinations

Higher 2

CANDIDATE NAME	
CLASS	2T

CHEMISTRY

9729/04

Paper 4 Practical

16 August 2017

2 hour 30 minutes

Candidates answer on the Question Paper.

Additional Materials: As listed in the Confidential Instructions

---

READ THESE INSTRUCTIONS FIRST

Write your name and class 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 15 and 16.

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

Shift
Laboratory

For Examiner's Use	
1	
2	
3	
Total	

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

[Turn over

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

1 'Washing soda' is made from crystals of sodium carbonate, which contains 62.94 % water and 37.06 % sodium carbonate. When stored, these crystals lose some of the water in the crystals to the atmosphere.

FA 1 is solid 'washing soda', originally sodium carbonate decahydrate, $Na_2CO_3.10H_2O$.
FA 2 is 0.100 mol dm^{-3} hydrochloric acid, HC*l*.

In this question, you will perform a titration to determine the amount of water in **FA 1** that has been lost to the atmosphere.

(a) Method

(i) Preparation of FA 3

- Weigh the 100 cm^3 beaker provided. Record the mass in the space below.
- Tip the 'washing soda' crystals, **FA 1**, into the beaker. Weigh the beaker with **FA 1** and record the mass.
- Calculate the mass of **FA 1** used and record this in the space below.
- Add distilled water to the beaker to dissolve the crystals. Carefully transfer the solution to a 250 cm^3 graduated (volumetric) flask labelled **FA 3**. Wash the beaker twice with small quantities of water and add these washings to the volumetric flask.
- Make the solution up to the mark using distilled water. Stopper the flask and invert a number of times to ensure thorough mixing.

[1]

(ii) Titration of FA 3 against FA 2

- Fill the burette with **FA 2**.
- Pipette 25.0 cm^3 of **FA 3** into a conical flask and add a few drops of the indicator provided.
- Titrate the solution with **FA 2**. Record your results in the space provided on page **3**. Make certain that the recorded results show the precision of your practical work.
- Repeat the titration until consistent results are obtained.

Titration Results:

[6]

(iii) 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]

(b) **(i)** Calculate the amount of hydrochloric acid run from the burette.

amount of HC*l* =……………………...… [1]

(ii) Sodium carbonate reacts with hydrochloric acid as follows.

$$Na_2CO_3(aq) + 2HCl(aq) \rightarrow 2NaCl(aq) + CO_2(g) + H_2O(l)$$

Calculate the amount of sodium carbonate, Na_2CO_3, in 250 cm^3 of **FA 3**.

amount of Na_2CO_3 in 250 cm^3 of **FA 3** =……………………...… [2]

(iii) Calculate the mass of sodium carbonate, Na_2CO_3, dissolved in 250 cm^3 of **FA 3**.
[A_r: C, 12.0; O, 16.0; Na, 23.0]

mass of Na_2CO_3 in 250 cm^3 of **FA 3** =……………………...… [1]

(iv) Calculate the mass of water present in the washing soda crystals.

mass of water =……………………...… [1]

(v) Hence calculate the percentage of water in the sodium carbonate crystals, **FA 1**.

percentage of water in **FA 1** =……………………...… [1]

(c) The maximum error for a 25 cm^3 pipette commonly used in schools is ± 0.06 cm^3.
The maximum error in any single burette reading is ± 0.05 cm^3.

Calculate the maximum percentage error in each of the following.

(i) The volume of **FA 3** pipetted into the conical flask.

maximum percentage error in pipette volume =……………………...… %

(ii) The titre volume calculated in **(a)(iii)**.

maximum percentage error in titre volume =……………………...… %

[2]

[Total: 16]

2 The enthalpy change for the reaction of sodium carbonate, Na_2CO_3, with water and carbon dioxide to form sodium hydrogencarbonate, $NaHCO_3$ cannot be determined directly. However both $Na_2CO_3(s)$ and $NaHCO_3(s)$ react with dilute hydrochloric acid.

Reaction 1 $NaHCO_3(s) + HCl(aq) \rightarrow NaCl\ (aq) + H_2O(l) + CO_2(g)$ ΔH_1

Reaction 2 $Na_2CO_3(s) + 2HCl(aq) \rightarrow 2NaCl\ (aq) + H_2O(l) + CO_2(g)$ ΔH_2

In this experiment you will determine the enthalpy change ΔH_1 for **reaction 1** and ΔH_2 for **reaction 2**, and then use your results to calculate ΔH_3 for the reaction:

$$Na_2CO_3(s) + H_2O(l) + CO_2(g) \rightarrow 2NaHCO_3(s) \qquad \Delta H_3$$

FA 4 is sodium hydrogen carbonate, $NaHCO_3$.
FA 5 is sodium carbonate, Na_2CO_3.
FA 6 is 2.0 mol dm^{-3} hydrochloric acid, HC*l*.

(a) Method

(i) Experiment 1: $NaHCO_3(s) + HCl(aq) \rightarrow NaCl\ (aq) + H_2O(l) + CO_2(g)$

- Use a measuring cylinder to transfer 25 cm^3 of the acid, **FA 6**, into the plastic cup supported in a 250 cm^3 beaker. The acid is in excess.
- Weigh the container with **FA 4** and record the balance reading.
- Place the thermometer in the acid and record its temperature at 1 minute interval for the first two minutes.
- At 2½ minutes, carefully tip all the **FA 4**, in small portions, into the acid and stir to dissolve.
- Record the temperature of the solution at 1 minute interval from 3 minutes up to 8 minutes.
- Reweigh the container with any residual **FA 4** and record the balance reading and the mass of **FA 4** used.
- Rinse out the plastic cup and shake it to remove excess water.

Results

Record **all** weighings and temperature readings in the space below.

[5]

(ii) Plot on the grid below, a graph of temperature on the *y*-axis against time on the *x*-axis. The scale for the temperature should extend at least 1°C below the lowest recorded temperature.

Draw two straight lines of best fit and extrapolate the two lines to 2½ minutes. Determine the change in temperature at this time.

temperature change at 2½ minutes = ... °C

[4]

(iii) **Experiment 2**: $Na_2CO_3(s) + 2HCl(aq) \rightarrow 2NaCl(aq) + H_2O(l) + CO_2(g)$

- Use a measuring cylinder to transfer 25 cm^3 of the acid, **FA 6**, into the plastic cup supported in a 250 cm^3 beaker. The acid is in excess.
- Weigh the container with **FA 5** and record the balance reading.
- Place the thermometer in the acid and record its initial temperature.
- Carefully tip all the **FA 5**, in small portions, into the acid and stir to dissolve.
- Record the highest temperature reached.
- Reweigh the container with any residual **FA 5** and record the balance reading and the mass of **FA 5** used.

Results

Record **all** weighings and temperature readings in the space below.

[3]

(b) **(i)** Using your answer to **2(a)(ii)**, calculate the heat energy absorbed when **FA 4** was added to the acid in **Experiment 1**.
[Assume that 4.3 J of heat energy changes the temperature of 1.0 cm^3 of solution by 1.0 °C.]

heat energy absorbed =…………..…. J [1]

(ii) Calculate the enthalpy change, in kJ mol^{-1}, when 1 mol of **FA 4**, $NaHCO_3$, reacts with the acid. [A_r: H, 1.0; C, 12.0; O, 16.0; Na, 23.0]

enthalpy change, ΔH_1 = ... kJ mol^{-1} [1]

(iii) Using your results in **2(a)(iii)**, calculate the heat energy produced when **FA 5** was added to the acid in **Experiment 2**.
[Assume that 4.3 J of heat energy changes the temperature of 1.0 cm^3 of solution by 1.0 °C.]

heat energy produced =……………..… J [1]

(iv) Calculate the enthalpy change, in kJ $mol^{–1}$, when 1 mol of **FA 5**, Na_2CO_3, reacts with the acid. [A_r: C, 12.0; O, 16.0; Na, 23.0].

enthalpy change, ΔH_2 = ... kJ $mol^{–1}$ [1]

(v) Using your answers to **2(b)(ii)** and **2(b)(iv)** and the equations for **Experiment 1** and **Experiment 2**, determine the enthalpy change for the reaction:

$$Na_2CO_3(s) + H_2O(l) + CO_2(g) \rightarrow 2NaHCO_3(s)$$

enthalpy change, ΔH_3 = ... kJ $mol^{–1}$ [3]

(c) Planning

You are provided with **FA 4**, solid sodium hydrogencarbonate, $NaHCO_3$, distilled water and apparatus commonly found in the school laboratory.

Using only these materials, you are to plan an additional experiment to determine a further enthalpy change, ΔH_4, which can be put together with those from **Experiment 1** and **Experiment 2** to determine the enthalpy change for the reaction:

$$Na_2CO_3(s) + H_2O(l) + CO_2(g) \rightarrow 2NaHCO_3(aq) \qquad \Delta H_5$$

In your plan, you should include details of:

- the quantity of reactants and apparatus that you would use,
- the procedure you would follow,
- the measurements you would take, and
- an outline of how you would use your results to determine ΔH_5.

DO NOT CARRY OUT YOUR PLAN.

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

[5]

[Total: 24]

3 **Qualitative Analysis**

In this question, you will carry out tests, make observations and come to conclusions about the compounds.

If the evolution of a gas is observed at any stage, the gas should be tested and identified. Details of the test carried out, the observations from the test and the identity of the gas should be given with the observations.

If it appears that no reaction has taken place, this should be clearly recorded

(a) **FA 7** is an organic solid. Carry out the tests described in Table 3.1 and use the observations to identify two functional groups present in **FA 7**.

Table 3.1

tests	*observations*
Add 10 cm^3 of ethanol to your **FA 7** in a boiling tube. Stopper the boiling tube and shake to dissolve the solid. Then add 10 cm^3 of deionised water. Shake again to ensure complete mixing. Divide the solution into four clean test-tubes and use a fresh tube for each of the following tests:	
(i) add a piece of magnesium ribbon to the solution	
(ii) add solid sodium carbonate to the solution	
(iii) add a few drops of aqueous iron(III) chloride to the solution	
(iv) add 2 cm depth of bromine water. (Take care: bromine water is corrosive.)	

[4]

(v) Complete Table 3.2, using the observations in Table 3.1 to identify the two functional groups present in **FA 7**. In each case, give evidence to support your conclusion.

Table 3.2

functional group	*evidence*

[2]

(b) **Plan**

You are provided with four solutions, labelled **FA 8**, **FA 9**, **FA 10** and **FA 11**.

Each solution contains one of the following compounds.

- lead nitrate, $Pb(NO_3)_2$
- sodium chloride, NaC*l*
- sodium hydroxide, NaOH
- zinc sulfate, $ZnSO_4$

The order in the list of solutions does **not** correspond to the **FA** numbers.

(i) Using the *Qualitative Analysis Notes* on page 14, complete Table 3.3 to show the expected observations when pairs of the solutions are mixed. Solutions should be added a little at a time, with shaking, until no further change is observed.

Expected observations for $Pb(NO_3)_2$ have already been recorded in Table 3.3.

Table 3.3

	NaC*l*	**NaOH**	**$ZnSO_4$**
$Pb(NO_3)_2$	white ppt.	white ppt. soluble in excess NaOH	white ppt.
NaC*l*			
NaOH			

Explain how you could use the expected observations in Table 3.3 to identify **each** of the solutions.

....

....

....

....

....

.... [5]

(ii) Carry out the experiment using **FA 8**, **FA 9**, **FA 10** and **FA 11** and record your results in a suitable table.

[3]

(iii) Identify the substance present in each of the solutions.

FA 8 ....

FA 9 ....

FA 10 ....

FA 11 ....

[1]

[Total: 15]

Qualitative Analysis Notes
[*ppt. = precipitate*]

(a) Reactions of aqueous cations

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

(b) Reactions of anions

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

(c) Tests for gases

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

(d) Colour of halogens

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

BLANK PAGE

Catholic Junior College
JC 2 Preliminary Examinations
Higher 2

CHEMISTRY

9729/01

Paper 1 Multiple Choice

29 August 2017

Additional Materials: Multiple Choice Answer Sheet
Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name, HT group and NRIC/FIN number on the Answer Sheet in the spaces provided.
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.

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.

MARK SCHEME

This document consists of **25** 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 When an unknown organic compound is burned completely in excess oxygen, 90 cm^3 of gaseous products is collected. When cooled to room temperature, the gaseous volume decreased to 50 cm^3. A further decrease of 40 cm^3 in the gaseous volume was observed when the gaseous mixture is passed through aqueous potassium hydroxide.

What is the possible identity of the organic compound?

1 CH_2CH_2

2 CH_3CO_2H

3 $CH_3CH_2CH_3$

4 CH_2CHCH_2OH

A 1 and 3 only

B 1 and 4 only

C 1, 2 and 4 only

D 2 and 4 only

Concept: MCS: rxn stoichiometry, molar volume of gas at r.t.p,

Start with volume of CO_2 given and use the equation to work out the mole ratio.

Answer: C

First reduction of gaseous vol due to cooling

→ hot $H_2O(g)$ has condensed to form $H_2O(l)$ at r.t.p.

→ thus, vol of $H_2O(g)$ = 90 – 50 = 40 cm^3

Second reduction of gaseous vol due to reaction with KOH(aq)

→ $CO_2(g)$ is an acidic gas and reacts with KOH(aq) via acid-base reaction

→ vol of $CO_2(g)$ = 40 cm^3

Thus, $CO_2(g) : H_2O(g)$ Thus, C : H
= 40 : 40 ➡ = 1 : 2
= 1 : 1

Thus the organic compound must have a ratio C : H = 1: 2.

1	CH_2CH_2	→ C_2H_4	→ correct
2	CH_3CO_2H	→ $C_2H_4O_2$	→ correct
3	$CH_3CH_2CH_3$	→ C_3H_8	→ incorrect
4	CH_2CHCH_2OH	→ C_3H_6O	→ correct

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

A vanadium salt of unknown oxidation state was dissolved in water to form a solution of 0.500 mol dm^{-3}. It was found that 20.4 cm^3 of this solution will react with 1.00 g of zinc powder to form vanadium(II) solution.

What is the possible identity of the vanadium salt used?

A V^{2+} **B** V^{3+} **C** VO^{2+} **D** VO_2^+

Concept: Redox: determination of oxidation state

Answer: D

Let the vanadium salt of unknown oxidation state be V^{x+}

Amt of zinc used = 1 ÷ 65.4 = 0.0153 mol

Amt of V^{x+} reacted = $\frac{20.4}{1000} \times 0.500 = 0.0102$ mol

Ratio of Zn : V^{x+} = 0.0153 : 0.0102

= 3 : 2

Given that $Zn \rightarrow Zn^{2+} + 2e^-$,

3 mol of Zn will donate 6 mol of e^- and 2 mol of V^{x+} will accept 6 mol of e^-.

Therefore, 1 mol of V^{x+} will accept 3 mol of e^-.

Since V^{x+} is reduced to V^{2+}, its original oxidation state is +5.

species	V^{2+}	V^{3+}	VO^{2+}	VO_2^+
Oxidation state	+2	+3	+4	+5

Thus, only VO_2^+ is the possible identities of the unknown salt solution.

3 The table below gives some data about four ions.

ions	number of neutrons	number of nucleons
$Q^–$	16	33
R^+	19	39
$S^{2–}$	17	33
T^{2+}	18	35

Which of the following pairs consists of ions that are isoelectronic?

A **$Q^–$** and **$S^{2–}$**

B **R^+** and **$S^{2–}$**

C **$S^{2–}$** and **T^{2+}**

D **$Q^–$** and **T^{2+}**

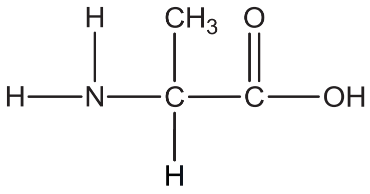
Concept: Atomic Structure: determination of no. of protons and electrons from given species, isoelectronic species

Isoelectronic species have the same number of electrons.

particle	number of neutrons	number of nucleons	number of protons	number of electrons
$Q^–$	16	33	33 – 16 = 17	17 + 1 = **18**
R^+	19	39	39 – 19 = 20	20 – 1 = 19
$S^{2–}$	17	33	33 – 17 = 16	16 + 2 = **18**
T^{2+}	18	35	35 – 18 = 17	17 – 2 = 15

ANS: A

4 Which bond angle is present in a molecule of alanine, $H_2NCH(CH_3)CO_2H$, but is **not** present in its zwitterion?



alanine

A 90°

B 107°

C 109°

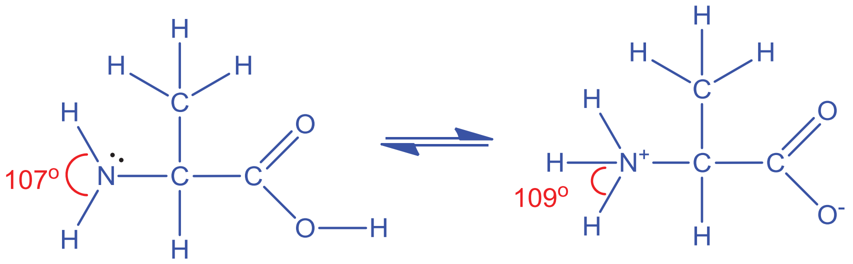
D 120°

Concept: Chemical Bonding: Structure of zwitterion of amino acid

Predict bond angles based on number of bond and lone pairs, and shape around central atom.

Answer: B

Zwitterion of alanine is $^{+}H_3NCH(CH_3)COO^{-}$



alanine

3 bp, 1 lp around N
bond angle = 107°

zwitterion of alanine

4 bp, 0 lp around N
bond angle = 109°

In the zwitterion, $–NH_2$ group (trigonal pyramidal about N, bond angle = 107°) becomes $–NH_3^{+}$ (tetrahedral about N, bond angle = 109°) and $–CO_2H$ (trigonal planar about sp^2 hybridised carbon, 120°) group becomes CO_2^{-} (trigonal planar about sp^2 hybridised carbon, 120°).

Option A: bond angle of 90° is not present in both alanine and its zwitterion.

5 What are the types of chemical bonds present in solid phenylammonium chloride, $C_6H_5NH_3Cl$?

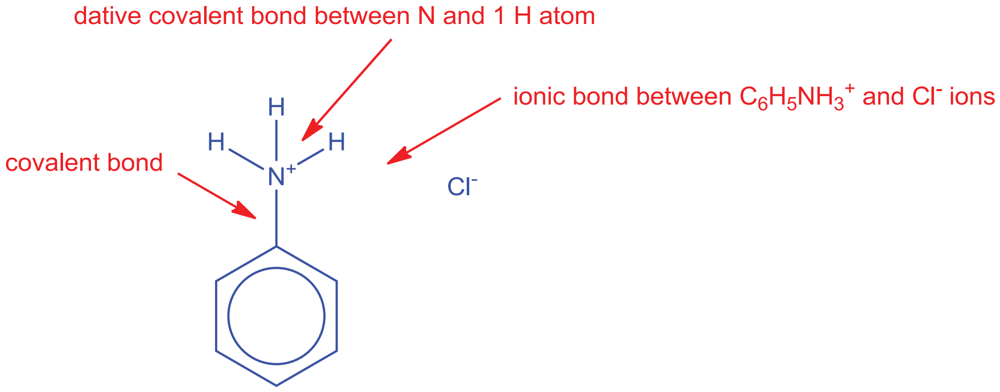
1 dative covalent bonds
2 ionic bonds
3 hydrogen bonds

A 2 only
B 1 and 2 only
C 2 and 3 only
D 1, 2 and 3

Concept: Chemical Bonding: Identify type of chemical bonds within an ionic compound, consisting of polyatomic ions.

Identify structure to be giant ionic, with covalent bonds within the polyatomic cation, $C_6H_5NH_3^{+}$

Answer: B



phenylammonium chloride

absence of hydrogen bond; absence of lone electron pair on N

$C_6H_5NH_3Cl$ is an ionic compound, consisting of polyatomic cations, $C_6H_5NH_3^+$ and Cl^-. Hence ionic bonds exist between $C_6H_5NH_3^+$ and Cl^- ions while covalent bond and dative covalent bonds exist between the C, N and H atoms within the $C_6H_5NH_3^+$ cation. Hydrogen bonds are not present as no lone electron pair is present on N atom in $C_6H_5NH_3^+$.

6 Which one of the following shows the standard enthalpy change of formation of carbon monoxide?

A $C(s) + ½O_2(g) \rightarrow CO(g)$

B $C(s) + CO_2(g) \rightarrow 2CO(g)$

C $C(g) + ½O_2(g) \rightarrow CO(g)$

D $C(g) + CO_2(g) \rightarrow 2CO(g)$

Concept: Chemical Energetics, Definition of enthalpy change of formation.

Answer: A

The **standard enthalpy change of formation,** $\Delta H_f^\ominus$, of a substance (usually a compound) is defined as the enthalpy change when one mole of the substance is formed **(Hence options B and D are incorrect as 2 moles of CO are formed)** from its elements under standard conditions of 298 K and 1 bar. (Elements must be in most stable physical form.) **The most stable physical form of carbon is graphite (solid). Hence option C is incorrect and the answer is option A.**

7 Nitrogen dioxide, NO_2, has an unpaired electron and dimerises to form N_2O_4.

$$2NO_2(g) \rightarrow N_2O_4(g)$$

Which of the following statements about the spontaneity of the reaction is true?

A The reaction is only spontaneous at low temperatures.

B The reaction is only spontaneous at high temperatures.

C The reaction is spontaneous at all temperatures.

D The reaction is non-spontaneous at all temperatures.

ΔH of the reaction is negative since the reaction involves bond formation which is exothermic.

ΔS of the reaction is negative as there is a decrease in the number of moles of gaseous particles.

$\Delta G = \Delta H - T\Delta S$
Since ΔH is negative and $-T\Delta S$ is positive, a higher temperature would cause ΔG to become more positive and less spontaneous. Hence the reaction is only spontaneous at low temperatures.

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

Gas canisters used in camping stoves contain partially liquefied hydrocarbon. A canister was connected to a gas syringe and the valve opened slightly to allow some gas into the syringe. 0.200 g of the gas occupied a volume of 96.0 cm^3 at a temperature of 30.0 °C and a pressure of 101 kPa.

What is the average M_r of the gas mixture?

A 31 **B** 52 **C** 479 **D** 519

Concept: Gaseous State; application of Ideal gas equation, pV = nRT & unit conversion

Rearrange pV = nRT equation to solve for M_r

Answer: B

$pV = nRT$

$= \frac{m}{M_r}RT \qquad \therefore M_r = \frac{mRT}{pV} = \frac{(0.200)(8.31)(30 + 273)}{(101 \times 10^3)(96.0 \times 10^{-6})} = 52$

9 At a certain temperature, three gases N_2, O_2 and HCl were mixed and the following reaction occurred:

$$2N_2(g) + 3O_2(g) + 4HCl(g) \rightleftharpoons 4NOCl(g) + 2H_2O(g)$$

The initial partial pressures of N_2, O_2 and HCl are 0.800 atm, 0.800 atm and 0.400 atm respectively. After equilibrium has been established, it is found that the partial pressure of steam is 0.15 atm.
What is the numerical value of K_p for this reaction at this temperature?

A 1.20 **B** 22.7 **C** 0.0217 **D** 0.0251

Concept: Chemical Equilibria, Finding equilibrium values and calculating K_p, keeping in mind the stoichiometric ratios reacted / formed while achieving equilibrium.

Answer: B

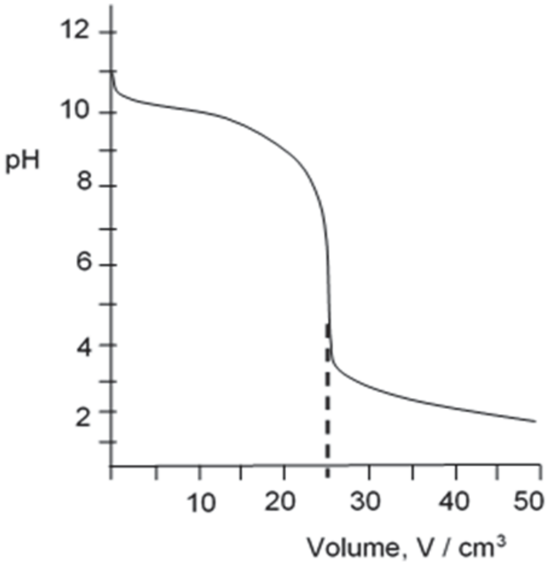
To find the pressures at equilibrium, the ICE table can be drawn.

	$2N_2(g)$	$+ 3O_2(g)$	$+ 4HCl(g)$	$\rightleftharpoons 4NOCl(g)$	$+ 2H_2O$ (g)
Initial p / atm	0.800	0.800	0.400	0	0
Change in p / atm	- (0.15)	-3/2(0.15)	-2(0.15)	+2(0.15)	+0.15
Eqm p / atm	0.65	0.575	0.100	0.300	0.15

$$K_p = \frac{pNOCl^4\ pH_2O^2}{pN_2{}^2 pO_2{}^3 pHCl^4} = \frac{(0.300)^4(0.15)^2}{(0.65)^2(0.575)^3(0.100)^4} = 22.7\text{atm}^{-3}$$

10 In an acid-base titration, a 0.10 mol dm^{-3} solution of an acid is added to a 25 cm^3 of a 0.10 mol dm^{-3} solution of a base.

The pH value of the solution is plotted against the volume, V, of acid added as shown in the diagram.



Which of the following statements is **incorrect**?

A The titration involved a strong acid and a weak base.

B The pair of solutions could have been HC*l*(aq) and CH_3NH_2(aq).

C Methyl orange is a suitable indicator for the above titration.

D When concentration of acid is doubled, the end point volume of the titration would be halved while the pH at equivalence point would remain unchanged.

Concept: Chemistry of Aqueous Solutions, interpreting titration curve

Using equivalence point pH to determine type of acid-base reaction

Answer: D

pH at equivalence point < 7; implies presence of acidic salt. Hence strong acid-weak base titration has occurred. Hence Option A is correct.

As the stoichiometry of acid: base = 1:1, hence the solutions involved should be a monoprotic base and a monobasic acid. Hence Option B is correct.

For strong acid-weak base titration, methyl orange is a suitable indicator. Hence Option C is correct too.

When concentration of acid is doubled, the amount of salt formed at equivalence point is fixed though total volume of the solution is now lower.

Compared to $[salt]_{original}$ = 25.0 x 0.1 / (25+25) = 0.05 mol dm^{-3}

$[salt]_{new}$ = 12.5 x 0.2 / (12.5 + 25) = 0.0667 mol dm^{-3}

Since $NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+$

And $[H^+] = \sqrt{Ka} \times [acidic\ salt]$

when [salt] is higher, new $[H^+]$ will work out to be higher, hence new equivalence pH will decrease.

11 The following two reactions are examples of acid-base reactions.

Reaction 1: $HNO_3 + H_2SO_4 \rightleftharpoons H_2NO_3^+ + HSO_4^-$

Reaction 2: $NH_3 + BF_3 \rightarrow NH_3BF_3$

Which of the following correctly describes the behaviour of each species?

	Brønsted acid	Brønsted base	Lewis acid	Lewis base
A	HNO_3	NH_3	H_2SO_4	HSO_4^-
B	H_2SO_4	HNO_3	BF_3	NH_3
C	HSO_4^-	NH_3	BF_3	$H_2NO_3^+$
D	$H_2NO_3^+$	HSO_4^-	NH_3BF_3	NH_3

Concept: Definition of Bronsted acids and bases, Lewis acids and bases

For Reaction 1

HNO_3 donated a proton to form $H_2NO_3^+$. HNO_3 is a Brønsted base whereas $H_2NO_3^+$ is the conjugate acid.

H_2SO_4 donated a proton to form HSO_4^- and is a Brønsted acid, whereas HSO_4^- is the conjugate base.

For Reaction 2

NH_3 has a lone pair of electrons on N and donates a pair of electrons to B in BF_3 (which is electron-deficient). NH_3 thus acts as a Lewis base whereas BF_3 acts as the Lewis acid.

12 The decomposition of hydrogen peroxide is known to be a first order reaction.

$$2H_2O_2 \rightarrow 2H_2O + O_2$$

The rate constant is found to be 4.95×10^{-2} min^{-1}. If the initial concentration of H_2O_2 is 4.00 mol dm^{-3}, what will be the concentration of H_2O_2 after 64 min?

A 0.50 mol dm^{-3}

B 0.20 mol dm^{-3}

C 0.17 mol dm^{-3}

D 0.13 mol dm^{-3}

Concept: Calculations involving first order reactions, making use of the formula t1/2 = ln 2 / k

Half life = ln 2 / (4.95×10^{-2}) = 14 min

Number of half-lives = 64 / 14 = 4.57

$$\frac{Ct}{Co} = (\frac{1}{2})^{n}$$

$$\frac{Ct}{4} = (\frac{1}{2})^{4.57}$$

C_t = 0.168 mol dm^{-3}

13 The rate equation for the reaction 2**W** + **X** → **Y** + **Z** is given as rate = k[**W**][**X**]. In an experiment to study the kinetics of the reaction, the initial concentration of **W** used is 0.20 mol dm^{-3} and the initial concentration of **X** used is 0.001 mol dm^{-3}.

Which of the following statements regarding the experiment is correct?

A The half-life for the [**X**] against time curve is approximately constant.

B The mechanism for the above reaction involves one step.

C The units of the rate constant is $mol^{-2}dm^{6}s^{-1}$.

D Doubling the initial concentration of **W** to 0.40 mol dm^{-3} will not affect the half-life of **X**.

Concept: relationship of mechanism to rate equation and overall equation, interpretation of units for rate constant

The concentration of **W** is 200 times larger than **X**, hence the reaction is pseudo zero order wrt **W** and the reaction becomes overall pseudo first-order.

Rate = k' [**X**], where k' = k [**W**]

Therefore half-life of **X** will be approximately constant having a value of $t_{½} = \frac{\ln 2}{0.2\ k}$

D: when initial [**W**] is doubled, $t_{½}$ will be halved.

B: Since stoichiometry shows that 2 W are involved, the reaction will have more than one step as the slow step involves only 1W and 1X leaving the other W molecule/ion to be involved in the fast step.

C: Since rate = k[**W**][**X**], and units of rate = $moldm^{-3}s^{-1}$, the units for k = $mol^{-1}dm^{3}s^{-1}$

14 The oxide and chloride of an element **E** are mixed separately with water. The two resulting solutions have the same effect on litmus.

What is element **E**?

A Mg **B** A*l* **C** Si **D** P

Concept: Trends across Period 3, and oxides and chlorides of Period 3

Answer: D
For Option B and C
Note that both SiO_2 and Al_2O_3 are insoluble in water. The resulting solution would thus be neutral. Both $SiCl_4$ and $AlCl_3$ will give undergo hydrolysis to give acidic solutions.

PCl_5 undergoes hydrolysis to form H_3PO_4 and HC*l*, which causes the resulting solution to be acidic and turn blue litmus red. P_4O_{10} would also undergo hydrolysis to give H_3PO_4 which is an acidic solution.

MgO is gives $Mg(OH)_2$ in water which is weakly basic whereas $MgCl_2$ is weakly acidic.

15 Which of the following statements about iodine or its compounds are correct?

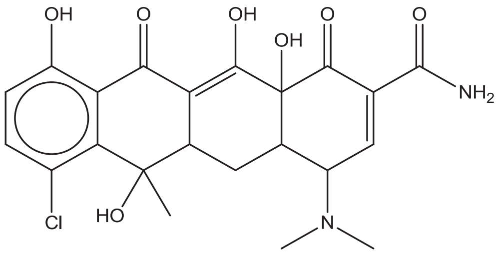
1 A crystal of iodine contains covalent bonds and instantaneous dipole-induced dipole forces of attraction.
2 When aqueous chlorine is added to potassium iodide and the aqueous mixture shaken with tetrachloromethane, a purple organic layer is obtained.
3 The first ionisation energy of iodine is less than that of bromine.
4 The thermal stability of hydrogen iodide is higher than that of hydrogen bromide.

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

Concept: Group 17 Halogen and Halide properties

1: I_2 is a non-polar simple covalent molecule. Thus, there are strong covalent bonds between I atoms and instantaneous dipole-induced dipole forces of attraction between iodine molecules.
2: Cl_2 can oxidise KI to form I_2 which is purple in the organic layer.
Ecell = 1.36 – 0.54 > 0 V (thus the reaction is spontaneous)
3: Ionisation energy decreases down the group. I_2 has a lower first ionisation energy than Br_2.
4: H- I bond is longer and weaker than H-Br and thus HI has a lower thermal stability.

16 *Aureomycin* is a powerful oral antibiotics that is effective against a wide range of infections.



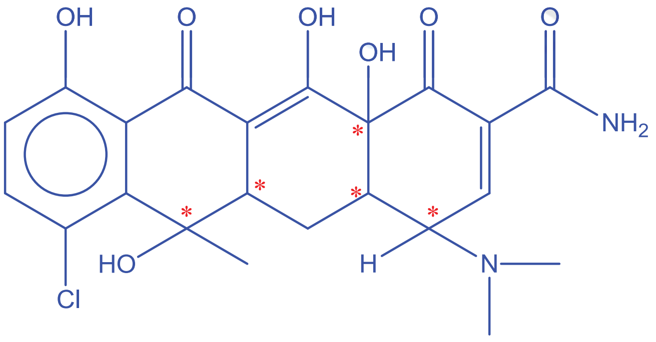
Aureomycin

Which row correctly indicates the number of chiral centres and sp^2 hybridised carbon in a molecule of *aureomycin*?

	Number of chiral centres	Number of sp^2 hybridised C
A	4	10
B	4	13
C	5	10
D	5	13

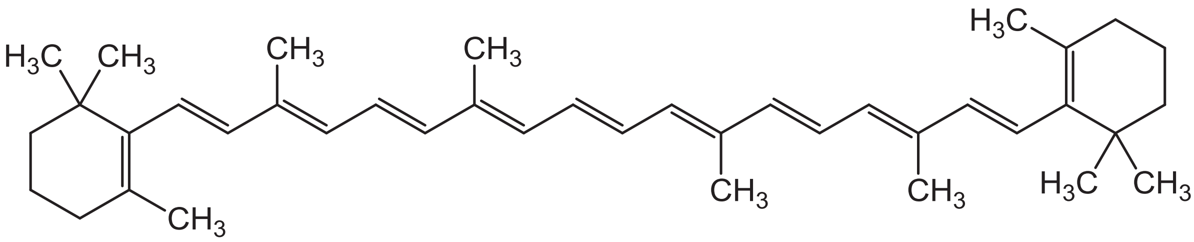
Concept: Introduction to Organic Chem; identification of chiral C & hybridisation

Answer: D



5 chiral centres
13 sp^2 C

17 β-carotene is responsible for the orange colour of carrots.



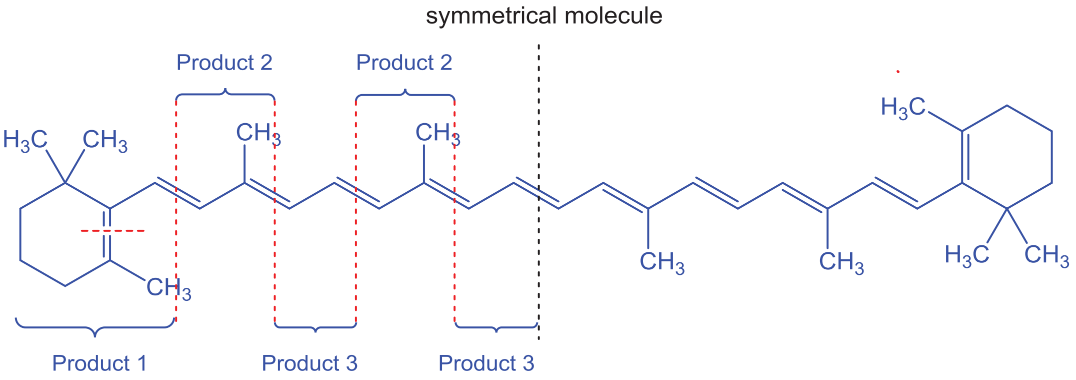
β–carotene

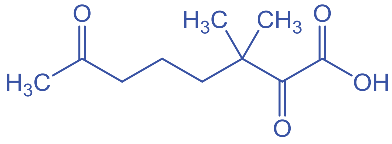
β-carotene is oxidised by hot, concentrated, acidified $KMnO_4$.

How many different products formed from the above reaction contain the ketone functional group?

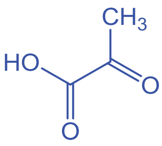
A 2 **B** 4 **C** 6 **D** 8

Concept: oxidative cleavage of C=C and identifying the ketone functional group

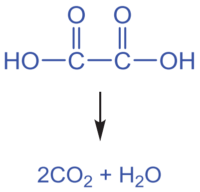




Product 1



Product 2

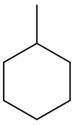


$$HO-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-OH \rightarrow 2CO_2 + H_2O$$

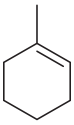
Product 3

Since the molecule is symmetrical, there are only 2 different products that contained ketone groups.

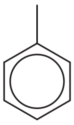
18 Which of the statements are true regarding the three compounds below?



I



II



III

1 Compounds **I** and **III** will not decolourise Br_2 in CCl_4.

2 Compounds **I** and **II** will decolourise acidified $KMnO_4$ at 298 K.

3 Compound **III** will not react with chlorine in the presence of uv light.

4 Compound **III** will react with bromine in the presence of a homogeneous catalyst.

A 1 and 4 only

B 2 and 3 only

C 1, 3 and 4 only

D 1, 2, 3 and 4

Concept: Chemical properties of Hydrocarbons

Reagents and conditions of Free Radical Substitution, Electrophilic Addition and Electrophilic Substitution

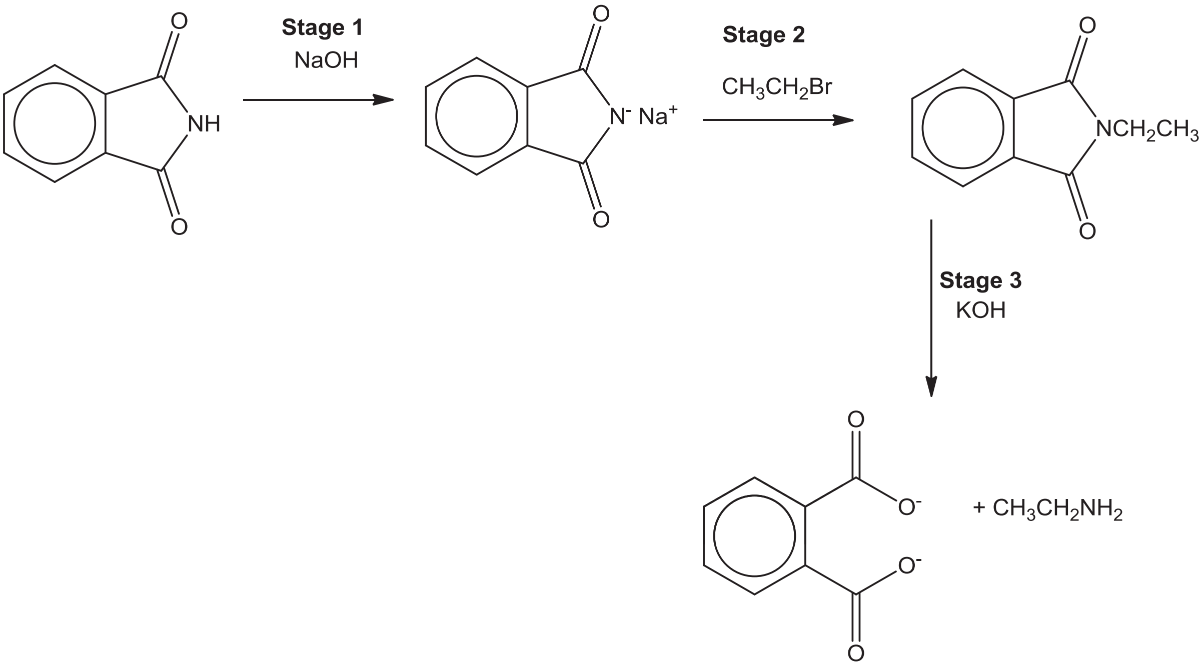
addition. Thus, both compounds **I** and **III** will not decolourise Br_2.

Statement 2: False. Compound **I** will not decolourise purple $KMnO_4$ at room temp.

Statement 3: False. The alkyl side-chain of compound **III** will be able to undergo free radical substitution with Cl_2 gas when exposed to uv light.

Statement 4: True. Compound **III** requires $FeBr_3$ catalyst for electrophilic substitution to occur.

19 A sequence of reactions is shown below.



Which of the following correctly describes the type of reactions for Stages **1** to **3**?

Stage 1	**Stage 2**	**Stage 3**

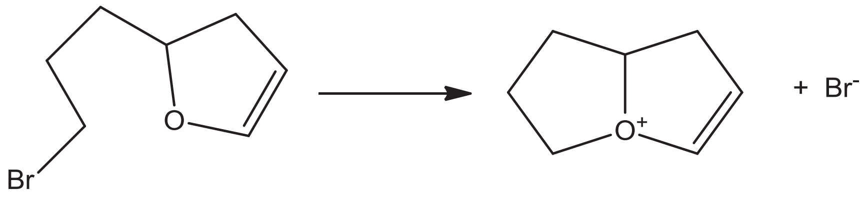
A	neutralisation	electrophilic substitution	nucleophilic substitution
B	hydrolysis	nucleophilic substitution	hydrolysis
C	redox	nucleophilic addition	nucleophilic substitution
D	neutralisation	nucleophilic substitution	hydrolysis

Concept: identifying types of reaction for organic compounds

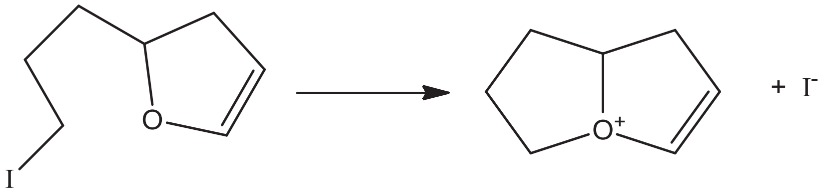
Stage 1: The diamide donated a proton and is a Bronsted acid. The OH^- accepted a H^+ to form H_2O. Thus this is an acid-base reaction.
Stage 2: Bromoethane undergoes nucleophilic substitution, with the negatively charged ion acting as the nucleophile.
Stage 3: The amide undergoes base-catalysed hydrolysis.

20 The intramolecular reactions below occur via nucleophilic substitution mechanism.

Reaction 1



Reaction 2



Reaction 2 is faster than reaction 1 under identical conditions.

Which statement explains this difference?

A Br is more electronegative than I.

B The I^- ion is a stronger nucleophile than Br^-.

C The C–Br bond is more polar than the C–I bond.

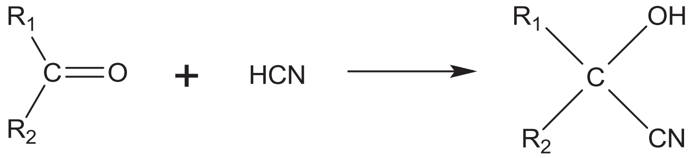
D The C–Br bond is stronger than the C–I bond.

Concept: Halogen Derivatives; effect of C-Hal bond strength on reactivity towards nucleophilic substitution

To recall weaker C-Hal bond leads to faster substitution by nucleophile

Answer: D
C-Br bond is stronger than C-I bond, hence rate of S_N2 nucleophilic substitution in reaction 1 is slower.

21 Cyanohydrins can be made from carbonyl compounds by generating CN^- ions from HCN in the presence of a weak base.



In a similar reaction, $^-CH_2COOCH_3$ ions are generated from CH_3COOCH_3 by strong bases.

Which compound can be made from an aldehyde and CH_3COOCH_3?

A $CH_3CH(OH)COOCH_3$
B $CH_3COOCH_2CH(OH)CH_3$
C $CH_3CH_2CH(OH)CH_2COOCH_3$
D $(CH_3)_2C(OH)CH_2COOCH_3$

Concept: Pattern identification and interpreting condensed structural formula

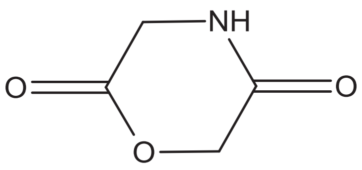
A is incorrect. The nucleophile used is $^-COOCH_3$.

B is incorrect. The nucleophile used is $CH_3COOCH_2^-$.

C is correct. The nucleophile used is $^-CH_2COOCH_3$ and it reacts with an aldehyde CH_3CH_2CHO.

D is incorrect. The nucleophile used is $^-CH_2COOCH_3$ but it reacts with a ketone CH_3COCH_3

22 The cyclic compound **X** is heated with acidified $KMnO_4$.



Compound **X**

What are the final organic products of the reaction?

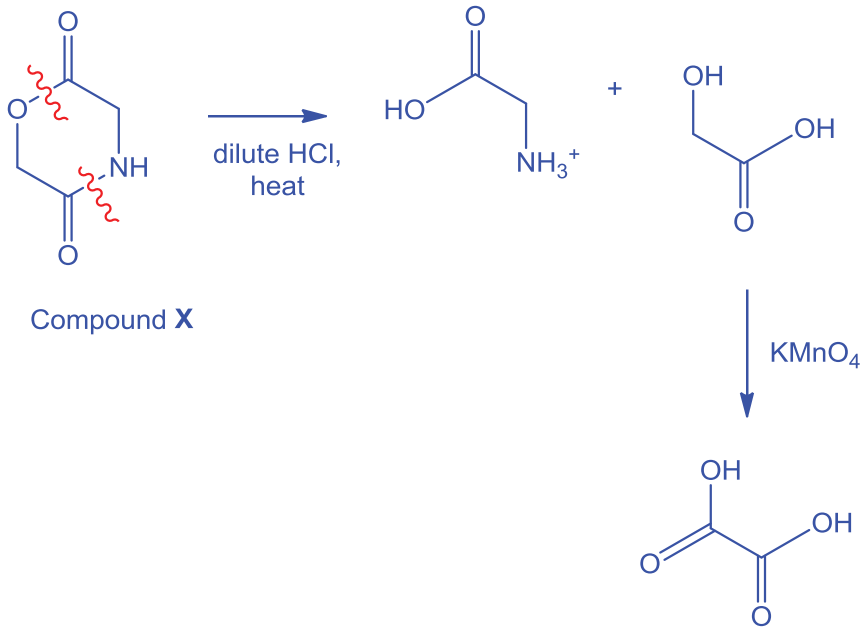
A $HOCH_2CO_2H$ and $HO_2CCH_2NH_3^+$

B $HO_2CCH_2NH_3^+$

C $HOCH_2CHO$ and $H_2NCH_2CO_2H$

D H_2NCOCH_2OH and $HOCH_2CHO$

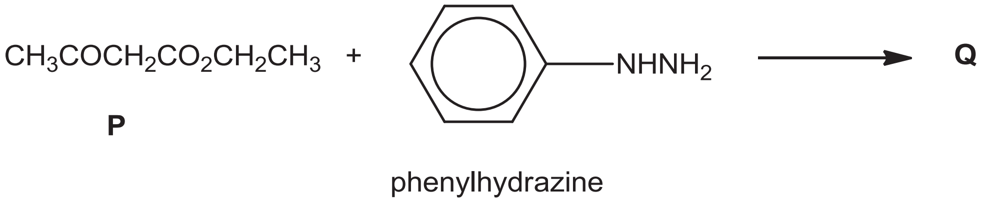
Concept: hydrolysis of amides and esters



Compound **X**

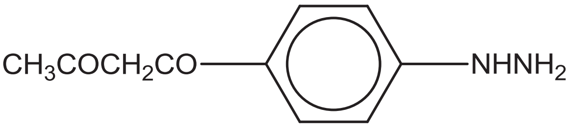
ethanedioic acid undergoes further oxidation to give CO_2 and H_2O

23 The first stage in the synthesis of *Antipyrine,* a fever medication, is the reaction between compound **P** and phenylhydrazine.

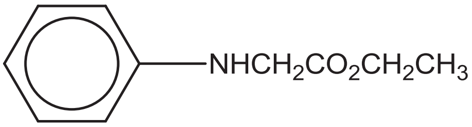


Which of the following correctly represents the structure of product **Q**?

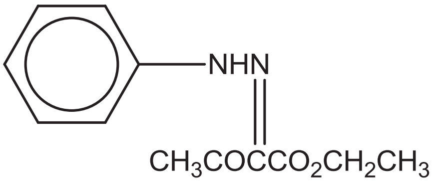
A



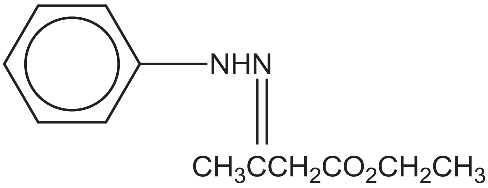
B



C



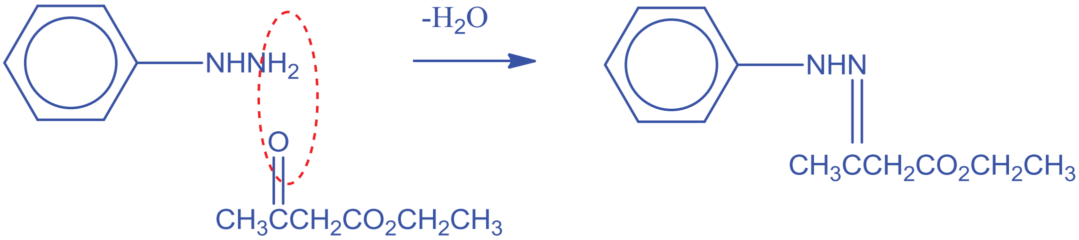
D



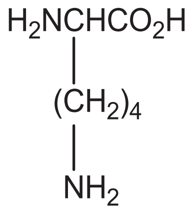
Concept: Carbonyl Compounds & Carboxylic acids derivatives

Predicting product formed from condensation reaction between a ketone and phenylhydrazine (extension of knowledge from reaction between carbonyl compounds and 2,4-DNPH.

Answer: D

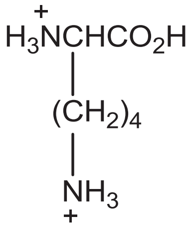


24 Lysine is an α-amino acid.



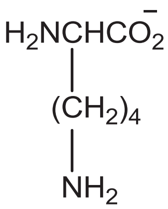
$$\begin{array}{c} H_2NCHCO_2H \\ | \\ (CH_2)_4 \\ | \\ NH_2 \end{array}$$

Which structure is predominant when lysine is in an aqueous solution of pH 9.5, given that lysine has three pK_a values of 2.2, 8.9 and 10.5?



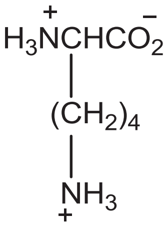
$$\begin{array}{c} \overset{+}{H_3N}CHCO_2H \\ | \\ (CH_2)_4 \\ | \\ \underset{+}{NH_3} \end{array}$$

A



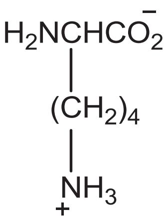
$$\begin{array}{c} H_2NCHCO_2^- \\ | \\ (CH_2)_4 \\ | \\ NH_2 \end{array}$$

B



$$\begin{array}{c} \overset{+}{H_3N}CHCO_2^- \\ | \\ (CH_2)_4 \\ | \\ \underset{+}{NH_3} \end{array}$$

C



$$\begin{array}{c} H_2NCHCO_2^- \\ | \\ (CH_2)_4 \\ | \\ \underset{+}{NH_3} \end{array}$$

D

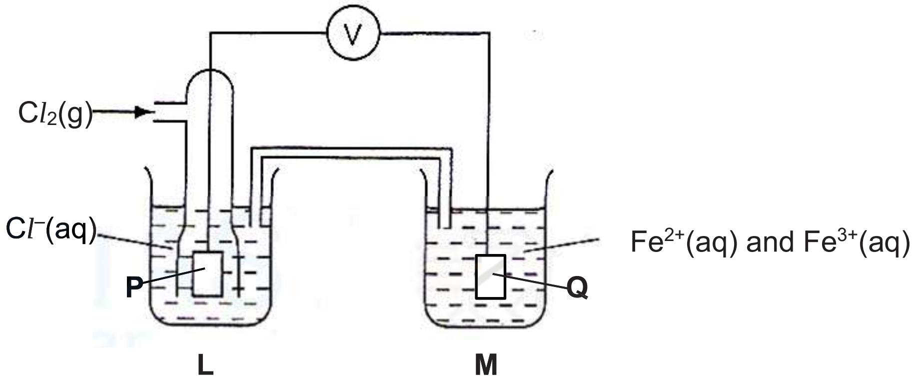
Concept: Nitrogen Compounds; assigning pK_a values, determining predominant structure of amino acid in alkaline solution.

Answer: D

Side-chain -NH_3+ group will not dissociate as its pK_a value (10.5) is above pH 9.5.

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

The cell shown below is set up under standard conditions where **P** and **Q** are platinum electrodes.



Which of the following statements is correct?

A Addition of KCN to half-cell **M** will not affect $E_{cell}^{\ominus}$.

B The voltmeter will show a reading of about 2.13 V.

C The electrons will flow from **Q** to **P** through the voltmeter.

D **P** will be the negative electrode.

Concept: Electrochemical cell setup, determining cell emf.

Answer: C

A. Wrong. By introducing CN^- Ligands, the $E(Fe^{3+}/Fe^{2+})$ changes and therefore the cell emf will change. , it will participate in reaction.

B. Wrong. Cell emf = 1.36 – 0.77 = 0.59 V

C. Correct. Half-cell **M** is undergoing oxidation (loss of electrons) since the $E(Fe^{3+}/Fe^{2+})$ is less positive than $E(Cl_2/Cl^-)$.

D. Wrong. In electrochemical cell, the half-cell where reduction takes place, the electrode will have positive polarity. Oxidation is taking place in half-cell **M**.

26 During electroplating, a current is passed through a cell containing aqueous silver nitrate using inert electrodes. After some time, 1.35 g of silver was deposited at one electrode. What volume of gas would be produced at the other electrode at r.t.p.?

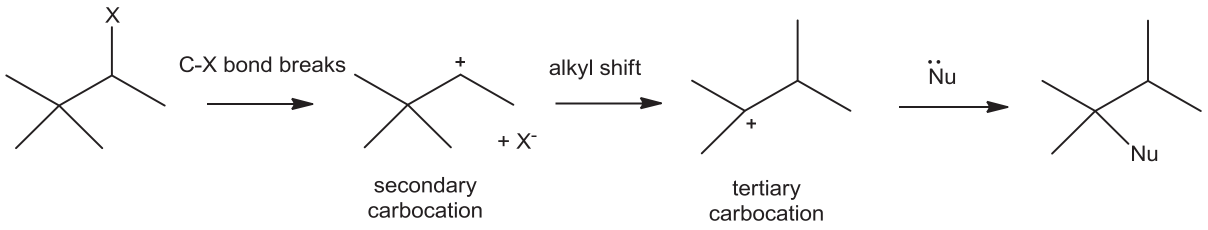
A 70 cm^3 **B** 75 cm^3 **C** 140 cm^3 **D** 150 cm^3

Concept: Electrolytic calculations via half-cell reactions.

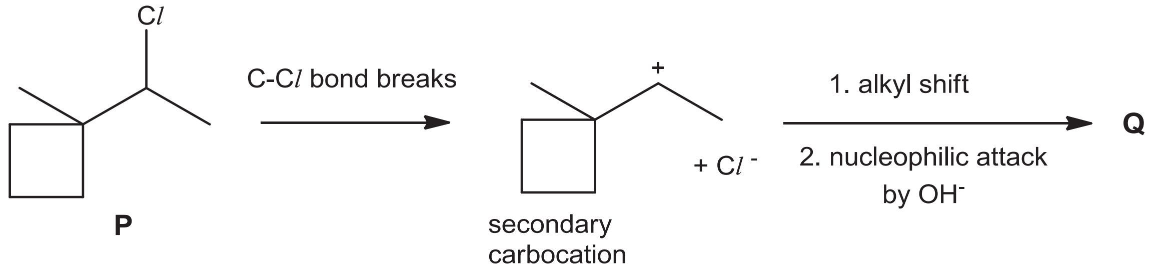
Answer: B

$Ag^+ + e^- \rightarrow Ag$ is formed at the cathode
1 mol of Ag requires 1 mol of electrons
No. of mole of electrons = 1.35/108 = 0.0125 mol
$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$
1 mol O_2 give 4 mol of electrons
No. of mole of oxygen formed = 0.0125/4 = 0.003125 mol
Volume of oxygen = 0.03125 x 24000 = 75 cm^3

27 In S_N1 reactions involving secondary halogenoalkanes, alkyl shift can sometimes occur after the breaking of C–X bond to form a more stable tertiary carbocation.

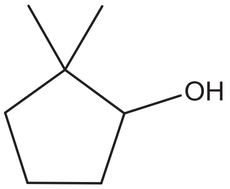


Rearrangements need not always involve methyl groups. In situation when the carbocation is formed adjacent to a strained ring, such as a cyclobutane, it is more favourable for one of the alkyl groups in the ring, rather than the methyl group, to shift so as to cause **ring expansion** and the formation of a less strained ring.

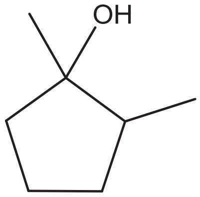


Which of the following is a possible identity of **Q**?

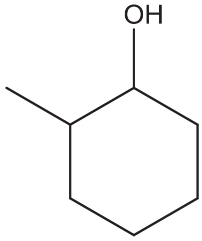
A



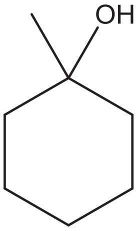
B



C

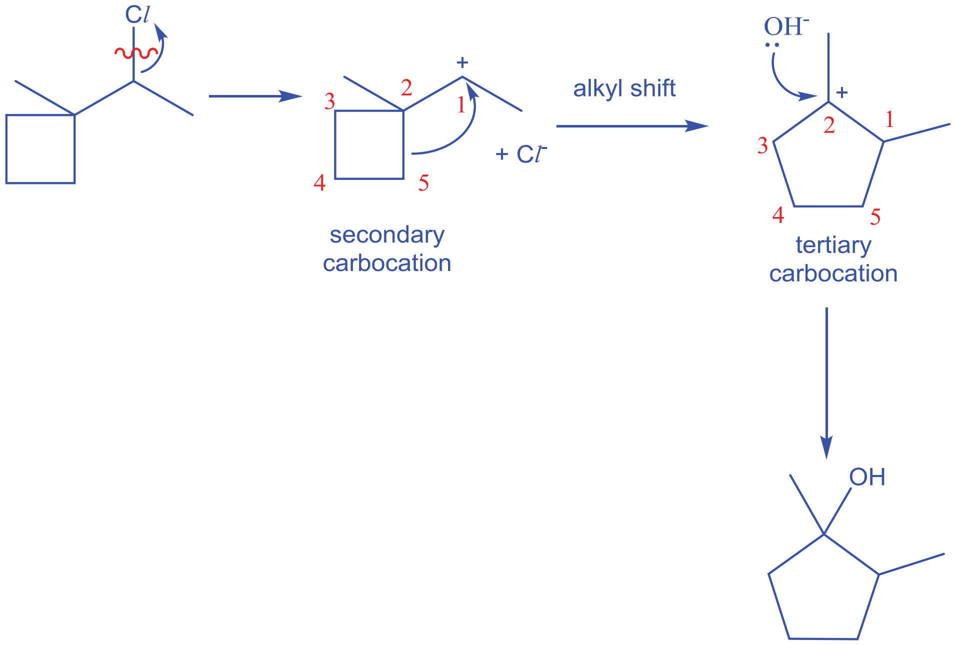


D

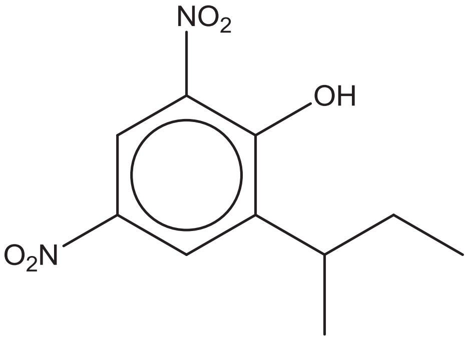


Concept: Pattern recognition of novel reaction; predicting structure of product

Answer: B



28 *Binapacryl* is used as a fungicide.



Binapacryl

Which of the following statements about *Binapacryl* are correct?

1 It dissolves in water to give a neutral solution.

2 It is inert towards acidified potassium dichromate(VI) solution.

3 It decolourises aqueous bromine to form a white precipitate.

4 It reacts with ethanoic acid in the presence of concentrated sulfuric acid to form an ester.

A 2 only

B 2 and 3 only

C 1 and 4 only

D 1, 2, 3 and 4 only

Concept: Hydroxy compounds (phenols); reactions of phenols; chirality.

Answer: A

1 It dissolves in water to give a neutral solution. **False; Binapacryl is not soluble in water.**

2 It is inert towards acidified potassium dichromate solution. **True; acidified $K_2Cr_2O_7$ is not strong enough to oxidise the alkyl side-chain.**

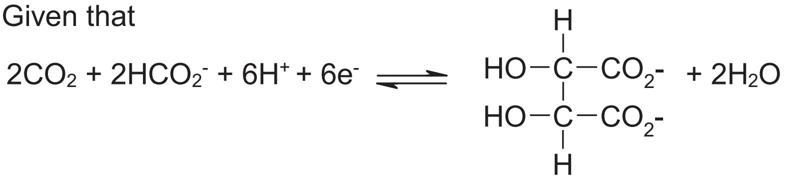
3 It decolourises aqueous bromine to form a white precipitate. **False; phenolic group in Binapacryl is already 2, 4 substituted. Hence will not be able to undergo further electrophilic substitution with aq. Br_2.**

4 It reacts with ethanoic acid in the presence of concentrated sulphuric acid to form an ester. **False; phenol and ethanoic acid are both weak acids; no reaction between both compounds. To form ester with phenol, acyl chloride is required instead.**

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

The reaction between peroxodisulfate(VI) ion, $S_2O_8^{2-}$, and tartrate ion, $[CH(OH)CO_2^-]_2$, is slow due to a high activation energy.

The reaction can be catalysed by a homogeneous catalyst.
Given that



$$2CO_2 + 2HCO_2^- + 6H^+ + 6e^- \rightleftharpoons \begin{array}{c} H \\ | \\ HO-C-CO_2^- \\ | \\ HO-C-CO_2^- \\ | \\ H \end{array} + 2H_2O \qquad E^\ominus = +0.56\ V$$

Which metal ion is **not** a suitable catalyst for this reaction?

A Co^{2+}

B Cr^{2+}

C Mn^{3+}

D Fe^{3+}

Concept tested: Transition metal ions as suitable homogeneous catalyst

From data booklet, $E^\ominus$ ($S_2O_8^{2-}$ / SO_4^{2-}) = +2.01V
Hence $E^\ominus$ value of suitable catalyst should be between +0.56 V and +2.01 V

$E^\ominus$ (Co^{3+}/Co^{2+}) = +1.89 V
$E^\ominus$ (Mn^{3+}/Mn^{2+}) = +1.54 V

$E^\ominus$ (Fe^{3+}/Fe^{2+}) = +0.77 V
$E^\ominus$ (Cr^{3+}/Cr^{2+}) = -0.41 V

Hence Cr^{3+} is not a suitable catalyst for this reaction.
Answer: B

30 Chromium forms a series of compounds with the general formula $CrCl_3 \bullet 6H_2O$. One of these compounds, **X** is violet and produces an aqueous solution from which all the chlorine can be precipitated as $AgCl$ upon addition of aqueous silver nitrate.
Another compound **Y** is green and produces an aqueous solution from which only one third of the chlorine can be precipitated with silver nitrate.

Which of the following statements about **X** and **Y** is **incorrect**?

A **X** is an ionic compound consisting of $[Cr(H_2O)_6]^{3+}$ and Cl^- ions.

B **Y** is an ionic compound consisting of $[Cr(Cl)_2(H_2O)_4]^+$ and Cl^- ions.

C Oxidation number of Cr in **X** is +3 while the oxidation number of Cr in **Y** is +1.

D Oxidation number of Cr in **X** and **Y** remains unchanged during precipitation of $AgCl$.

Concept: Introduction to Transition Elements; complex ion formation and oxidation number of central metal ion.

Determining formula of Cr-containing complex ions and oxidation number of central metal ion based on given information.

Answer: C

A **X** is an ionic compound consisting of $[Cr(H_2O)_6]^{3+}$ and Cl^- ions. **True; since all chlorine can be precipitated, it implies all chlorine exists as free Cl- ions in the aqueous solution.**

B **Y** is an ionic compound consisting of $[Cr(Cl)_2(H_2O)_4]^+$ and Cl^- ions. **True; since only 1/3 of the chlorine can be precipitated, it implies 2/3 of the chlorine are bonded to the Cr in the complex ion.**

C Oxidation number of Cr in **X** is +3 while the oxidation number of Cr in **Y** is +1. **False; Oxidation number of Cr in both X and Y is +3.**

D Oxidation number of Cr in **X** and **Y** remains unchanged during precipitation of $AgCl$; **True; precipitation is not a redox reaction.**

Catholic Junior College
JC2 Preliminary Examinations
Higher 2

CANDIDATE NAME	
CLASS	2T

CHEMISTRY 9729/02

Paper 2 Structured Questions

18 August 2017

2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name and class on all the work you hand in.
Write in dark blue or black pen.
You may use an HB pencil for any diagrams or graphs.
Do **not** use staples, paper clips, glue or correction fluid.

Answer **all** questions in the spaces provided on the Question Paper.
The use of an approved scientific calculator is expected, where appropriate.
A Data Booklet is provided.

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

For Examiner's Use			
Paper 1			**30**
Paper 2	**Q 1**	**12**	
	Q 2	**19**	
	Q 3	**18**	
	Q 4	**9**	
	Q 5	**10**	
	Q 6	**7**	**75**
Paper 3	**Q 1**	**22**	
	Q 2	**20**	
	Q 3	**18**	
	Q 4	**20**	
	Q 5	**20**	**80**
Total			**185**

Suggested Solutions

This document consists of **14** printed pages.

1 Sedimentary rocks formed at the earth's surface by the accumulation of particulate matter are usually transported to the place of deposition by water, wind, or mass movement of glaciers. Dolostone, a sedimentary rock, consists of a mixture of minerals such as calcium and magnesium carbonates.

Table 1.1 below shows some properties of calcium carbonate and magnesium carbonate.

	Numerical values of K_{sp} at 25 °C	Decomposition temperature / ˚C
calcium carbonate	5.0×10^{-9}	900
magnesium carbonate	1.0×10^{-5}	540

Table 1.1

(a) **(i)** Write an expression for the solubility product, K_{sp}, of calcium carbonate.

K_{sp}= $[Ca^{2+}]\ [CO_3^{2-}]$

.... [1]

(ii) Calculate the solubility, in mol dm^{-3}, of calcium carbonate in water at 25 °C.

Let solubility of $CaCO_3$ be x
$[Ca^{2+}] = [CO_3^{2-}] = x$
$K_{sp} = [Ca^{2+}][CO_3^{2-}]$
$x^2 = 5.0 \times 10^{-9}$
x = $\underline{7.07 \times 10^{-5} \text{ mol dm}^{-3}}$

[1]

(iii) A saturated solution **X** containing calcium hydroxide and calcium carbonate has a pH of 13 at 25 °C.

Given that the K_{sp} of calcium hydroxide is 5.5×10^{-6} mol^3 dm^{-9} and using your answer in **(a)(i)**, calculate the solubility of calcium carbonate in solution **X**.

pOH = 14 - 13
$[OH^-] = 10^{-(14-13)} = 0.100$ mol dm^{-3}
$[Ca^{2+}][OH^-]^2 = 5.5 \times 10^{-6}$
$[Ca^{2+}] = 5.5 \times 10^{-4}$ mol dm^{-3}
$[Ca^{2+}][CO_3^{2-}] = 5.0 \times 10^{-9}$
$[CO_3^{2-}] = 5.0 \times 10^{-9} / 5.5 \times 10^{-4}$
$[CO_3^{2-}] = 9.09 \times 10^{-6}$ mol dm^{-3}
Since mol $CaCO_3$ dissolved ≡ CO_3^{2-} in saturated solution
Solubility of $CaCO_3$= = $\underline{9.09 \times 10^{-6} \text{ mol dm}^{-3}}$

[2]

(iv) Comment on, and explain, the discrepancy in the solubilities of calcium carbonate in water and in solution **X**.

Solubility of calcium carbonate in solution X is lower . Presence of common ion, Ca^{2+}, shifts position of equilibrium (1) to the left by Le Chatelier's Principle.

[2]

$CaCO_3\ (s) \rightleftharpoons Ca^{2+}\ (aq) + CO_3^{2-}\ (aq)$ ---------(1)

(v) When rainwater runs over dolostone, a chemical reaction occurs as shown below:

$$\mathbf{M}CO_3(s) + CO_2(aq) + H_2O(l) \rightleftharpoons 2HCO_3^-(aq) + \mathbf{M}^{2+}(aq)$$

where **M** is a group 2 metal

I. Suggest the source of CO_2 (aq) for the reaction.

Air containing CO_2 that is dissolved in the rainwater. [1]

II. When a sample of saturated solution of $Ca(HCO_3)_2$ is heated, a reaction occurs and a precipitate is formed. Using the equation above, suggest why this happens.

Boiling causes CO_2 to be released from the solution. Based on Le Chatelier's Principle, position of equilibrium of above equation shifts left, which results in the precipitation of $CaCO_3$ (s).

[2]

(b) Calcium carbonate can be decomposed by heating at high temperatures.

(i) Write an equation for the thermal decomposition of calcium carbonate.

$CaCO_3\ (s) \rightarrow CaO\ (s) + CO_2\ (g)$ [1]

(ii) Calcium carbonate decomposes at a higher temperature than magnesium carbonate. Explain why this is so.

Ca^{2+} has a larger ionic size than Mg^{2+}, thus charge density of Ca^{2+} is lower, leading to lower polarising power of the cation Ca^{2+} compared to Mg^{2+}. As a result, the CO_3^{2-} ion is polarised (or distorted) to a smaller extent and the C-O bond is weakened to a larger extent. Hence, decomposition of the $CaCO_3$ occurs with greater difficulty and at higher temperature compared to $MgCO_3$. [2]

[Total: 12]

2 **(a)** Table 2.1 gives data about some physical properties of the elements calcium and copper.

physical property	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
melting point / °C	839	1085
boiling point / °C	1484	2562

Table 2.1

(i) Explain why the atomic radius of copper is smaller than that of calcium.

$_{29}$Cu: [Ar] 3d^{10} 4s^{1} $_{20}$Ca:[Ar] 4s^{2}

Copper has more protons and hence higher nuclear charge than calcium. Since the 3d electrons in copper provide poor shielding, the shielding effect is similar. Hence, the atomic radius of copper is smaller than that of calcium. [2]

(ii) Explain why copper has a higher melting point than calcium.

Copper has more electrons available for delocalisation (3d and 4s electrons) than calcium (only 4s electrons). In copper, the metal cation has a smaller ionic radius (or higher charge density) than in calcium. Hence there is stronger metallic bonding between the metal cations and 'sea' of delocalised electrons, and more energy required to break. [2]

(iii) Apart from the properties given in Table 2.1, state clearly the difference in one other physical property between copper and calcium.

Copper has higher density than calcium.
Or
Copper has higher electrical conductivity than calcium. [1]

(b) Copper, scandium and zinc are d-block elements. However, copper is a transition element while scandium and zinc are not.

(i) Define the term *transition element*.

A transition element is a d-block element which forms one or more stable ions with partially filled d subshells. [1]

(ii) Explain why scandium is not classified as a transition element.

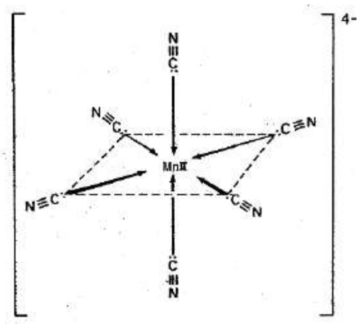
Sc is not a transition element as it only forms Sc^{3+} ion which has empty d subshell. ....[1]

(c) Manganese is also a transition element and shows great tendency to form stable coloured complexes with ligands.

(i) Define the term *ligand*.

A ligand is an ion or molecule that has at least one lone pair of electrons available for donation to the central metal atom/ion. ....[1]

(ii) Draw the shape of the complex ion, $[Mn(CN)_6]^{4-}$.



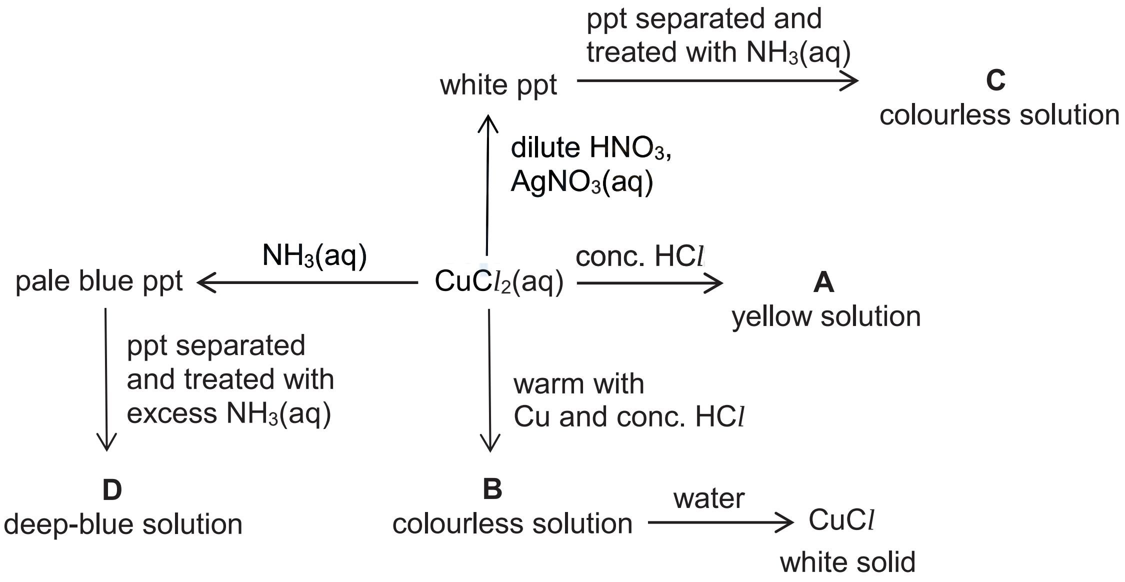
[2]

(d) Copper has more than one oxidation state and many of its compounds have colours in the blue-green-yellow part of the visible spectrum.

Write the *spdf* electronic configuration of copper(II) ions.

Cu^{2+} **$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^9$** .... [1]

(e) Aqueous copper(II) chloride, $CuCl_2$, is a blue solution which gives the following reactions.



Both **A** and **B** contain complex ions of copper and chlorine.

(i) State the formula of compound **C**.

$[Ag(NH_3)_2]Cl$ ....[1]

(ii) Suggest the formula and shape of the complex ion present in **D**.

Formula $[Cu(NH_3)_4]^{2+}$ / $[Cu(NH_3)_4(H_2O)_2]^{2+}$ .... [1]

Shape square planar / distorted octahedral .... [1]

(iii) What type of reaction occurs when **A** is formed from $CuCl_2(aq)$?

Ligand exchange / ligand displacement .... [1]

(iv) Explain why **A** is yellow in colour.

In the presence of Cl^- ligands, the partially filled degenerate d orbitals of Cu^{2+} ions split into two groups of non-degenerate d orbitals with a small energy gap. When exposed to visible light, d electron absorb energy in the violet region and is promoted to a higher energy d* orbital from a lower energy d orbital. This process is called *d-d** *electronic transition* . The complementary colour i.e. yellow is not absorbed and thus seen as the colour of the complex. [3]

(v) Explain why **B** is colourless.

Cu^+ in B has a fully filled d subshell (d^{10} configuration).

No d-d* electronic transition is possible.

.... [1]

[Total: 19]

3 Industrially, ethanol, CH_3CH_2OH, is manufactured by reacting ethene with steam in the presence of a catalyst. The reaction is reversible and the equation is as follows:

$$CH_2{=}CH_2(g) + H_2O(g) \rightleftharpoons CH_3CH_2OH(g)$$

At equilibrium, only 5 % of the ethene is converted into ethanol. To increase the overall yield of ethanol, ethanol is regularly removed from the equilibrium mixture as it is formed and more ethene is added into the reaction mixture. The volume of steam is not increased as this may disable the catalyst.

(a) Apart from the methods mentioned above, suggest one other method which will increase the conversion of ethene into ethanol. Explain your answer briefly.

By Le Chatelier's Principle, **increasing the pressure** will shift the position of equilibrium to favour the production of **fewer number of moles of gas molecules**. Hence the equilibrium shifts forward and more ethanol is produced. [2]

Alcoholic beverages can contain up to 40 % of ethanol. Excessive consumption of ethanol depresses the activity of the central nervous system. The blood alcohol concentration (BAC) is a good measure of the extent to which the activity of the central nervous system is depressed. It is usually defined as follows

BAC = mg of ethanol per 100 cm^3 of blood

Ethanol is sufficiently volatile to pass from the blood into the air in the lungs and the following equilibrium is set up:

$$CH_3CH_2OH(blood) \rightleftharpoons CH_3CH_2OH(g)$$

(b) **(i)** Suggest an expression for K_c for the equilibrium of ethanol between the blood and the air in the lungs.

$$K_c = \frac{[C_2H_5OH_{(g)}]}{[C_2H_5OH_{(blood)}]}$$

State symbols are required in the K_c expression to distinguish between ethanol in blood and ethanol in one's breath.

[1]

(ii) Using your answer to **(b)(i)** and given that the equilibrium constant, K_c, for this process is 4.35×10^{-4}, calculate the breath alcohol concentration (in mg of ethanol / 100 cm^3 of air) which corresponds to the 80 mg / 100 cm^3 of blood legal limit for BAC.

$[C_2H_5OH\ (g)] = 4.35 \times 10^{-4} \times 80 = 0.0348$ mg/ 100 cm^3 of air

[1]

(iii) Hence determine the legal limit of breath alcohol concentration in mol dm^{-3}.

[C_2H_5OH (g)] in g/ 100cm^3 = 3.48×10^{-5} g / 100 cm^3 of air
[C_2H_5OH (g)] in g/ dm^3 = 3.48×10^{-4} g / dm^3 of air

$$[C_2H_5OH\ (g)] \text{ in mol/ dm}^3 = \frac{3.48 \times 10^{-4}}{46.0} = 7.56 \times 10^{-6} \text{ mol dm}^{-3}$$

[2]

(c) The handheld breathalyser contains an electrochemical cell in which ethanol is oxidised. At one electrode, atmospheric oxygen is reduced to water and the other electrode ethanol is oxidised to ethanoic acid. The electric current produced gives an approximation of the overall blood alcohol concentration (BAC).

Give the half–equation for each electrode reaction and hence give the overall equation showing the oxidation of ethanol.

anode: $CH_3CH_2OH(g) + H_2O(l) \rightarrow CH_3CO_2H(l) + 4H^+(aq) + 4e^-$

cathode, atmospheric oxygen is reduced:

$O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$

The overall reaction is the oxidation of ethanol to ethanoic acid and water.

$CH_3CH_2OH(l) + O_2(g) \rightarrow CH_3CO_2H(aq) + H_2O(l)$

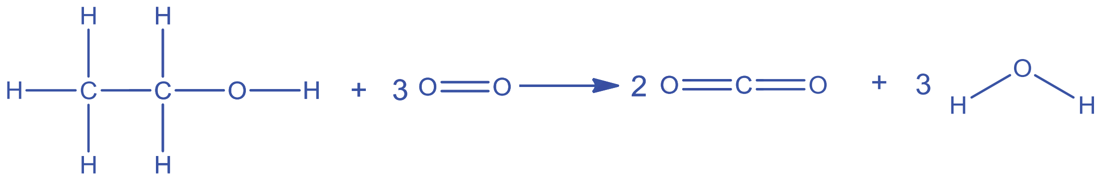
[2]

(d) Ethanol can be burned in excess oxygen as fuel. Complete combustion of ethanol releases 1367 kJ mol^{-1} of heat energy.

(i) Write an equation to show the standard enthalpy change of combustion of ethanol.

$C_2H_5OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l)$ [1]

(ii) Use the bond energies given in the *Data Booklet* to calculate another value for the standard enthalpy change of combustion of ethanol.



Bonds broken	kJ mol^{-1}	Bonds formed	kJ mol^{-1}
5(C-H)	5(410)	4(C=O)	-4(805)
1(C-C)	(350)	6(O-H)	-6(460)
1(C-O)	(360)		
1(O-H)	(460)		
3(O=O)	3(496)		
Total:	+4708	Total:	-5980

Enthalpy change = +4708 – 5980 = -1272 kJ mol^{-1} = -1270 kJ mol^{-1} (3 sf)

[3]

(iii) Suggest a reason for the discrepancy between this value and that quoted in **(d)**.

The values in *the Data Booklet* were average values and hence the calculated value is an approximation.

OR [1]

Bond energies are based on calculations from reaction in the gas phase, but at standard state, ethanol and water are liquids.

(e) **(i)** The complete combustion of ethanoic acid, CH_3CO_2H, releases 873 kJ mol^{-1} of energy. Use this value and the enthalpy change of combustion of ethanol given in **(d)** to construct an energy cycle to calculate the enthalpy change when 1.0 mol of ethanol in the body is oxidised to ethanoic acid and water only.

$$\begin{tikzcd}
C_2H_5OH + O_2 \arrow[rr, "\Delta H_{reaction}"] \arrow[dr, "\Delta H_c \text{ of } C_2H_5OH = -1367 \text{ kJ mol}^{-1}"'] & & CH_3CO_2H + H_2O \arrow[dl, "\boldsymbol{\Delta H_c \textbf{ of } CH_3CO_2H = -873 \textbf{ kJ mol}^{-1}}"] \\
& 2CO_2 + 3H_2O &
\end{tikzcd}$$

Using Hess' Law,

$\Delta H_{reaction} + \Delta H_c$ of $CH_3CO_2H = \Delta H_c$ of C_2H_5OH

$\Delta H_{reaction} = -1367 - (-873) = -494$ kJ mol^{-1}

[3]

(ii) The metabolism of ethanol in the human body leads to partial oxidation which releases 770 kJ mol^{-1} of energy. Assuming that ethanol is oxidised to ethanoic acid and carbon dioxide only, use your answer to **(e)(i)** and any other relevant data to calculate the proportion of ethanol metabolised to ethanoic acid and to carbon dioxide respectively.

Energy released when 1 mole of ethanol is oxidised to CO_2 and CH_3CO_2H = 770 kJ

Let % of ethanol oxidised to CH_3CO_2H be x

% of ethanol oxidised to CO_2 = 100 –x

$$770 \text{ kJ} = \frac{x}{100} \times \Delta H_{reaction} \text{ (answer in } \textbf{(e)}\text{(i))} + \frac{100-x}{100} \times \Delta H_c \text{ of } C_2H_5OH$$

$770000 = 494x + (100-x)(1367)$

$x = 68.4\%$

Proportion of ethanol metabolized to CO_2 is 31.6% while proportion of ethanol metabolised to CH_3COOH is 68.4%

[2]

[Total: 18]

4 **(a)** Aerosol spray is a type of dispensing system which creates an aerosol mist of liquid particles. This is used with a can that contains a product and propellant under pressure. Hair spray is a common example of an aerosol spray where butane is often used as the propellant.

(i) A typical can of hair spray has a volume of 300 ml and 70 % of which is the hair product. Given that the can has an internal pressure of 100 psi, at 27 °C, calculate the maximum amount of butane present in the can. (1 psi = 6894.76 Pa)

$pV = nRT$

$(100 \times 6894.76)(300 \times 10^{-6} \times 30\%) = n(8.31)(273 + 27)$

$n = 0.0249$ mol of butane

[2]

(ii) The can of hair spray is used such that only the propellant, butane gas, remained and the internal pressure of the can decreased to 20 psi. If the can is left in a car that reaches 50 °C on a hot afternoon, what is the new pressure in the can?

Since V is constant

$$\frac{P_1}{T_1} = \frac{P_2}{T_2}$$

$$\frac{20}{273 + 27} = \frac{P_2}{273 + 50}$$

$P_2 = 21.5$ psi or 148 kPa

[1]

(iii) As a safety precaution, the propellant has to be completely expelled from the can prior to disposal and subsequent incineration. Using concepts from the Ideal Gas Law, explain qualitatively, why this precaution is necessary.

As the can will be incinerated, it will be subjected to high temperatures. Given that volume of the can is constant, pressure of butane increases when temperature increases.

.... [1]

(b) In 1873, Johannes D. van der Waals, a physicist proposed a modification to the ideal gas equation to better model real gas behaviour. The new equation, usually referred to as the van der Waals equation, has the following expression.

$$\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT$$

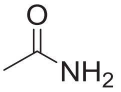
P is the observed pressure exerted by the gas.
V is the volume of the container in which the gas is contained.
The constants a and b have positive values and are characteristic of a gas.

Suggest why the term $\frac{an^2}{V^2}$ is **added** to P and the term nb is **subtracted** from V respectively.

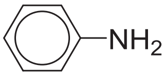
$P + \frac{an^2}{V^2}$: **Real gas particles have significant forces of attraction, the pressure exerted by a real gas is smaller than expected for an ideal gas. Thus, a term is added to P.** [1]

$V - nb$: **As real gas particles have a significant volume compared to the volume of the container, the volume of space in which the gas particles can move about is smaller than that of the container. Thus a term is subtracted from V.** [1]

(c) Arrange the following three compounds in increasing order of basicity.


ethanamide


ethylamine


phenylamine

Order of basicity:

ethanamide < phenylamine < ethylamine

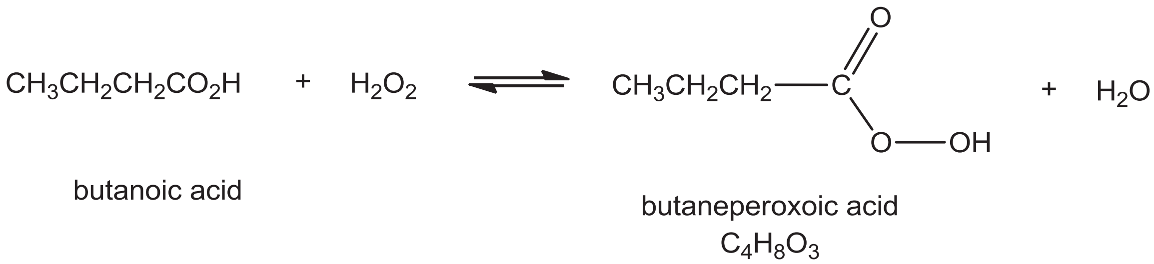
Explain your answer.

Ethanamide is an amide and the lone pair of electrons on N is delocalised into the π bond of C=O, thus it is not available to accept H^+, making ethanamide neutral and less basic than phenylamine and ethylamine. Ethylamine is more basic than phenylamine as it has an electron-donating ethyl group. Thus the lone pair of electrons on N is more available to accept H^+ compared to phenylamine.

OR Ethylamine is the most basic. Phenylamine is less basic than ethylamine due to the lone pair of electrons on N being delocalised into the benzene ring. Thus, the lone pair of electron is less available to accept H^+. Ethanamide is neutral (least basic among the three) as lone pair of electrons on N is delocalised into the π bond of C=O, thus it is not available to accept H^+. [3]

[Total: 9]

5 **(a)** Butaneperoxoic acid, a type of peroxyacid, is produced when butanoic acid reacts with hydrogen peroxide.



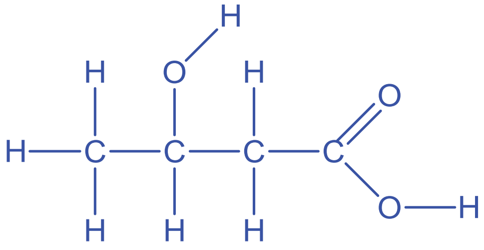
(i) Identify the type of hybridisation involved for the C atom of O=C-O in butaneperoxoic acid and hence state its bond angle.

Hybridisation of C ..sp^2..................................

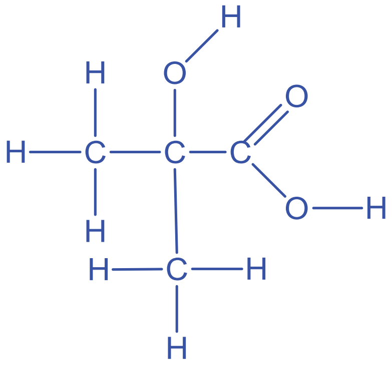
Bond angle ..120°.................................. [2]

(ii) Non-cyclic compounds **A** and **B** are functional group isomers of butaneperoxoic acid. 1 mole of hydrogen gas is produced when 1 mole of **A** and 1 mole of **B** are reacted with Na metal separately. **A** produces yellow precipitate when reacted with aqueous alkaline iodine while **B** does not. When reacted with hot acidified $K_2Cr_2O_7$, orange $K_2Cr_2O_7$ turns green in the presence of **A** but not **B**.

Draw the displayed formula of **A** and **B**, hence state the specific type of isomerism between **A** and **B**.



Compound **A**

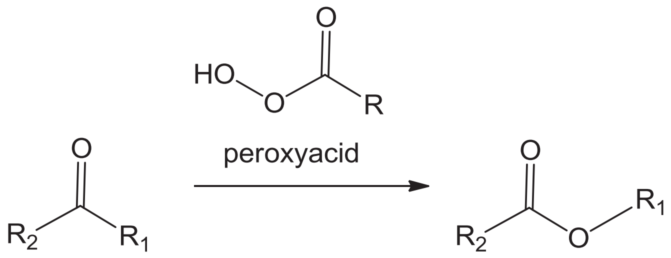


Compound **B**

[2]

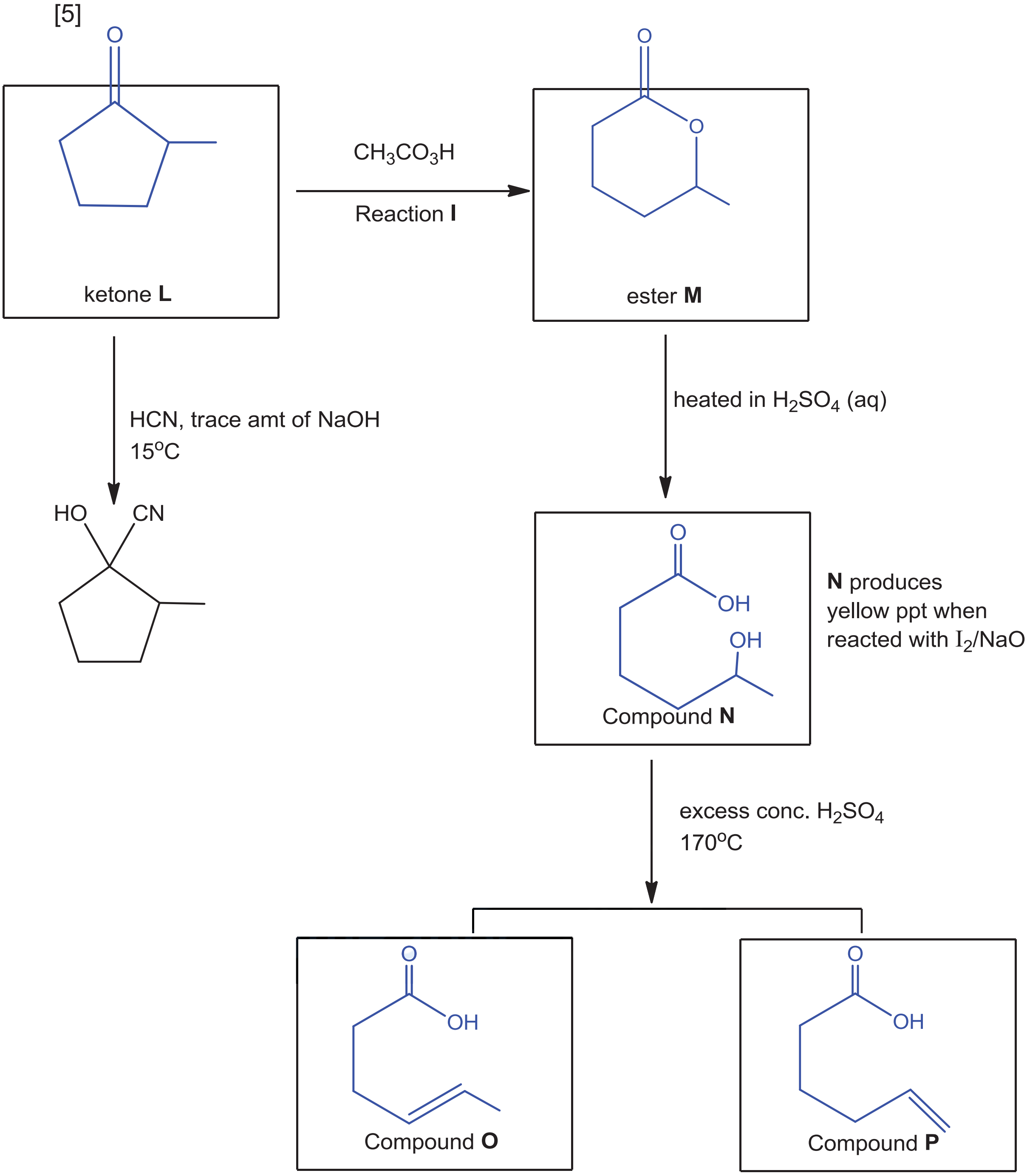
Type of isomerism between **A** and **B** ....Chain isomerism.................... [1]

(b) The Baeyer-Villiger oxidation is an organic reaction that converts ketones into esters using peroxyacids.



In the following reaction scheme, reaction **I** is a Baeyer-Villiger oxidation. Give the structural formulae of compounds **L**, **M**, **N**, **O** and **P**.

[5]



N produces yellow ppt when reacted with I_2/NaOH

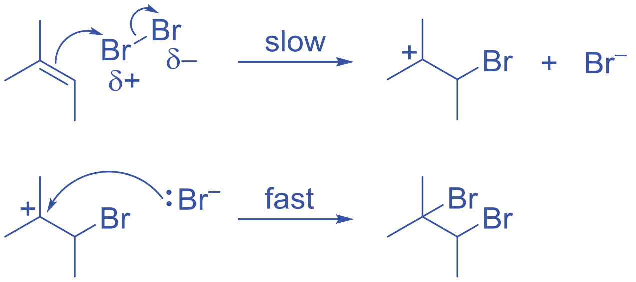
Both Compounds **O** and **P** decolourise aqueous bromine

[Total: 10]

6 2-methylbut-2-ene is reacted with bromine in an inert solvent in the absence of light.

(a) Describe the mechanism for the above reaction.

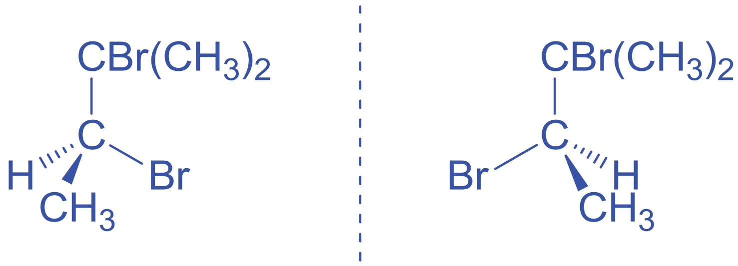
Electrophilic addition



[3]

(b) State the type of isomerism exhibited by the organic product(s) formed in the above reaction, and hence, draw the structures of the isomers.

Enantiomerism [1]



[1]

(ii) It was found that the product(s) formed from **(a)** do not rotate plane of polarised light. Using the mechanism drawn in **(a)**, suggest why this is so.

Since the C in the C=C is sp^2 hybridised and thus has a trigonal planar shape about C, the δ+ Br electrophile has a 50% chance to attack the electron rich C from either side of the plane, resulting in racemic mixture. Thus the products do not rotate plane of polarised light. [2]

[Total: 7]

Catholic Junior College
JC2 Preliminary Examinations
Higher 2

CHEMISTRY 9729/03

Paper 3 Free Response **25 August 2017**

Candidates answer on separate paper. **2 hours**

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.

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.

Suggested Solutions

[Turn over

Section A

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

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

(a) Under acidic conditions, ethanol reacts with dichromate(VI) ions quantitatively to give ethanoic acid and chromium(III) ions.

$$3CH_3CH_2OH + 2Cr_2O_7^{2-} + 16H^+ \rightarrow 3CH_3CO_2H + 4Cr^{3+} + 11H_2O$$

A student carried out the following experiment to determine the concentration of ethanol in a brand of wine.

A 10.0 cm^3 sample of the wine was diluted to 250 cm^3. He then added 25.0 cm^3 of 0.156 mol dm^{-3} $K_2Cr_2O_7$(aq) and excess dilute H_2SO_4 to a 25.0 cm^3 portion of the diluted solution. After allowing the mixture to stand for about an hour at room temperature, the excess $K_2Cr_2O_7$ in the mixture was then titrated with 0.118 mol dm^{-3} $(NH_4)_2Fe(SO_4)_2$(aq) using an appropriate indicator. At the end-point of the titration, he used 12.25 cm^3 of the Fe^{2+}(aq) solution.

(i) Write an ionic equation for the reaction that occurs during titration. [1]

$Cr_2O_7^{2-} + 6Fe^{2+} + 14H^+ \rightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O$

(ii) Calculate the concentration, in mol dm^{-3}, of ethanol in this brand of wine. [4]

mol of excess $Cr_2O_7^{2-}$ = $\frac{1}{6}\times$ mol of Fe^{2+} used in titration

$= \frac{1}{6} \times 0.118 \times \frac{12.25}{1000}$

$= 2.41 \times 10^{-4}$ mol

mol of $Cr_2O_7^{2-}$ added initially = cV = $0.156 \times \frac{25.0}{1000}$

$= 3.90 \times 10^{-3}$ mol

mol of $Cr_2O_7^{2-}$ that react with CH_3CH_2OH = $(3.90 \times 10^{-3}) - (2.41 \times 10^{-4})$

$= 3.66 \times 10^{-3}$ mol

$3CH_3CH_2OH + 2Cr_2O_7^{2-} + 16H^+ \rightarrow 3CH_3CO_2H + 4Cr^{3+} + 11H_2O$

mol of CH_3CH_2OH in 25.0 cm^3 of diluted soln = $\frac{3}{2}\times$ mol of $Cr_2O_7^{2-}$ reacted

$= \frac{3}{2} \times 3.66 \times 10^{-3}$

$= 5.49 \times 10^{-3}$ mol

mol of CH_3CH_2OH in 250 cm^3 of diluted soln = $\frac{250}{25.0} \times 5.49 \times 10^{-3}$

$= 0.0549$ mol

Since 10.0 cm^3 of the sample of spirit was diluted to 250 cm^3,

$\therefore$ mol of CH_3CH_2OH in 10.0 cm^3 of spirit = 0.0549 mol

$\Rightarrow$ [CH_3CH_2OH] in the brand of spirit = $\frac{1000}{10.0} \times 0.0549$

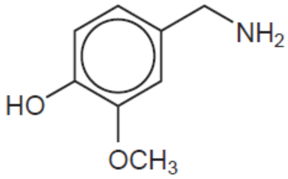
$= 5.49$ mol dm^{-3}

(b) The relatively high alcohol content in wine makes it difficult to pair wine with spicy food because the combination can create a painful burning sensation on the lips and tongue that cannot be wiped or rinsed away.

Capsaicin, $C_{18}H_{27}NO_3$, is the active ingredient in spicy food that gives the hot taste of chilli peppers. The structure of capsaicin can be deduced from the following reactions.

When capsaicin is boiled with dilute sulfuric acid, compound **A**, $C_{10}H_{18}O_2$, and the salt of compound **B**, are produced. Compound **B**, $C_8H_{11}NO_2$, has the structure shown, where the CH_3O– group can be regarded as inert.

compound **B**



When **A** is heated with concentrated acidified $KMnO_4$, compound **C**, $C_6H_{10}O_4$, and compound **D**, $C_4H_8O_2$, are produced. **C** can be prepared from $Br(CH_2)_4Br$ in two steps whereas **D** can be prepared directly from $(CH_3)_2CHCH_2OH$.

Compounds **A**, **C** and **D** all react with aqueous sodium carbonate.

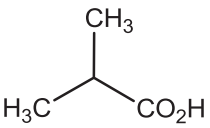
(i) What observations and deductions could be made from the reaction of **A**, **C** and **D** with aqueous sodium carbonate? [2]

effervescence of CO_2 ; A, C and D are acidic/contains –CO_2H group.

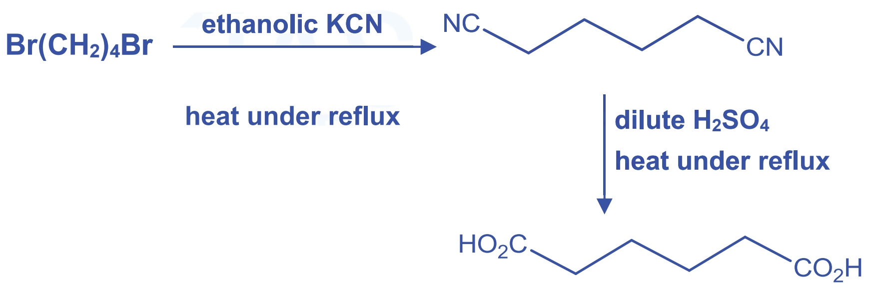
(ii) Draw the structural formula of **D** and state the reagents and conditions required for its preparation from $(CH_3)_2CHCH_2OH$. [2]

$K_2Cr_2O_7$ + dil. H_2SO_4; heat under reflux

D is



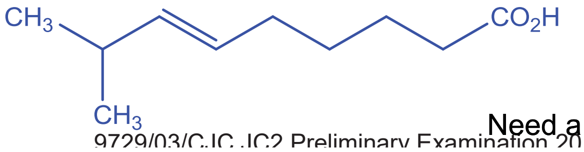
(iii) Show how compound **C** can be prepared from $Br(CH_2)_4Br$, stating clearly the reagents and conditions required for each step, and give the structural formulae of **C** and the intermediate formed. [4]



C

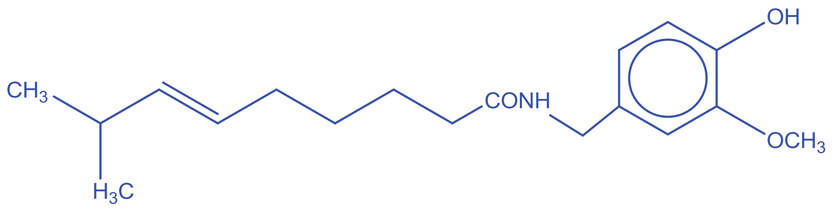
(iv) Hence suggest the structure for **A** and two possible structures for capsaicin. [3]

A is

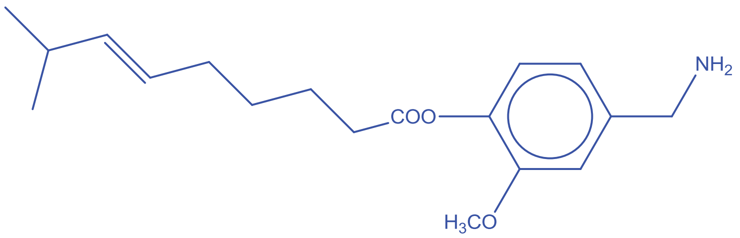


[Turn over

capsaicin is



and



(c) Methanol, CH_3OH, is the simplest alcohol that could be used to power a fuel cell in an electric car.

Figure 1.1 shows a preliminary design of a methanol fuel cell. The fuel and oxygen are fed continuously to the two electrodes which are made of platinum. Methanol is oxidised when the fuel cell is operated.

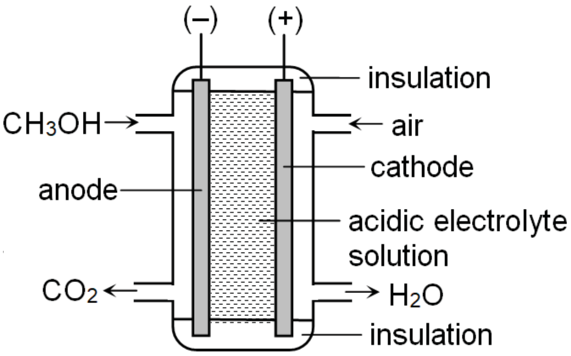


Fig. 1.1

(i) Write balanced equations for the half reactions at each electrode and for the overall cell reaction. [2]

Cathode: $O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$

Anode: $CH_3OH(l) + H_2O \rightarrow CO_2(g) + 6H^+ + 6e^-$

Overall reaction: $2CH_3OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 4H_2O(l)$

(ii) Write a cell representation, indicating clearly on the cell representation the direction of electron flow in the external circuit. [1]

e^- flow

$Pt(s) \mid CH_3OH(l)/CO_2(g) \,//\, O_2(g)/H_2O(l), H^+(aq) \mid Pt(s)$

(iii) Use appropriate data from the *Data Booklet* to explain why an acidic electrolyte is often preferred to an alkaline electrolyte. [1]

In an acidic medium, $E^\ominus_{O_2/H_2O}$ = +1.23 V

In an alkaline medium, $E^\ominus_{O_2/OH^-}$ = +0.40 V

Acidic electrolyte is preferred because oxygen is a stronger oxidising agent in an acidic medium.

(iv) The design of the above fuel cell could be improved by replacing the acidic electrolyte solution with a film of solid H^+ ion-conducting polymer.

Suggest a reason for doing so. [1]

Using a film of solid H^+ ion-conducting polymer as electrolyte would eliminate the possibility of acid leakage from the fuel cell.

(v) Methanol could also be used as fuel in an internal combustion engine.

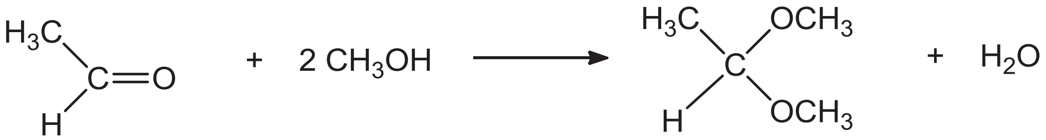
Suggest one advantage of the methanol fuel cell over such an internal combustion engine that uses methanol. [1]

In the methanol fuel cell, there is complete combustion of CH_3OH and so, no C nor CO (atmospheric pollutants) is produced.

[Total: 22]

[Turn over

2 Acetals are molecules that contain 2 –OR groups bonded to the same carbon and are formed when aldehydes are reacted with an alcohol in the presence of an acid. The reaction between ethanal and methanol in the presence of acid, to produce acetal **A** was studied.



acetal **A**

(a) When the initial rate of this reaction was measured at various starting concentrations of ethanal, methanol and H^+, the following results were obtained:

Experiment number	**$[CH_3CHO]$ / mol dm^{-3}**	**$[CH_3OH]$ / mol dm^{-3}**	**$[H^+]$ / mol dm^{-3}**	**relative rate**
1	0.20	0.10	0.05	1.00
2	0.25	0.10	0.05	1.25
3	0.25	0.32	0.05	4.00
4	0.10	0.16	0.10	1.60

(i) Use the data in the table to determine the order with respect to

I ethanal

By inspection

Using experiments 1 and 2,

when $[CH_3CHO]$ increased by 0.25/0.20 = 1.25 times and the concentration of other reactants remain constant, the relative rate increases by 1.25 times.

Order of reaction wrt ethanal = 1

II methanol and

By inspection

Using experiments 2 and 3,

when $[CH_3OH]$ increased by 0.32/0.1 = 3.2 times and the concentration of other reactants remain constant, the relative rate increases by 4.00/1.25 = 3.2 times.

Order of reaction wrt ethanal = 1

III H^+.

[3]

By inspection

Using experiments 1 and 4,

when $[CH_3CHO]$ is halved and $[CH_3OH]$ is increased by 0.16/0.1 = 1.6 times, relative rate should be 0.8 since orders of reaction wrt ethanal and methanol are 1. However, the relative rate is 1.60 which means when the $[H^+]$ is doubled, rate is doubled.

Order of reaction wrt H^+ = 1

Alternatively, mathematical method

Let n be the order of reaction wrt H^+

$\text{rate}_{exp1} = k[\text{ethanal}]_{exp1}[\text{methanol}]_{exp1}[H^+]^n$

$1.00 = k(0.20)(0.10)(0.05)^n$---- (1)
$rate_{exp2} = k[ethanal]_{exp2}[methanol]_{exp2}[H^+]^n$
$1.60 = k(0.10)(0.16)(0.10)^n$---- (2)
(2) ÷ (1)
$1.6 = (0.5)(1.6)(2)^n$
$n = 1$

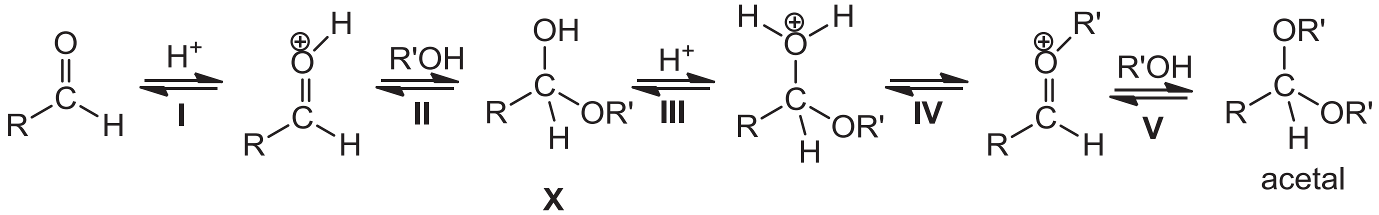
(ii) Use your results from **(a)(i)** to write the rate equation for the reaction. [1]

rate = $k[CH_3CHO][CH_3OH][H^+]$

(iii) Calculate the relative rate of reaction for a mixture in which the starting concentrations of all three reactants are 0.20 mol dm^{-3}. [1]

rate will be 2 × 4 = 8 times as fast as reaction 1 (i.e. relative rate = 8)

(b) The mechanism of acetal formation is proposed to proceed through the following steps.



X

(i) The protonation of the carbonyl group in step **I** is necessary for step **II** to take place. Suggest a reason for this. [1]

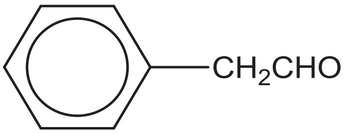
The protonation of the carbonyl group makes the carbonyl carbon more electron deficient (greater partial positive charge on carbonyl carbon) and thus more susceptible for the alcohol to attack.

(ii) Using your answer to **(a)(ii)**, state with reasons, which one is the rate-determining step of the reaction mechanism. [2]
Step II
Based on the rate equation, the slow step should involve 1 molecule of the carbonyl compound, 1 H^+ ion and 1 alcohol molecule

(iii) The species in the mechanism have various roles. They can be reactants, products, catalysts or intermediates. Suggest, with a reason in each case, the roles of H^+ and **X**. [2]
H^+ is a catalyst as H^+ is regenerated in steps II and V

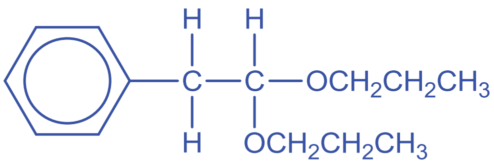
X is an intermediate as it is being produced in step II but used in step III .

(c) Draw the structure of the acetal **B** formed from the reaction between phenylethananl and propan-1-ol.



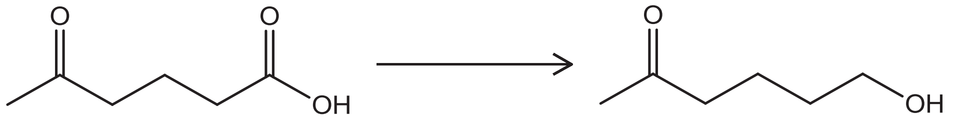
$+ \; 2\,CH_3CH_2CH_2OH \longrightarrow$ acetal **B** $+ \; H_2O$

[1]

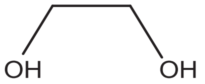


(d) Acetal formation is useful in organic synthesis. When an aldehyde or ketone is converted to an acetal, the carbonyl group is protected from attack by reagents such as bases and reducing agents. The acetal can later be hydrolysed by a strong acid to form the original aldehyde or ketone since the formation of acetals is a reversible reaction.

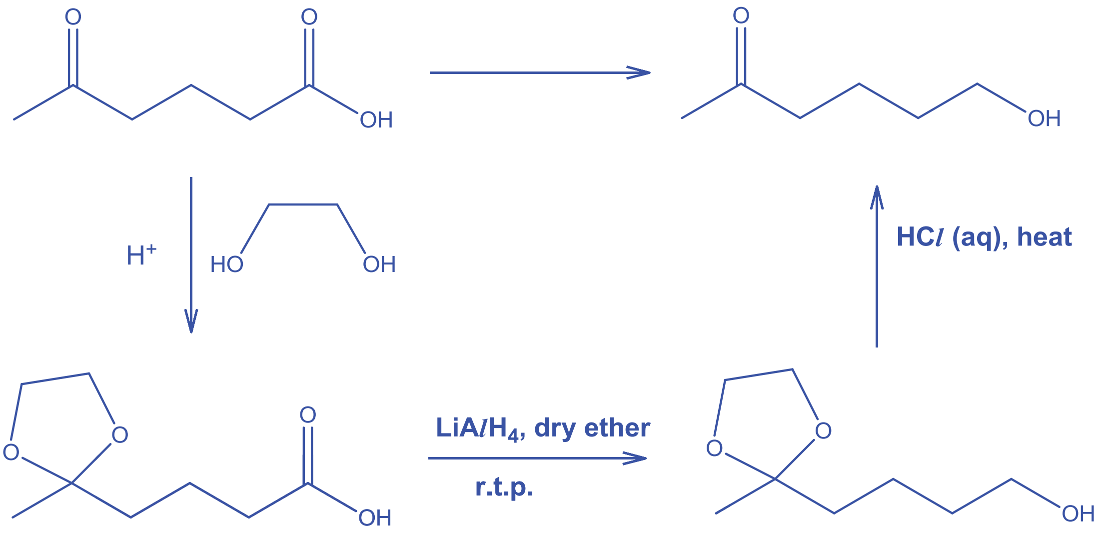
Suggest a suitable synthesis route for the following conversion



which involves the initial formation of an acetal group using ethane-1,2-diol,


.

[2]



(e) Methanol is currently studied as a potential green fuel that greatly reduces the pollution to the environment.

$$CH_3OH(l) + \frac{3}{2}O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$$

(i) The standard molar entropy, $S^\ominus$ is the entropy content of one mole of substance under standard conditions. Given the following standard molar entropy values, calculate the standard entropy change of combustion of methanol. [1]

	$S^\ominus$ /J K^{-1} mol^{-1}
$CH_3OH(l)$	126.8

O_2(g)	205.0
CO_2(g)	213.6
H_2O(*l*)	69.9

$\Delta S_c^\ominus$ $CH_3OH(l)$ = $S^\ominus_{products}$ – $S^\ominus_{reactants}$

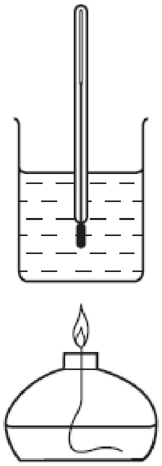
= 213.6 + 2 x 69.9 – (126.8 + 3/2 x 205)

= – 80.9 J K^{-1} mol^{-1}

(ii) Hence, explain the significance of the sign of the standard entropy change of combustion of methanol. [1]

The standard entropy change of combustion reaction has a negative sign. Since the amount of gaseous particles produced is less than the initial amount, there is a decrease in the number of ways to arrange the gaseous particles, giving rise to a decrease in disorder.

(iii) A student carried out an experiment to determine the enthalpy change for the combustion of methanol. A sample of methanol was burnt under laboratory conditions and the following results were obtained by the student.



initial temperature of the water	25.0 °C
final temperature of the water	48.2°C
mass of alcohol burner before burning	259.65 g
mass of alcohol burner after burning	259.15 g
mass of glass beaker and water	150.00 g
mass of glass beaker	50.00 g

Given that the theoretical enthalpy change of combustion of methanol is -726 kJ mol^{-1}, calculate the percentage of heat evolved used to heat up the water. [2]

(Experimental) Heat absorbed by water = (150 – 50)(4.18)(48.2 – 25)

[Turn over

= 9697.6J

Theoretical heat evolved by combustion of methanol = 726 000 x $\frac{0.5}{32}$ = 11343J

% of heat evolved used to heat up the water = 9697.6 / 11343 x 100 = 85.5%

(iv) Using the theoretical enthalpy change of combustion and other relevant information given above, calculate the change in standard Gibbs free energy for the combustion reaction. [1]

$\Delta G_c^o = \Delta H_c^o - T\Delta S_c^o$

$= -726 - (298)(-80.9/1000)$

$= -702$ kJmol^{-1}

(v) Predict and explain the effect on the spontaneity of this reaction of increasing the temperature. [2]

$\Delta G = \Delta H - T\Delta S$

ΔH is negative while -TΔS is positive. Increasing the temperature increases the magnitude of -TΔS and ΔG becomes more positive.
Thus, reaction becomes less spontaneous .

[Total: 20]

3 **(a)** Water pollution is any chemical, physical or biological change in the quality of water that has a harmful effect on any living thing that consumes it. In 2008, a cholera outbreak in Zimbabwe occurred due to a lack of proper water treatment. It is possible to stop the spread of cholera by treating water with chlorine or solid calcium chlorate(I). Calcium chlorate(I), $Ca(ClO)_2$, reacts with water to form chloric(I) acid, $HClO$, which acts as a general biocide.

(i) Write an ionic equation for the reaction of calcium chlorate(I) with water. [1]

$ClO^- + H_2O \rightleftharpoons HClO + OH^-$

(ii) Chloric(I) acid, $HClO$, can also be formed by adding chlorine dioxide gas, ClO_2, to water as shown in the equation below:

$$4ClO_2 + 2H_2O \rightarrow HClO + HClO_3$$

Identify the specific type of reaction that chlorine has undergone by stating the oxidation states of chlorine in the relevant species. [2]

Disproportionation reaction

$$\underset{+4}{4ClO_2} + 2H_2O \rightarrow \underset{+1}{HClO} + \underset{+5}{HClO_3}$$

(iii) An environmental scientist decides to analyse a sample of treated water to find out the amount of chlorine it contains. A 250 cm^3 sample of the chlorine containing water was treated with an excess of potassium iodide solution.

$$Cl_2(aq) + 2I^-(aq) \rightarrow I_2(aq) + 2Cl^-(aq)$$

The sample was subsequently titrated with 12.30 cm^3 of 0.001 mol dm^{-3} sodium thiosulfate solution to find out how much iodine had been formed.

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

Calculate the concentration of Cl_2, in mol dm^{-3}, in the original sample of treated water. [2]

No. of moles of $S_2O_3^{2-}$ $= \frac{12.30}{1000} \times 0.001$

$= 1.23 \times 10^{-5}$ mol

Since $I_2 \equiv 2S_2O_3^{2-}$,

No. of moles of I_2 formed = $\frac{1}{2} \times 1.23 \times 10^{-5}$

$= 6.15 \times 10^{-6}$ mol

[Turn over

Since $Cl_2 \equiv I_2$,

Concentration of $Cl_2 = \frac{1000}{250} \times 6.15 \times 10^{-6}$

$= 2.46 \times 10^{-5}$ mol dm^{-3}

(iv) Suggest a reason why it may be preferable to use calcium chlorate(I) rather than chlorine for treating drinking water. [1]

calcium chlorate(I) is a solid which makes it easier and safer to handle compared to chlorine gas.

or calcium chlorate(I) is more soluble in water than chlorine.

(b) The extraction of aluminium from its ore is highly energy intensive and often results in pollution of the environment. Phosphorus, however, poses a threat to biodiversity in aquatic ecosystems through the depletion of oxygen via the excessive growth and decomposition of aquatic plants and algae.

When heated in chlorine, both aluminium and phosphorus form chlorides.

(i) Describe the observations when a **limited** amount of water is added to the chlorides of aluminium and phosphorus respectively and write equations for any reactions that occur. [2]

$AlCl_3 + 3H_2O \rightarrow Al(OH)_3 + 3HCl$
[white ppt & white fumes observed]

$PCl_5 + H_2O \rightarrow POCl_3 + 2HCl$
[white fumes observed]

(ii) Write equations for any reactions that might occur when an **excess** amount of water is added to the chlorides of aluminium and phosphorus respectively and suggest the pH of each solution formed. [2]

$AlCl_3 + 6H_2O \rightarrow [Al(H_2O)_6]^{3+} + 3Cl^-$

$[Al(H_2O)_6]^{3+} + H_2O \rightleftharpoons [Al(H_2O)_5(OH)]^{2+} + H_3O^+$

pH 3

$PCl_5 + 4H_2O \rightarrow H_3PO_4 + 5HCl$

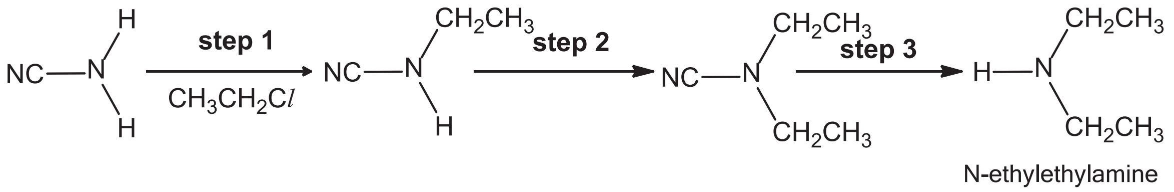
pH 1-2

(c) Cyanamide, CH_2N_2, is a compound commonly used in fertilisers that could also cause eutrophication, which deplete the water's oxygen supply through excessive growth and decomposition of algae and water plants.

$$N\equiv C-NH_2$$

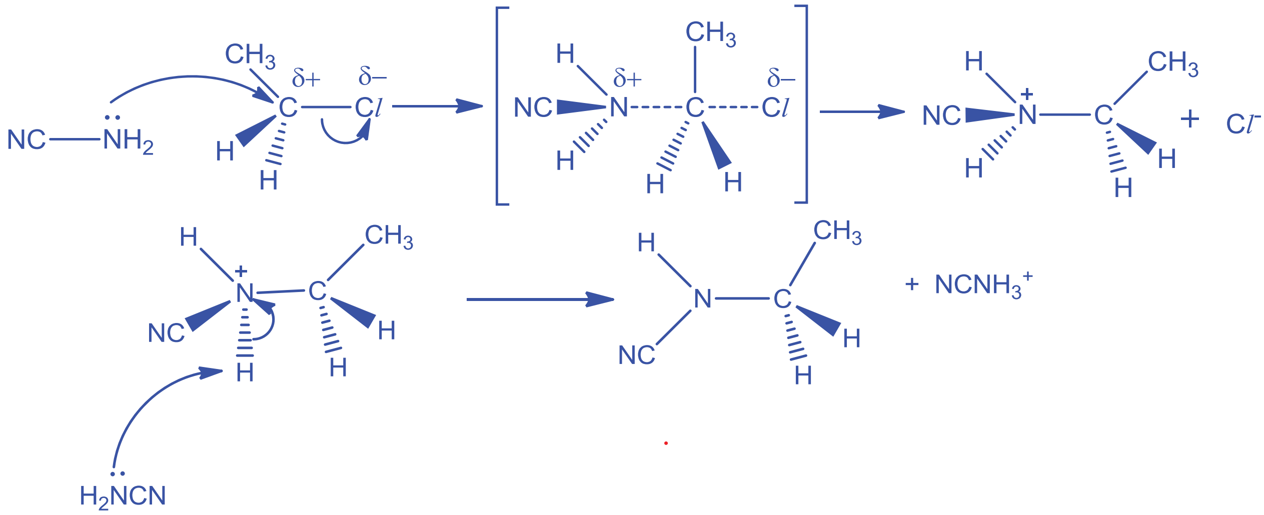
cyanamide

Cyanamide is a useful precursor for the synthesis of secondary amines with a relatively high yield. Below is the sequence of steps for the synthesis of N-ethylethylamine.



(i) Describe the mechanism for the reaction in **step 1**. In your answer, show any relevant charges, lone pairs of electrons and movement of electrons. [4]

Mechanism: Nucleophilic substitution reaction (S_N2)



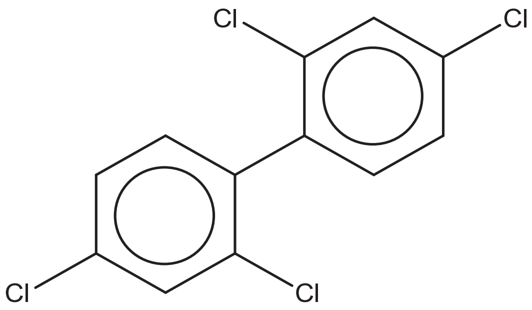
(ii) Identify the two roles of cynnamide in your mechanism. [1]

Nucleophile and Base

(iii) Besides using a specific catalyst and heating under reflux for steps 1 and 2, suggest another condition which would allow a high yield of the intermediate formed in step 2. [1]

Excess CH_3CH_2Cl

(d) 2,2',4,4'-tetrachlorobiphenyl is a common organic pollutant that is immiscible in water.



2,2',4,4'-tetrachlorobiphenyl

Suggest two reasons why 2,2',4,4'-tetrachlorobiphenyl is typically inert and chemically unreactive to nucleophilic reagents. [2]

The p-orbital of the chlorine atoms overlap with the π electron cloud system of the benzene rings. The lone pair of electrons on each C*l* atom is delocalised into the benzene rings. This results in the C–C*l* bond having a partial double-bond character which makes the C–C*l* bond stronger and less ready to undergo reaction.

The C of the C–C*l* bond also has a lower partial positive charge and is less susceptible to nucleophilic attacks.

The π-electron cloud of the benzene ring will repel the lone pair of electrons of an incoming nucleophile, rendering attack of the nucleophile difficult.

[Total: 18]

Section B

Answer **one** question from this section.

4 Transition elements show unique properties that distinguish them from s-block elements, such as calcium. These include variable oxidation states in their compounds, and the formation of coloured complex ions.

(a) Chromium, a transition element, forms two common series of compounds. One containing chromium in the +3 oxidation state while the other containing chromium in +6 oxidation state.

The complex ion $[Cr(OH)_6]^{3-}$ is green whereas the complex ion $[Cr(NH_3)_6]^{3+}$ is purple. Both of these complexes are octahedral.

In an octahedral complex, the d subshell of a transition metal ion is split into two energy levels.

(i) Using the Cartesian axes, like those shown in Fig 4.1, draw fully-labelled diagrams of the following.

- One of the d orbitals at the lower energy level in an octahedral complex. Label this diagram 'lower'.
- One of the d orbitals at the upper energy level in an octahedral complex. Label this diagram upper.

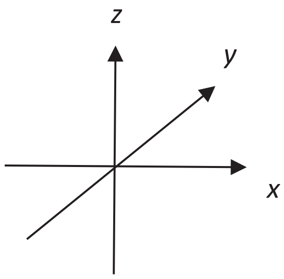
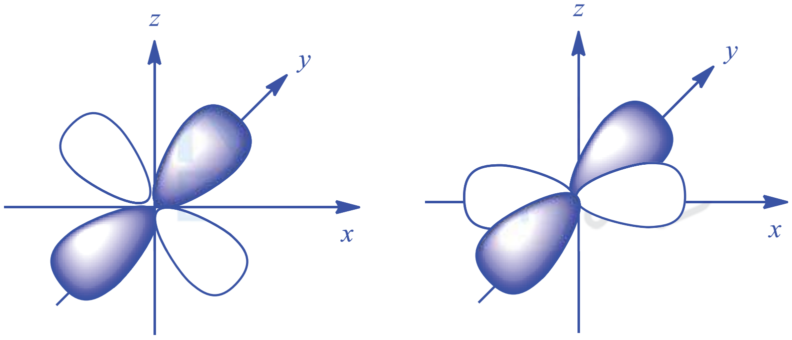


Fig. 4.1

[2]



lower d-orbital upper d-orbital

[Turn over

(ii) Explain why splitting of the d-subshell occurs in an octahedral complex, using your d orbital diagrams in **(a)(i).** [2]

During formation of an octahedral complex, the ligands would approach the central metal ion with partially filled d-subshell along the x, y and z axes.

As the ligands would approach the $d_{x^2-y^2}$ and d_{z^2} orbitals 'head-on' (along the x, y and z axes), the inter-electronic repulsion is stronger between the ligands and the d_{z^2} and $d_{x^2-y^2}$ orbitals.

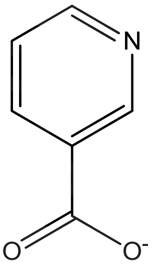
The ligands approach the d_{xy}, d_{xz} and d_{yz} orbitals between the orbital lobes (between the x, y and z axes). Hence the inter-electronic repulsion is not as strong between the ligands and the d_{xy}, d_{xz} and d_{yz} orbitals.

Hence the splitting of the degenerate d orbitals into two slightly different energy levels with a small energy gap will occur.

(iii) By considering your answer to **(a)(ii)**, suggest why $[Cr(OH)_6]^{3-}$ and $[Cr(NH_3)_6]^{3+}$ have different colours. [1]

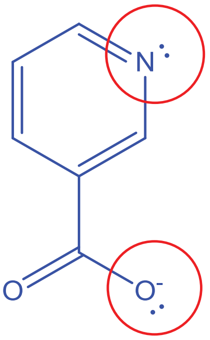
$[Cr(OH)_6]^{3-}$ complex has a different d-d* energy gap from $[Cr(NH_3)_6]^{3+}$ complex, hence visible light of different wavelength / frequency is absorbed during d-d* transition in both complexes.

(b) Chromium(III) nicotinate is commonly used as chromium supplementation for medical conditions associated with diabetes mellitus type 2. This octahedral complex contains three nicotinate ions per chromium ion. The nicotinate ion has the structure shown below.



nicotinate ion

(i) Copy the structure of nicotinate ion and circle the atoms that are bonded to chromium(III) ion. Explain your choice of atoms. [2]



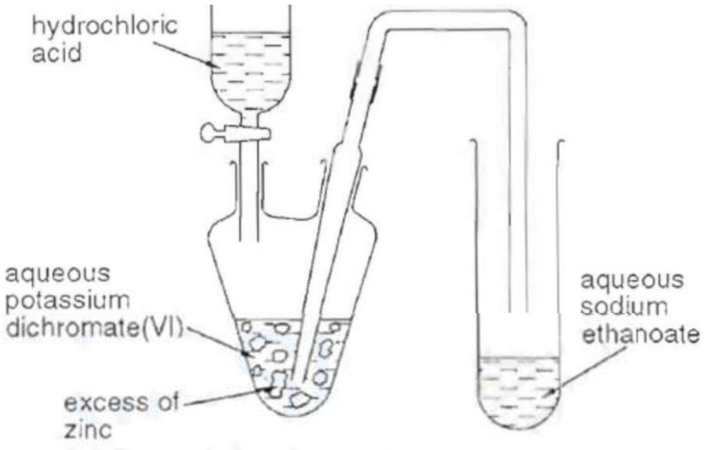
Presence of lone pairs of electrons on both N and O^- which allows nicotinate ion to <u>donate two lone pairs of electrons</u> to form a stable 6-membered ring structure with the central Cr^{3+} ion.

(ii) What is the overall charge of this complex? [1]

0 / no charge

(c) Chromium-containing compounds are useful reagents in the laboratory.

The apparatus and reagents shown in the diagram are used to prepare chromium(II) ethanoate, which is a reducing agent.



All the acid is added to the dichromate solution and the zinc in the flask. The tap funnel is left open. The flask is shaken and chromium soon reaches the Cr^{3+} state.

(i) Write balanced equations for the **two** reactions involving zinc which take place initially in the flask. [2]

[Turn over

$Zn + 2HCl \rightarrow ZnCl_2 + H_2$

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

$(Zn \rightarrow Zn^{2+} + 2e^-) \times 3$

$Cr_2O_7^{2-} + 3Zn + 14H^+ \rightarrow 2Cr^{3+} + 3Zn^{2+} + 7H_2O$

The colour of the solution in the flask subsequently changes as $Cr^{2+}(aq)$ is produced.

(ii) Using relevant redox potential values in the *Data Booklet*, show why the reduction of Cr^{3+} to Cr^{2+} is likely to proceed. [2]

$Cr^{3+} + e^- \rightleftharpoons Cr^{2+}$ $E^\ominus = -0.41$ V (less negative)

$Zn^{2+} + 2e^- \rightleftharpoons Zn$ $E^\ominus = -0.76$ V

Since $E^\ominus_{Cr3+/Cr2+}$ is less negative than $E^\ominus_{Zn2+/Zn}$,

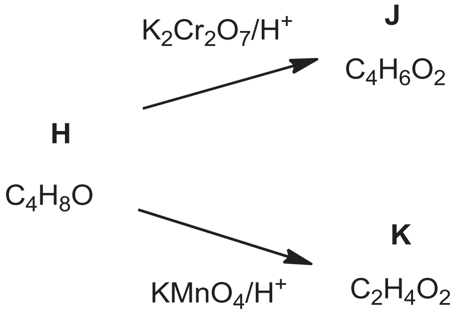
$E^\ominus_{cell} = -0.41 - (-0.76) = +0.35$ V > 0 (spontaneous reaction)

The tap funnel is subsequently closed and the liquid in the flask forced over into the tube containing the aqueous sodium ethanoate to form chromium(II) ethanoate.

(iii) By considering your answers to **(c)(i)**, suggest what causes the liquid to be forced over into the tube. [1]

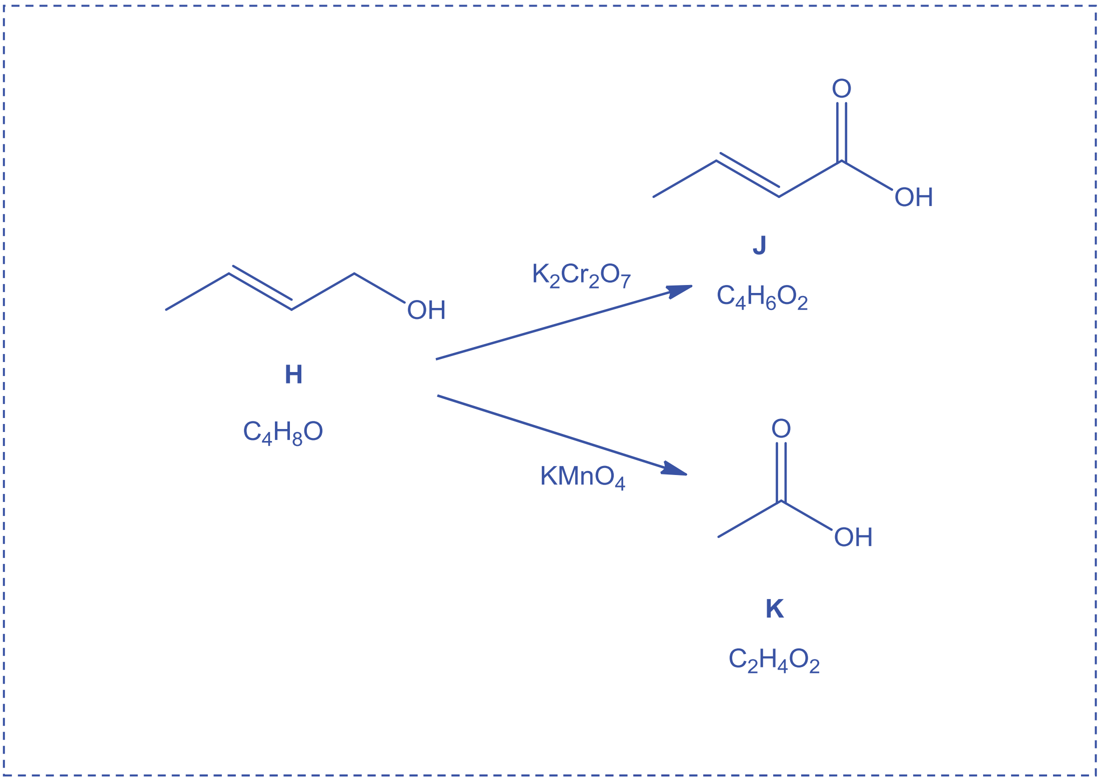
Build-up of pressure from the formation of $H_2(g)$ caused liquid to be forced over.

(d) Another chromium-containing compound, $K_2Cr_2O_7$, together with $KMnO_4$ are common oxidising agents used in organic synthesis. $KMnO_4$ is the more powerful of the two, as shown by the following scheme.

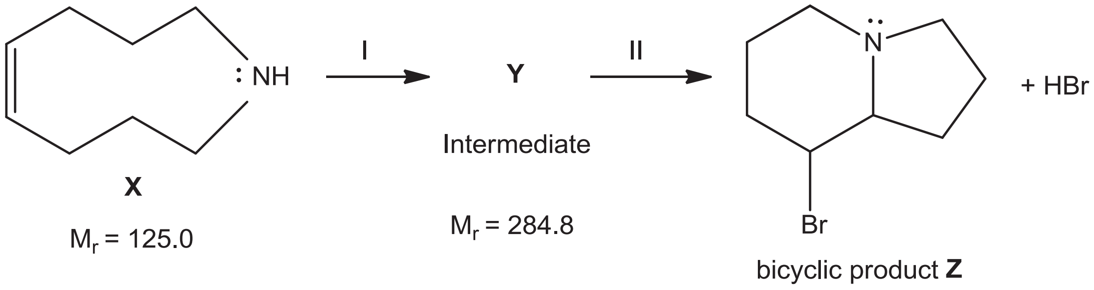


All three compounds, **H**, **J** and **K** react with sodium metal. **J** and **K** react with Na_2CO_3, but **H** does not. **H** and **J** decolourise aqueous bromine.

Suggest structures for **H**, **J** and **K**. [3]

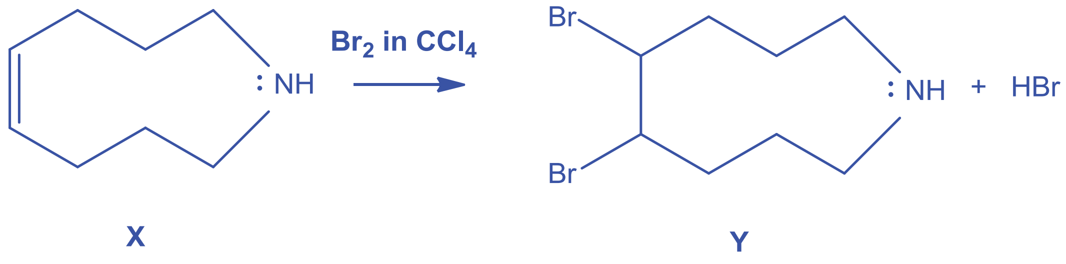


(e) The bicyclic product **Z** shown below can be formed from **X** in the following scheme:

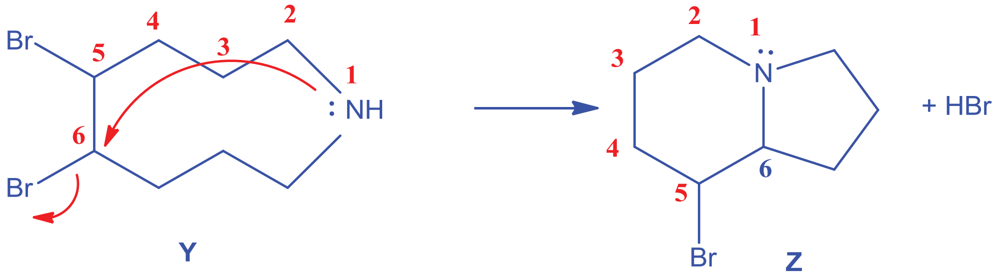


[Turn over

(i) Suggest reagents and conditions for Step I and the structure of **Y**. [2]



(ii) Given that Step II is an intramolecular reaction, explain the conversion of **Y** into **Z**, drawing curly arrows to show the movement of electron pair where necessary. State the type of reaction in Step II. [2]



intramolecular **nucleophilic substitution** occurs

[Total: 20]

5 Hydroformylation is used commercially for producing aldehydes from alkenes. The aldehyde produced is then converted into other organic compounds.

Butanal is synthesised from propene from the following hydroformylation reaction at 500 K.

$$CH_3CH{=}CH_2(g) + CO(g) + H_2(g) \rightleftharpoons CH_3CH_2CH_2CHO(g) \qquad \Delta H < 0$$

(a) An equimolar mixture of $CH_3CH{=}CH_2$, CO and H_2 at an initial total pressure of 150 atm is allowed to reach dynamic equilibrium. Figure 5.1 below shows the graphs of partial pressure of $CH_3CH{=}CH_2$ and $CH_3CH_2CH_2CHO$ against time.

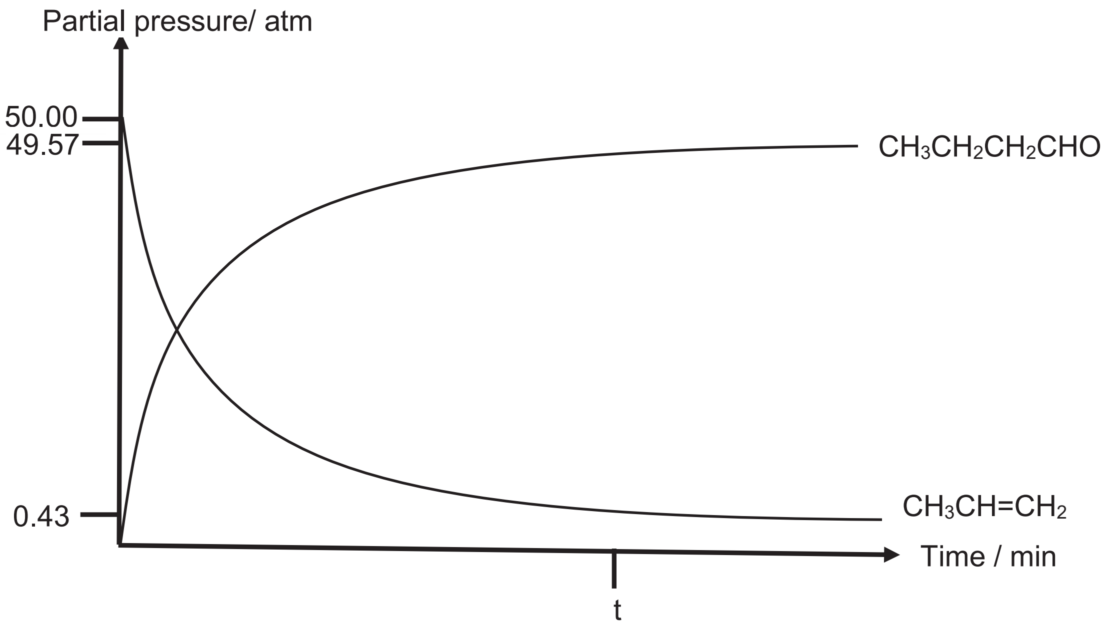


Figure 5.1

(i) Define the term *dynamic equilibrium*. [1]

Dynamic equilibrium refers to a reversible reaction in which the rates of forward and reverse reactions have become equal and there is no change in the concentration of the reactants and the products.

(ii) Write an expression for K_p for the above reaction. [1]

$$K_p = \frac{P_{CH3CH2CH2CHO}}{(P_{CH3CH=CH2})(P_{CO})(P_{H2})}$$

[Turn over

(iii) Using Figure 5.1 above, calculate K_p for the hydroformylation reaction at 500 K, stating its units. [3]

	$CH_3CH=CH_2(g)$ +	$CO(g)$ +	$H_2(g)$	$\rightleftharpoons$	$CH_3CH_2CH_2CHO(g)$
Initial Partial Pressure/ atm	**50**	**50**	**50**		**0**
Change in partial pressure/ atm	**- 49.57**	**- 49.57**	**- 49.57**		**+ 49.57**
Equilibrium Partial Pressure/ atm	**0.43**	**0.43**	**0.43**		**49.57**

$$K_p = \frac{49.57}{(0.43)(0.43)(0.43)} = 623.46\ \text{atm}^{-2}$$

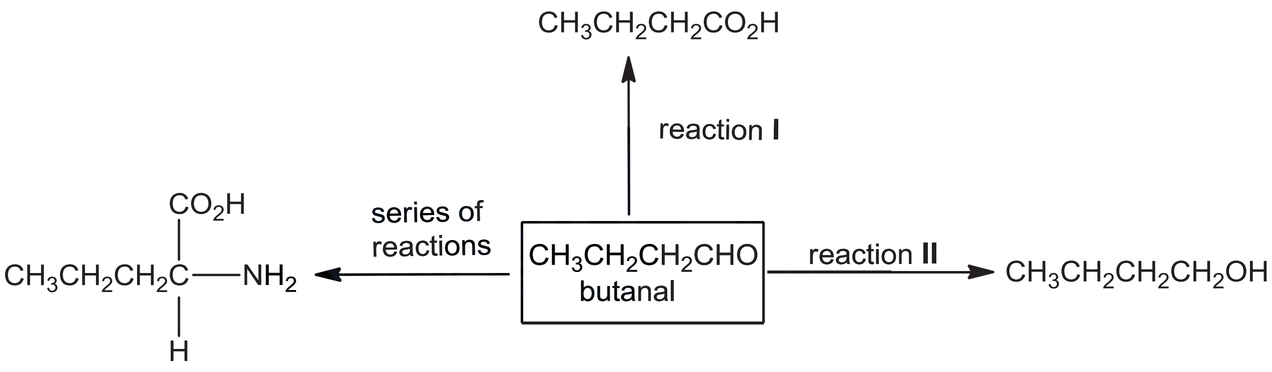
$$= 623\ \text{atm}^{-2}$$

(iv) State how the graphs of partial pressure against time for $CH_3CH=CH_2$ and $CH_3CH_2CH_2CHO$ would differ from that shown in Figure 5.1 when the experiment is repeated at a higher temperature. [2]

The gradients of the graphs will be steeper Or the equilibrium will be established at a shorter time (before time t).

The equilibrium partial pressure of $CH_3CH_2CH_2CHO$ would decrease while the equilibrium partial pressure of $CH_3CH=CH_2$ will increase.

Butanal, synthesised from hydroformylation reaction, can undergo further reactions as shown in the reaction scheme below.



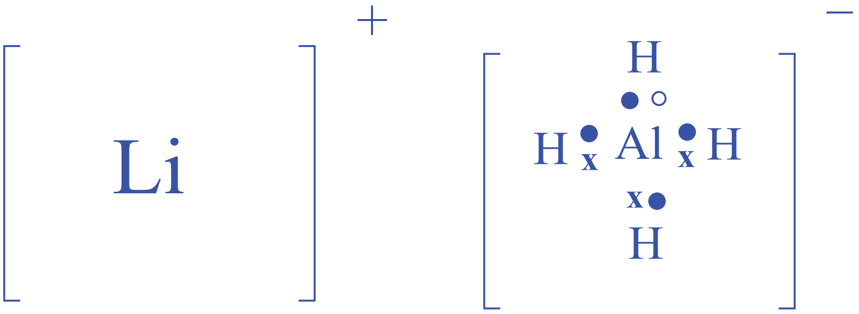
Compound **X**

(b) From reaction **I** above, butanoic acid is produced. Comment on the difference in the solubility of butanal and butanoic acid in water. [2]

Butanoic acid is more soluble than butanal. Butanoic acid molecules contains both electron deficient H atoms as well as highly electronegative O atoms with lone pair of electrons, therefore they are able to form more extensive hydrogen bonds with water molecules on average as compared to butanal molecules which only contains highly electronegative O atoms with lone pair of electrons.

(c) In reaction **II**, butanal is reduced to give butan-1-ol. One of the commonly used reducing agents is lithium aluminium hydride, $LiAlH_4$, which is usually dissolved in dry ether.

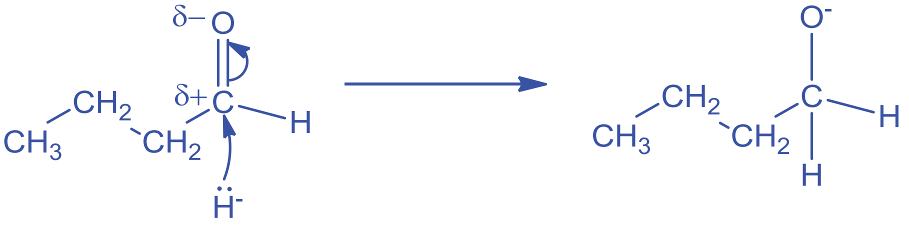
(i) Given that $LiAlH_4$ exist as $Li^+[AlH_4]^-$, draw the dot-and-cross diagram for $LiAlH_4$. [1]



(ii) The reaction between $LiAlH_4$ and butanal to form butan-1-ol happens in two-steps.

The first step involves a nucleophilic addition reaction between the hydride ion, H^-, from $LiAlH_4$ and butanal to form an anion.
The second step involves the protonation of the anion to form butan-1-ol.

Using the information above, show how the anion in the first step is formed with the use of curly arrows showing the movement of electrons and charges. [2]



(iii) Other than $LiAlH_4$, $NaBH_4$ can also be used to convert butanal to butan-1-ol. By considering the chemical bonds in $LiAlH_4$ and $NaBH_4$, suggest why $LiAlH_4$ is a more powerful reducing agent $NaBH_4$. [1]

The size of Al atom is larger compared to B and the orbital overlap of Al and H is less effective. Thus the bond length of Al–H bond is longer than that of B–H bond and less energy is required to break the weaker Al–H bond, resulting in a greater ease of generating the H^- nucleophile. Or There is greater electronegativity difference between Al and H than B and H, therefore the tendency of forming H^- is higher in $LiAlH_4$ than $NaBH_4$.

[Turn over

(iv) State a reason why $LiAlH_4$ cannot be used to reduce alkenes even though it is a powerful reducing agent. [1]

The electron rich C=C will not attract the H^- nucleophiles.

(v) Expain how the rate of the reaction in **(c)(ii)** would differ if butanone is used in place of butanal. [2]

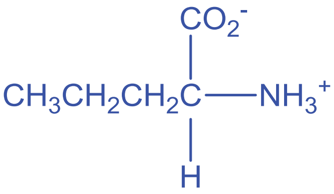
The rate of reaction will be slower with butanone.

In butanone, there are two electron-donating alkyl groups directly attached to the carbonyl carbon. Hence the partial positive charge on the carbonyl carbon in butanone is less pronounced than that in butanal which only has 1 alkyl group.

Or

The presence of 2 alkyl groups in butanone contributes to greater steric hindrance.

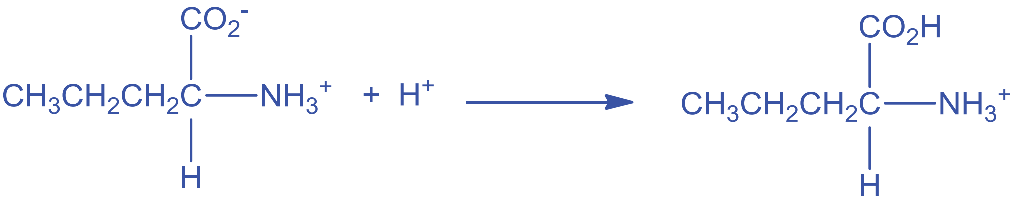
(d) Draw the structure of the predominant form produced when compound **X** is in an aqueous solution of pH 7. [1]



$CH_3CH_2CH_2C(H)(CO_2^-)-NH_3^+$

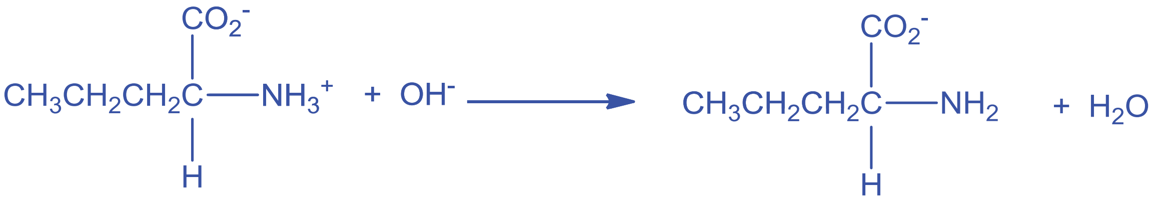
(e) Write two equations to show how the solution in **(d)** is able to resist the change in pH upon addition of small amounts of acid and base. [2]

When small amounts of acid is added,



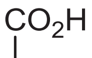
$CH_3CH_2CH_2C(H)(CO_2^-)-NH_3^+ + H^+ \longrightarrow CH_3CH_2CH_2C(H)(CO_2H)-NH_3^+$

When small amounts of base is added,



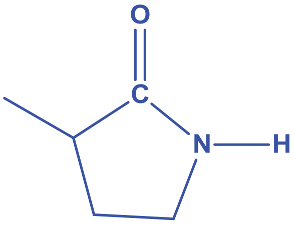
$CH_3CH_2CH_2C(H)(CO_2^-)-NH_3^+ + OH^- \longrightarrow CH_3CH_2CH_2C(H)(CO_2^-)-NH_2 + H_2O$

(f) Compound **Y** is an isomer of compound **X**. Draw the structural formula of the **final** product when compound **Y** reacts with PCl_5. [1]



CO_2H

Final product formed:



[Total: 20]

[Turn over

Catholic Junior College
JC2 Preliminary Examinations
Higher 2

CANDIDATE NAME	
CLASS	2T

CHEMISTRY

9729/04

Paper 4 Practical

16 August 2017

2 hour 30 minutes

Candidates answer on the Question Paper.

Additional Materials: As listed in the Confidential Instructions

READ THESE INSTRUCTIONS FIRST

Write your name and class 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 15 and 16.

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

Shift
Laboratory

For Examiner's Use	
1	
2	
3	
Total	

Suggested Solutions

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

[Turn over

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

1 'Washing soda' is made from crystals of sodium carbonate, which contains 62.94 % water and 37.06 % sodium carbonate. When stored, these crystals lose some of the water in the crystals to the atmosphere.

FA 1 is solid 'washing soda', originally sodium carbonate decahydrate, $Na_2CO_3.10H_2O$.
FA 2 is 0.100 mol dm^{-3} hydrochloric acid, HC*l*.

In this question, you will perform a titration to determine the amount of water in **FA 1** that has been lost to the atmosphere.

(a) Method

(i) Preparation of FA 3

- Weigh the 100 cm^3 beaker provided. Record the mass in the space below.
- Tip the 'washing soda' crystals, **FA 1**, into the beaker. Weigh the beaker with **FA 1** and record the mass.
- Calculate the mass of **FA 1** used and record this in the space below.
- Add distilled water to the beaker to dissolve the crystals. Carefully transfer the solution to a 250 cm^3 graduated (volumetric) flask labelled **FA 3**. Wash the beaker twice with small quantities of water and add these washings to the volumetric flask.
- Make the solution up to the mark using distilled water. Stopper the flask and invert a number of times to ensure thorough mixing.

mass of beaker + **FA1** / g	**21.138**
mass of beaker / g	**17.746**
mass of **FA 1** used / g	**3.392**

[1]

(ii) Titration of FA 3 against FA 2

- Fill the burette with **FA 2**.
- Pipette 25.0 cm^3 of **FA 3** into a conical flask and add a few drops of the indicator provided.
- Titrate the solution with **FA 2**. Record your results in the space provided on page **3**. Make certain that the recorded results show the precision of your practical work.
- Repeat the titration until consistent results are obtained.

Titration Results:

	1	2
final burette reading / cm^3	28.50	30.50
initial burette reading / cm^3	3.00	5.00
volume of FA 2 used / cm^3	25.50	25.50
	✓	✓

[6]

(iii) 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 = $\frac{25.50+25.50}{2}$

= 25.50 cm^3

volume of **FA 2** = ……25.50 cm^3………… [1]

(b) **(i)** Calculate the amount of hydrochloric acid run from the burette.

mol of HC*l* = cV = 0.100 × $\frac{25.50}{1000}$

= 2.55 x 10^{-3} mol

amount of HC*l* =……2.55 x 10^{-3} mol……… [1]

(ii) Sodium carbonate reacts with hydrochloric acid as follows.

$Na_2CO_3(aq) + 2HCl(aq) \rightarrow 2NaCl(aq) + CO_2(g) + H_2O(l)$

Calculate the amount of sodium carbonate, Na_2CO_3, in 250 cm^3 of **FA 3**.

mol of Na_2CO_3 in 25.0 cm^3 of FA3 = $\frac{1}{2}$ × mol of HC*l*

= $\frac{1}{2}$ × 2.55 x 10^{-3}

= 1.275 x 10^{-3} mol

mol of Na_2CO_3 in 250 cm^3 of FA 3 = $\frac{250}{25.0}$ × 1.275 x 10^{-3}

= 1.275 x 10^{-2} mol

amount of Na_2CO_3 in 250 cm^3 of **FA 3** =……1.275 x 10^{-2} mol……… [2]

(iii) Calculate the mass of sodium carbonate, Na_2CO_3, dissolved in 250 cm^3 of **FA 3**.
[A_r: C, 12.0; O, 16.0; Na, 23.0]

M_r of Na_2CO_3 = 2(23.0) + 12.0 + 3(16.0) = 106.0

mass of Na_2CO_3 in 250 cm^3 FA 3 = nM_r = (1.275 x 10^{-2}) x 106.0
= 1.351 g

mass of Na_2CO_3 in 250 cm^3 of **FA 3** =……**1.351 g**………...… [1]

(iv) Calculate the mass of water present in the washing soda crystals.

mass of water = mass of FA 1 – mass of Na_2CO_3 in 250 cm^3 of FA 3
= 3.392 – 1.351
= 2.041 g

mass of water =……**2.041 g**………...… [1]

(v) Hence calculate the percentage of water in the sodium carbonate crystals, **FA 1**.

% of water = $\frac{2.041}{3.392}$ x 100

= 60.2 %

percentage of water in **FA 1** =……**60.2 %**………...… [1]

(c) The maximum error for a 25 cm^3 pipette commonly used in schools is ±0.06 cm^3.
The maximum error in any single burette reading is ±0.05 cm^3.

Calculate the maximum percentage error in each of the following.

(i) The volume of **FA 3** pipetted into the conical flask.

max % error = $\frac{0.06}{25.0}$ × 100 = $\underline{0.240\ \%}$

maximum percentage error in pipette volume =……**0.240**………...… %

(ii) The titre volume calculated in **(a)(iii)**.

max % error = $\frac{(2\times0.05)}{25.50}$ × 100 = $\underline{0.392\ \%}$

maximum percentage error in titre volume =……**0.392**………...… %
[2]

[Total: 16]

2 The enthalpy change for the reaction of sodium carbonate, Na_2CO_3, with water and carbon dioxide to form sodium hydrogencarbonate, $NaHCO_3$ cannot be determined directly. However both $Na_2CO_3(s)$ and $NaHCO_3(s)$ react with dilute hydrochloric acid.

Reaction 1 $NaHCO_3(s) + HCl(aq) \rightarrow NaCl\,(aq) + H_2O(l) + CO_2(g)$ ΔH_1

Reaction 2 $Na_2CO_3(s) + 2HCl(aq) \rightarrow 2NaCl\,(aq) + H_2O(l) + CO_2(g)$ ΔH_2

In this experiment you will determine the enthalpy change ΔH_1 for **reaction 1** and ΔH_2 for **reaction 2**, and then use your results to calculate ΔH_3 for the reaction:

$$Na_2CO_3(s) + H_2O(l) + CO_2(g) \rightarrow 2NaHCO_3(s) \qquad \Delta H_3$$

FA 4 is sodium hydrogen carbonate, $NaHCO_3$.
FA 5 is sodium carbonate, Na_2CO_3.
FA 6 is 2.0 mol dm^{-3} hydrochloric acid, HCl.

(a) Method

(i) Experiment 1: $NaHCO_3(s) + HCl(aq) \rightarrow NaCl\,(aq) + H_2O(l) + CO_2(g)$

- Use a measuring cylinder to transfer 25 cm^3 of the acid, **FA 6**, into the plastic cup supported in a 250 cm^3 beaker. The acid is in excess.
- Weigh the container with **FA 4** and record the balance reading.
- Place the thermometer in the acid and record its temperature at 1 minute interval for the first two minutes.
- At 2½ minutes, carefully tip all the **FA 4**, in small portions, into the acid and stir to dissolve.
- Record the temperature of the solution at 1 minute interval from 3 minutes up to 8 minutes.
- Reweigh the container with any residual **FA 4** and record the balance reading and the mass of **FA 4** used.
- Rinse out the plastic cup and shake it to remove excess water.

Results

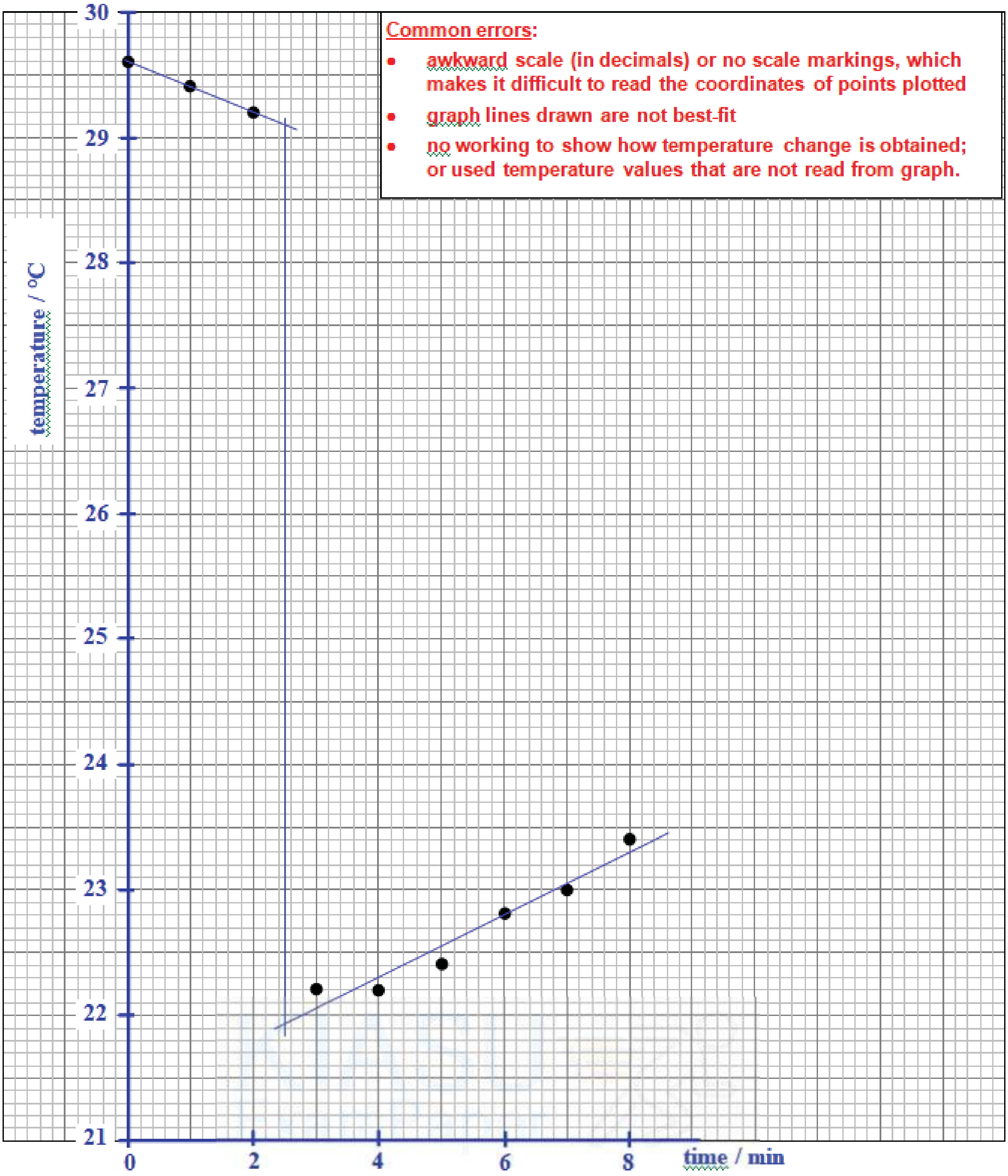
Record **all** weighings and temperature readings in the space below.

mass of container + **FA 4** / g	**5.976**
mass of container + residual **FA 4** / g	**3.489**
mass of **FA 4** used / g	**2.487**

time / min	0	1	2	3	4	5	6	7	8
temperature / °C	29.6	29.4	29.2	22.2	22.2	22.4	22.8	23.0	23.4

[5]

(ii) Plot on the grid below, a graph of temperature on the *y*-axis against time on the *x*-axis. The scale for the temperature should extend at least 1°C below the lowest recorded temperature.



Common errors:

- awkward scale (in decimals) or no scale markings, which makes it difficult to read the coordinates of points plotted
- graph lines drawn are not best-fit
- no working to show how temperature change is obtained; or used temperature values that are not read from graph.

Draw two straight lines of best fit and extrapolate the two lines to 2½ minutes. Determine the change in temperature at this time.

temperature change = 29.10 – 21.95 = 7.15 °C

temperature change at 2½ minutes = ...7.15......... °C

[4]

(iii) **Experiment 2**: $Na_2CO_3(s) + 2HCl(aq) \rightarrow 2NaCl(aq) + H_2O(l) + CO_2(g)$

- Use a measuring cylinder to transfer 25 cm^3 of the acid, **FA 6**, into the plastic cup supported in a 250 cm^3 beaker. The acid is in excess.
- Weigh the container with **FA 5** and record the balance reading.
- Place the thermometer in the acid and record its initial temperature.
- Carefully tip all the **FA 5**, in small portions, into the acid and stir to dissolve.
- Record the highest temperature reached.
- Reweigh the container with any residual **FA 5** and record the balance reading and the mass of **FA 5** used.

Results

Record **all** weighings and temperature readings in the space below.

mass of container + **FA 5** / g	**5.535**
mass of container + residual **FA 5** / g	**3.521**
mass of **FA 5** used / g	**2.014**
initial temperature of **FA 5** / °C	**30.0**
highest temperature / °C	**35.7**
temperature rise / °C	**5.7**

[3]

(b) **(i)** Using your answer to **2(a)(ii)**, calculate the heat energy absorbed when **FA 4** was added to the acid in **Experiment 1**.
[Assume that 4.3 J of heat energy changes the temperature of 1.0 cm^3 of solution by 1.0 °C.]

heat absorbed $= mc\,\Delta T$

$= 25 \times 4.3 \times 7.15$

$= 768.6$ J

heat energy absorbed =……**768.6**…… J [1]

(ii) Calculate the enthalpy change, in kJ mol^{-1}, when 1 mol of **FA 4**, $NaHCO_3$, reacts with the acid. [A_r: H, 1.0; C, 12.0; O, 16.0; Na, 23.0]

M_r of $NaHCO_3$ $= 23.0 + 1.0 + 12.0 + 3(16.0) = 84.0$

mol of $NaHCO_3 = \frac{2.487}{84.0} = 0.0296$ mol

$\therefore \quad \Delta H_1 = +\frac{768.6}{0.0296}$ J mol^{-1}

$= +25970$ J mol^{-1}

$= +26.0$ kJ mol^{-1}

enthalpy change, ΔH_1 = ……**+26.0**…… kJ mol^{-1} [1]

(iii) Using your results in **2(a)(iii)**, calculate the heat energy produced when **FA 5** was added to the acid in **Experiment 2**.
[Assume that 4.3 J of heat energy changes the temperature of 1.0 cm^3 of solution by 1.0 °C.]

heat evolved = mc ΔT

= 25 × 4.3 × 5.7

= 612.8 J

heat energy produced =……**612.8**……... J [1]

(iv) Calculate the enthalpy change, in kJ mol^{-1}, when 1 mol of **FA 5**, Na_2CO_3, reacts with the acid. [A_r: C, 12.0; O, 16.0; Na, 23.0].

M_r of Na_2CO_3 = 2(23.0) + 12.0 + 3(16.0) = 106.0

mol of Na_2CO_3 = $\frac{2.014}{106.0}$ = 0.0190 mol

$\therefore \quad \Delta H_2 = -\frac{612.8}{0.0190}$ Jmol^{-1}

$= -$ 32250 J mol^{-1}

$= -$ 32.3 kJ mol^{-1}

enthalpy change, ΔH_2 = ...**–32.3**........... kJ mol^{-1} [1]

(v) Using your answers to **2(b)(ii)** and **2(b)(iv)** and the equations for **Experiment 1** and **Experiment 2**, determine the enthalpy change for the reaction:

$$\begin{tikzcd}
Na_2CO_3(s) + H_2O(l) + CO_2(g) \arrow[r] \arrow[dr, "+ 2HCl(aq)", "\Delta H_2"'] & 2NaHCO_3(s) \arrow[d, "+ 2 HCl(aq)"', "2\Delta H_1"] \\
& 2NaCl(aq) + 2H_2O(l) + 2CO_2(g)
\end{tikzcd}$$

By Hess' Law,

$\Delta H = \Delta H_2 - 2\Delta H_1$

$= (-32.3) - 2(+26.0)$

$= -84.3$ kJ mol^{-1}

enthalpy change, ΔH_3 = ...**–84.3**............. kJ mol^{-1} [3]

(c) **Planning**

You are provided with **FA 4**, solid sodium hydrogencarbonate, $NaHCO_3$, distilled water and apparatus commonly found in the school laboratory.

Using only these materials, you are to plan an additional experiment to determine a further enthalpy change, ΔH_4, which can be put together with those from **Experiment 1** and **Experiment 2** to determine the enthalpy change for the reaction:

$$Na_2CO_3(s) + H_2O(l) + CO_2(g) \rightarrow 2NaHCO_3(aq) \qquad \Delta H_5$$

In your plan, you should include details of:

- the quantity of reactants and apparatus that you would use,
- the procedure you would follow,
- the measurements you would take, and
- an outline of how you would use your results to determine ΔH_5.

DO NOT CARRY OUT YOUR PLAN.

Plan

- **Weigh a sample (say, 2.50 g of FA 4), adds to known volume of water (say, 25 cm^3) and measure change in temperature (record initial temperature of water (T_i) and lowest temperature (T_f) reached on adding FA 4 to water).**

Treatment of results

Let mass of FA 4 added be m_1 g

temperature change, $\Delta T = (T_f) - (T_i) = x$ °C

heat energy absorbed = $mc\Delta T = (25)(4.3)(x)$ J = $108x$ J

mol of $NaHCO_3$ = $\frac{m_1}{84.0}$ mol

$$\Delta H_4 = \frac{\text{energy absorbed}}{\text{mol of NaHCO}_3} = +\frac{108x}{m_1/84.0}\ \text{J mol}^{-1} = +9072\frac{x}{m_1}\ \text{J mol}^{-1} = +9.07\frac{x}{m_1}\ \text{kJ mol}^{-1}$$

From (b)(iv), $Na_2CO_3(s) + H_2O(l) + CO_2(g) \rightarrow 2NaHCO_3(s) \qquad \Delta H_3 = -84.3\ \text{kJ mol}^{-1}$

$NaHCO_3(s) \rightarrow NaHCO_3(aq) \qquad \Delta H_4 = +9.07\frac{x}{m_1}\ \text{kJ mol}^{-1}$

$Na_2CO_3(s) + H_2O(l) + CO_2(g) \rightarrow 2NaHCO_3(aq) \qquad \Delta H_5$

$$\therefore \quad \Delta H_5 = \Delta H_3 + 2\Delta H_4$$

$$= -83.4 + 2(+9.07\frac{x}{m_1}) = (-83.4 + 18.1\frac{x}{m_1})\ \text{kJ mol}^{-1}$$

[5]

[Total: 24]

3 Qualitative Analysis

In this question, you will carry out tests, make observations and come to conclusions about the compounds.

If the evolution of a gas is observed at any stage, the gas should be tested and identified. Details of the test carried out, the observations from the test and the identity of the gas should be given with the observations.

If it appears that no reaction has taken place, this should be clearly recorded

(a) **FA 7** is an organic solid. Carry out the tests described in Table 3.1 and use the observations to identify two functional groups present in **FA 7**.

Table 3.1

tests	*observations*
Add 10 cm^3 of ethanol to your **FA 7** in a boiling tube. Stopper the boiling tube and shake to dissolve the solid. Then add 10 cm^3 of deionised water. Shake again to ensure complete mixing. Divide the solution into four clean test-tubes and use a fresh tube for each of the following tests:	
(i) add a piece of magnesium ribbon to the solution	**brisk effervescence;** **gas gives a "pop" sound with a lighted splint.** **$H_2(g)$ evolved.** ***Need to include identity of gas***
(ii) add solid sodium carbonate to the solution	**effervescence;** **gas gives a white ppt with limewater.** **$CO_2(g)$ evolved.** ***Need to include identity of gas***
(iii) add a few drops of aqueous iron(III) chloride to the solution	**violet (or purple) coloration**
(iv) add 2 cm depth of bromine water. (Take care: bromine water is corrosive.)	**orange $Br_2(aq)$ decolourised;** **white ppt.** ***accept reddish-brown $Br_2(aq)$***

[4]

(v) Complete Table 3.2, using the observations in Table 3.1 to identify the two functional groups present in **FA 7**. In each case, give evidence to support your conclusion.

Table 3.2

functional group	*evidence*
phenol	**- violet coloration with aq. $FeCl_3$** **- white ppt with aq. bromine water** ***correct functional group & with underlined evidence***
carboxylic acid ***'carboxyl group' not acceptable***	**- $CO_2(g)$ with solid sodium carbonate** **- $H_2(g)$ with magnesium ribbon** ***correct functional group & with underlined evidence***

[2]

(b) **Plan**

You are provided with four solutions, labelled **FA 8**, **FA 9**, **FA 10** and **FA 11**.

Each solution contains one of the following compounds.

- lead nitrate, $Pb(NO_3)_2$
- sodium chloride, NaC*l*
- sodium hydroxide, NaOH
- zinc sulfate, $ZnSO_4$

The order in the list of solutions does **not** correspond to the **FA** numbers.

(i) Using the *Qualitative Analysis Notes* on page 14, complete Table 3.3 to show the expected observations when pairs of the solutions are mixed. Solutions should be added a little at a time, with shaking, until no further change is observed.

Expected observations for $Pb(NO_3)_2$ have already been recorded in Table 3.3.

Table 3.3

	NaC*l*	**NaOH**	**$ZnSO_4$**
$Pb(NO_3)_2$	white ppt.	white ppt. soluble in excess NaOH	white ppt.
NaC*l*		**no ppt.**	**no ppt.**
NaOH			**white ppt. soluble in excess NaOH**

complete table (with correct observations)

Explain how you could use the expected observations in Table 3.3 to identify **each** of the solutions.

- **$Pb(NO_3)_2$ - gives white ppt with the other 3 solutions**
- **NaC*l* - gives white ppt with only 1 other solution**
- **NaOH - gives white ppt with 2 other solutions (ppt soluble in both cases)**
- **$ZnSO_4$ - gives white ppt with 2 other solutions (ppt soluble in only one)** [5]

(ii) Carry out the experiment using **FA 8**, **FA 9**, **FA 10** and **FA 11** and record your results in a suitable table.

	FA 8 (excess)	**FA9 (excess)**	**FA 10 (excess)**	**FA 11 (excess)**
FA 8		no ppt	no ppt.	white ppt.
FA 9	no ppt.		white ppt. soluble in excess **FA 10**	white ppt.
FA10	no ppt.	white ppt.		white ppt.
FA 11	white ppt.	white ppt.	white ppt. soluble in excess **FA 10**	

[3]

(iii) Identify the substance present in each of the solutions.

FA 8 **NaC*l***

FA 9 **$ZnSO_4$**

FA 10 **NaOH**

FA 11 **$Pb(NO_3)_2$**

[1]

[Total: 15]

Qualitative Analysis Notes
[*ppt. = precipitate*]

(a) Reactions of aqueous cations

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

(b) Reactions of anions

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

(c) Tests for gases

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

(d) Colour of halogens

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

BLANK PAGE

Name:		**Index Number:**		**Class:**	

DUNMAN HIGH SCHOOL
Preliminary Examination 2017
Year 6

H2 CHEMISTRY

9729/01

Paper 1 Multiple Choice

25 September 2017
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 t**hirty** 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”.

This question paper consists of **17** printed pages and **1** blank page.

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

Which sample of gas contains twice the number of atoms as 4 g of helium gas, He?

A 22 g of carbon dioxide, CO_2

B 8 g of methane, CH_4

C 4 g of hydrogen, H_2

D 12 g of steam, H_2O

2 When 10 cm^3 of a gaseous hydrocarbon was sparked with excess oxygen gas and cooled to room temperature, the gaseous mixture contracted by 30 cm^3. When the residual gas was passed through aqueous potassium hydroxide, there was a further contraction of 40 cm^3.

What is the hydrocarbon?

A 2–methylpropene

B propane

C butadiene

D butane

3 Ethanedioate ions, $C_2O_4^{2-}$, are oxidised by acidified aqueous potassium manganate(VII) to give carbon dioxide. What volume of 0.020 mol dm^{-3} potassium manganate(VII) is required to completely oxidise 2.0 x 10^{-3} mol of the salt $NaHC_2O_4.H_2C_2O_4$?

The half equation for MnO_4^- is given below:

$$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$$

A 20 cm^3 **B** 40 cm^3

C 80 cm^3 **D** 100 cm^3

4 The successive ionisation energies, in kJ mol^{-1}, of elements **G** and **H** are given below.

G	580	1820	2740	11600	14800	18400	23300
H	940	2050	2970	4140	6590	7880	14900

Which statements about elements **G** and **H** are true?

1 The first ionisation energy of **G** is lower than that of the element preceding it in the Periodic Table.

2 **G** and **H** forms a compound with the formula $\mathbf{G_3H_2}$.

3 **H** has an outer electronic configuration ns^2 np^4.

4 When oxides of **G** and **H** are added separately to water containing Universal Indicator solution, the solution turns blue and red respectively.

A **1** and **3** only

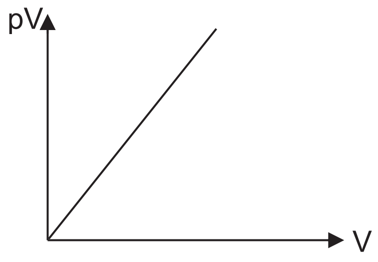
B **3** and **4** only

C **2**, **3** and **4** only

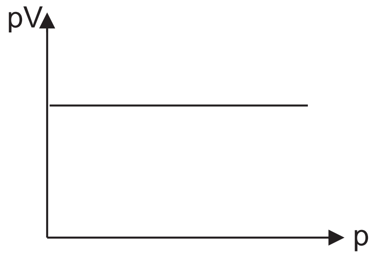
D **1**, **2** and **4** only

5 Which graph does **not** describe the relationship between volume and pressure for a fixed mass of an ideal gas under constant temperature?

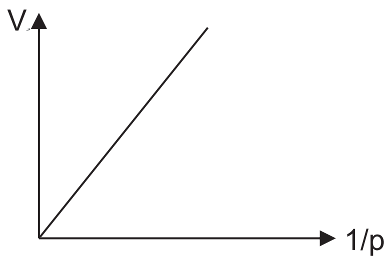
A



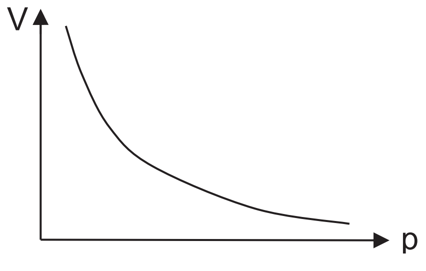
B



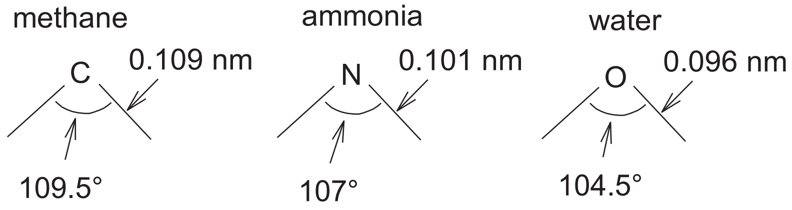
C



D



6 The bond lengths and bond angles in the molecules of methane, ammonia and water may be represented as follow:



What causes this trend in the bond angles shown?

1 Increasing repulsion between hydrogen atoms as the bond length decreases.

2 Number of non–bonding electron pairs of the central atom in the molecule.

3 Non-bonding electron pair–bonding electron pair repulsion is greater than bonding electron pair–bonding electron pair repulsion.

A **3** only

B **1** and **2** only

C **2** and **3** only

D **1**, **2** and **3**

7 Equimolar samples of gaseous NH_3 and HBr were injected into an evacuated flask maintained at a fixed temperature. Some white crystals of NH_4Br were observed in the flask.

Which is the only piece of information you would need to calculate the value of K_p?

A initial amount of HBr used

B mass of NH_4Br formed at equilibrium

C base dissociation constant, K_b, of NH_3

D total pressure of the system at equilibrium

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

Nickel tetracarbonyl, $Ni(CO)_4$, is an intermediate in the Mond process. It has a melting point of –17.2°C and a boiling point of 43°C.

A 40.3 g sample of nickel tetracarbonyl is placed in a 10 dm^3 vessel under an atmosphere of neon gas at 20°C and a pressure of 1.0 atm. When the vessel is warmed to 60°C and the contents are allowed to reach equilibrium, 10% of the nickel tetracarbonyl has dissociated into nickel metal and carbon monoxide.

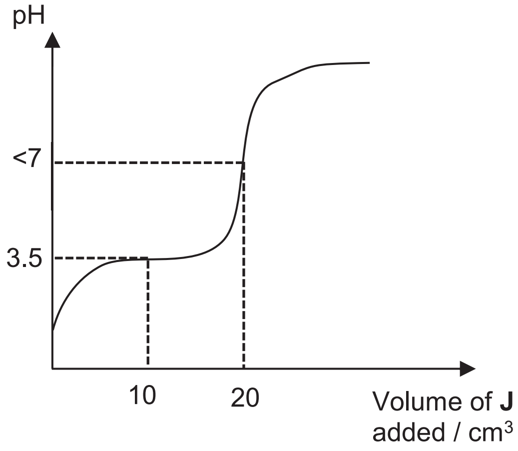
What is the total pressure of the gases in the vessel at 60°C?
[M_r of $Ni(CO)_4$ = 170.7]

A 2.04 atm **B** 1.97 atm **C** 1.37 atm **D** 0.837 atm

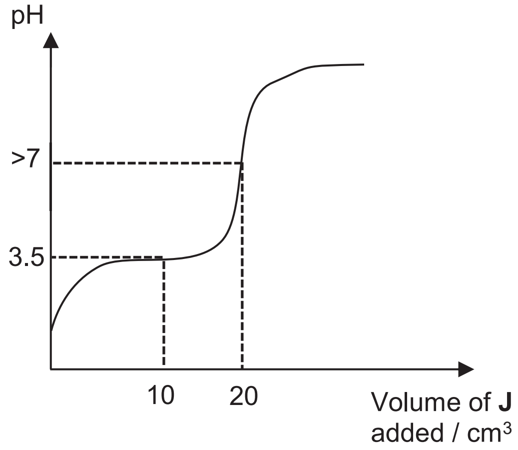
9 **J** is a monoacidic weak base with a pK_b of 3.5.

A total of 50 cm^3 of 0.1 mol dm^{-3} of **J** was added dropwise to 20 cm^3 of 0.1 mol dm^{-3} HNO_3. Which pH curve correctly describes the changes in the pH of the resultant solution as **J** was added to HNO_3?

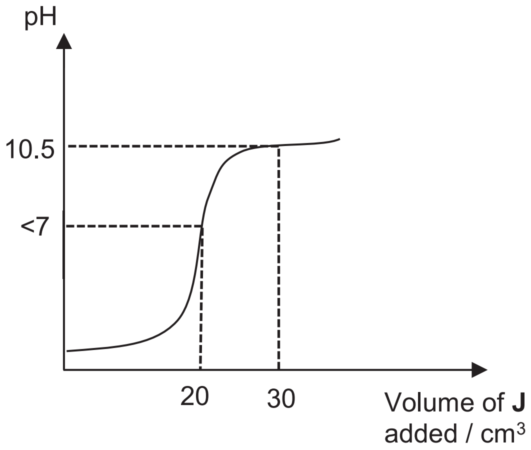
A



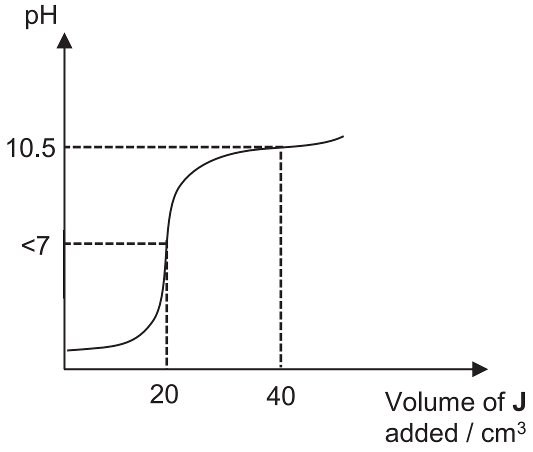
B



C



D



10 Consider the following solutions at 298K:

solutions	concentration / mol dm^{-3}
NH_3 (K_b = 1.8 × 10^{-5} mol dm^{-3})	0.010
CH_3COOH (K_a = 1.8 × 10^{-5} mol dm^{-3})	0.010
NH_4Cl	0.10
$CH_3COO^-Na^+$	0.10

Which sequence correctly ranks these solutions in increasing pH?

A $NH_4Cl < CH_3COO^-Na^+ < CH_3COOH < NH_3$

B $NH_4Cl < CH_3COOH < NH_3 < CH_3COO^-Na^+$

C $CH_3COOH < NH_4Cl < CH_3COO^-Na^+ < NH_3$

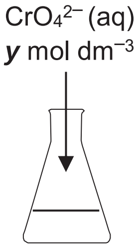
D $CH_3COOH < NH_4Cl = CH_3COO^-Na^+ < NH_3$

11 The table below lists the K_{sp} values of some lead containing salts.

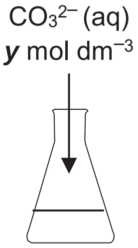
salts	K_{sp} value
$PbCrO_4$	2.8 × 10^{-13}
$PbCO_3$	7.4 × 10^{-14}
$Pb(OH)_2$	1.2 × 10^{-15}
$Pb_3(AsO_4)_2$	4.0 × 10^{-36}

A student prepared four solutions containing ***x*** mol dm^{-3} of Pb^{2+} ions. She then added solutions containing an anion drop–wise to one of these Pb^{2+} containing solutions, as shown below.

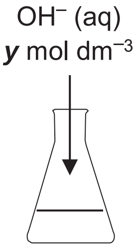
Which set–up will allow for the greatest volume of anion–containing solution to be added before a precipitate is formed?



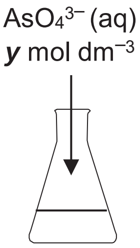
A



B



C



D

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

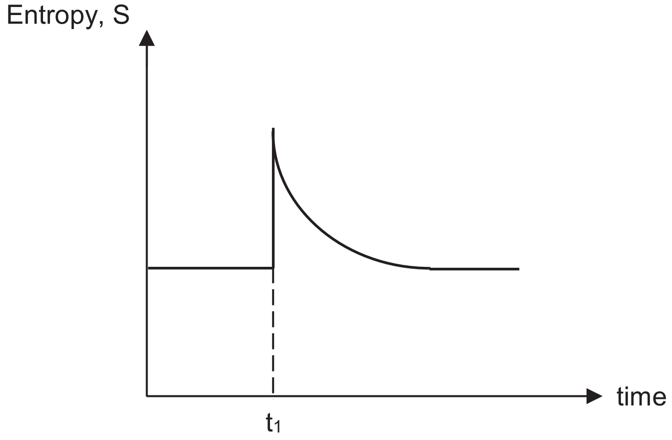
Hexamine has an enthalpy change of combustion of –4288 kJ mol^{-1}.

12.4 g of hexamine tablets were burnt to heat up 850 g of water. Given that the process was 75% efficient and temperature of the water increased from 10°C to 90°C, what is the molar mass of hexamine?

A 124.7 g mol^{-1} **B** 140.3 g mol^{-1}

C 187.1 g mol^{-1} **D** 249.4 g mol^{-1}

13 1 mol of unknown organic compound **W** was placed in a closed vessel. This closed system was kept at room temperature and pressure. The absolute entropy, S, of the system was measured over a period of time as shown in the graph below:



At time t$_1$, 1 mol of unknown compound **X** was added into the closed vessel and the vessel was sealed again.

What could be compounds **W** and **X**?

	W	**X**
A	ethanol	sodium metal
B	pent–2–ene	liquid bromine
C	propanoic acid	sodium carbonate
D	propanoic acid	sodium borohydride

14 Aqueous solutions **Y** and **Z** react according to the following equation:

$$\mathbf{Y} + 2\mathbf{Z} \rightarrow \mathbf{YZ}_2$$

The reaction rate of the above reaction is determined to follow the rate equation:

$$\text{rate} = k[\mathbf{Y}][\mathbf{Z}]$$

Which statements must be true regarding the above reaction?

1 The reaction mechanism has at least 2 steps.

2 Adding water to the reaction will not affect the rate of reaction.

3 When **Y** is present in large excess, the half–life of **Z** is independent of [**Z**].

4 The half–lives of **Y** and **Z** remain constant when an initial concentration of 1 mol dm^{-3} of each reactant is used.

A **1** and **3** only

B **1** and **4** only

C **2** and **3** only

D **1**, **2** and **4** only

15 Which statement about Group 2 metals is correct?

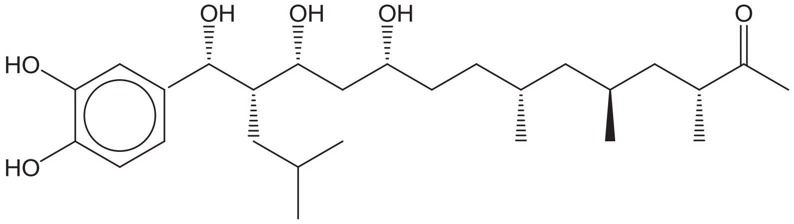
A Melting point increases down the group.

B Reducing strength increases down the group.

C Each ground state atom contains 2 unpaired electrons in its valence shell.

D The second electron is lost more easily than the first electron, forming the M^{2+} cation with a noble gas configuration.

16 Baulamycin B is found to halt the growth of methicillin–resistant *Staphylococcus aureus* (MRSA) and anthrax.



Baulamycin B

What is true of its enantiomer?

A It has 256 stereoisomers.

B It is inactive against MRSA.

C It reacts with 5 mol of sodium hydroxide.

D It forms a violet colouration with neutral iron(II) chloride.

17 Halothane, $CF_3CHBrCl$ is a common anaesthetic.

Which reaction is a termination step in the chain reaction between chlorine and halothane, in the presence of ultraviolet light?

A $\overset{\bullet}{C}F_2CHBrCl + \overset{\bullet}{C}l \rightarrow CF_2ClCHBrCl$

B $CF_3\overset{\bullet}{C}HCl + \overset{\bullet}{H} \rightarrow CF_3CH_2Cl$

C $CF_3\overset{\bullet}{C}BrCl + Cl_2 \rightarrow CF_3CBrCl_2 + \overset{\bullet}{C}l$

D $2\ CF_3\overset{\bullet}{C}HBr \rightarrow (CF_3CHBr)_2$

18 A comparison is made of the nitration reactions of some aromatic compounds.

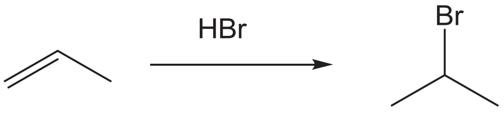
How will the reaction temperatures required compare?

	lowest	⟶	highest
A	benzoic acid	benzene	phenylamine
B	phenylamine	benzene	ethylbenzene
C	phenylamine	ethylbenzene	benzaldehyde
D	benzoic acid	benzaldehyde	ethylbenzene

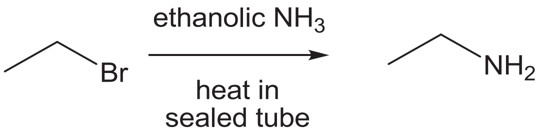
19 As a reaction progresses, there is no change in the hybridisation state of a reactive carbon from the reactant to the **reaction intermediate**.

Which reaction does this statement apply to?

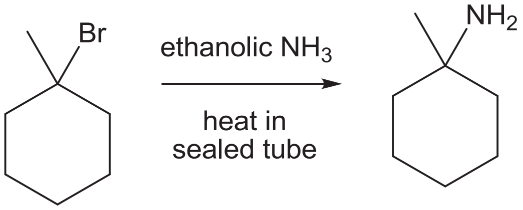
A



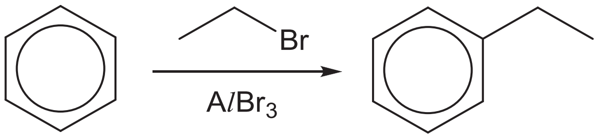
B



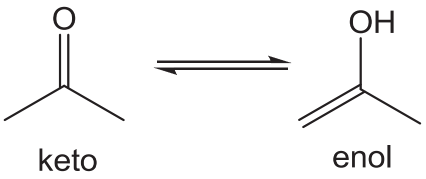
C



D



20 Carbonyl compounds exist as an equilibrium between its keto and enol forms. For propanone, the K_c of the tautomerism process is 3 x 10^{-7}.



Which statement explains the equilibrium position for the tautomerism of propanone?

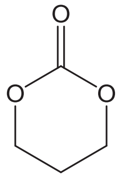
A The C=O bond is stronger that the C=C bond.

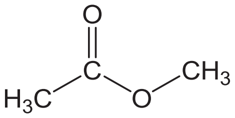
B The O–H bond is stronger than the C–H bond.

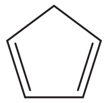
C The hydroxyl group exerts an electron–withdrawing effect.

D A lone pair of electrons on oxygen moves to the C–O bond in enol, resulting in partial double bond character.

21 Which compounds liberate carbon dioxide gas when heated with acidified potassium manganate(VII)?

1 

2 

3 

A **3** only

B **1** and **2** only

C **2** and **3** only

D **1**, **2** and **3**

22 How may the ester, phenyl 2–methylpropanoate, be made in the laboratory?

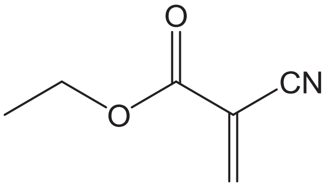
A $CH_3CH(CH_3)COOH + C_6H_5OH \xrightarrow[\text{heat}]{\text{conc. } H_2SO_4,} \text{ester} + H_2O$

B $CH_3CH(CH_3)CH_2OH + C_6H_5COOH \xrightarrow[\text{heat}]{\text{conc. } H_2SO_4,} \text{ester} + H_2O$

C $CH_3CH(CH_3)COCl + C_6H_5OH \longrightarrow \text{ester} + HCl$

D $CH_3CH(CH_3)CH_2OH + C_6H_5COCl \longrightarrow \text{ester} + HCl$

23 Ethyl cyanoacrylate, $C_6H_7O_2N$, is the major component of superglue.



ethyl cyanoacrylate

Which statements about the molecule are true?

1 It contains 3 lone pairs of electrons.

2 It reacts with H_2 in the presence of Ni catalyst to form $C_6H_{11}O_2N$.

3 It contains 4 π bonds.

4 It is hydrolysed by dilute H_2SO_4 to give a diacid and an alcohol.

A **1** and **2** only

B **3** and **4** only

C **1**, **2** and **3** only

D **1**, **2**, **3** and **4**

24 When a compound **O** is heated in a tube containing reagent **P**, a colour change is observed. The product formed is then heated with reagent **Q**, giving compound **R**. **R** can react with reagent **S** to give an observable change.

Which combination could be **O**, **P**, **Q** and **S**?

	O	**P**	**Q**	**S**
1	$CH_2=CH_2$	Br_2 in CCl_4	excess conc. NH_3	$Cu^{2+}(aq)$
2	$CH_2=CHCH_3$	acidified $KMnO_4(aq)$	methanolic $NaBH_4$	Tollens' reagent
3	$CH_2=CH_2$	HBr(g)	NaOH(aq)	hot alkaline $I_2(aq)$

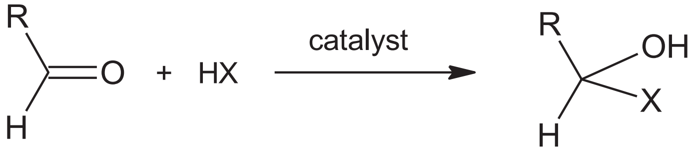
A **1** only

B **1** and **2** only

C **2** and **3** only

D **1**, **2** and **3**

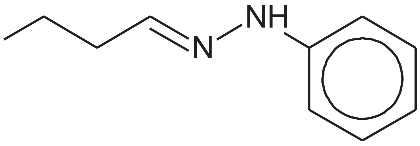
25 There is a range of reactions of the aldehyde group which have the pattern



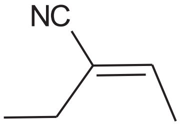
of which the formation of the cyanohydrin (where X = CN) is one.

Which compounds could be obtained by such an addition to an aldehyde group, followed by dehydration?

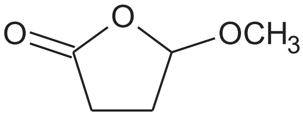
1



2



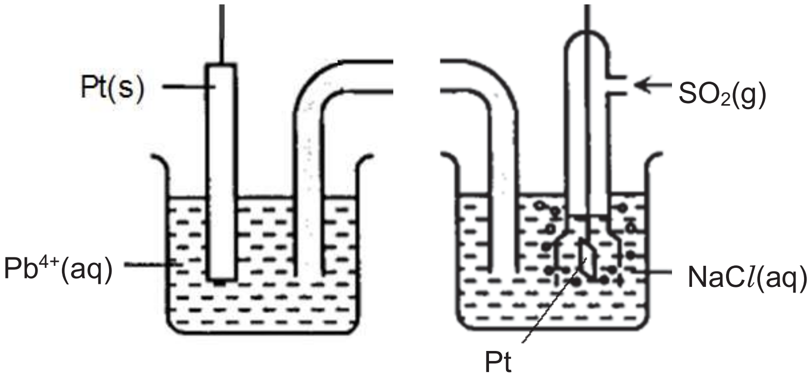
3



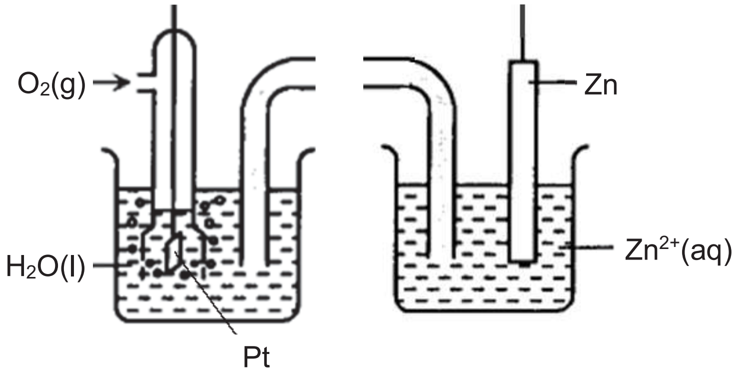
A	**1** and **2** only	**B**	**1** and **3** only
C	**2** and **3** only	**D**	**1** only

26 Which pair of half-cells will form an electrochemical cell that generates electricity?

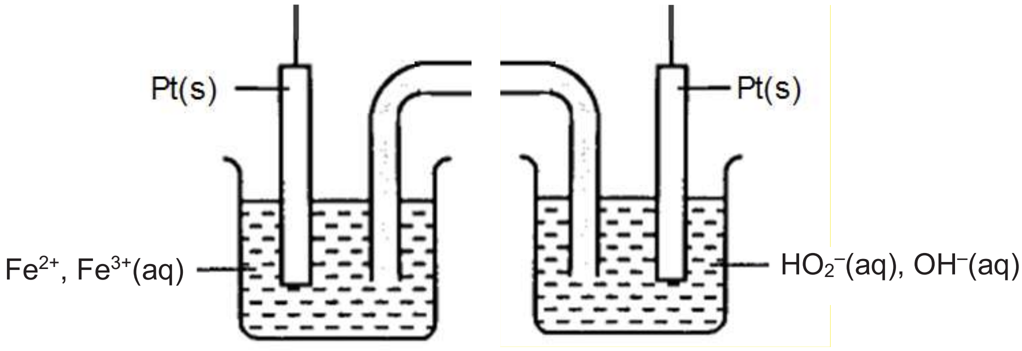
A



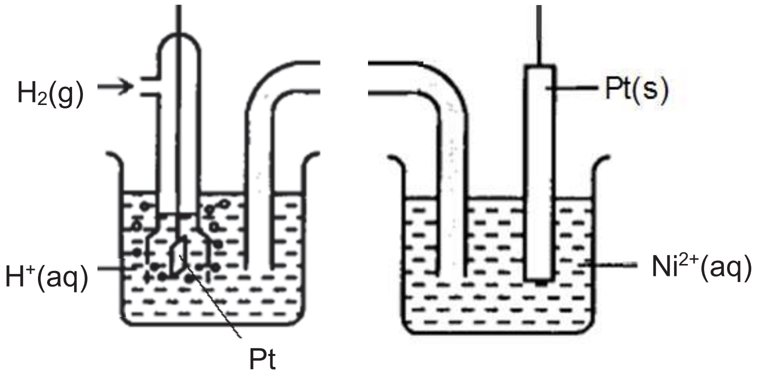
B



C

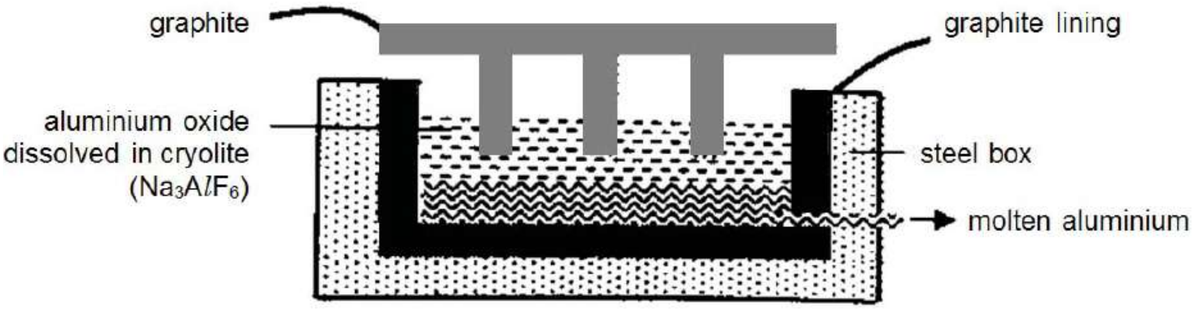


D



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

Aluminium ore is called bauxite. The bauxite can be purified to yield a white powder, aluminium oxide, from which aluminium can be extracted by electrical means. A current of 100 A is passed through the cell for 15 minutes. At the end of the extraction, one of the graphite electrodes has decreased in mass.



Which statement about the extraction is correct?

A Cryolite should not be used as its sodium ions will be discharged in the process.

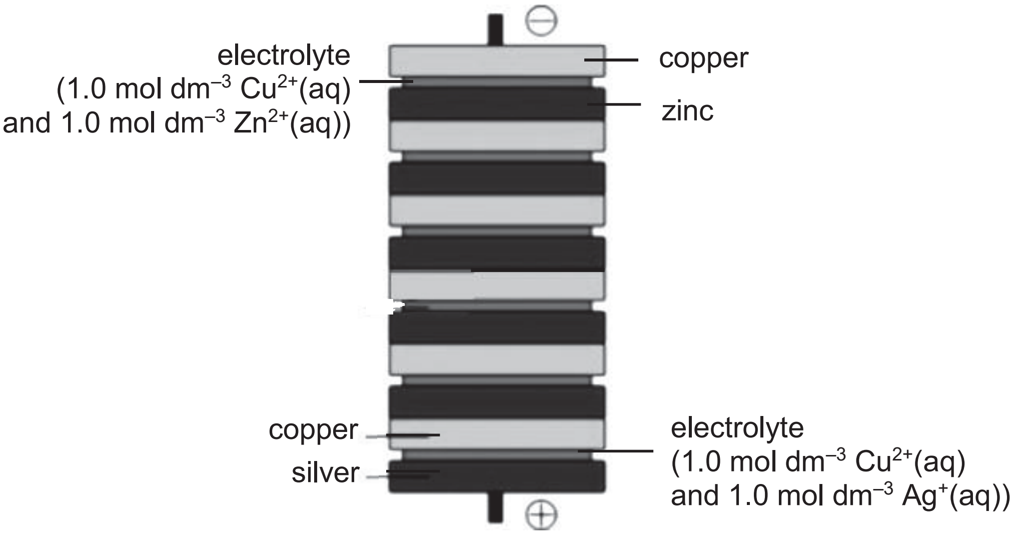
B Molten aluminium is obtained at the cathode and oxygen is produced at the anode.

C A maximum mass of 16.8 g of aluminium can be obtained from this extraction process.

D The graphite cathode reacts with oxygen produced to give CO_2, hence its mass decreases.

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

The voltaic pile was the first modern electric battery invented by Alessandro Volta in 1800. The pairs of alternating discs of copper, silver and zinc are separated by cardboard soaked in an aqueous electrolyte to increase the conductivity.



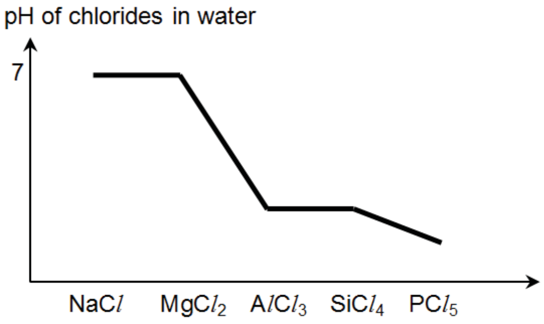
The voltaic pile above has four pairs of Cu and Ag discs and two pairs of Cu and Zn discs, which will be connected to a voltmeter. The voltage of the voltaic pile is the sum of the voltages of each component cell.

What is the reading on the voltmeter?

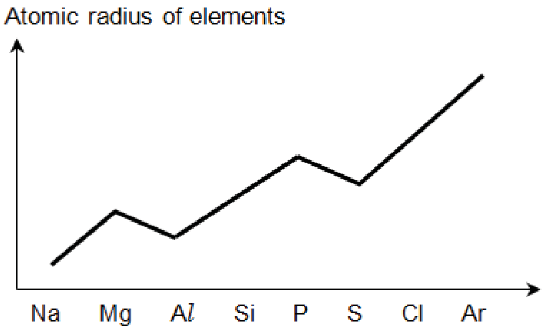
A	1.00 V	**B**	1.56 V
C	4.04 V	**D**	6.76 V

29 Which sketch below is correct?

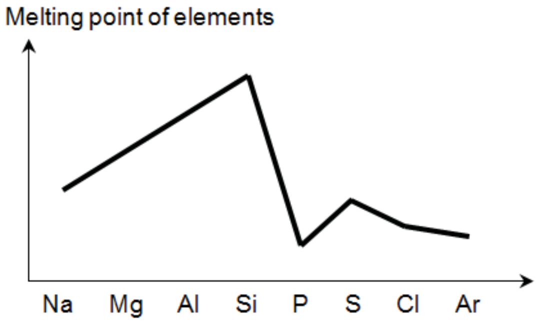
A



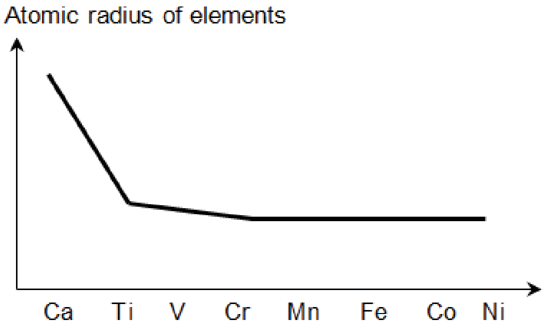
B



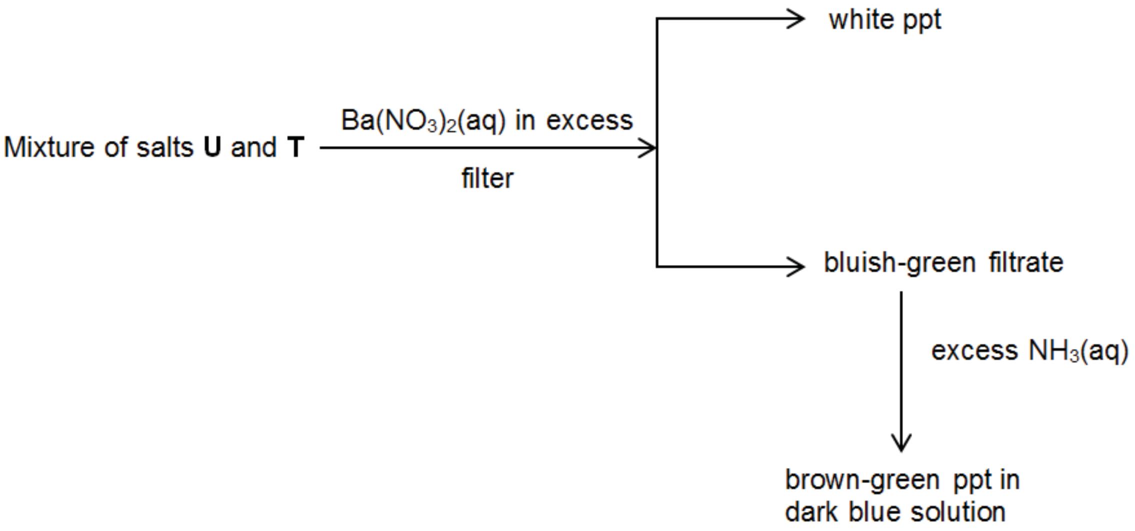
C



D



30 Below is a reaction scheme of salts **U** and **T**.



What are the identities of salts **U** and **T**?

A chromium(III) chloride and copper(II) chloride

B chromium(III) sulfate and copper(II) sulfate

C copper(II) chloride and iron(II) chloride

D copper(II) sulfate and iron(II) sulfate

BLANK PAGE

Name:		**Index Number:**		**Class:**	

DUNMAN HIGH SCHOOL
Preliminary Examination 2017
Year 6

H2 CHEMISTRY

9729/02

Paper 2 (Structured)

11 Sep 2017
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 Answer **all** questions in the spaces provided on the Question Paper.

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

You are advised to show all workings in calculations.

You are reminded of the need for good English and clear presentation in your answers.

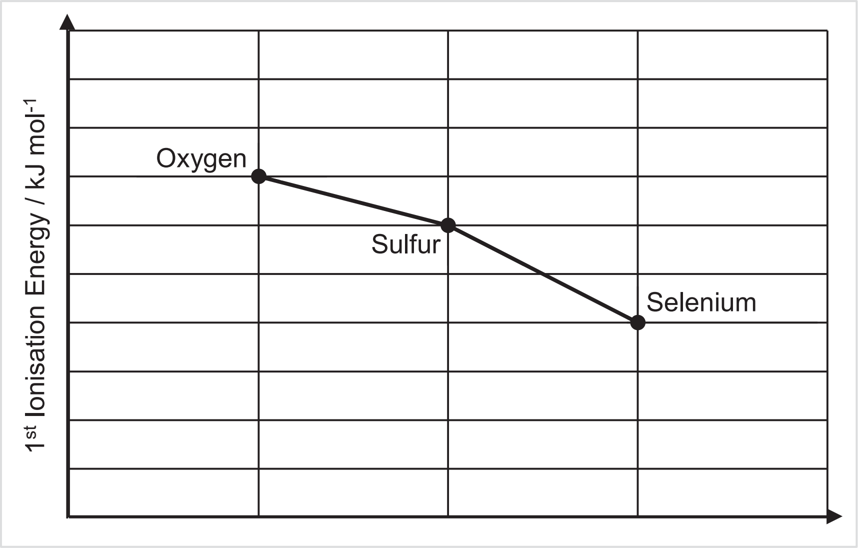
For Examiner's Use	
Question No.	**Section A Marks**
1	**13**
2	**13**
3	**20**
4	**14**
5	**15**
Total	**75**

This question paper consists of **21** printed pages and **1** blank page.

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

1 The chalcogens, or the oxygen family, are the elements in group 16 of the Periodic Table. These elements are common in both organic and inorganic compounds.

(a) The graph below shows the trend in the first ionisation energies of oxygen, sulfur and selenium.



(i) Explain the trend in the first ionisation energies of oxygen, sulfur and selenium.

....

....

....

....

[2]

(ii) On the same grid above, sketch the trend in the first ionisation energies of nitrogen, phosphorus and arsenic.

[1]

(b) A common chalcogen-containing reagent used in both organic and inorganic synthesis is hydrogen peroxide, H_2O_2. Hydrogen peroxide readily decomposes at room temperature. However, this process is slow.

Iodide ions, I^-, catalyse this decomposition, as shown below:

Step I: $H_2O_2 + I^- \rightarrow H_2O + IO^-$ (slow)
Step II: $H_2O_2 + IO^- \rightarrow H_2O + O_2 + I^-$

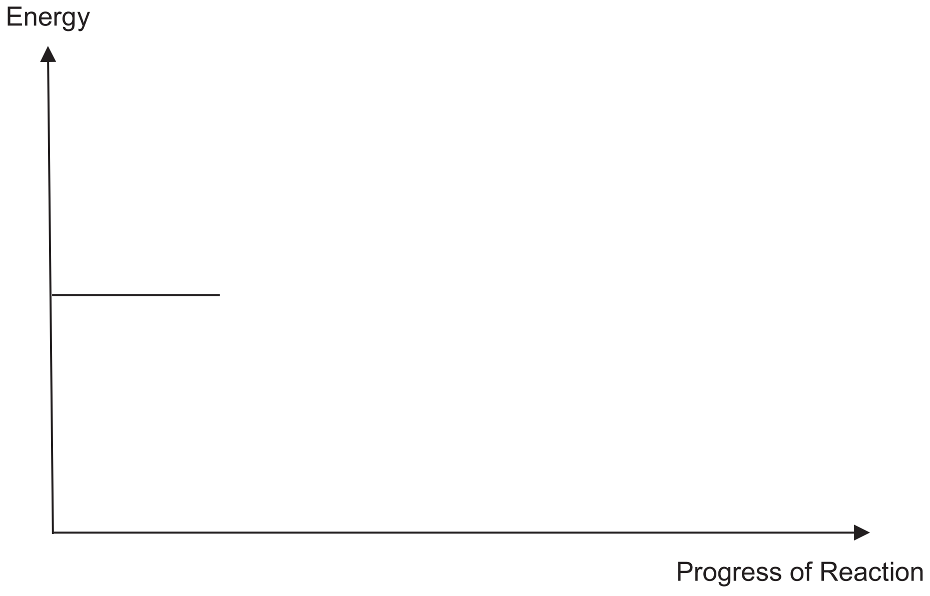
The overall equation for the decomposition of hydrogen peroxide is shown below:

$$2H_2O_2 \rightarrow 2H_2O + O_2$$

The enthalpy and entropy changes for the reaction above are shown in the table below:

Enthalpy change / kJ mol^{-1}	–98
Entropy change / J K^{-1} mol^{-1}	+71

(i) Using the data above, complete the diagram below to show the energy profile diagram for the decomposition of hydrogen peroxide in the presence of iodide ions.



[2]

(ii) An unknown amount of hydrogen peroxide was allowed to decompose in a 5 dm^3 closed vessel at 120 °C. When all the hydrogen peroxide was decomposed, a pressure of 177 kPa was measured in the vessel.

Determine the amount of hydrogen peroxide that decomposed in the vessel.

(Assume that H_2O and O_2 are ideal gases under the above reaction conditions)

[2]

(c) Chalcogens are also very commonly found in organic compounds. Table 1 below shows some common oxygen or sulfur containing organic functional groups.

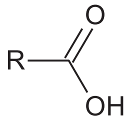
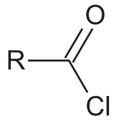
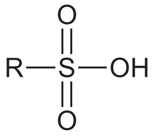
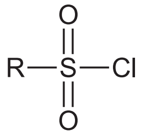
Oxygen-containing functional groups	Alcohols R–OH	Carboxylic acids 	Acyl chlorides 
Sulfur-containing functional groups	Thiols R–SH	Sulfonic acids 	Sulfonyl chlorides 

Table 1

(i) Explain why carboxylic acids are generally more acidic than alcohols.

....

.... [1]

(ii) Hence, suggest a reason why carboxylic acids are generally less acidic than their corresponding sulfonic acids.

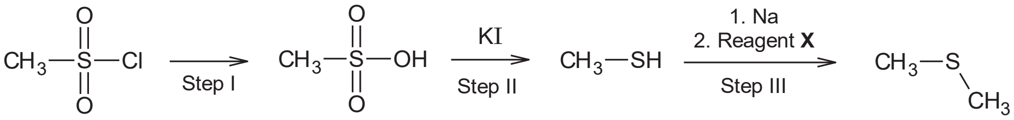
....

....

....

.... [1]

(iii) A reaction scheme for the synthesis of dimethyl sulfide (CH_3SCH_3) from methylsulfonyl chloride (CH_3SO_2Cl) is shown below:



Given that sulfur-containing functional groups undergo similar reactions as their corresponding oxygen-containing functional groups (Table 1), suggest:

I. The reagent(s) and condition(s) required for Step I.

.... [1]

II. The role of KI in Step II.

.... [1]

III. The identity of Reagent **X** in Step III.

.... [1]

IV. The structure of the product(s) formed when methylsulfonic acid (CH_3SO_3H) is reacted with ethylamine ($CH_3CH_2NH_2$) at room temperature.

[1]

[Total: 13]

2 The electrolysis of dilute sulfuric acid was carried out using two different currents at room temperature and pressure.

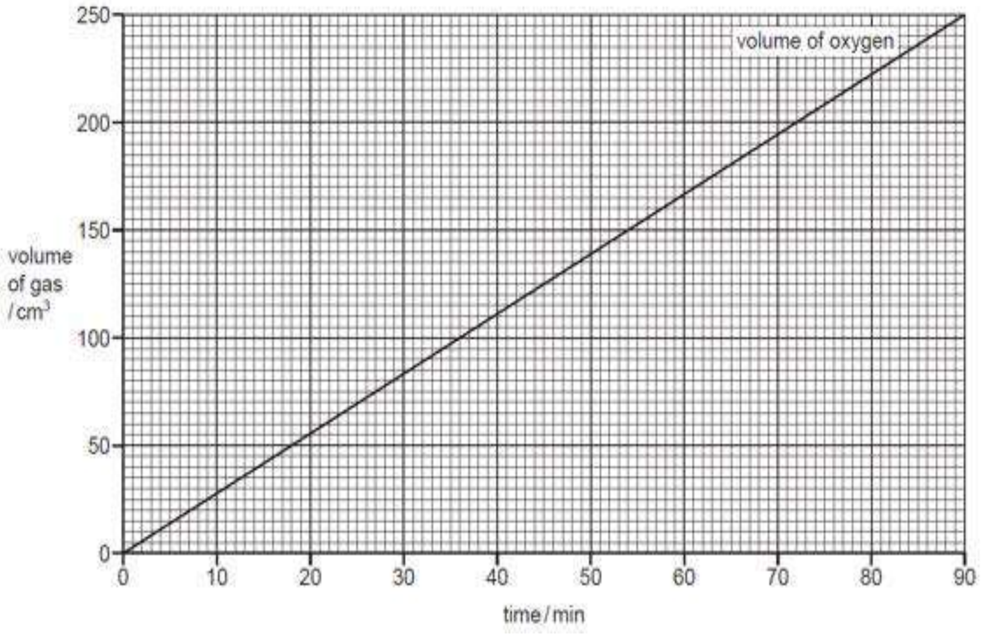
	Current / A	Duration / min
Experiment 1	0.75	90
Experiment 2	0.45	90

Oxygen gas is collected at one of the electrodes.

(a) **(i)** Calculate the final volume of oxygen produced in experiment 2.

[2]

(ii) The volume of oxygen collected for experiment 1 is shown below.



On the graph above, draw a line to show each of the following:

I. the volume of H_2 gas that would be given off in experiment 1 (Label this line **1**)

II. the volume of oxygen that would be produced in experiment 2 (Label this line **2**)

[2]

(b) In another experiment, electrolysis of aqueous potassium butanedioate, $(OOCCH_2CH_2COO)K_2$, was carried out. It was found that two gases, **Y** and **Z**, were liberated at the anode in a 2:1 ratio by volume.

Gas **Y** formed is absorbed by soda lime while gas **Z** is able to decolourise bromine water.

(i) Suggest the identities of gases **Y** and **Z**.

Gas **Y** is …………………. Gas **Z** is ……………………… [1]

(ii) Construct the half-equation for the reaction that occurs at the anode and the cathode respectively.

Anode ………………………………………………………………………

Cathode ………………………………………………………………………

[2]

(iii) Predict the main organic product that would be obtained at the anode when a solution of potassium pentanedioate is electrolysed.

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

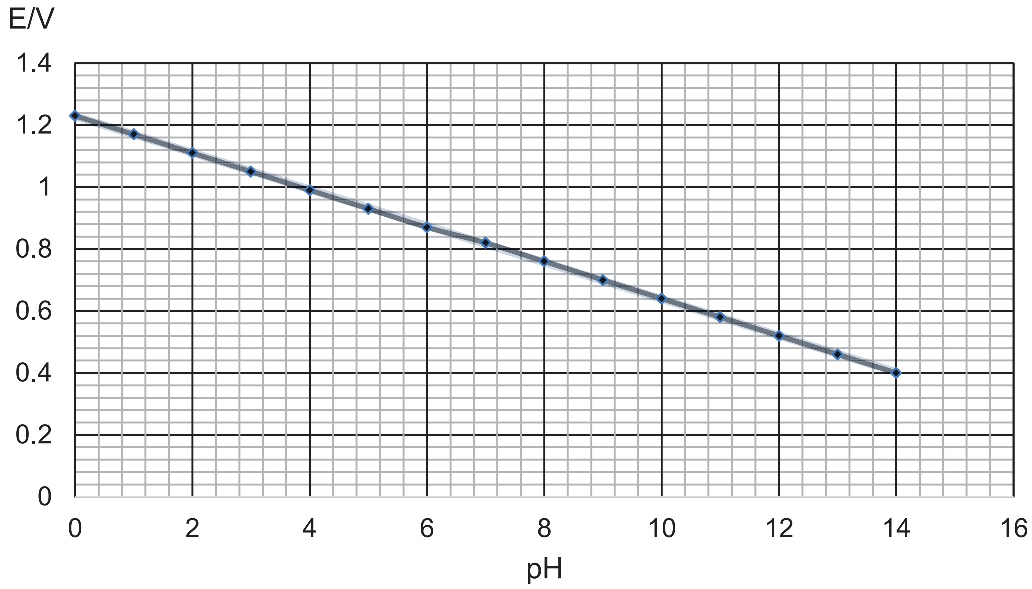
(c) Nicotinamide adenine dinucleotide (NAD^+) is involved in redox chemistry throughout the respiratory system. Aerobic respiration is the process of producing cellular energy involving oxygen.

The electrode potential for the reduction of NAD^+ in a *biological* system, *E*(pH 7), at 1 mol dm^{-3}, 25 °C and pH 7, is as shown.

Its oxidised and reduced forms are represented as NAD^+ and NADH respectively.

$$NAD^+ + H^+ + 2e^- \rightleftharpoons NADH \qquad E(\text{pH } 7) = -0.320\ \text{V}$$

The reduction electrode potential of oxygen at different pH is given below.



(i) With reference to the *Data Booklet* and the graph given above, calculate the value of E_{cell} for aerobic respiration. Write a balanced equation for this reaction.

[3]

(ii) State how the E_{cell} will differ if the aerobic reaction is performed at a pH of 7.4.

....

[1]

(iii) Using your answer in **(c)(i),** calculate ΔG(pH 7) for the aerobic respiration process.

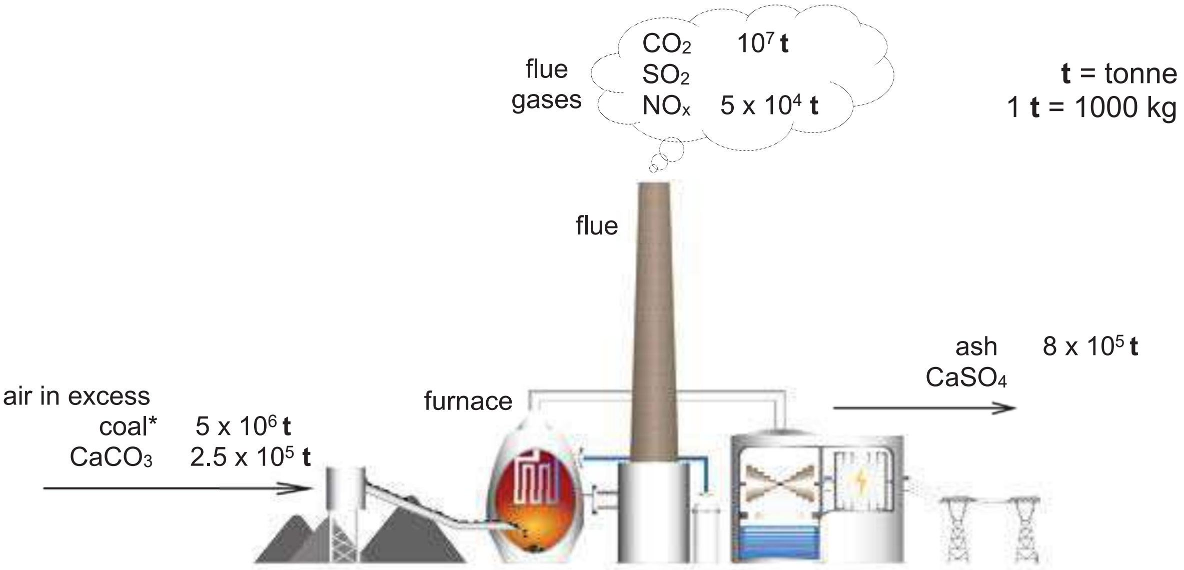
[1]

[Total: 13]

3 A coal-fired power station is fitted with a Flue Gas Desulfurisation (FGD) plant, which removes some of the sulfur dioxide from flue (waste) gases.

In the FGD plant, the flue gases are treated with powdered limestone, $CaCO_3$, where sulfur dioxide is absorbed and reacted to produce calcium sulfite, $CaSO_3$, which is oxidised by air to form solid calcium sulfate, $CaSO_4$.

The diagram below shows the amounts of substances used, and produced, by such a coal-fired power station with an FGD plant in **one** year.



Power station & FGD plant

**coal is chiefly hydrocarbons*

(a) **(i)** State the process that produces the energy in the power station.

....

[1]

(ii) Identify a gas, not listed in the diagram, which will be a chief component of the flue gases.

....

[1]

(iii) Explain why oxides of nitrogen (NO_x) are present in the flue gases.

....

....

[1]

(b) Write a balanced equation in each case to show how

- sulfur dioxide is removed from flue gases;

....

- calcium sulfate is formed.

....

[2]

(c) Using your answer in **(b)**, determine the maximum mass of sulfur dioxide which could be removed in the FGD plant.
[1**t** = 1 tonne = 1000 kg]

[1]

(d) Given that your answer in **(c)** was only 90% of the sulfur dioxide removed from the flue gases, calculate the mass of sulfur dioxide which is released into the atmosphere in **five** years by this power station when the same mass of coal is burnt each year.

[1]

(e) Another method for removing sulfur dioxide from the flue gases is to absorb it in a slurry of magnesium oxide, to produce magnesium sulfite, $MgSO_3$.

(i) Explain why magnesium oxide can also be used to remove sulfur dioxide.

....

....

[1]

(ii) Magnesium sulfite decomposes readily to give magnesium oxide and sulfur dioxide. Magnesium oxide could be recycled, while sulfur dioxide could be used to make sulfuric acid.

Explain whether it would be easier to obtain magnesium oxide or calcium oxide from its respective sulfite.

....

....

....

....

[3]

(f) When 1 mol of magnesium oxide, calcium oxide and other Group 2 metal oxides were separately dissolved in 1 dm^3 of deionised water, the pH of the resulting solutions were obtained.

Some data regarding these Group 2 metal oxides, **M**O, and their resulting solutions are provided in the table below.

ion	ionic radius/ nm	$\Delta H_{hydration}$ / kJ mol^{-1}	pH of **M**O in water	Electronegativity difference (ΔEN) in **M**O
O^{2-}	0.140			
Be^{2+}	0.031	–2370	7.0	1.87
Mg^{2+}	0.065	–2024	9.0	2.13
Ca^{2+}	0.099	–1680	9.5	2.44
Sr^{2+}	0.113	?	11	2.49
Ba^{2+}	0.135	–1314	12	2.55

(i) Suggest why there is no value for $\Delta H_{hydration}$ of the oxide ion, O^{2-}.

....

[1]

(ii) Using the data given, estimate $\Delta H_{hydration}$ of Sr^{2+}.

enthalpy change of hydration of Sr^{2+} = ...

[1]

(iii) State and explain the trend in $\Delta H_{hydration}$ in the table, in terms of the interaction between cations and water.

....

....

....

....

[2]

(iv) With reference to the relevant data given in **(f)**, suggest explanations for the increasing pH of the resulting solution from BeO to BaO in terms of:

I. Lattice energy and enthalpy change of solution of **M**O

....

....

....

....

....

.... [3]

II. ΔEN and the nature of the bonding in **M**O

....

....

....

.... [2]

[Total: 20]

4 Vitamin C is an essential nutrient also known as ascorbic acid. A deficiency of vitamin C leads to a disease known as scurvy.

Ascorbic acid is known to have a M_r of 176.0 and contains 40.9% of carbon and 54.5% of oxygen by mass.

(a) Determine the molecular formula of ascorbic acid.

[2]

(b) Ascorbic acid is a monobasic acid, H**A**, and has a pK_a of 4.10. The amount of ascorbic acid contained in dietary supplement tablets can be verified by titration. A tablet containing 500 mg of ascorbic acid was dissolved in 25.0 cm^3 of deionised water.

(i) Calculate the volume of 0.100 mol dm^{-3} sodium hydroxide required for complete neutralisation.

[1]

(ii) Calculate the initial pH of the ascorbic acid solution.

[2]

(iii) Suggest a suitable indicator for the titration. Describe the expected colour change at the endpoint.

[1]

(iv) With the aid of a suitable equation, explain your choice of indicator in **(iii)**.

[2]

(c) When a vitamin C tablet is swallowed, it dissolves in the stomach. The pH of the stomach is 2.

(i) Determine the percentage of ascorbic acid that is ionised in the stomach.

[2]

The pH of blood is maintained at 7.35 by a H_2CO_3/HCO_3^- buffer.

(ii) Using appropriate equations, explain how the buffer minimises changes in pH.

....

....

....

....
[2]

(d) Organic acids like ascorbic acid react with amines in aqueous medium.

(i) State the type of bond formed during the reaction.

....
[1]

(ii) Account for the increasing basicity of primary, secondary and tertiary amines in gas phase.

....

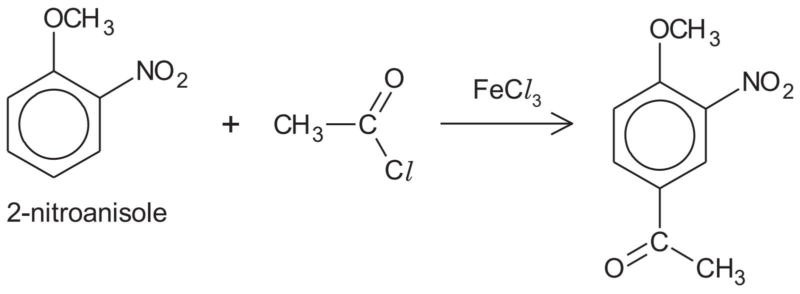
....

....
[1]

[Total: 14]

5 **(a)** In Friedel-Crafts acylation, $FeCl_3$ is employed to attach an acyl group to an aromatic ring via electrophilic substitution.

For example, compound **A** can be prepared by the reaction of 2-nitroanisole with ethanoyl chloride in the presence of $FeCl_3$.



2-nitroanisole

compound **A**

(i) Draw the displayed formula of the electrophile and write an equation to show how it is generated.

equation: ....
[2]

(ii) Using your answer in **(i)**, draw the mechanism of the acylation of 2-nitroanisole by ethanoyl chloride. Show all charges and relevant lone pairs and show the movement of electron pairs by using curly arrows.

[2]

Empirical evidence shows that the electrophile generated in **(i)** is not exceptionally reactive. As such, the Friedel-Crafts acylation of nitrobenzene by ethanoyl chloride does not take place under any conditions.

(iii) Explain why nitrobenzene does not undergo acylation but the presence of the $–OCH_3$ group in 2-nitroanisole permits acylation.

[2]

(b) Another iron compound, $Na_2[Fe(CO)_4]$, is used in the reaction between alkyl halides and carbon monoxide to synthesise ketones. This iron-based reagent is made as follows.

$$Fe(CO)_5 \xrightarrow{Na/Hg} \xrightarrow{-CO} 2Na^+ + [Fe(CO)_4]^{2-}$$

(i) Draw the structure of $Fe(CO)_5$ to show its shape clearly.

[1]

(ii) The oxidation state of Fe in $Fe(CO)_5$ is 0 and the CO ligands are neutral. Suggest the oxidation state of Fe in the $[Fe(CO)_4]^{2-}$ anion.

oxidation state of Fe in $[Fe(CO)_4]^{2-}$: ....

[1]

(iii) Besides the oxidation states exhibited in the above reaction, iron also exists in other oxidation states like +2 and +3.

State a property of iron that allows its compounds to behave in this manner and give a reason why this property arises in iron.

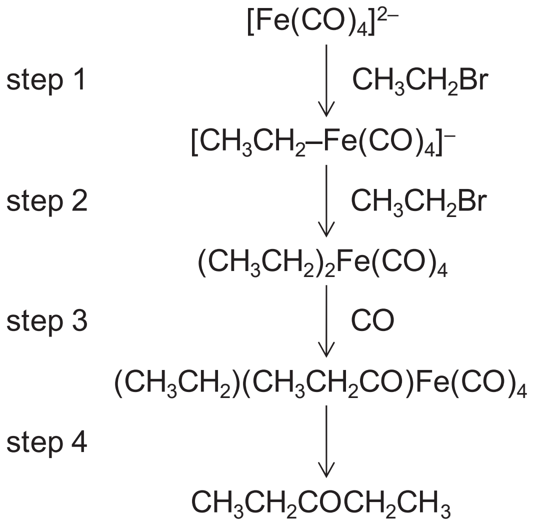
Property of iron: ....

Reason: ....

....

.... [2]

The reaction between $[Fe(CO)_4]^{2-}$ and bromoethane takes place under an applied pressure of carbon monoxide via the following steps.



(iv) Explain what is meant by the term *coordination number* in the context of a metal complex.

State the coordination number of iron in $[Fe(CO)_4]^{2-}$ and $(CH_3CH_2)(CH_3CH_2CO)Fe(CO)_4$.

....

....

Coordination number of iron in $[Fe(CO)_4]^{2-}$: ....

Coordination number of iron in $(CH_3CH_2)(CH_3CH_2CO)Fe(CO)_4$: ....

[2]

(v) Studies show that steps 1 and 2 proceed via nucleophilic substitution.

If bromoethane were replaced by bromobenzene, the above reaction with $Na_2[Fe(CO)_4]$ would not work. With reference to the bonding and structure of bromobenzene, give **two** reasons why both S_N1 and S_N2 cannot occur.

....

....

....

....

....

....

.... [3]

[Total: 15]

BLANK PAGE

Name:		**Index Number:**		**Class:**	

DUNMAN HIGH SCHOOL
Preliminary Examination 2017
Year 6

H2 CHEMISTRY

9729/03

Paper 3 Section A and B (Free Response)

18 September 2017
2 hours

Additional Materials: Data Booklet
Writing Paper
Cover Sheet

INSTRUCTIONS TO CANDIDATES

1 Write your **name**, **index number** and **class** on this cover page and on the Cover Sheet provided.

2 Write your answers on the separate writing papers provided.

3 Write in dark blue or black pen.

4 You may use an HB pencil for any diagrams or graphs.

5 Start each question on a fresh sheet of paper.

6 At the end of the examination:

- Fasten all your work securely together with the Cover Sheet on top.

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

Section A

8 Answer **all** questions in this section.

Section B

9 Answer **one** question from this section.

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

You are advised to show all workings in calculations.

You are reminded of the need for good English and clear presentation in your answers.

This question paper consists of **14** printed pages and **0** blank page.

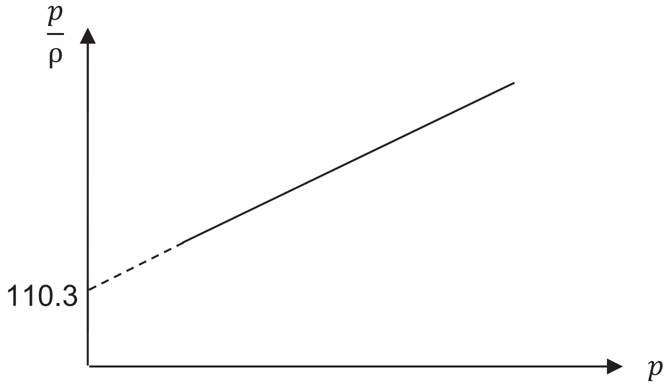
Section A

Answer **all** questions.

1 (a) Singapore has been affected by severe smoke haze due to forest fires in the region periodically. The National Environment Agency (NEA) is taking action to ensure that its population is better equipped to deal with haze.

During one of the sample analysis of air, the air sample was found to contain elevated amounts of NO_2 and gas **S**.
By careful measurements and extrapolation, the value of $\frac{p}{\rho}$ for gas **S** has been found to be approximately 110.3, at 100 °C and at very low pressure.

[p is the pressure of the gas in Pa and ρ is the density of the gas in g m^{-3}]



(i) State two main assumptions of the kinetic theory, and use these to explain why you might expect the behaviour of nitrogen dioxide to be less ideal compared to that of hydrogen. [3]

(ii) Calculate an approximate value for the relative molecular mass of **S**. [1]

(iii) Hence, identify gas **S**, where **S** is a diatomic neutral pollutant. [1]

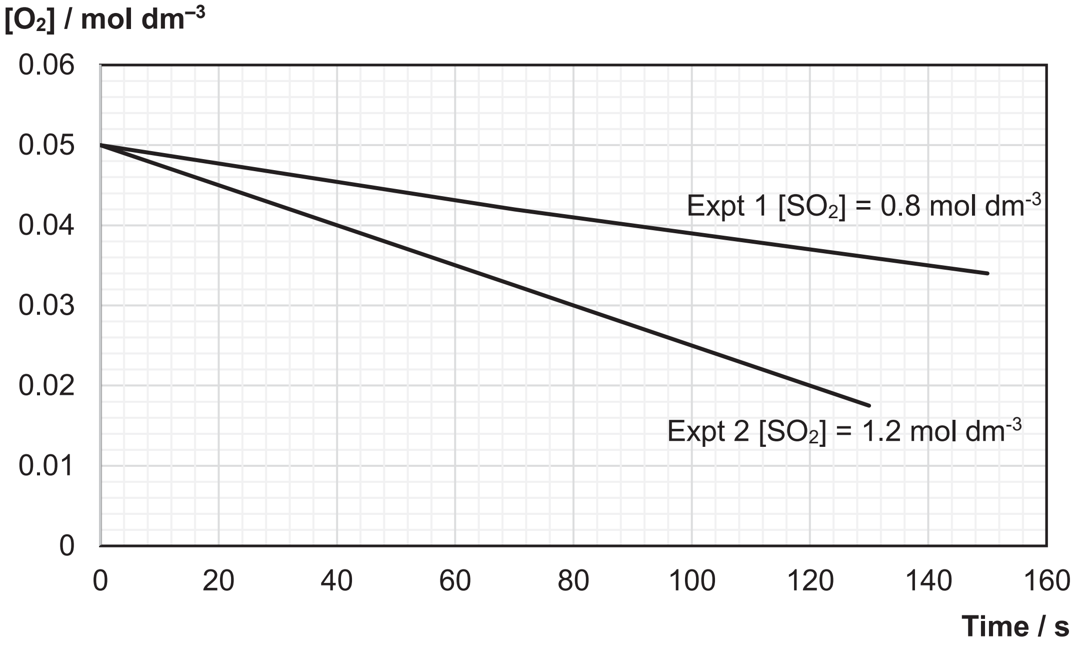
(b) Atmospheric sulfur dioxide is a major air pollutant that forms acid rain. The pollution problem caused by sulfur dioxide is amplified in the presence of atmospheric oxides of nitrogen, which act as a homogeneous catalyst.

Explain, with the aid of equation(s), how atmospheric oxides of nitrogen act as a homogeneous catalyst to amplify the pollution problems of sulfur dioxide. [3]

(c) The Contact Process is an important industrial process that occurs at 450 °C. The key stage in this process is the reaction between sulfur dioxide and oxygen.

$$2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$$

Two laboratory experiments were conducted at 450 °C to investigate the kinetics of this reaction. The graph below shows the results obtained when concentrations of sulfur dioxide were varied.



(i) Use the graphs above to deduce the order of reaction with respect to sulfur dioxide and oxygen. [3]

(ii) Using one of the graphs above, calculate the value of rate constant, stating its units. [2]

(iii) Using your answer in **(i)**, sketch the graph of concentration of sulfur dioxide against time for this reaction, while keeping $[O_2]$ constant. Use construction lines to label the first and second half-lives in your sketch. [1]

(iv) Sketch and label clearly, on the same axes as in **(iii)**, how the graph would look like if the experiment was conducted at 200 °C. [1]

[Total: 15]

2 (a) Two 1.0 mol samples of hexane are mixed with separate 1.0 mol samples of cyclohexane and ethanol. The following results were obtained.

hexane mixed with	*observations*
cyclohexane	no heat is absorbed or given out
ethanol	1.0 kJ of heat is absorbed

For each mixture, consider interactions between molecules of the two liquids mixed and explain the observations. [4]

(b) In the presence of peroxides, H*X* may be added to alkenes by a free radical mechanism. The addition is said to be *anti-Markovnikov*, that is, the H atom from H*X* attaches itself to the C atom in the carbon-carbon double bond with the least number of H atoms.

The propagation steps for propene are as follows.

step 1 $CH_3CH{=}CH_2 + X\bullet \longrightarrow CH_3\overset{\bullet}{C}HCH_2X$

step 2 $CH_3\overset{\bullet}{C}HCH_2X + HX \longrightarrow CH_3CH_2CH_2X + X\bullet$

The table below shows values of the enthalpy changes, ΔH, for the propagation steps 1, 2, and for the overall reaction for H*X* respectively.

X	Cl	Br	I
$\Delta H_{\text{step 1}}$ / kJ mol^{-1}	–80	–20	+20
$\Delta H_{\text{step 2}}$ / kJ mol^{-1}	+21	–44	–111
$\Delta H_{\text{overall}}$ / kJ mol^{-1}	–59	–64	–91

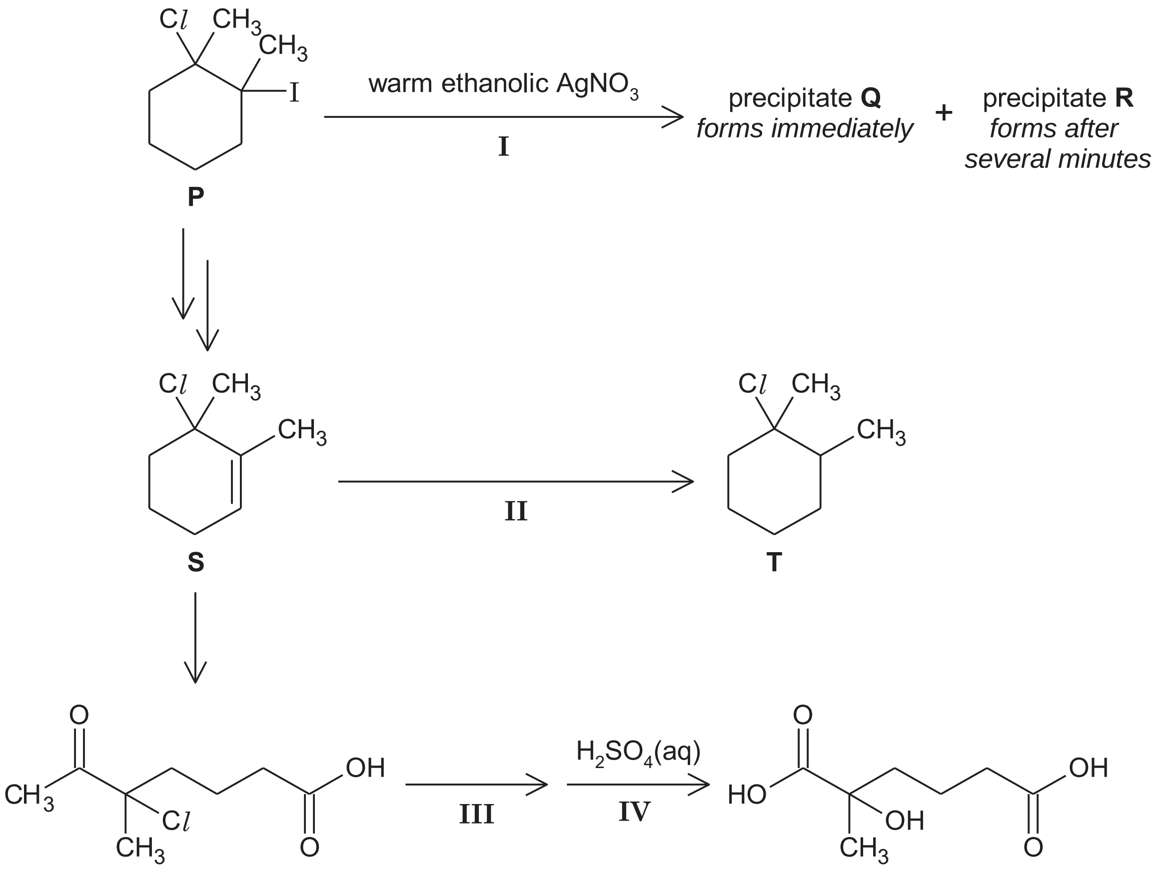
(i) By selecting relevant data from the *Data Booklet*, show that $\Delta H_{\text{step 1}}$ for HI and $\Delta H_{\text{step 2}}$ for HCl are +20 kJ mol^{-1} and +21 kJ mol^{-1} respectively. [2]

(ii) Experiments show that only HBr adds across an alkene via free radical mechanism.

With reference to the ΔH values given above, explain why HBr is most likely to do so and why the other two H*X* does **not** undergo the same mechanism. [2]

(iii) Hence suggest the structure of the major product formed when HI that is contaminated with small amount of peroxides is added to propene. [1]

(c) The following scheme shows the reactions of **P**, a dihalogen derivative of 1,2-dimethylcyclohexane.



(i) Identify precipitates **Q** and **R**.

With reference to the type of reaction that **P** has undergone in reaction **I**, explain the sequence in which **Q** and **R** are formed. Support your answer with suitable data from the *Data Booklet*. [3]

(ii) $LiAlH_4$ is a powerful reducing agent commonly used in organic chemistry to reduce carbonyl compounds, carboxylic acids and their derivatives. However when $LiAlH_4$ is used to reduce **S** in reaction **II**, **T** is **not** formed.

Explain these observations. [2]

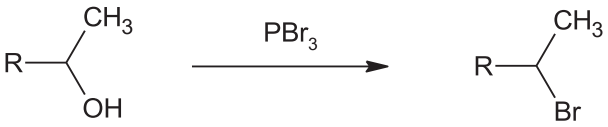
(iii) State the reagents and conditions required for reaction **III**. [1]

[Total: 15]

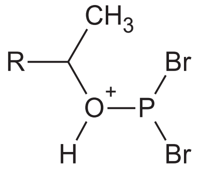
3 The chemistry of Group 15 elements, also known as Pnictogens, is discussed in this question.

(a) Common phosphorous halides contain phosphorous in oxidation states of +3 or +5 (e.g. PX_3 or PX_5). Such compounds are useful in organic or inorganic syntheses as they can function as both Lewis acids or Lewis bases.

In the synthesis of an aesthetic, Methohexital, phosphorous tribromide is used for the conversion of a secondary alcohol to an alkyl bromide.



The mechanism of the above reaction involves two steps:

step 1:	• the secondary alcohol attacks PBr_3 to form the following as an intermediate, along with a bromide ion: 
step 2: (rate-determining step)	• the bromide ion attacks the electrophilic carbon on the intermediate, facilitating the breaking of the C–O bond.

(i) Using the information given above, draw the mechanism to describe the conversion of the secondary alcohol to an alkyl bromide, showing dipoles, lone pairs, and curly arrows. [3]

(ii) State and explain if PBr_3 acts as a Lewis acid or Lewis base in the above synthesis. [1]

(iii) With reference your answer in **(i)**, explain why the reaction of phenol, instead of a secondary alcohol, with PBr_3 will result in the first step of the mechanism being relatively slower. [1]

(iv) Phenol undergoes substitution when reacted with aqueous bromine. Explain why phenol undergoes substitution instead of addition with aqueous bromine. [1]

(v) Other than using aqueous bromine or any phosphorous halides, suggest a simple chemical test to distinguish phenol from the secondary alcohol used in **(a)**.

(You can assume that the R group in the molecule does not react in any way.) [2]

(b) Both phosphorous trichloride and phosphorous pentachloride can be used in the synthesis of tricresylphosphate, a common waterproofing agent.

Phosphorous pentachloride can be formed by reacting phosphorous trichloride with chlorine gas.

$$PCl_3(g) + Cl_2(g) \rightleftharpoons PCl_5(g)$$

2 atm of PCl_3 and 1.5 atm of Cl_2 were left to equilibrate in a closed vessel at 600 K. At equilibrium, the total pressure in the vessel was determined to be 3.3 atm.

(i) Calculate the K_p of the above equlibrium. [2]

(ii) Hence, comment on the position of the equilibrium and the sign for the Gibbs free energy change of the forward reaction at 600 K. [2]

(c) The table below shows common chlorides and oxides of other Group 15 elements.

	Nitrogen	Arsenic
Chlorides	NCl_3	$AsCl_3$ $AsCl_5$
Oxides	NO N_2O NO_2	As_2O_3 As_2O_5

(i) Write an equation to show why arsenic pentachloride ($AsCl_5$) dissolves in water to give a solution with a very low pH. [1]

(ii) Draw the dot-and-cross diagram of N_2O and state its bond angle. [2]

[Total: 15]

4 The fragrance of perfume is created using a range of scents such as citrus, fresh, floral, oriental or woody. Hex-3-en-1-ol has a fresh scent with a strong ‘leafy’ smell of newly cut grass, Geraniol is the main ingredient of rose oil and Linalool has the scent of sweet lavender. Usually, some ethanol and water were also present in a bottle of perfume.

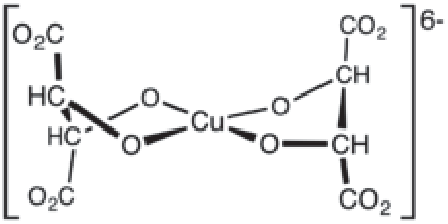
Compound	**Molecular formula**	**Structural formula**
Hex-3-en-1-ol	$C_6H_{12}O$	$CH_3CH_2CHCHCH_2CH_2OH$
Geraniol	$C_{10}H_{18}O$	$(CH_3)_2CCH(CH_2)_2C(CH_3)CHCH_2OH$
Linalool	$C_{10}H_{18}O$	$(CH_3)_2CCH(CH_2)_2C(CH_3)(OH)CHCH_2$

(a) **(i)** Geraniol and Linalool are constitutional isomers. Explain what is meant by *constitutional isomers* are. [1]

(ii) Using skeletal formula, draw the stereoisomers of hex-3-en-1-ol. [1]

(b) A compound **X**, $CH_2CCH_3(CH_2)_3C_aH_bO$, is a constitutional isomer of Geraniol. It exhibits stereoisomerism and has a particular functional group that can be tested positively by Fehling’s solution, an alkaline solution of complexed $Cu^{2+}(aq)$, in a redox reaction.

In Fehling’s solution, the tartrate ion forms a *complex* with Cu^{2+} as shown below.



(i) Suggest why the copper ion needs to be complexed for the test to work. [1]

(ii) Explain why such a complex can be formed between copper and tartrate ion, while no such complex is formed between potassium and tartrate ion. [2]

(iii) Suggest the structural formula of the compound **X**. [1]

(iv) A 2.0 g of fluid sample in a perfume vial containing compound **X** is treated with an excess of the Fehling’s solution. The red solid obtained was collected, washed and dried. It had a mass of 0.282 g.

Given that 1 mol of **X** reacts completely with 2 mol of the Fehling’s solution, calculate the percentage of compound **X** present in the fluid sample. [2]

(v) Compound **X** has a citrus scent. The human nose is able to detect the citrus scent at a minimum concentration of 10 ppm (parts per million) by mass in the air. (1 ppm by mass is 1 g in 1 x 10^6 g).

Assuming that all the fluid were vapourised, using your answer in **(iv)**, calculate the volume of a room above which the smell of compound **X** can no longer be detected by the human nose.

You may assume density of the air in the room is 1.20 kg m^{-3}. [2]

(c) When copper was added to a solution of copper(II) chloride in concentrated hydrochloric acid, a colourless solution, **Y** was obtained. During the reaction, one mole of copper(II) chloride reacts with exactly two moles of HCl, and no product other than compound **Y** was formed.

(i) Explain why solution **Y** is colourless. [1]

(ii) Write a balanced equation for the reaction. [1]

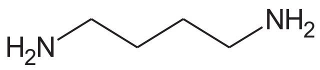
(d) When solid sodium chloride is added to a solution containing $Cu^{2+}(aq)$, the colour changes to pale yellow-green. No such colour change occurs when solid sodium sulfate is added to $Cu^{2+}(aq)$. Addition of water to the yellow-green solution produces the original pale blue colour. Suggest an explanation for these observations. [3]

[Total: 15]

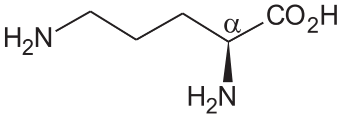
Section B

Answer **one** question from this section.

5 **(a)** A polyamine, butane-1,4-diamine, can be prepared from the decarboxylation of the α-COOH of an amino acid, L-ornithine, under suitable conditions.



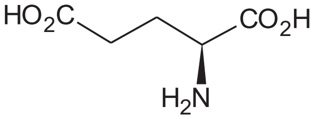
butane-1,4-diamine



L-ornithine

(i) Deduce the identity of the gaseous by-product of the reaction and hence write an equation for the formation of butane-1,4-diamine from L-ornithine. [1]

(ii) Draw and name the organic product formed when L-glutamic acid undergoes decarboxylation in a similar manner.



L-glutamic acid

[2]

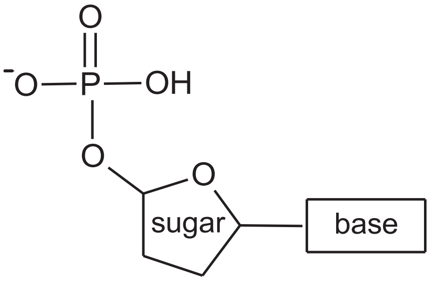
(iii) α-NH_2 and R-NH_2 of L-ornithine have different base dissociation constants, K_b.

Explain what is meant by the term K_b as applied to a weak base, **B**. [1]

(iv) State and explain how the K_b values of α-NH_2 and R-NH_2 of L-ornithine would differ. [2]

(b) Suggest a reaction scheme to synthesise butane-1,4-diamine from ethene. State the reagents and conditions required, and draw the structures of the intermediates formed. [4]

Each strand of deoxyribonucleic acid (DNA) is a macromolecule made by the polymerisation of units called nucleotides. Nucleotides are themselves made from three components (a sugar, a phosphate group and a nitrogen-containing organic base) as shown in the simplified diagram below.



Nucleotide

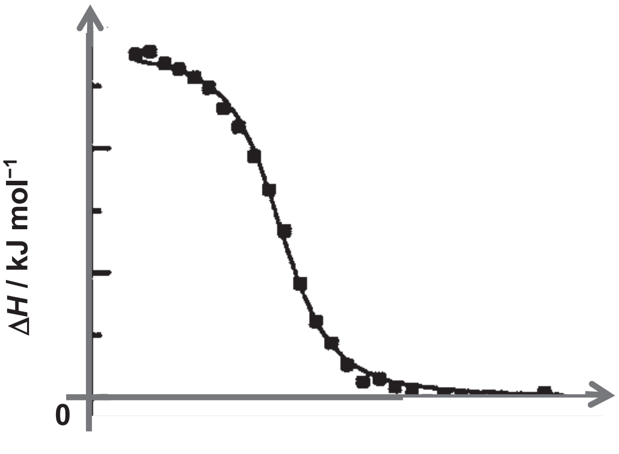
In this question, the sugar and base group remain unaltered and do not take part in any interaction.

A series of experiments was carried out in a buffer solution of pH 7.0 to investigate how butane-1,4-diamine binds with a DNA sample. The binding of butane-1,4-diamine with DNA sample occurs spontaneously.

(c) **(i)** Draw the predominant form of butane-1,4-diamine when it is added to the buffer solution at pH 7.0. [1]

(ii) Hence suggest the type of interaction that facilitates the binding of butane-1,4-diamine to the DNA sample. [1]

The DNA sample was dissolved in a buffer solution of pH 7.0 before it was titrated with butane-1,4-diamine at 293 K. When butane-1,4-diamine was added to the DNA sample, the following graph showing enthalpy change (kJ per mole of butane-1,4-diamine) against molar ratio (of butane-1,4-diamine to DNA sample) was obtained.



Molar ratio of butane-1,4-diamine to DNA sample

(d) **(i)** It is observed from the graph that the enthalpy change is zero at the higher molar ratios. Suggest why this is so. [1]

(ii) Using the graph above, deduce whether the binding of butane-1,4-diamine with the DNA sample is an endothermic or exothermic process. [1]

(iii) Using your answer in **(ii)**, deduce the sign of the entropy change when butane-1,4-diamine binds with the DNA sample. [2]

(iv) A DNA molecule is closely surrounded by water molecules upon hydration.

Use this information to suggest a reason for the sign of the entropy change in **(iii)**. [1]

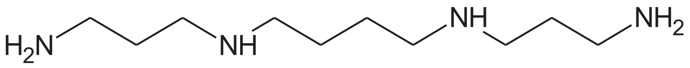
(e) The affinity of a polyamine for a DNA sample can be described by the binding constant, K, for the following equilibrium.

$$\text{polyamine} + \text{DNA} \rightleftharpoons \text{polyamine–DNA complex}$$

The binding constant, K, is further related to the standard Gibbs free energy change, $\Delta G^\ominus$, for the reaction by the equation below.

$$\Delta G^\ominus = -RT\ln K$$

(i) Given that the numerical value of K for the binding between another polyamine, spermine, and the DNA sample at 290 K is 4.88×10^5, calculate the standard Gibbs free energy change in **J mol^{-1}**.



spermine

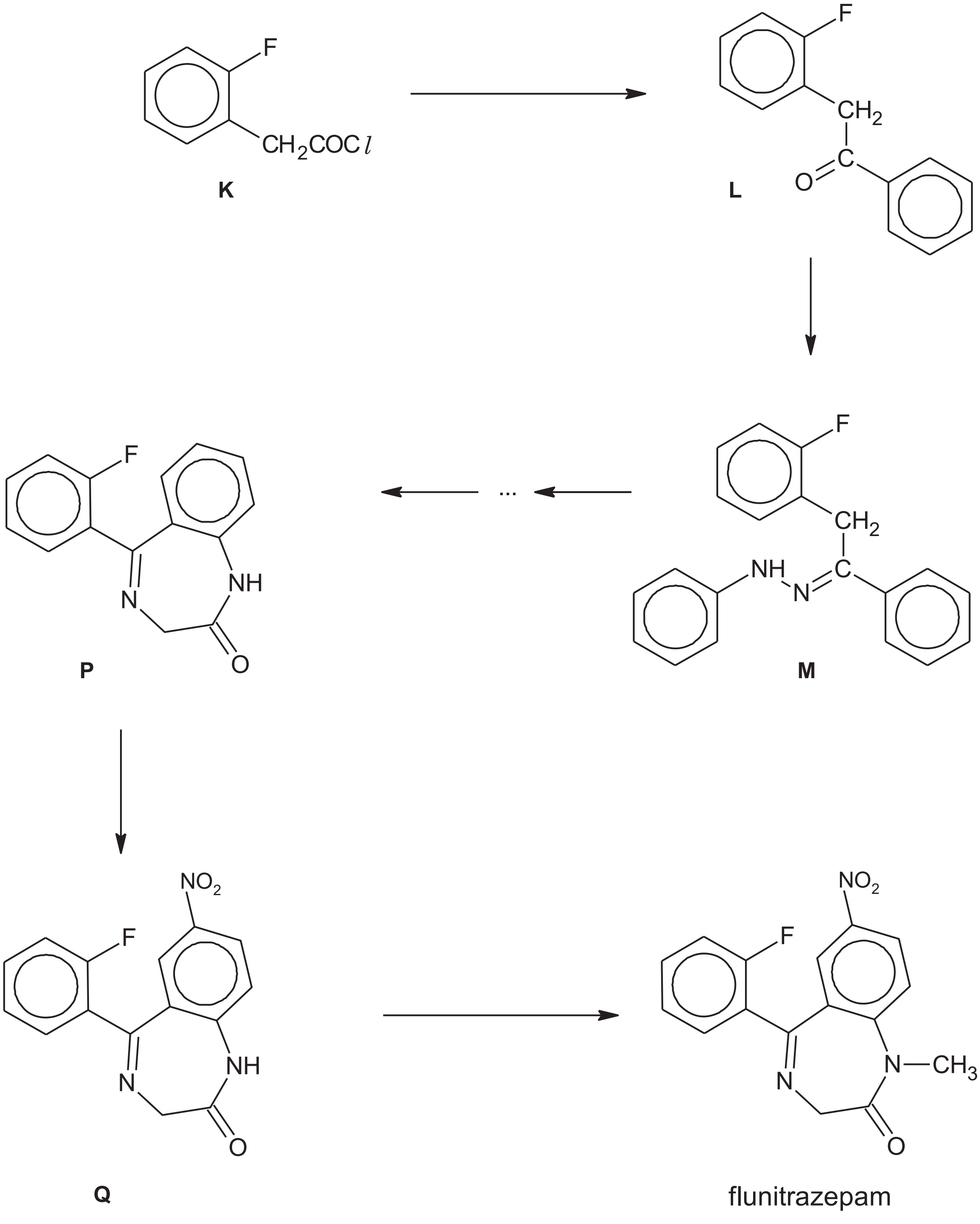
[1]

(ii) When the binding was repeated under similar conditions with butane-1,4-diamine, the standard Gibbs free energy change was found to be -2.62×10^4 J mol^{-1}.

Deduce the relative strength of interaction of the two polyamines with the same DNA sample. [2]

[Total: 20]

6 (a) Flunitrazepam is a potent sleep-inducing drug used to treat severe insomnia. Its use is under strict control in many countries. The reaction scheme below shows the synthesis of flunitrazepam from compound **K**.



(i) Propose a synthetic route, with no more than four steps, for the synthesis of **K** from 2-fluoromethylbenzene. [5]

(ii) Suggest the reagent(s) and conditions and name the type of reaction for each of the following conversions:

(I) K to L

(II) L to M

(III) P to Q [6]

(iii) The metabolism of flunitrazepam in human bodies is a first order reaction with a half-life of about 23.5 hours. Suggest an undesirable effect of using flunitrazepam as a sleep-inducing drug. [1]

(iv) A patient suffering insomnia took 1 tablet containing 1mg of flunitrazepam each night for consecutive 3 days. Assuming only about 80% of the flunitrazepam in each tablet can be absorbed by the body, estimate the mass of residual flunitrazepam in the patient's body on the 5th night. [2]

(b) Flunitrazepam acts as a sedative and hypnotic drug by enhancing the effect of the neurotransmitter γ-aminobutyric acid (GABA) at the GABA receptor in the brain. The IUPAC name of GABA is 4-aminobutanoic acid, $C_4H_9NO_2$.

(i) Explain why GABA exists as white crystalline powder. [1]

(ii) Experimentally, it is difficult to determine the melting point of GABA as it decomposes readily under high temperature to form a liquid compound, R of molecular formula C_4H_7NO.

By using the following thermochemical data, draw an appropriate energy cycle and calculate the standard enthalpy change of decomposition of GABA.

Standard enthalpy change of formation of solid GABA	-581.1 kJ mol^{-1}
Standard enthalpy change of formation of gaseous R	-197.4 kJ mol^{-1}
Standard enthalpy change of vapourisation of R	$+73.6$ kJ mol^{-1}
Standard enthalpy change of combustion of hydrogen	-286 kJ mol^{-1}

[4]

(iii) Suggest the structure of compound R. [1]

[Total: 20]

Dunman High School
2017 Year 6 H2 Chemistry Preliminary Examination
Paper 1

Answer Key

1	2	3	4	5	6	7	8	9	10
D	**A**	**C**	**A**	**A**	**C**	**D**	**B**	**D**	**C**

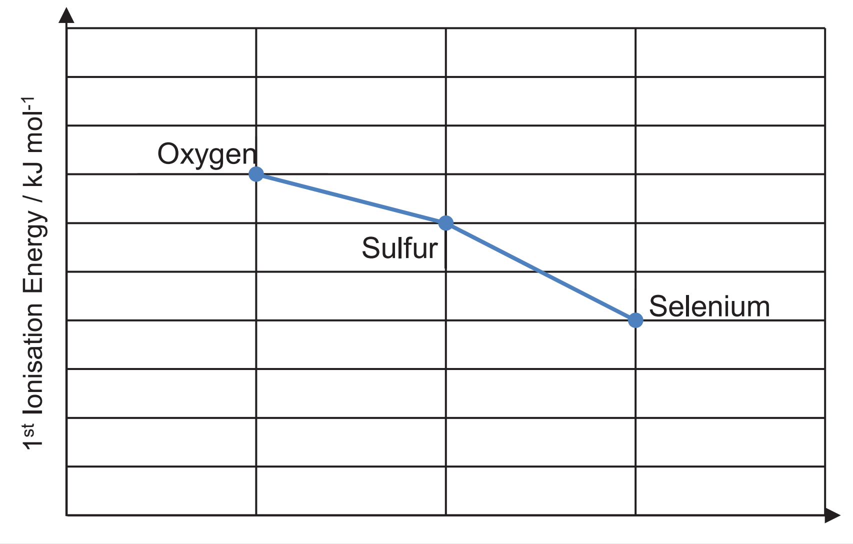
11	12	13	14	15	16	17	18	19	20
C	**B**	**B**	**A**	**B**	**B**	**D**	**C**	**A**	**A**

21	22	23	24	25	26	27	28	29	30
D	**C**	**B**	**A**	**B**	**C**	**B**	**C**	**D**	**D**

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

1 The chalcogens, or the oxygen family, are the elements in group 16 of the Periodic Table. These elements are common in both organic and inorganic compounds.

(a) The graph below shows the trend in the first ionisation energies of oxygen, sulfur and selenium.



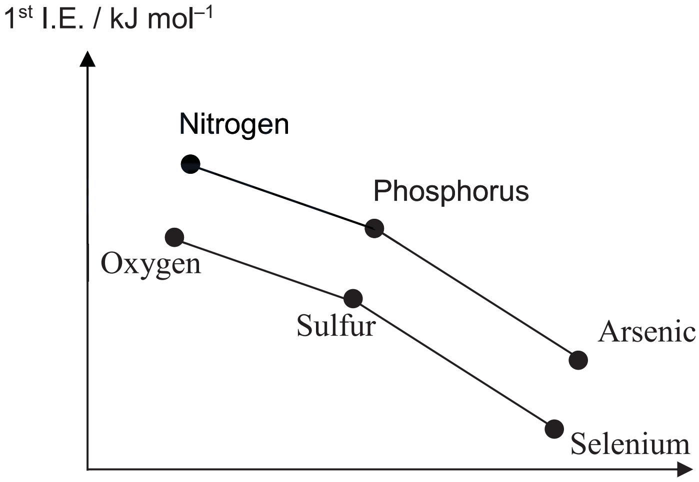
(i) Explain the trend in the first ionisation energies of oxygen, sulfur and selenium.

The first ionisation energy decreases from oxygen to selenium. This is because down the group while the nuclear charge increases, number of quantum shells increases and valence electrons are further away from the nucleus.

Hence, down the group, the valence electrons experience weaker attraction to the nucleus and a smaller amount of energy is required to remove this electron from the atom.

[2]

(ii) On the same grid above, sketch the trend in the first ionisation energies of nitrogen, phosphorus and arsenic.



[1]

(b) A common chalcogen-containing reagent used in both organic and inorganic synthesis is hydrogen peroxide, H_2O_2. Hydrogen peroxide readily decomposes at room temperature.

Iodide ions, I^-, catalyse this decomposition, as shown below:

$$\text{Step I: } H_2O_2 + I^- \rightarrow H_2O + IO^- \text{ (slow)}$$
$$\text{Step II: } H_2O_2 + IO^- \rightarrow H_2O + O_2 + I^-$$

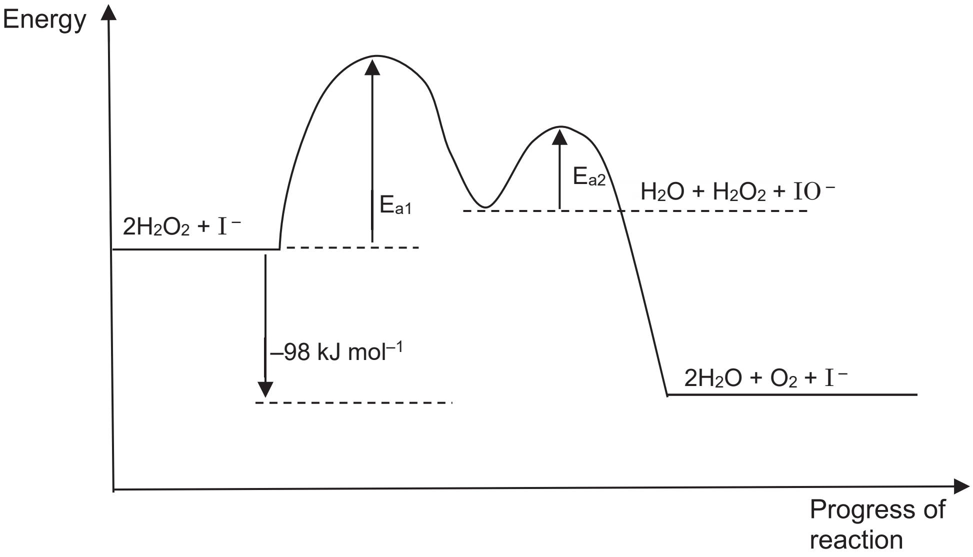
The overall equation for the decomposition of hydrogen peroxide is shown below:

$$2H_2O_2 \rightarrow 2H_2O + O_2$$

The enthalpy and entropy changes for the reaction above are shown in the table below:

Enthalpy change / kJ mol^{-1}	–98
Entropy change / J K^{-1} mol^{-1}	+71

(i) Using the data above, complete the diagram below to show the energy profile diagram for the decomposition of hydrogen peroxide in the presence of iodide ions.



[2]

(ii) An unknown amount of hydrogen peroxide was allowed to decompose in a 5 dm^3 closed vessel at 120 ºC. When all the hydrogen peroxide was decomposed, a pressure of 177 kPa was measured in the vessel.

Determine the amount of hydrogen peroxide that decomposed in the vessel. (Assume that H_2O and O_2 are ideal gases under the above reaction conditions)

pV = nRT

Total moles of gas in vessel, n = $\frac{177000 \times 5 \times 10^{-3}}{8.31 \times (273+120)}$ = **<u>0.27098 mol</u>**

Hence, moles of hydrogen peroxide that decomposed
= 0.27098 ÷ 3 × 2
= **<u>0.181 mol</u>**

[2]

(c) Chalcogens are also very commonly found in organic compounds. Table 1 below shows some common oxygen or sulfur containing organic functional groups.

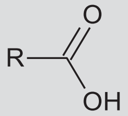
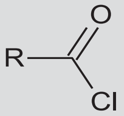
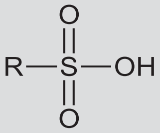
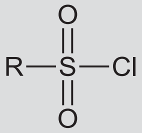
Oxygen-containing functional groups	Alcohols R–OH	Carboxylic Acids 	Acyl chlorides 
Sulfur-containing functional groups	Thiols R–SH	Sulfonic Acids  $R-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-OH$	Sulfonyl chlorides  $R-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-Cl$

Table 1

(i) Explain why carboxylic acids are generally more acidic than alcohols.

This is because the lone pair of electrons on the negatively charged oxygen of the carboxylate anion is able to delocalise over two oxygen atoms. This results in the dispersal of the negative charge and hence, the conjugate base of carboxylic acids are more stable than that of alcohols.

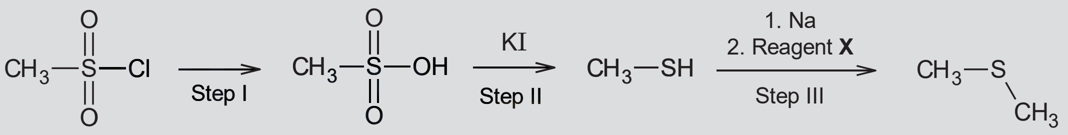
[1]

(ii) Hence, suggest a reason why carboxylic acids are generally less acidic than their corresponding sulfonic acids.

The conjugate base of the sulfonic acids are more stable due to the presence of an additional (electronegative) oxygen atom, which allows the delocalisation of electrons over more atoms.This reduces the intenisty of the negative charge on a single atom.

[1]

(iii) A reaction scheme for the synthesis of dimethyl sulfide (CH_3SCH_3) from methylsulfonyl chloride (CH_3SO_2Cl) is shown below:



Given that sulfur-containing functional groups undergo similar reactions as their corresponding oxygen-containing functional groups (Table 1), suggest:

I. The reagent(s) and condition(s) required for Step I.

H_2O

[1]

II. The role of KI in Step II.

Reducing agent

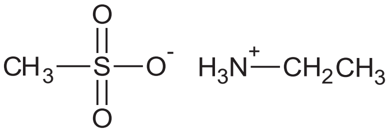
[1]

III. The identity of reagent **X** in Step III.

CH_3Cl or CH_3Br or CH_3I

[1]

IV. The structure of the product(s) formed when methylsulfonic acid (CH_3SO_3H) is reacted with ethylamine ($CH_3CH_2NH_2$) at room temperature.



$CH_3SO_2O^- \quad H_3\overset{+}{N}CH_2CH_3$

[1]

[Total: 13]

2 The electrolysis of dilute sulfuric acid was carried out using two different currents at room temperature and pressure.

	Current / A	Duration / min
Experiment 1	0.75	90
Experiment 2	0.45	90

Oxygen gas is collected at one of the electrodes.

(a) **(i)** Calculate the final volume of oxygen produced in experiment 2.

$Q = It$

$= 0.45 \times (90 \times 60) = 2430$ C

At the anode, $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$

$4F \equiv 1O_2$

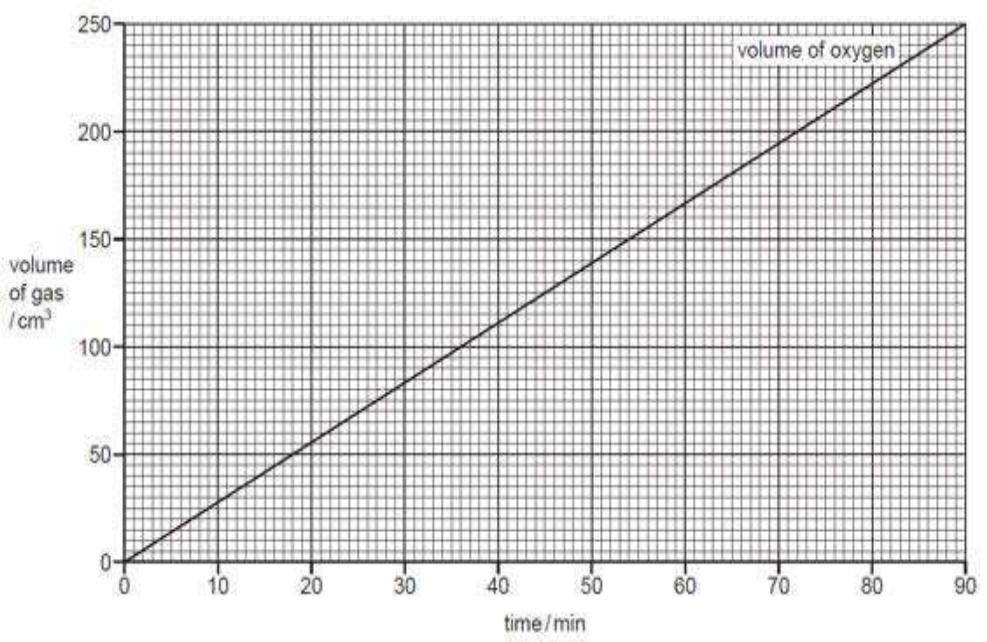
Moles of oxygen produced $= \dfrac{Q}{nF} = \dfrac{2430}{4 \times 96500}$

$= 6.30 \times 10^{-3}$

Final volume of O_2 produced $= (6.30 \times 10^{-3}) \times 24\ 000\ cm^3 =$ **$\underline{151\ cm^3}$**

[2]

(ii) The volume of oxygen collect at one of the electrodes for experiment 1 is shown below.



On the graph above, draw a line to show each of the following:

I. the volume of H_2 gas that would be given off in experiment 1 (Label this line **1**)

II. the volume of oxygen that would be produced in experiment 2 (Label this line **2**)

[2]

I. A straight line from the origin which has double the oxygen volume at a given time.

II. A straight line from the origin which has 0.45/0.75 of the volume of oxygen at a given time.

(b) In another experiment, electrolysis of aqueous potassium butanedioate, $(OOCCH_2CH_2COO)K_2$ as the electrolyte was carried out. It was found that two gases, **Y** and **Z**, were liberated at the anode in a 2:1 ratio by volume.

Gas **Y** formed is absorbed by soda lime while gas **Z** is able to decolourise bromine water.

(i) Suggest the identities of gases **Y** and **Z**. [1]

Gas **Y** is CO_2 Gas **Z** is C_2H_4

(ii) Construct the half-equation for the reaction that occurs at the anode and the cathode respectively. [2]

Anode $^{-}OOCCH_2CH_2COO^{-} \rightarrow 2CO_2 + CH_2CH_2 + 2e^{-}$

Cathode $2H_2O + 2e^{-} \rightarrow H_2 + 2OH^{-}$

(iii) Predict the main organic product that would be obtained at the anode when a solution of potassium pentanedioate is electrolysed. [1]

Propene

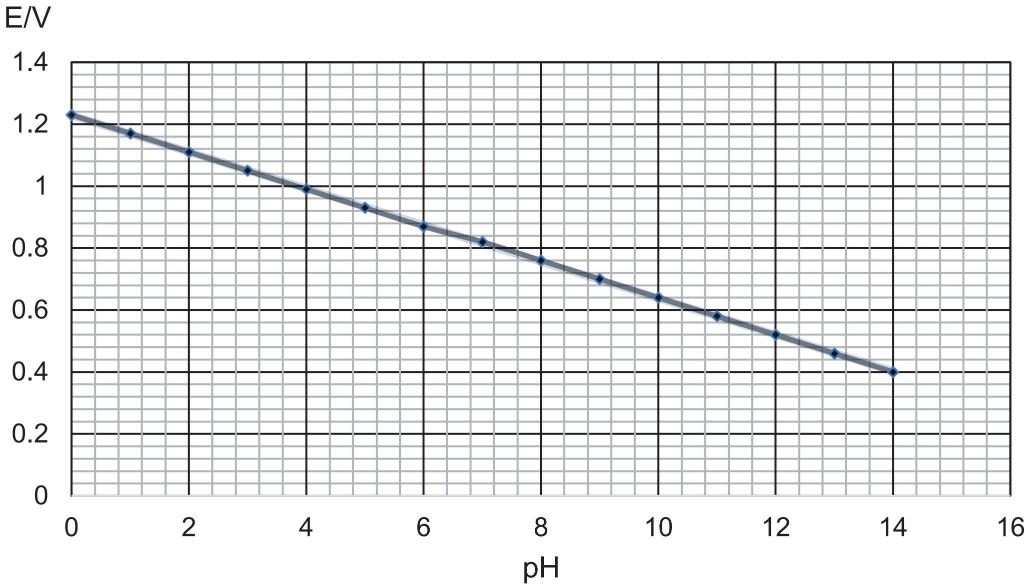
(c) Nicotinamide adenine dinucleotide (NAD^+) is involved in redox chemistry throughout the respiratory system. Aerobic respiration is the process of producing cellular energy involving oxygen.

The electrode potential for the reduction of NAD^+ in a *biological* system, *E*(pH 7), at 1 mol dm^{-3}, 25 °C and pH 7, is as shown.

Its oxidised and reduced forms are represented as NAD^+ and NADH respectively.

$$NAD^+ + H^+ + 2e^- \rightleftharpoons NADH \qquad E(\text{pH } 7) = -0.320\ V$$

The reduction electrode potential of oxygen at different pH is given below.



(i) With reference to the *Data Booklet* and the graph given above, calculate the value of E_{cell} for aerobic respiration. Write a balanced equation for this reaction. [3]

At pH 7, reduction potential of oxygen is **<u>+0.82 V</u>**. That is,

$O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O$ $\qquad E(\text{pH } 7) = +0.82$ V
OR
$O_2 + 2H_2O + 4e^- \rightleftharpoons 4OH^-$

$$E_{cell} = E_{cathode} - E_{anode} = +0.82 - (-0.32) = +1.14\ V$$

<u>Equation:</u>

$2NADH + O_2 + 2H^+ \rightarrow 2H_2O + 2NAD^+$
OR
$2NADH + O_2 \rightarrow 2NAD^+ + 2OH^-$

(ii) State how will the *E_{cell}* differ if the aerobic reaction is performed at a pH of 7.4. [1]

At a higher pH, i.e. lower $[H^+(aq)]$, the aerobic respiration reaction is *less* favourable and so E_{cell} will be less positive.

(iii) Based on your answer in **(c)(i),** calculate ΔG(pH 7) for the aerobic respiration process. [1]

$$\begin{aligned}\Delta G(\text{pH } 7) &= -nFE(\text{pH } 7)\\ &= -(4)(96500)(+1.14)\\ &= -440\ 040\ \text{J mol}^{-1}\\ &= \underline{\mathbf{-440\ kJ\ mol^{-1}}}\end{aligned}$$

[correct answer + units]

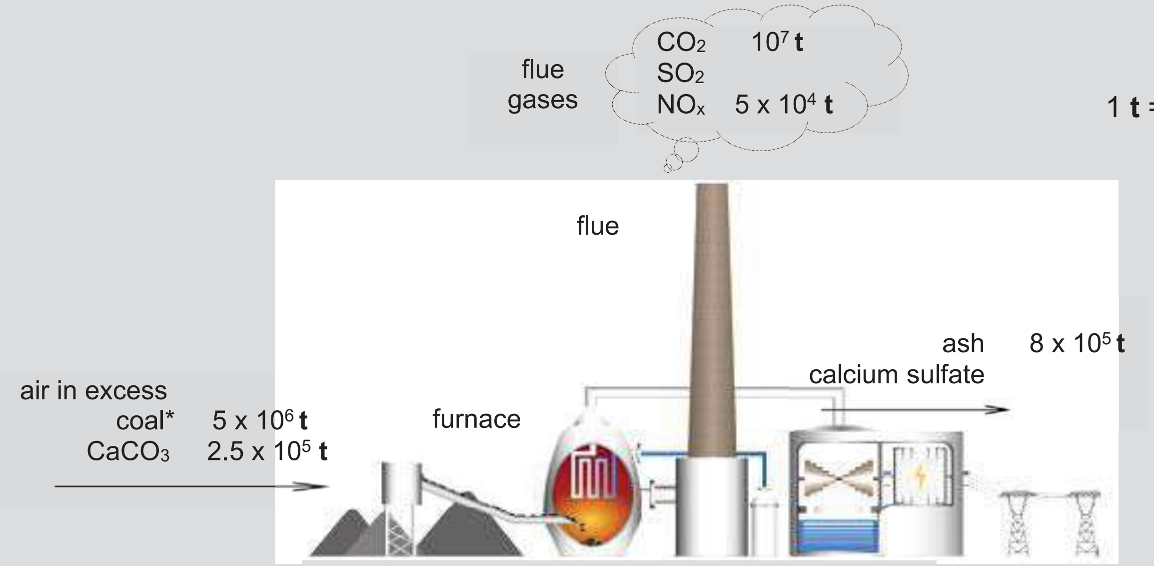
[Total:13]

3 A coal-fired power station is fitted with a Flue Gas Desulfurisation (FGD) plant, which removes some of the sulfur dioxide from flue (waste) gases.

In the FGD plant, the flue gases are treated with powdered limestone, $CaCO_3$, where sulfur dioxide is absorbed and reacted to produce calcium sulfite, $CaSO_3$, which is oxidised by air to form solid calcium sulfate, $CaSO_4$.

The diagram below shows the amounts of substances used, and produced, by such a coal-fired power station with an FGD plant in **one** year.

t = tonne
1 **t** = 1000 kg



Power station & FGD plant

**coal is chiefly* hydrocarbons

(a) **(i)** State the process that produces the energy in the power station. [1]

Combustion of coal.

(ii) Identify a gas, not listed in the diagram, which will be a chief component of the flue gases. [1]

H_2O(g) or water vapour.

(iii) Explain why oxides of nitrogen (NO_x) are present in the flue gases. [1]

NO_x is likely formed from reaction of oxygen and nitrogen in the air at high temperatures during combustion of coal.

(b) Write a balanced equation in each case to show how

- sulfur dioxide is removed from flue gases;

$SO_2 + CaCO_3 \rightarrow CaSO_3 + CO_2$

- calcium sulfate is formed. [2]

$CaSO_3 + \frac{1}{2} O_2 \rightarrow CaSO_4$

(c) Using your answer in **(b)**, determine the maximum mass of sulfur dioxide which could be removed in the FGD plant.
[1**t** = 1 tonne = 1000 kg] [1]

Mass of SO_2 that could be removed in FGD plant depends on mass of $CaCO_3$ used.

Moles of $CaCO_3$ used = $2.5 \times 10^5 \times 10^6 / 100.1 = 2.4975 \times 10^9$ mol
Maximum moles of SO_2 can be removed = Moles of $CaCO_3$ used

Maximum mass of SO_2 removed = $2.4975 \times 10^9 \times 64.1$
= 1.60×10^{11} g or 1.60×10^8 kg or 1.60×10^5 t

(d) Given that your answer in **(c)** was only 90% of the sulfur dioxide removed from the flue gases, calculate the mass of sulfur dioxide which is released into the atmosphere in **five** years by this power station when the same mass of coal is burnt each year. [1]

Mass of SO_2 released in 5 years = $(1.6009 \times 10^{11} \text{ g} \times \frac{0.10}{0.90}) \times 5$
= 8.89×10^{10} g or 8.89×10^7 kg or 8.89×10^4 t

(e) Another method for removing sulfur dioxide from the flue gases is to absorb it in a slurry of magnesium oxide, to produce magnesium sulfite, $MgSO_3$.

(i) Explain why magnesium oxide can also be used to remove sulfur dioxide. [1]

Magnesium oxide is basic and can undergo acid-base reaction with (acidic) sulfur dioxide.

(ii) Magnesium sulfite decomposes readily, upon heated, to give magnesium oxide and sulfur dioxide. Magnesium oxide could be recycled, while sulfur dioxide could be used to make sulfuric acid.

Explain whether it would be easier to obtain magnesium oxide or calcium oxide from its respective sulfite. [3]

It will require less energy to decompose magnesium sulfite as magnesium sulfite is less thermally stable, due to the higher charge density, hence higher polarising power, of Mg^{2+} ion. The electron cloud of SO_3^{2-} ion will be polarised to a larger extent by Mg^{2+}, resulting in $MgSO_3$ decomposing more readily to give MgO. Therefore it will be easier to obtain magnesium oxide from its respective sulfite.

(f) When 1 mol of magnesium oxide, calcium oxide and other Group 2 metal oxides were separately dissolved in 1 dm^3 of deionised water, the pH of the resulting solutions were obtained.

Some data regarding these Group 2 metal oxides, **M**O, and their resulting solutions are provided in the table below.

ion	ionic radius/ nm	$\Delta H_{hydration}$ / kJ mol^{-1}	pH of **M**O in water	Electronegativity difference (ΔEN) in **M**O
O^{2-}	0.140			
Be^{2+}	0.031	–2370	7.0	1.87
Mg^{2+}	0.065	–2024	9.0	2.13
Ca^{2+}	0.099	–1680	9.5	2.44
Sr^{2+}	0.113	?	11	2.49
Ba^{2+}	0.135	–1314	12	2.55

(i) Suggest why there is no value for $\Delta H_{hydration}$ of the oxide ion, O^{2-}. [1]

O^{2-} reacts with water to give OH^-.
OR equation: $O^{2-} + H_2O \rightarrow 2OH^-$

(ii) Using the data given, estimate $\Delta H_{hydration}$ of Sr^{2+}. [1]

enthalpy change of hydration of Sr^{2+} = **<u>–1538 kJ mol^{-1}</u>**

(iii) State and explain the trend in $\Delta H_{hydration}$ in the table, in terms of the interaction between cations and water. [2]

$\Delta H_{hydration}$ of cations becomes less exothermic (or its magnitude decreases) with increasing cationic radius. The increase in cationic radius results in decrease in charge density of cations. Cations will polarise the electron cloud of water molecules to a smaller extent, hence there is a decrease in strength of ion–dipole interactions formed between cations and water molecules. This results in less amount of energy evolved when cations are hydrated.

(iv) With reference to the relevant data given in **(f)**, suggest explanations for the increasing pH of the resulting solution from BeO to BaO in terms of:

(I) Lattice energy and enthalpy change of solution of **M**O [3]

Increasing cationic radius from Be^{2+} to Ba^{2+}, hence lattice energy becomes less exothermic (or magnitude decreases) resulting in a more exothermic (or increasing magnitude of) enthalpy change of solution from BeO to BaO.

Thus, solubility of Group 2 MO increases down the group.
As a result, $[OH^-]$ increases and pH of resulting solution increases.

(II) ΔEN and the nature of the bonding in **M**O [2]

ΔEN increases from BeO to BaO. This means that the metal-oxygen bond gets more ionic from BeO to BaO, thus MO gets more basic / $[OH^-]$ increases, and the pH of the resulting solution becomes higher.

[Total: 20]

4 **(a)** Vitamin C is an essential nutrient also known as ascorbic acid. A deficiency of vitamin C leads to a disease known as scurvy.

Ascorbic acid is known to have a M_r of 176.0 and contains 40.9% of carbon and 54.5% of oxygen by mass.

(i) Determine the molecular formula of ascorbic acid.

	C	O	H
% mass	40.9	54.5	4.6
Divide by A_r	3.41	3.41	4.6
Simplest ratio	3	3	4

The empirical formula of ascorbic acid is $C_3O_3H_4$.
n[(3 x 12.0) + (3 x 16.0) + (4 x 1.0)] = 176.0
n = 2
The molecular formula of ascorbic acid is $C_6O_6H_8$.

[2]

(b) Ascorbic acid is a monobasic acid, H**A**, and has a pK_a of 4.10. The amount of ascorbic acid contained in dietary supplement tablets can be verified by titration. A tablet containing 500 mg of ascorbic acid was dissolved in 25.0 cm^3 of deionised water.

(i) Calculate the volume of 0.100 mol dm^{-3} sodium hydroxide required for complete neutralisation.

$$n_{acid} = \frac{0.500}{176.0} = 2.841 \times 10^{-3} mol$$
$$v_{NaOH} \times 0.100 = 2.841 \times 10^{-3}$$
$$v_{NaOH} = 28.4\ cm^3$$

[1]

(ii) Calculate the initial pH of the ascorbic acid solution.

$[HA] = \frac{2.841\times10^{-3}}{(25.0)\div1000} = 0.1136$ mol dm^{-3}
$K_a = 10^{-4.10}$
$[H^+] = \sqrt{K_a \times [HA]} = 3.00 \times 10^{-3}$ mol dm^{-3}
$pH = -\lg[3.00 \times 10^{-3}] = 2.52$

[2]

(iii) Suggest a suitable indicator the titration. Describe the expected colour change at the endpoint.

Phenolphthalein (colorless to pink) or
Thymol blue (yellow to blue)

[1]

(iv) With the aid of a suitable equation, explain your choice of indicator in **(iii)**.

$A^- + H_2O \rightleftharpoons HA + OH^-$

At end point, the salt / conjugate base of ascorbic acid undergoes salt hydrolysis to form hydroxide ions. [1] with equation

The pH of the resultant solution is > 7.

The pH transition range of selected indicator lies within the range of rapid pH change over the equivalence point of the neutralisation reaction.

[2]

(c) When a vitamin C tablet is swallowed, it dissolves in the stomach. The pH of the stomach is 2.

(i) Determine the percentage of ascorbic acid that is ionised in the stomach.

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

$$10^{-4.10} = \frac{[10^{-2}][A^-]}{[HA]}$$

$$\frac{[A^-]}{[HA]} = 10^{-2.1} = 7.93 \times 10^{-3}$$

Alternative method:

$$pH = pK_a + lg\frac{[A^-]}{[HA]}$$

$$2 = 4.10 + lg\frac{[A^-]}{[HA]}$$

$$\frac{[A^-]}{[HA]} = 10^{-2.1} = 7.93 \times 10^{-3}$$

Let α represent the percentage ionisation.

$$\frac{\alpha}{100-\alpha} = 7.93 \times 10^{-3}$$

$$\alpha = 0.788\%$$

Alternative method:

Since [HA]>>[A^-] or since K_a is small,

% ionisation = 0.793%

[2]

The pH of blood is maintained at 7.35 by a H_2CO_3/HCO_3^- buffer.

(ii) Using appropriate equations, explain how the buffer minimises changes in pH.

Excess acid in blood is removed by hydrogen carbonate.

$HCO_3^- + H^+ \rightarrow H_2CO_3$

Excess alkali in blood is removed by carbonic acid.

$H_2CO_3 + OH^- \rightarrow HCO_3^- + H_2O$

[2]

(d) Organic acids like ascorbic acid react with amines in aqueous medium.

(i) State the type of bond formed during the reaction.

Type of bond: Ionic

[1]

(ii) Account for the increasing basicity of primary, secondary and tertiary amines in gas phase.

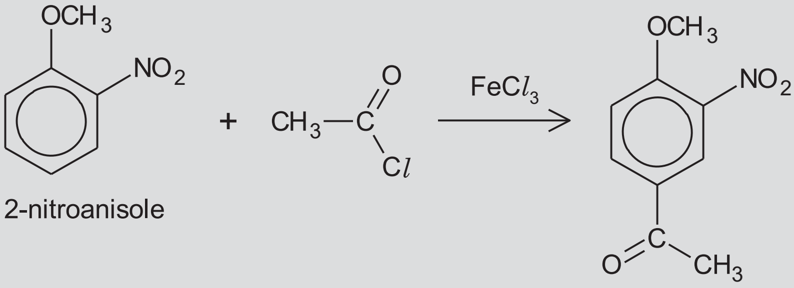
As the number of electron-donating alkyl groups increases, electron density on the N atom increases or lone pair of electrons is more available for donation.

[1]

[Total: 15]

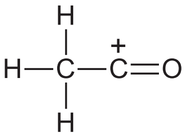
5 **(a)** In Friedel-Crafts acylation, $FeCl_3$ is employed to attach an acyl group to an aromatic ring via electrophilic substitution.

For example, compound **A** can be prepared by the reaction of 2-nitroanisole with ethanoyl chloride in the presence of $FeCl_3$.



compound **A**

(i) Draw the displayed formula of the electrophile and write an equation to show how it is generated.

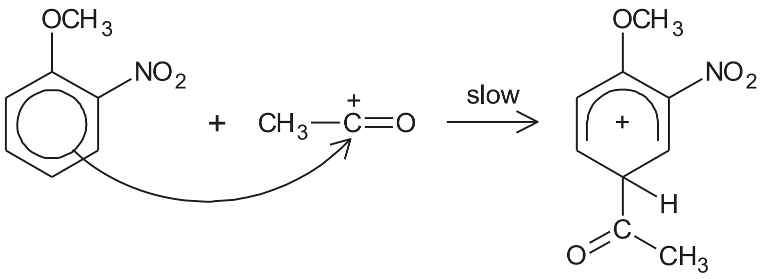


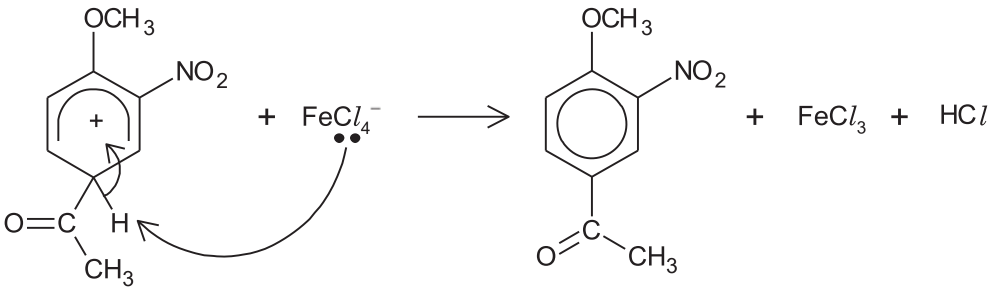
$$\mathrm{H{-}\overset{\displaystyle H}{\underset{\displaystyle H}{C}}{-}\overset{+}{C}{=}O}$$

$CH_3COCl + FeCl_3 \rightarrow CH_3CO^+ + FeCl_4^-$

[2]

(ii) Using your answer in **(i)**, draw the mechanism of the acylation of 2-nitroanisole by ethanoyl chloride. Show all charges and relevant lone pairs and show the movement of electron pairs by using curly arrows.





[2]

Empirical evidence shows that the electrophile generated in **(i)** is not exceptionally reactive. As such, the Friedel-Crafts acylation of nitrobenzene by ethanoyl chloride does not take place under any conditions.

(iii) Explain why nitrobenzene does not undergo acylation but the presence of the –OCH_3 group in 2-nitroanisole permits acylation.

- The –NO_3 group is a highly deactivating substituent.
- It reduces the electron density of benzene ring such that it becomes less susceptible to an electrophilic attack by a rather unreactive electrophile like CH_3CO^+.

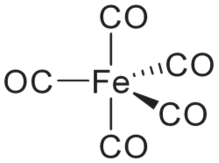
- The presence of a second strongly activating group like –OCH_3 increases the electron density of benzene ring sufficiently for it be susceptible to electrophilic attack by CH_3CO^+.

[2]

(b) Another iron compound, $Na_2[Fe(CO)_4]$, is used in the reaction between alkyl halides and carbon monoxide to synthesise ketones. This iron-based reagent is made as follows.

$$Fe(CO)_5 \xrightarrow{Na/Hg} \xrightarrow{-CO} 2Na^+ + [Fe(CO)_4]^{2-}$$

(i) Draw the structure of $Fe(CO)_5$ to show its shape clearly.



[1]

(ii) The oxidation state of Fe in $Fe(CO)_5$ is 0 and the CO ligands are neutral. Suggest the oxidation state of Fe in the $[Fe(CO)_4]^{2-}$ anion.

–2

[1]

(iii) Besides the oxidation states exhibited in the above reaction, iron also exists in other oxidation states like +2 and +3.

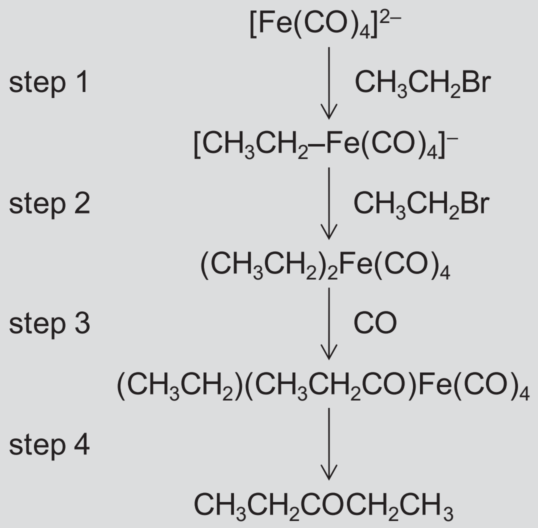
State a property of iron that allows its compounds to behave in this manner and give a reason why this property arises in iron.

- Fe exhibits variable oxidation states.

- In transition elements, 3d and 4s orbitals / electrons are similar in energy *OR* 3d orbitals which are partially filled, which allows the removal or accepting of electrons without requiring much more energy.

[2]

The reaction between $[Fe(CO)_4]^{2-}$ and bromoethane takes place under an applied pressure of carbon monoxide via the following steps.



(iv) Explain what is meant by the term *coordination number* in the context of a metal complex.

State the coordination number of iron in $[Fe(CO)_4]^{2-}$ and in $(CH_3CH_2)(CH_3CH_2CO)Fe(CO)_4$.

The coordination number is the number of dative covalent bonds formed between ligands and the central metal atom or ion.

	coordination number of iron
$[Fe(CO)_4]^{2-}$	4
$(CH_3CH_2)(CH_3CH_2CO)Fe(CO)_4$	6

[2]

(v) Studies show that steps 1 and 2 proceed via nucleophilic substitution.

If bromoethane were replaced by bromobenzene, the above reaction with $Na_2[Fe(CO)_4]$ would not work. With reference to the bonding and structure of bromobenzene, give **two** reasons why both S_N1 and S_N2 cannot occur.

- A p orbital of Br atom overlaps with the p orbitals of C atoms in benzene ring.
- The lone pair of electrons in this p orbital delocalises into the benzene ring to form a delocalised π electron cloud.
- This results in a partial double bond character in the C–Br bond.
- Large amount of energy is needed to break the C–Br bond, making it very difficult for both S_N1 and S_N2 o occur.

- The rear end of the C–Br bond in bromobenzene is sterically hindered by the

bulky benzene ring.
OR

- The π electron cloud repels the lone pair of electrons of the incoming nucleophile and hinders the rear end attack of the electrophilic C bearing the Br atom.
- This makes it difficult for S_N2 to occur.

[3]

[Total: 15]

Dunman High School
2017 Year 6 H2 Chemistry
Preliminary Examination Paper 3 (Answer Scheme)
Section A

1 **(a)** **(i)**

1. The gas *particles* have negligible volume compared to the volume of the container.
2. There are no intermolecular forces of attraction between gas particles.

Its electron cloud size is larger hence volume of NO_2 molecules is significant compared to the volume of the gas, unlike H_2.

Both NO_2 and H_2 have simple molecular structure. Since NO_2 has stronger permanent dipole-permanent dipole interaction than instantaneous dipole-induced dipole interactions in H_2 $\boxed{\textit{OR}}$ NO_2 has a larger electron cloud size than H_2, the electron cloud of NO_2 is more polarisable and hence stronger intermolecular forces of attraction.

(ii) $pV = nRT = (m/M)RT$
$p = (m/V)(RT/M)$
$\frac{p}{\rho} = RT/M$
At 100 °C and very low pressure,
$RT/M = 110.3$
$M = (8.31 \times 373) / 110.3$
$= 28.1 \text{ g mol}^{-1}$
$M_r = 28.1$

(iii) CO

(b) $NO_2 + SO_2 \rightarrow SO_3 + NO$
$NO + ½ O_2 \rightarrow NO_2$

NO_2 catalyses by oxidising SO_2 to SO_3, while itself is reduced to NO. NO is rapidly re-oxidised to NO_2 by oxygen, regenerating the catalyst, NO_2.

$SO_3 + H_2O \rightarrow H_2SO_4$ *OR*
SO_3 dissolves in the water vapour in the atmosphere/ rain to form sulfuric acid, which causes acid rain.

(c) **(i)** Order w.r.t $[O_2]$ is zero as the graph of $[O_2]$ against time is a downward sloping straight line / the gradient of the line, i.e. rate of reaction, is constant with changing $[O_2]$.

When $[SO_2] = 0.8 \text{ mol dm}^{-3}$,
r_1, rate of reaction = $\left|\frac{0.04 - 0.05}{88}\right| = 1.13 \times 10^{-4} \text{ mol dm}^{-3} \text{ s}^{-1}$
When $[SO_2] = 1.2 \text{ mol dm}^{-3}$,
r_2, rate of reaction = $\left|\frac{0.030 - 0.05}{80}\right| = 2.50 \times 10^{-4} \text{ mol dm}^{-3} \text{ s}^{-1}$
$r_2/r_1 = 2.21 \approx 2.25$

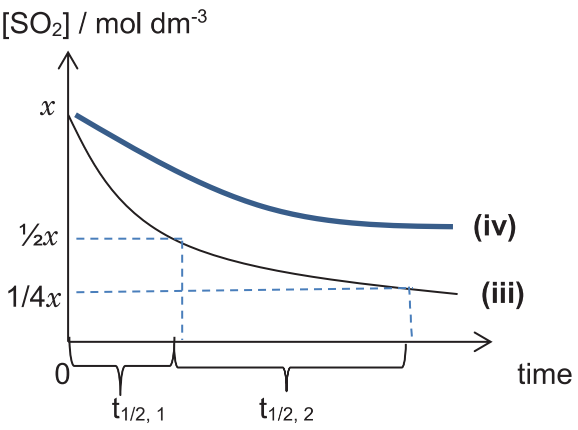
When $[SO_2]$ x 1.5 times, rate of reaction x 2.25 times, reaction is second order w.r.t $[SO_2]$.

(ii) rate = $k[SO_2]^2$

When $[SO_2] = 0.8\ \text{mol dm}^{-3}$,
$k = 1.77 \times 10^{-4}\ \text{mol}^{-1}\ \text{dm}^3\ \text{s}^{-1}$

($k = 1.74 \times 10^{-4}\ \text{mol}^{-1}\ \text{dm}^3\ \text{s}^{-1}$, if $[SO_2] = 1.2\ \text{mol dm}^{-3}$)

(iii)



2 **(a)** For hexane / cyclohexane mixture,

- Energy produced from instantaneous dipole – induced dipole (id-id) interactions between hexane and cyclohexane molecules after mixing
- is just sufficient to overcome id-id interactions between hexane molecules and between cyclohexane molecules before mixing.
- Thus no heat change is observed.

For hexane / ethanol mixture,

- Energy produced from weak id-id interactions between hexane and ethanol molecules after mixing
- is insufficient to overcome stronger hydrogen bonds between ethanol molecules before mixing.
- Thus heat is absorbed from the surroundings for mixing to occur.

(b) **(i)**

	bonds broken	bonds formed	ΔH / kJ mol^{-1}
step 1	1 C=C	1 C–C 1 C–I	(–350 – 240) + 610 = +20
step 2	1 H–C*l*	1 C–H	–410 + 431 = +21

(ii)

- Only the free radical addition of HBr to an alkene is likely to occur since $\Delta H_{\text{step 1}}$, $\Delta H_{\text{step 2}}$ are all exothermic.

- This reaction is however unlikely to occur if HC*l* and HI were used.
- In each case, there is one propagation step which is endothermic — step 2 for HC*l* and step 1 for HI.

(iii) CH_3CHICH_3

2 **(c)** **(i)**

Q : AgI
R : AgC*l*

- Reaction **I** is the nucleophilic substitution of a halogenoalkane in which C–*X* bonds (where *X* = C*l*, I) are broken to release X^- ions into solution to be precipitated as Ag*X*.
- Rate of substitution depends on the strength of C–*X* bond.

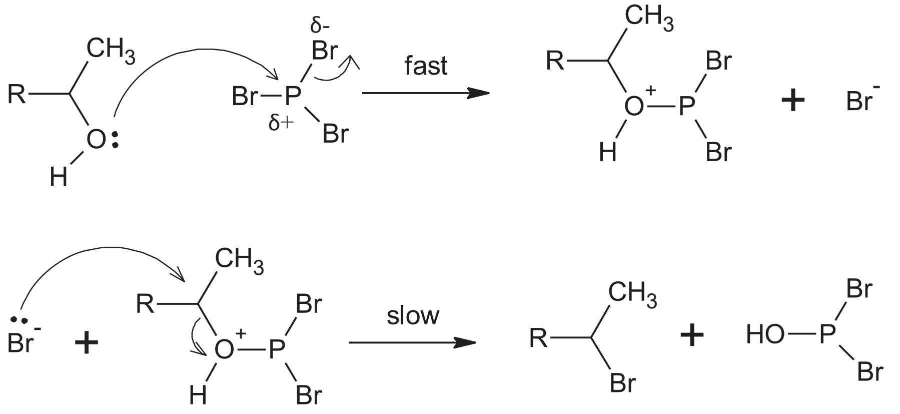
From the *Data Booklet*, BE(C–C*l*) : 340 kJ mol^{-1}
BE(C–I) : 240 kJ mol^{-1}

- C–I bond is weaker *OR* more easily broken than C–C*l* bond *OR* less amount of energy is needed to break C–I than C–C*l* bond.
- Thus, time taken for I^- ions to be released is shorter than that for Cl^- ions *OR* C–I bond is broken first *OR* AgI is precipitated first.

(ii)
- $LiAlH_4$ is a nucleophilic reducing agent *OR* is electron-rich.
- It attacks the electrophilic *OR* electron-deficient carbonyl C atom in carbonyl compounds, carboxylic acids and their derivatives but does not reduce electron-rich C=C bonds in alkenes.

(iii) Step **III**: I_2(aq) with NaOH(aq), heat

3 (a) (i)



3 (a) (ii) Lewis acid. PBr_3 accepts a lone pair of electrons from oxygen in the first step of the mechanism.

(iii) For phenol, the lone pair of electron on the oxygen atom is delocalised into the benzene ring and hence less available for donation and hence, phenol will be a weaker nucleophile, resulting in a relatively slower first step.

(iv) Phenol undergoes electrophilic substitution instead of addition to prevent the loss of its aromaticity (and resonance stability).

(v) Chemical test 1: Add $KMnO_4$ and dilute H_2SO_4, heat (in water bath)
Observation for phenol: Purple $KMnO_4$ does not decolourise
Observation for 2° alcohol used in (a): Purple $KMnO_4$ decolourises

OR

Chemical test 2: Add I_2 and NaOH, warm/heat (in water bath)
Observation for phenol: No yellow ppt forms
Observation for 2° alcohol used in (a): Yellow precipitate forms

OR

Chemical test 3: Add neutral $FeCl_3$(aq)
Observation for phenol: Violet colouration observed

Observation for 2° alcohol used in (a): No violet colouration observed

OR
Chemical test 4: Add $K_2Cr_2O_7$ and dilute H_2SO_4, heat (in a water bath)
Observation for phenol: Solution remains orange
Observation for 2° alcohol used in (a): Orange solutions turns green

3 (b) (i)

	$PCl_3(g)$ +	$Cl_2(g)$ $\rightleftharpoons$	$PCl_5(g)$
Initial partial pressure / atm	2	1.5	0
Change in partial pressure / atm	–x	–x	+x
Eqm Partial pressure/ atm	2 – x	1.5 – x	x

Hence, $(2 - x) + (1.5 - x) + x = 3.3$
Partial pressure of PCl_5 at eqm, $x = 0.2$ atm

$$K_p = \frac{(0.2)}{(2-0.2)(1.5-0.2)} = 0.0855 \text{ atm}^{-1}$$

(ii) Since K_p is much less than 1, the position of the equilibrium lies to the left (or to the reactant side). This means that the forward reaction is not likely to be spontaneous and hence, ΔG should be positive.

(c) (i) $AsCl_5 + 4H_2O \rightarrow H_3AsO_4 + 5HCl$

Or

$AsCl_5 + H_2O \rightarrow AsOCl_3 + 2HCl$

$AsCl_5$ completely hydrolyses in water to produce a strong acid, HCl, which is responsible for the very low pH.

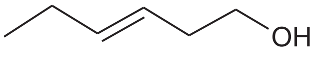
(ii)

OR

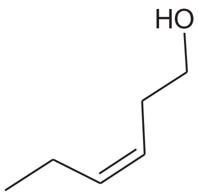
Bond angle: **180°**

4 (a) (i) Constitutional isomers are compounds with the same molecular formula but differs in structural formula.

(ii)



trans



cis

(b) **(i)** If Cu^{2+} is not complexed, it will form $Cu(OH)_2$ solid in alkaline medium and hence will not be able to react with the (aldehyde) functional group.

(ii) Cu^{2+} is a transition metal ion while K^+ is not.
Cu^{2+} has low lying partially–filled orbitals (or vacant subshell of low energy) which allows it to accept lone pair of electrons from tartrate ions to form a dative bond in complex formation.
K^+, however, does not low lying orbitals to form dative bonds with tartrate ligands.

(iii) $CH_2CCH_3(CH_2)_3CH(CH_3)CH_2CHO$ $\boxed{OR}$

$CH_2CCH_3(CH_2)_3CH_2CH(CH_3)CHO$ OR

$CH_2CCH_3(CH_2)_3CH(C_2H_5)CHO$

(iv) Amount of $Cu_2O = \dfrac{0.282}{143} = 0.00197$ mol

General equation (unbalanced):

$$X + 2\,Cu^{2+}(\text{complexed}) + OH^- \rightarrow Cu_2O(s) + \text{products}$$

$1\,X \equiv 2\,Cu^{2+}(\text{complexed}) \equiv 1\,Cu_2O(s)$

Amount of X present = 0.00197 mol
Mass of X present = 0.00197 x M_r of X
= 0.00197 x 154.0
= 0.3037 g
Percentage of compound X present = $\dfrac{0.3037}{2.0}$ x 100% = 15.2%

(v) From (iv), (max) mass of X vapourised/ present = 0.3037 g

Given that minimum concentration of X in the air to be "detectable" is 10 ppm,

i.e. 10 g of X in 1 x 10^6 g of air,

(Max) Mass of air for 0.3037 g of X to be detectable = 0.3037 x $\left(\dfrac{1 \times 10^6}{10}\right)$
= 30 370 g
= 30.37 kg

Given that the density of air is 1.20 kg m^{-3},
Volume of air = $\dfrac{30.37}{1.20}$ = 25.3 m^3

(c) **(i)** Copper in solution Y has oxidation state of +1. Electronic configuration of Cu(I) is $1s^2\ 2s^22p^6\ 3s^23p^63d^{10}$
The ion has a fully–filled d orbitals (or no vacant or partially–filled d orbitals, hence a d electron from lower energy orbital cannot be promoted to a higher energy d orbital. Therefore, solution Y is colourless.

(ii) $CuCl_2 + Cu + 2HCl \rightarrow 2H[CuCl_2]$

$\boxed{OR}$

$Cu^{2+} + Cu + 4Cl^- \rightarrow 2CuCl_2^-$

(d) $Cu^{2+}(aq)$ which is $[Cu(H_2O)_6]^{2+}(aq)$ is blue in colour. When solid sodium chloride is added, it provides high $[Cl^-]$, causing H_2O ligands to be displaced by Cl^- ligands, forming $CuCl_4^{2-}(aq)$ complex, which is yellow in colour. When the following equilibrium is established, the presence of both $[Cu(H_2O)_6]^{2+}(aq)$ and $CuCl_4^{2-}(aq)$ makes the solution appear yellow-green.

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

Upon addition of water, the equilibrium system is diluted. The aqueous reactants are diluted to a larger extent. By Le Chatelier's Principle, addition of water causes equilibrium position to shift to the left. Thus, the $[Cu(H_2O)_6]^{2+}(aq)$ ion dominates, reproducing the blue colour.

In the presence of sulfate ions, no ligand exchange reaction takes place, hence no change is observed as sulfate is a weaker ligand than H_2O.

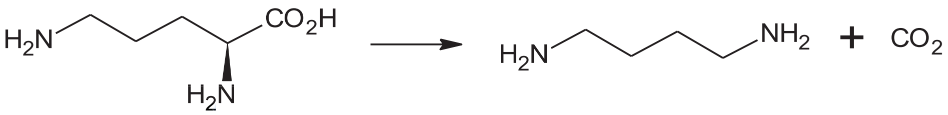
Section B

Answer **one** question from this section.

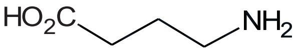
5 **(a)** **(i)** Gaseous by-product: CO_2

AND

Equation (stereochemistry not required):



(ii) Structure:



Name: 4-aminobutanoic acid

(iii) K_b is a measure of the strength/ basicity of a weak base.

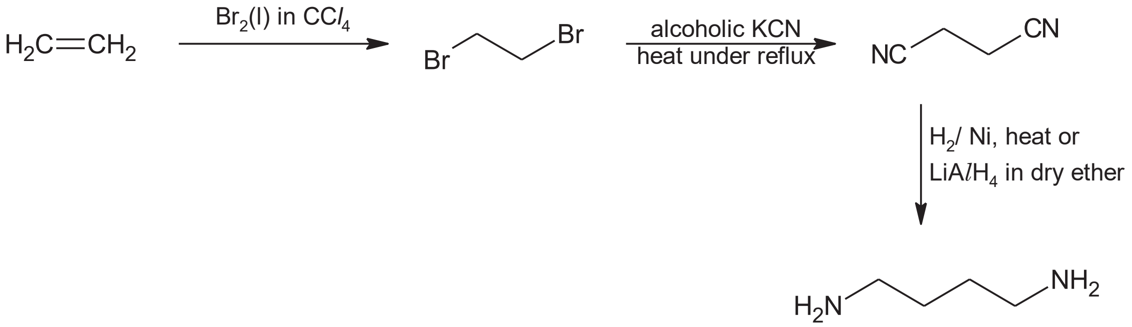
$\boxed{OR}$

K_b of a weak base, B = $\dfrac{[BH^+][OH^-]}{[B]}$

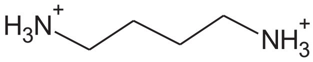
(iv) K_b: α-NH_2 of L-ornithine < R-NH_2 of L-ornithine

α-NH_2 of L-ornithine is closer to the electron-withdrawing $–CO_2H$/ $–CO_2^-$ group which decreases the availability of the lone pair of electrons on N atom of α-NH_2. Hence, α-NH_2 is a weaker base than R-NH_2 of L-ornithine.

5 (b)



5 (c) (i)



(ii) Ionic bonding

(d) (i) At the higher molar ratios, there is a large excess of unbound butane-1,4-diamine as binding sites of the DNA sample become saturated so energy change per mole of butane-1,4-diamine added is zero.

(ii) Endothermic since enthalpy change is positive when butane-1,4-diamine is added to the DNA sample.

(iii) $\Delta G < 0$ since binding of butane-1,4-diamine with the DNA sample is spontaneous.

Since $\Delta G = \Delta H - T\Delta S$ and $\Delta H > 0$, $\Delta S > 0$ and $|T\Delta S| > |\Delta H|$ in order for $\Delta G < 0$.

(iv) The displacement of water molecules surrounding the DNA molecule disrupts the orderly arrangement which leads to an increase in disorder of the system.
OR
The moles of water molecules displaced from the DNA molecule are more than the moles of butane-1,4-diamine that bind with it, leading to an increase in disorder of the system.

5 (e) (i)

$$\Delta G^\ominus = -(8.31)(290)(\ln 4.88 \times 10^5)$$
$$= -315650$$
$$= -31\,600 \text{ J mol}^{-1}$$

(ii) Since $\Delta G^\ominus$ for butane-1,4-diamine is less negative than that for spermine, the binding constant K for butane-1,4-diamine is smaller than that for spermine.

Hence butane-1,4-diamine interacts/ binds less strongly with the DNA than spermine.

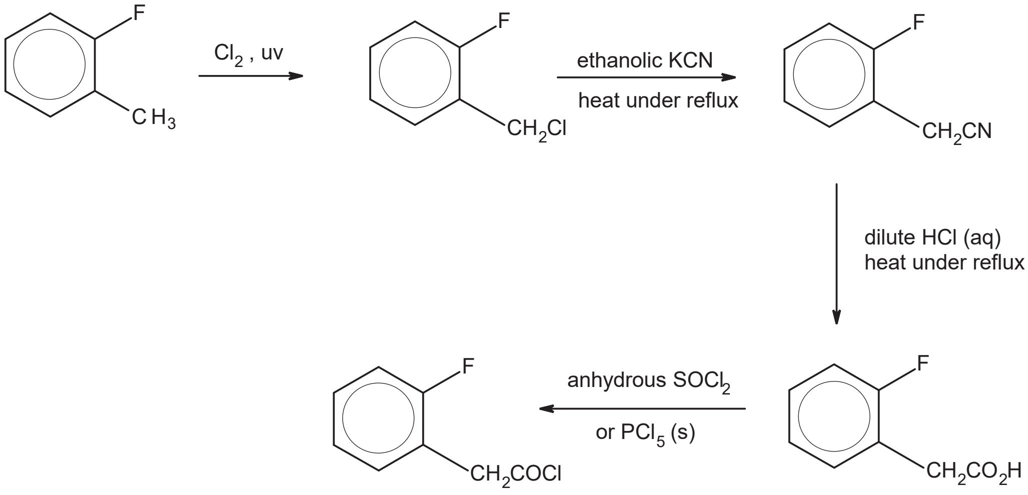
$\boxed{OR}$

$-2.62 \times 10^4 = -(8.31)(290)(\ln K)$

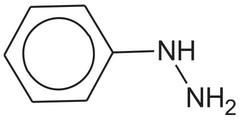
K = 52 671
= 5.27×10^4

Since the magnitude of K for butane-1,4-diamine is lower than that of spermine, butane-1,4-diamine interacts/ binds less strongly with the DNA than spermine.

6 (a) (i)



(ii)

	reagent(s) and conditions	*type of reaction*
(I)	C_6H_6, (anhydrous) $AlCl_3$ or $FeCl_3$	Electrophilic substitution
(II)	 $\boxed{\text{OR}}$ phenylhydrazine	Condensation
(III)	dilute HNO_3	Electrophilic substitution

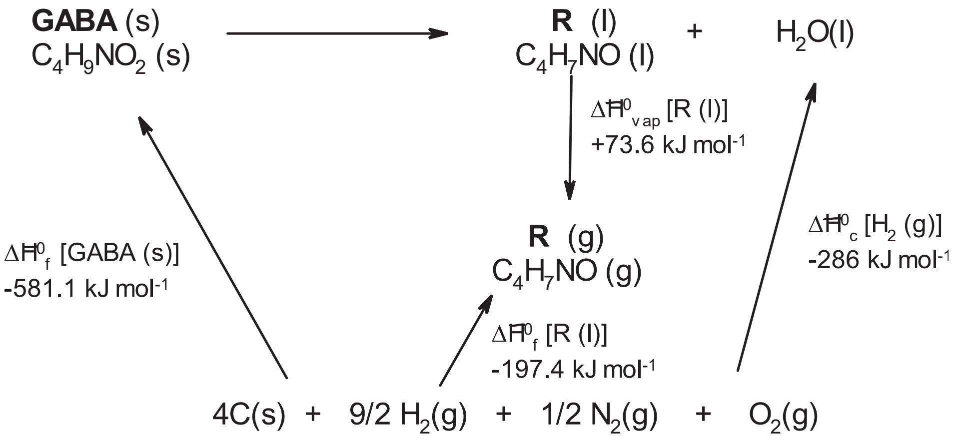
(iii) The half-life is too long and the patient will still be in a drowsy/ hangover state in the following day. / The effect of taking flunitrazepam at night will persist in the next day. / It takes too long for the sleep inducing effect of the drug to kick in. / There could be an overdose of the drug, due to its slow metabolism which results in accumulation of drug, if the patient continues to take drug on consecutive days.

(iv) Approximating $t_{½}$ of 23.5 h as 24 h or a day,

Day	Active mass absorbed / mg	Mass remained from previous day / mg	Total mass left / mg
1	0.8		
2	0.8	0.4	1.2
3	0.8	0.4 + 0.2	1.4
4	-	0.4 + 0.2 + 0.1	0.7
5	-	0.2 + 0.1 + 0.05	**0.35**

(b) **(i)** GABA exists as zwitterion in its natural form which results in strong electrostatic attraction between the zwitterions. Hence, it exists as solid at r.t.p.

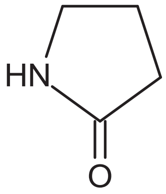
(ii)



By Hess Law,

$\Delta H^{\ominus}_{\text{decomposition}}$ = –(–581.1) + (–197.4) – (+73.6) + (–286)
= +24.1 kJ mol^{-1}

(iii)



HWA CHONG INSTITUTION
C2 Preliminary Examinations
Higher 2

CANDIDATE NAME		**CT GROUP**	**16S**
CENTRE NUMBER		**INDEX NUMBER**	

CHEMISTRY

9729/01

Paper 1 Multiple Choice

20 September 2017

1 hour

Additional Materials: Multiple Choice Answer Sheet
Data Booklet

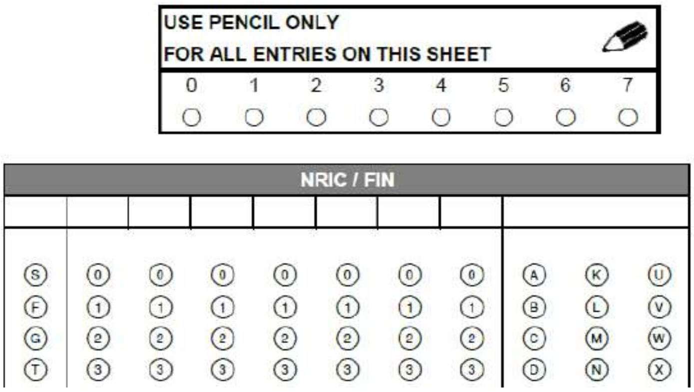
READ THESE INSTRUCTIONS FIRST

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.

1 Why is the second ionisation energy of sodium higher than that of magnesium?

A Magnesium has more protons than sodium.

B Sodium has a complete octet, but magnesium does not.

C The ionic radius of Na^+ ion is larger than that of Mg^+ ion.

D The electron to be removed from sodium is closer to the nucleus.

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

A mass of 0.457 g of solid carbon dioxide was vapourised into an evacuated gas syringe at r.t.p. A small amount of inert gas was introduced into the gas syringe and the volume of the gas syringe was 334.5 cm^3. The temperature was kept constant throughout.

How much inert gas was introduced into the gas syringe?

A 1.4×10^{-2} mol

B 3.3×10^{-3} mol

C 3.5×10^{-3} mol

D 4.3×10^{-3} mol

3 Propadiene and propyne both have the same molecular formula, C_3H_4. They exist in equilibrium as shown:

$$\underset{\text{propadiene}}{H_2C{=}C{=}CH_2} \rightleftharpoons \underset{\text{propyne}}{CH_3C{\equiv}CH}$$

Which bond is present in propadiene but **not** present in propyne?

A a σ bond formed by 1s – 2sp overlap

B a π bond formed by 2p – 2p overlap

C a σ bond formed by 2sp – $2sp^2$ overlap

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

4 Which molecules contain a 90° bond angle?

1 SF_6 2 $\mathrm{PC}l_5$ 3 XeF_4 4 $\mathrm{SiC}l_4$

A 1, 2, 3 and 4

B 1, 2 and 3 only

C 1 and 2 only

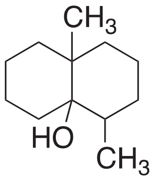
D 3 and 4 only

5 When $\mathrm{T}l^{+}$(aq) ions are reacted with VO_3^{-}(aq) ions, $\mathrm{T}l^{3+}$(aq) ions and V^{2+}(aq) ions are formed.

Assuming the reaction goes to completion, how many moles of $\mathrm{T}l^{+}$(aq) and VO_3^{-}(aq) would result in a mixture containing equal number of moles of VO_3^{-}(aq) and V^{2+}(aq) once the reaction had taken place?

	moles of $\mathrm{T}l^{+}$(aq)	moles of VO_3^{-}(aq)
A	1	2
B	1	3
C	3	2
D	3	4

6 Compound G is produced by actinobacteria in the soil and is responsible for the “it just rained” smell.



compound G

How many moles of oxygen gas are needed to completely burn 1 mole of compound G?

A 16.75 **B** 17.00 **C** 17.25 **D** 17.50

7 Which of the following changes will result in an increase in entropy?

A forward reaction of $[Fe(H_2O)_6]^{2+}(aq) + edta^{4-}(aq) \rightleftharpoons [Fe(edta)]^{2-}(aq) + 6H_2O(l)$

B mixing of 1 mol of N_2 with 1 mol of Ar at constant volume and temperature

C cooling of liquid ethanol from 50 °C to 20 °C

D condensation of water vapour

8 Which equation correctly represents both the enthalpy change of combustion, ΔH_c, and the enthalpy change of formation, ΔH_f, of the respective species?

	ΔH_c	ΔH_f	equation
1	$Na(s)$	$Na_2O(s)$	$2Na(s) + \frac{1}{2}O_2(g) \rightarrow Na_2O(s)$
2	$C(s)$	$CO_2(g)$	$C(s) + O_2(g) \rightarrow CO_2(g)$
3	$H_2(g)$	$H_2O(l)$	$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l)$

A 1 and 2 only

B 2 and 3 only

C 2 only

D 1, 2 and 3

9 The mechanism below has been proposed for the reaction between $CHCl_3$ and Cl_2.

Step 1: $Cl_2(g) \rightleftharpoons 2Cl(g)$ fast

Step 2: $Cl(g) + CHCl_3(g) \rightarrow CCl_3(g) + HCl(g)$ slow

Step 3: $CCl_3(g) + Cl(g) \rightarrow CCl_4(g)$ fast

Which rate equation is consistent with this mechanism?

A rate = $k[CHCl_3]^1[Cl]^1$

B rate = $k[CHCl_3]^1[Cl_2]^1$

C rate = $k[CHCl_3]^1[Cl_2]^{\frac{1}{2}}$

D rate = $k[Cl_2]^1$

10 Iodine–131 is a radioactive isotope with a half-life of 8 days. Given that radioactive decay is a first-order reaction, what fraction of the isotope would remain after 80 days?

A $\frac{1}{20}$ **B** $\frac{1}{160}$ **C** $\frac{1}{2^8}$ **D** $\frac{1}{2^{10}}$

11 The enthalpy change of reaction for the conversion of sulfur dioxide to sulfur trioxide is shown below.

$$2SO_2\,(g) + O_2\,(g) \rightleftharpoons 2SO_3\,(g) \qquad \Delta H = -196 \text{ kJ mol}^{-1}$$

Which of the following statements is correct?

A When the volume of the system increases at constant temperature, the yield of SO_3 increases.

B When a catalyst is introduced to the system, the yield of SO_3 increases.

C The forward reaction is spontaneous at all temperatures.

D When the temperature is increased, K_c decreases.

12 Which of the following silver compounds would give the highest concentration of silver ions in its saturated solution?

	compound	magnitude of solubility product
A	AgCN	6×10^{-17}
B	AgSCN	1×10^{-12}
C	Ag_2SO_3	2×10^{-14}
D	Ag_3PO_4	9×10^{-17}

13 Which of the following is a satisfactory indicator for the titration of 0.1 mol dm^{-3} methylamine and 0.1 mol dm^{-3} hydrochloric acid?

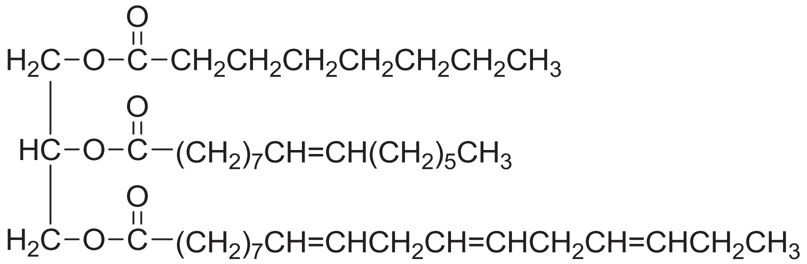
A methyl red (pH range 4.2 – 6.3)

B bromothymol blue (pH range 6.0 – 7.6)

C phenolphthalein (pH range 8.2 – 10.0)

D There is no satisfactory indicator.

14 Triglycerides are the main constituents of body fat in humans and animals. The diagram shows the structure of a triglyceride.

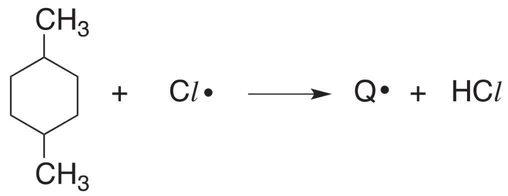


$$H_2C{-}O{-}\overset{O}{\overset{\|}{C}}{-}CH_2CH_2CH_2CH_2CH_2CH_2CH_3$$
$$HC{-}O{-}\overset{O}{\overset{\|}{C}}{-}(CH_2)_7CH{=}CH(CH_2)_5CH_3$$
$$H_2C{-}O{-}\overset{O}{\overset{\|}{C}}{-}(CH_2)_7CH{=}CHCH_2CH{=}CHCH_2CH{=}CHCH_2CH_3$$

What is the total number of stereoisomers possible for this triglyceride?

A 2^1 **B** 2^3 **C** 2^4 **D** 2^5

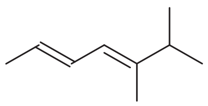
15 When heated with chlorine, the following hydrocarbon undergoes free radical substitution. In the propagation step, the free radical Q• is formed by the loss of one hydrogen atom.



Ignoring any stereoisomers, how many different forms of Q• are theoretically possible?

A 3 **B** 4 **C** 6 **D** 8

16 Compound W is heated with excess acidified $KMnO_4$ for a prolonged period.

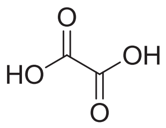


compound W

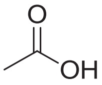
Which of the following compounds is **least likely** to be a product of this reaction?

A CO_2

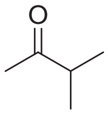
C



B



D



17 Liquid bromine is added separately to the following pairs of compounds under various conditions.

Which of the following pairs of compounds will give the same observations?

A Benzene and phenol, in the presence of *uv* light.

B Hexane and methylbenzene, in the presence of *uv* light.

C Pentene and pentane, in the absence of *uv* light.

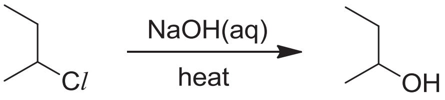
D Phenylamine and benzene, in the absence of *uv* light.

18 Enantiomeric excess is the measure of the excess of one enantiomer over another in a mixture.

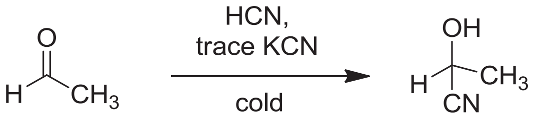
Consider a pair of enantiomers, R and S. If the R enantiomer makes up 75% of the mixture while the S enantiomer makes up 25% of the mixture, R has an enantiomeric excess of 50%.

Which of the following reactions would result in a mixture which gives an enantiomeric excess of 0%?

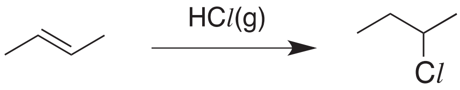
1



2



3



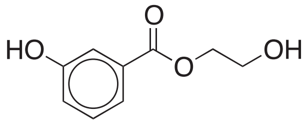
A 1 and 2 only

B 1 and 3 only

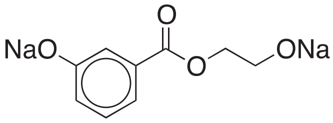
C 2 and 3 only

D 1, 2 and 3

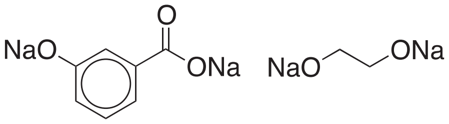
19 What will be produced when the following compound is reacted with cold NaOH(aq)?



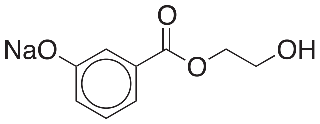
A



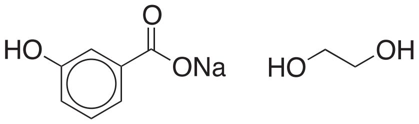
C



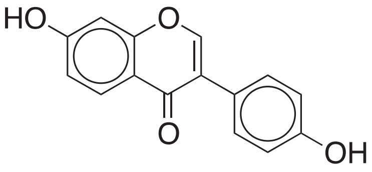
B



D



20 Diadzein belongs to a class of compounds known as isoflavenoids, and is a major component of soya beans.



diadzein

Which statement about diadzein is **not** correct?

A When diadzein reacts with aqueous Br_2, the product contains chiral centres.

B When heated with ethanoic acid and concentrated sulfuric acid, diadzein forms an ester.

C When neutral $FeCl_3$ is added to diadzein, a purple colouration is observed.

D When 2,4-DNPH is added to diadzein, an orange precipitate is observed.

21 Which reaction yields a carbon compound incorporating deuterium, D? [D = ^{2}H]

A $CH_3CH_2CN \xrightarrow[\text{heat}]{\text{NaOD, } D_2O}$

B $CH_3CD(OD)CO_2H \xrightarrow[\text{heat}]{\text{acidified } KMnO_4}$

C $CH_3COCI_3 \xrightarrow[\text{heat}]{\text{NaOD, } D_2O}$

D $(CH_3)_3COH \xrightarrow[\text{heat}]{\text{conc. } D_2SO_4}$

22 Which of the following statements about the reaction with Fehling's reagent is correct?

1 In a positive test, Cu^{2+} is reduced to produce an oxide.

2 Propanone will react to form a propanoate ion.

3 Benzaldehyde will give a brick-red precipitate.

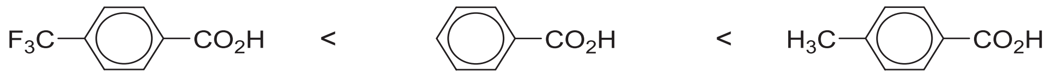
A 1 only

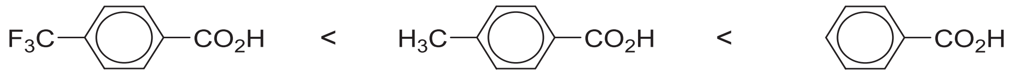
B 1 and 2 only

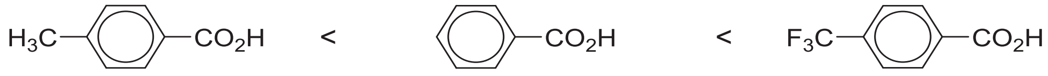
C 1 and 3 only

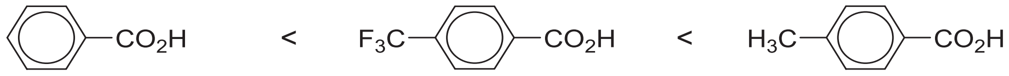
D 2 and 3 only

23 Which of the following shows an increasing trend in pK_a ?

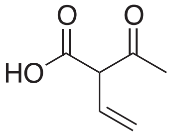
A


B


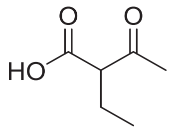
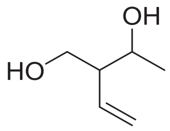
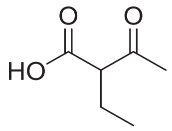
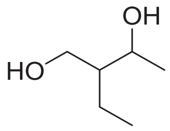
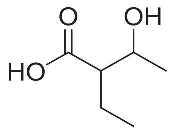
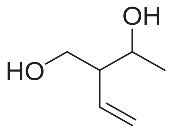
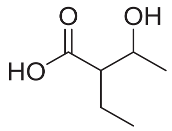
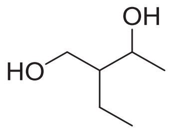
C


D


24 Which are the products formed when compound Z reacts with the following reducing agents?

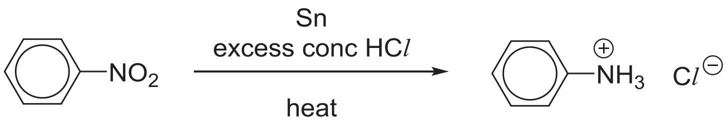


compound Z

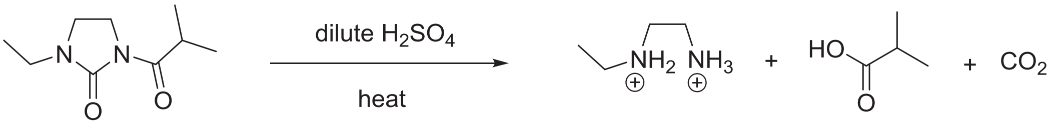
	H_2, Pt	$LiAlH_4$ in dry ether
A		
B		
C		
D		

25 Which of the following transformations is **not** correct?

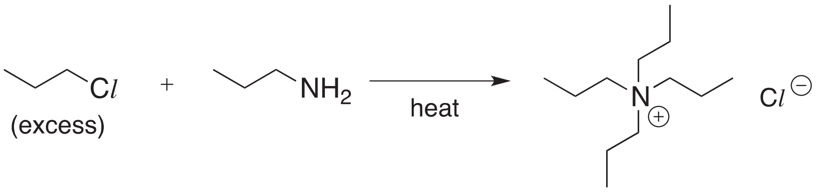
A



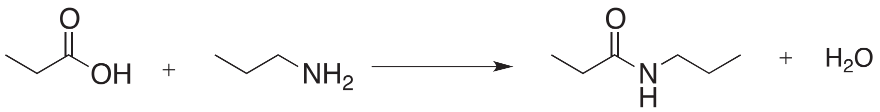
B



C



D



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

By considering the relevant $E^\ominus$ values, which halogen will oxidise $Fe^{2+}(aq)$ to $Fe^{3+}(aq)$?

A bromine and chlorine only

B bromine and iodine only

C chlorine only

D iodine only

27 Which of the following about the anodising of aluminium using dilute sulfuric acid is correct?

1 The thickness of the solid Al_2O_3 layer on the surface of the aluminium object is increased.

2 Oxygen is produced at the cathode.

3 The Al object to be anodised is the positive electrode.

A 1 only

B 1 and 3 only

C 2 and 3 only

D 1, 2 and 3

28 Y is an element in Period 3. When water is added to a chloride of Y, an acidic solution will be obtained. When water is added to an oxide of Y, a basic solution will be obtained.

Which of the following could Y be?

A Na **B** Mg **C** Al **D** Si

29 Which of the following correctly describes the complex formed when different reagents are added to solid copper(II) sulfate?

	reagent added	colour of resultant solution	shape of complex ion formed
1	H_2O	pale blue	octahedral
2	conc. HC*l*	yellow	tetrahedral
3	excess NH_3(aq)	dark blue	tetrahedral

A 1 and 2 only

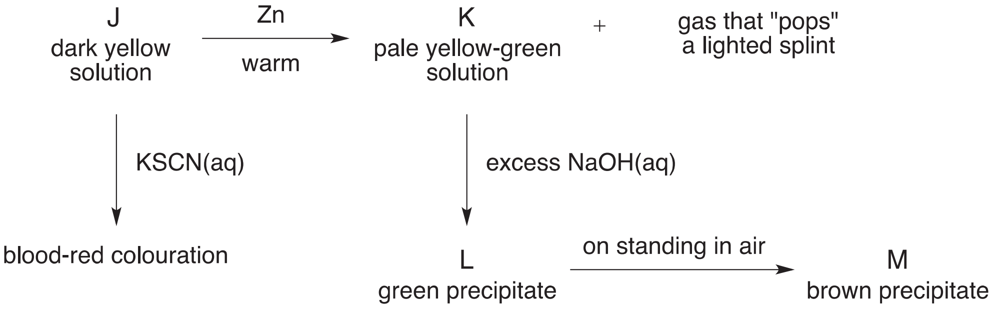
B 1 and 3 only

C 2 and 3 only

D 1, 2 and 3

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

Consider the following reaction scheme starting from solution J, which contains one metal cation.



Which of the following statements is correct?

A The metal cation present in solution J is Fe^{2+}.

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

C The reaction from K to L is a ligand exchange reaction.

D The metal cation present in solution J and in precipitate M is the same.

HWA CHONG INSTITUTION
C2 Preliminary Examinations
Higher 2

CANDIDATE NAME		**CT GROUP**	**16S**
CENTRE NUMBER		**INDEX NUMBER**	

CHEMISTRY

9729/02

Paper 2 Structured Questions

11 September 2017

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	**/ 12**
2	**/ 14**
3	**/ 16**
4	**/ 12**
5	**/ 13**
6	**/8**
Deductions	
Total	**/ 75**

Calculator Model:

1 **(a)** Atmospheric hydrogen and iodine, each 0.10 mol, are placed in a 2 dm^3 evacuated flask at 400 °C. After 30 minutes, the following equilibrium was established and the amount of HI was found to be 0.12 mol.

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

(i) Write the expression for K_c and calculate its value at 400 °C.

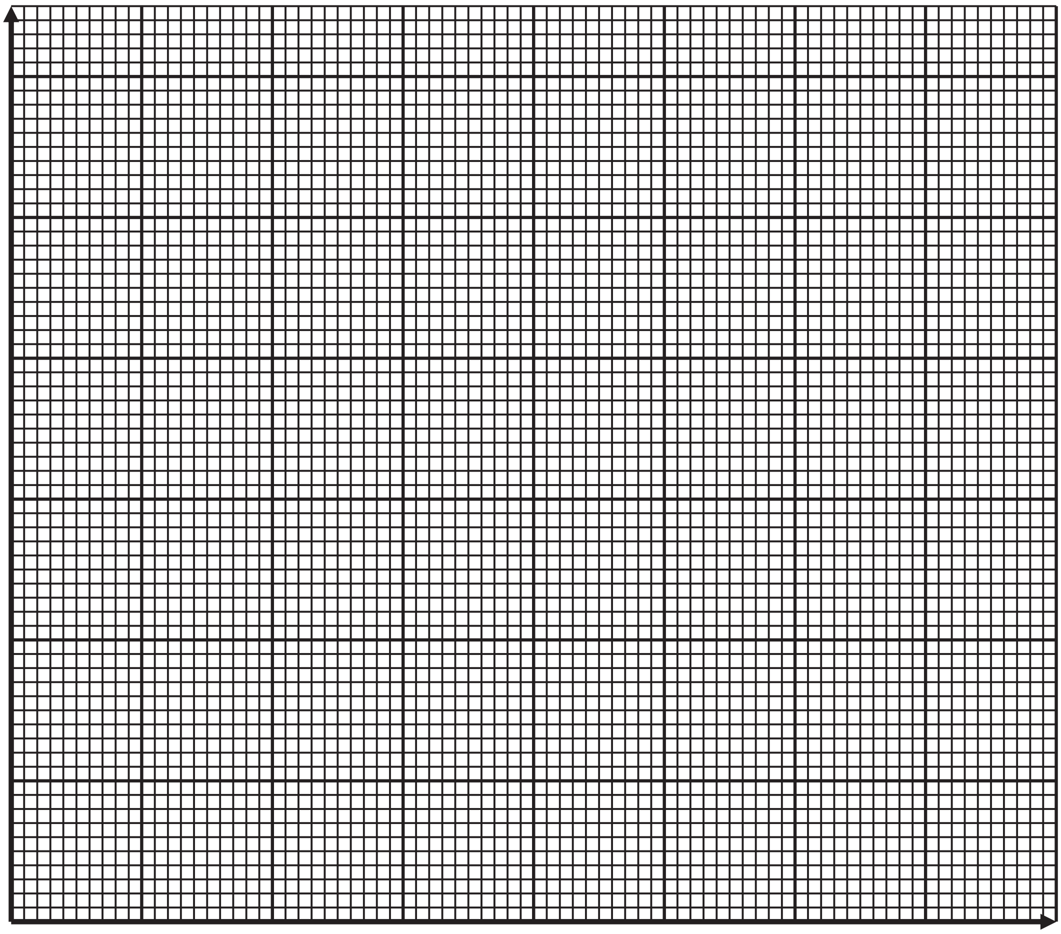
[2]

(ii) At 40 minutes, the temperature of the system was raised to 600 °C and equilibrium was re-established at 60 minutes.

Given that the K_c at 600 °C was 0.36, show that the equilibrium concentrations of H_2, I_2 and HI in the equilibrium mixture at 60 min are 0.0385 mol dm^{-3}, 0.0385 mol dm^{-3} and 0.0231 mol dm^{-3} respectively.

[2]

(iii) On the grid below, sketch the concentration versus time graphs for I_2 and HI respectively under the conditions as described in **(a)(i)** and **(a)(ii)** from 0 to 70 minutes. Label the graphs and indicate significant values on the axes.



[4]

(iv) To find the amount of HI present at equilibrium at 30 minutes, the flask can be rapidly cooled and the HI is dissolved in water. The solution obtained can be titrated against NaOH(aq). Explain why the flask has to be rapidly cooled.

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

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

[1]

(b) When I_2 combines with I^-, it forms the I_3^- ion which is responsible for the characteristic brown colour of aqueous I_2.

Draw a dot-and-cross diagram to show the bonding in I_3^-.

[1]

(c) Explain, in terms of structure and bonding, why I_2 has a higher boiling point than HI.

………

………

………

………

………

[2]

[Total: 12]

2 **(a)** Metal ions, especially transition metal ions, possess the ability to form complexes with both organic and inorganic *ligands*.

1,10-phenanthroline (also known as 'phen') and ferrozine are organic ligands that can form complexes with Fe^{2+} ions.

(i) Explain the term '*ligand*'.

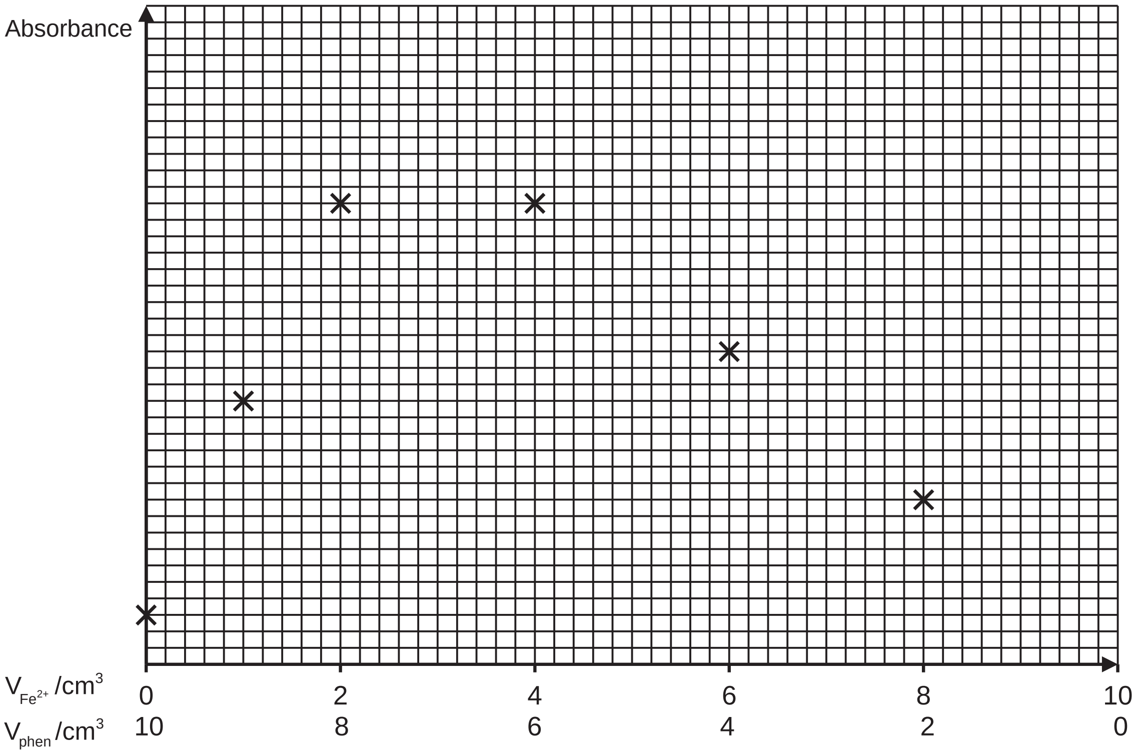
…………………………………………………………………………………………………

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

(ii) In the following experiment, varying volumes of solutions of 0.1 mol dm^{-3} Fe^{2+} and 0.1 mol dm^{-3} phen are mixed to produce a complex of orange-red colour.

$$x\text{Fe}^{2+} + y\text{phen} \rightarrow [\text{Fe}_x(\text{phen})_y]^{2+}$$

The concentration of the orange-red complex formed is proportional to the absorbance of the solution which is measured using a colorimeter. The following graph is plotted using the results of the experiment.



By drawing suitable lines on the graph, deduce the formula of the complex formed between Fe^{2+} and phen.

Formula of the complex ………………………………….

[2]

(iii) Explain why the solution of the complex formed between Fe^{2+} and phen exhibits an orange-red colour.

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

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

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

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

(iv) Ferrozine reacts with Fe^{2+} in solutions to give a purple complex. Suggest why the colour of this complex is different from that formed with phen, by considering your answer to **(iii)**.

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

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

(b) Alkyl groups can be substituted into a benzene ring in the presence of a suitable catalyst. This is known as a Friedel-Crafts alkylation.

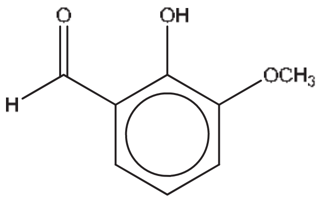
(i) Suggest a suitable reagent and condition to convert benzene to ethylbenzene.

Reagent: …………………………………. Condition: ………………………………….
[1]

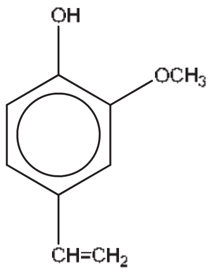
(ii) Name and outline the mechanism to convert benzene to ethylbenzene using the reagent and condition you proposed in **(b)(i)**. Show all charges and use curly arrows to show the movement of electron pairs.

[3]

(c) Fermentation produces phenolic compounds that give wheat beer its distinctive spicy, clove-like flavor. This flavor comes from phenolic molecules such as vanillin and 4-VG.

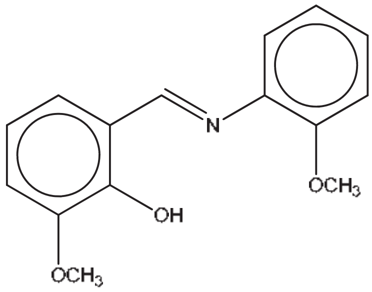


vanillin



4-vinylguaiacol
(4-VG)

(i) Schiff bases are an important class of ligands that form complexes which can be used as antimicrobial agents. They are derived when a condensation reaction takes place between an amine and a carbonyl group. Vanillin can be used to synthesise the Schiff base ligand below.



Give the structure of the molecule that reacted with vanillin to form this Schiff base ligand.

[1]

(ii) Suggest a simple chemical test to distinguish between vanillin and 4-VG. State the reagent and condition used and the expected observation for **each** compound.

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

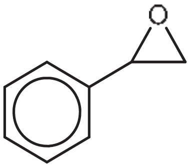
……………………………………………………………………………………………………

[2]

[Total: 14]

3 Epoxides are a class of organic compounds with a three-membered ring structure containing two carbon atoms and one oxygen atom. The three-membered ring in epoxides makes them highly reactive and susceptible to "ring-opening reactions" whereby one of the C–O bonds breaks. Hence, epoxides are important precursors for many industrial and commercial applications.

One such epoxide is styrene oxide.



styrene oxide

(a) **(i)** State the hybridisation of the carbon atoms in the three-membered ring in styrene oxide, and the typical bond angle around a carbon atom with the same hybridisation.

hybridisation: ……………………….

typical bond angle: …………………

[2]

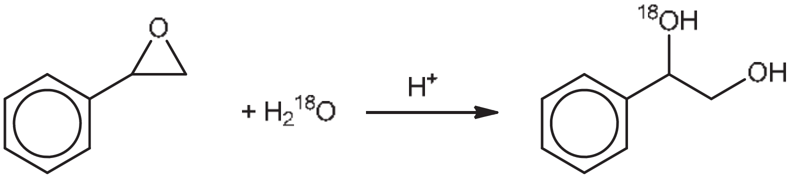
(ii) The actual bond angle in the three-membered ring in styrene oxide is 60°. By comparing this bond angle with your answer in **(a)(i)**, suggest why epoxides are susceptible to "ring-opening reactions".

……………………………………………………………………………………………….

……………………………………………………………………………………………….

[1]

(b) An example of an epoxide ring-opening reaction is the hydrolysis of styrene oxide in the presence of a strong acid catalyst to form styrene glycol. To determine the reaction mechanism, isotopic labelling was used. The hydrolysis was carried out using "heavy-oxygen water", $H_2{}^{18}O$.

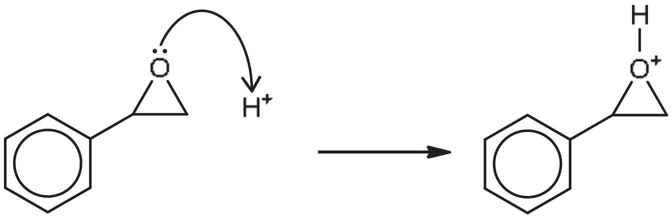


styrene glycol

It is found that the reaction follows a unimolecular nucleophilic substitution mechanism. Some details of the mechanism are as given.

1. Protonation of the oxygen atom by a strong acid catalyst
2. Heterolytic fission of the C–O bond to generate a carbocation intermediate
3. Attack of the carbocation by one molecule of $H_2{}^{18}O$ to form a new C–O bond
4. Loss of a proton to form styrene glycol and regenerate the acid catalyst

(i) Step 1 of the mechanism has been drawn for you:



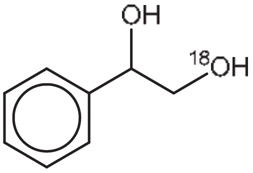
Describe steps 2 to 4 of the mechanism for this unimolecular nucleophilic substitution reaction. Show all relevant lone pairs and charges, and indicate the movement of electron pairs with curly arrows. You do not need to label the ^{18}O atom in any water molecules.

[3]

(ii) Draw the structure of a side product formed if the acid catalyst used is dilute hydrochloric acid.

[1]

(iii) Analysis of the styrene glycol product formed from the hydrolysis showed the presence of trace amounts of an isotopic isomer **A** (in which the oxygen-18 atom is bonded to a different carbon atom).



isotopic isomer **A**

Suggest how isotopic isomer **A** could have been formed during the reaction and why it was formed only in trace amounts.

……

……

……

[2]

(c) Compound **D** can be synthesised from styrene glycol by the following route.

styrene glycol

D

State the reagents and conditions for steps 1 to 3, and draw the structures of the intermediate compounds **B** and **C**.

step 1 ……………………………………………………………………………………………

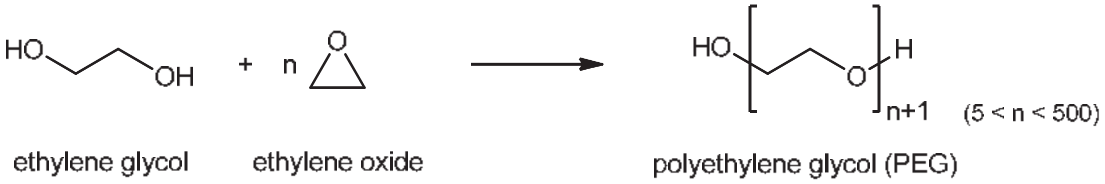
step 2 ……………………………………………………………………………………………

step 3 ……………………………………………………………………………………………

Compound **B**	Compound **C**

[5]

(d) Ethylene oxide is another epoxide, and can undergo polymerisation with a small amount of ethylene glycol to form polyethylene glycol (PEG).



PEG is highly soluble in water, in contrast to long-chain fatty acids such as lauric acid, $CH_3(CH_2)_{10}CO_2H$, which are only sparingly soluble.

With the aid of a labelled diagram, explain why PEG is highly soluble in water despite its large M_r.

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

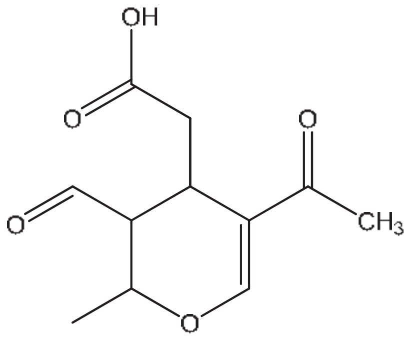
……………………………………………………………………………………………………..

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

[2]

[Total: 16]

4 The olive tree has been used for centuries in the Mediterranean region for culinary and medicinal practices. The leaves and the fruit contain a number of organic compounds which are responsible for these benefits. One of these compounds is elenolic acid. The structure of elenolic acid is shown below.



elenolic acid

(a) Name **four** functional groups, other than the ether functional group (–C–O–C–), that are present in the elenolic acid molecule.

………

………

[4]

(b) Draw the structural formula of all the organic products formed when elenolic acid is treated with the following reagents. Assume the ether functional group is inert.

(i) $LiAlH_4$ in dry ether

[1]

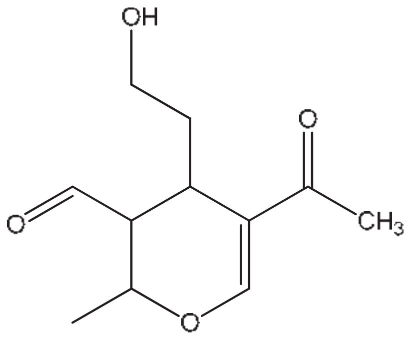
(ii) hot aqueous iodine in an excess of sodium hydroxide

[2]

(iii) hot aqueous $KMnO_4$ in an excess of dilute sulfuric acid

[2]

(c) Explain how the acidity of elenolic acid compares with that of compound **M**.



M

……

……

……

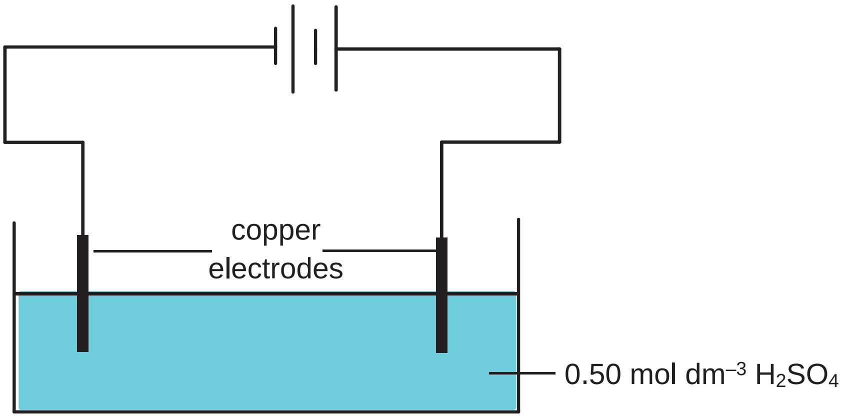
……

……

[3]

[Total: 12]

5 **(a)** The Avogadro constant may be determined via an electrolytic method in a school laboratory. In a typical experiment, copper electrodes are connected to a battery and dipped into an electrolyte of dilute sulfuric acid.



The experimental results are tabulated as follows.

Initial mass of anode/ g	0.968
Final mass of anode/ g	0.254
Time of electrolysis/ s	3100
Average current/ A	0.700

(i) Write an equation for the reaction that occurs at the anode. Include state symbols in your answer.

.... [1]

(ii) Using the above experimental results, calculate a value for the Avogadro constant.

[3]

(b) A 10-cent coin is typically made up of cupronickel, an alloy consisting of both copper and nickel. In another electrolytic experiment, a 10-cent coin is made the anode and dipped in an electrolyte of 6.0 mol dm^{-3} HC*l*. Graphite is used as the cathode.

The 10-cent coin is gradually but completely dissolved, resulting in an intensely green-coloured electrolyte. Copper is deposited at the cathode.

(i) Explain, by quoting relevant $E^{\ominus}$ values, why copper instead of nickel is deposited at the cathode.

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

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

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

[2]

(ii) The complex responsible for the colour of the electrolyte is $NiCl_4^{2-}$. State the electronic configuration of Ni in $NiCl_4^{2-}$.

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

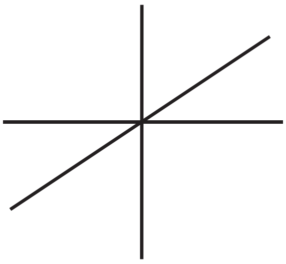
[1]

(iii) $NiCl_4^{2-}$ is an example of a tetrahedral complex. Similar to an octahedral complex, the d subshell of a transition metal ion in a tetrahedral complex is split into two energy levels. However, the d orbitals found in the upper energy level in the octahedral complex are now found in the lower energy level of the tetrahedral complex and vice versa.

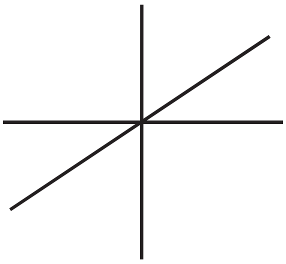
Using the Cartesian axes given below, draw **fully-labelled** diagrams of the following.

- One of the d orbitals at the upper energy level in a tetrahedral complex.
- One of the d orbitals at the lower energy level in a tetrahedral complex.

upper



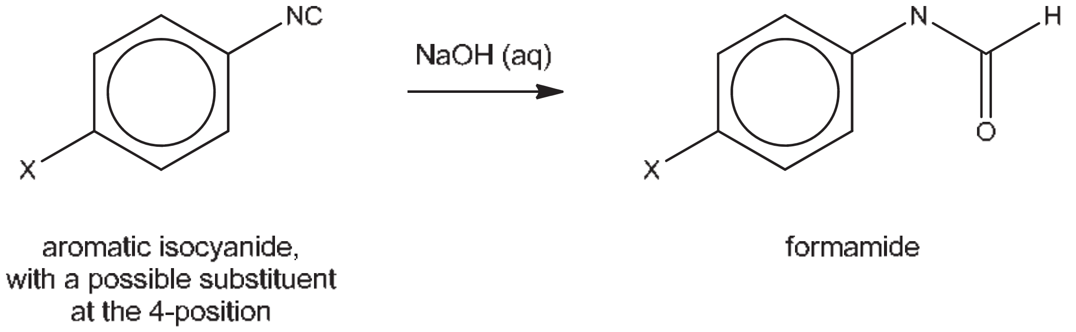
lower



[2]

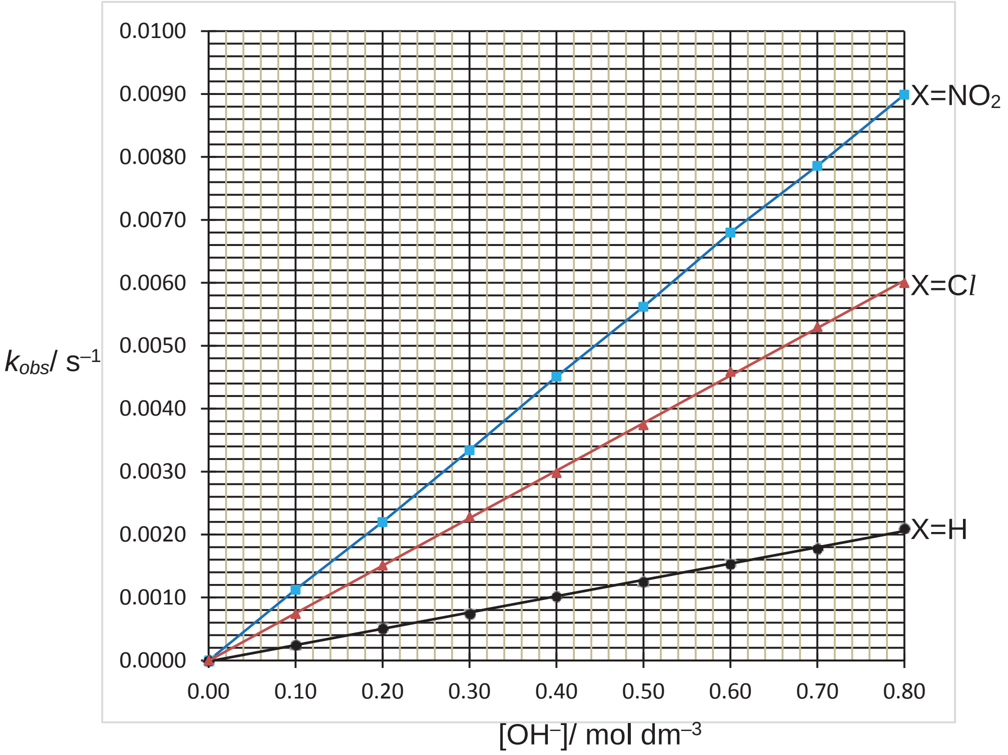
(c) An isocyanide is an organic compound with the functional group –NC. When the –NC group is attached to a benzene ring, the compound is called an aromatic isocyanide.

Aromatic isocyanides have been found to react in NaOH (aq) yielding the corresponding formamides.



The order of reaction with respect to the aromatic isocyanide was found to be one in an earlier series of experiments.

In further experiments, to determine the order of reaction with respect to OH^-, the concentration of aromatic isocyanide used was kept at 5.0×10^{-4} mol dm^{-3} while the concentration of OH^- used was varied between 0.10 and 0.80 mol dm^{-3}. To determine the effect of different substituents X, the reaction was carried out using different aromatic isocyanides. The graph of the observed rate constant, k_{obs} against $[OH^-]$ is plotted as follows.



(i) Given that $k_{obs} = k[OH^-]^m$, deduce the order of reaction with respect to OH^-.

....

[1]

(ii) Hence or otherwise, write a rate equation for the reaction between aromatic isocyanides and OH^- and use it to determine the rate of the reaction for X = C*l* when $[OH^-] = 0.74$ mol dm^{-3}.

[2]

(iii) In the reaction, OH^- acts as a nucleophile to attack the carbon atom of the isocyanide group. Explain why the gradients of the graph for X = NO_2 and X = C*l* were steeper than that for X = H.

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

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

[1]

[Total: 13]

6 A common magic demonstration where containers of “water” are mixed to obtain “milk” makes use of the following reaction between methanal and sulfite:

$$HCHO + SO_3^{2-} + H_2O \rightarrow CH_2(OH)(SO_3^-) + OH^-$$

As the reaction produces hydroxide ions, the pH of the solution rises. If a buffer solution is present, this rise is gradual at first. Eventually, when the buffer is exhausted, the pH rises quickly. If the cation Mg^{2+} is also present, the solution soon becomes saturated in magnesium hydroxide and a white precipitate appears.

The procedure of the demonstration is given below.

Procedure (steps 1 to 3 are prepared ahead of the demonstration whereas step 4 is performed in front of the audience)

To the same beaker, the following solutions are added:

1. Add 100 cm^3 of 0.100 mol dm^{-3} Na_2SO_3 (solution A).
2. Add 100 cm^3 of 0.400 mol dm^{-3} $NaHSO_3$ (solution B).
3. Add 5 cm^3 of 2.00 mol dm^{-3} $MgCl_2$ (solution C).
4. Add 200 cm^3 of 0.300 mol dm^{-3} HCHO (solution D) and swirl.

20 s after step 4 is carried out, a white cloudy solution (“milk”) suddenly appears in the beaker owing to the precipitation of magnesium hydroxide.

The following information are relevant.

K_a of HSO_3^-	1.02×10^{-7} mol dm^{-3}
K_{sp} of $Mg(OH)_2$	5.66×10^{-12} mol^3 dm^{-9}

(a) What do you understand by the term *buffer solution*?

……

…… [1]

(b) Calculate the pH of the buffer solution in the beaker after Step 2.

[1]

(c) Write **one** equation to show how this buffer performs its function in **(a)**, in the process delaying the appearance of the white precipitate.

……

[1]

(d) Show that the white precipitate first appears when the pH in the beaker is 9.18.

[2]

(e) State a solution (A, B, C or D) whose concentration you would **decrease** in order for the white precipitate to appear earlier.

………
[1]

(f) The procedure can be slightly amended as follows to produce “tea” instead of “milk”.

- Steps 1, 2 and 4 are unchanged.
- In step 3, instead of solution C, add 5 cm^3 of 3-nitrophenol indicator.

Indicator	**colour in acidic solution**	**colour in alkaline solution**	**working pH range**
3-nitrophenol	colourless	yellow	6.7 – 8.7

In this way, a yellow solution suddenly appears at the end of the demonstration.

Previously, “milk” appeared 20 s after step 4 was carried out. Explain whether “tea” appears earlier, later or also at 20 s after step 4 was carried out.

………

………
[1]

(g) Suggest another indicator you could use in place of 3-nitrophenol so that “red wine” may be obtained instead of “tea”.

………
[1]

[Total: 8]

HWA CHONG INSTITUTION
C2 Preliminary Examinations
Higher 2

CANDIDATE NAME		**CT GROUP**	**16S**
CENTRE NUMBER		**INDEX NUMBER**	

CHEMISTRY

9729/03

Paper 3 Free Response

18 September 2017

2 hours

Candidates answer on separate paper.

Additional Materials: Answer Paper
Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your **name**, **CT group, centre number** and **index number** clearly in the spaces above.

Write in dark blue or black pen.

You may use a HB pencil for any diagrams or graphs.

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

Section A

Answer **all** questions.

Section B

Answer **one** question.

Begin each question on a **new sheet of writing paper**.

A Data Booklet is provided.

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

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.

Circle the question numbers for the questions that you have attempted on the cover page provided.

This document consists of **12** printed pages.

Section A

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

1 (a) *Azurite* is a deep blue copper-containing mineral. For many centuries, finely ground rock containing azurite has been used as a pigment in blue paints. Azurite is a mixture of copper(II) carbonate and copper(II) hydroxide. The formula of pure azurite is $Cu_3(CO_3)_2(OH)_2$, which has a relative formula mass of 344.5.

The percentage by mass of pure azurite in a sample of finely ground rock can be determined by back titration. 3.70 g of the sample is added to 100 cm^3 of 0.425 mol dm^{-3} sulfuric acid. The resulting solution was made up to 250 cm^3 with distilled water. 25.0 cm^3 of the diluted solution required 26.50 cm^3 of 0.100 mol dm^{-3} sodium hydroxide for neutralization.

Dilute sulfuric acid reacts with pure azurite as shown in the following equation.

$$Cu_3(CO_3)_2(OH)_2(s) + 3H_2SO_4(aq) \rightarrow 3CuSO_4(aq) + 4H_2O(l) + 2CO_2(g)$$

Calculate the percentage by mass of pure azurite in the sample. You may assume that azurite is the only substance in the rock that reacts with sulfuric acid. [3]

(b) The brick-red precipitate, Cu_2O, dissolves in concentrated ammonia solution to form a colourless complex ion **P**, $[Cu(NH_3)_x]^{n+}$, which has a linear geometry about the central metal ion. When left exposed to air, the colourless complex ion **P** turns into a deep blue solution, containing the complex ion $[Cu(NH_3)_4]^{2+}$.

(i) State the value of x and write the formula of complex ion **P**. [2]

(ii) With the help of the *Data Booklet*, write the two half equations, and hence the overall equation for the reaction of the colourless complex ion **P** to form $[Cu(NH_3)_4]^{2+}$. [2]

(c) Iodine and chlorine react together to give iodine trichloride.

$$I_2(s) + 3Cl_2(g) \rightarrow 2ICl_3(s)$$

(i) Construct a fully labelled energy cycle relating the reactants and products of this reaction to their gas phase atoms. Use your cycle to calculate the average bond energy of the I–Cl bond in ICl_3.

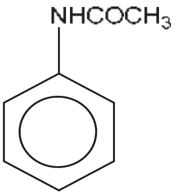
Your cycle should include relevant data from the *Data Booklet* together with the following data.

standard enthalpy change of formation ($\Delta H_f^\ominus$) of $ICl_3(s)$ = –81 $kJmol^{-1}$
enthalpy change of sublimation of $I_2(s) \rightarrow I_2(g)$ = +38 $kJmol^{-1}$
enthalpy change of sublimation of $ICl_3(s) \rightarrow ICl_3(g)$ = +60 $kJmol^{-1}$

[4]

(ii) The standard Gibbs free energy of formation, $\Delta G_f^\ominus$, of $ICl_3(s)$ is –40.4 $kJmol^{-1}$. Calculate $\Delta S_f^\ominus$ and comment on its sign with respect to the reaction. [2]

(d) The antipyretic (fever-reducing) drug *antifebrin* can be made via a 3-step synthetic route, starting from benzene.



antifebrin

(i) State the 3 types of reactions involved (in sequence) in the formation of antifebrin from benzene. [3]

(ii) Draw the structures of the products formed when antifebrin was subjected to prolonged heating with dilute sulfuric acid. [1]

[Total: 17]

2 Thiols are a group of organic compounds which may be represented as $C_nH_{2n+1}SH$ or RSH, where R is an alkyl group.

(a) In an experiment a sample of thiol was completely burnt in a stoichiometric amount of oxygen. The product mixture was collected in a 1.65 dm^3 flask at 110 °C and 1 atm total pressure. The partial pressure of sulfur dioxide was found to be 16.9 kPa.

(i) Write a balanced equation for the complete combustion of one mole of a thiol with *n* carbon atoms. [1]

(ii) Show that when a thiol with *n* carbon atoms is completely burnt in a stoichiometric amount of oxygen, the mole fraction of sulfur dioxide in the product mixture is 1/(2*n*+2). Assume that all products are gaseous. [1]

(iii) Use the above data, together with the information in **(ii)** to deduce the value of *n* for the thiol burnt in the experiment. [1]

(iv) Hence find the mass of thiol burnt. [2]

(b) Thiols are suitable starting materials for the synthesis of organic sulfides. An example is given below.

$$\underset{\text{ethanethiol}}{CH_3CH_2SH} \xrightarrow[\text{Reaction 1}]{NaOH} CH_3CH_2S^-Na^+ \xrightarrow[\text{Reaction 2}]{\text{heat with } CH_3CH_2Br} \underset{\text{diethyl sulfide}}{CH_3CH_2SCH_2CH_3}$$

(i) How would the acid strength of ethanethiol compare to that of ethanol, given that Reaction 1 is effectively complete? [1]

(ii) State the type of reaction occurring in Reaction 2. [1]

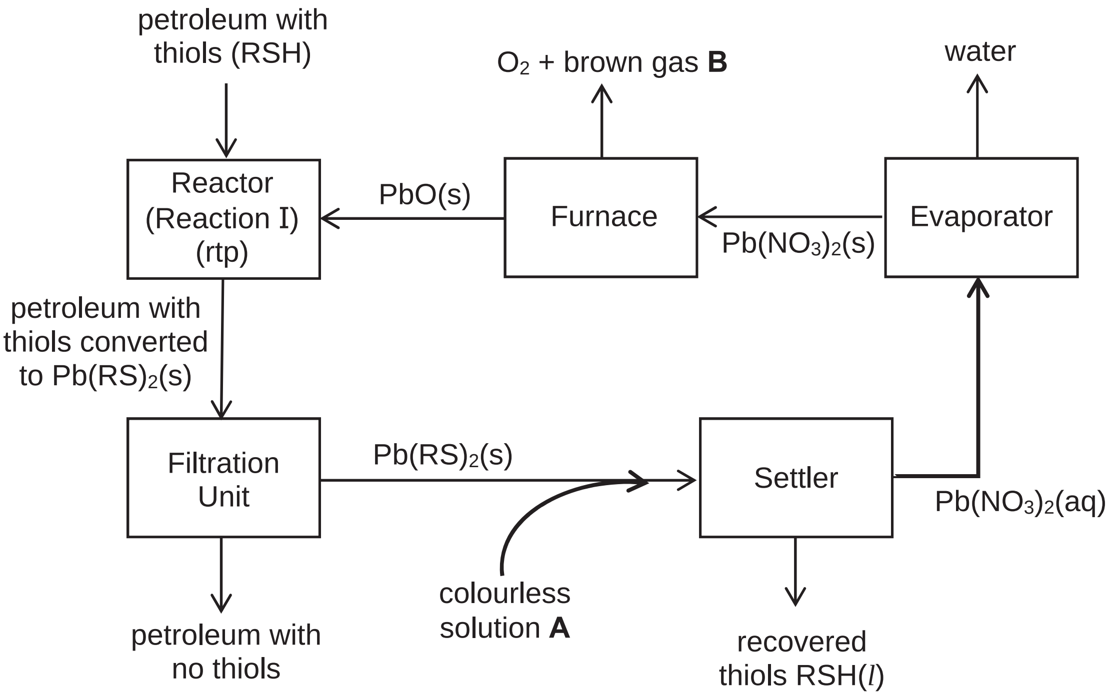
(iii) Suggest why Reaction 1 was carried out in the above synthesis. [1]

(iv) Give **two** reasons to explain why ethylphenyl sulfide, $C_6H_5SCH_2CH_3$, cannot be obtained by changing bromoethane in Reaction 2 to bromobenzene. [2]

(c) The following diagram shows a process which may be used for the removal and recovery of thiols from petroleum. The process utilizes the reaction between thiols and lead(II) oxide, as given in the equation below.

$$2RSH(l) + PbO(s) \rightleftharpoons Pb(RS)_2(s) + H_2O(l) \qquad \text{Reaction I}$$

As the equilibrium position for Reaction I lies very much towards the products, the overall recovery of thiols in the process is high.



(i) State the role of lead(II) oxide in Reaction I. [1]

(ii) Comment on the sign and magnitude of $\Delta G^\ominus$ for Reaction I. [2]

(iii) Suggest the identity of colourless solution **A** and brown gas **B**. [2]

(iv) Suggest the temperature in the furnace, explaining your reasoning with the use of relevant data from the *Data Booklet*. For reference, copper(II) nitrate and barium nitrate decompose at 170 °C and 630 °C respectively. [4]

(d) Thermal cracking, which is a process where large alkane molecules are broken down into smaller alkanes and alkenes, proceeds via a free radical mechanism.

The following are reactions which are thought to occur, using propane as the starting alkane.

$CH_3CH_2CH_3 \rightarrow \bullet CH_3 + \bullet CH_2CH_3$ -- (A)

$CH_3CH_2CH_3 \rightarrow \bullet H + \bullet CH_2CH_2CH_3$ -- (B)

$\bullet CH_3 + CH_3CH_2CH_3 \rightarrow CH_4 + \bullet CH_2CH_2CH_3$ -- (C)

$\bullet CH_2CH_3 \rightarrow \bullet H + CH_2{=}CH_2$ -- (D)

$\bullet CH_3 + CH_2{=}CH_2 \rightarrow \bullet CH_2CH_2CH_3$ -- (E)

$\bullet CH_3 + \bullet CH_3 \rightarrow CH_3CH_3$ -- (F)

$2\ \bullet CH_2CH_3 \rightarrow CH_3CH_3 + CH_2{=}CH_2$ -- (G)

(i) Reactions (A) and (B) are termed initiation steps. With the use of the *Data Booklet*, deduce which one is more likely to occur. [1]

(ii) Of reactions (C) to (G), identify those which may be termed propagation steps in the mechanism. [1]

(iii) Which gas, if detected in the product mixture, would offer support for the occurrence of both Reactions (B) and (D)? [1]

(iv) Explain why Reaction (G) may be termed a disproportionation. [1]

[Total: 23]

3 Phosphorus forms a wide range of compounds that are essential for life and have many applications in the industry and in the laboratory.

(a) Many detergents contain sodium dodecylbenzenesulfonate, $C_{18}H_{29}SO_3Na$ (M_r = 348), that can react with calcium ions in 'hard' water to give a precipitate, making the detergent ineffective.

The solubility product, K_{sp}, for $(C_{18}H_{29}SO_3)_2Ca(s)$ is given by

$$[Ca^{2+}][C_{18}H_{29}SO_3^-]^2 = 1.20 \times 10^{-17}\ mol^3\ dm^{-9}$$

A particular brand of detergent contains 17.4% by mass of sodium dodecylbenzenesulfonate. The manufacturer states that in 'hard' water, 1.00 g of the detergent should be used with 1.00 dm^3 of water. A typical sample of 'hard' water contains 2.50×10^{-4} mol dm^{-3} of Ca^{2+}.

You may assume that the volume of 1.00 g of detergent is negligible compared to 1.00 dm^3 of 'hard' water.

(i) Explain why it is not necessary to include the concentration of $(C_{18}H_{29}SO_3)_2Ca(s)$ in the K_{sp} expression. [1]

(ii) Explain whether a precipitate will form when 1.00 g of the detergent is added to 1.00 dm^3 of 'hard' water. [3]

(iii) Calculate the maximum concentration of Ca^{2+} in 'hard' water for the detergent to be effective when it is used as recommended by the manufacturer. [1]

In order for detergents to be used in 'hard' water, sodium tripolyphosphate, $Na_5P_3O_{10}$, is added as a water softening agent. It 'softens' water by complexing with the calcium ions which can help to prevent the formation of precipitate.

$$Ca^{2+}(aq) + P_3O_{10}^{5-}(aq) \rightleftharpoons CaP_3O_{10}^{3-}(aq) \qquad K_c = 7.70 \times 10^8\ mol^{-1}\ dm^3$$

(iv) Write an expression for the equilibrium constant of the above reaction. [1]

(v) Some solid sodium tripolyphosphate was added to 'hard' water containing the detergent. After forming the complex, the concentration of $P_3O_{10}^{5-}$ decreased to **one-tenth** of its original value at equilibrium.

Using the K_c value, calculate the concentration of Ca^{2+} in the equilibrium mixture. [1]

(vi) Hence, with reference to your answers in **(a)(iii)** and **(a)(v)**, comment on whether the amount of solid sodium tripolyphosphate added was sufficient to make the detergent effective. [1]

(b) Phosphorus also forms a class of compounds with nitrogen known as phosphazenes.

A commercially available phosphazene is $(Cl_2PN)_3$ which is the starting material for many biomedical polymers. It can be synthesized by reacting PCl_5 with NH_4Cl. HCl is formed as a byproduct.

(i) Write an equation for the synthesis of $(Cl_2PN)_3$. [1]

(ii) $(Cl_2PN)_3$ has a cyclic backbone consisting of alternating phosphorus and nitrogen atoms. Each chlorine atom forms a single bond with a phosphorus atom.

Draw the structure of $(Cl_2PN)_3$. [1]

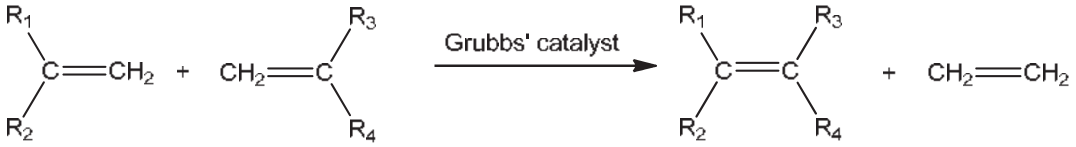
(iii) Like PCl_5, $(Cl_2PN)_3$ undergoes a similar reaction with water, forming $(PN(OH)_2)_3$.

Suggest the type of reaction undergone by $(Cl_2PN)_3$ and predict what would be observed when a few drops of water was added to $(Cl_2PN)_3$. [2]

(iv) The atomic radii of P, N and C*l* are listed in the *Data Booklet*.

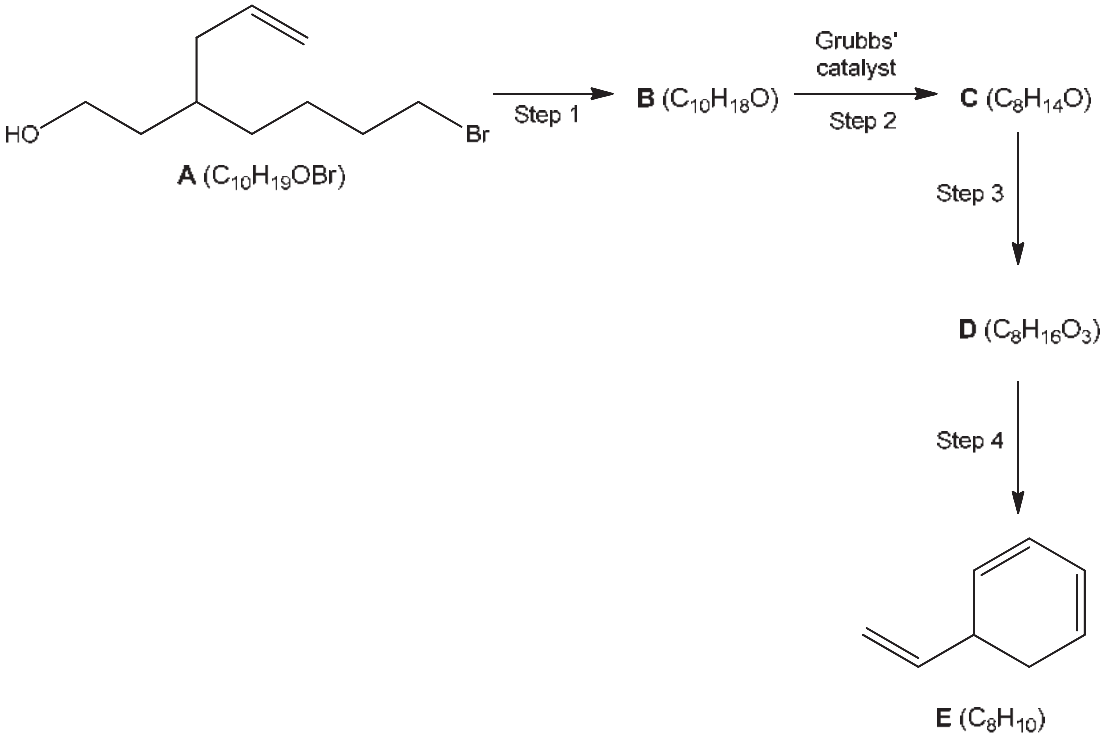
State and explain the differences between the atomic radii of these three atoms. [2]

(c) Many transition metal complexes contain phosphorus-containing ligands. An example is the Grubbs' catalyst that is used in alkene metathesis, a reaction that involves the redistribution of carbon-carbon double bonds.



(R_1, R_2, R_3 and R_4 are alkyl groups)

The reaction scheme below shows the synthesis of compound **E** via alkene metathesis. Compound **A** is the only starting organic compound.



Compound **C** is a cyclic compound that reacts with one mole of PCl_5. Compound **D** reacts with three moles of PCl_5.

(i) Draw the structures of compounds **B**, **C** and **D**. [3]

(ii) State the reagents and conditions for Steps 1, 3 and 4. [3]

[Total: 20]

Section B

Answer **one** question from this section.

4 **(a)** Organic compounds like ethanol can be used as fuels in fuel cells.

In an ethanol fuel cell, an aqueous solution of ethanol undergoes oxidation at the anode, which is layered with a metal catalyst, to produce carbon dioxide gas and hydrogen ions, while oxygen undergoes reduction at the cathode.

(i) Write a half equation for the reaction that occurs at the anode in the ethanol fuel cell. [1]

(ii) Describe the mode of action of the metal catalyst that helps to increase the rate of reaction at the anode in the fuel cell. [4]

(iii) Draw a fully labelled diagram of a separate electrochemical cell you would set up in order to measure the standard reduction potential, $E^{\ominus}_{CO_2/\text{ethanol}}$. [3]

(iv) Deduce how $E^{\ominus}_{CO_2/\text{ethanol}}$ will change when the pH in the CO_2/ethanol half-cell increases. [2]

(b) **A,** $C_6H_8O_3$, is a fungal metabolite that is known to inhibit the formation of biofilms. To determine its identity, **A** was boiled in dilute HC*l* to give **B**, $C_6H_{10}O_4$.

(i) The degree of unsaturation uses the molecular formula of an organic compound to find the number of double/ triple bonds or rings present in the compound. A double bond or a ring accounts for one degree of unsaturation, while a triple bond accounts for two degrees of unsaturation.

The degree of unsaturation for a compound $C_xH_yO_z$ is found using this expression: $\frac{1}{2}(2 + 2x - y)$.

Calculate the degree of unsaturation of **A** and of **B.** [2]

(ii) Deduce the **functional groups** present in **B**. Provide supporting evidence from the information below.

- **B** reacts with Na_2CO_3 to give effervescence.
- When **B** was warmed with alkaline I_2(aq), a yellow precipitate was observed.
- No orange precipitate was formed upon reaction of **B** with 2,4–dinitrophenylhydrazine.
- When **B** was heated with acidified $K_2Cr_2O_7$, it formed **C**, $C_6H_6O_4$. However, when acidified $KMnO_4$ was used instead, **D**, $C_5H_4O_5$ was produced.
- Both **C** and **D** formed an orange precipitate when reacted with 2,4–dinitrophenylhydrazine. [3]

(iii) By considering the reaction of **A** to give **B** and your answer in **b(ii)**, deduce the identity of the functional group present in **A** that is **not** present in **B**. [1]

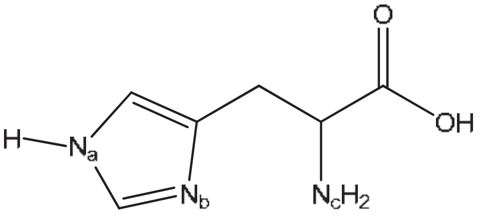
(iv) **A** was subjected to a series of tests. The observations are recorded in the table below.

Test	Observation
Br_2 (aq)	Yellow solution decolourised
$SOCl_2$	White fumes of HC*l* observed
I_2, NaOH(aq), heat	No yellow ppt
2,4–dinitrophenylhydrazine	No orange ppt observed
Na_2CO_3(aq)	No effervescence observed

Using all the information in **(b)**, suggest the structures of **A**, **B**, **C** and **D**. [4]

[Total: 20]

5 Histidine is one of the essential amino acids that is present in many proteins and enzymes. It exists as a crystalline solid with a melting point of 282 °C. There are three pK_a values associated with histidine: 1.82, 6.00 and 9.17.



histidine

(a) Account for the crystalline state and high melting point of histidine in terms of its structure and bonding. [3]

(b) State the hybridisation of the nitrogen atom N_b and sketch a diagram showing all the hybrid orbitals around it. [2]

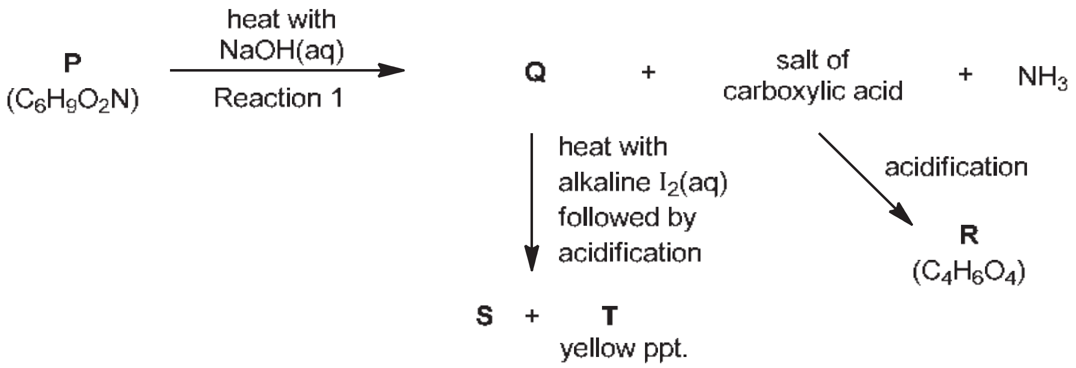
(c) **(i)** In the fully protonated form of histidine, nitrogen atoms N_b and N_c are protonated. N_a is not considered basic.

Sketch the titration curve obtained when 20 cm^3 of the fully-protonated form of histidine is titrated with 60 cm^3 of NaOH(aq) of the same concentration. Your sketch should show clearly where the three pK_a values occur and mark the isoelectric point of histidine on your sketch with an "**X**". [3]

(ii) Calculate the final pH, to 2 decimal places, of the resultant solution obtained when 10 cm^3 of 0.010 mol dm^{-3} NaOH was added to 100 cm^3 of a solution of 0.10 mol dm^{-3} histidine at pH 6.

You may represent the acid as HA and the conjugate base as A^- in your working. [3]

(d) Compound **P** does not rotate plane-polarised light and is insoluble in both dilute hydrochloric acid and aqueous sodium hydroxide at room temperature. The following scheme shows reactions of compound **P** and its products.



(i) State the type of reaction that occurs in Reaction 1 and identify **two** possible functional groups in **P** which can produce ammonia in this reaction. [2]

(ii) Draw the structures of compounds **P** to **T.** [5]

(iii) On treatment of **P** with hydrogen and a platinum catalyst, compound **U**, $C_6H_{13}NO_2$, is produced. However, reaction of **P** with lithium aluminium hydride forms **Q** and compound **V**, $C_4H_{11}NO$. Both **Q** and **V** contain a common functional group. Suggest the structures of **U** and **V**. [2]

[Total: 20]

HWA CHONG INSTITUTION
C2 Preliminary Examination
Higher 2

NAME		**CT GROUP**	**16S**

CHEMISTRY

9729/04

Paper 4 Practical

25 August 2017

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 15 and 16.

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

Shift
Laboratory

For Examiner's Use	
1	
2	
3	
4	
Total	

Thi ank page.

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

1 Determination of concentrations of sodium hydroxide, and of sodium carbonate in a mixture

FA 1 is a solution containing sodium hydroxide, NaOH, and sodium carbonate, Na_2CO_3.
FA 2 is an aqueous solution containing 0.90 mol dm^{-3} of hydrochloric acid, HC*l*.

Sodium hydroxide reacts with hydrochloric acid according to the equation below:

Reaction 1 $NaOH + HCl \rightarrow NaCl + H_2O$

Sodium carbonate reacts with hydrochloric acid in two separate stages. The reactions that occur are:

Reaction 2 $Na_2CO_3 + HCl \rightarrow NaCl + NaHCO_3$
Reaction 3 $NaHCO_3 + HCl \rightarrow NaCl + CO_2 + H_2O$

You are required to find the concentrations of sodium hydroxide, and of sodium carbonate, in **FA 1**, by means of a *double-indicator* titration.

In a *double-indicator* titration, **two different** indicators are used, separately, in the **same** titration. In this experiment, thymolphthalein indicator, followed by methyl orange indicator, will be used.

Thymolphthalein indicates the end-point when **Reaction 1** and **2** are complete, while methyl orange indicates the end-point when **Reaction 3** is complete.

(a) (i) Dilution of FA 2

Using a burette, measure between 35.00 cm^3 and 36.00 cm^3 of **FA 2** into the 250 cm^3 volumetric flask.

Record your burette readings and the volume of **FA 2** added to the flask in the space below.

Make up the contents of the flask to the 250 cm^3 mark with deionised water. Place the stopper in the flask and mix the contents thoroughly by slowly inverting the flask a number of times. This solution is **FA 3**.

(ii) Titration of FA 1 against FA 3

Fill a second burette with **FA 3**.

Pipette 25.0 cm^3 of **FA 1** into a conical flask.
Replace the cap over the FA 1 bottle to prevent absorption of carbon dioxide from the atmosphere.

Add a few drops of thymolphthalein indicator and titrate **FA 1** with **FA 3**. The end-point is reached when the solution turns colourless. Ignore any cloudiness that you may observe in the conical flask. Record your titration results in the space below. **The volume of FA 3 used to reach the first end-point need not be consistent.**

Do not discard this solution.

To **this** solution, add a few drops of methyl orange indicator and **continue** to titrate with **FA 3** until the second end-point is reached. Record your titration results in the space below.

Perform sufficient titrations to obtain accurate results for the **second end-point**, which refers to the **total** volume of **FA 3** required for the whole titration.

Make certain that all your recorded results show the precision of your working.

[3]

(b) From your titrations, obtain suitable volumes of **FA 3** for the:

- first end-point
- second end-point.

Show clearly how you obtained these volumes.

volume of **FA 3** for first end-point = ...

volume of **FA 3** for second end-point = ...

[3]

(c) **(i)** Calculate the concentration, in mol dm^{-3}, of HC*l* in **FA 3**.

concentration of HC*l* in **FA 3** = ... [1]

(ii) Calculate the amount of sodium carbonate, Na_2CO_3, present in 25.0 cm^3 of **FA 1**.

amount of Na_2CO_3 in 25.0 cm^3 of **FA 1** = ... [1]

(iii) Calculate the amount of sodium hydroxide, NaOH, present in 25.0 cm^3 of **FA 1**.

amount of NaOH in 25.0 cm^3 of **FA 1** = ... [2]

(iv) Use your answers from **(c)(ii)** and **(c)(iii)**, calculate the concentrations, in mol dm^{-3}, of Na_2CO_3 and NaOH in **FA 1**.

concentration of Na_2CO_3 in **FA 1** = ...

concentration of NaOH in **FA 1** = ...

[1]

(d) The maximum error in a single burette reading is ±0.05 cm^3.

When making up the diluted acid, **FA 3,** a student recorded that 35.00 cm^3 of **FA 2** was used. What are the smallest and largest possible volumes of acid that were run into the volumetric flask?

smallest volume used = ... cm^3 largest volume used = ... cm^3

[1]

(e) A student suggested doing the titration in **(a)(ii)** differently – **FA 3** is placed in the conical flask and **FA 1** in the burette, using methyl orange indicator followed by thymolphthalein indicator.

Explain if this method will allow you to determine the concentrations of NaOH and Na_2CO_3 in **FA 1**.

....

....

....[1]

[Total: 13]

2 Heat of reaction between copper(II) ions and iron metal

In this experiment, you will measure the heat given out by the reaction of excess iron with copper(II) sulfate solution and use this to find the concentration of the copper(II) sulfate.

$$Fe(s) + CuSO_4(aq) \rightarrow FeSO_4(aq) + Cu(s)$$

FA 4 is iron powder.
FA 5 is aqueous copper(II) sulfate, $CuSO_4$.

In an appropriate format in the space below, prepare a table in which you may record each temperature and the time it was taken.

1. Wash thoroughly a burette and fill it with **FA 5**. Place a Styrofoam cup into a 250 cm^3 beaker to prevent it from tipping over. Transfer 40.00 cm^3 of **FA 5** into the Styrofoam cup.

2. Place the lid onto the cup and insert the thermometer through the lid. Measure and record the initial temperature of the **FA 5** solution in the cup.

3. Start the stopwatch. Measure and record the temperature of the solution in the cup **every <u>half minute</u>** up to and including the temperature at 1.5 min. Stir the solution using the thermometer.

4. At time *t* = 2.0 min, add all the powdered iron **FA 4** to the solution. Stir the mixture **thoroughly** with the thermometer to **ensure the solid mixes well with the solution**.

5. Record the temperature of the mixture **every <u>minute</u>** from *t* = 2.5 min. Continue stirring **thoroughly** and mixing the contents of the cup well **throughout** your recordings.

6 Once the temperature starts to drop, continue recording **every <u>half minute</u>** for a **further 3 minutes**. Constantly stir the solution **thoroughly**.

(a) Experimental Results

[4]

(b) **(i)** Plot on the grid below, a graph of the temperature on the y-axis, against time, *t*, on the x-axis. The scale for the temperature axis must allow you to plot a point with temperature 5 °C greater than the maximum temperature you recorded.

Draw the following **best-fit** straight lines on the graph.

- a line through the points before addition of **FA 4**.
- a line through the points once temperature starts to drop.

(ii) Use the best-fit straight lines to determine the theoretical temperature change at time t = 2.0 min.

change in temperature = ……………………………………… [5]

(c) **(i)** Use your answer to **(b)(ii)** to calculate the heat energy produced in the reaction. (Assume that **4.2 J** are required to increase the temperature of 1 cm^3 of solution by 1 ^{o}C.)

heat energy produced = ... [1]

(ii) The molar enthalpy change, ΔH, for the reaction shown below is –152 kJ mol^{-1}.

$$Fe(s) + CuSO_4(aq) \rightarrow FeSO_4(aq) + Cu(s)$$

Use this value and your answer to **(c)(i)** to calculate the concentration of copper(II) sulfate, in mol dm^{-3}, in **FA 5**.

concentration of copper(II) sulfate = ... [5]

(d) **(i)** Calculate the maximum percentage error in the highest temperature that you recorded in your results table.

maximum percentage error = ... [1]

(ii) What would be the expected change in temperature obtained in **(b)(ii)** if the volume of copper(II) sulfate used was halved? Explain your answer.

....

....

....

....[1]

[Total: 17]

3 Planning

The concentration of copper(II) sulfate in **FA 5** in Question 2 may be determined instead, by titration of the aqueous solution obtained after step 5, with aqueous potassium manganate(VII).

The reaction mixture obtained after step 5 in Question 2 contains $FeSO_4$(aq) and solids iron and copper. This mixture needs to be first filtered. The filtrate is then diluted to obtain a solution suitable for titration with aqueous potassium manganate(VII) of known concentration, in the presence of acid.

The manganate(VII) ions react with iron(II) ions as shown in the following equation.

$$MnO_4^- + 5Fe^{2+} + 8H^+ \rightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$$

(a) Using information from Question 2, determine a suitable concentration of aqueous potassium manganate(VII) to use in this titration. The concentration of manganate(VII) should not exceed 0.0500 mol dm^{-3}.

You are to assume that the concentration of copper(II) sulfate in **FA 5** is 0.800 mol dm^{-3}. (Note that this is not the correct value.)

Show clearly your calculations and any assumptions.

[3]

(b) Plan an experiment to determine the concentration of copper(II) sulfate in **FA 5** using the titration method described above.

In your plan, you should include details of:

- the quantities of chemicals you would use,
- the apparatus you would use and the procedure you would follow,
- the measurements you would take.

....[5]

[Total: 8]

4 Qualitative analysis

In this question you will perform a series of test-tube reactions and use the observations to help you deduce the identities of two solids present in a given mixture **FA 6**.

You will also **devise a plan**, consisting of test-tube reactions, and **carry out** the plan to distinguish between three solutions **FA 9**, **FA 10** and **FA 11**, so that each is identified.

At each stage of any test you are to record details of the following:

- details of colour changes and precipitates formed
- the names of gases evolved and details of the test used to identify each one

You should indicate clearly at what stage in a test a change occurs.
No additional tests for ions present should be attempted.

(a) **FA 6** is a mixture of two solids: **FA 7**, which is soluble in water and **FA 8**, which is insoluble in water. Each contains one cation and one anion listed in the Qualitative Analysis Notes on pages 15 and 16.

Carry out the following tests and record your observations in the table.

	test	*observations*
(i)	Place all of the solid, **FA 6**, into a boiling tube. Add 10 cm^3 of deionised water and shake to dissolve **FA 7**. Filter the mixture, collecting the filtrate in a test-tube. Keep the filtrate for tests **(ii)** to **(iv)**. Wash the residue, **FA 8**, with deionised water. Collect the washings in the previous boiling tube. Keep the residue for tests **(v)** to **(vii)**.	
(ii)	To a 1 cm depth of filtrate, **FA 7**, in a test-tube, add aqueous sodium hydroxide. Carefully warm the mixture.	
(iii)	To a 1 cm depth of filtrate, **FA 7**, in a test-tube, add aqueous ammonia.	
(iv)	To a 1 cm depth of filtrate, **FA 7**, in a test-tube, add 5 drops of aqueous silver nitrate, followed by aqueous ammonia.	

	test	*observations*
(v)	Transfer half a spatula of the residue, **FA 8**, into a clean boiling tube. Using a measuring cylinder, measure out 10 cm^3 of dilute nitric acid. Transfer the acid to the boiling tube in portions. Mix the contents of the boiling tube thoroughly. Filter if necessary. This solution is **FA 12**.	
(vi)	To a 1 cm depth of **FA 12** in a test-tube, add 1 cm depth aqueous edta.	
(vii)	To a 1 cm depth of **FA 12** in a test-tube, add 1 cm depth aqueous sodium hydroxide, followed by aqueous ammonia. **Do not discard the remaining FA 12. Keep the solution for (b).**	

[4]

(viii) From the observations, identify the ions in **FA 7** and **FA 8**.

FA 7 contains the cation .... and the anion ....

FA 8 contains the cation .... and the anion ....

[2]

(ix) Explain in terms of the chemistry involved, your observations in **(a)(iv)**.

....

....

....

....

.... [2]

(x) State the type of reaction that occurred in **(a)(vi)**.

.... [1]

(b) Planning

FA 9, **FA 10** and **FA 11** each contains one of the following but not in that order:

hydrogen peroxide   iron(II) sulfate   potassium iodide

You are required to plan and **perform** a series of test-tube reactions using only **FA 9**, **FA 10**, **FA 11** and, **FA 12** from **(a)(v)**, to identify the three solutions, **FA 9** to **FA 11**.

You should commence your plan by adding **FA 12** to each of **FA 9**, **FA 10** and **FA 11**.

Each solution should be identified by at least one positive test. It is **not** sufficient to identify a solution simply by eliminating all the others.

You should aim to use the **minimum number** of reactions.

You may find it useful to consider the standard electrode potentials given below.

$$\begin{array}{llll}
O_2 + 2H^+ + 2e & \rightleftharpoons & H_2O_2 & +0.68\text{ V} \\
H_2O_2 + 2H^+ + 2e & \rightleftharpoons & 2H_2O & +1.77\text{ V} \\
Fe^{3+} + e & \rightleftharpoons & Fe^{2+} & +0.77\text{ V} \\
Fe^{2+} + 2e & \rightleftharpoons & Fe & -0.44\text{ V} \\
I_2 + 2e & \rightleftharpoons & 2I^- & +0.54\text{ V}
\end{array}$$

You may use the space below to plan your tests.

In the table in the next page, record

- details of the tests, including quantity of solutions used,
- observations of the tests,
- identities of the products that gave rise to the observations,
- identity of each solution.

....

....

....

....

....

....

....

....

....

....

....

....

	observations, identities of products and identity of each solution		
tests	**FA 9**	**FA 10**	**FA 11**

Conclusion

Solution **FA 9** contains ....

Solution **FA 10** contains ....

Solution **FA 11** contains ....

[8]

[Total: 17]

Qualitative Analysis Notes
[ppt. = precipitate]

(a) Reactions of aqueous cations

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

(b) Reactions of 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) 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

BLANK PAGE

You should have the following apparatus and chemicals.

Apparatus

2 x burette (50 cm^3);
1 x pipette (25.0 cm^3);
1 x pipette filler;
1 x retort stand and burette clamp;
2 x filter funnel;
1 x white tile;
2 x 250 cm^3 conical flasks;
1 x volumetric flask (250 cm^3)
1 x Styrofoam cup;
1 x 250 cm^3 beaker;
1 x thermometer with range –5 ^{o}C to +50 ^{o}C, graduated to 0.2 ^{o}C;
1 x stopwatch, reading to at least 0.1s;
1 x 10 cm^3 measuring cylinder;
1 x Bunsen burner;
1 x lighter (shared by 2 students);
10 x test-tube;
2 x boiling tube;
1 x test-tube rack;
1 x test-tube holder;
1 x delivery tube with rubber stopper (fits boiling tube);
1 x marker for writing on glass;
1 x pair of disposable vinyl gloves;
1 x pair of safety goggles;
1 x wash bottle containing deionised water;
A clear plastic bag containing:
    6 x plastic dropping pipettes;
    1 x lid for Styrofoam cup;
    1 x plastic spatula;
    1 x wooden splint;
    filter papers;
    litmus papers;
    paper towels.

Chemicals

Reagents labelled FA	Bench reagents
FA 1	methyl orange
FA 2	thymolphthalein
FA 4	limewater
FA 5	dilute nitric acid
FA 6	aqueous ammonia
FA 9	aqueous silver nitrate
FA 10	aqueous sodium hydroxide
FA 11	aqueous edta (ethylenediaminetetraacetic acid)

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

HWA CHONG INSTITUTION
2017 C2 CHEMISTRY PRELIMINARY EXAMINATIONS
PAPER 2 MARK SCHEME

1

(a) **(i)**

	H_2(g)	+	I_2(g)	⇌	2HI(g)
Initial conc/ mol dm^{-3}	0.05		0.05		0
Change / mol dm^{-3}	- 0.03		- 0.03		+ 0.06
Eqm conc / mol dm^{-3}	0.02		0.02		0.06

$K_c = \frac{[HI]^2}{[H_2][I_2]}$ **[1]**

$K_c = \frac{(0.06)^2}{(0.02)^2} = 9$ **[1]**

(ii)

	H_2(g)	+	I_2(g)	⇌	2HI(g)
Initial conc/ mol dm^{-3}	0.02		0.02		0.06
Change / mol dm^{-3}	+x		+x		-2x
Eqm conc / mol dm^{-3}	0.02+x		0.02+x		0.06-2x

$K_c = \frac{(0.06-2x)^2}{(0.02+x)^2} = 0.36$

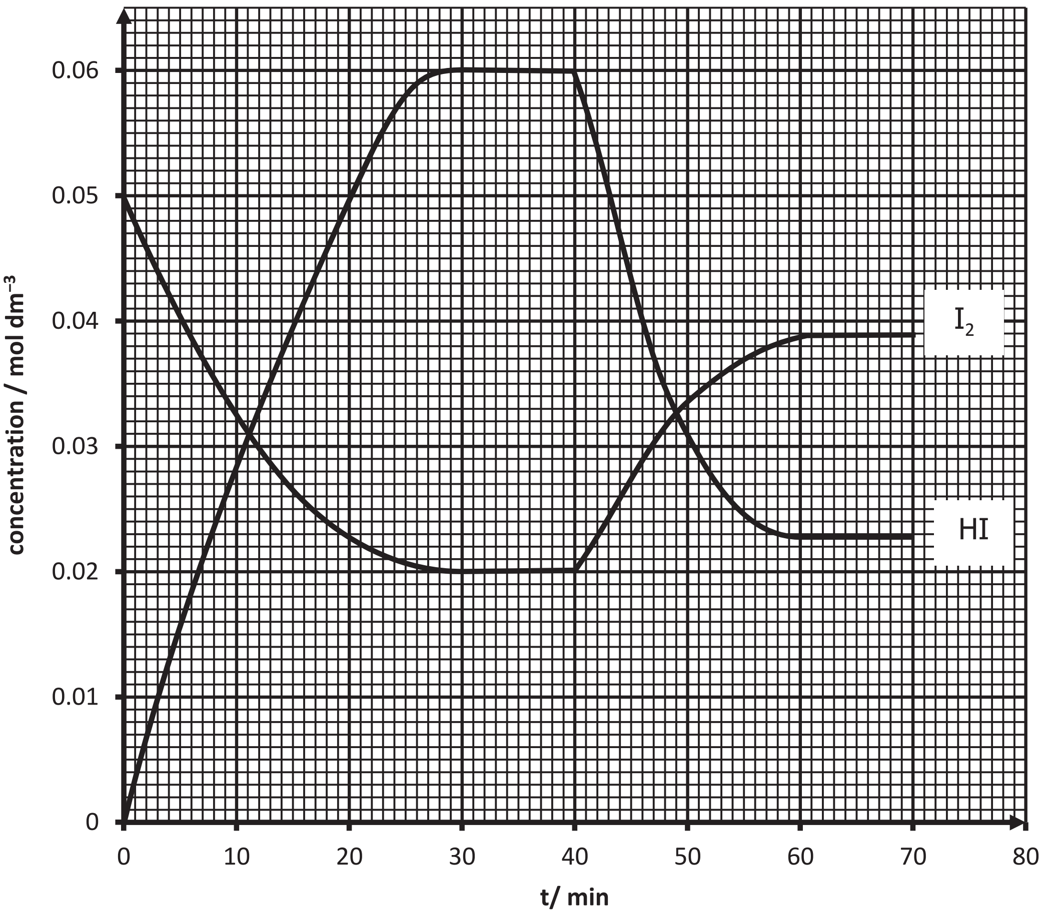
$\frac{(0.06-2x)}{(0.02+x)} = 0.6$

x = 0.01846 **[1]**

$[H_2] = [I_2]$ = 0.02+x = **<u>0.0385 mol dm^{-3}</u>**

[HI] = 0.06-2x = **<u>0.0231 mol dm^{-3}</u>** shown **[1]**

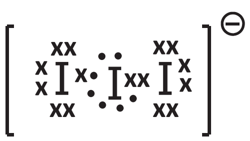
(iii)



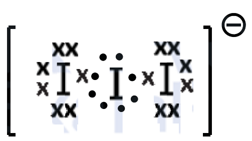
Correct axis labels [0.5]
Appropriate scale [0.5]
Correct shape of curves [0.5]
Horizontal lines from 30 – 40 mins and 60 – 70 mins [0.5]
***Correct concentration and time values for HI at t = 0, 30 and 60 min [1]**
***Correct concentration and time values for I_2 at t = 0, 30 and 60 min [1]**
***-[0.5] for every wrong plot**

(iv) To <u>prevent the position of equilibrium from shifting</u> during the cooling process or when HI is removed when dissolved in water. **[1]**

(b)



or



[1]

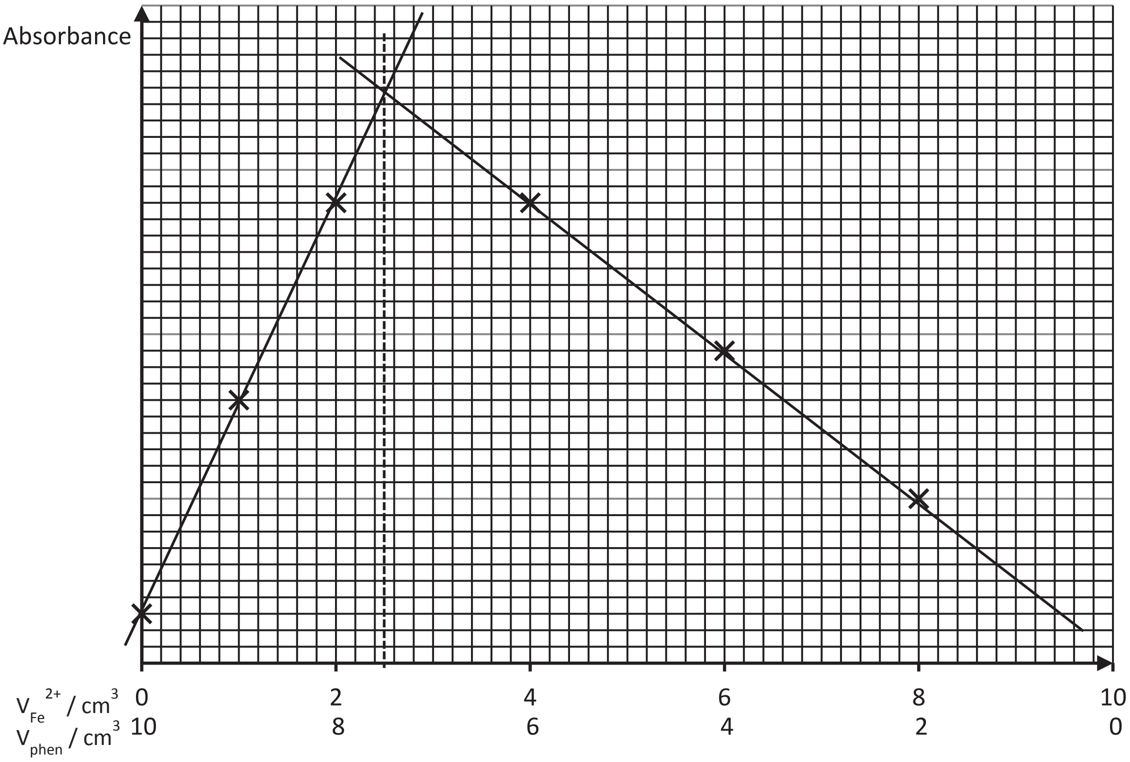
(c) Both I_2 and HI have <u>simple molecular structure</u> / consist of simple discrete molecules **[0.5]** held together by <u>dispersion forces</u>. However, I_2 has a larger number of electrons, therefore a <u>larger electron cloud than HI</u>, leading to <u>stronger</u> dispersion forces. **[1]**

So, a <u>larger amount of heat energy</u> **[0.5]** is needed to separate the molecules, leading to a higher boiling point.

2

(a) **(i)** A ligand is an ion or molecule with one or more lone pairs of electrons available to be donated into the vacant orbitals of transition metal atom or ion.

(ii)



From the graph, V_{Fe2+}:V_{phen} = 2.5:7.5 therefore you can deduce the following reacting ratio - Fe^{2+}:phen is 1:3

Formula of the complex: **$[Fe(phen)_3]^{2+}$**

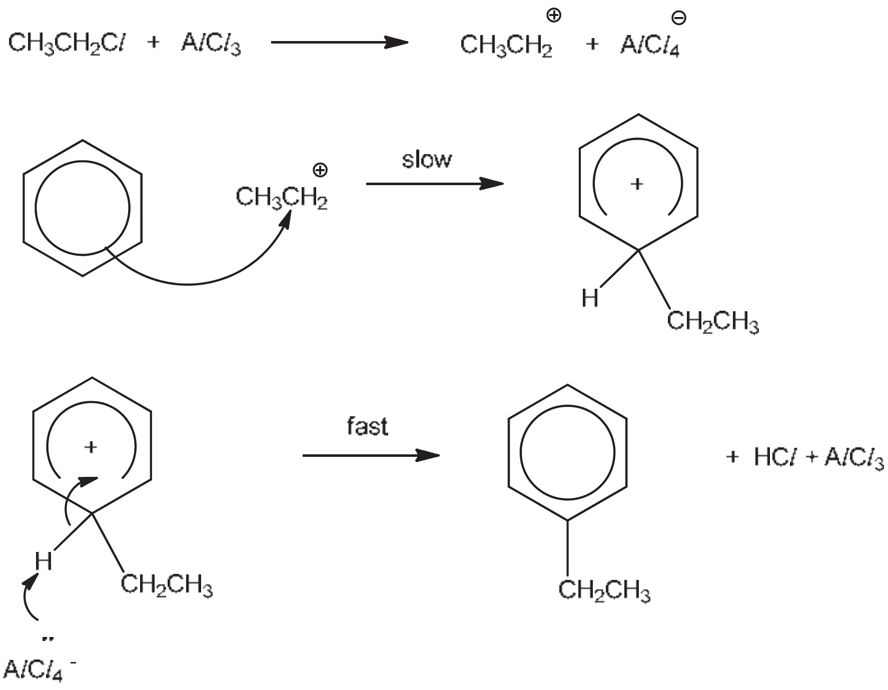
(iii)

- Fe^{2+} has an incomplete/ partially filled 3d subshell (insufficient to just give electronic configuration)
- In the presence of ligands (phen), the degenerate 3d orbitals of Fe^{2+} split into **two** different energy levels with an energy gap ΔE
- ΔE falls within the visible region of the electromagnetic spectrum
- An electron in a lower energy d-orbital can absorb energy from the visible spectrum and be promoted to a higher energy d orbital that is vacant
- The orange-red colour seen is the complement of the blue light absorbed.

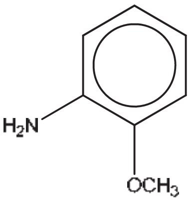
(iv) The energy gap, ΔE, is of a different magnitude in both complexes. Hence wavelength of light absorbed by the ferrozine complex is different from that absorbed by the phen complex and different colours are observed. (no need details on the exact colour of wavelength).

(b) **(i)** Reagent: CH_3CH_2Cl ; condition: $AlCl_3$, warm

(ii) Electrophilic substitution



(c) **(i)**



[1]

(ii) Accepted answers:

- 2,4-dinitrophenylhydrazine. Orange precipitate observed for vanillin but no precipitate for 4-VG
- Tollen's reagent with heating. Silver mirror observed for vanillin but no silver mirror for 4-VG
- Hot acidified KMnO4. Solution turns from purple to colourless for both but only 4-VG gives an effervescence that formed white ppt when passed through limewater
- Hot acidified $K_2Cr_2O_7$. Orange solution turned green for vanillin but solution remained orange for 4-VG.

3 **(a)** **(i)** hybridisation: sp^3 **[1]**

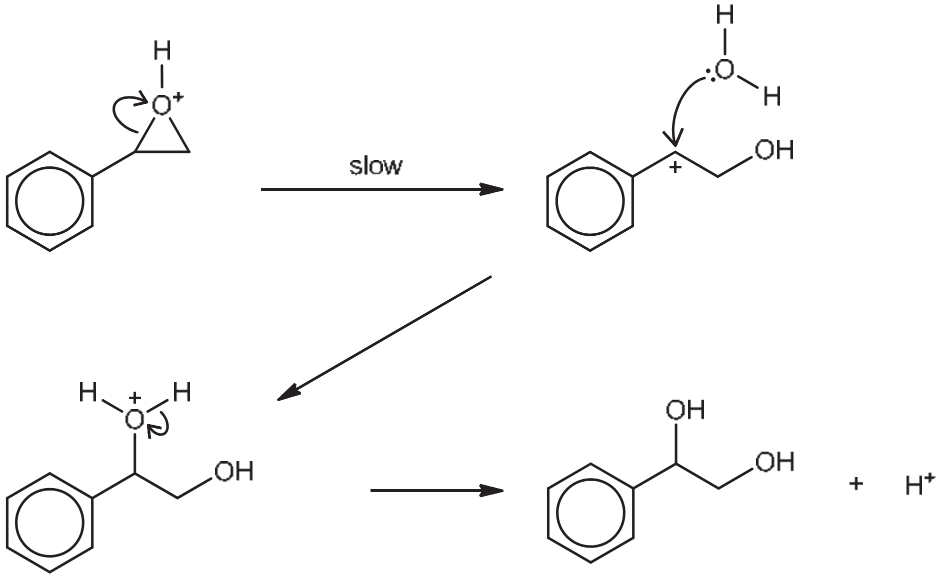
typical bond angle: 109.5° **[1]**

(ii) Forcing the bond angle in the epoxide ring to 60° brings electron pairs in the covalent bonds closer and they experience increased repulsion, weakening the C–O bonds and making them easier to break. **[1]**

or

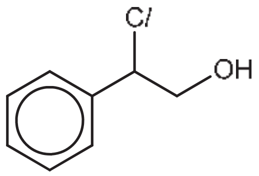
After opening the ring, the resulting product is able to attain an optimal bond angle of 109.5° around the carbon atoms, minimising electron repulsion and eliminating the ring strain.

(b) **(i)**



curly arrow from benzylic C–O^+ bond to O^+ [½], correct carbocation [½]
curly arrow from lone pair on O in H_2O to C bearing the positive charge [½], correct intermediate formed [½]
curly arrow from O^+–H bond to O^+ and H^+ regenerated [1]

(ii)



[1]

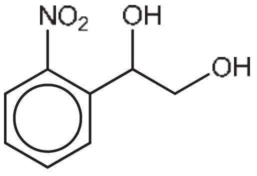
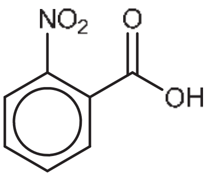
(iii) The other C–O bond was broken instead, forming a primary carbocation intermediate. $H_2{}^{18}O$ was then able to attack the primary carbocation to form isotopic isomer **A**. **[1]**

The primary carbocation formed is much more unstable than the secondary carbocation (which is particularly stable as it is resonance stabilised). The reaction mechanism is therefore much less likely to proceed via the 1° carbocation intermediate to form **A**. **[1]**

(c) step 1: conc HNO_3, conc H_2SO_4 **[½]**, maintained at 55 °C or < 55 °C **[½]**

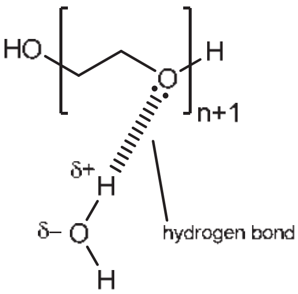
step 2: $KMnO_4$(aq), H_2SO_4(aq), heat **[1]**

step 3: CH_3CH_2OH (accept ethanol), few drops of conc H_2SO_4, heat (under reflux) **[1]**

 **B**	 **C**

[1] each

(d)



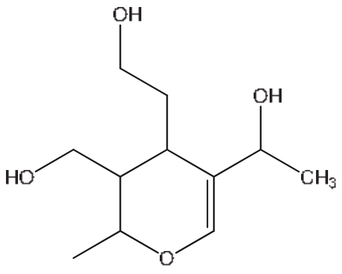
[1]

Extensive hydrogen bonding exists between PEG and water molecules. Energy released from this intermolecular hydrogen bonding with water is able to compensate for dispersion and p.d.-p.d. interactions between PEG, and intermolecular hydrogen bonding in water. **[1]**

4

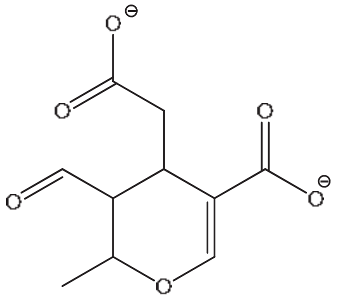
(a) Carboxylic acid, aldehyde, ketone, alkene **4 x [1]**

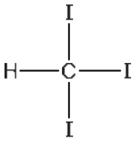
(b) **(i)**



[1]

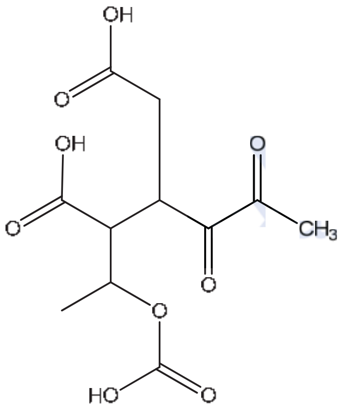
(ii)





2 x [1]

(iii)



1 mark for correct structure for oxidative cleavage of C = C bond
1 mark for correct structure for the oxidation of –CHO to –CO_2H

(c) Elenolic acid is a <u>stronger acid</u> / has <u>higher acidity</u> than compound M, which is a primary alcohol. [1]

The <u>negative charge</u> on the carboxylate ion (conjugate base of elenolic acid) is <u>delocalised</u> equally over two highly <u>electronegative</u> oxygen atoms. The negative charge is dispersed and the carboxylate ion is greatly <u>stabilised</u>. [1]

Whereas the electron-donating alkyl group <u>intensifies the negative charge</u> on the alkoxide ion (conjugate base of compound M) and the alkoxide ion is <u>destabilised</u>. [1]

5

(i) $Cu (s) \rightarrow Cu^{2+} (aq) + 2e^-$ **[1]**

(ii) Q = 3100 x 0.700 = 2170 C **[1]**

Amount of electrons transferred = (0.714/63.5) x 2 = 0.02249 mol **[1]**

Since $Q = \eta_e \times L \times e$

$2170 = 0.02249 \times L \times 1.60 \times 10^{-19}$

$L = 6.03 \times 10^{23}\ mol^{-1}$ **[1]**

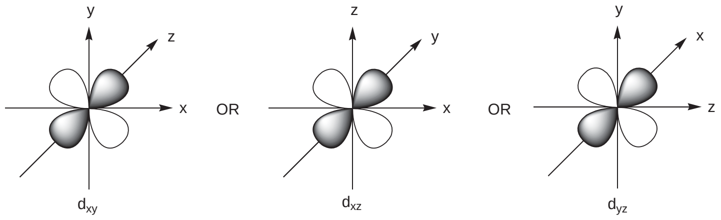
(b) **(i)** $Ni^{2+}(aq) + 2e^- \rightleftharpoons Ni(s)$ –0.25V

$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$ +0.34V **[1] (correct quotation)**

The reduction potential of the Cu^{2+}/Cu half cell is more positive than that of Ni^{2+}/Ni half cell and therefore Cu^{2+} will be preferentially reduced at the cathode. **[1]**

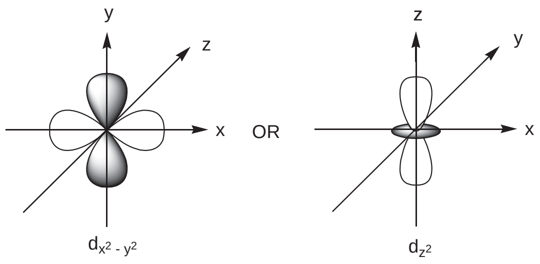
(ii) $1s^2 2s^2 2p^6 3s^2 3p^6 3d^8$ **[1]**

(iii) <u>**Upper**</u>



[1] for <u>**any**</u> of the three being drawn + <u>**correct label**</u> (shading not required; ignore if drawn)

<u>**Lower**</u>



[1] for <u>**any**</u> of the two being drawn + <u>**correct label**</u> (shading not required; ignore if drawn)

(c) **(i)** From the graph, since the plot of k_{obs} against OH^- is a straight line that passes through the origin, m=1. **[1]**

(ii) Rate = $k[OH^-]$[isocyanide] **[1]**

When $[OH^-] = 0.74$ mol dm^{-3}, $k_{obs} = 5.6 \times 10^{-3}$ s^{-1}
rate = k_{obs} [isocyanide] = $5.6 \times 10^{-3} \times (5.0 \times 10^{-4}) = 2.8 \times 10^{-6}$ mol dm^{-3} s^{-1} **[1]**
OR
Gradient for X=C*l* graph, $k = 0.6 \times 10^{-3}/0.8 = 7.5 \times 10^{-3}$ mol dm^{-3} s^{-1}
rate = $k[OH^-]$[isocyanide] = $7.5 \times 10^{-3} \times 0.74 \times (5.0 \times 10^{-4}) = 2.8 \times 10^{-6}$ mol dm^{-3} s^{-1}

(iii) The OH^- nucleophile approaches the electron deficient carbon of isocyanide. The substituents NO_2 and C*l* are electron withdrawing and they enhance the electron deficiency of isocyanide, making it more susceptible to nucleophilic attack. Their rate of reaction (as reflected in the rate constant represented by the gradient) thus exceeds that when X=H (when there is no substituent). **[1]**

6
(a) A buffer solution is a solution that resists changes in pH upon addition of small amounts of acid or base. **[1]**

(b)
$$pH = pK_a + \lg\frac{[SO_3^{2-}]}{[HSO_3^-]} = -\lg(1.02 \times 10^{-7}) + \lg(1/4)$$

pH = 6.39 **[1]**

(c) $HSO_3^- + OH^- \rightarrow SO_3^{2-} + H_2O$ **[1]**

(d) $K_{sp} = [Mg^{2+}][OH^-]^2$
$5.66 \times 10^{-12} = (5 \div 405 \times 2)\,[OH^-]^2$
$[OH^-] = 1.51 \times 10^{-5}$ mol dm^{-3} **[1]**

pH = 14−pOH = 14 + lg(1.51×10^{-5})
pH = 9.18 shown. **[1]**

(e) Solution B **[1]**

(f) "Tea" appears earlier because the working pH range of 3-nitrophenol indicator (6.7-8.7) is lower than the pH at which white precipitate occurs (9.18). **[1]**

(g) Phenolphthalein **[1]**

2017 C2 Prelims Paper 3 Mark Scheme

1 **(a)** No. of moles of NaOH = 0.100 x 26.50/1000 = 2.65 x 10^{-3} mol

No. of moles of H_2SO_4 (in 25cm^3) = ½ x 2.65 x 10^{-3}
= **1.325 x 10^{-3}** mol **[1/2]**

No. of moles of H_2SO_4 (in 250cm^3) = 1.35 x 10^{-3} x **250/25.0** **[1/2]**
= 0.01325 mol

No. of moles of H_2SO_4 reacted = (0.425 x 100/1000) – 0.01325 **[1/2]**
= 0.02925 mol

No. of moles of $Cu_3(CO_3)_2(OH)_2$ = 0.02925 **x 1/3** **[1/2]**
= 9.75 x 10^{-3} mol

Mass of azurite = 9.75 x 10^{-3} **x 344.5** **[1/2]**
= 3.359 g

% by mass of pure azurite in the powdered rock = 3.359/3.70 x 100%
= 90.8% **[1/2]**

(b) **(i)** x = 2 **[1]**

$[Cu(NH_3)_2]^+$ **[1]**

(ii) [O] $[Cu(NH_3)_2]^+ + 2NH_3 \longrightarrow [Cu(NH_3)_4]^{2+} + e^-$

[R] $O_2 + 2H_2O + 4e^- \longrightarrow 4OH^-$

Overall: $4[Cu(NH_3)_2]^+ + O_2 + 8NH_3 + 2H_2O \rightarrow 4[Cu(NH_3)_4]^{2+} + 4OH^-$

2 half-equations: **[1/2 each]**
Overall equation: **[1]**

(c) **(i)**

$$\begin{tikzcd}
I_2(s) \arrow[d, "+38"'] & + & 3Cl_2(g) \arrow[dd, "3(244)"] \arrow[r] & 2ICl_3(s) \arrow[d, "2(+60)"] \\
I_2(g) \arrow[d, "+151"'] & & & 2ICl_3(g) \arrow[dl, bend left, "6BE(I\text{–}Cl)"] \\
2I(g) & + & 6Cl(g) &
\end{tikzcd}$$

$$-162 = +38 + 151 + 3(244) - 6BE(I\text{–}Cl) - 120$$

$$BE(I\text{–}Cl) = +160.5\ kJmol^{-1}$$

energy cycle: **[2]**
application of Hess's Law: **[1]**
correct stoichiometry coefficients: **[1]**

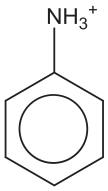
(ii)

$$\Delta G_f^{\ominus} = \Delta H_f^{\ominus} - T\Delta S_f^{\ominus}$$
$$-40.4 = -81 - 298\Delta S_f^{\ominus}$$
$$\Delta S_f^{\ominus} = -0.136 \text{ kJ mol}^{-1}\text{ K}^{-1}$$
$$= -136 \text{ J mol}^{-1}\text{ K}^{-1}$$
[1]

$\Delta S_f^{\ominus}$ is negative as there is a **decrease in the number of gaseous molecules**, resulting in **fewer number of ways** that the particles and the energy can be distributed. **[1]**

(d) (i) Electrophilic substitution, reduction and condensation. **[1 each] x 3**

(ii)



and CH_3CO_2H **[1/2 each]**

2 **(a)** **(i)** $C_nH_{2n+1}SH + 3(n+1)/2\ O_2 \rightarrow n\ CO_2 + SO_2 + (n+1)H_2O$ **[1]**

(ii) $\chi_{SO_2} = \dfrac{\eta_{SO_2}}{\eta_{CO_2} + \eta_{SO_2} + \eta_{H_2O}}$ = 1/(n+1+n+1) = 1/(2n+2) shown **[1]**

(iii) $\chi_{SO_2} = \dfrac{p_{SO_2}}{p_{total}}$

1/(2n+2) = 16900 / 101325

n = 2 **[1]**

(iv) $\eta_{SO_2} = \dfrac{p_{SO_2}V}{RT} = \dfrac{16900(1.65x10^{-3})}{8.31(110+273)} = 0.00876\text{ mol} =$ $\eta_{ethanethiol}$ reacted **[1]**

Mass of ethanethiol = 0.00876 x 62.1 = 0.544 g **[1]**

(b) **(i)** As Reaction 1 is effectively complete whereas ethanol does not react with NaOH, this shows that ethanethiol is a stronger acid than ethanol. **[1]**

(ii) Nucleophilic substitution **[1]**

(iii) Reaction 1 was carried out to generate $CH_3CH_2S^-$, a stronger nucleophile than CH_3CH_2SH. **[1]**

(iv) For bromobenzene, the lone pair of electrons on the bromine atom is delocalised into the ring. As a result, there is partial double bond character to the C-Br bond, so its bond strength is higher than a typical C-Br in a halogenoalkane and it is very difficult to break. **[1]**

Sterically, the rear side of the C-Br bond in bromobenzene is blocked by the benzene ring.
Or
The pi-electron cloud of the benzene ring will repel the lone pair of electrons of the incoming nucleophile, rendering attack of the nucleophile difficult. **[1]**

(c) **(i)** Base **[1]**

(c) **(ii)** As the equilibrium position lies towards the products (K>1), $\Delta G^{\ominus}$ is negative. **[1]**

As the equilibrium constant for Reaction 1 is a very large number, as $\Delta G^{\ominus}=-RT\ln K$, the magnitude of $\Delta G^{\ominus}$ is very large. **[1]**

(iii) A: HNO_3 **[1]**
B: NO_2 **[1]**

(iv) The temperature in the furnace is 400 °C. **[1]** (accept any temperature between 170 °C and 630 °C)

The ionic radii of Cu^{2+}, Pb^{2+} and Ba^{2+} are 0.073nm, 0.120nm and 0.135nm respectively. **[1/2]**

The charge density of the cation decreases from Cu^{2+} to Pb^{2+} to Ba^{2+}. **[1]**

The polarising power of the cation decreases from Cu^{2+} to Pb^{2+} to Ba^{2+}. OR the cation is less able to distort the electron cloud of the nitrate, weakening the N-O bonds within the nitrate anion to a smaller extent. **[1]**
Hence more energy is required to decompose $Pb(NO_3)_2$ compared to $Cu(NO_3)_2$ but less compared to $Ba(NO_3)_2$. **[1/2]** (accept "ease of decomposition" / "decomposition temperature")

(d) **(i)** Reaction (A) 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) Reactions (C), (D) and (E) **[1]**

(iii) Hydrogen **[1]**

(iv) The $\bullet CH_2CH_3$ radical loses a hydrogen (is oxidised) to form ethene and gains a hydrogen (is reduced) to form ethane. As it is both oxidised and reduced, this is a disproportionation. **[1]**

OR
The average oxidation number of carbon in the $\bullet CH_2CH_3$ radical is -2.5, but -2 in ethene and -3 in ethane. As carbon is both oxidised and reduced, this is a disproportionation. **[1]**

3 **(a)** **(i)** Concentration of a solid is constant. **[1]**

(ii) $\eta(C_{18}H_{29}SO_3Na)$ present in 1.00 g of detergent

$= \left(\frac{17.4}{100} \times 1.00\right) \div 348 = 5.00 \times 10^{-4}$ mol

$\therefore [C_{18}H_{29}SO_3^-] = 5.00 \times 10^{-4}$ mol dm^{-3} **[1]**

IP = $(2.50 \times 10^{-4})(5.00 \times 10^{-4})^2 = 6.25 \times 10^{-11}$ mol^3 dm^{-9} **[1]**

Since IP > K_{sp}, a precipitate will form. **[1]**

(iii) For the detergent to be effective, no precipitate is formed

$\Rightarrow$ IP < K_{sp}

$\therefore [Ca^{2+}][C_{18}H_{29}SO_3^-]^2 < 1.20 \times 10^{-17}$

From **(a)(ii)**, $[C_{18}H_{29}SO_3^-] = 5.00 \times 10^{-4}$ mol dm^{-3}

$\therefore [Ca^{2+}] < \frac{1.20 \times 10^{-17}}{(5.00 \times 10^{-4})^2} = 4.80 \times 10^{-11}$ mol dm^{-3}

Maximum $[Ca^{2+}] = 4.80 \times 10^{-11}$ mol dm^{-3} **[1]**

(iv) $K_c = \frac{[CaP_3O_{10}^{3-}]}{[Ca^{2+}][P_3O_{10}^{5-}]}$ **[1]**

(v) $K_c = \frac{[CaP_3O_{10}^{3-}]}{[Ca^{2+}][P_3O_{10}^{5-}]}$

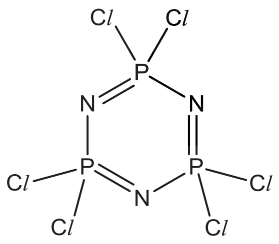
$7.70 \times 10^8 = \frac{0.90}{[Ca^{2+}] \times 0.10}$

$[Ca^{2+}] = 1.17 \times 10^{-8}$ mol dm^{-3} **[1]**

(vi) Since $[Ca^{2+}]$ is **more than 4.80×10^{-11}**, the added solid sodium tripolyphopshate was **insufficient** to make the detergent effective. **[1]**

(b) **(i)** $3PCl_5 + 3NH_4Cl \rightarrow (Cl_2PN)_3 + 12HCl$ **[1]**

(ii)



[1]

(iii) $(Cl_2PN)_3$ undergoes hydrolysis. **[1]** (Accept nucleophilic substitution)

White fumes of HCl is observed. **[1]**

(iv) From the Data Booklet, atomic radius of P = 0.110 nm, atomic radius of N = 0.074 nm and atomic radius of C*l* = 0.099 nm

Atomic radius of N is the smallest as it has one less principle quantum shell than P and C*l* and hence their valence electrons are closer to the nucleus. **[1]**

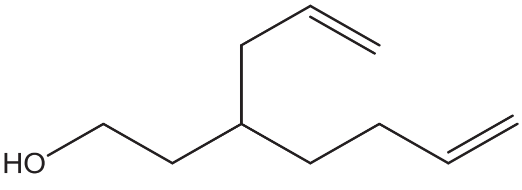
Atomic radius of C*l* is smaller than P. C*l* has higher nuclear charge / higher proton number but similar shielding effect **[1]** as P. Hence C*l* has higher effective nuclear charge and the valence electrons are held closer to the nucleus.

(Idea of valence electron closer to nucleus just need to be mentioned once in answer).

Note: atomic radius of N must be compared to C*l*. Explaining atomic radius of N < P and atomic radius of C*l* < P does not fully explain the trend atomic radius of N < C*l* < P.

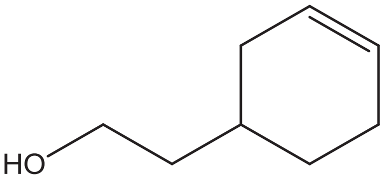
(c) (i)

B =



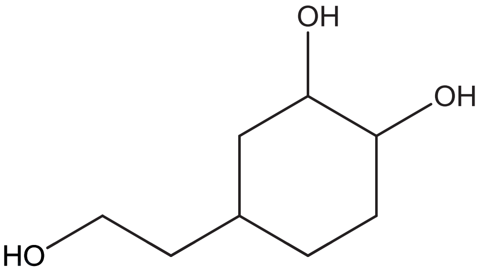
[1]

C =



[1]

D =



[1]

(ii) Step 1: alcoholic KOH, heat or alcoholic NaOH, heat **[1]**

Step 3: $KMnO_4$, NaOH(aq), cold **[1]**

Step 4: excess concentrated H_2SO_4, heat or concentrated H_3PO_4, heat or Al_2O_3, heat **[1]**

4 (a) (i) $CH_3CH_2OH + 3H_2O \rightarrow 2CO_2 + 12H^+ + 12e$ **[1]**

(ii)
- Reactant molecules diffuse towards the catalyst surface and are **adsorbed onto the active sites**.
- The **bonds in the reactant molecules weaken**, and the **activation energy is lowered**.
- Reactant molecules are **brought closer together**, and are **correctly orientated.**
- When the product is formed, it **desorbs** and diffuses away from the catalyst surface **freeing up the active sites**.

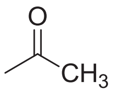
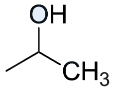
[4]

(iii)
- Correctly drawn CO_2/ ethanol half cell
  - [H^+] and ethanol to 1mol dm^{-3}
  - Temperature and pressure of CO_2 to 298K and 1 bar
  - Electrode: graphite/ metal catalyst/ platinum (coated with metal catalyst)
- Correctly drawn standard hydrogen electrode
  - [H^+] to 1 mol dm^{-3}
  - Temperature and pressure of H_2 to 298K and 1 bar
  - Platinum electrode
- Salt bridge and voltmeter

[1] for each point

(iv)
- When pH increases, **[H+] decreases**. This **favours the oxidation** of ethanol.
- Reduction potential should become **more negative**. **[2]**

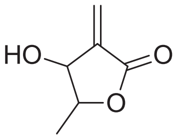
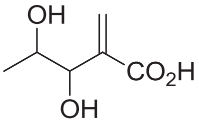
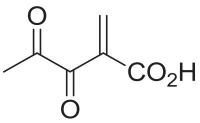
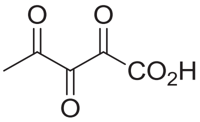
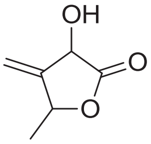
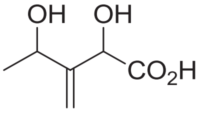
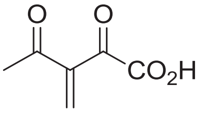
(b) (i) Degree of unsaturation of **A** = 3
Degree of unsaturation of **B** = 2 **[2]**

(ii)
- **Carboxylic acid**
  - reacts with Na_2CO_3 in an acid–carbonate reaction.
- **(Two) 2° alcohol**
  - oxidation with I_2, NaOH(aq), suggest that either  or  is present. Since **B** does not react with 2, 4 – DNPH, a 2° alcohol is present
  - oxidation with $K_2Cr_2O_7$ does not increase the number of oxygen atoms in C. No primary alcohol was oxidized.
- **(Terminal) Alkene**
  - Oxidative cleavage with $KMnO_4$.
  - Oxidative cleavage causes the molecule to lose one carbon.

[3]

(b) (iii)
- Since **B** contains a carboxylic acid and alcohol and is formed from the acid hydrolysis of **A**, **A** contains an **ester functional group**. **[1]**

(iv)
- Of the two secondary alcohols, it is the secondary alcohol with the CH_3 that forms the ester since **A** does not give a yellow ppt with alkaline $I_2(aq)$

A	B	C	D
			
			

[1] each

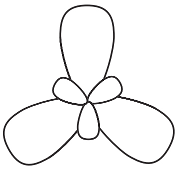
5 **(a)** Histidine exists as zwitterions due to the internal neutralization of amino and carboxylic acid groups. **Zwitterions** are **arranged in an orderly manner** in solid crystalline state. **[1]**

It has a **giant ionic structure with** strong **ionic bonds** between the zwitterions.

[1] both

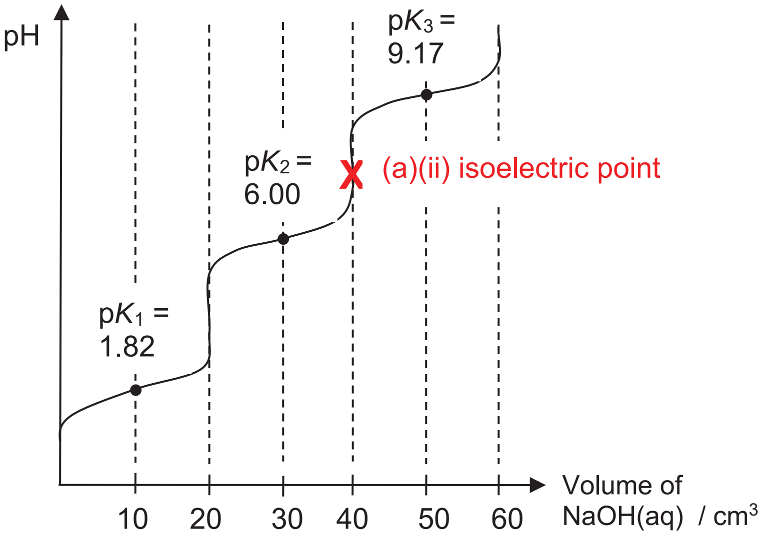
A lot of energy is required to separate the zwitterions due to the **strong** ionic bonds, thus it has high melting point. **[1]**

(b) sp^2 **[1]**



[1]

(c) **(i)**



[1] axis labels and shape of curve

[1] 3 equivalence points at correct volumes & mark pK_1, pK_2 & pK_3

[1] Mark X at the correct volume

(c) **(ii)** pH = pK_{a2} + lg [A^-]/[HA]
6 = 6.00 + lg [A^-]/[HA]
[A^-]/[HA] = <u>1</u>

<u>Before addition of OH^-</u>
Amount of histidine present = 0.100 dm^3 x 0.10 mol dm^{-3} = 0.01 mol
Amount of HA = Amount of A^- = 0.01 $\times \frac{1}{2}$ = <u>0.00500 mol</u>

<u>On addition of OH^-:</u>
Amount of OH^- added = 0.01 dm^3 x 0.01 mol dm^{-3} = 0.0001 mol

	HA	+	OH^-(aq)	$\rightleftharpoons$	A^-(aq)	+	H_2O
Before adding NaOH	0.00500				0.00500		
After adding NaOH	0.00500 – 0.0001 = 0.00490				0.00500 + 0.0001 = 0.00510		

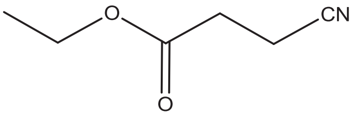
pH = 6.00 + lg (0.00510/0.00490)
= <u>6.017 ≈ 6.02</u>

[1] for original [A^-]/[HA]
[1] for amount of A^- & HA before addition of NaOH
[1] pH with 2 dp

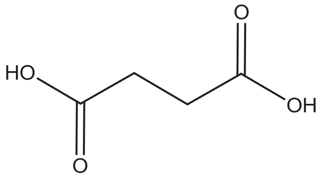
(d) **(i)** (Alkaline) Hydrolysis **[1] reject acid hydrolysis**

Amide and nitrile **[1/2 each]**

(ii)

P: 

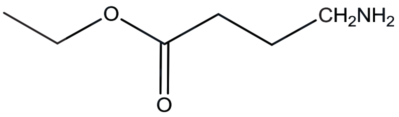
Q: CH_3CH_2OH

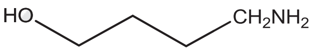
R: 

S: HCO_2H **T:** CHI_3

[1] each

(iii)

U: 

V: 

[1] each

2017 HCI C2 H2 Chemistry Prelim Paper 4 Preparation Instructions

Safety

Supervisors are advised to remind candidates that **all** substances in the examination should be treated with caution. Only those tests described in the Question Paper should be attempted.

Attention is drawn in particular, to certain materials used in the examination. The following codes are used where relevant.

- Explosives
- Self-Reactives
- Organic peroxides

- Flammables
- Self Reactives
- Pyrophorics
- Self-Heating
- Emit Flammable Gas
- Organic Peroxides

- Oxidisers

- Gases Under Pressure

- Corrosives

- Acute Toxicity (severe)

- Irritant
- Dermal Sensitizer
- Acute toxicity (harmful)
- Narcotic Effects
- Respiratory Tract Irritation

- Carcinogen
- Respiratory Sensitizer
- Reproductive Toxicity
- Target Organ Toxicity
- Mutagenicity
- Aspiration Toxicity

- Environmental Toxicity

'Hazard Data Sheets', relating to materials used in this examination, should be available from your chemical supplier.

Before the Examination

1 **Preparation of materials**
Where quantities are specified for each candidate, they are sufficient for the experiments described in the Question Paper to be completed.
In preparing materials, the bulk quantity for each substance should be increased by 25% as spare material should be available to cover accidental loss. More material may be supplied if requested by candidates, without penalty.
All solutions should be bulked and mixed thoroughly before use to ensure uniformity.

2 **Labelling of materials**
Materials must be labelled as specified in these instructions. Materials with an **FA** code number should be so labelled **without** the identities being included on the label. Where appropriate the identity of an **FA** coded chemical is given in the Question Paper itself.

3 **Identity of materials**
It should be noted that descriptions of solutions given in the Question Paper may not correspond exactly with the specifications in these Instructions. **The candidates must assume the descriptions given in the Question Paper.**

Apparatus

1 *For each candidate*

2 x burette (50 cm^3);
1 x pipette (25.0 cm^3);
1 x pipette filler;
1 x retort stand and burette clamp;
2 x filter funnel;
1 x white tile;
2 x 250 cm^3 conical flasks;
1 x volumetric flask (250 cm^3)
1 x Styrofoam cup;
1 x 250 cm^3 beaker;
1 x thermometer with range –5 ^oC to +50 ^oC, graduated to 0.2 ^oC;
1 x stopwatch, reading to at least 0.1s;
1 x 10 cm^3 measuring cylinder;
1 x Bunsen burner;
1 x lighter (shared by 2 students);
10 x test-tube;
2 x boiling tube;
1 x test-tube rack;
1 x test-tube holder;
1 x delivery tube with rubber stopper (fits boiling tube);
1 x marker for writing on glass;
1 x pair of disposable vinyl gloves;
1 x pair of safety goggles;
1 x wash bottle containing deionised water;
A clear plastic bag containing:
    6 x plastic dropping pipettes;
    1 x lid for Styrofoam cup;
    1 x plastic spatula;
    1 x wooden splint;
    filter papers;
    litmus papers;
    paper towels.

FA reagents (1 set for every candidate)

hazard	label	per candidate	identity	notes
	**FA 1**	150 cm^3	0.0625 mol dm^{-3} NaOH + 0.05 mol dm^{-3} Na_2CO_3 (anhydrous)	
	**FA 2**	80 cm^3	0.9 mol dm^{-3} HC*l*	
	**FA 4**	1.5 g	Fe powder (as purchased)	
	**FA 5**	100 cm^3	0.400 mol dm^{-3} $CuSO_4$ (5 hydrate)	
	**FA 6**	2 g	50:50 solid sodium chloride & solid copper carbonate basic mixture	NaC*l* is used as “substitute” for BaC*l*$_2$
	**FA 9**	10 cm^3	5% w/v acidified ferrous sulfate (7 hydrate) (in equal volume of 1M H_2SO_4 and DI water)	
	**FA 10**	10 cm^3	3% H_2O_2	
	FA 11	10 cm^3	5% w/v KI	

Bench reagents (1 set per seat for 3 shifts)

hazard	label	per candidate	identity
	lime water	2 cm^3 per shift	saturated calcium hydroxide, $Ca(OH)_2$
	nitric acid	10 cm^3 per shift	2 mol dm^{-3}
  	aqueous ammonia	25 cm^3 per shift	2 mol dm^{-3}
	aqueous sodium hydroxide	10 cm^3 per shift	2 mol dm^{-3}
	aqueous silver nitrate	5 drops per shift	0.05 mol dm^{-3}
	aqueous EDTA (sodium salt) (ethylenediaminetetraacetic acid)	2 cm^3 per shift	168.0 g $C_{10}H_{14}N_2O_8Na_2$ in 1 dm^3 or 186.0g $C_{10}H_{14}N_2O_8Na_2.2H_2O$ in 1 dm^3
	methyl orange indicator	10 drops per shift	as purchased
	thymolphthalein indicator	10 drops per shift	2 g in 1 dm^3 ethanol

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

1 Determination of concentrations of sodium hydroxide, and of sodium carbonate in a mixture

FA 1 is a solution containing sodium hydroxide, NaOH, and sodium carbonate, Na_2CO_3.
FA 2 is an aqueous solution containing 0.90 mol dm^{-3} of hydrochloric acid, HC*l*.

Sodium hydroxide reacts with hydrochloric acid according to the equation below:

Reaction 1 $NaOH + HCl \rightarrow NaCl + H_2O$

Sodium carbonate reacts with hydrochloric acid in two separate stages. The reactions that occur are:

Reaction 2 $Na_2CO_3 + HCl \rightarrow NaCl + NaHCO_3$
Reaction 3 $NaHCO_3 + HCl \rightarrow NaCl + CO_2 + H_2O$

You are required to find the concentrations of sodium hydroxide, and of sodium carbonate, in **FA 1**, by means of a *double-indicator* titration.

In a *double-indicator* titration, **two different** indicators are used, separately, in the **same** titration. In this experiment, thymolphthalein indicator, followed by methyl orange indicator, will be used.

Thymolphthalein indicates the end-point when **Reaction 1** and **2** are complete, while methyl orange indicates the end-point when **Reaction 3** is complete.

(a) (i) Dilution of FA 2

Using a burette, measure between 35.00 cm^3 and 36.00 cm^3 of **FA 2** into the 250 cm^3 volumetric flask.

Record your burette readings and the volume of **FA 2** added to the flask in the space below.

Final (burette) reading /cm^3	46.30
Initial (burette) reading / cm^3	11.00
Volume of FA2 (used for dilution) /cm^3	35.30

Make up the contents of the flask to the 250 cm^3 mark with deionised water. Place the stopper in the flask and mix the contents thoroughly by slowly inverting the flask a number of times. This solution is **FA 3**.

(ii) Titration of FA 1 against FA 3

Fill a second burette with **FA 3**.

Pipette 25.0 cm^3 of **FA 1** into a conical flask.
Replace the cap over the FA 1 bottle to prevent absorption of carbon dioxide from the atmosphere.

Add a few drops of thymolphthalein indicator and titrate **FA 1** with **FA 3**. The end-point is reached when the solution turns colourless. Ignore any cloudiness that you may observe in the conical flask. Record your titration results in the space below. **The volume of FA 3 used to reach the first end-point need not be consistent.**

Do not discard this solution.

To **this** solution, add a few drops of methyl orange indicator and **continue** to titrate with **FA 3** until the second end-point is reached. Record your titration results in the space below.

Perform sufficient titrations to obtain accurate results for the **second end-point**, which refers to the **total** volume of **FA 3** required for the whole titration.

Make certain that all your recorded results show the precision of your working.

Initial (burette) reading /cm^3	4.90	4.30
Final (burette) reading 1 /cm^3	24.60	24.10
Final (burette) reading 2 / cm^3	35.50	34.90
Titre 1 /cm^3	19.70	19.80
Titre 2 /cm^3	30.60	30.60

Tables have correct headers and units [1]
All readings recorded to correct precision [1]
Dilutes between 35.00 cm^3 and 36.00 cm^3 of **FA 2**. [1]

[3]

(b) From your titrations, obtain suitable volumes of **FA 3** for the:

- first end-point
- second end-point.

Show clearly how you obtained these volumes.

mean titre 1 = ½ (19.70 + 19.80) = 19.75 cm^3
mean titre 2 = ½ (30.60 + 30.60) = 30.60 cm^3

Correct average titre from values within 0.10 cm^3 [1]
Accuracy (difference between teacher's and student's scaled mean titre) [2]

volume of **FA 3** for first end-point = ...

volume of **FA 3** for second end-point = ...

[3]

(c) **(i)** Calculate the concentration, in mol dm^{-3}, of HC*l* in **FA 3**.

[HC*l*] in FA3 = 35.30 / 250 × 0.90 = 0.127 mol dm^{-3}

concentration of HC*l* in **FA 3** = ... [1]

(ii) Calculate the amount of sodium carbonate, Na_2CO_3, present in 25.0 cm^3 of **FA 1**.

vol. FA3 reacted with $NaHCO_3$ formed = 30.60 – 19.75
= 10.85 cm^3

ηNa_2CO_3 in 25 cm^3 **FA 1**
= $\eta NaHCO_3$ formed
= ηHC*l* reacted
= 0.1271 × 10.85/1000
= 0.00138 mol

amount of Na_2CO_3 in 25.0 cm^3 of **FA 1** = ... [1]

(iii) Calculate the amount of sodium hydroxide, NaOH, present in 25.0 cm^3 of **FA 1**.

vol. FA3 reacted with NaOH = 19.75 – 10.85
= 8.90 cm^3 [1]

ηNaOH in 25 cm^3 **FA 1** = ηHC*l* reacted
= 0.1271 × 8.90/1000 = 0.00113 mol [1]

amount of NaOH in 25.0 cm^3 of **FA 1** = ... [2]

(iv) Use your answers from **(c)(ii)** and **(c)(iii)**, calculate the concentrations, in mol dm^{-3}, of Na_2CO_3 and NaOH in **FA 1**.

[Na_2CO_3] in **FA 1** = 0.001379 x 1000/25 = 0.0552 mol dm^{-3}

[NaOH] in **FA 1** = 0.001131 x 1000/25 = 0.0452 mol dm^{-3}

concentration of Na_2CO_3 in **FA 1** = ...

concentration of NaOH in **FA 1** = ...
[1]

(d) The maximum error in a single burette reading is ±0.05 cm^3.

When making up the diluted acid, **FA 3,** a student recorded that 35.00 cm^3 of **FA 2** was used. What are the smallest and largest possible volumes of acid that were run into the volumetric flask?

smallest volume used = 34.90 cm^3 largest volume used = 35.10 cm^3

[1]

(e) A student suggested doing the titration in **(a)(ii)** differently – **FA 3** is placed in the conical flask and **FA 1** in the burette, using methyl orange indicator followed by thymolphthalein indicator.

Explain if this method will allow you to determine the concentrations of NaOH and Na_2CO_3 in **FA 1**.

As there is **excess HC*l*** in the conical flask, methyl orange only changes colour when **both** Na_2CO_3 and NaOH have completely reacted i.e. only **one end-point** will be obtained. Hence this method does **not** allow [Na_2CO_3] and [NaOH] to be determined.

....

....

....[1]

[Total: 13]

2 Heat of reaction between copper(II) ions and iron metal

In this experiment, you will measure the heat given out by the reaction of excess iron with copper(II) sulfate solution and use this to find the concentration of the copper(II) sulfate.

$$Fe(s) + CuSO_4(aq) \rightarrow FeSO_4(aq) + Cu(s)$$

FA 4 is iron powder.
FA 5 is aqueous copper(II) sulfate, $CuSO_4$.

In an appropriate format in the space below, prepare a table in which you may record each temperature and the time it was taken.

1. Wash thoroughly a burette and fill it with **FA 5**. Place a Styrofoam cup into a 250 cm^3 beaker to prevent it from tipping over. Transfer 40.00 cm^3 of **FA 5** into the Styrofoam cup.

2. Place the lid onto the cup and insert the thermometer through the lid. Measure and record the initial temperature of the **FA 5** solution in the cup.

3. Start the stopwatch. Measure and record the temperature of the solution in the cup **every <u>half minute</u>** up to and including the temperature at 1.5 min. Stir the solution using the thermometer.

4. At time *t* = 2.0 min, add **all** the powdered iron **FA 4** to the solution. Stir the mixture **thoroughly** with the thermometer to **ensure the solid mixes well with the solution**.

5. Record the temperature of the mixture **every <u>minute</u>** from *t* = 2.5 min. Continue stirring **thoroughly** and mixing the contents of the cup well **throughout** your recordings.

6 Once the temperature starts to drop, continue recording **every <u>half minute</u>** for a **further 3 minutes**. Constantly stir the solution **thoroughly**.

(a) Experimental Results

Time / min	Temperature / °C
0.0	29.6
0.5	29.6
1.0	29.6
1.5	29.6
2.0	–
2.5	29.8
3.5	32.4
4.5	35.8
5.5	38.6
6.5	40.6
7.5	41.8
8.5	42.5
9.5	42.6
10.5	42.3
11.0	42.2
11.5	42.0
12.0	41.8
12.5	41.7
13.0	41.6

Correct headers and units [1]
All temperatures recorded to correct precision [1]
Full set of results with **at least 6 more readings** once the temperature starts to drop [1]
Accuracy (difference between teacher's and student's highest recorded T) [1]

Correct axes + labels + units + sensible scale + plotted points (inclusive of 5 °C) occupy at least half the graph grid in both x and y directions [1]
Correct plotting [1]
Correctly draws the two best-fit lines [1]

[4]

(b) **(i)** Plot on the grid below, a graph of the temperature on the y-axis, against time, *t*, on the x-axis. The scale for the temperature axis must allow you to plot a point with temperature 5 ^{o}C greater than the maximum temperature you recorded.

Draw the following **best-fit** straight lines on the graph.

- a line through the points before addition of **FA 4**.
- a line through the points once temperature starts to drop.

(ii) Use the best-fit straight lines to determine the theoretical temperature change at time t = 2.0 min.

45.0 – 29.6 = 15.4 °C

Correctly determines theoretical T_{max} using graph [1]

Accuracy (difference between teacher's and student's change in T) [1]

change in temperature = ……………………………………………

[5]

(c) (i) Use your answer to **(b)(ii)** to calculate the heat energy produced in the reaction. (Assume that **4.2 J** are required to increase the temperature of 1 cm^3 of solution by 1 °C.)

q = 40.00 x 4.2 x 15.4 = 2587.2 = 2590 J

heat energy produced = ... [1]

(ii) The molar enthalpy change, ΔH, for the reaction shown below is –152 kJ mol^{-1}.

$$Fe(s) + CuSO_4(aq) \rightarrow FeSO_4(aq) + Cu(s)$$

Use this value and your answer to **(c)(i)** to calculate the concentration of copper(II) sulfate, in mol dm^{-3}, in **FA 5**.

nCu^{2+} in 40.00 cm^3 of **FA 4** = 2587 / 152000 = 0.01702 mol [1]

[Cu^{2+}] in **FA 4** = 0.01702 / (40.00/1000) = 0.426 mol dm^{-3} [1]

Shows working in **all** calculations in Q1 and Q2 [1]

Shows appropriate significant figures in **all** final answers [1]

Shows appropriate units in **all** answers [1]

concentration of copper(II) sulfate = ... [5]

(d) (i) Calculate the maximum percentage error in the highest temperature that you recorded in your results table.

maximum percentage error = 0.1 / 42.6 x 100 % = 0.23 %

maximum percentage error = ... [1]

(ii) What would be the expected change in temperature obtained in **(b)(ii)** if the volume of copper(II) sulfate used was halved? Explain your answer.

Since $CuSO_4$ is the limiting reagent, using half the volume of $CuSO_4$ means only half the original amount of Cu^{2+} is reacted, hence only half the heat will be released. However, the volume of solution to be heated is also halved. Hence the change in temperature will be the same.

....

....[1]

[Total: 17]

3 Planning

The concentration of copper(II) sulfate in **FA 5** in Question 2 may be determined instead, by titration of the aqueous solution obtained after step 5, with aqueous potassium manganate(VII).

The reaction mixture obtained after step 5 in Question 2 contains $FeSO_4(aq)$ and solids iron and copper. This mixture needs to be first filtered. The filtrate is then diluted to obtain a solution suitable for titration with aqueous potassium manganate(VII) of known concentration, in the presence of acid.

The manganate(VII) ions react with iron(II) ions as shown in the following equation.

$$MnO_4^- + 5Fe^{2+} + 8H^+ \rightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$$

(a) Using information from Question 2, determine a suitable concentration of aqueous potassium manganate(VII) to use in this titration. The concentration of manganate(VII) should not exceed 0.0500 mol dm^{-3}.

You are to assume that the concentration of copper(II) sulfate in **FA 5** is 0.800 mol dm^{-3}. (Note that this is not the correct value.)

Show clearly your calculations and any assumptions.

n(Cu^{2+}) in 40.00 cm^3 of **FA 5**
= 0.800 x 40/1000 = 0.032 mol = n(Fe^{2+}) produced in mixture [1]

Assume pipette 25 cm^3 (out of 40 cm^3) of Fe^{2+} and dilute to 250 cm^3, then draw out 25 cm^3 for titration,

n(Fe^{2+}) used for titration = 0.032 x 25/40 x 1/10 = 0.0020 mol

n(MnO_4^-) needed for titration = 0.0020 / 5 = 0.00040 mol [1]

Assume titre to be 25 cm^3,
[$KMnO_4$] = 0.00040 / (25/1000) = **0.0160 mol dm^{-3}** [1]

[3]

(b) Plan an experiment to determine the concentration of copper(II) sulfate in **FA 5** using the titration method described above.

In your plan, you should include details of:

- the quantities of chemicals you would use,
- the apparatus you would use and the procedure you would follow,
- the measurements you would take.

1. Filter the mixture into a dry conical flask, using dry filter funnel and dry filter paper.
2. Pipette 25.0 cm^3 of the filtrate into a 250 cm^3 volumetric flask. Top up to the mark with deionised water. Stopper and shake to ensure a homogeneous solution.
3. Fill a burette with 0.0160 mol dm^{-3} aqueous $KMnO_4$ solution. Record the initial burette reading.
4. Pipette 25.0 cm^3 of the diluted solution into a conical flask.
5. Add 10 cm^3 of 1.0 mol dm^{-3} H_2SO_4 solution into the conical flask.
6. Titrate the solution in the conical flask with $KMnO_4$ until the end-point where the solution turns from yellow to orange/pink. Record the final burette reading.
7. Repeat steps 4-6 until consistent results within +/-0.10 cm^3 are obtained.

Filters reaction mixture into volumetric flask and ensure quantitative transfer of all Fe^{2+}
OR: Filters reaction mixture using dry filter funnel, dry filter paper and dry conical flask into beaker/conical flask and draws out suitable volume of filtrate using pipette for dilution [1]
Proposes correct dilution steps and apparatus from Question 1 [1]
Proposes correct titration steps and apparatus from Question 1 [1]
Adds excess dilute H_2SO_4 into conical flask before titration [1]
Gives correct colour change at end-point (yellow to orange/pink) [1]

....

....

....

..........[5]

[Total: 8]

4 Qualitative analysis

In this question you will perform a series of test-tube reactions and use the observations to help you deduce the identities of two solids present in a given mixture **FA 6**.

You will also **devise a plan**, consisting of test-tube reactions, and **carry out** the plan to distinguish between three solutions **FA 9**, **FA 10** and **FA 11**, so that each is identified.

At each stage of any test you are to record details of the following:

- details of colour changes and precipitates formed
- the names of gases evolved and details of the test used to identify each one

You should indicate clearly at what stage in a test a change occurs.
No additional tests for ions present should be attempted.

(a) **FA 6** is a mixture of two solids: **FA 7**, which is soluble in water and **FA 8**, which is insoluble in water. Each contains one cation and one anion listed in the Qualitative Analysis Notes on pages 15 and 16.

Carry out the following tests and record your observations in the table.

	test	*observations*
(i)	Place all of the solid, **FA 6**, into a boiling tube. Add 10 cm^3 of deionised water and shake to dissolve **FA 7**. Filter the mixture, collecting the filtrate in a test-tube. Keep the filtrate for tests **(ii)** to **(iv)**. Wash the residue, **FA 8**, with deionised water. Collect the washings in the previous boiling tube. Keep the residue for tests **(v)** to **(vii)**.	colourless filtrate green residue
(ii)	To a 1 cm depth of filtrate, **FA 7**, in a test-tube, add aqueous sodium hydroxide. Carefully warm the mixture.	no ppt no pungent/NH_3 gas evolved
(iii)	To a 1 cm depth of filtrate, **FA 7**, in a test-tube, add aqueous ammonia.	no ppt
(iv)	To a 1 cm depth of filtrate, **FA 7**, in a test-tube, add 5 drops of aqueous silver nitrate, followed by aqueous ammonia.	white ppt white ppt soluble in NH_3(aq)

	test	*observations*
(v)	Transfer half a spatula of the residue, **FA 8**, into a clean boiling tube. Using a measuring cylinder, measure out 10 cm^3 of dilute nitric acid. Transfer the acid to the boiling tube in portions. Mix the contents of the boiling tube thoroughly. Filter if necessary. This solution is **FA 12**.	green residue dissolves to give blue solution effervescence, gas gives white ppt with limewater
(vi)	To a 1 cm depth of **FA 12** in a test-tube, add 1 cm depth aqueous edta.	blue solution turns dark blue
(vii)	To a 1 cm depth of **FA 12** in a test-tube, add 1 cm depth aqueous sodium hydroxide, followed by aqueous ammonia. **Do not discard the remaining FA 12. Keep the solution for (b).**	blue ppt blue ppt dissolves to give dark blue solution

[4]

10 observations [4]

(viii) From the observations, identify the ions in **FA 7** and **FA 8**.

FA 7 contains the cation Ba^{2+}/Ca^{2+} and the anion Cl^{-}

FA 8 contains the cation Cu^{2+} and the anion CO_3^{2-}

[2]

(ix) Explain in terms of the chemistry involved, your observations in **(a)(iv)**.

Cl^{-} reacts with $AgNO_3$ to form white ppt of **$AgCl$**. With $NH_3(aq)$, complex **$[Ag(NH_3)_2]^+$** is formed. [1]
This reduces $[Ag^+]$ and shifts the equilibrium: $AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$ to the right / ionic product becomes lower than K_{sp}, so $AgCl$ solid dissolves. [1]

....

.... [2]

(x) State the type of reaction that occurred in **(a)(vi)**.

Ligand exchange
.... [1]

(b) Planning

FA 9, **FA 10** and **FA 11** each contains one of the following but not in that order:

hydrogen peroxide iron(II) sulfate potassium iodide

You are required to plan and **perform** a series of test-tube reactions using only **FA 9**, **FA 10**, **FA 11** and, **FA 12** from **(a)(v)**, to identify the three solutions, **FA 9** to **FA 11**.

You should commence your plan by adding **FA 12** to each of **FA 9**, **FA 10** and **FA 11**.

Each solution should be identified by at least one positive test. It is **not** sufficient to identify a solution simply by eliminating all the others.

You should aim to use the **minimum number** of reactions.

You may find it useful to consider the standard electrode potentials given below.

$$\begin{array}{lcll} O_2 + 2H^+ + 2e & \rightleftharpoons & H_2O_2 & +0.68\ V \\ H_2O_2 + 2H^+ + 2e & \rightleftharpoons & 2H_2O & +1.77\ V \\ Fe^{3+} + e & \rightleftharpoons & Fe^{2+} & +0.77\ V \\ Fe^{2+} + 2e & \rightleftharpoons & Fe & -0.44\ V \\ I_2 + 2e & \rightleftharpoons & 2I^- & +0.54\ V \end{array}$$

You may use the space below to plan your tests.

In the table in the next page, record
- details of the tests, including quantity of solutions used,
- observations of the tests,
- identities of the products that gave rise to the observations,
- identity of each solution.

....

....

....

....

....

....

....

....

....

....

....

....

	observations, identities of products and identity of each solution		
tests	**FA 9**	**FA 10**	**FA 11**
1. To 1 cm depth FA solution, add 1 cm depth **FA 12**	no yellow/ orange/ brown solution formed	no yellow/ orange/ brown solution formed	cream ppt in brown solution cream ppt is CuI brown solution is I_2 ∴ **FA 11** is KI
2. To 1 cm depth FA solution, add 1 cm depth **FA 11**	no yellow/ orange/ brown solution formed	yellow solution formed, effervescence of gas which relights a glowing splint yellow solution is I_2 gas is O_2 ∴ **FA 10** is H_2O_2	
3. To 1 cm depth FA solution, add 1 cm depth **FA 10**	yellow solution formed, effervescence of gas which relights a glowing splint yellow solution is Fe^{3+} gas is O_2 ∴ **FA 9** is $FeSO_4$		

Correct sequence and quantities [1]
All negative tests observations correct [1]
5 positive observations, 5 products and 3 identities [6]

Conclusion

Solution **FA 9** contains ....

Solution **FA 10** contains ....

Solution **FA 11** contains ....

[8]

[Total: 17]

INNOVA JUNIOR COLLEGE
JC2 PRELIMINARY EXAMINATION
in preparation for General Certificate of Education Advanced Level
Higher 2

CANDIDATE NAME			
CLASS		INDEX NUMBER	

CHEMISTRY 9729/01

Paper 1 Multiple Choice **15 September 2017**

1 hour

Additional Materials: *Data Booklet*
Multiple Choice Answer Sheet

READ THESE INSTRUCTIONS FIRST

Write your name and class on all the work you hand in.
Write in soft pencil.
Do not use staples, paper clips, highlighters, glue or correction fluid.

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

Read the instructions on the Answer Sheet very carefully.

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

This document consists of **13** 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 A given mass of ideal gas occupies a volume V and exerts a pressure p at 30 °C.

At which temperature will the same mass of the ideal gas occupy a volume $\frac{V}{3}$ and exert a pressure $2p$?

A	20 °C	**C**	202 °C
B	20 K	**D**	202 K

2 Which equation corresponds to the third ionisation energy of titanium (Ti)?

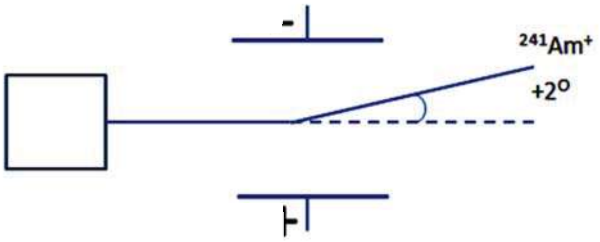
A $Ti(g) \rightarrow Ti^{3+}(g) + 3e^{-}$

B $Ti^{2+}(s) \rightarrow Ti^{3+}(g) + e^{-}$

C $Ti^{2+}(g) \rightarrow Ti^{3+}(g) + e^{-}$

D $Ti^{3+}(g) + e^{-} \rightarrow Ti^{2+}(g)$

3 A sample of the element Americium (Am) was vaporised, ionised and passed through an electric field. It was observed that a beam of $^{241}Am^{+}$ particles gave an angle of deflection of +2°.



Assuming an identical set of experimental conditions, by what angle would a beam of $^{32}S^{-}$ particles be deflected?

A +15.1°

B –15.1°

C +30.1°

D –30.1°

4 Which of the following statements describes a phenomenon which **cannot** be explained by hydrogen bonding?

A Ice floats on water.

B The boiling point of carboxylic acid increases with increasing relative molecular mass.

C 2-nitrophenol is more volatile than 4-nitrophenol.

D Ethanoic acid molecules form dimers when dissolved in benzene.

5 A tertiary amine, R_3N, reacts with boron trifluoride, BF_3 to give an addition product. Which of the following statements is **not** true?

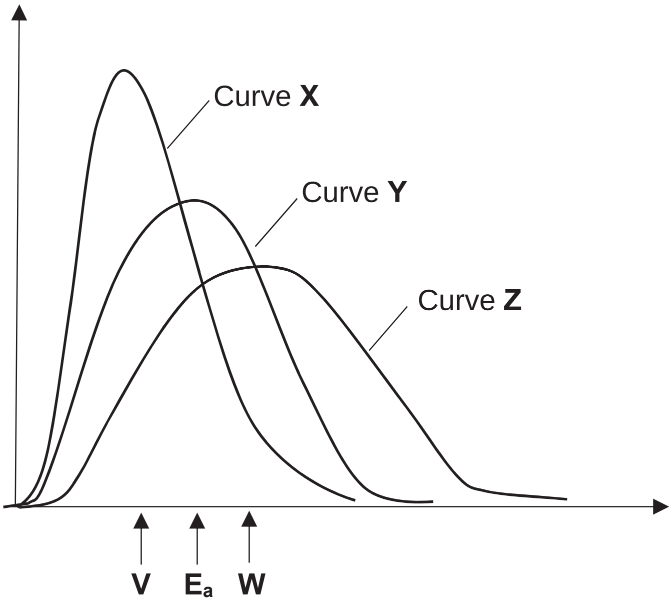
A R_3N acts as a Lewis base.

B The product is a polar molecule.

C There are six σ bonds in the product.

D The product contains a dative covalent bond.

6 The curve **Y** and the value E_a represent the distribution of energies of the molecules and the activation energy for an uncatalysed gaseous reaction.



What is a possible outcome if the reaction is catalysed?

A The distribution of energies will be given by curve **X** and the activation energy by value **V**

B The distribution of energies will be given by curve **Y** and the activation energy by value **V**.

C The distribution of energies will be given by curve **Y** and the activation energy by value **W**.

D The distribution of energies will be given by curve **Z** and the activation energy by value **W**.

7 If the rate of decay of a radioactive isotope decrease from 300 counts per minute to 37.5 counts per minute after 1 day, what is its half-life?

A	4 hours	**C**	8 hours
B	6 hours	**D**	12 hours

8 Which of the following statements does **not** describe a reaction at equilibrium?

A Forward and backward reactions occur at equal rate.

B The system must be closed.

C K_c increases as the reaction progresses.

D Concentrations of reactants and products are constant.

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

The enthalpy change of formation of carbon monoxide and carbon dioxide are given below.

$$\Delta H_f \text{ CO} = -110 \text{ kJmol}^{-1}$$
$$\Delta H_f \text{ CO}_2 = -393 \text{ kJmol}^{-1}$$

Which of these statements are correct?

1 CO_2(g) has lower energy content than CO(g).

2 The enthalpy change of combustion of carbon is –393 kJmol^{-1}.

3 CO_2(g) is formed exothermically from CO(g).

4 A larger amount of energy is required to atomise CO_2(g) than CO(g).

A 1, 2, 3 and 4

B 1, 2 and 3 only

C 1, 2 and 4 only

D 2 and 3 only

10 A sparingly soluble calcium salt ionises in aqueous solution according to the equation given:

$$Ca_3X_2(s) \rightleftharpoons 3Ca^{2+}(aq) + 2X^{3-}(aq)$$

If the solubility product K_{sp} of Ca_3X_2 is S, what is the value of the concentration of $Ca^{2+}(aq)$ at equilibrium?

A $S^{\frac{1}{2}}$

B $\left[\dfrac{S}{108}\right]^{\frac{1}{5}}$

C $\left[\dfrac{3S}{5}\right]^{\frac{1}{2}}$

D $\left[\dfrac{9S}{4}\right]^{\frac{1}{5}}$

11 The K_{sp} of AgC*l* and AgI are 1.80 x 10^{-10} mol^2 dm^{-6} and 8.3 x 10^{-17} mol^2 dm^{-6} respectively. Which of the following statements is correct when equal volumes of 1 x 10^{-4} mol dm^{-3} aqueous $AgNO_3$ was added to a mixture containing 3.0 x 10^{-6} mol dm^{-3} $BaCl_2$ and 3.0 x 10^{-6} mol dm^{-3} BaI_2?

A AgC*l* is precipitated only.

B AgI is precipitated only.

C AgC*l* is precipitated followed by AgI.

D AgI is precipitated followed by AgC*l*.

12 The dissociation constant, K_w, for the ionisation of water, $H_2O \rightleftharpoons H^+ + OH^-$, at different temperatures is given below.

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 The equilibrium lies furthest to the right at 0 °C.

C The forward reaction is exothermic.

D The pH of pure water decreases with temperature.

13 Calculate the standard Gibbs free energy change, $\Delta G^{\ominus}$ for the following reaction:

$$2Al\,(s) + 3Cu^{2+}(aq) \longrightarrow 2Al^{3+}(aq) + 3Cu(s)$$

A –386 kJ mol^{-1}

B –579 kJ mol^{-1}

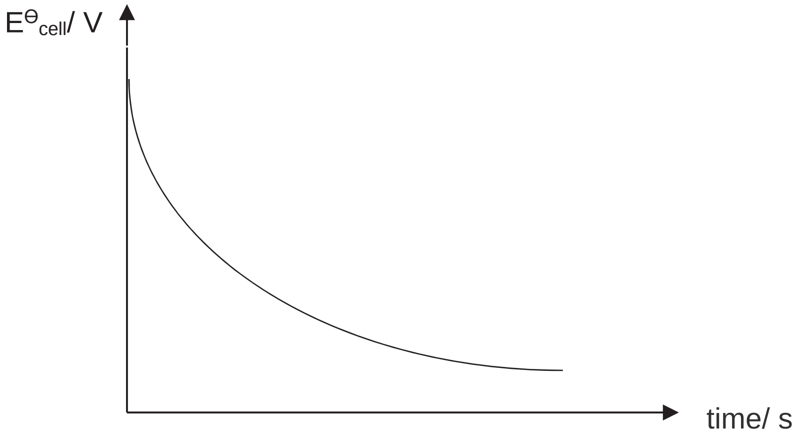
C –1045 kJ mol^{-1}

D –1158 kJ mol^{-1}

14 An experiment is carried out with the following cell.

$$Fe\,(s)\,|\,Fe^{2+}\,(aq)\,||\,Ni^{2+}\,(aq)\,|\,Ni\,(s)$$

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 these results?

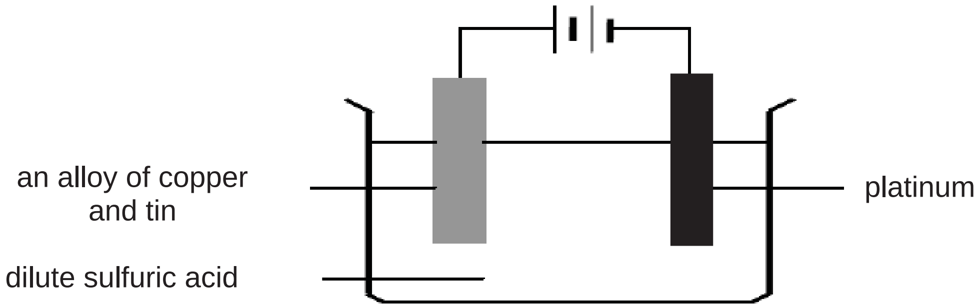
A Add nickel (II) chloride to the nickel half-cell.

B Add aqueous cyanide ions to the iron half-cell.

C Add water to the nickel half-cell.

D Increases the surface area of iron immersed in the solution.

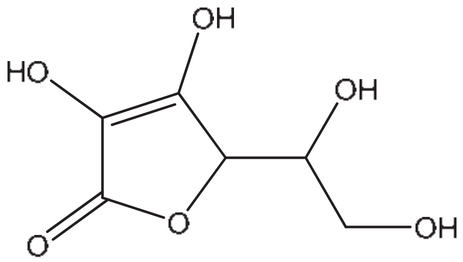
15 The circuit shown in the diagram was set up.



Which reactions will occur at the electrodes?

	anode reaction	*cathode reaction*
A	Oxygen gas is evolved.	Hydrogen gas is evolved.
B	Tin dissolves preferentially.	Hydrogen gas is evolved.
C	Copper dissolves preferentially.	Copper is deposited.
D	Copper and tin both dissolve.	Sulfur dioxide gas is evolved.

16 The diagram shows the structure of vitamin C.



vitamin C

How many stereoisomers are there in one molecule of vitamin C?

A 2 **B** 4 **C** 8 **D** 16

17 Propyne, C_3H_4, has the following structure.

$$H-C\equiv C-CH_3$$

Which row correctly describes the bonding and hybridisation in a molecule of propyne?

	number of π bonds	number of sp C atoms	number of sp^2 C atoms
A	1	1	1
B	2	2	0
C	2	2	1
D	3	3	0

18 During the nitration of benzene, a nitro group substitutes at a carbon atom. Which one of the following gives the arrangement of the bonds at this carbon atom during the reaction?

	at the start of the reaction	*in the intermediate complex*	*at the end of the reaction*
A	planar	planar	planar
B	planar	tetrahedral	tetrahedral
C	planar	tetrahedral	planar
D	tetrahedral	planar	tetrahedral

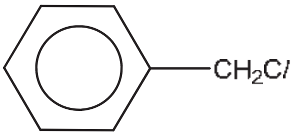
19 When a halogen compound **S** was boiled under reflux for some time with silver nitrate in a mixture of ethanol and water, little or no precipitate was seen.

Which of the following formulae could represent **S**?

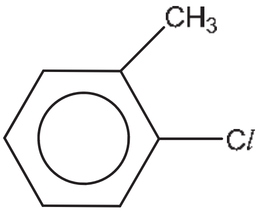
A $CH_3CH_2CHClCH_2CH_3$

B $CH_3CH_2CH_2COCl$

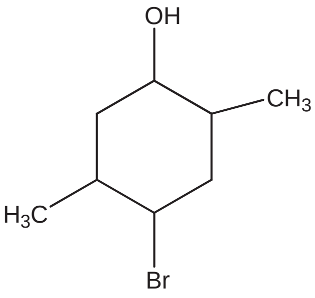
C



D



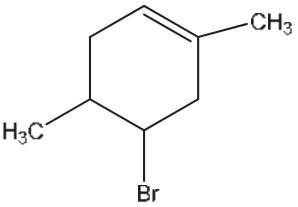
20 Compound **P** was heated with ethanolic potassium hydroxide.



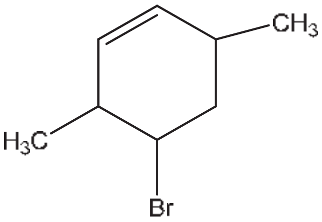
compound **P**

Which of the following would be the major product?

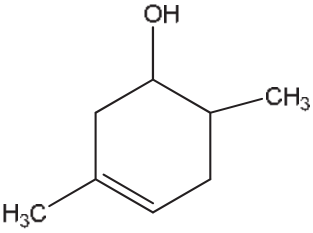
A



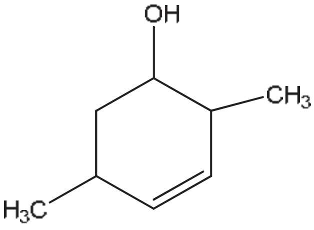
B



C



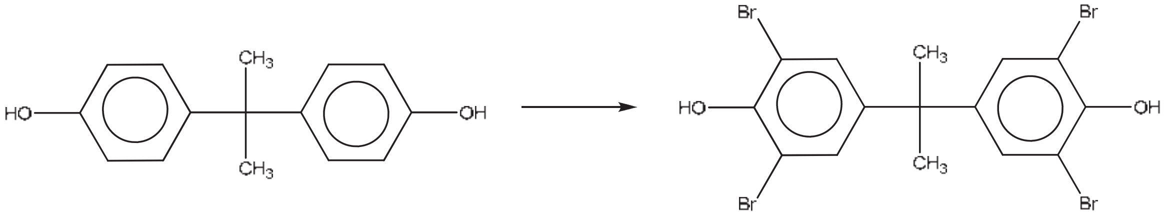
D



21 How many isomers (including both structural isomers and stereoisomers) with molecular formula $C_4H_{10}O$ liberate hydrogen gas on reaction with sodium?

A 2 **B** 3 **C** 4 **D** 5

22 Bisphenol A was used to make products such as plastic polycarbonate baby bottles and food containers. It is now regarded as toxic and has been withdrawn from use.



bisphenol A compound **Q**

Which reagent will convert bisphenol A into compound **Q**?

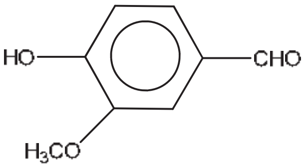
A A*l*Br$_3$(s)

B Br$_2$(aq)

C HBr(g)

D NaBr(aq)

23 Vanillin is the active ingredient of vanilla.



vanillin

Which of the following will be observed with vanillin?

1 Warm acidified potassium dichromate (VI) turns green.
2 2,4-dinitrophenylhydrazine reagent gives an orange precipitate.
3 A yellow precipitate is formed on warming with aqueous alkaline iodine.

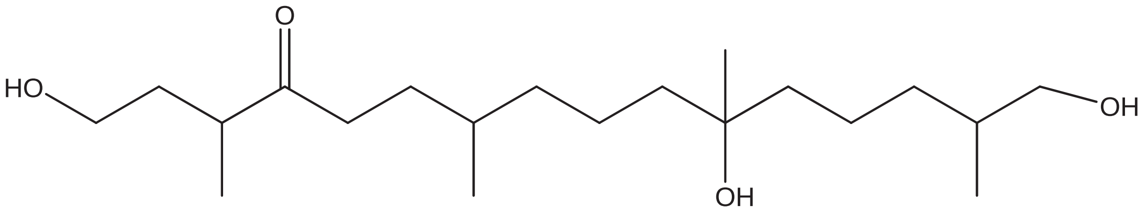
A 1 only

B 2 only

C 1 and 2 only

D 2 and 3 only

24 The mould *Phytophthora* damages many plants, destroying agricultural crops such as potatoes. A hormone-like compound called alpha1 regulates the reproduction of all species of *Phytophthora*. The structure of alpha1 is now known, giving scientist a key to the possible future eradication of the mould.



alpha1

Which of the following reagents will react with alpha1?

1 Br_2
2 $SOCl_2$
3 H_2/Pt

A 1 and 2 only

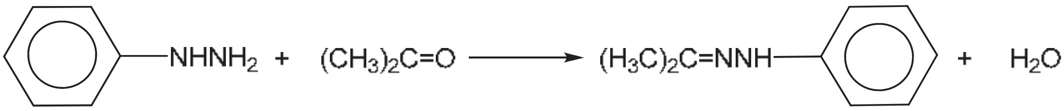
B 2 and 3 only

C 1 and 3 only

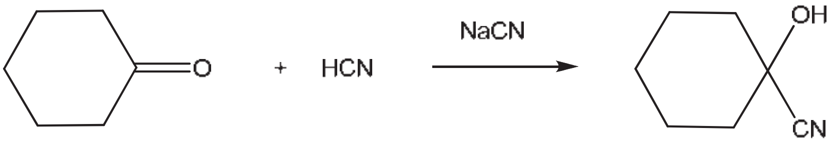
D 1, 2 and 3 only

25 Which transformations involve a nucleophile?

1



2



3 $CH_3CH_2COCl + NH_3 \longrightarrow CH_3CH_2CONH_2 + HCl$

A 1 only

B 3 only

C 1 and 2 only

D 1, 2 and 3 only

26 Which of the following properties are identical for the two enantiomers of 2-hydroxypropanoic acid, $CH_3CH(OH)COOH$?

1 $\Delta H_f^{\ominus}$

2 pK_a

3 melting point

A 2 only

B 3 only

C 1 and 2 only

D 1, 2 and 3 only

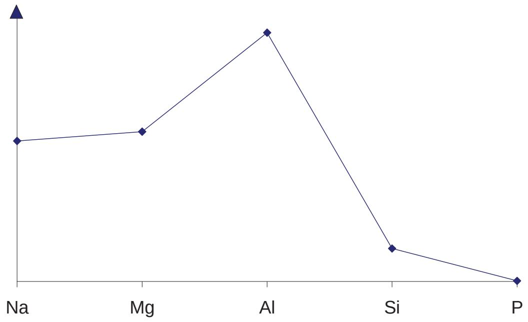
27 When organic compounds **E**, **F**, **G** and **H** are added separately to water, solutions of increasing pH values are obtained. The possible identities of compounds **E** to **H** (not necessarily in that order) are given below.

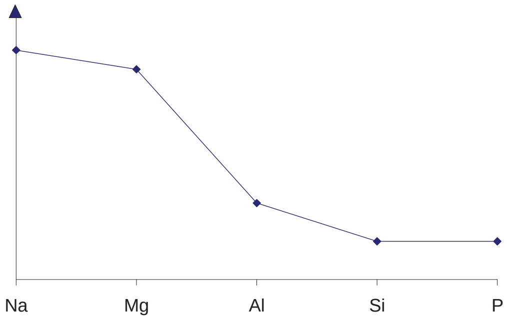
$CH_3CH_2CO_2H$ CH_3CH_2COCl $(CH_3)_2CHNH_2$ $CH_3CH_2NH_2$

Which is the correct set of identities of compounds **E**, **F**, **G** and **H**?

	E	**F**	**G**	**H**
A	$CH_3CH_2CO_2H$	CH_3CH_2COCl	$CH_3CH_2NH_2$	$(CH_3)_2CHNH_2$
B	$CH_3CH_2CO_2H$	CH_3CH_2COCl	$(CH_3)_2CHNH_2$	$CH_3CH_2NH_2$
C	CH_3CH_2COCl	$CH_3CH_2CO_2H$	$(CH_3)_2CHNH_2$	$CH_3CH_2NH_2$
D	CH_3CH_2COCl	$CH_3CH_2CO_2H$	$CH_3CH_2NH_2$	$(CH_3)_2CHNH_2$

28 The graphs below show the variation in two properties of the elements Na to P and their compounds.


Graph I


Graph II

Which properties are illustrated in Graphs I and II?

	Graph I	Graph II
A	electrical conductivity of the element	pH of the chloride when added to water
B	electrical conductivity of the element	pH of the oxide when added to water
C	melting point of the element	pH of the chloride when added to water
D	melting point of the element	pH of the oxide when added to water

29 Which of the following elements is expected to show the greatest tendency to form some covalent compounds?

A Barium

B Calcium

C Magnesium

D Potassium

30 Why is hydrogen iodide a stronger acid than hydrogen chloride?

A A molecule of hydrogen chloride is more polar than a molecule of hydrogen iodide.

B The enthalpy change of formation of hydrogen iodide is greater than that of hydrogen chloride.

C The covalent bond in the hydrogen iodide molecule is weaker than that in the hydrogen chloride molecule.

D The dissociation of hydrogen chloride molecules is suppressed by the stronger permanent dipole–permanent dipole interactions.

Blank Page

INNOVA JUNIOR COLLEGE
JC2 PRELIMINARY EXAMINATION
in preparation for General Certificate of Education Advanced Level
Higher 2

CANDIDATE NAME ☐

CLASS ☐ INDEX NUMBER ☐

CHEMISTRY

9729/02

Paper 2 Structured Questions

24 August 2017

Candidates answer on the question paper.

2 hours

Additional Materials: *Data Booklet*

READ THESE INSTRUCTIONS FIRST

Write your index number, name and civics group on all the work you hand in.
Write in dark blue or black pen.
You may use pencil for any diagrams, graphs or rough working.
Do not use staples, paper clips, highlighters, glue or correction fluid.

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

You are advised to show all working in calculations.
You are reminded of the need for good English and clear presentation in your answers.
You are reminded of the need for good handwriting.
Your final answers should be in 3 significant figures.

You may use a calculator.

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

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

For Examiner's Use	
1	19
2	12
3	10
4	10
5	24
Significant Figures and Units	
Handwriting and Presentation	
Total	75

This document consists of **18** printed pages.

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

1 Halogens are highly reactive and form compounds with many other elements, including metals and non-metals.

(a) Fluorine reacts with bromine to form liquid bromine trifluoride, BrF_3.

Two molecules of BrF_3 react to form ions as shown by the following equation.

$$2BrF_3 \longrightarrow BrF_2^+ + BrF_4^-$$

(i) Draw the structures and suggest the shape of each of these species.

BrF_3

Shape: ……………………………..

BrF_4^-

Shape: ……………………………..

[3]

(ii) BrF_4^- ions are also formed when potassium fluoride, KF dissolves in liquid BrF_3 to form $KBrF_4$. Explain, in terms of structure and bonding, why $KBrF_4$, has a high melting point.

…………………………………………………………………………………………

…………………………………………………………………………………………

…………………………………………………………………………………………

…………………………………………………………………………………………

…………………………………………………………………………………………

[2]

(b) Magnesium bromide, $MgBr_2$ is a chemical compound of magnesium and bromine and is often used in the pharmaceutical industries.

In this part of the question, you will construct an energy cycle for magnesium bromide to determine the enthalpy change of hydration of magnesium ions.

(i) Magnesium bromide has a lattice energy of –2440 kJ mol^{-1}.
Define in words the *lattice energy of magnesium bromide*.

……………………………………………………………………………………………

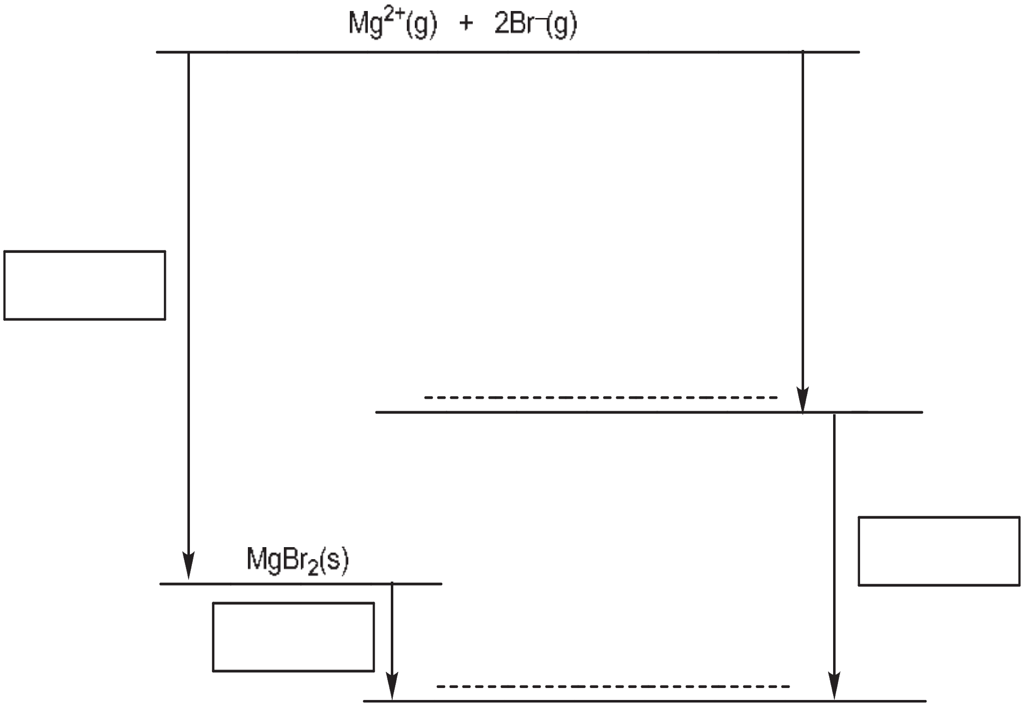
……………………………………………………………………………………………

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

(ii) The table below shows the enthalpy changes that are needed to determine the enthalpy change of hydration of magnesium ions.

enthalpy change	**energy /kJ mol^{-1}**
lattice energy of magnesium bromide	–2440
enthalpy change of solution of magnesium bromide	–89
enthalpy change of hydration of bromide ions	–304

On the two dotted lines, add the species present and label the numerical values of the three arrows in the boxes provided.



[2]

(iii) Calculate the enthalpy change of hydration of magnesium ions.

[1]

(iv) Given that the enthalpy change of formation of Mg^{2+}(aq) is +413 kJ mol^{-1} , use your answer in **(b)(iii)** as well as relevant values from the *Data Booklet* to calculate the enthalpy change of atomisation of magnesium.

[1]

(v) The enthalpy change of hydration of magnesium ions is more exothermic than the enthalpy change of hydration of calcium ions. Explain why.

……………………………………………………………………………………….

……………………………………………………………………………………….

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

(c) Nickel is a typical transition element in the d-block of the Periodic Table. Many nickel ions are able to interact with ligands to form complex ions, such as $[Ni(H_2O)_6]^{2+}$.

A student dissolves nickel(II) sulfate in water. A green solution forms containing the complex ion $[Ni(H_2O)_6]^{2+}$. The student then reacts separate portions of the green solution of nickel(II) sulfate as outlined below.

- Concentrated hydrochloric acid is added to the green solution of nickel(II) sulfate until there is no further change. The solution turns a lime-green colour and contains the four-coordinate complex ion **A**.
- Aqueous sodium hydroxide is added to the green solution of nickel(II) sulfate. A pale-green precipitate **B** forms.
- Concentrated aqueous ammonia is added to the green solution of nickel(II) sulfate until there is no further change. The solution turns a violet colour and contains the complex ion **C**. **C** has a molar mass of 160.7 g mol^{-1}.

(i) Explain why aqueous nickel(II) sulfate is green.

…………………………………………………………………………………………

…………………………………………………………………………………………

…………………………………………………………………………………………

…………………………………………………………………………………………

…………………………………………………………………………………………

…………………………………………………………………………………………

…………………………………………………………………………………………

[2]

(ii) Draw a three dimensional diagram for the $[Ni(H_2O)_6]^{2+}$ ion.

[1]

(iii) Suggest the formulae of **A**, **B** and **C**.

A: ……………………………………………………………

B: ……………………………………………………………

C: ……………………………………………………………

[3]

(iv) What type of reaction has taken place in the formation of **C** from $[Ni(H_2O)_6]^{2+}$? Write an equation for this reaction.

…………………………………………………………………………………………

…………………………………………………………………………………………

[2]

[Total: 19]

2 **(a)** In a school lab, magnesium strips can be stored in a normal container. However, barium metal has to be submerged in oil when it is stored. With reference to relevant data from the *Data Booklet*, explain the above observation.

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

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

(b) When solid barium carbonate is heated, no carbon dioxide is detected as it is thermally stable.
However, magnesium carbonate decomposes on heating as shown by the equation below.

$$MgCO_3(s) \longrightarrow MgO(s) + CO_2(g)$$
$$\Delta H^\ominus = +117\ \text{kJ mol}^{-1}; \qquad \Delta S^\ominus = +175\ \text{J mol}^{-1}\ \text{K}^{-1}$$

(i) Explain why barium carbonate is thermally stable while magnesium carbonate is not.

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

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

(ii) Account for the sign of $\Delta S^\ominus$ in this reaction.

……………………………………………………………………………………………

……………………………………………………………………………………………

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

(iii) Calculate the standard Gibbs free energy change, $\Delta G^\ominus$, for the decomposition of magnesium carbonate.

[1]

(iv) Assuming that $\Delta H^{\ominus}$ and $\Delta S^{\ominus}$ for the reaction are independent of temperature, calculate the temperature at which the decomposition reaction becomes feasible.

[1]

(c) The labels of group 2 metal carbonates fell off the bottles. In an attempt to identify the compound in one of the bottles, the following experiment was carried out.

1.68 g of an insoluble metal carbonate, $\mathbf{D}CO_3$ was reacted with 100 cm^3 of hydrochloric acid of concentration 0.500 mol dm^{-3}. The resulting solution was then made up to 250 cm^3 with distilled water. 25.0 cm^3 of this solution required 25 cm^3 of 0.04 mol dm^{-3} sodium hydroxide for titration.

(i) Write a balanced equation for the reaction between the metal carbonate and hydrochloric acid.

……………………………………………………………………………………………

[1]

(ii) Calculate the relative atomic mass of **D** and hence using the Periodic Table, identify **D**.

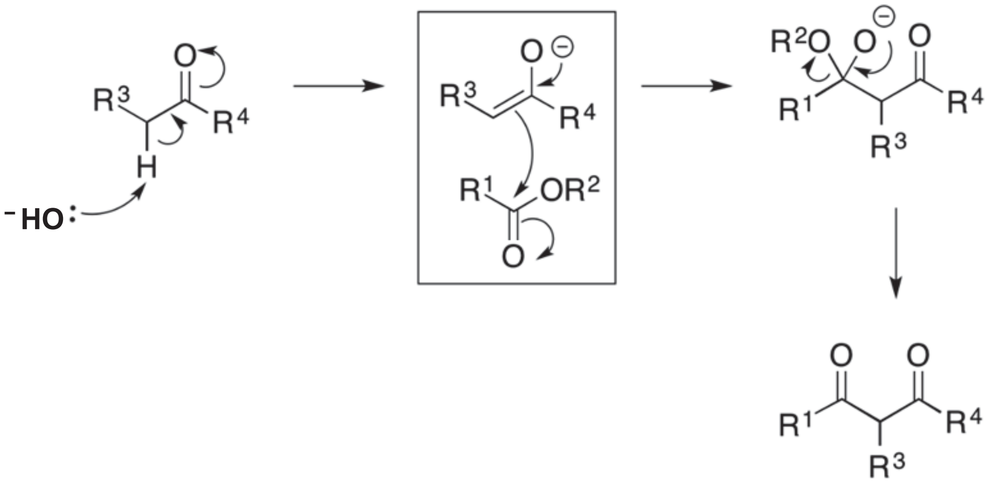
[4]

[Total: 12]

3 Claisen condensation is a carbon-carbon bond forming reaction between 2 esters or an ester and a carbonyl compound in the presence of strong base to form β-ketoesters or diketones respectively.

The following is the general equation for the reaction between an ester and a ketone.

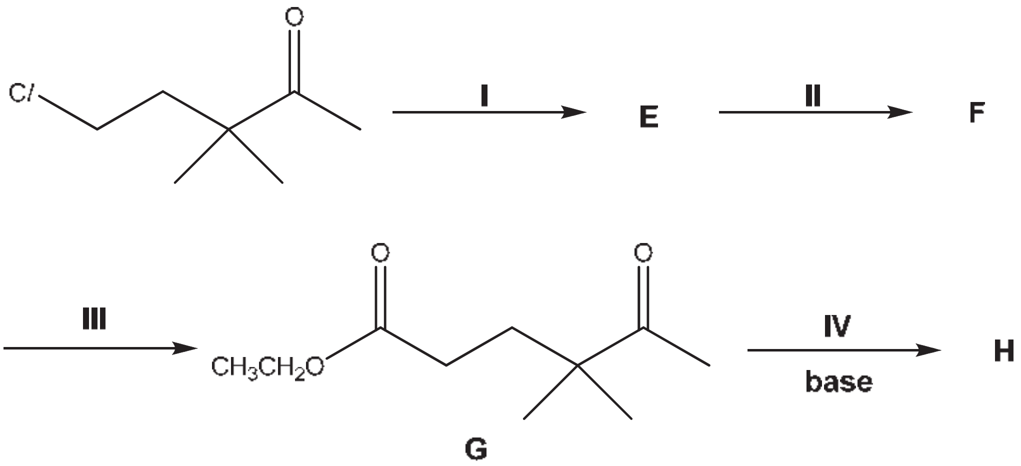
The mechanism of the Claisen condensation reaction is given below.



(a) Name the type of reaction for the step shown in the box above.

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

The Claisen condensation reaction can be used in step **IV** of the following synthesis.



(b) **(i)** Suggest reagents and conditions for steps **I** to **III**.

Step **I**: …………………………………………………………………………………..

Step **II**: ……………………………………………………………………………….

Step **III**: ………………………………………………………………………………

[3]

(ii) State the type of reactions for step **I** to **III**

Step **I**: …………………………………………………………………………………..

Step **II**: ……………………………………………………………………………….

Step **III**: ………………………………………………………………………………

[3]

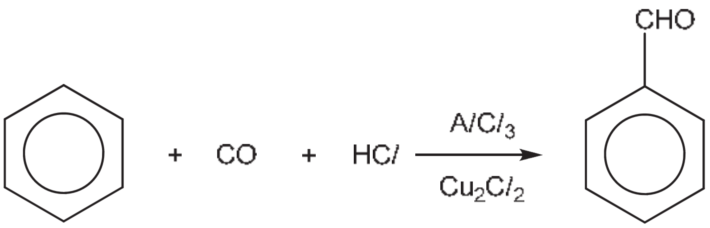
(iii) Propose the structures of compounds **E**, **F** and **H**.

E	**F**	**H**

[3]

[Total: 10]

4 **(a)** The Gattermann-Koch reaction, named after the German chemists Ludwig Gattermann and Julius Arnold Koch in organic chemistry, refers to a Friedel-Crafts acylation reaction in which carbon monoxide and hydrochloric acid are used in-situ with Friedel-Crafts catalyst, namely $AlCl_3$. The reaction involves an acylium ion as an electrophile and tetrachloroaluminate ion, $AlCl_4^-$. An example is provided below.

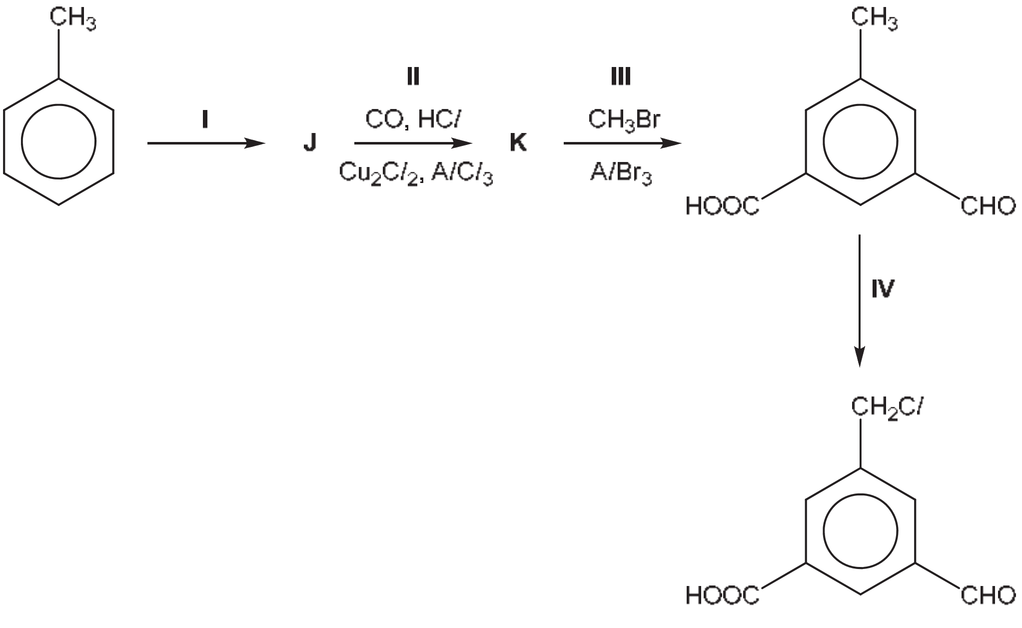


(i) Give the formula of the acylium ion in this reaction.

....
[1]

(ii) The synthesis of compound **L** involves the Gattermann-Koch reaction in Step **II**.

Complete the reaction scheme below by providing the appropriate reagents and conditions for Step **I** and **IV** and give the structural formula for **J** and **K**.



L

Step **I**: ……………………………………………………………………………………

Step **IV**: …………………………………………………………………………………

J

K

[4]

(b) Three non-cyclic organic compounds, **M**, **N** and **P** each have the same empirical formula CH_2O.
The number of carbon atoms in their molecules are shown in the table below.

compound	number of C atoms
M	2
N	3
P	3

All the carbon atoms are bonded directly to one another in **M** and in **N** but not in **P**.

M and **N** each give a brisk effervescence with $Na_2CO_3(aq)$ but not **P**.

P does not give a silver mirror when treated with Tollens' reagent.

(i) Draw the structural formula of **M**.

[1]

(ii) When **N** is heated under reflux with acidified $K_2Cr_2O_7$, the product, **Q**, gives a orange precipitate with 2,4-dinitrophenylhydrazine.

Draw the structural formulae of **N** and **Q**.

N

Q

[2]

(iii) When **N** is warmed with concentrated sulfuric acid, compound **R** is formed. **R** has the molecular formula $C_6H_8O_4$.

Draw the structural formula of **R.**

[1]

(iv) **P** is optically active. Draw the displayed formula of **P**.

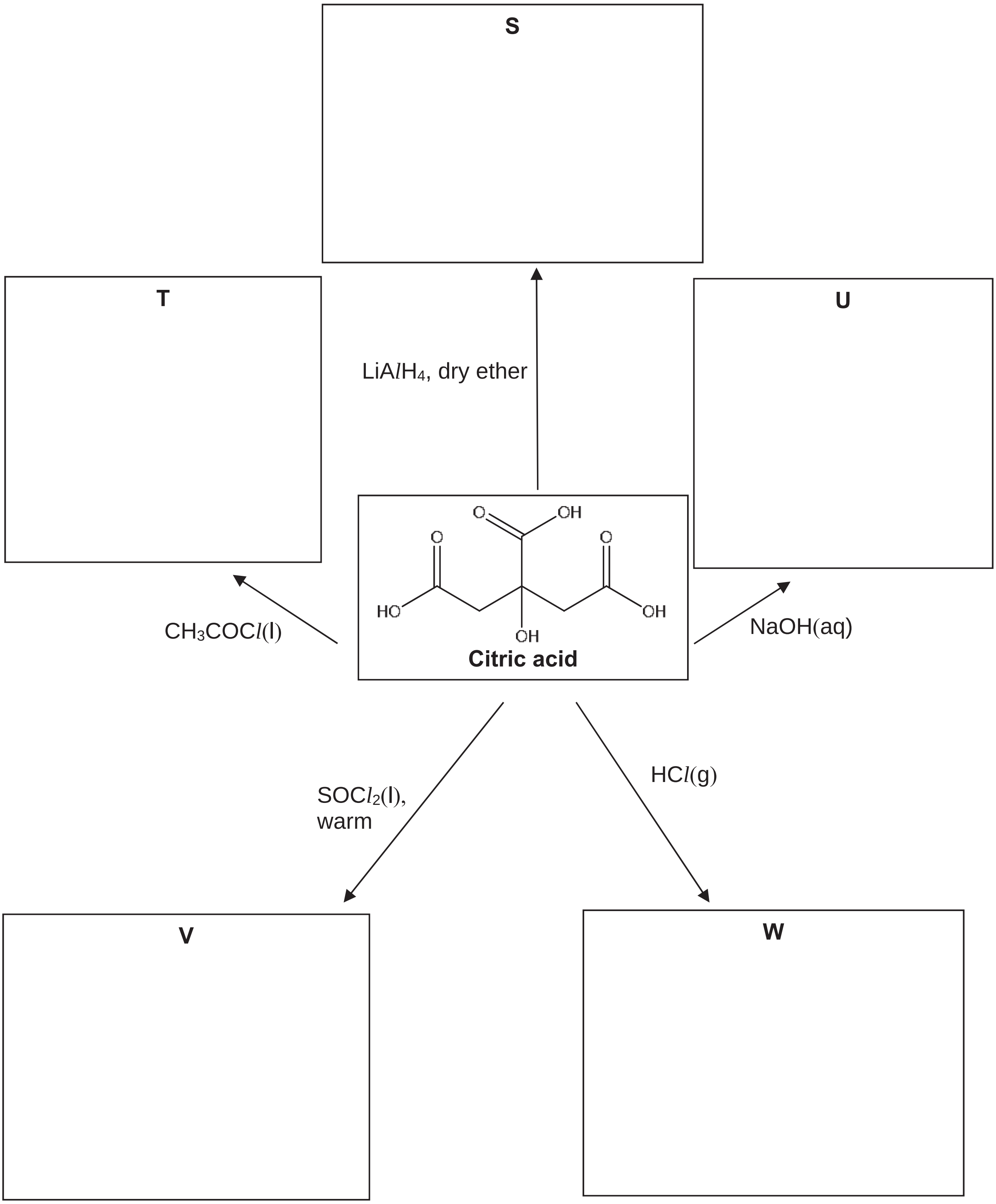
[1]

[Total: 10]

5 Citric acid, $C_6H_8O_7$ is produced commercially by the fermentation of sugars. Citric acid is used in the production of beverages and foods; in detergents; and in cosmetics and pharmaceuticals.

Fruits such as oranges, lemons and strawberries also contain citric acid.

(a) Citric acid can undergo the following reactions:



Suggest structures for the organic compounds **S, T, U, V** and **W**.

[5]

(b) As citric acid is a user-friendly, inexpensive, water-soluble crystalline solid, it is often used for finding the concentration of alkalis e.g. sodium hydroxide and potassium hydroxide.

Citric acid is a tribasic acid with the following pK_a values:

$pK_1 = 3.14$, $pK_2 = 4.75$, $pK_3 = 6.40$

(i) Explain why citric acid is soluble in water.

…………………………………………………………………………………….

…………………………………………………………………………………….
[1]

(ii) The pK_a value of ethanoic acid, CH_3COOH is 4.76.

Suggest why the pK_1 value of citric acid is lower than the pK_a value of ethanoic acid.

…………………………………………………………………………………….

…………………………………………………………………………………….

…………………………………………………………………………………….

…………………………………………………………………………………….

…………………………………………………………………………………….

…………………………………………………………………………………….
[2]

(iii) Calculate the pH of a solution that is a mixture of equal volumes of 0.100 mol dm^{-3} of citric acid and 0.060 mol dm^{-3} of sodium hydroxide.

[2]

(c) The neutralisation equivalent (N.E.) of a carboxylic acid is defined as the mass in g of the acid required to neutralise one mole of a strong alkali such as sodium hydroxide. Each carboxylic acid has a unique N.E. value.

N.E. values can be used to determine the identity of a carboxylic acid.

A student carried out a titration experiment between a sample of citric acid and sodium hydroxide solution. 3.68 g of the citric acid was dissolved in 500 cm^3 of water in a volumetric flask. It was found that 5.00 cm^3 of the citric acid solution needed 5.29 g of 4.43 g dm^{-3} sodium hydroxide solution for complete reaction.

(i) Calculate the mass, in g, of the citric acid used in the 5 cm^3 sample.

[1]

(ii) Calculate the amount, in moles, of sodium hydroxide that reacted with the 5 cm^3 of citric acid.

The density of the sodium hydroxide solution is 1.01 g cm^{-3}.

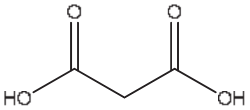
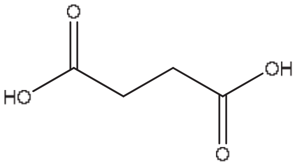
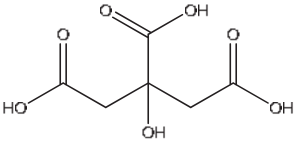
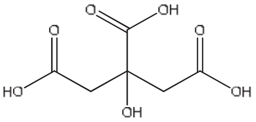
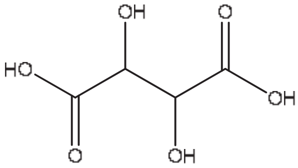
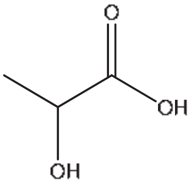
[2]

(iii) Calculate the neutralisation equivalent (N.E.) for this sample of citric acid.

[1]

(d) Table 5.1 gives the neutralisation equivalent (N.E.) values for some organic acids.

Table 5.1

Acid name	**Structure**	**Molar mass/ g mol^{-1}**	**N.E. / g**
Malonic acid		104.0	52.0
Succinic acid		118.0	59.0
Anhydrous citric acid		192.0	64.0
Citric acid monohydrate	 . H_2O	210.0	70.0
Tartaric acid		150.0	*m*
Lactic acid		90.0	90.0

(i) Suggest whether the student's sample of citric acid is a hydrated sample or anhydrous sample. Support your answer with appropriate evidence.

……………………………………………………………………………………..

……………………………………………………………………………………..

……………………………………………………………………………………..

[2]

(ii) Determine the value of m in Table 5.1.

[1]

(e) Another student determines the N.E. of an unknown aliphatic acid to be 82.0 g.

The unknown aliphatic acid has the following formula, $C_xH_y(COOH)_n$ where x and y are integers and n = 1, 2 or 3.

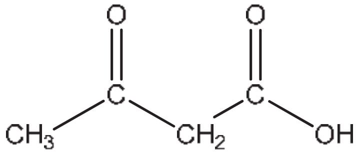
Determine the molecular formula of the unknown aliphatic acid.

[3]

(f) The loss of carbon dioxide from a carboxylic acid is called decarboxylation.

$$RCOOH \longrightarrow RH + CO_2$$

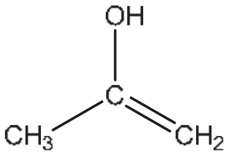
Certain types of carboxylic acids are readily decarboxylated. Beta-keto acids such as acetoacetic acid readily decarboxylate at room temperature in an acidic solution.



acetoacetic acid

The decarboxylation of acetoacetic acid occurs via a two-step mechanism.

- the H atom from the COOH group is transferred to the carbonyl oxygen atom via a cyclic transition state to form CO_2 and the following compound, an enol,



enol

- the enol then extracts a H atom from a H_2O molecule to form a ketone and H^+ and OH^- ions.

Suggest the mechanism for this reaction. Show any relevant lone pairs, dipoles and charges, and indicate the movement of electron pairs with curly arrows.

[4]

[Total: 24]

For
Examiner's
Use

INNOVA JUNIOR COLLEGE
JC 2 PRELIMINARY EXAMINATION
in preparation for General Certificate of Education Advanced Level
Higher 2

CHEMISTRY 9729/03

Paper 3 Free Response **13 September 2017**

2 hours

Candidates answer on separate paper.

Additional Materials: Writing Papers
Data Booklet
Cover Page

READ THESE INSTRUCTIONS FIRST

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

Section A
Answer **all** questions.

Section B
Answer **one** question.

You are advised to show all working in calculations.
You are reminded of the need for good English and clear presentation in your answers.
You are reminded of the need for good handwriting.
Your final answers should be in 3 significant figures.

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

This document consists of **12** printed pages.

Section A

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

1 Benzoic acid, C_6H_5COOH is a colourless crystalline solid and a simple aromatic carboxylic acid. Benzoic acid occurs naturally in many plants. Salts of benzoic acid are used as food preservatives and benzoic acid is an important precursor for the industrial synthesis of many other organic substances.

(a) In the identification of benzoic acid, a commonly used reagent is neutral iron(III) chloride solution, in which a buff precipitate of iron(III) benzoate, $Fe(C_6H_5CO_2)_3$ is formed. When 50.0 cm^3 of iron(III) chloride solution was added to 50.0 cm^3 of benzoic acid solution, 0.0532 g of the buff precipitate was formed in the mixture.

The reactions that take place are shown below:

$$C_6H_5CO_2H \rightleftharpoons C_6H_5CO_2^- + H^+$$

$$Fe^{3+} + 3C_6H_5CO_2H \longrightarrow Fe(C_6H_5CO_2)_3 + 3H^+$$

(Given: M_r of $Fe(C_6H_5CO_2)_3 = 418.8$)

(i) Calculate the number of moles of benzoic acid that reacted with the neutral iron(III) chloride solution.

[1]

(ii) Given that the pH of the solution after the reaction is 2.33, calculate the number of moles of H^+ in the mixture.

[1]

(iii) Assuming that the H^+ ions in solution are formed only from the dissociation of benzoic acid in solution, as well as the reaction of benzoic acid with iron(III) chloride, calculate the concentration of benzoate ions in the mixture.

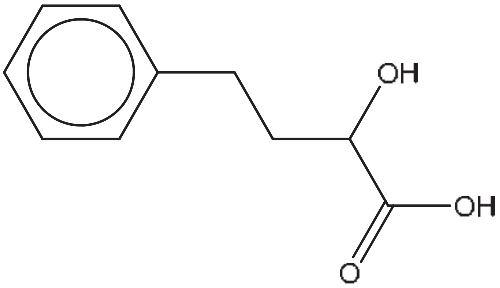
[2]

(iv) Iron(III) benzoate is a sparingly soluble salt.

Calculate the K_{sp} of iron(III) benzoate, given that the concentration of Fe^{3+} in the mixture was 1.83×10^{-3} mol dm^{-3} at equilibrium.

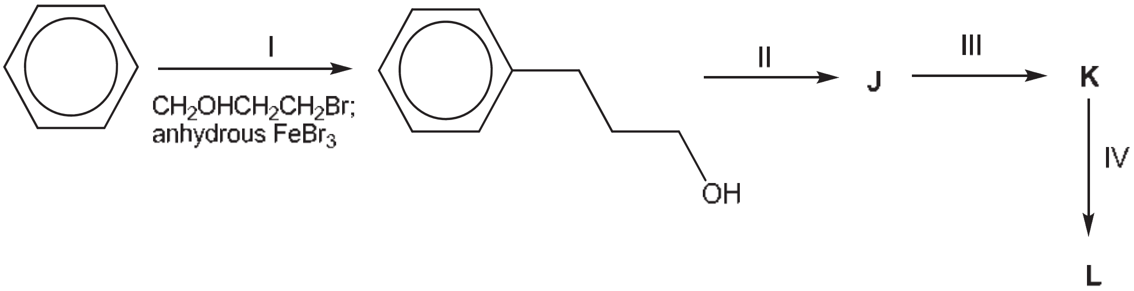
[1]

(b) Benzoic acid can be produced by oxidising compound **L**.



Compound **L**

Compound **L** can be synthesised by the following reaction scheme.



(i) State the *type of reaction* in step I and hence explain the need for $FeBr_3$ to be anhydrous. [2]

(ii) Suggest the identities of **J** and **K**. [2]

(iii) State the reagents and conditions for steps II to IV. [3]

(iv) State the *type of reaction* for stage IV. [1]

[Total: 13]

2 Sulfur is a chemical element with the symbol S and an atomic number of 16. It is an abundant, multivalent non-metal. It can be found in amino acids and it is a precursor to other chemicals such as H_2SO_4. H_2SO_4 is a common mineral acid with many uses. It can be used as an electrolyte in batteries.

(a) In the cells of a lead-acid car battery the following reactions take place.

anode: $Pb(s) \longrightarrow Pb^{2+}(aq) + 2e^-$

cathode $PbO_2(s) + 4H^+(aq) + 2e^- \longrightarrow Pb^{2+}(aq) + 2H_2O(l)$

(i) Use the *Data Booklet* to calculate E^θ_{cell} for this reaction.

[1]

(ii) Construct an equation for the overall reaction.

[1]

The electrolyte in a lead-acid cell is $H_2SO_4(aq)$. Most of the $Pb^{2+}(aq)$ ions that are produced at the electrodes are precipitated as a highly insoluble $PbSO_4(s)$.

(iii) Construct an equation for the overall cell reaction in the presence of H_2SO_4.

[1]

(iv) By considering the effect of decreasing $[Pb^{2+}(aq)]$ on the electrode potentials of the cathode and the anode, state and explain whether the overall E^θ_{cell} will *increase*, *decrease* or *remain the same*.

[1]

(b) H_2SO_4 is also used as an electrolyte in the anodising of aluminium. Anodising of aluminium is the process of coating aluminium metal with aluminium oxide (Al_2O_3) via electrolysis with the aluminium metal as the anode.

(i) Using $H_2SO_4(aq)$ as the electrolyte and an inert electrode, draw an electrolysis set-up to show how a piece of aluminium metal can be anodised.

[1]

(ii) Write chemical equations to show the reactions at the anode and cathode during anodising. Include in your answers, the overall equation.

[3]

(iii) The aluminum piece to be anodised has a surface area of 29.2 cm^2. Calculate the time taken to form a 0.2 mm protective layer of Al_2O_3 on the aluminum piece if a current of 2.0 A is passed through the set-up.

(Density of Al_2O_3 is 3.95 g cm^{-3})

[4]

(iv) Give one example of an anodised aluminium object, and explain the advantages of anodising it.

[1]

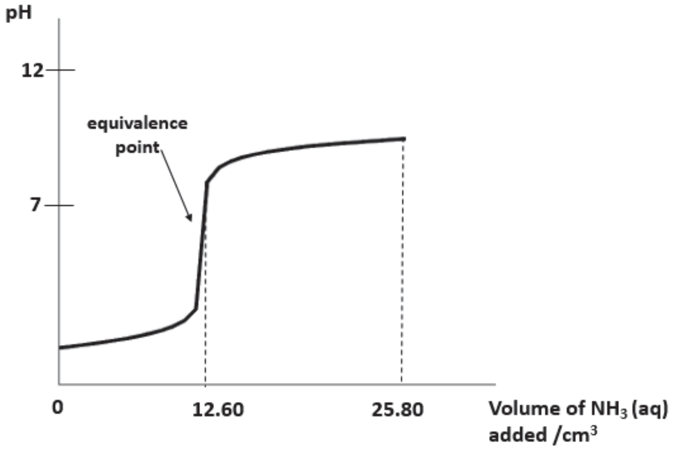
(c) H_2SO_4, can be produced when sulfur trioxide is added to water, according to the following equation:

$$SO_3(g) + H_2O(l) \rightarrow H_2SO_4(aq)$$

Calculate the volume of gaseous SO_3, under room temperature and pressure, needed to form 30.0 cm^3 of 0.0200 mol dm^{-3} of H_2SO_4.

[1]

(d) 25.0 cm^3 of 0.0200 mol dm^{-3} of H_2SO_4 was titrated against $NH_3(aq)$. The following graph was obtained.



(i) Calculate the initial pH of the sulfuric acid solution.

[1]

(ii) Calculate the concentration of $NH_3(aq)$ used in this titration.

[2]

(iii) Suggest a suitable indicator for this titration, giving a reason for your choice.

[2]

(e) Thiophenol are the sulfur analogue of phenol, that is, sulfur takes the place of oxygen in the hydroxyl group of phenol. A common reaction that phenol and thiophenol have is shown in **Figure 1** below.

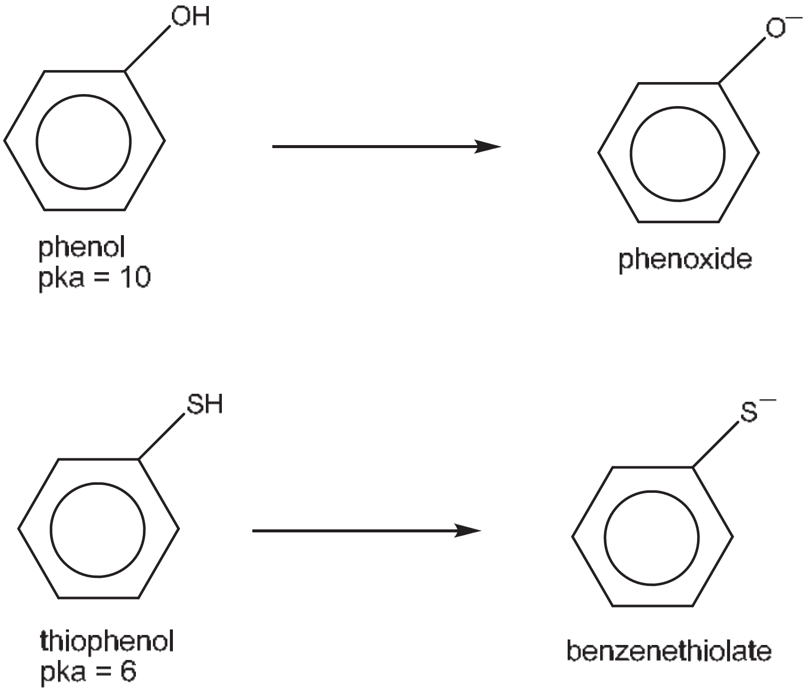
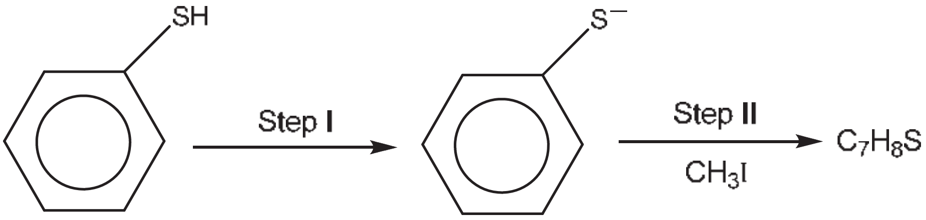


Figure 1

Consider the reaction scheme below.



(i) Suggest reagent and condition for step **I**.

[1]

(ii) What *type of reaction* is step **I** and step **II**?

[2]

(iii) Suggest the structure of C_7H_8S.

[1]

[Total: 23]

3 Halogenated organic compounds are widespread throughout nature and have a vast array of uses in modern industrial processes. They find many uses in the industries such as solvents and pesticides.

The rate of hydrolysis of $CH_3CH_2CH_2CH_2Br$ with aqueous NaOH was studied in a series of 3 experiments in which the initial rate of the reaction was measured. The following results were obtained.

Experiment	$[OH^-]$ / mol dm^{-3}	$[CH_3CH_2CH_2CH_2Br]$ / mol dm^{-3}	Initial Rate / mol dm^{-3} s^{-1}
1	0.100	0.010	4×10^{-6}
2	0.200	0.010	8×10^{-6}
3	0.200	0.020	16×10^{-6}

(a) Explain the meaning of the following terms.

(i) order of reaction

[1]

(ii) half-life

[1]

(iii) Using the data given, derive the rate equation for the hydrolysis of $CH_3CH_2CH_2CH_2Br$.

[3]

(iv) Using your rate equation, determine a value for the rate constant, including units for this reaction.

[2]

(v) Using the Maxwell-Boltzmann distribution curve, explain how the reaction rate might change with an increase in temperature.

[4]

(vi) Given that the rate equation for the hydrolysis of $(CH_3)_3CBr$ is rate = $k[(CH_3)_3CBr]$, suggest possible mechanisms for **both** of the reactions of $(CH_3)_3CBr$ and $CH_3CH_2CH_2CH_2Br$ with aqueous NaOH which are consistent with the observed kinetics.

[6]

(b) Bromine reacts with 2-methylpropane in the presence of sunlight to produce mono-brominated products via a free radical mechanism.

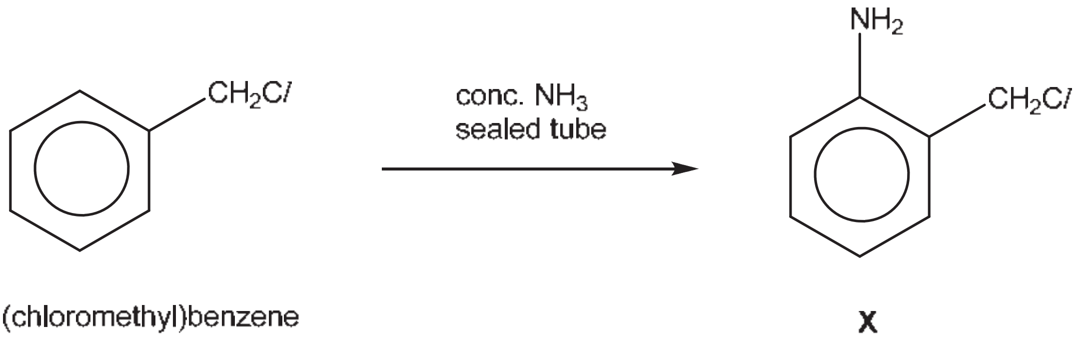
(i) Explain why the mono-bromination of 2-methylpropane results in the formation of two products in unequal amounts.

[1]

(ii) By quoting appropriate data from the *Data Booklet,* explain the difference in the reactivity of fluorine with 2-methylpropane compare with that of bromine.

[2]

(c) A student was not successful in making **X** from (chloromethyl)benzene with the proposed reaction route as shown.



Instead, a different product with molecular formula C_7H_9N was obtained.

(i) Draw the displayed formula of the product obtained.

[1]

(ii) Suggest how **X** can be synthesised from (chloromethyl)benzene. You should include the reagents, conditions and intermediate(s) formed in your answer.

[3]

[Total: 24]

Section B

Answer **one** question from this section

4 Hydrogen gas is needed in a large number of processes in the chemical industries such as hydrocracking of petroleum, production of margarine and production of ammonia.

Hydrogen gas can be produced in many chemical reactions.

(a) One of the reactions that produces hydrogen is the reaction of sodium with ethanol.

$$C_2H_5OH(l) + Na(s) \longrightarrow C_2H_5ONa(s) + \frac{1}{2}H_2(g)$$

This is also a chemical test for the presence of alcohol.

(i) Write the full electronic configuration of Na.

[1]

(ii) Describe how you would use the ionisation energies found in the *Data Booklet* to conclude that sodium is in group 1 of the periodic table.

[1]

(iii) Ethanoic acid reacts with sodium in a similar way. However, when ethanol and ethanoic acid is reacted with solid sodium carbonate separately, only ethanoic acid gives off a gas that forms white precipitate with calcium hydroxide.

Explain the difference in reactions of ethanol and ethanoic acid with sodium carbonate.

[3]

(iv) An unknown compound **M**, $C_8H_{10}O$ was found to be an alcohol when tested with sodium metal.

When **M** is treated with hot acidified potassium dichromate, compound **N**, C_8H_8O is formed. **N** gives a yellow precipitate, **P** when warmed with alkaline aqueous iodine.

When **M** is heated with concentrated H_2SO_4, compound **R**, C_8H_8 is formed. **R** gives compound **S** when reacted with hydrogen chloride gas.

M also gave compound **S** when reacted with phosphorous pentachloride at room temperature.

Deduce the structures of **M**, **N**, **P**, **R** and **S.**

[5]

(b) Another reaction that produces hydrogen is the reaction of methane with steam at 1000–1400 K.

$$CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g) \qquad \Delta H = +206 \text{ kJ mol}^{-1}$$

This reaction produces large quantities of hydrogen for industrial use.

(i) State and explain the effect of decreasing the temperature of the reaction on the equilibrium position.

[1]

(ii) Deduce the sign of entropy change for the forward reaction.

[1]

(iii) Hence, or otherwise, predict and explain the spontaneity of the forward reaction at low temperature.

[1]

(iv) Comment and explain if there is any discrepancy in your answers in **b(i)** and **b(iii)**.

[1]

(v) Calculate the enthalpy change of vaporisation of water using the data in **Table 1**.

Table 1

Enthalpy change of formation of carbon monoxide	-111 kJ mol^{-1}
Enthalpy change of formation of methane	-75 kJ mol^{-1}
Enthalpy change of formation of water	-285 kJ mol^{-1}

[2]

(c) Hydrogen gas can also be produced from the reaction of carbon monoxide with steam.

$$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g) \quad K_c = 6.40 \times 10^{-1} \text{ at 1100K}$$

A mixture containing 0.8 mol of CO and 0.8 mol of H_2O was placed in a 2 dm^3 flask and allowed to come to equilibrium at 1100K.

(i) Write an expression for an expression for K_c of this reaction.

[1]

(ii) Calculate the amount of each substance present in the equilibrium mixture at 1100K.

[2]

(iii) State and explain the effect of decreasing pressure on the equilibrium constant.

[1]

[Total: 20]

5 Methanol can be prepared industrially by reacting together carbon monoxide and hydrogen. This is a reversible reaction:

$$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g) \quad \Delta H = -94 kJmol^{-1}$$

A chemist mixes together 0.114 mol CO(g) and 0.152 mol H_2(g) in a container. The container is pressurised and then sealed and the total volume is 200 cm^3. The mixture is heated to 500 K at constant volume and left to reach equilibrium. The chemist analyses the equilibrium mixture and finds that 0.052 mol CH_3OH has formed.

(a) Calculate the value of K_c for the equilibrium at 500 K. [2]

(b) The chemist repeats the experiment using the same initial amounts of CO and H_2. The same procedure is used but the mixture is heated in the 200 cm^3 sealed container to a temperature higher than 500 K.
As the gas volume is kept at 200 cm^3, the increased temperature also increases the pressure.

Explain why it is difficult to predict how the yield of CH_3OH would change and state what happens to the value of K_c. [2]

(c) Methanol can be oxidised to formaldehyde, HCHO, by passing its vapour over copper heated to 300 °C.

Explain why the boiling point of methanol (65 °C) is higher than that of formaldehyde (–19 °C). [2]

(d) State the type of hybridisation shown by the C atom in formaldehyde and draw its hybrid orbitals. [2]

(e) Benzaldehyde, C_6H_5CHO, is the simplest aromatic aldehyde and has a characteristic smell of almonds.
In the presence of a solution of potassium hydroxide, benzaldehyde undergoes disproportionation to give a mixture of two organic products, **E** and **F**. **F** has a higher solubility in water compared to **E**.

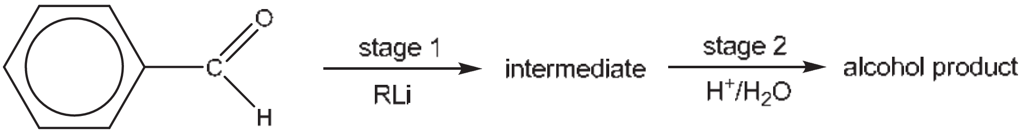
(i) Suggest the structures of **E** and **F**. [2]

(ii) Explain why **F** is soluble in water. [1]

(f) Alkyllithium compounds, RLi, can be used to increase the number of carbon atoms in an organic compound. Different alkyl groups, R, add carbon chains with different chain lengths.

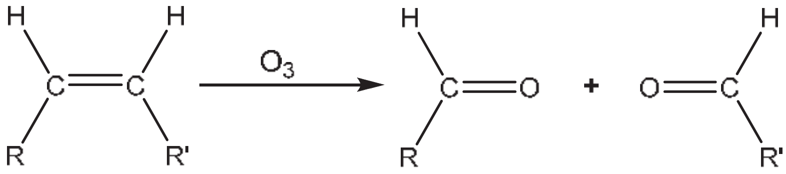
RLi provides a source of R^- ions, which act as a nucleophile.

(i) RLi reacts with benzaldehyde to give an intermediate in stage 1, followed by reaction with aqueous acid to form an alcohol in stage 2.



Describe the mechanism for the above reaction, including curly arrows and relevant dipoles. [3]

(ii) 'Ozonolysis' is a technique used in organic chemistry to break open a C=C double bond. During ozonolysis, an alkene reacts with ozone, O_3. The products are carbonyl compounds as shown below.



An aromatic alkene, **A** undergoes ozonolysis to give benzaldehyde and **B**, C_4H_8O. **B** has no reaction with $[Ag(NH_3)_2]^+$(aq) but gives a yellow precipitate with aqueous alkaline iodine.

B undergoes a reaction with an alkyllithium compound, **C**, followed by reaction with aqueous acid to give an alcohol, **D**, which is optically active. The elimination of H_2O from **D** produces a mixture of four different isomeric alkenes with the formula, C_7H_{14}, only two of which are cis-trans isomers of each other. Suggest the structural formulae of compounds **A** to **D** and the two cis-trans isomers.

[6]

[Total: 20]

CHEMISTRY LAB PREPARATION LIST FOR JC2 H2 CHEMISTRY

2017 PRELIM

APPARATUS

S/N	Apparatus	Quantity
1	25cm^3 Pipette	1
2	Pipette Filler	1
3	Burette stand and clamp	2
4	250cm^3 conical flask	2
5	250cm^3 volumetric flask	1
6	250cm^3 beaker	1
7	Funnel (for filling burette)	1
8	White tile	1
9	spatula	1
10	Wash bottle containing distilled water	1
11	Marker pen or labels(suitable for labelling glassware)	1
12	100cm^3 beaker	2
13	25cm^3 measuring cylinder	1
14	10cm^3 measuring cylinder	2
14	50cm^3 burette	2
15	Glass rod	1
16	Stopwatch	1
17	Paper towels	
18	Dropping pipettes	4
19	**DRY** Boiling tube	4
20	**DRY** Test tubes	8

CHEMICALS NEEDED (PER STUDENT)

S/N	Chemical
1	**FA1**
2	Magnesium Ribbon
3	Bromophenol blue
4	**FA3**
5	**FA4**
6	**FA5**
7	**FA6**
8	Starch indicator
9	**FA7**
10	**FA8**
11	**FA9**

CHEMISTRY LAB PREPARATION LIST FOR JC2 H2 CHEMISTRY

2017 PRELIM

APPARATUS NEEDED (PER STUDENT)

S/N	**Apparatus**	**Quantity**	**Location**	**Remarks**
1	25cm^3 Pipette	1	Student's bench	Reuse
2	Pipette Filler	1	Student's bench	Reuse
3	Burette stand and clamp	2	Student's bench	Reuse
4	250cm^3 conical flask	2	Student's bench	Reuse
5	250cm^3 volumetric flask	1	Student's bench	Reuse
6	250cm^3 beaker	1	Student's bench	Reuse
7	Funnel (for filling burette)	1	Student's bench	Reuse
8	White tile	1	Student's bench	Reuse
9	spatula	1	Student's bench	Reuse
10	Wash bottle containing distilled water	1	Student's bench	Reuse
11	Marker pen or labels(suitable for labelling glassware)	1	Student's bench	Reuse
12	100cm^3 beaker	2	Student's bench	Reuse
13	25cm^3 measuring cylinder	1	Student's bench	Reuse
14	10cm^3 measuring cylinder	2	Student's bench	Reuse
14	50cm^3 burette	2	Student's bench	Reuse
15	Glass rod	1	Student's bench	Reuse
16	Stopwatch	1	Student's bench	Reuse
17	Paper towels		Student's bench	Must change to new one per shift
18	Dropping pipettes	4	Student's bench	Must change to new one per shift
19	Boiling tube	~~3~~ 4	Student's bench	Must change to new one per shift
20	Test tubes	8	Student's bench	Must change to new one per shift
~~**21**~~	~~Hard glass test tube~~	~~1~~	~~Student's bench~~	~~Must change to new one per shift~~
22	Access to weighing balance			4 per lab

CHEMICALS NEEDED (PER STUDENT)

S/N	Chemical	Concentration	Quantity	Location	Remarks
1	**FA1** Hydrochloric acid **[H]**	2.00 mol dm^{-3}	40cm^3	Student's bench	Dilute 170cm^3 of concentrated (35-37%; approximately 11 mol dm^{-3}) hydrochloric acid to 1 dm^3
2	Magnesium Ribbon **[F]**		0.20g (in one strip) - Place in a ziplock bag and label.	Student's bench - together with FA1 to FA9 **REMOVE the small strips in the bottle found with the common QA reagents	One strip of Mg ribbon, lightly cleaned with emery paper or sand paper if appropriate, of mass 0.20g. All Mg strips supplied to candidates must be cut to the same length, to within 0.2cm, using scissors and a ruler.
3	Bromophenol blue		5cm^3	Student's bench/ Shared by two students per bench	Dissolve 0.4g of the solid indicator in 200cm^3 ethanol and make up to 1 dm^3 with distilled water.
4	**FA3** Sodium hydroxide **[H]**	0.120 mol dm^{-3}	150 cm^3	Student's bench	Dissolve 4.80g of NaOH in each dm^3 of solution.
5	**FA4** Acidified iron(III) chloride **[C][H]**	0.060 mol dm^{-3}	150 cm^3	Student's bench	Dissolve 16.22g of $FeCl_3.6H_2O$ in each dm^3 of 0..20 mol dm^{-3} hydrochloric acid. 0.20 mol dm^{-3} hydrochloric acid made by diluting 2.0 mol dm^{-3} hydrochloric acid 10 fold.(see above in FA1)
6	**FA5** Potassium iodide	0.060 mol dm^{-3}	80cm^3	Student's bench	Dissolve 9..96g of KI in each dm^3 of solution.
7	**FA6** Sodium thiosulfate	0.0060 mol dm^{-3}	150 cm^3	Student's bench	Dissolve 29.78g of $Na_2S_2O_3.5H_2O$ in each dm^3 of solution. Dilute this solution 20-fold.
8	Starch indicator	Freshly prepared aqueous starch indicator	80cm^3	Student's bench	Mix 2g of soluble starch with a little cold water until a smooth paste is obtained. Add 100cm^3 of boiling water and stir. Boil until a clear solution is obtained (about 5 minutes).

		(approx. 2% solution w/v)			
9	**FA7**	A mixture of aluminium sulfate and sodium chloride	0.5g	Student's bench	Approximately equal masses of $Al_2(SO_4)_3.16H_2O$ and NaCl thoroughly mixed.
10	**FA8**	A mixture of magnesium carbonate and potassium iodide	0.5g	Student's bench	Approximately equal masses of $MgCO_3$ and KI thoroughly mixed. Note: "basic" forms of magnesium carbonate are suitable.
11	**FA9 [H]**	Ammonium iron(II) sulfate	1.5g	Student's bench	Approximately 1.5g of $(NH_4)_2Fe(SO_4).6H_2O$

STANDARD BENCH REAGENTS

Hazard	Label	Identity	Notes (hazards given in this column are for the raw materials)
[MH]	Dilute hydrochloric acid	2.0 mol dm^{-3} HCl	Dilute 170 cm^3 of concentrated (35 – 37%; approximately 11 mol dm^{-3}) hydrochloric acid to 1 dm^{-3}
[C]	Dilute nitric acid	2.0 mol dm^{-3} HNO_3	Dilute 128 cm^3 of concentrated (70% w/v) nitric acid to 1 dm^3
[MH]	Dilute sulfuric acid	1.0 mol dm^{-3} H_2SO_4	Cautiously pour 55 cm^3 of concentrated (98%) sulfuric acid into 500 cm^3 of distilled water with continuous stirring. Make the solution up to 1 dm^3 with distilled water. **Care:** concentrated H_2SO_4 is very corrosive
[C][MH][N]	Aqueous ammonia	2.0 mol dm^{-3} NH_3	Dilute 112 cm^3 of concentrated (35%) ammonia to 1 dm^3
[C]	Aqueous sodium hydroxide	2.0 mol dm^{-3} NaOH	Dissolve 80.0 g of NaOH in each dm^3 of solution. **Care:** the process of solution is exothermic and any concentrated solution is very corrosive.
[MH]	Aqueous barium nitrate	0.1 mol dm^{-3} barium nitrate	Dissolve 26.1 g of $Ba(NO_3)_2$ in each dm^3 of solution.
[N]	Aqueous silver nitrate	0.05 mol dm^{-3} silver nitrate	Dissolve 8.5g of $AgNO_3$ in each dm^3 of solution.
[MH]	Limewater	Saturated aqueous calcium hydroxide, $Ca(OH)_2$	Prepare fresh limewater by leaving distilled water to stand over solid calcium hydroxide for several days, shaking occasionally. Decant or filter the solution.
	Aqueous potassium iodide	0.1 mol dm^{-3} KI	Dissolve 16.6g of KI in each dm^3 of solution

	Acidified aqueous potassium manganate (VII)	0.02 mol dm^{-3} potassium manganate (VII)	Dissolve 3.16g of $KMnO_4$ in each dm^3 of solution. Mix equal volumes of 0.02 mol dm^{-3} $KMnO_4$ and 1.0 mol dm^{-3} sulfuric acid.
	hexane	Hexane	

The following materials and apparatus should be available **FOR EACH STUDENT**.

Red and blue litmus papers, plain filter strips for use with acidified manganate(VII), aluminium foil for testing nitrate/nitrite, wooden splints and the apparatus normally used in the Centre for use with limewater testing for carbon dioxide.

INNOVA JUNIOR COLLEGE
JC2 PRELIMINARY EXAMINATION
in preparation for General Certificate of Education Advanced Level
Higher 2

CANDIDATE NAME **WORKED SOLUTIONS**

CLASS

INDEX NUMBER

CHEMISTRY

9729/01

Paper 1 Multiple Choice

27 June 2017

1 hour

Additional Materials: *Data Booklet*
Multiple Choice Answer Sheet

READ THESE INSTRUCTIONS FIRST

Write your name and class on all the work you hand in.
Write in soft pencil.
Do not use staples, paper clips, highlighters, glue or correction fluid.

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

Read the instructions on the Answer Sheet very carefully.

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

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

This document consists of **19** 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 given mass of ideal gas occupies a volume *V* and exerts a pressure *p* at 30 °C.

At which temperature will the same mass of the ideal gas occupy a volume $\frac{V}{3}$ and exert a pressure 2*p*?

A	20 °C	**C**	202 °C
B	20 K	**D**	202 K

Answer: **D**

pV = nRT

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

$$\frac{P_1V_1}{T_1} = \frac{2P_1\frac{V_1}{3}}{T_2}$$

$$T_2 = \frac{2}{3}T_1$$

Original T = 30 + 273 = 303 K
New T = $\frac{2}{3}$ × 303 = 202 K

2 Which equation corresponds to the third ionisation energy of titanium (Ti)?

A $Ti(g) \rightarrow Ti^{3+}(g) + 3e^-$

B $Ti^{2+}(s) \rightarrow Ti^{3+}(g) + e^-$

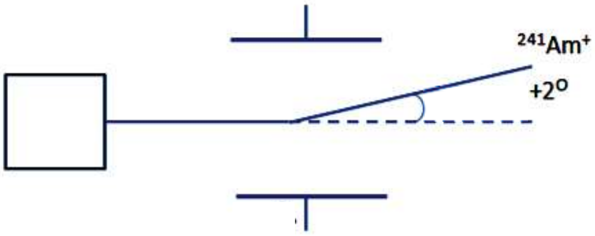
C $Ti^{2+}(g) \rightarrow Ti^{3+}(g) + e^-$

D $Ti^{3+}(g) + e^- \rightarrow Ti^{2+}(g)$

Answer: **C**

Third ionization energy of Ti is defined as the amount of energy required to remove 1 mole of electrons from one mole of doubly charged gaseous Ti (Ti^{2+}) to form one mole of triply charged gaseous Ti (Ti^{3+}).

3 A sample of the element Americium (Am) was vaporised, ionised and passed through an electric field. It was observed that a beam of $^{241}Am^+$ particles gave an angle of deflection of +2°.



Assuming an identical set of experimental conditions, by what angle would a beam of $^{32}S^-$ particles be deflected?

A +15.1°

B –15.1°

C +30.1°

D –30.1°

Answer: **B**

$$\text{angle of deflection } \alpha \frac{\text{charge}}{\text{mass}}$$

angle of deflection of $^{241}Am^+$ = +2°

For $^{241}Am^+$, $\frac{q}{m} = \frac{1}{241}$

$$k\frac{1}{241} = (2)$$
$$k = 482$$

For $^{32}S^-$, $\frac{q}{m} = \frac{1}{32}$

angle of deflection of $^{32}S^-$ = $= \frac{1}{32} \times 482$ = –15.1°

4 Which of the following statements describes a phenomenon which **cannot** be explained by hydrogen bonding?

A Ice floats on water.

B The boiling point of carboxylic acid increases with increasing relative molecular mass.

C 2-nitrophenol is more volatile than 4-nitrophenol.

D Ethanoic acid molecules form dimers when dissolved in benzene.

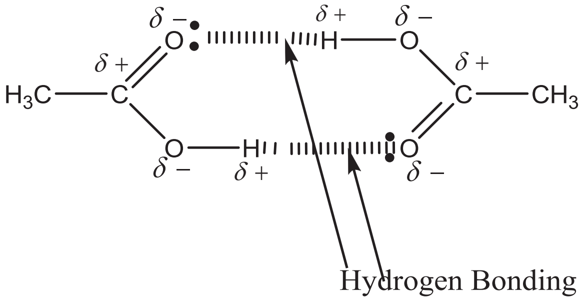
Answer: **B**

Option **A** is incorrect as in ice, each H_2O molecule forms the maximum of **four** hydrogen bonds with 4 other H_2O molecules. This results in an **open structure** of ice and hence ice is **less dense** than water and so, floats on water.

Option **B** is correct as the boiling point of carboxylic acid increases with increasing M_r due to **stronger instantaneous dipole-induced dipole interactions between the non-polar R group** as the size of electron cloud of R group increases and hence become more polarisable.

Option C is incorrect as in 2-nitrophenol, due to close proximity between –OH and $-NO_2$ groups, they can be used for formation of **intramolecular hydrogen bonds.** Hence, there are **fewer available sites** for **intermolecular hydrogen bonds**. Thus, 2-nitrophenol has a lower boiling point (and hence more volatile) as **lesser energy is required** to overcome the **less extensive hydrogen bonds** between molecules.

Option **D** is incorrect as in benzene, CH_3COOH molecules can form a dimer via hydrogen bonding.



5 A tertiary amine, R_3N, reacts with boron trifluoride, BF_3 to give an addition product. Which of the following statements is **not** true?

A R_3N acts as a Lewis base.

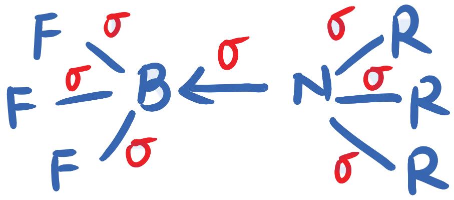
B The product is a polar molecule.

C There are six σ bonds in the product.

D The product contains a dative covalent bond.

Answer: **C**

Addition product:



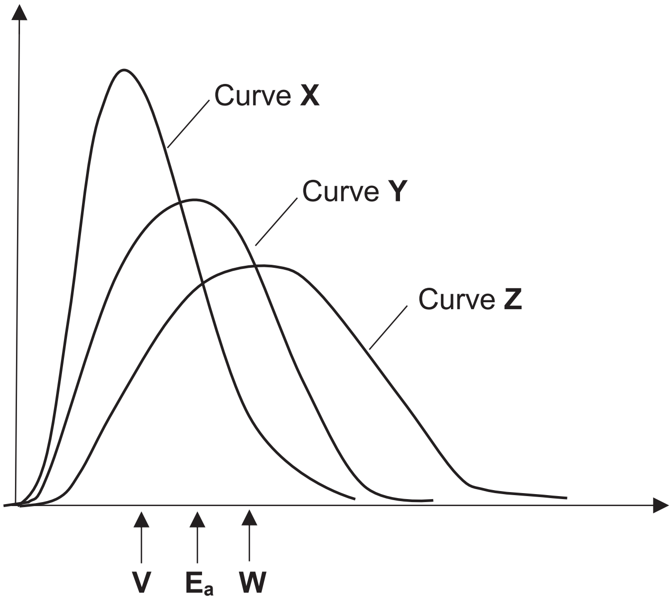
Option **A** is incorrect as R_3N is a lewis base as it **donates an electron pair** to BF_3.

Option **B** is incorrect as the molecule is polar due to presence of **polar bonds** (C–N, B–F and B–N) and the **dipole moments do not cancel out**.

Option **C** is correct as there is a **minimum of 7 σ bonds** in the addition product (not taking into account the C–H and C–C σ bonds present in the R groups).

Option D is correct as there is a **dative covalent bond from N to B**.

6 The curve **Y** and the value E_a represent the distribution of energies of the molecules and the activation energy for an uncatalysed gaseous reaction.



What is a possible outcome if the reaction is catalysed?

A The distribution of energies will be given by curve **X** and the activation energy by value **V**

B The distribution of energies will be given by curve **Y** and the activation energy by value **V**.

C The distribution of energies will be given by curve **Y** and the activation energy by value **W**.

D The distribution of energies will be given by curve **Z** and the activation energy by value **W**.

Answer: **B**

When catalyst is added, the graph distribution of energies of molecules will not change, it is affected only by temperature. Hence the curve should be **Y.**
However, when catalyst is added E_a will become lowered, hence value **V.**

7 If the rate of decay of a radioactive isotope decrease from 300 counts per minute to 37.5 counts per minute after 1 day, what is its half-life?

A	4 hours	**C**	8 hours
B	6 hours	**D**	12 hours

Answer: **C**

First half-life occurs when 300 counts per minute is reduced to 150 counts per minute.
Second half-life occurs when 150 counts per minute is reduced to 75 counts per minute.
Third half-life occurs when 75 counts per minute is reduced to 37.5 counts per minute.

3 half-life in 24 hours means each half-life is 8 hours.

8 Which of the following statements does **not** describe a reaction at equilibrium?

A Forward and backward reactions occur at equal rate.

B The system must be closed.

C K_c increases as the reaction progresses.

D Concentrations of reactants and products are constant.

Answer: **C**

At dynamic equilibrium, rate of forward reaction = rate of backward reaction, hence there is no change in concentration of reactants and products.

K_c is only affected by **temperature changes**.

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

The enthalpy change of formation of carbon monoxide and carbon dioxide are given below.

$$\Delta H_f \text{ CO} = -110 \text{ kJmol}^{-1}$$
$$\Delta H_f \text{ CO}_2 = -393 \text{ kJmol}^{-1}$$

Which of these statements are correct?

1 CO_2(g) has lower energy content than CO(g).

2 The enthalpy change of combustion of carbon is –393 kJmol^{-1}.

3 CO_2(g) is formed exothermically from CO(g).

4 A larger amount of energy is required to atomise CO_2(g) than CO(g).

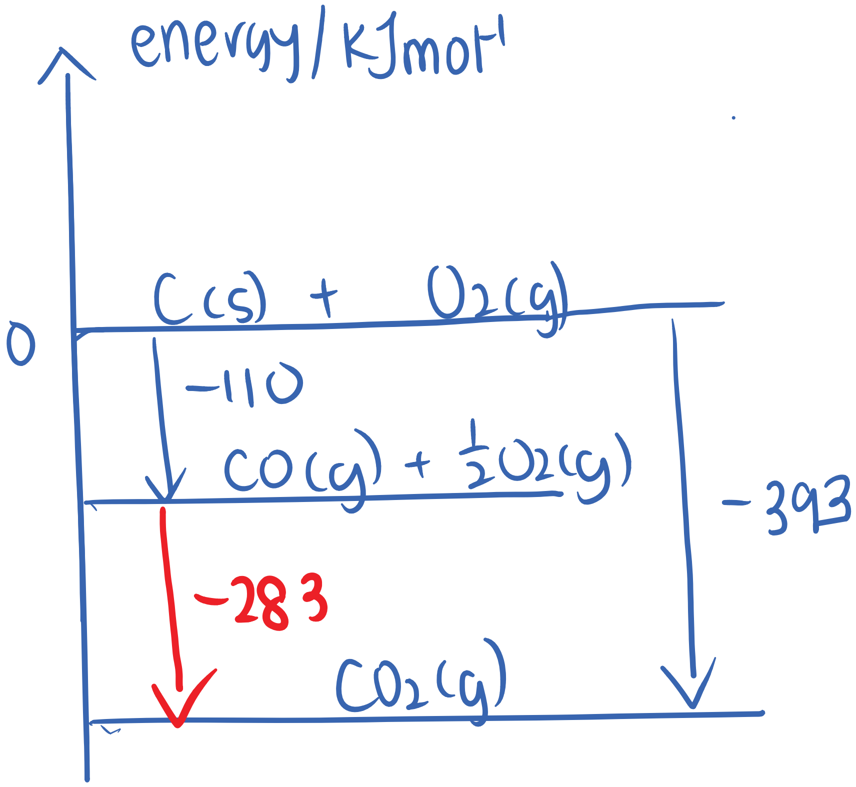
A 1, 2, 3 and 4

B 1, 2 and 3 only

C 1, 2 and 4 only

D 2 and 3 only

Answer: **A**



Option **1** is correct as from the energy level diagram, CO_2(g) has a lower energy content than CO(g).

Option **2** is correct as ΔH_c(C) = ΔH_f(CO_2) = –393 kJmol^{-1} from the diagram

Option **3** is correct as from the energy level diagram, CO_2(g) is formed exothermically from CO(g). [–283 kJmol^{-1}]

Option **4** is correct as atomisation means to produce free gaseous C and O atoms (an endothermic process). More energy is required to atomise CO_2(g) than CO(g) as CO_2(g) has a lower energy content.

10 A sparingly soluble calcium salt ionises in aqueous solution according to the equation given:

$$Ca_3X_2(s) \rightleftharpoons 3Ca^{2+}(aq) + 2X^{3-}(aq)$$

If the solubility product K_{sp} of Ca_3X_2 is S, what is the value of the concentration of Ca^{2+} (aq) at equilibrium?

A $S^{\frac{1}{2}}$

B $\left[\frac{S}{108}\right]^{\frac{1}{5}}$

C $\left[\frac{3S}{5}\right]^{\frac{1}{2}}$

D $\left[\frac{9S}{4}\right]^{\frac{1}{5}}$

Answer: **D**

$$Ca_3X_2\,(s) \rightleftharpoons 3\,Ca^{2+}\,(aq) + 2\,X^{3-}\,(aq)$$

$K_{sp} = [Ca^{2+}]^3\,[X^{3-}]^2$
$S = (3x)^3\,(2x)^2$
$= (27x^3)\,(4x^2)$
$= 108\,x^5$

$$X = \left(\frac{S}{108}\right)^{\frac{1}{5}}$$

$$[Ca^{2+}] \text{ at eqm} = 3x = 3\left(\frac{S}{108}\right)^{\frac{1}{5}} = \left(\frac{243S}{108}\right)^{\frac{1}{5}} = \left[\frac{9S}{4}\right]^{\frac{1}{5}}$$

11 The K_{sp} of AgC*l* and AgI are 1.80×10^{-10} mol^2 dm^{-6} and 8.3×10^{-17} mol^2 dm^{-6} respectively. Which of the following statements is correct when equal volumes of 1×10^{-4} mol dm^{-3} aqueous $AgNO_3$ was added to a mixture containing 3.0×10^{-6} mol dm^{-3} $BaCl_2$ and 3.0×10^{-6} mol dm^{-3} BaI_2?

A AgC*l* is precipitated only.

B AgI is precipitated only.

C AgC*l* is precipitated followed by AgI.

D AgI is precipitated followed by AgC*l*.

Answer: **B**

$[Ag^+] = [AgNO_3] = 1 \times 10^{-4}$ mol dm^{-3}

$[Cl^-] = 2 \times [BaCl_2] = 6 \times 10^{-6}$ mol dm^{-3}

$[I^-] = 2 \times [BaI_2] = 6 \times 10^{-6}$ mol dm^{-3}

Take note that the mixture consists of equal volumes of $AgNO_3$ and $BaCl_2$. Hence, the new concentration will be halved.
$[Ag^+]$ in mixture = 0.5×10^{-4}

$[Cl^-]$ in mixture = 3×10^{-6}

IP of AgC*l* = $(0.5 \times 10^{-4})(3.0 \times 10^{-6}) = 1.5 \times 10^{-10}$

IP < Ksp → AgC*l* will not ppt out

IP of AgI = $(0.5 \times 10^{-4})(3.0 \times 10^{-6}) = 1.5 \times 10^{-10}$

IP > Ksp → AgI will ppt out

12 The dissociation constant, K_w, for the ionisation of water, $H_2O \rightleftharpoons H^+ + OH^-$, at different temperatures is given below.

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 The equilibrium lies furthest to the right at 0 °C.

C The forward reaction is exothermic.

D The pH of pure water decreases with temperature.

Answer: **D**

Option **A** is incorrect as the $[H^+]$ and $[OH^-]$ of water are equal at all temperatures.
Option **B** is incorrect as the value of K_w is the smallest at 0 °C. Hence, equilibrium lies most to the left.
Option **C** is incorrect as K_w increases with temperature, the forward reaction is favoured.
Option **D** is correct as an increase in temperature favours the endothermic reaction, hence the forward reaction is endothermic.

Option **D**:
$K_w = [H^+][OH^-]$
$K_w = [H^+]^2$
$pH = -\log \sqrt{(K_w)}$
as K_w increases with temperature, pH will decrease.

13 Calculate the standard Gibbs free energy change, $\Delta G^\ominus$ for the following reaction:

$$2Al\,(s) + 3Cu^{2+}(aq) \longrightarrow 2Al^{3+}(aq) + 3Cu(s)$$

A –386 kJ mol^{-1}

B –579 kJ mol^{-1}

C –1045 kJ mol^{-1}

D –1158 kJ mol^{-1}

Answer: **D**

$E_{cell} = +0.34 - (-1.66) = +2.00$ V

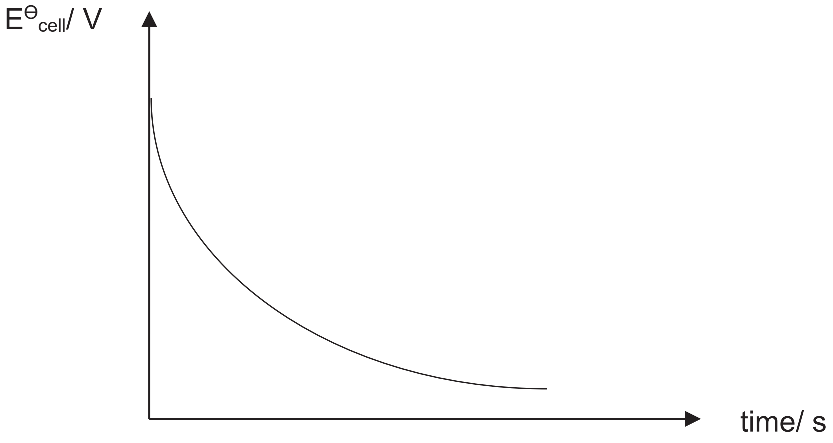
$\Delta G^\ominus = -nFE_{cell} = -6 \times 96500 \times 2.00 = -1158\,000$ J mol^{-1}

$= \underline{\mathbf{-1158\ kJ\ mol^{-1}}}$

14 An experiment is carried out with the following cell.

$$Fe\ (s)\ |\ Fe^{2+}\ (aq)\ ||\ Ni^{2+}\ (aq)\ |\ Ni\ (s)$$

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 these results?

A Add nickel (II) chloride to the nickel half-cell.

B Add aqueous cyanide ions to the iron half-cell.

C Add water to the nickel half-cell.

D Increases the surface area of iron immersed in the solution.

Answer: **C**

$E_{cell} = E_{Ni^{2+}/Ni} - E_{Fe^{3+}/Fe^{2+}}$ (graph states that E_{cell} should decrease)

Option **A** is incorrect as

$$Ni^{2+} + 2e^- \rightleftharpoons Ni$$

When nickel (II) chloride is added to the nickel half-cell, $[Ni^{2+}]$ increase, eqm position shift right. $E_{Ni^{2+}/Ni}$ is more positive (incorrect)

Option **B** is incorrect as

$$Fe^{3+} + e^- \rightleftharpoons Fe^{2+} \qquad +0.77$$

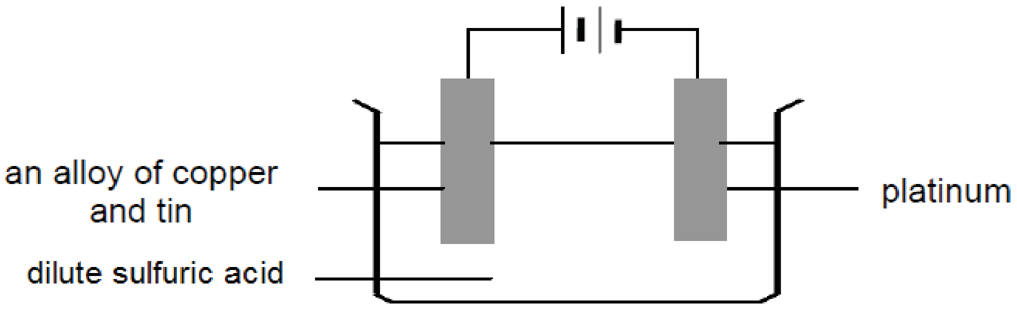
$$[Fe(CN)_6]^{3-} + e^- \rightleftharpoons [Fe(CN)_6]^{4-} \qquad +0.36$$

When aqueous cyanide ions is added to the iron half-cell. $E_{Fe^{3+}/Fe^{2+}}$ is less positive (incorrect)

Option **C** is correct as when water is added to the nickel half-cell, $[Ni^{2+}]$ decrease, eqm position shift left. $E_{Ni^{2+}/Ni}$ is less positive (correct)

Option **D** is incorrect as increases in the surface area of iron affects rate not E values.

15 The circuit shown in the diagram was set up.



Which reactions will occur at the electrodes?

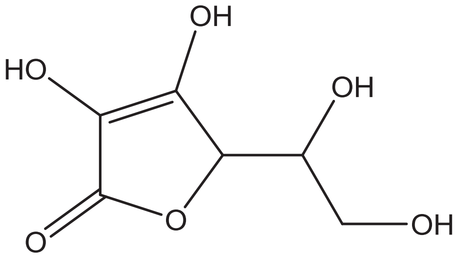
	anode reaction	*cathode reaction*
A	Oxygen gas is evolved.	Hydrogen gas is evolved.
B	Tin dissolves preferentially.	Hydrogen gas is evolved.
C	Copper dissolves preferentially.	Copper is deposited.
D	Copper and tin both dissolve.	Sulfur dioxide gas is evolved.

Answer: **B**

At the anode: (oxidation will occur)
Species present: Cu and Sn
Consider
$Sn^{2+} + 2e^- \longrightarrow Sn$ $\quad E^\ominus$/ V = - 0.14
$Cu^{2+} + 2e^- \longrightarrow Cu$ $\quad E^\ominus$/ V = +0.34
Based on the $E^\ominus$/ V values, a less positive value indicates that tin will be selectively oxidised.

At the cathode: (reduction will occur)
Species present: H_2O and H^+
Consider
$2H_2O + 2e^- \longrightarrow H_2 + 2OH^-$ $\quad E^\ominus$/ V = –0.83
$2H^+ + 2e^- \longrightarrow H_2$ $\quad E^\ominus$/ V = 0.00
$Sn^{2+} + 2e^- \longrightarrow Sn$ $\quad E^\ominus$/ V = - 0.14
Based on the $E^\ominus$/ V values, a more $E^\ominus$/ V positive value indicates that H^+ will be selectively reduced to produce H_2 gas.

16 The diagram shows the structure of vitamin C.

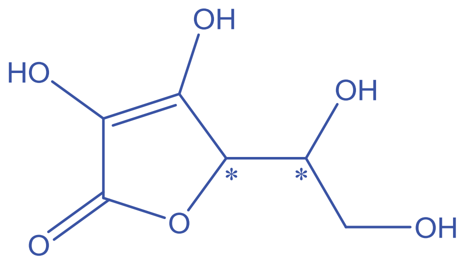


vitamin C

How many stereoisomers are there in one molecule of vitamin C?

A	2	**B**	4	**C**	8	**D**	16

Answer: **B**



2 chiral centres so number of enantiomers are $2^2 = 4$

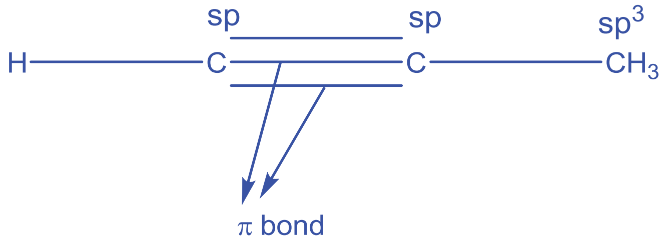
17 Propyne, C_3H_4, has the following structure.

$$H-C\equiv C-CH_3$$

Which row correctly describes the bonding and hybridisation in a molecule of propyne?

	number of π bonds	number of sp C atoms	number of sp^2 C atoms
A	1	1	1
B	2	2	0
C	2	2	1
D	3	3	0

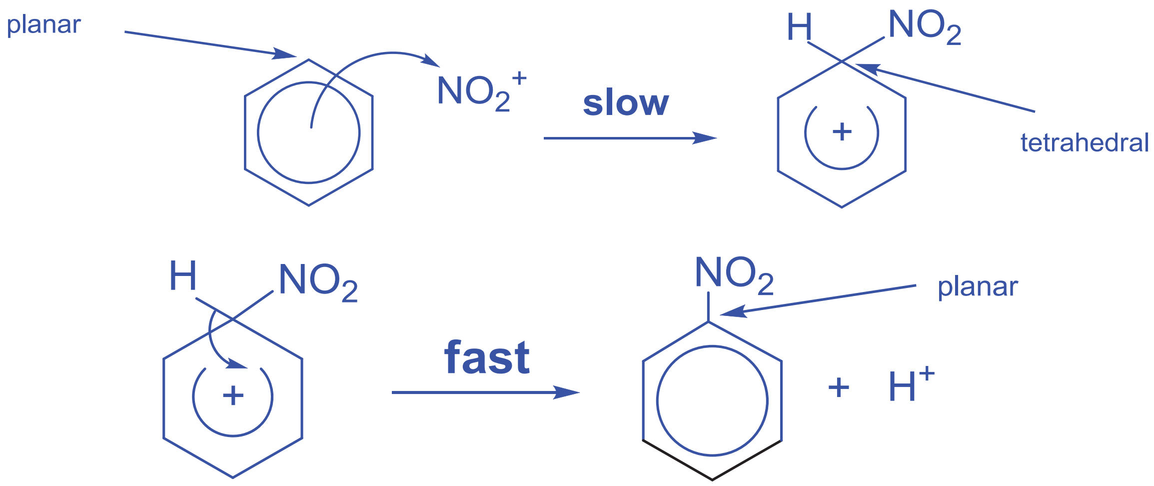
Answer: **B**



18 During the nitration of benzene, a nitro group substitutes at a carbon atom. Which one of the following gives the arrangement of the bonds at this carbon atom during the reaction?

	at the start of the reaction	*in the intermediate complex*	*at the end of the reaction*
A	planar	planar	planar
B	planar	tetrahedral	tetrahedral
C	planar	tetrahedral	planar
D	tetrahedral	planar	tetrahedral

Answer: **C**



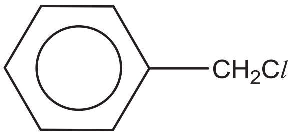
19 When a halogen compound **S** was boiled under reflux for some time with silver nitrate in a mixture of ethanol and water, little or no precipitate was seen.

Which of the following formulae could represent **S**?

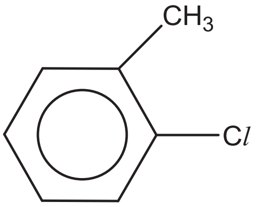
A $CH_3CH_2CHClCH_2CH_3$

B $CH_3CH_2CH_2COCl$

C



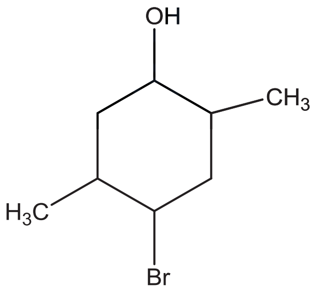
D



Answer: **D**

Given that there is little or no ppt seen, it shows that the C-Cl bond is strong, hence it is referring to the Cl bonded to a benzene ring as the p orbital of Cl will overlap with the π orbital of the benzene ring.

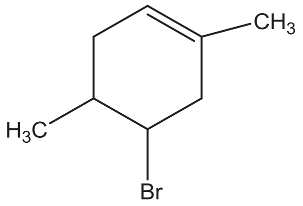
20 Compound **P** was heated with ethanolic potassium hydroxide.



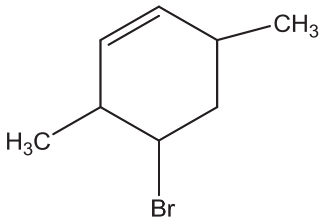
compound **P**

Which of the following would be the major product?

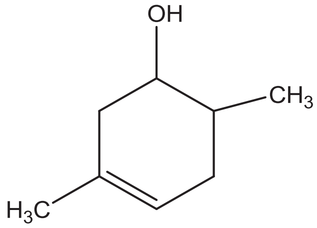
A



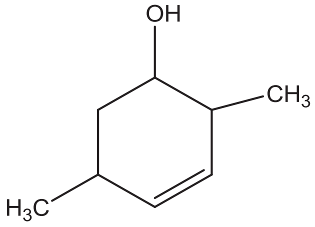
B



C



D



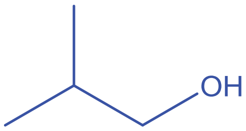
Answer: **C**

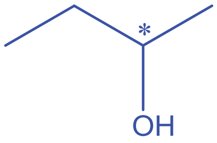
Ethanolic KOH is the reagent to eliminate H and Br → **A** and **B** will be wrong
Using Saytzeff rule whereby the "poor get poorer"

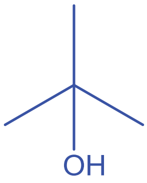
21 How many isomers (including both structural isomers and stereoisomers) with molecular formula $C_4H_{10}O$ liberates hydrogen on reaction with sodium?

A 2 **B** 3 **C** 4 **D** 5

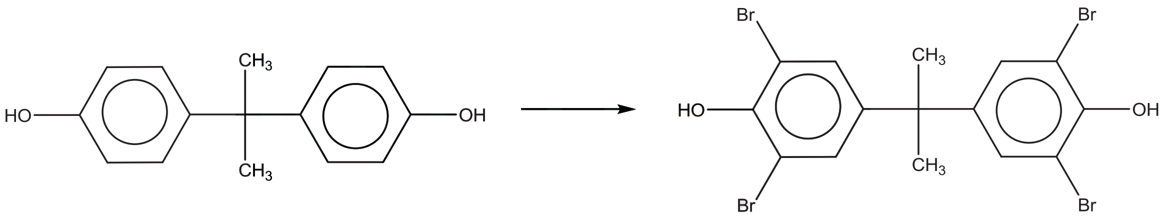
Answer: **D**







22 Bisphenol A was used to make products such as plastic polycarbonate baby bottles and food containers. It is now regarded as toxic and has been withdrawn from use.



bisphenol A compound **Q**

Which reagent will convert bisphenol A into compound **Q**?

A $AlBr_3(s)$

B $Br_2(aq)$

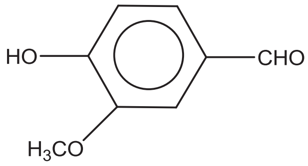
C HBr(g)

D NaBr(aq)

Answer: **B**

Based on the product, the reaction is electrophilic substitution. Since the starting reactant is a phenol, catalyst will not be necessary. Hence Br_2(aq) will be sufficient.

23 Vanillin is the active ingredient of vanilla.



vanillin

Which of the following will be observed with vanillin?

1 Warm acidified potassium dichromate (VI) turns green.
2 2,4-dinitrophenylhydrazine reagent gives an orange precipitate.
3 A yellow precipitate is formed on warming with aqueous alkaline iodine.

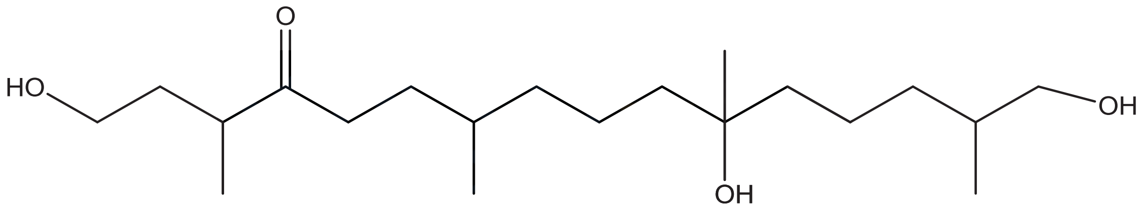
A 1 only
B 2 only
C 1 and 2 only
D 2 and 3 only

Answer: **C**

Option **1** and **2** are correct as Vanillin has the aldehyde group which can be oxidised by potassium dichromate and react with 2,4-DNPH.

Option **3** is not correct as there is no presence of CH_3CO- or $CH_3CH(OH)$- group in vanillin hence it does not react with aqueous alkaline iodine.

24 The mould *Phytophthora* damages many plants, destroying agricultural crops such as potatoes. A hormone-like compound called alpha1 regulates the reproduction of all species of *Phytophthora*. The structure of alpha1 is now known, giving scientist a key to the possible future eradication of the mould.



alpha1

Which of the following reagents will react with alpha1?

1 Br_2
2 $SOCl_2$
3 H_2/Pt

A 1 and 2 only

B 2 and 3 only

C 1 and 3 only

D 1, 2 and 3 only

Answer: **B**

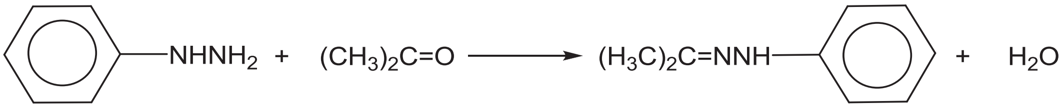
Alpha1 is not able to react with aqueous Br_2 since there is no C=C.

OH group on Alpha1 is able to react with $SOCl_2$ to form halogenoalkane.

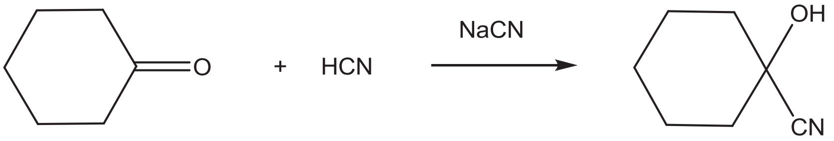
Carbonyl group on alpha1 can be reduced by H_2/Pt to form secondary alcohol.

25 Which transformations involve a nucleophile?

1



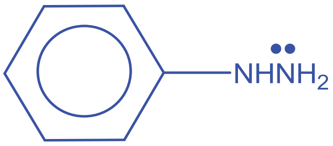
2



3 $CH_3CH_2COCl + NH_3 \longrightarrow CH_3CH_2CONH_2 + HCl$

A 1 only
B 2 and 3 only
C 1 and 2 only
D 1, 2 and 3 only

Answer: **D**



Option **1** is correct as is the nucleophile. Similar to 2,4-DNPH
Option **2** is correct as CN^- is the nucleophile. Reaction is nucleophilic addition.
Option **3** is correct as NH_3 is the nucleophile. Reaction is nucleophilic acyl substitution.

26 Which of the following properties are identical for the two enantiomers of 2-hydroxypropanoic acid, $CH_3CH(OH)COOH$?

1 ΔH^o_f
2 pK_a
3 melting point

A 2 only

B 3 only

C 1 and 2 only

D 1, 2 and 3 only

Answer: **D**

Enantiomers will only differ in their biological properties. Given that they have the same functional group, their chemical and physical properties should remain the same.

27 When organic compounds **E**, **F**, **G** and **H** are added separately to water, solutions of increasing pH values are obtained. The possible identities of compounds **E** to **H** (not necessarily in that order) are given below.

$CH_3CH_2CO_2H$ CH_3CH_2COCl $(CH_3)_2CHNH_2$ $CH_3CH_2NH_2$

Which is the correct set of identities of compounds **E**, **F**, **G** and **H**?

	E	**F**	**G**	**H**
A	$CH_3CH_2CO_2H$	CH_3CH_2COCl	$CH_3CH_2NH_2$	$(CH_3)_2CHNH_2$
B	$CH_3CH_2CO_2H$	CH_3CH_2COCl	$(CH_3)_2CHNH_2$	$CH_3CH_2NH_2$
C	CH_3CH_2COCl	$CH_3CH_2CO_2H$	$(CH_3)_2CHNH_2$	$CH_3CH_2NH_2$
D	CH_3CH_2COCl	$CH_3CH_2CO_2H$	$CH_3CH_2NH_2$	$(CH_3)_2CHNH_2$

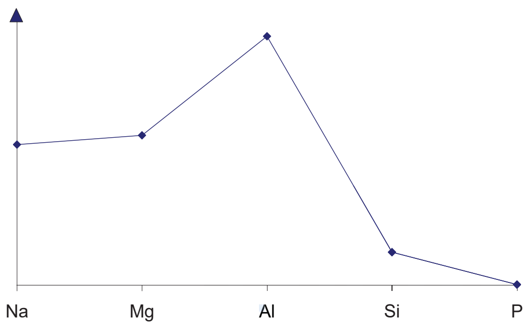
Answer: **D**

Between CH_3CH_2COCl and $CH_3CH_2CO_2H$, $CH_3CH_2CO_2H$ is a weaker acid as one mole of CH_3CH_2COCl will form one mole of CH_3CH_2COOH and one mole of HCl in aqueous solution while CH_3CH_2COOH will only partially dissociate to form H^+. CH_3CH_2COCl will have a lower pH than CH_3CH_2COOH.

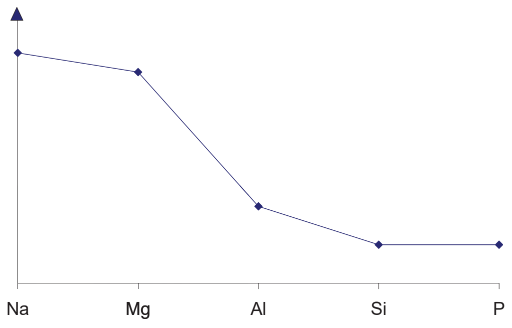
$(CH_3)_2CHNH_2$ is a stronger base as compared to $CH_3CH_2NH_2$ as it has one more methyl electron donating group, hence the lone pair is more available to accept H^+. $(CH_3)_2CHNH_2$ will have a higher pH as compared to $CH_3CH_2NH_2$.

28 The graphs below show the variation in two properties of the elements Na to P and their compounds.

Graph I



Graph II



Which properties are illustrated in Graphs I and II?

	Graph I	Graph II
A	electrical conductivity of the element	pH of the chloride when added to water
B	electrical conductivity of the element	pH of the oxide when added to water
C	melting point of the element	pH of the chloride when added to water

D	melting point of the element	pH of the oxide when added to water

Answer: **A**

Graph 1:
Electrical conductivity increases from Na to A*l* due to the increasing amount of delocalised electrons. Si is a semiconductor / metalloid hence it is able to conduct electricity. Phosphorus is a non-metal with a simple covalent structure. Hence it is unable to conduct electricity.

Melting point of graph should increase from Na to A*l* and peak at Si as Si has a giant covalent structure. Hence, options C and D are eliminated.

Graph 2:
$NaCl$ - pH 7
$MgCl_2$ – pH 6.5
$AlCl_3$ – pH 3
$SiCl_4$ – pH 2
PCl_5 – pH 2

Na_2O – pH 13
MgO – pH 10
Al_2O_3 – not soluble hence pH 7
SiO_4 – not soluble hence pH 7
P_4O_{10} – pH 2

29 Which of the following elements is expected to show the greatest tendency to form some covalent compounds?

A Barium

B Calcium

C Magnesium

D Potassium

Answer: **C**

The metal cation with the highest charge density will have the greatest polarising power and hence the greatest tendency to form covalent compounds.

Charge density = charge / ionic radius

Since Mg has a charge of +2 and the smallest size, it has the highest charge density

30 Why is hydrogen iodide a stronger acid than hydrogen chloride?

A A molecule of hydrogen chloride is more polar than a molecule of hydrogen iodide.

B The enthalpy change of formation of hydrogen iodide is greater than that of hydrogen chloride.

C The covalent bond in the hydrogen iodide molecule is weaker than that in the hydrogen chloride molecule.

D The dissociation of hydrogen chloride molecules is suppressed by the stronger permanent dipole–permanent dipole interactions.

Answer: **C**

For HI and HC*l* to form acids, the H – X bond must be broken and the molecules need to dissociate in water to form H^+ and X^- ions.
Hence, the molecule with the weaker H – X bond will be able to dissociate to a greater extent to form more H^+ ions to be the stronger acid.

INNOVA JUNIOR COLLEGE
JC2 PRELIMINARY EXAMINATION
in preparation for General Certificate of Education Advanced Level
Higher 2

CANDIDATE NAME	**WORKED SOLUTIONS**
CLASS	
INDEX NUMBER	

CHEMISTRY

9729/02

Paper 2 Structured Questions

24 August 2017

Candidates answer on the question paper.

2 hours

Additional Materials: *Data Booklet*

READ THESE INSTRUCTIONS FIRST

Write your index number, name and civics group on all the work you hand in.
Write in dark blue or black pen.
You may use pencil for any diagrams, graphs or rough working.
Do not use staples, paper clips, highlighters, glue or correction fluid.

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

You are advised to show all working in calculations.
You are reminded of the need for good English and clear presentation in your answers.
You are reminded of the need for good handwriting.
Your final answers should be in 3 significant figures.

You may use a calculator.

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

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

For Examiner's Use	
1	19
2	12
3	10
4	10
5	24
Significant Figures and Units	
Handwriting and Presentation	
Total	75

This document consists of **18** printed pages.

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

1 Halogens are highly reactive and form compounds with many other elements, including metals and non-metals.

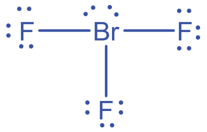
(a) Fluorine reacts with bromine to form liquid bromine trifluoride, BrF_3.

Two molecules of BrF_3 react to form ions as shown by the following equation.

$$2BrF_3 \longrightarrow BrF_2^+ + BrF_4^-$$

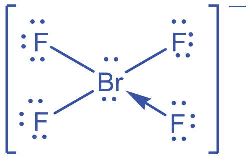
(i) Draw the structures and suggest the shape of each of these species. [3]

BrF_3



T-shaped

BrF_4^-



Square planar

(ii) BrF_4^- ions are also formed when potassium fluoride, KF dissolves in liquid BrF_3 to form $KBrF_4$. Explain, in terms of structure and bonding, why $KBrF_4$, has a high melting point.

[2]

$KBrF_4$ has a **giant ionic structure** with **strong electrostatic forces of attraction between oppositely charged ions**, K^+ and BrF_4^-.

Large amount of energy is required to break the strong ionic bonds, thus it has a high melting point.

(b) Magnesium bromide, $MgBr_2$ is a chemical compound of magnesium and bromine and is often used in the pharmaceutical industries.

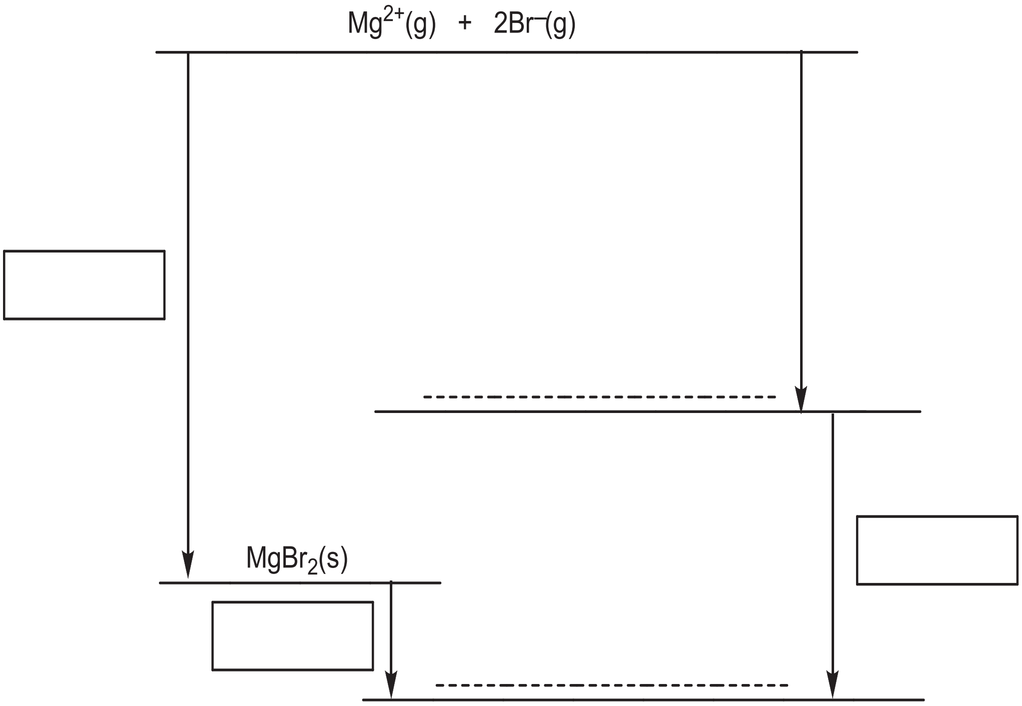
In this part of the question, you will construct an energy cycle for magnesium bromide to determine the enthalpy change of hydration of magnesium ions.

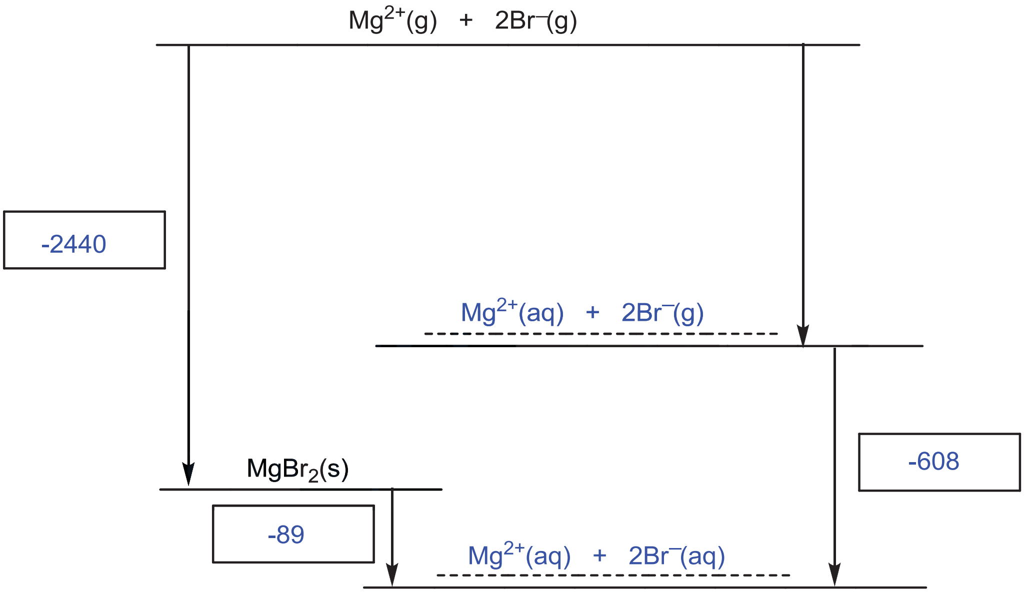
(i) Magnesium bromide has a lattice energy of –2440 kJ mol^{-1}.
Define in words the *lattice energy of magnesium bromide*. [1]
Lattice energy of $MgBr_2$ is the **enthalpy change/ energy released** when **ONE mole of solid $MgBr_2$ is formed from its separate gaseous ions, $Mg^{2+}(g)$ and $Br^-(g)$**.

(ii) The table below shows the enthalpy changes that are needed to determine the enthalpy change of hydration of magnesium ions.

enthalpy change	**energy /kJ mol^{-1}**
lattice energy of magnesium bromide	–2440
enthalpy change of solution of magnesium bromide	–89
enthalpy change of hydration of bromide ions	–304

On the two dotted lines, add the species present and label the numerical values of the three arrows in the boxes provided. [2]





Species on the 2 dotted lines
Three numerical values

(iii) Calculate the enthalpy change of hydration of magnesium ions. [1]

Enthalpy change of hydration = –2440 – 89 + 608 = –1921

= **–1920 kJ mol^{-1}**

(iv) Given that the enthalpy change of formation of $Mg^{2+}(aq)$ is +413 kJ mol^{-1}, use your answer in **(b)(iii)** as well as relevant values from the *Data Booklet* to calculate the enthalpy change of atomisation of magnesium. [1]

$$\begin{tikzcd}
Mg(s) \arrow[r, "\Delta H_{atom}"] \arrow[dr, "413"'] & Mg(g) \arrow[r, "736 + 1450"] & Mg^{2+}(g) \arrow[dl, "-1921"] \\
& Mg^{2+}(aq) &
\end{tikzcd}$$

$\Delta H_{atomisation} = 413 + 1921 - 736 - 1450$
$= \mathbf{+148\ kJ\ mol^{-1}}$

(v) The enthalpy change of hydration of magnesium ions is more exothermic than the enthalpy change of hydration of calcium ions. Explain why. [1]

- $\Delta H_{hydration} \propto \frac{q_+}{r_+}$ or in words
- Mg^{2+} has **higher charge density than Ca^{2+} since Mg^{2+} has a smaller ionic size than Ca^{2+}** and hence a more exothermic $\Delta H_{hydration}$.

(c) Nickel is a typical transition element in the d-block of the Periodic Table. Many nickel ions are able to interact with ligands to form complex ions, such as $[Ni(H_2O)_6]^{2+}$.

A student dissolves nickel(II) sulfate in water. A green solution forms containing the complex ion $[Ni(H_2O)_6]^{2+}$. The student then reacts separate portions of the green solution of nickel(II) sulfate as outlined below.

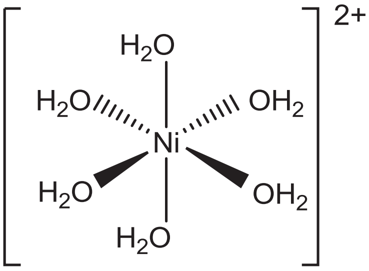
- Concentrated hydrochloric acid is added to the green solution of nickel(II) sulfate until there is no further change. The solution turns a lime-green colour and contains the four-coordinate complex ion **A**.
- Aqueous sodium hydroxide is added to the green solution of nickel(II) sulfate. A pale-green precipitate **B** forms.
- Concentrated aqueous ammonia is added to the green solution of nickel(II) sulfate until there is no further change. The solution turns a violet colour and contains the complex ion **C**. **C** has a molar mass of 160.7 g mol^{-1}.

(i) Explain why aqueous nickel(II) sulfate is green. [2]

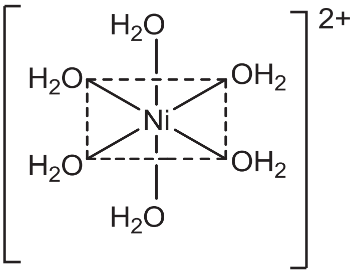
$NiSO_4$ (aq) is coloured due to:

- the presence of **partially filled 3d–orbitals** in the Ni^{2+} metal ions.
- In the **presence of ligands**, **3d orbitals split into two groups with small energy gap**
- Some of the **light energy is used to promote an electron from a d-orbital of lower energy into the unfilled/ partially filled d-orbital of higher energy.**
- Green colour seen is the **complement of the red colour absorbed** in the visible region of the spectrum.

(ii) Draw a three dimensional diagram for the $[Ni(H_2O)_6]^{2+}$ ion. [1]



OR



(iii) Suggest the formulae of **A**, **B** and **C**. [3]

A: $[NiCl_4]^{2-}$

B: $Ni(OH)_2$ or $Ni(H_2O)_4(OH)_2$

C: $[Ni(NH_3)_6]^{2+}$, do not allow $[Ni(NH_3)_4(H_2O)_2]^{2+}$ due to M_r of C given

(iv) What type of reaction has taken place in the formation of **C** from $[Ni(H_2O)_6]^{2+}$?
Write an equation for this reaction. [2]

Ligand exchange

$[Ni(H_2O)_6]^{2+} + 6NH_3 \rightarrow [Ni(NH_3)_6]^{2+} + 6H_2O$

[Total: 19]

2 **(a)** In a school lab, magnesium strips can be stored in a normal container. However, barium metal has to be submerged in oil when it is stored. With reference to relevant data from the *Data Booklet*, explain the above observation. [2]

Reduction potential for Ba^{2+} **(-2.92V)** **is more negative** than Mg^{2+} **(-2.38V)** . **Ba is more reactive OR undergoes oxidation more readily than Mg**, thus has to be kept in oil to prevent it from reacting OR avoid direct contact with atmospheric O_2 .

(b) When solid barium carbonate is heated, no carbon dioxide is detected as it is thermally stable.

However, magnesium carbonate decomposes on heating as shown by the equation below.

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

$$\Delta H^\ominus = +117 \text{ kJ mol}^{-1}; \quad \Delta S^\ominus = +175 \text{ J mol}^{-1} \text{ K}^{-1}$$

(i) Explain why barium carbonate is thermally stable while magnesium carbonate is not. [2]

Ba^{2+} ion is **larger and has a smaller charge density** than Mg^{2+}.

Ba^{2+} ion (has a smaller polarizing power) is able to **polarize/ distort the large electron cloud of the carbonate ion less effectively** than Mg^{2+} , **weakening the C-O bond to a smaller extent**.

More energy is required to break the C – O bond in $BaCO_3$ than $MgCO_3$.

(ii) Account for the sign of $\Delta S^\ominus$ in this reaction. [1]

There is an **increase in disorderliness** due to increase in the number of **moles** of gaseous particles , resulting in more ways to arrange the particles in the system.

(iii) Calculate the standard Gibbs free energy change, $\Delta G^\ominus$, for the decomposition of magnesium carbonate. [1]

$$\Delta G^\ominus = \Delta H^\ominus - T\Delta S^\ominus$$

$$= +117 - (298 \times \frac{+175}{1000}) = +117 - 52.15$$

$$\approx +64.9 \text{ kJ mol}^{-1}$$

(iv) Assuming that $\Delta H^\ominus$ and $\Delta S^\ominus$ for the reaction are independent of temperature, calculate the temperature at which the decomposition reaction becomes feasible. [1]

$$\Delta G^\ominus = 0 = \Delta H^\ominus - T\Delta S^\ominus = +117 - (\mathbf{T} \times \frac{+175}{1000})$$

T = 669K = 396^0C

At 669K, the decomposition reaction becomes feasible.

(c) The labels of group 2 metal carbonates fell off the bottles. In an attempt to identify the compound in one of the bottles, the following experiment was carried out.

1.68 g of an insoluble metal carbonate, **D**CO_3 was reacted with 100 cm^3 of hydrochloric acid of concentration 0.500 mol dm^{-3}. The resulting solution was then made up to 250 cm^3 with distilled water. 25.0 cm^3 of this solution required 25 cm^3 of 0.04 mol dm^{-3} sodium hydroxide for titration.

(i) Write a balanced equation for the reaction between the metal carbonate and hydrochloric acid. [1]

$DCO_3 (s) + 2HCl (aq) \rightarrow DCl_2 (aq) + H_2O (l) + CO_2 (g)$

(ii) Calculate the relative atomic mass of **D** and hence using the Periodic Table, identify **D**. [4]

Amount of sodium hydroxide that was used for the titration

= (25/1000) x 0.04

= $\underline{\mathbf{1.00 \times 10^{-3}}}$ mol (3sf)

Amount of HC*l* present originally = $\frac{100}{1000}$ x 0.500 = 0.05000 mol

Amount of HC*l* in **<u>25.0 cm³</u>** after reaction with **D**CO_3

= 1.00×10^{-3} mol

Amount of unreacted HC*l* in $\underline{\mathbf{250\ cm^3}}$ = $1.00 \times 10^{-3} \times \frac{250}{25.0}$

= 1.00×10^{-2} mol

Amount of HC*l* reacted with **D**CO_3

= Amount of HC*l* initially – amount of unreacted HC*l*

= 0.05000 - 1.00×10^{-2} = 0.0400 mol

Amount of **D**CO_3 reacted = 0.0400/2 = 0.0200 mol

M_r of **D**CO_3 = 1.68 / 0.0200 = 84

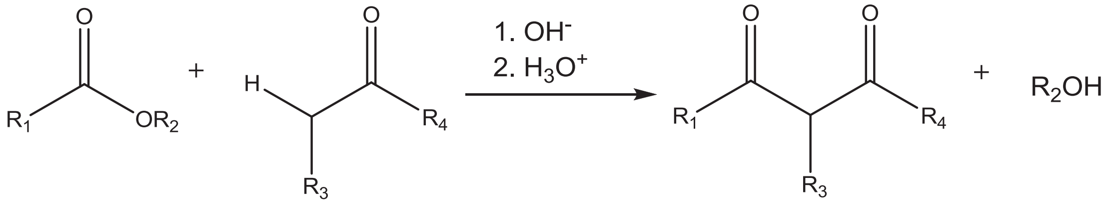
A_r of **D** = 84 – 12.0 – 3 x 16.0 = 24.0 **(must be 1d.p.)**

D = Mg

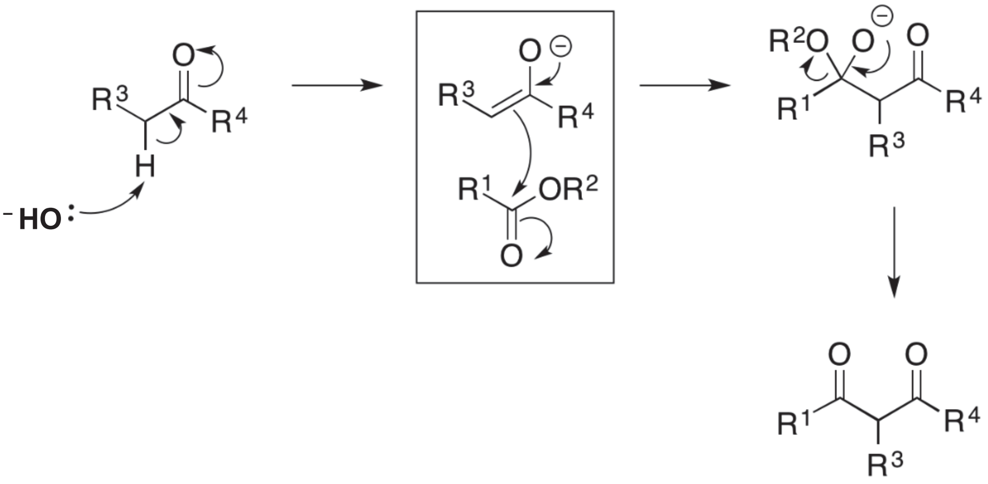
[Total: 12]

3 Claisen condensation is a carbon-carbon bond forming reaction between 2 esters or an ester and a carbonyl compound in the presence of strong base to form β-ketoesters or diketones respectively.

The following is the general equation for the reaction between an ester and a ketone.



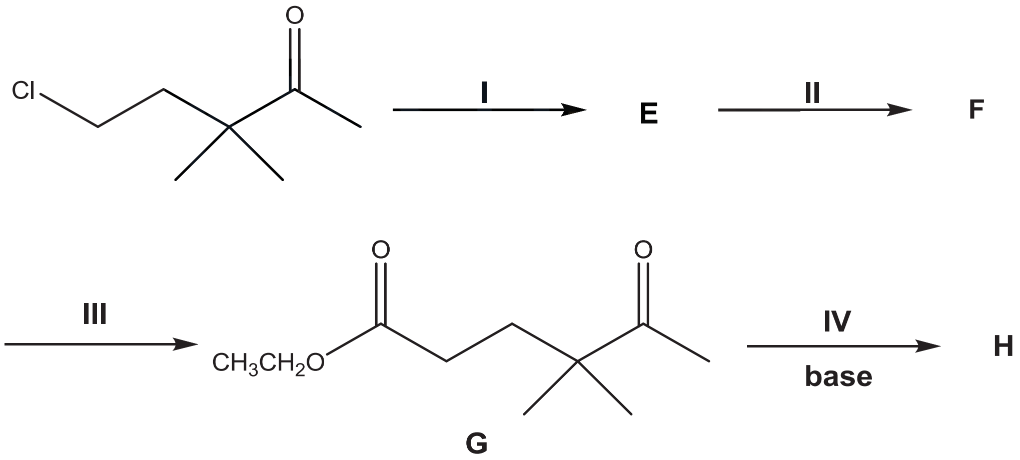
The mechanism of the Claisen condensation reaction is given below.



(a) Name the type of reaction for the step shown in the box above. [1]

Nucleophilic addition

The Claisen condensation reaction can be used in step **IV** of the following synthesis.



(b) **(i)** Suggest reagents and conditions for steps **I** to **III**. [3]

Step I : ethanolic KCN, heat with reflux

Step II : HC*l* (aq) or H_2SO_4 (aq), heat

Step III : C_2H_5OH, trace amount of conc H_2SO_4, heat with reflux

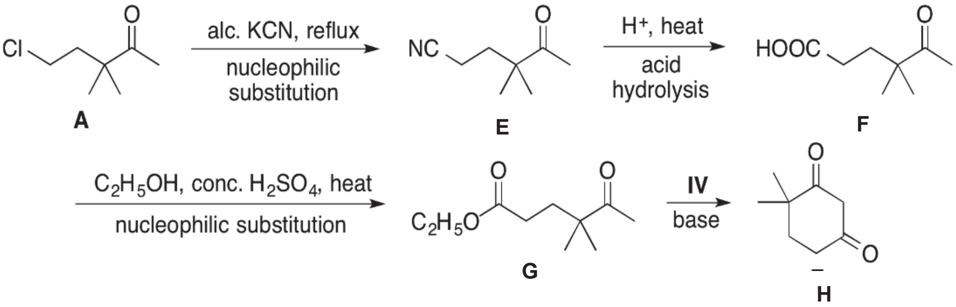
(ii) State the type of reactions for step **I** to **III** [3]

Step I: Nucleophilic substitution

Step II: Acidic hydrolysis

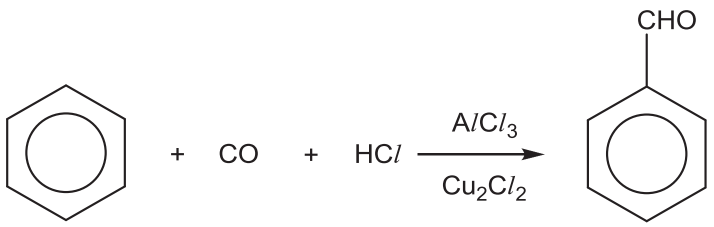
Step III: Condensation or Nucleophilic acyl substitution

(iii) Propose the structures of compounds **E**, **F** and **H**. [3]



[Total: 10m]

4 **(a)** The Gattermann-Koch reaction, named after the German chemists Ludwig Gattermann and Julius Arnold Koch in organic chemistry, refers to a Friedel-Crafts acylation reaction in which carbon monoxide and hydrochloric acid are used in-situ with Friedel-Crafts catalyst, namely $AlCl_3$. The reaction involves an acylium ion as an electrophile and tetrachloroaluminate ion, $AlCl_4^-$. An example is provided below.



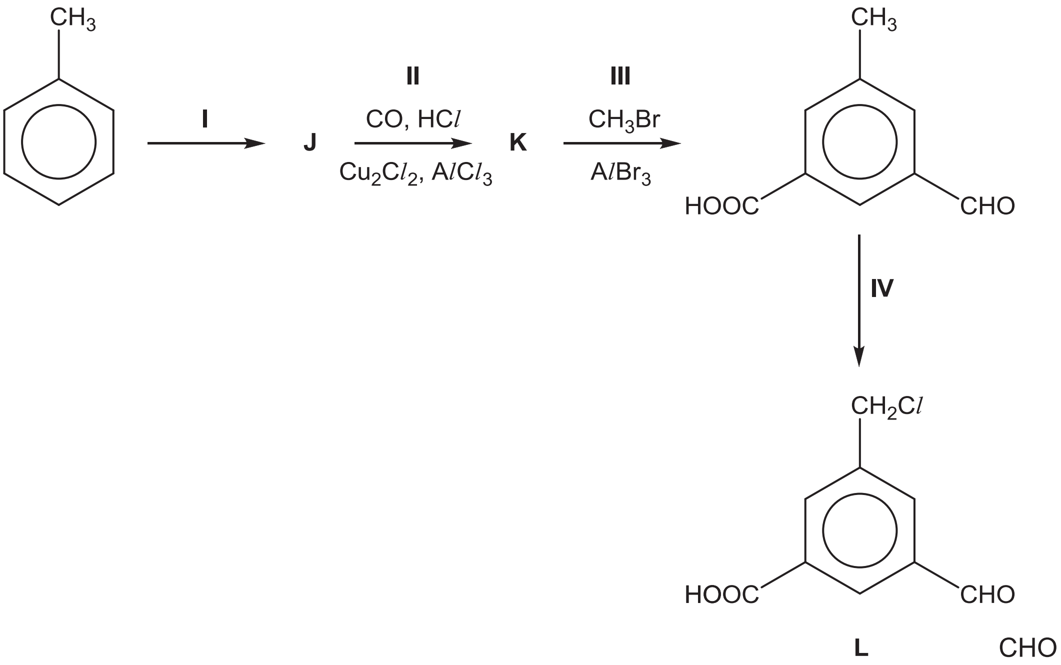
(i) Give the formula of the acylium ion in this reaction.

[1]

^{+}CHO

(ii) The synthesis of compound **L** involves the Gattermann-Koch reaction in Step **II**.

Complete the reaction scheme below by providing the appropriate reagents and conditions for Step **I** and **IV** and give the structural formula for **J** and **K**.

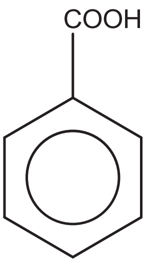


[4]

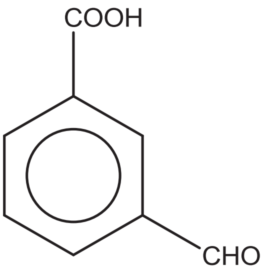
Step I: $KMnO_4$, dil H_2SO_4, heat with reflux

Step IV: limited Cl_2 (g) or limited Cl_2 in CCl_4, UV light

J:



K:



(b) Three non-cyclic organic compounds, **M**, **N** and **P** each have the same empirical formula CH_2O.
The number of carbon atoms in their molecules are shown in the table below.

compound	number of C atoms
M	2
N	3
P	3

All the carbon atoms are bonded directly to one another in **M** and in **N** but not in **P**.

M and **N** each give a brisk effervescence with Na_2CO_3(aq) but not **P**.

P does not give a silver mirror when treated with Tollens' reagent.

(i) Draw the structural formula of **M**.

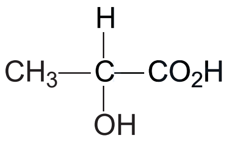
[1]

CH_3COOH

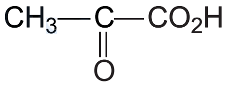
(ii) When **N** is heated under reflux with acidified $K_2Cr_2O_7$, the product, **Q**, gives a orange precipitate with 2,4–dinitrophenylhydrazine.

Draw the structural formulae of **N** and **Q**.

[2]



$CH_3-CH(OH)-CO_2H$



$CH_3-C(=O)-CO_2H$

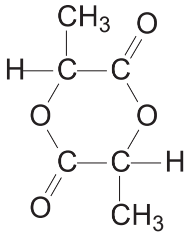
Compound **N**

Compound **Q**

(iii) When **N** is warmed with concentrated sulfuric acid, compound **R** is formed. **R** has the molecular formula $C_6H_8O_4$.

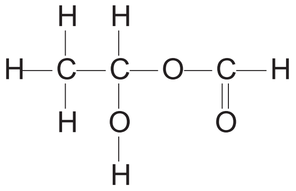
Draw the structural formula of **R.**

[1]



(iv) **P** is optically active. Draw the displayed formula of **P**.

[1]

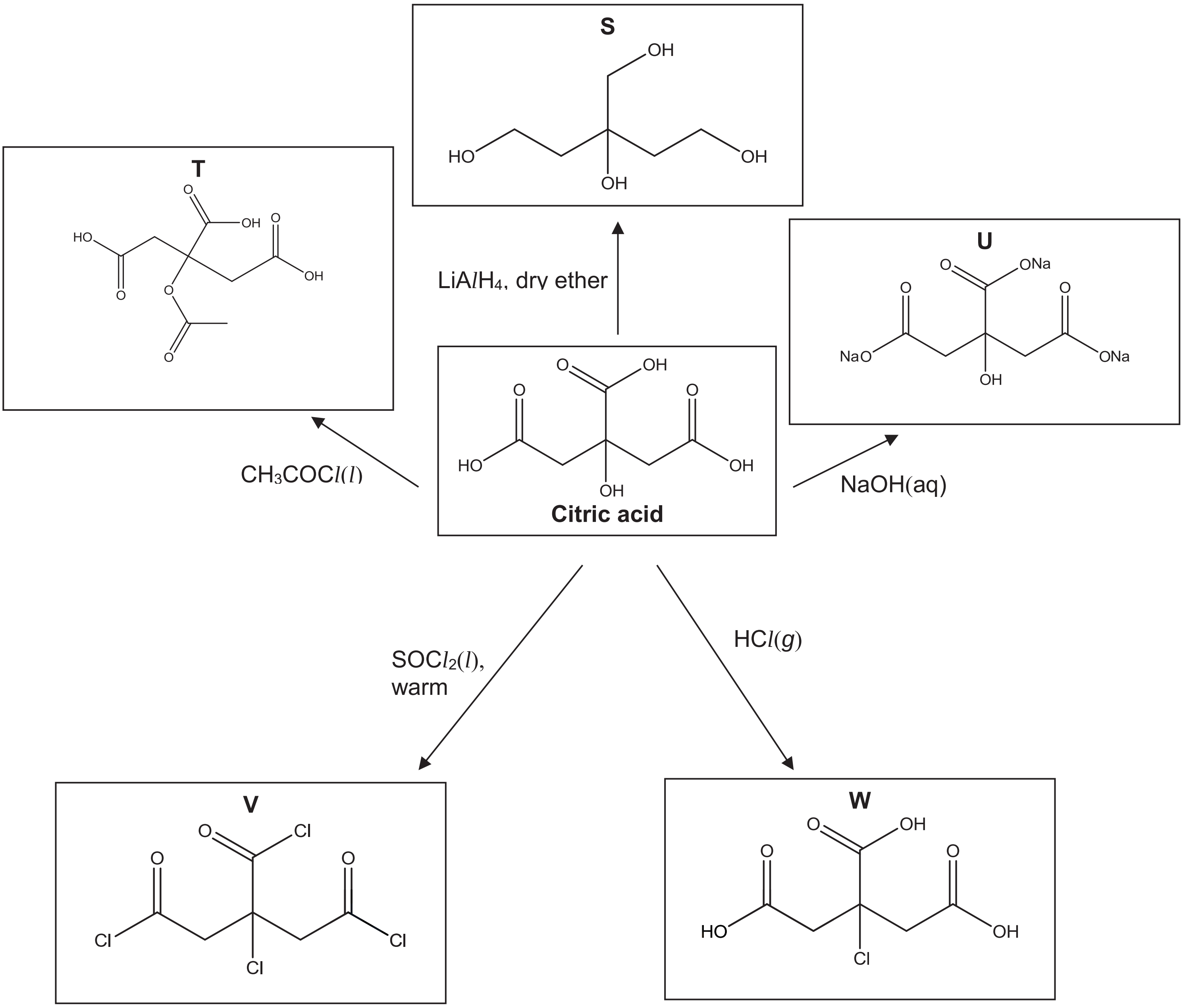


[Total: 10]

5 Citric acid, $C_6H_8O_7$ is produced commercially by the fermentation of sugars. Citric acid is used in the production of beverages and foods; in detergents; and in cosmetics and pharmaceuticals.

Fruits such as oranges, lemons and strawberries also contain citric acid.

(a) Citric acid can undergo the following reactions:



Suggest structures for the organic compounds **S, T, U, V** and **W**.

[5]

(b) As citric acid is a user-friendly, inexpensive, water-soluble crystalline solid, it is often used for finding the concentration of alkalis e.g. sodium hydroxide and potassium hydroxide.

Citric acid is a tribasic acid with the following pK_a values:

pK_1 = 3.14, pK_2 = 4.75 , pK_3 = 6.40

(i) Explain why citric acid is soluble in water.
Citric acid has (3 **COOH groups)** which can form **hydrogen bonds** with water molecules.

[1]

(ii) The pK_a value of ethanoic acid, CH_3COOH is 4.76.

Suggest why the pK_1 value of citric acid is lower than the pK_a value of ethanoic acid.

The anion formed by citric acid contains **two electron withdrawing –COOH group** which **disperses the negative charge** on the oxygen atom of the anion.
Thus, the anion formed by citric acid is **more stable than the ethanoate anion** and hence citric acid is **stronger**/ has a lower pK_a value**.**

OR

The anion formed by citric acid is further **stabilised by intramolecular hydrogen bonding** with the neighbouring COOH groups.
Thus, the anion formed by citric acid is **more stable than the ethanoate anion** and hence citric acid is **stronger**/ has a lower pK_a value .

[2]

(iii) Calculate the pH of a solution that is a mixture of equal volumes of 0.100 mol dm^{-3} of citric acid and 0.060 mol dm^{-3} of sodium hydroxide.

A buffer solution is formed.

New initial concentration of citric acid = 0.100 / 2 = 0.050 mol dm^{-3}

New initial concentration of NaOH = 0.060 / 2 = 0.030 mol dm^{-3}

$C_6H_8O_7 + OH^- \rightarrow C_6H_7O_7^- + H_2O$

After reaction

Final concentration of citric acid salt, $C_6H_7O_7^-$ = **0.030 mol dm^{-3}**

Final concentration of citric acid = 0.050 – 0.030 = **0.020 mol dm^{-3}**

$$\text{pH of solution} = \mathrm{p}K_1 + \log_{10}\frac{[C6H7O7-]}{[C6H8O7\,]}$$
$$= 3.14 + \log_{10}\left[\frac{0.030}{0.020}\right] = 3.316 = \mathbf{3.32}$$

[2]

(c) The neutralisation equivalent (N.E.) of a carboxylic acid is defined as the mass in g of the acid required to neutralise one mole of a strong alkali such as sodium hydroxide. Each carboxylic acid has a unique N.E. value.

N.E. values can be used to determine the identity of a carboxylic acid.

A student carried out a titration experiment between a sample of citric acid and sodium hydroxide solution. 3.68 g of the citric acid was dissolved in 500 cm^3 of water in a volumetric flask. It was found that 5.00 cm^3 of the citric acid solution needed 5.29 g of 4.43 g dm^{-3} sodium hydroxide solution for complete reaction.

(i) Calculate the mass, in g, of the citric acid used in the 5 cm^3 sample.

Mass of citric acid = 3.68 x $\frac{5.00}{500}$ = 0.0368 g

[1]

(ii) Calculate the amount, in moles, of sodium hydroxide that reacted with the 5 cm^3 of citric acid.

The density of the sodium hydroxide solution is 1.01 g cm^{-3}.

Concentration of NaOH = $\frac{4.43}{40}$ = 0.11075 mol dm^{-3}

Volume of NaOH used = 5.29/1.01 = 5.2376 cm^3

Moles of NaOH used = $\frac{5.2376}{1000} \times 0.11075$ = 5.801 x 10^{-4} mol (4 s.f.)
= 5.80 x 10^{-4} mol (3 s.f.)

[2]

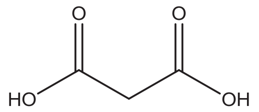
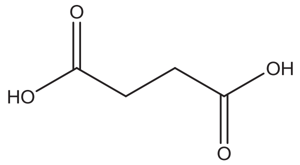
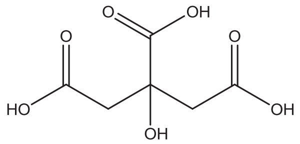
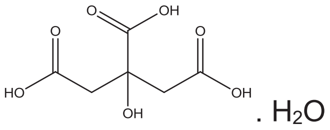
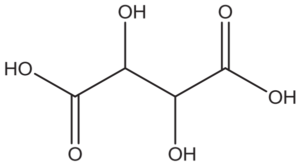
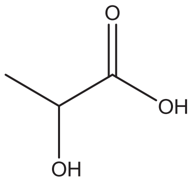
(iii) Calculate the neutralisation equivalent (N.E.) for this sample of citric acid.

Neutralisation Equivalent = $\frac{0.0368}{5.801 \times 10^{-4}}$ = 63.4

[1]

(d) Table 5.1 gives the neutralisation equivalent (N.E.) values for some organic acids.

Table 5.1

Acid name	**Structure**	**Molar mass/ g mol^{-1}**	**N.E. / g**
Malonic acid		104.0	52.0
Succinic acid		118.0	59.0
Anhydrous citric acid		192.0	64.0
Citric acid monohydrate		210.0	70.0
Tartaric acid		150.0	*m*
Lactic acid		90.0	90.0

(i) Suggest whether the student's sample of citric acid is a hydrated sample or anhydrous sample. Support your answer with appropriate evidence.

Anhydrous citric acid. The calculated value of N.E. is 63.4 and this is close to the theoretical value of 64.0.

[2]

(ii) Determine the value of *m* in Table 5.1.

N.E. for tartaric acid = $\frac{150.0}{2}$ = 75.0

[1]

(e) Another student determines the N.E. of an unknown aliphatic acid to be 82.0 g.

The unknown aliphatic acid has the following formula, $C_xH_y(COOH)_n$ where *x* and *y* are integers and n = 1, 2 or 3.

Determine the molecular formula of the unknown aliphatic acid.

The molar mass of the acid is either:

82.0 g mol^{-1} for a monobasic acid, n = 1
82.0 x 2 = 164.0 g mol^{-1} for a dibasic acid, n = 2
82.0 x 3 = 246.0 g mol^{-1} for a tribasic acid, n= 3

The molar mass of a -COOH group = 12.0 + 2 x 16.0 + 1.0 = 45.0 g mol^{-1}
The molar mass of a $–CH_2–$ group = 12.0 + 2.0 = 14.0 g mol^{-1}

It is a tribasic acid as **246.0 – (3 x 45.0) - (14.0 x 7) = 13.0** g mol^{-1} (equivalent to 1C and 1 H)

The tribasic acid consists of **3 –COOH groups**, **7 $–CH_2–$ groups** and **one C** and one H atom. It is possible to form a molecule using these groups.

The molecular formula is **$C_{11}H_{18}O_6$** or **$C_8H_{15}(COOH)_3$**

Marking guidelines

- 1 mark for calculating the molar mass of the tribasic acid
- 1 mark for explaining why it has to be the tribasic acid using the calculated molar mass
- 1 mark for giving the correct molecular formula
- Working must be shown for the mark to be obtained. No marks to be given if the correct answer is given without any working.

Additional note (not marking points):

It cannot be a monobasic acid as 85.0 = 12.0 + 45.0 + 2 x14.0
There cannot be a structure for 1 –COOH group and 2 $–CH_2–$ groups and 1 C atom. (Molecular formula $C_4H_5O_2$)

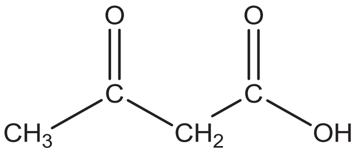
It cannot be a dibasic acid as 164.0 = 2 x 45.0 + 5 x 14.0 + 4.0
There cannot be a structure for 2 –COOH groups and 5 $–CH_2–$ groups and 4 H atoms. (Molecular formula $C_7H_{16}O_4$)

[3]

(f) The loss of carbon dioxide from a carboxylic acid is called decarboxylation.

$$RCOOH \longrightarrow RH + CO_2$$

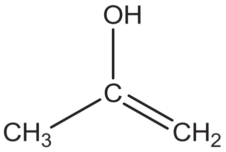
Certain types of carboxylic acids are readily decarboxylated. Beta-keto acids such as acetoacetic acid readily decarboxylate at room temperature in an acidic solution.



acetoacetic acid

The decarboxylation of acetoacetic acid occurs via a two-step mechanism.

- the H atom from the COOH group is transferred to the carbonyl oxygen atom via a cyclic transition state to form CO_2 and the following compound, an enol,

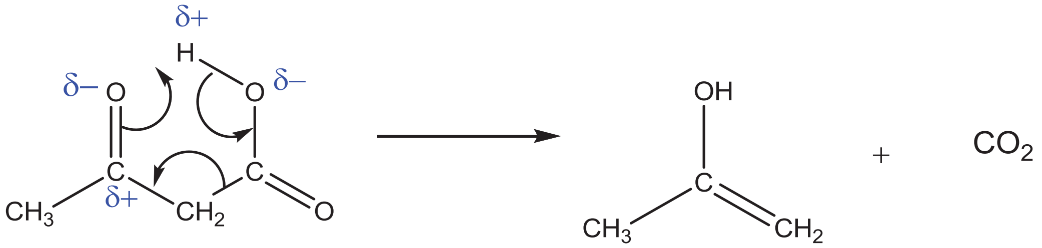


enol

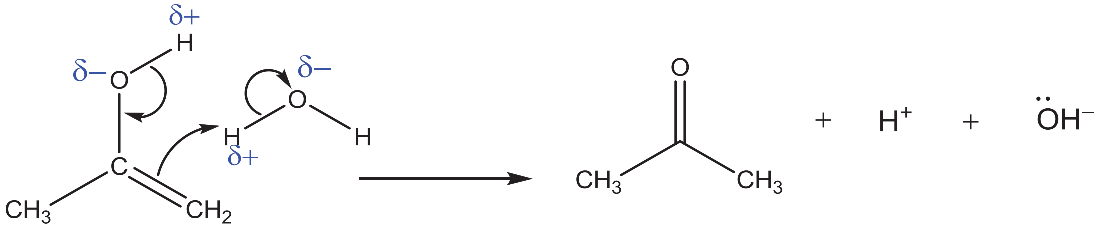
- the enol then extracts a H atom from a H_2O molecule to form a ketone and H^+ and OH^- ions.

Suggest the mechanism for this reaction. Show any relevant lone pairs, dipoles and charges, and indicate the movement of electron pairs with curly arrows.

Step 1



Step 2



[4]

[Total: 24]

INNOVA JUNIOR COLLEGE
JC 2 PRELIMINARY EXAMINATION
in preparation for General Certificate of Education Advanced Level
Higher 2

CHEMISTRY 9729/03

Paper 3 Free Response **13 September 2017**
2 hours

Candidates answer on separate paper.

Additional Materials: Writing Papers
Data Booklet
Cover Page

READ THESE INSTRUCTIONS FIRST

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

Section A
Answer **all** questions.

Section B
Answer **one** question.

You are advised to show all working in calculations.
You are reminded of the need for good English and clear presentation in your answers.
You are reminded of the need for good handwriting.
Your final answers should be in 3 significant figures.

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

This document consists of **20** printed pages.

Section A

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

1 Benzoic acid, C_6H_5COOH is a colourless crystalline solid and a simple aromatic carboxylic acid. Benzoic acid occurs naturally in many plants. Salts of benzoic acid are used as food preservatives and benzoic acid is an important precursor for the industrial synthesis of many other organic substances.

(a) In the identification of benzoic acid, a commonly used reagent is neutral iron(III) chloride solution, in which a buff precipitate of iron(III) benzoate, $Fe(C_6H_5CO_2)_3$ is formed. When 50.0 cm^3 of iron(III) chloride solution was added to 50.0 cm^3 of benzoic acid solution, 0.0532 g of the buff precipitate was formed in the mixture.

The reactions that take place are shown below:

$$C_6H_5CO_2H \rightleftharpoons C_6H_5CO_2^- + H^+$$

$$Fe^{3+} + 3C_6H_5CO_2H \longrightarrow Fe(C_6H_5CO_2)_3 + 3H^+$$

(Given: M_r of $Fe(C_6H_5CO_2)_3 = 418.8$)

(i) Calculate the number of moles of benzoic acid that reacted with the neutral iron(III) chloride solution.

[1]

Number of moles of $Fe(C_6H_5CO_2)_3$ = 0.0532 / 418.8
= 1.2703×10^{-4} mol

$C_6H_5CO_2^- \equiv C_6H_5CO_2H$

Number of moles of benzoic acid reacted = $3 \times 1.2703 \times 10^{-4}$
= 3.8108×10^{-4}
= 3.81×10^{-4} mol

(ii) Given that the pH of the solution after the reaction is 2.33, calculate the number of moles of H^+ in the mixture.

[1]

$[H^+] = 10^{-2.33} = 4.677 \times 10^{-3}$ mol dm^{-3}

Number of moles of H^+ = $0.100 \times 4.677 \times 10^{-3}$
= 4.677×10^{-4}
= 4.68×10^{-4} mol

(iii) Assuming that the H^+ ions in solution are formed only from the dissociation of benzoic acid in solution, as well as the reaction of benzoic acid with iron(III) chloride, calculate the concentration of benzoate ions in the mixture.

[2]

Since the H^+ comes from both dissociation of benzoic acid and reaction of benzoic acid with iron (III) chloride,

Number of moles of benzoate in solution = $4.677 \times 10^{-4} - 3.8108 \times 10^{-4}$
= 8.6655×10^{-5} mol

Concentration of benzoate in solution = moles / volume
= 8.6655×10^{-5} / [(50 + 50)/1000]
= 8.67×10^{-4} mol dm^{-3}

Allow ecf

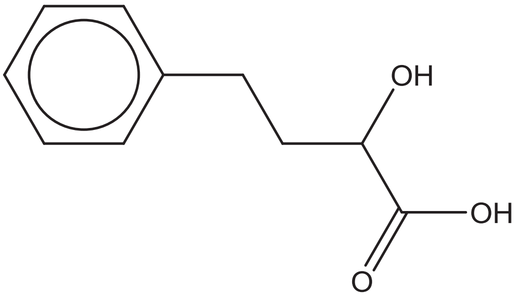
(iv) Iron(III) benzoate is a sparingly soluble sa

Calculate the K_{sp} of iron(III) benzoate, given that the concentration of Fe^{3+} in the mixture was 1.83×10^{-3} mol dm^{-3} at equilibrium.

[1]

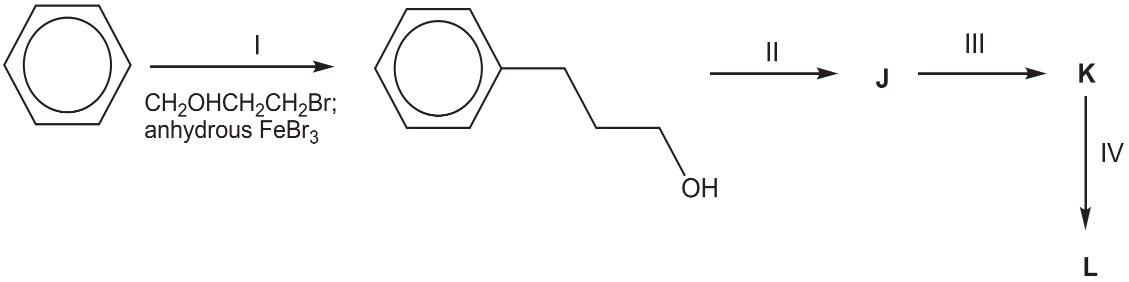
K_{sp} = $[Fe^{3+}] [C_6H_5CO_2^-]^3$
= $(1.83 \times 10^{-3}) (8.6655 \times 10^{-4})^3$
= 1.1908×10^{-12}
= 1.19×10^{-12} mol^4 dm^{-12}
Allow ecf

(b) Benzoic acid can be produced by oxidising compound **L**.



Compound **L**

Compound **L** can be synthesised by the following reaction scheme.



(i) State the *type of reaction* in step I and hence explain the need for $FeBr_3$ to be anhydrous.

[2]

Electrophilic substitution

The catalyst will be hydrolysed and lose its catalytic property if it is dissolved in water.

$FeBr_3$ has to be anhydrous as it has to be electron deficient to accept a lone pair of electron from the Br in $CH_3(CH_2)_3Br$ to form the electrophile $CH_3(CH_2)_3^+$ for electrophilic substitution to take place.

If water is present, $Fe^{3+}(aq)$ will be present and the electrophile $CH_3(CH_2)_3^+$ will not be formed.

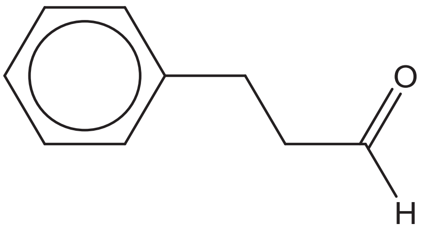
$Fe^{3+}(aq)$ will undergo hydrolysis:

$[Fe(H_2O)_6]^{3+} + H_2O \rightleftharpoons [Fe(H_2O)_5(OH^-)]^{2+} + H_3O^+$

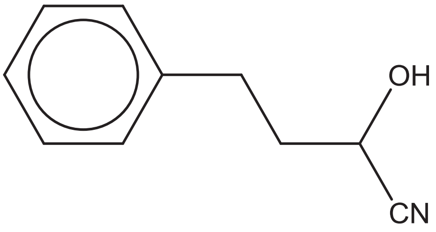
(ii) Suggest the identities of **J** and **K**.

[2]

J:



K:



(iii) State the reagents and conditions for steps II to IV. [3]

II: $K_2Cr_2O_7$, dilute H_2SO_4, heat with immediate distillation

III: HCN, trace amount of NaCN or NaOH, cold

IV: dilute H_2SO_4 or dilute HCl, heat

(iv) State the *type of reaction* for stage IV. [1]

Acidic hydrolysis

[Total: 13]

2 Sulfur is a chemical element with the symbol S and an atomic number of 16. It is an abundant, multivalent non-metal. It can be found in amino acids and as a precursor to other chemicals such as H_2SO_4. H_2SO_4 is a common mineral acid with many uses. It can be used as an electrolyte in batteries.

(a) In the cells of a lead-acid car battery the following reactions take place.

anode: $Pb(s) \longrightarrow Pb^{2+}(aq) + 2e^-$

cathode $PbO_2(s) + 4H^+(aq) + 2e^- \longrightarrow Pb^{2+}(aq) + 2H_2O(l)$

(i) Use the *Data Booklet* to calculate E^θ_{cell} for this reaction. [1]

E^θ cell = 1.47–(–0.13) = +1.60V

(ii) Construct an equation for the overall reaction. [1]

$PbO_2 + Pb + 4H^+ \longrightarrow 2Pb^{2+} + 2H_2O$

The electrolyte in a lead-acid cell is $H_2SO_4(aq)$. Most of the $Pb^{2+}(aq)$ ions that are produced at the electrodes are precipitated as a highly insoluble $PbSO_4(s)$.

(iii) Construct an equation for the overall cell reaction in the presence of H_2SO_4. [1]

$PbO_2 + Pb + 4H^+ + 2SO_4^{2-} \longrightarrow 2PbSO_4 + 2H_2O$

(iv) By considering the effect of decreasing [Pb^{2+}(aq)] on the electrode potentials of the cathode and the anode, state and explain whether the overall E^{θ}_{cell} will *increase*, *decrease* or *remain the same*.

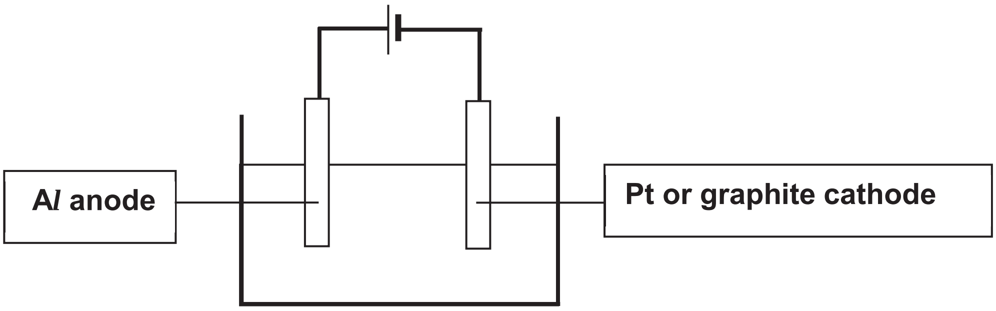
[1]

Overall E^{θ}_{cell} will increase as [Pb^{2+}] decreases, $E^{\theta}(PbO_2/Pb^{2+})$will become more positive, but $E^{\theta}(Pb^{2+}/Pb)$ will become more negative

(b) H_2SO_4 is also used as an electrolyte in the anodising of aluminium. Anodising of aluminium is the process of coating aluminium metal with aluminium oxide (Al_2O_3) via electrolysis with the aluminium metal as the anode.

(i) Using H_2SO_4(aq) as the electrolyte and an inert electrode, draw an electrolysis set-up to show how a piece of aluminium metal can be anodised.

[1]



- Correct orientation of the battery
- Correct labeling of both the electrodes with the material used
- Correct cell. i.e. An electrolytic cell and not a electrochemical cell

(ii) Write chemical equations to show the reactions at the anode and cathode during anodising. Include in your answers, the overall equation.

[3]

Reaction at the A*l* anode:
$2H_2O\ (l) \longrightarrow O_2\,(g) + 4H^+\,(aq) + 4e$
The oxygen liberated then reacts with the aluminium to produce aluminium oxide protective surface.
$4Al\ (s) + 3O_2\,(g) \longrightarrow 2Al_2O_3\ (s)$
Reaction at the Pt cathode:
$2H^+\ (aq) + 2e \longrightarrow H_2\,(g)$

Overall reaction: $2Al\ (s) + 3H_2O\ (l) \longrightarrow Al_2O_3\ (s) + 3H_2\,(g)$

(iii) The aluminium piece to be anodised has a surface area of 29.2 cm^2. Calculate the time taken to form a 0.2 mm protective layer of Al_2O_3 on the aluminium piece if a current of 2.0 A is passed through the set-up.

(Density of Al_2O_3 is 3.95 g cm^{-3})

[4]

Volume of Al_2O_3 layer = 29.2×0.02
= 0.58400 cm^3
Mass of Al_2O_3 = 3.95×0.584
= 2.3068 g

Amount of Al_2O_3 = $\dfrac{2.3068}{2\times27.0+3\times16.0}$

= 0.022616 mol
Amount of O_2 = 0.0226 × 3/2
= 0.033923 mol
Amount of electrons passed through the anode = 0.0339 × 4
= 0.13569 mol
Q = 0.13569 × 96500
= 13094 C
Time needed =13094 ÷ 2.0
= 6547.2 s = 6550 s (3s.f)

Alternatively from here,
It = n_eF approach

t = (n_eF) / I
= (0.13569 × 96500) / 2.0
= 6547.2 s = 6550 s (3s.f)

(iv) Give one example of an anodised aluminium object, and explain the advantages of anodising it.

[1]

Examples of anodized aluminium objects: drink cans, windows frames and grilles

Anodised aluminium objects are more resistant to corrosion. Moreover, they can be decorative as well since the aluminium oxide layer is able to absorb dyes.

(c) H_2SO_4, can be produced when sulfur trioxide is added to water, according to the following equation:

$$SO_3(g) + H_2O(l) \longrightarrow H_2SO_4(aq)$$

Calculate the volume of gaseous SO_3 under room temperature and pressure, needed to form 30.0 cm^3 of 0.0200 mol dm^{-3} of H_2SO_4.

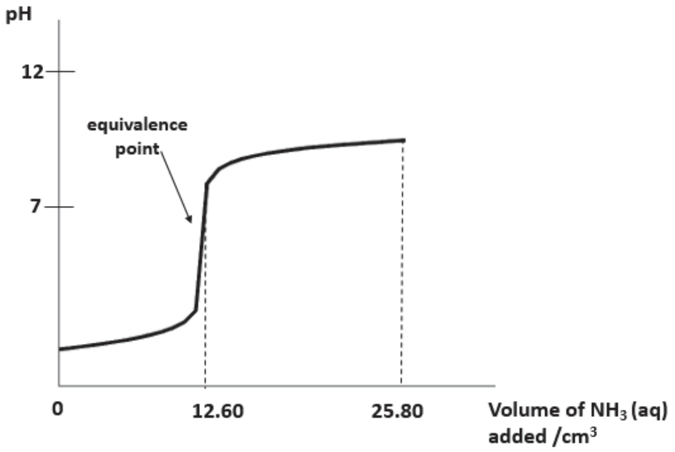
[1]

Amount of H_2SO_4 to be produced = $\frac{30}{1000}$ X 0.02 = 6.00 x 10^{-4}

Amount of SO_3 needed = 6.00 x 10^{-4}

Volume of SO_3 needed at r.t.p = 6.00 x 10^{-4} X 24.0 dm^3
= 0.0144 dm^3

(d) 25.0 cm^3 of 0.0200 mol dm^{-3} of H_2SO_4 was titrated against $NH_3(aq)$.The following graph was obtained.



(i) Calculate the initial pH of the sulfuric acid solution.

[1]

$[H_2SO_4]$ = 0.02 mol dm^{-3}
$[H^+]$ = 0.04 mol dm^{-3}
pH = 1.40

(ii) Calculate the concentration of NH_3 (aq) used in this titration.

[2]

H_2SO_4 (aq) + $2NH_3$ (aq) → $(NH_4)_2SO_4$ (aq)

Amount of H_2SO_4 used in titration = $\frac{25}{1000} \times 0.02 = 5.000 \times 10^{-4}$

Amount of NH_3 used in titration = $\frac{25}{1000} \times 0.02 \times 2 = 1.000 \times 10^{-3}$

$[NH_3] = \frac{1 \times 10^{-3}}{12.60/1000} = 0.0794$ mol dm^{-3}

(iii) Suggest a suitable indicator for this titration, giving a reason for your choice.

[2]

Methyl orange.

The working range for methyl orange (is in the region of 3 to 5 and) coincides with the equivalence point of a strong acid-weak base titration (<7).

[5]

(e) Thiophenol are the sulfur analogue of phenol, that is, sulfur takes the place of oxygen in the hydroxyl group of phenol. A common reaction that phenol and thiophenol have is shown in **Figure 1** below.

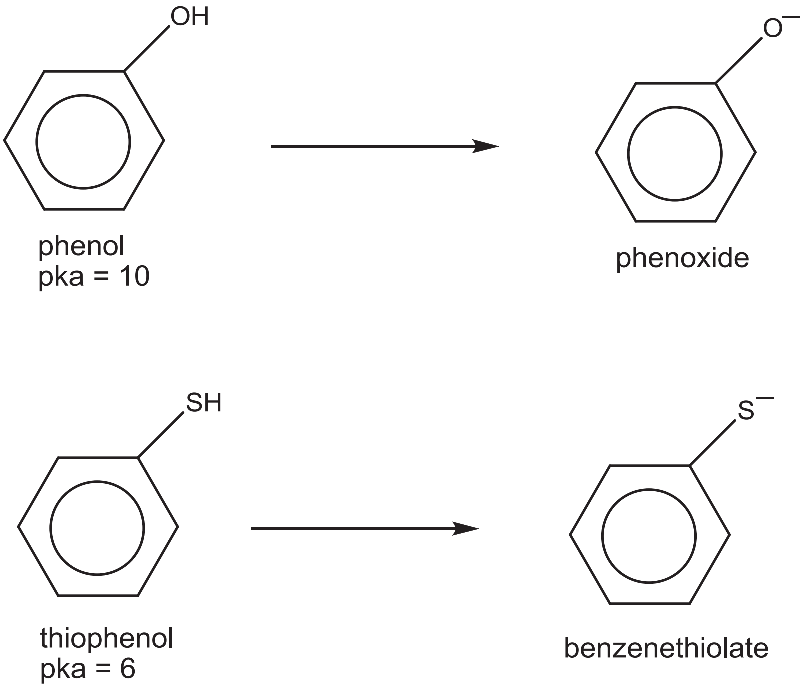
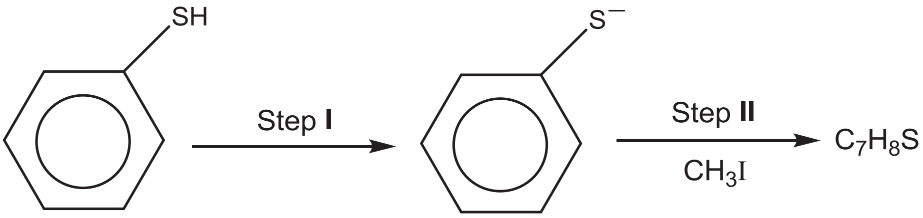


Figure 1

Consider the reaction scheme below.



(i) Suggest reagent and condition for step **I**. [1]

Reagents and Conditions: Na metal at room temperature

OR

Reagents and Conditions: NaOH (aq) at room temperature

(ii) What *type of reaction* is step **I** and step **II**? [2]

Step I

Acid- Metal (if student answer is Na metal)

Accept: Redox

OR

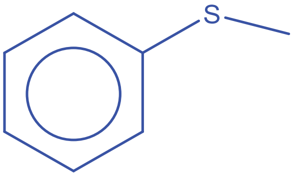
Acid-base if student answer is NaOH(aq)

Step II

Nucleophilic substitution

(iii) Suggest the structure of C_7H_8S.

[1]



[Total: 23]

3 Halogenated organic compounds are widespread throughout nature and have a vast array of uses in modern industrial processes. They find many uses in the industries such as solvents and pesticides.

The rate of hydrolysis of $CH_3CH_2CH_2CH_2Br$ with aqueous NaOH was studied in a series of 3 experiments in which the initial rate of the reaction was measured. The following results were obtained.

Experiment	$[OH^-]$ / mol dm^{-3}	$[CH_3CH_2CH_2CH_2Br]$ / mol dm^{-3}	Initial Rate / mol dm^{-3} s^{-1}
1	0.100	0.010	4×10^{-6}
2	0.200	0.010	8×10^{-6}
3	0.200	0.020	16×10^{-6}

(a) Explain the meaning of the following terms.

(i) order of reaction

(ii) half-life

The order of reaction with respect to a given reactant is the power to which the concentration of that reactant is raised to in the rate equation.

The half-life ($t_{1/2}$) of a reaction is the time taken for the concentration of a reactant to decrease to half its initial value.

[2]

(iii) Using the data given, derive the rate equation for the hydrolysis of $CH_3CH_2CH_2CH_2Br$.

For $CH_3CH_2CH_2CH_2Br$

(inspection method)
Using experiment 1 and 2, when $[OH^-]$ doubles, keeping $[CH_3CH_2CH_2CH_2Br]$ constant, rate doubled. Hence order of reaction with respect to $[OH^-]$ is one.

Using experiment 2 and 3, when $[CH_3CH_2CH_2CH_2Br]$ is doubled, keeping $[OH^-]$ constant, rate doubled. Hence order of reaction with respect to $[CH_3CH_2CH_2CH_2Br]$ is one.

(Substitution method)
Let the rate law be:
Rate = $k[OH^-]^a[CH_3CH_2CH_2CH_2Br]^b$

Using experiment 1 and 2

$$\frac{4\times10^{-6}}{8\times10^{-6}}=\frac{k(0.100)^a(0.010)^b}{k(0.200)^a(0.010)^b}$$

$$(\frac{1}{2})^a=\frac{1}{2}$$

$$a=1$$

Using experiment 2 and 3

$$\frac{8\times10^{-6}}{16\times10^{-6}}=\frac{k(0.010)^b}{k(0.020)^b}$$

$$(\frac{1}{2})^b=\frac{1}{2}$$

$$b=1$$

Rate = k [OH^-][$CH_3CH_2CH_2CH_2Br$]

[3]

(iv) Using your rate equation, determine a value for the rate constant, including units for this reaction.

Rate = k [OH^-][$CH_3CH_2CH_2CH_2Br$]

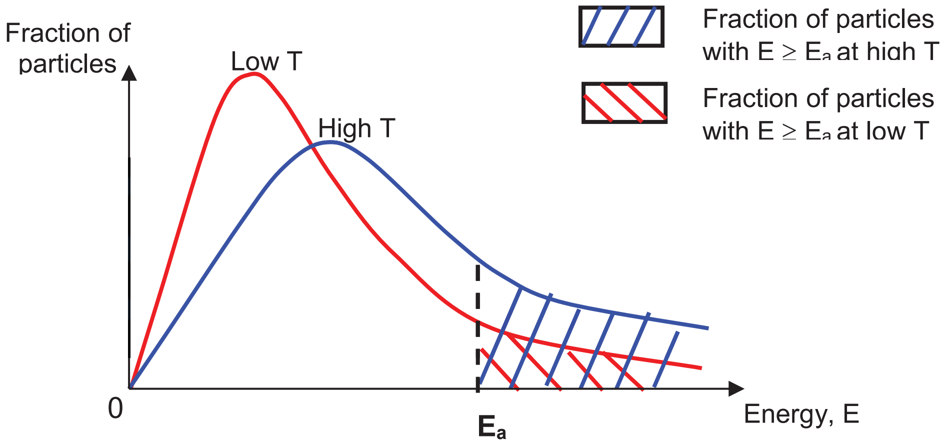
6×10^{-6} = k(0.100)(0.010)
k = 6.00×10^{-3} allow ecf

$$k=\frac{Rate}{[CH_3CH_2CH_2CH_2Br][OH^-]}$$

$$k=\frac{moldm^{-3}s^{-1}}{(moldm^{-3})^2}=mol^{-1}dm^3s^{-1}[1]$$

[1]

(v) Using the Maxwell-Boltzmann distribution curve, explain how the reaction rate might change with an increase in temperature.



- correct axes
- two graphs with higher temperature graph shifted to the left and lower peak, both graph must start from origin.
- both graphs should be labelled, Ea indicated with shading
- legend of shading provided.

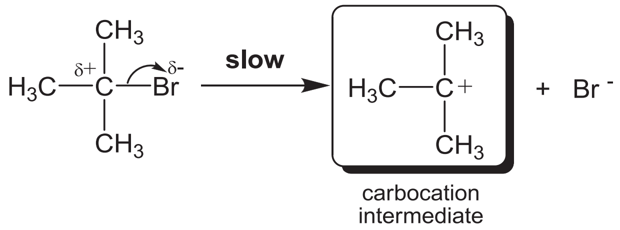
An increase in temperature will result in an increase in the average kinetic energy of the particles.
There is an increase in the fraction of particles with energy equal to or greater than the activation energy, E_a. This is as shown by the larger shaded area at a higher temperature in the above diagram.
This result in an increase in the frequency of effective collisions.
Since rate is proportional to the frequency of effective collision, rate increases.

[4]

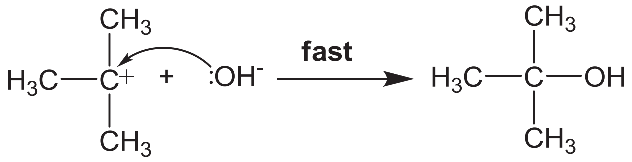
(vi) Given that the rate equation for the hydrolysis of $(CH_3)_3CBr$ is rate = k[$(CH_3)_3CBr$], suggest possible mechanisms for **both** of the reactions of $(CH_3)_3CBr$ and $CH_3CH_2CH_2CH_2Br$ with aqueous NaOH which are consistent with the observed kinetics.

For $(CH_3)_3CBr$

Nucleophilic substitution, S_N1
Step 1 (formation of carbocation):

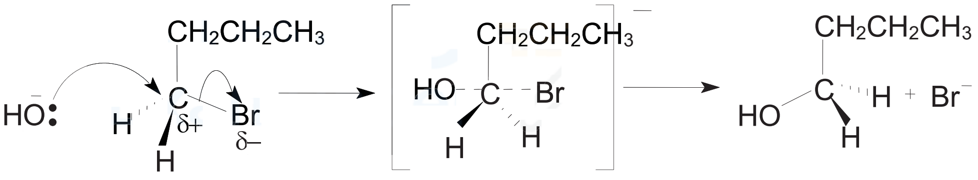


Step 2 (attack by nucleophile)



- δ+ and δ- on C-Br
- arrow to show breaking of C-Br bond, arrow must start from the bond
- slow and fast step
- Correct intermediate and Br^- formed
- lone pair on O of OH−
- arrow starting from lone pair to C+

For $CH_3CH_2CH_2CH_2Br$
Nucleophilic substitution, S_N2



- δ+ and δ- on C-Br
- arrow to show breaking of C-Br bond, arrow must start from the bond
- lone pair on O of OH−
- arrow starting from lone pair to C
- square bracket and negative charge for transition state
- initial reactant and final product should be inversed (solid wedge and dash is not necessary) and Br^- as product

[6]

(b) Bromine reacts with 2-methylpropane in the presence of sunlight to produce mono-brominated products via a free radical mechanism.

(i) Explain why the mono-bromination of 2-methylpropane results in the formation of two products in unequal amounts.

In the propagation step, two alkyl radicals will be formed. Tertiary $(CH_3)C\bullet$ is more stable than primary $(CH_3)_2CCH_2\bullet$. / There are 9 primary H atom and only 1 tertiary H atom.

[1]

(ii) By quoting appropriate data from the *Data Booklet,* explain the difference in the reactivity of fluorine with 2-methylpropane compare with that of bromine.

Bond energy of F_2 = 158kJ mol^{-1} Bond energy of Br_2 = 193 kJ mol^{-1}

Fluorine will react more vigorously/ more reactive because the F-F bond is weaker than Br-Br bond.

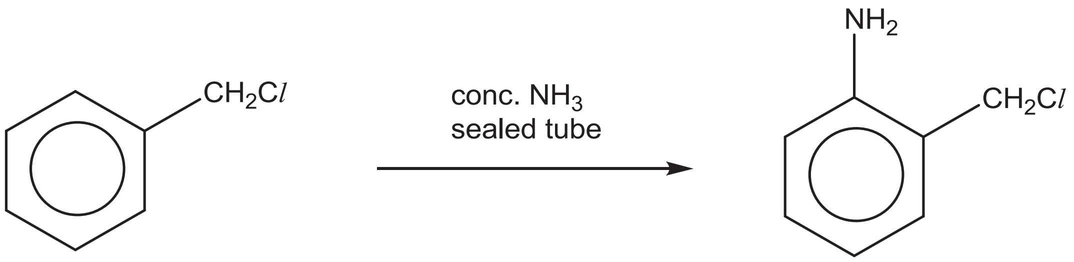
Or

Bond energy of C-F = 485 kJ mol^{-1} Bond Energy of C-Br = 280 kJ mol^{-1}

Fluorine will react more vigorously because C-F bond formed is stronger than C-Br bond.

[2]

(c) A student was not successful in making **X** from (chloromethyl)benzene with the proposed reaction route as shown.

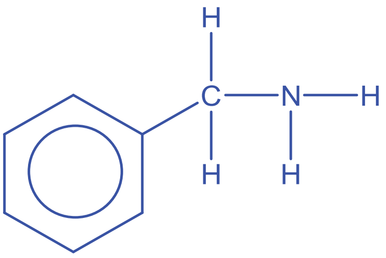


(chloromethyl)benzene

X

Instead, a different product with molecular formula C_7H_9N was obtained.

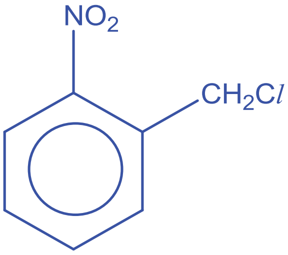
(i) Draw the displayed formula of the product obtained.



[1]

(ii) Suggest how **X** can be synthesised from (chloromethyl)benzene. You should include the reagents, conditions and intermediate(s) formed in your answer.

Step 1: Conc HNO_3, Conc H_2SO_4, **30°C < temp < 55°C (30/55 will not be accepted)**



Step 2:
1) Sn, conc HCl, heat
2) aq NaOH, rtp

[3]

[Total: 24]

Section B

Answer **one** question from this section

4 Hydrogen gas is needed in a large number of processes in the chemical industries such as hydrocracking of petroleum, production of margarine and production of ammonia.

Hydrogen gas can be produced in many chemical reactions.

(a) One of the reactions that produces hydrogen is the reaction of sodium with ethanol.

$$C_2H_5OH(l) + Na(s) \longrightarrow C_2H_5ONa(s) + \frac{1}{2}H_2(g)$$

This is also a chemical test for the presence of alcohol.

(i) Write the full electronic configuration of Na.

Electronic configuration of sodium: $1s^2 2s^2 2p^6 3s^1$

(ii) Describe how you would use the ionisation energies found in the *Data Booklet* to conclude that sodium is in group 1 of the periodic table.

[1]

Since there is a large increase between the first ionisation energy (494 kJ mol^{-1}) and the second ionisation energy (4560 kJ mol^{-1}) of sodium. This means that the second electron is removed from the inner principal quantum shell, hence there is only one valence electron in sodium.

(iii) Ethanoic acid reacts with sodium in a similar way. However, when ethanol and ethanoic acid is reacted with solid sodium carbonate separately, only ethanoic acid gives off a gas that forms white precipitate with calcium hydroxide.

Explain the difference in reactions of ethanol and ethanoic acid with sodium carbonate.

[3]

Reasons: Ethanoic acid is a stronger acid than ethanol hence it is acidic enough to react with sodium carbonate.

$CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$
For the ethanoate anion, the negative charge can be delocalised over two electronegative oxygen atoms. This disperses the negative charge on the oxygen atom and leads to a stabilisation of the ethanoate anion.
Hence, ethanoic acid is the more acidic.

$CH_3CH_2OH + H_2O \rightleftharpoons CH_3CH_2O^- + H_3O^+$

For the ethoxide anion, the electron-donating ethyl group intensifies the negative charge on the oxygen atom. Thus, the ethoxide anion is less stable.

(iv) An unknown compound **M**, $C_8H_{10}O$ was found to be an alcohol when tested with sodium metal.

When **M** is treated with hot acidified potassium dichromate, compound **N**, C_8H_8O is formed. **N** gives a yellow precipitate, **P** when warmed with alkaline aqueous iodine.

When **M** is heated with concentrated H_2SO_4, compound **R**, C_8H_8 is formed. **R** gives compound **S** when reacted with hydrogen chloride gas.

M also gave compound **S** when reacted with phosphorous pentachloride at room temperature.

Deduce the structures of **M**, **N**, **P**, **R** and **S.**

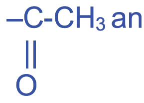
[5]

Explanation not required.

Comparable number of C and H → **M** contained benzene ring.
M undergoes oxidation with hot acidified potassium dichromate → **N** is aldehyde or ketone

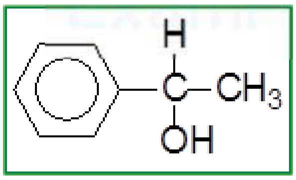
N undergoes oxidation with alkaline aqueous iodine to give yellow precipitate,

P: <u>CHI_3</u>

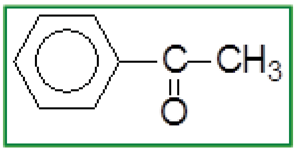


→ **N** has structure $-\underset{\underset{O}{\|}}{C}-CH_3$ and so **M** has $CH(OH)CH_3$ structure.

M:

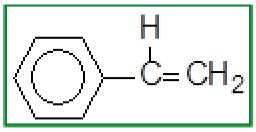


N:



M undergoes dehydration when heated with concentrated H_2SO_4 → **R** is an alkene

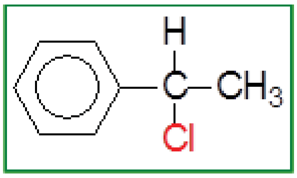
R:



R undergoes electrophilic addition when heated with hydrogen chloride gas → **S** is halogenoalkane

M undergoes substitution with phosphorous pentachloride at room temperature→ **S** is halogenoalkane

S:



(b) Another reaction that produces hydrogen is the reaction of methane with steam at 1000–1400 K.

$$CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g) \qquad \Delta H = +206 \text{ kJ mol}^{-1}$$

This reaction produces large quantities of hydrogen for industrial use.

(i) State and explain the effect of decreasing the temperature of the reaction on the equilibrium position.

[1]

When temperature of the system is decreased, by Le Chatelier's Principle, the equilibrium will favour exothermic reaction to release heat. Hence, the backward reaction is favoured and equilibrium position shifted left.

(ii) Deduce the sign of entropy change for the forward reaction.

[1]

Since the no. of moles of gas increases for the forward reaction, disorderness increased as there are more ways to arrange the particles so entropy change (ΔS) is positive.

(iii) Hence, or otherwise, predict and explain the spontaneity of the forward reaction at low temperature.

[1]

Since $\Delta G = \Delta H - T\Delta S$

When temperature is low, magnitude of $-T\Delta S$ will be smaller than that of magnitude of ΔH. or similar reasoning.

Since ΔS is positive and hence $-T\Delta S$ is negative and ΔH is positive, ΔG would be positive and hence the reaction is not spontaneous

(iv) Comment and explain if there is any discrepancy in your answers in **b(i)** and **b(iii)**.

[1]

No. Since at low temperature, forward reaction is not spontaneous (ΔG is positive) hence the position of equilibrium position should be on the left/ forward reaction is not favoured

(v) Calculate the enthalpy change of vaporisation of water of using the data in **Table 1**.

Table 1

Enthalpy change of formation of carbon monoxide	–111 kJ mol^{-1}
Enthalpy change of formation of methane	–75 kJ mol^{-1}
Enthalpy change of formation of water	–285 kJ mol^{-1}

[2]

For $CH_4(g) + H_2O(l) \longrightarrow CO(g) + 3H_2(g)$

Enthalpy change of reaction

$= \Sigma\Delta H_f$ product $- \Sigma\Delta H_f$ reactant

$= (-111 + 3(0)) - (-285 + -75)$
$= +249$ kJmol^{-1}

$$\begin{tikzcd} CH_4(g) + H_2O(g) \arrow[rr, "+206\text{ kJ mol}^{-1}"] & & CO(g) + 3H_2(g) \\ & CH_4(g) + H_2O(l) \arrow[ul, "\Delta H_{vap}^{\ominus}\ H_2O"] \arrow[ur, "+249\text{ kJmol}^{-1}"'] & \end{tikzcd}$$

By Hess' law,

$\Delta H_{vap}^{\ominus}\ H_2O = +249$ kJmol^{-1} – (+206 kJ mol^{-1})
$= +43.0$ kJ mol^{-1}

Or any other possible approaches.

(c) Hydrogen gas can also be produced from the reaction of carbon monoxide with steam.

$$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g) \quad K_c = 6.40\times10^{-1} \text{ at } 1100K$$

A mixture containing 0.8 mol of CO and 0.8 mol of H_2O was placed in a 2 dm^3 flask and allowed to come to equilibrium at 1100K.

(i) Write an expression for an expression for K_c of this reaction.

[1]

$$K_c = \frac{[H_2][CO_2]}{[CO][H_2O]}$$

(ii) Calculate the amount of each substance present in the equilibrium mixture at 1100K.

Let the change in number of moles be x.

[2]

	$CO(g)$ +	$H_2O(g)$ $\rightleftharpoons$	$CO_2(g)$ +	$H_2(g)$
initial moles	0.80	0.80	0	0
change in moles	–x	–x	+x	+x
eqm moles	(0.80 –x)	(0.80 –x)	+x	+x

$$K_c = \frac{\frac{x^2}{2}}{(\frac{0.80-x}{2})^2} = 6.40 \times 10^{-1}$$

0.8 x 0.8 – 0.8x = x

x = 0.356

At equilibrium

n(CO) =n(H_2O) = (0.80 – 0.356) = 0.444 mol

n(CO_2) = n(H_2) = 0.356 mol

(iii) State and explain the effect of decreasing pressure on the equilibrium constant. [1]

Decreasing pressure has no effect on the equilibrium constant as it is only affected by change in temperature.

[Total:20]

5 Methanol can be prepared industrially by reacting together carbon monoxide and hydrogen. This is a reversible reaction:

$$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g) \quad \Delta H = -94 kJmol^{-1}$$

A chemist mixes together 0.114 mol CO(g) and 0.152 mol H_2(g) in a container. The container is pressurised and then sealed and the total volume is 200 cm^3. The mixture is heated to 500 K at constant volume and left to reach equilibrium. The chemist analyses the equilibrium mixture and finds that 0.052 mol CH_3OH has formed.

(a) Calculate the value of K_c for the equilibrium at 500 K. [2]

	$CO(g)$ +	$2H_2(g)$ $\rightleftharpoons$	$CH_3OH(g)$
Initial amount/ mol	0.114	0.152	0
Change in amount/ mol	–0.052	–2(0.052)	+0.052
Equilibrium amount / mol	0.062	0.048	0.052
Equilibrium concentration/ mol dm^{-3}	0.31	0.24	0.26

All three equilibrium concentrations

$$K_c = \frac{[CH_3OH]}{[H_2]^2[CO]} = \frac{[0.26]}{[0.24]^2[0.31]}$$

= 14.6 mol^{-2} dm^6

(b) The chemist repeats the experiment using the same initial amounts of CO and H_2. The same procedure is used but the mixture is heated in the 200 cm^3 sealed container to a temperature higher than 500 K.
As the gas volume is kept at 200 cm^3, the increased temperature also increases the pressure.

Explain why it is difficult to predict how the yield of CH_3OH would change and state what happens to the value of K_c. [2]

At higher pressure, position of equilibrium shifts to the **right** with **fewer gas molecules**.

At higher temperature position of equilibrium shifts to the **left** to favour **endothermic reaction**.

Since **relative effect of pressure and temperature is unknown**, it is difficult to predict how the yield of CH_3OH would change.

The value of K_c **decreases**.

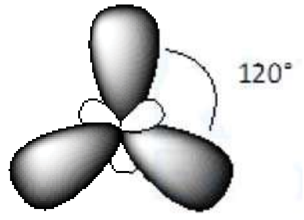
(c) Methanol can be oxidised to formaldehyde, HCHO, by passing its vapour over copper heated to 300 °C.

Explain why the boiling point of methanol (65 °C) is higher than that of formaldehyde (–19 °C). [2]

Both HCHO and CH_3OH have simple molecular structures.
CH_3OH have stronger hydrogen bonds between the molecules while HCHO have weaker permanent dipole-permanent dipole interactions between the molecules .
More energy is required to overcome the stronger hydrogen bonds between CH_3OH molecules, thus CH_3OH has a higher boiling point.

(d) State the type of hybridisation shown by the C atom in formaldehyde and draw its hybrid orbitals. [2]

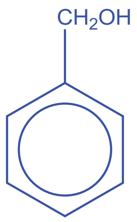
Type of hybridisation: sp^2



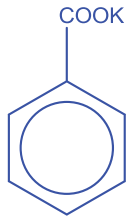
three sp^2 hybrid orbitals with correct shape

(e) Benzaldehyde, C_6H_5CHO, is the simplest aromatic aldehyde and has a characteristic smell of almonds.
In the presence of a solution of potassium hydroxide, benzaldehyde undergoes disproportionation to give a mixture of two organic products, **E** and **F**. **F** has a higher solubility in water compared to **E**.

(i) Suggest the structures of **E** and **F**. [2]



E



F

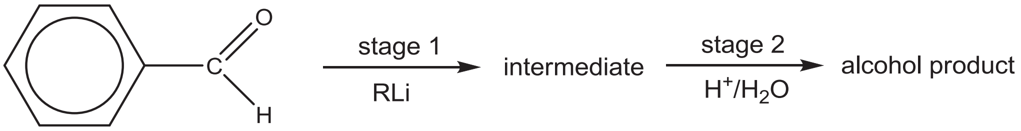
(ii) Explain why **F** is soluble in water. [1]

Ionic salt **F** is able to form ion-dipole interactions with water molecules .

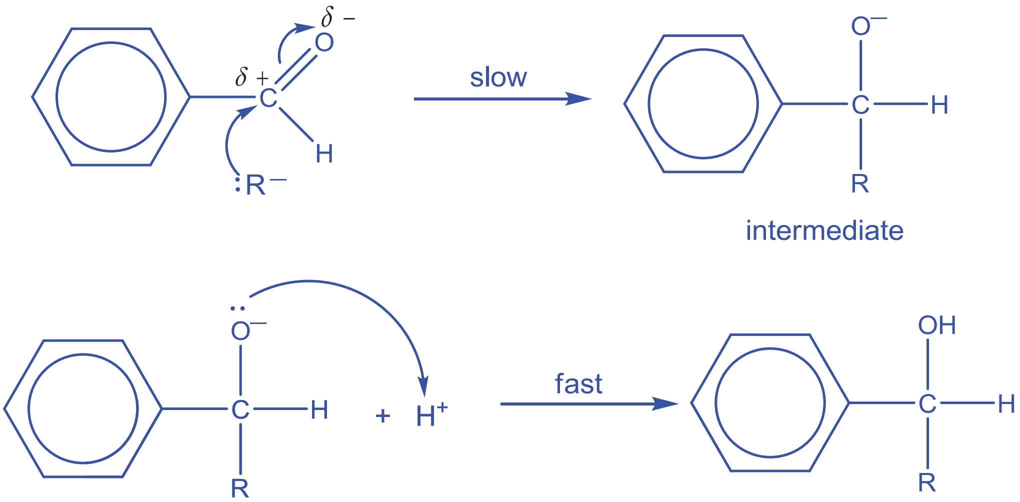
(f) Alkyllithium compounds, RLi, can be used to increase the number of carbon atoms in an organic compound. Different alkyl groups, R, add carbon chains with different chain lengths.

RLi provides a source of R^- ions, which act as a nucleophile.

(i) RLi reacts with benzaldehyde to give an intermediate in stage 1, followed by reaction with aqueous acid to form an alcohol in stage 2.

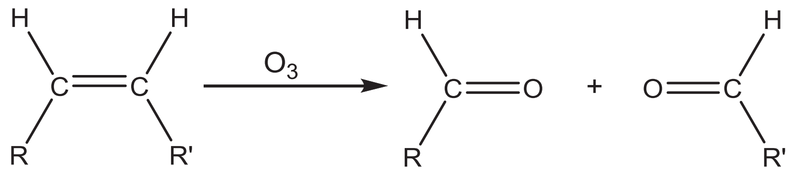


Describe the mechanism for the above reaction, including curly arrows and relevant dipoles. [3]



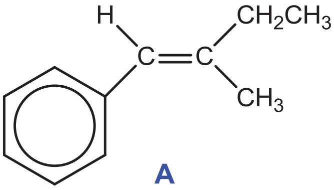
- dipoles on C = O bond & lone pair of electrons on R^- nucleophile
- 2 electron arrows in step 1
- slow and fast step
- correct intermediate
- lone pair of electrons on O^- and electron arrow in step 2
- alcohol product

(ii) 'Ozonolysis' is a technique used in Organic Chemistry to break open a C=C double bond. During ozonolysis, an alkene reacts with ozone, O_3. The products are carbonyl compounds as shown below.

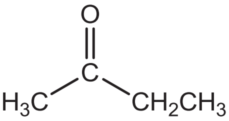


An aromatic alkene, **A** undergoes ozonolysis to give benzaldehyde and **B**, C_4H_8O. **B** has no reaction with $[Ag(NH_3)_2]^+$(aq) but gives a yellow precipitate with aqueous alkaline iodine.

B undergoes a reaction with an alkyllithium compound, **C**, followed by reaction with aqueous acid to give an alcohol, **D**, which is optically active. The elimination of H_2O from **D** produces a mixture of four different isomeric alkenes with the formula, C_7H_{14}, only two of which are cis-trans isomers of each other. Suggest the structural formulae of compounds **A** to **D** and the two cis-trans isomers. [6]



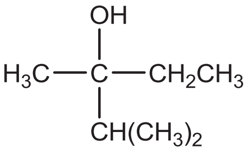
A



B

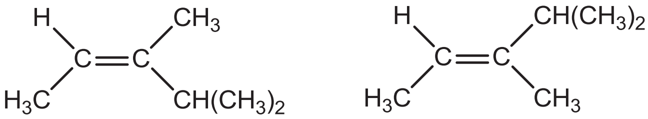
$(CH_3)_2CHLi$

C



$$H_3C-\overset{\overset{\large OH}{|}}{\underset{\underset{\large CH(CH_3)_2}{|}}{C}}-CH_2CH_3$$

D



Cis and trans isomers

[Total: 20]

INNOVA JUNIOR COLLEGE
JC2 PRELIMINARY EXAMINATION
in preparation for General Certificate of Education Advanced Level
Higher 2

CANDIDATE NAME	
CLASS	
INDEX NUMBER	

CHEMISTRY

9729/04

Paper 4 Practical

15 Aug 2017

2 hours 30 minutes

Candidates answer on the Question Paper.

READ THESE INSTRUCTIONS FIRST

Write your index number, name and class on all the work you hand in.
Give details of the practical shift and laboratory when appropriate, in the boxes provided.
Write in dark blue or black pen.
You may use an HB pencil for any diagrams or graphs.
Do not use staples, paper clips, glue or correction fluid.

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

The use of an approved scientific calculator is expected, where appropriate.
You may lose marks if you do not show your working or if you do not use appropriate units.
Qualitative Analysis Notes are printed on pages 18 and 19.

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

Shift
Laboratory

For Examiner's Use	
1	13
2	23
3	19
Total	55

This document consists of **19** printed pages and **1** blank page.

1 In this experiment you will determine the relative atomic mass, A_r, of magnesium by a titration method.

FA 1 is 2.00 mol dm^{-3} hydrochloric acid, HCl.
FA 3 is 0.120 mol dm^{-3} sodium hydroxide, NaOH
magnesium ribbon
bromophenol blue indicator

(a) Method

Reaction of magnesium with FA 1

- Pipette 25.0 cm^3 of **FA 1** into the 250 cm^3 beaker.
- Weigh the strip of magnesium ribbon and record its mass.

mass of magnesium = …………..g

- Coil the strip of magnesium ribbon loosely and then add it to the **FA 1** in the beaker.
- Stir the mixture occasionally and wait until the reaction has finished.

Dilution of the excess acid

- Transfer all the solution from the beaker into the volumetric flask.
- Make up the solution up to the mark using distilled water.
- Shake the flask to mix the solution before using it for your titrations.
- Label this solution of hydrochloric acid **FA 2**.

Titration

- Fill the burette with **FA 2**.
- Rinse the pipette out thoroughly. Then pipette 25.0 cm^3 of **FA 3** into a conical flask.
- Add several drops of bromophenol blue indicator.
- Run **FA 2** from the burette into this flask until the mixture just becomes yellow.
- Carry out as many titrations as you think necessary to obtain consistent results.
- Make certain that your recorded results show the precision of your working.
- Record in a suitable form below all your burette readings and the volume of **FA 2** added in each accurate titration.

Results

M1	
M2	
M3	
M4	
M5	
M6	

[6]

(b) From your titrations, obtain a suitable volume of **FA 2** to be used in your calculations. Show clearly how you obtained this volume.

M7

Volume of **FA 2** = …………………………….[1]

(c) Calculations

Show your working and appropriate significant figures in the final answer to **each** step of your calculations.

(i) Deduce the amount of hydrochloric acid in the volume of **FA 2** you calculated in **(b)**

M8

Amount of HC*l* = ………………… [1]

(ii) In **(a)**, you reacted 25.0 cm^3 of **FA 1** with your weighed piece of magnesium. After the reaction, the unreacted hydrochloric acid was used to prepare 250 cm^3 of **FA 2**.

Calculate the amount of hydrochloric acid that reacted with the magnesium ribbon.

M9

M10

Amount of HC*l* reacting with Mg = ……………………[2]

(iii) Hence, calculate the relative atomic mass , A_r, of magnesium.

M11

A_r of Mg = ……………………[1]

(d) A student carried out the same experiment but used 1.00 g of magnesium ribbon. State and explain why the student's experiment could not be used to determine the value for the A_r of magnesium.
Include a calculation in your answer.

[A_r: Mg, 24.3]

M12	
M13	

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

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

[Total: 13]

2 You will investigate the rate of reaction between iron(III) ions, Fe^{3+}, and iodide ions, I^-.

$$2Fe^{3+}(aq) + 2I^{-}(aq) \longrightarrow 2Fe^{2+}(aq) + I_2(aq)$$

The iodine, I_2, produced can be reacted immediately with thiosulfate ions, $S_2O_3^{2-}$.

$$I_2(aq) + 2S_2O_3^{2-}(aq) \longrightarrow 2I^{-}(aq) + S_4O_6^{2-}(aq)$$

When all the thiosulfate has been used, the iodine produced will turn starch indicator blue-black.

The rate of the reaction can therefore be measured by finding the time for the blue-black colour to appear.

FA 4 is aqueous iron(III) chloride, $FeCl_3$.
FA 5 is aqueous potassium iodide, KI.
FA 6 is 0.0060 mol dm^{-3} sodium thiosulfate, $Na_2S_2O_3$.
starch indicator

You are advised to read the instructions before starting any practical work and draw a table for your results in the space on page **6**.

(a) Method

Experiment 1

- Fill a burette with **FA 4**.
- Run 20.00 cm^3 of **FA 4** into a 100 cm^3 beaker.
- Use the measuring cylinder to place the following in a second 100 cm^3 beaker.
  - 10 cm^3 of **FA 5**
  - 20 cm^3 of **FA 6**
  - 10 cm^3 of starch indicator
- Add the contents of the second beaker to the first beaker and start timing.
- Stir the mixture once and place the beaker on the white tile.
- The mixture turns brown and then yellow before turning a blue-black colour. Stop timing when this **blue-black colour** appears.
- Record in your table the volume of **FA 4** used, the volume of distilled water used and the time to the **nearest second** for the blue-black colour to appear.
- Wash both beakers.

For each of **Experiments 1 - 6** you should complete your results table to show the volume of **FA 4** used, the volume of distilled water used and the time taken to the **nearest second** for the blue-black colour to appear.

Experiment 2

- Fill the other burette with distilled water.
- Run 10.00 cm^3 of **FA 4** into a 100 cm^3 beaker.
- Run 10.00 cm^3 of distilled water into the same beaker.
- Use the measuring cylinder to place the following in a second 100 cm^3 beaker.
  - 10 cm^3 of **FA 5**
  - 20 cm^3 of **FA 6**
  - 10 cm^3 of starch indicator
- Add the contents of the second beaker to the first beaker and start timing.
- Stir the mixture once and place the beaker on the white tile.
- Stop timing when a blue-black colour appears.

- Wash both beakers.

Experiments 3 - 6

Carry out **four** further experiments to investigate the effect of changing the concentration of Fe^{3+} (aq) by altering the volume of aqueous $FeCl_3$, **FA 4**, used.

You should not use a volume of **FA 4** that is less than 6.00 cm^3 and the total volume of the reaction mixture must always be 60 cm^3.

M14	
M15	
M16	
M17	
M18	
M19	

[6]

Calculations

The rate of reaction can be found by calculating the change in concentration of $Fe^{3+}(aq)$ that occurred when enough iodine was produced to change the colour of the indicator to blue-black.

Use your data and the equations on page **5** to carry out the following calculations.

Show your working and appropriate significant figures in the final answer to **each** step of your calculations.

(b) **(i)** Calculate the amount of thiosulfate ions, $S_2O_3^{2-}$ used in each experiment.

M20

Amount of $S_2O_3^{2-}$ ……………………….[1]

(ii) Calculate the amount of iron(III) ions, Fe^{3+}, that were used to produce the amount of iodine that react with the amount of $S_2O_3^{2-}$ in **(i)**.

M21

Amount of Fe^{3+} ………………………. [1]

(iii) Using your answer to **(ii)**, calculate the change in Fe^{3+} up to the time of appearance of the blue black colour.

M22

Change in concentration of Fe^{3+} ……………………….[1]

(iv) The following formula can be used as a measure of the 'rate of reaction'.

$$\text{‘rate of reaction’} = \frac{\text{change in concentration of Fe}^{3+}\left(\text{aq}\right)}{\text{reaction time}} \times 10^{6}$$

Complete the table to show the volume of **FA 4**, the reaction time and the rate in **Experiments 1- 6**. You should include units.

If you were unable to calculate a value for the change in concentration of Fe^{3+}(aq) in **(iv)**, you should assume it is 2.50 × 10^{-3} mol dm^{-3}. (Note: this is not the correct value.)

Experiment			
1			
2			
3			
4			
5			
6			

M23

[1]

(c) On the grid, plot the rate (*y*-axis) against the volume of **FA 4** (*x*-axis). Draw a line of best fit through the points. You should identify any points you consider anomalous.

M24	
M25	
M26	

[3]

(d) Using your graph, what conclusion can you reach about the effect of changing the concentration of $FeCl_3$ on the rate of the reaction between $Fe^{3+}(aq)$ and $I^-(aq)$?

…………………………………………………………………………………………………

………………………………………………………………………………………………… M27

…………………………………………………………………………………………………[2] M28

(e) It was found, by carrying out experiments similar to those used in **(a)**, that increasing the concentration of I^- increased the rate of the reaction.

The student suggested a modification to the method by using the same volumes of all reagents but with the concentration of **FA4** and **FA 5** being doubled their original values. State what the effect would be on the **reaction time** in Experiment 1 and explain how this change would affect any **possible errors** in the measurements.

…………………………………………………………………………………………………

…………………………………………………………………………………………………

…………………………………………………………………………………………………[1] M29

(f) Which of the experiments you carried out in **(a)** had the greatest percentage error in the reaction time? Calculate this percentage error. Assume that the error in measuring the reaction time is ±0.5 s.

M30

[1]

(g) Planning

Aqueous hydrogen peroxide decomposes into oxygen gas and water. The reaction is normally very slow but is catalysed by solid manganese (IV) oxide.

$$2H_2O_2(aq) \longrightarrow 2H_2O(l) + O_2(g)$$

You are to plan an experiment to investigate how the rate of the catalysed decomposition of aqueous hydrogen peroxide depends on its concentration.

(i) The rate of decomposition depends on the number of hydrogen peroxide molecules present in a given volume of solution.

Use this information to predict how the rate of decomposition of the hydrogen peroxide depends on the concentration.

Prediction……………………………………………………………………………………

…………………………………………………………………………………………………

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

M31

(ii) You are to design a laboratory experiment to test your prediction in **(g) (i)**.

In addition to the standard apparatus present in a laboratory you are provided with the following materials.

- 0.1 mol dm^{-3} aqueous hydrogen peroxide
- A supply of manganese (IV) oxide

Complete the table below to show how you would prepare five solutions of aqueous hydrogen peroxide. Make sure that the correct units are recorded.

expt No.	volume of H_2O_2	volume of H_2O	concentration of H_2O_2
1			
2			
3			
4			
5			

M32

[1]

(iii) Give a step by step description of how you would carry out **one** complete experiment.

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

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

M33	
M34	
M35	

(iv) State a problem which might be experienced by someone having to carry out these experiments alone.

……………………………………………………………………………………………..

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

M36	

[Total: 23]

3 Qualitative Analysis

At each stage of any test you are to record details of the following:

- colour changes seen
- the formation of any precipitate
- the solubility of such precipitates in an excess of the reagent added

Where gases are released they should be identified by a test, **described in the appropriate place in your observations.**

You should indicate clearly at which stage of the test a change occurs.
Marks are **not** given for chemical equations.
No additional tests for ions present should be attempted.

If any solution is warmed, a boiling tube MUST be used.

Rinse and reuse test-tubes and boiling tubes where possible.

Where reagents are selected for use in a test, the name or correct formula of the element or compound must be given.

(a) FA 7 and FA 8 are mixtures. Each mixture contains one cation and two anions from those listed on pages 18 and 19.

Carry out the following tests and record all your observations in the table below.

Test	Observations	
	FA 7	FA 8
(i) Place two spatula measure of FA 7 into a boiling tube, then add approximately 5 cm^3 of dilute nitric acid using the measuring cylinder. You are to repeat the steps for FA 8. Then		
add about 5 cm^3 of distilled water and shake to mix the solution. Use a 1 cm depth of the solution obtained in a test-tube for each of tests (ii) – (v).	No observation required.	
(ii) Add aqueous sodium hydroxide. Then add dilute nitric acid dropwise until in excess.		Do not carry out this test.
(iii) Add aqueous ammonia.		Do not carry out this test.
(iv) Add aqueous barium nitrate followed by dilute nitric acid.		

M37

	FA7	**FA8**
(v) Add aqueous silver nitrate followed by aqueous ammonia.		

M38	
M39	
M40	

[4]

(vi) Use your observations to identify the following ions.

FA 7 contains cation ………………………………..

FA 7 contains anions ………………………………. and ……………………………….
FA 8 contains anions ……………………………. and ……………………………….

State and explain all the evidence for your identification of the cation in **FA 7**.

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

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

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

M41	
M42	
M43	

(b) **FA 9** contains two cations from the list on page 18.

(i) Transfer approximately half of the **FA 9** into a hard-glass test-tube and heat gently at first, and then strongly, until no further change is seen.
Test with litmus papers while you are heating.
Record all your observations below.

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

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

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

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

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

M44	

(ii) Carry out further tests that will enable you to identify **both** cations in **FA 9**.
Describe your tests briefly and state your observations.

FA 9 contains cations ……………………………… and ……………………………….

[2]

M45	
M46	

(c) **Planning**

A solder is an alloy of metals which is used to join other metal pieces together.

A specialist solder that can be used to join together pieces of aluminium is made from a mixture by mass of 65% zinc, 20% aluminium and 15% copper.

You are to plan an experimental procedure to confirm the composition of a powdered sample of this solder, by adding reagents and then extracting from the mixture each of the following in sequence;

(i) the copper metal,
(ii) the aluminium as aluminium hydroxide,
(iii) the zinc as zinc hydroxide

You are provided with

- a sample of this solder, with approximate mass 4 g,
- 1.00 mol dm^{-3} sulfuric acid,
- 1.00 mol dm^{-3} ammonia

No other reagents should be used. Standard laboratory equipment is available including a balance, accurate to two decimal places.

(i) Complete the flowchart below to show the order in which the reagents would be added to the solder to allow you to extract and separate the components as copper metal, (**Step 1**), aluminium hydroxide, **(Step 2)**, and zinc hydroxide, **(Step 3)**.
You are reminded that aqueous ammonia contains both the base OH^- and the complex-forming molecule NH_3.

Step 1	**Step 2**	**Step 3**
reagent(s) added	reagent(s) added	reagent(s) added
………………………..........	…………………………	……………………………
…………………………....	…………………………	………………………….....
substance(s) present at the end of the reaction	substance(s) present at the end of the reaction	substance(s) present at the end of the reaction
…………………………....	………………………..........	……………………………
…………………………....	………………………..........	……………………………
…………………………....	……………………………	……………………………
substance(s) removed by filtration (if any)	substance(s) removed by filtration (if any)	substance(s) removed by filtration (if any)
…………………………....	……………………………	……………………………
…………………………....	……………………………	……………………………

M47	
M48	
M49	
M50	
M51	

[5]

(ii) For some of the steps in the procedure you would need to be careful to add an appropriate quantity of a reagent.
For each step of your procedure explain why particular quantities of reagent should be chosen.

Step 1

…………………………………………………………………………………………………

…………………………………………………………………………………………………

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

M52

Step 2

…………………………………………………………………………………………………

…………………………………………………………………………………………………

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

M53

Step 3

…………………………………………………………………………………………………

…………………………………………………………………………………………………

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

M54

(iii) If the mass of aluminium hydroxide obtained was 1.50 g, calculate the mass of aluminium that was present in the solder.
[A_r: A*l*, 27.0; O, 16.0]

[1]

M55

[Total: 19]

Qualitative Analysis Notes

[ppt. = precipitate]

(a) Reactions of aqueous cations

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

(b) Reactions of anions

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

(c) Tests for gases

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

(d) Colour of halogens

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

BLANK PAGE

INNOVA JUNIOR COLLEGE
JC2 PRELIMINARY EXAMINATION
in preparation for General Certificate of Education Advanced Level
Higher 2

CANDIDATE NAME	**WORKED SOLUTIONS**		
CLASS		INDEX NUMBER	

CHEMISTRY

9729/04

Paper 4 Practical

15 Aug 2017

2 hours 30 minutes

Candidates answer on the Question Paper.

READ THESE INSTRUCTIONS FIRST

Write your index number, name and class on all the work you hand in.
Give details of the practical shift and laboratory when appropriate, in the boxes provided.
Write in dark blue or black pen.
You may use an HB pencil for any diagrams or graphs.
Do not use staples, paper clips, glue or correction fluid.

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

The use of an approved scientific calculator is expected, where appropriate.
You may lose marks if you do not show your working or if you do not use appropriate units.
Qualitative Analysis Notes are printed on pages 18 and 19.

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

Shift
Laboratory

For Examiner's Use	
1	**17**
2	**24**
3	**14**
Total	**55**

This document consists of **15** printed pages.

1 In this experiment you will determine the relative atomic mass, A_r, of magnesium by a titration method.

FA 1 is 2.00 mol dm^{-3} hydrochloric acid, HC*l*.
FA 3 is 0.120 mol dm^{-3} sodium hydroxide, NaOH
magnesium ribbon
bromophenol blue indicator

(a) Method

Reaction of magnesium with FA 1

- Pipette 25.0 cm^3 of **FA 1** into the 250 cm^3 beaker.
- Weigh the strip of magnesium ribbon and record its mass.

mass of magnesium = ……………g

- Coil the strip of magnesium ribbon loosely and then add it to the **FA 1** in the beaker.
- Stir the mixture occasionally and wait until the reaction has finished.

Dilution of the excess acid

- Transfer all the solution from the beaker into the volumetric flask.
- Make up the solution up to the mark using distilled water.
- Shake the flask to mix the solution before using it for your titrations.
- Label this solution of hydrochloric acid **FA 2**.

Titration

- Fill the burette with **FA 2**.
- Rinse the pipette out thoroughly. Then pipette 25.0 cm^3 of **FA 3** into a conical flask.
- Add several drops of bromophenol blue indicator.
- Run **FA 2** from the burette into this flask until the mixture just becomes yellow.
- Carry out as many titrations as you think necessary to obtain consistent results.
- Make certain that your recorded results show the precision of your working.
- Record in a suitable form on below all your burette readings and the volume of **FA 2** added in each accurate titration.

Results

The following readings are recorded

- Mass of Mg used
- Initial and final burette reading for two (or more) accurate titrations **M1**

Titre values recorded for accurate titrations and appropriate headings for the accurate titration tables and cm^3 units.

- Initial (burette) reading
- Final (burette) reading
- Titre or volume of **FA 2** used/added (*not "difference" or "total"*)
- Unit: cm^3(for each heading)

If cm^3 units are not given in the headings, every entry in the table must have the correct unit. **M2**

All accurate burette reading are to the nearest 0.05 cm^3. *Do **not** award this mark if:*

- 50.00cm^3 is used as an initial burette reading
- Any burette reading is greater than 50.00cm^3
- There is only one accurate titration **M3**

There are two uncorrected **accurate** titres within 0.10 cm^3. *Do not award this mark if, having performed two titre within 0.10 cm' a further titration is performed.* **M4**

Calculate the student's mean titre based on the following hierarchy:
- Value of 2 identical titres
- Average of titres within 0.05 cm^3
- Average of titres within 0.1 cm^3

Award based on the difference, *Δtitre*, between Student's and Supervisor's mean titre.
Give 2 marks if $\Delta titre \leq 0.20$ cm^3
Give 1 marks if $0.20 < \Delta titre \leq 0.50$ cm^3 **M5,M6**

[6]

(b) From your titrations, obtain a suitable volume of **FA 2** to be used in your calculations. Show clearly how you obtained this volume.

Student obtains appropriate "average" to 2 d.p., from any experiments with uncorrected end – point titre values within 0.10 cm^3
Do not award this mark if the titres used are not identified either in the table (by, for example, a tick) or in a calculation.
*Do **not** award this mark if there are arithmetic error in the table.* **M7**

Volume of **FA 2** = ……………………………..[1]

(c) **Calculations**

Show your working and appropriate significant figures in the final answer to **each** step of your calculations.

Units should be either in final calculation **or** dotted line.
Sf will be deducted ½ for overall, max 1 mark
Units will be deducted ½ for overall, max 1 mark
Working must be shown for all parts.

(i) Deduce the amount of hydrochloric acid in the volume of **FA 2** you calculated in **(b)**

Amount of NaOH = $0.120 \times \frac{25.0}{1000} = 0.003000 mol$
$NaOH + HCl \rightarrow NaCl + H_2O$
Amount of HCl = amount of NaOH
= 0.00300 mol **M8**

Amount of HC*l* = ………………… [1]

(ii) In **(a)**, you reacted 25.0 cm^3 of **FA 1** with your weighed piece of magnesium. After the reaction, the unreacted hydrochloric acid was used to prepare 250 cm^3 of **FA 2**.

Calculate the amount of hydrochloric acid that reacted with the magnesium ribbon.

Amount of HCl in volumetric flask = $0.00300 \times \frac{250}{(b)}$ = **a** mol

Amount of HCl used initially = $2.00 \times \frac{25.0}{1000} = 0.0500 mol$ **M9**

Amount of hydrochloric acid that reacted with Mg = 0.0500 – **a**
= **b** mol **M10**

Amount of HC*l* reacting with Mg = ……………………[2]

(iii) Hence, calculate the relative atomic mass , A_r, of magnesium.

$Mg(s) + 2HCl(aq) \rightarrow MgCl_2(aq) + H_2(g)$
Amount of Mg = **b** /2 mol
A_r = mass of Mg / (**b**/2)
= $\frac{2 \times \text{mass of Mg}}{\text{b}}$ (1dp) **M11**
Must be 1dp otherwise 0 mark.

A_r of Mg = ……………………[1]

(d) A student carried out the same experiment but used 1.00 g of magnesium ribbon. State and explain why the student's experiment could not be used to determine the value for the A_r of magnesium.
Include a calculation in your answer.

[A_r: Mg, 24.3]
Amount of Mg = 1/24.3 = 0.0412 mol
Amount of HCl needed = 0.0412 x 2 = 0.0824 mol but only 0.05 mol present **M12**

If 1.0g of Mg is used, Mg would be in excess/ acid would be the limiting reagent/ all the acid would be used up. **M13**

[2]

[Total: 13]

2 You will investigate the rate of reaction between iron(III) ions, Fe^{3+}, and iodide ions, I^-.

$$2Fe^{3+}(aq) + 2I^-(aq) \longrightarrow 2Fe^{2+}(aq) + I_2(aq)$$

The iodine, I_2, produced can be reacted immediately with thiosulfate ions, $S_2O_3^{2-}$.

$$I_2(aq) + 2S_2O_3^{2-}(aq) \longrightarrow 2I^-(aq) + S_4O_6^{2-}(aq)$$

When all the thiosulfate has been used, the iodine produced will turn starch indicator blue-black.

The rate of the reaction can therefore be measured by finding the time for the blue-black colour to appear.

FA 4 is aqueous iron(III) chloride, $FeCl_3$.
FA 5 is aqueous potassium iodide, KI.
FA 6 is 0.0060 mol dm^{-3} sodium thiosulfate, $Na_2S_2O_3$.
starch indicator

You are advised to read the instructions before starting any practical work and draw a table for your results in the space on page **6**.

(a) Method

Experiment 1

- Fill a burette with **FA 4**.
- Run 20.00 cm^3 of **FA 4** into a 100 cm^3 beaker.
- Use the measuring cylinder to place the following in a second 100 cm^3 beaker.
    - 10 cm^3 of **FA 5**
    - 20 cm^3 of **FA 6**
    - 10 cm^3 of starch indicator
- Add the contents of the second beaker to the first beaker and start timing.
- Stir the mixture once and place the beaker on the white tile.
- The mixture turns brown and then yellow before turning a blue-black colour. Stop timing when this **blue-black colour** appears.
- Record in your table the volume of **FA 4** used, the volume of distilled water used and the time to the **nearest second** for the blue-black colour to appear.
- Wash both beakers.

For each of **Experiments 1 - 6** you should complete your results table to show the volume of **FA 4** used, the volume of distilled water used and the time taken to the **nearest second** for the blue-black colour to appear.

Experiment 2

- Fill the other burette with distilled water.
- Run 10.00 cm^3 of **FA 4** into a 100 cm^3 beaker.
- Run 10.00 cm^3 of distilled water into the same beaker.
- Use the measuring cylinder to place the following in a second 100 cm^3 beaker.
    - 10 cm^3 of **FA 5**
    - 20 cm^3 of **FA 6**
    - 10 cm^3 of starch indicator
- Add the contents of the second beaker to the first beaker and start timing.
- Stir the mixture once and place the beaker on the white tile.
- Stop timing when a blue-black colour appears.
- Wash both beakers.

Experiments 3 - 6

Carry out **four** further experiments to investigate the effect of changing the concentration of Fe^{3+}(aq) by altering the volume of aqueous $FeCl_3$, **FA 4**, used.

You should not use a volume of **FA 4** that is less than 6.00 cm^3 and the total volume of the reaction mixture must always be 60 cm^3.

Experiment	Vol. of FA4/ cm^3	Vol. of water/ cm^3	Time taken/s
1	20.00	0.00	20
2	10.00	10.00	27
3	7.00	13.00	32
4	13.00	7.00	24
5	15.00	5.00	22
6	18.00	2.00	21

Recording:

- Constructs a table for 6 results. **M14**
- Correct headings and units for FA4, distilled water and time. Volumes / V/vol in cm^3 or / cm^3 or (cm^3), time / t in seconds or / s or (s). **M15**

Precision:

- All times recorded to the nearest second and volumes of FA4 and distilled water to 0.05 cm^3. **M16**

Decision:

- Four further experiments chosen with intervals not less than 2 cm^3 and no volume less than 6 cm^3. At least one volume must be **less than 10 cm^3** and **at least one must be more than 10 cm^3. M17**

- Water added to make total volume of FA 4 and water 20 cm^3 in each experiment and no other changes in volume. **M18**

M17 and M18 penalised if students change volume of other reagents other than FA4 and water.

Accuracy:

- Times increase with decrease in volume FA 4.
- Examiner rounds times to nearest second and calculates (time for expt 2) / (time for expt 1) to 2 decimal place. Ratio is compared with that of Supervisor.
  Award marks as follows:
  if ratio within 0.2 of Supervisor. **M19**

[6]

Calculations

The rate of reaction can be found by calculating the change in concentration of Fe^{3+}(aq) that occurred when enough iodine was produced to change the colour of the indicator to blue-black.

Use your data and the equations on page **5** to carry out the following calculations.

Show your working and appropriate significant figures in the final answer to **each** step of your calculations.

(b) **(i)** Calculate the amount of thiosulfate ions, $S_2O_3^{2-}$ used in each experiment.

$$\text{Amount } S_2O_3^{2-} = \frac{20}{1000} \times 0.0060$$

= 1.20×10^{-4} mol **M20**

Amount of $S_2O_3^{2-}$ ……………………….[1]

(ii) Calculate the amount of iron(III) ions, Fe^{3+}, that were used to produce the amount of iodine that react with the amount of $S_2O_3^{2-}$ in **(i)**.

$2Fe^{3+} \equiv I_2 \equiv 2\ S_2O_3^{2-}$

Amount of Fe^{3+} = 1.20×10^{-4} mol **M21**

OR

Amount of iodine = $\frac{1}{2} \times 1.2 \times 10^{-4}$

=0.600×10^{-4} mol

Amount of Fe^{3+} = $2 \times 0.600 \times 10^{-4}$

= 1.20×10^{-4} mol **M21**

Amount of Fe^{3+} ……………………… [1]

(iii) Using your answer to **(ii)**, calculate the change in Fe^{3+} up to the time of appearance of the blue black colour.

$$\text{Change in concentration of } Fe^{3+} = \frac{1.20\times10^{-4}}{\frac{60}{1000}} = 0.00200 \text{ mol dm}^{-3}$$ **M22**

Change in concentration of Fe^{3+} ……………………….[1]

(iv) The following formula can be used as a measure of the 'rate of reaction'.

$$\text{'rate of reaction'} = \frac{\text{change in concentration of } Fe^{3+}(aq)}{\text{reaction time}} \times 10^6$$

Complete the table to show the volume of **FA 4**, the reaction time and the rate in **Experiments 1- 6**. You should include units.

If you **were unable** to calculate a value for the change in concentration of Fe^{3+}(aq) in **(iv)**, you should assume it is 2.50×10^{-3} mol dm^{-3}. (Note: this is not the correct value.)

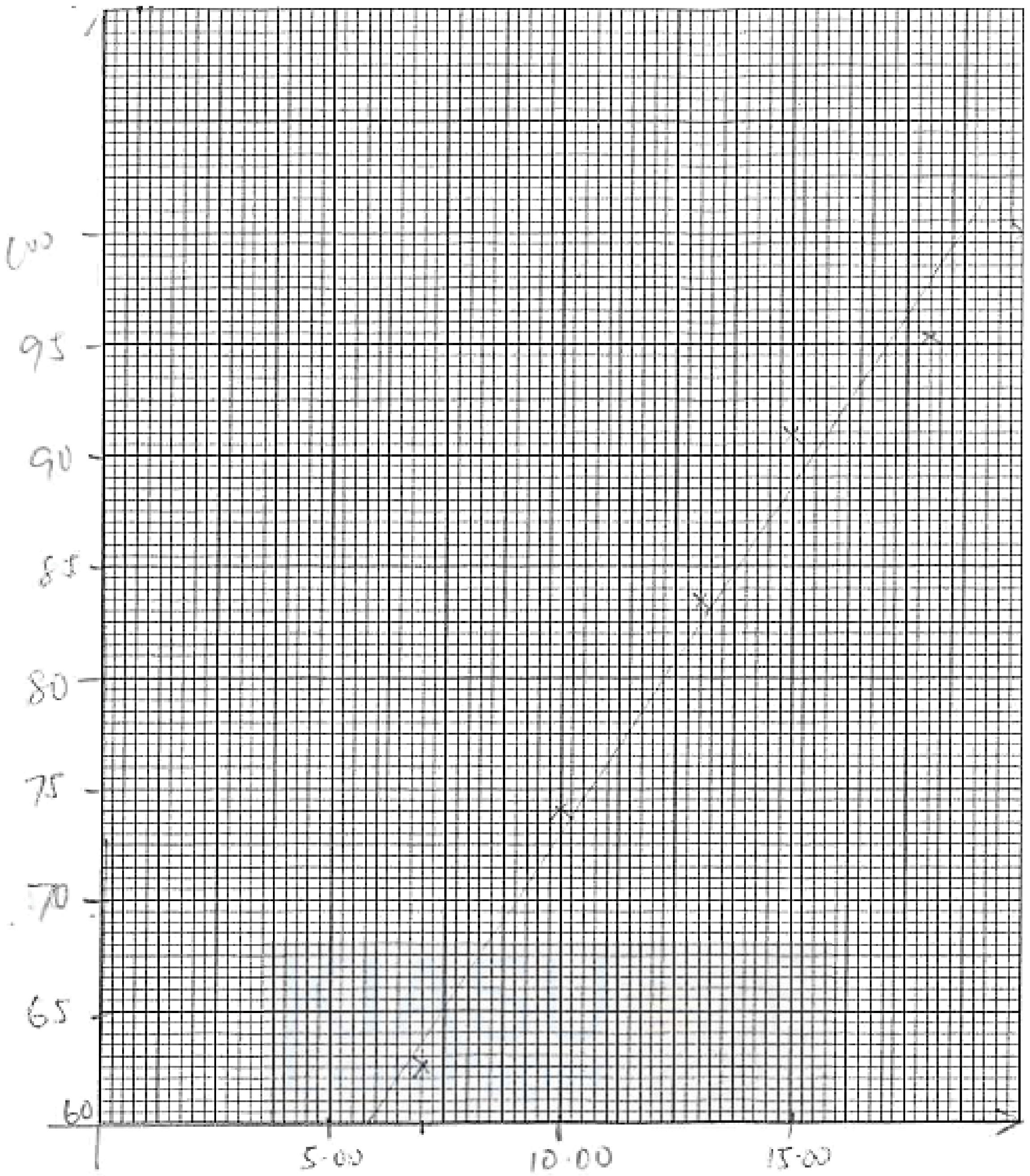
Experiment	Vol. of FA4/ cm^3	Time taken/s	Rate/ mol dm^{-3} s^{-1}
1	20.00	20	100
2	10.00	27	74.0
3	7.00	32	62.5
4	13.00	24	83.3
5	15.00	22	90.9
6	18.00	21	95.2

Rates correctly calculated using $\dfrac{0.00200}{\text{reaction time}} \times 10^6$

Units for volume given as cm^3. Units for time given as s. Units for rate given as mol dm^{-3} s^{-1}, 3 correct columns used and 3 sig fig. Ignore precision for volume of FA4 and time. **M23**

[1]

(c) On the grid, plot the rate (*y*-axis) against the volume of **FA 4** (*x*-axis). Draw a line of best fit through the points. You should identify any points you consider anomalous.



Axes labelled – rate/ mol dm^{-3} s^{-1} on *y*-axis and volume or FA 4 / cm^3 on *x*-axis. Scales to use at least half of each axis including 0.0 if point plotted. **M24**

Correct plotting – **all** points recorded plotted and within half a small square and within correct small square. Scale must be drawn correctly. **M25**

Draws a line of best fit (can be straight line or curve). Straight lines must be straight (single line with no kinks, drawn using a ruler) or a smooth curve (gradual change in gradient).
Points not on the line must be balanced on either side of the best fit line but any points ringed or labelled as anomalous should be ignored. **M26**

[3]

(d) Using your graph, what conclusion can you reach about the effect of changing the concentration of $FeCl_3$ on the rate of the reaction between Fe^{3+}(aq) and I^-(aq)?

Rate increases as concentration of Fe^{3+} increases/ rate directly proportional to concentration **M27** since **either straight line that pass through the origin shows** rate is directly proportional to concentration **or gradient is positive** **M28** shows that rate increase with increase in concentration (or other words to that effect).

[2]

(e) It was found, by carrying out experiments similar to those used in **(a)**, that increasing the concentration of I^- increased the rate of the reaction.

The student suggested a modification to the method by using the same volumes of all reagents but with the concentration of **FA4** and **FA 5** being doubled their original values. State what the effect would be on the **reaction time** in Experiment 1 and explain how this change would affect any **possible errors** in the measurements.

Reaction time less/shorter. (**Less accurate) since larger % error** (in time). **M29**
Not "Reaction time faster".

[1]

(f) Which of the experiments you carried out in **(a)** had the greatest percentage error in the reaction time? Calculate this percentage error. Assume that the error in measuring the reaction time is ±0.5 s.

Experiment 1.

percentage error = $\frac{0.5}{20} \times 100\%$ **M30**

[1]

(g) **Planning**

Aqueous hydrogen peroxide decomposes into oxygen gas and water. The reaction is normally very slow but is catalysed by solid manganese (IV) oxide.

$$2H_2O_2(aq) \longrightarrow 2H_2O(l) + O_2(g)$$

You are to plan an experiment to investigate how the rate of the catalysed decomposition of aqueous hydrogen peroxide depends on its concentration.

(i) The rate of decomposition depends on the number of hydrogen peroxide molecules present in a given volume of solution.

Use this information to predict how the rate of decomposition of the hydrogen peroxide depends on the concentration.

Prediction

Prediction: Predicts **any** direct proportionality e.g. Increasing concentration increases rate or doubling the molecules per unit volume (concentration) doubles the rate. **M31**

[1]

(ii) You are to design a laboratory experiment to test your prediction in **(g) (i)**.

In addition to the standard apparatus present in a laboratory you are provided with the following materials.

- 0.1 mol dm^{-3} aqueous hydrogen peroxide
- A supply of manganese (IV) oxide

Complete the table below to show how you would prepare five solutions of aqueous hydrogen peroxide. Make sure that the correct units are recorded.

expt No.	volume of H_2O_2 / cm^3	volume of H_2O / cm^3	concentration of H_2O_2 / mol dm^{-3}
1	40.00	0.00	0.100
2	35.00	5.00	0.0875
3	30.00	10.00	0.0750
4	25.00	15.00	0.0625
5	20.00	20.00	0.0500

Whole table completed. Correct units required for each column. 0 cm^3 of H_2O_2 not accepted. Total volume of solutions need not be constant. **M32**

Pre-calculation
Assuming burette is used, maximum volume of O_2 that can be collected will be 50 cm^3.

Amount of O_2 = 50/24000 = 2.0833×10^{-3} mol
Amount of H_2O_2 = 2 x 2.0833×10^{-3} = 4.1667×10^{-3} mol

Volume of original H_2O_2 = (4.1667×10^{-3})/ 0.1
= 41.67 cm^3

Note: If gas syringe is used in planning, maximum volume of original H_2O_2 will be around 80 cm^3.

[1]

(ii) Give a step by step description of how you would carry out **one** complete experiment.

1. Using a burette, introduce 35.00cm^3 of H_2O_2 solution into a 100 cm^3 conical flask.
2. Using another burette, introduce 5.00 cm^3 of distilled water into the same conical flask.
3. Attach a small tube containing some solid manganese (IV) oxide with a string and stopper it.
4. Record initial volume reading of the syringe.
5. Let the manganese (IV) oxide comes in contact with the solution by loosening the stopper.
6. Start the stopwatch immediately. Swirl to mix gently.
7. Stop the stopwatch once 20 cm^3 of gas has been collected.

Give marks for shaking to react the catalyst and solution present. If a thistle or dropping funnel used the mark is for adding the liquid reagent to the catalyst. In other situations give marks for adding solid catalyst to the solution and closing the vessel. **M33**

Start the reaction and a stopwatch simultaneously. **M34**

Recording the time taken to produce a chosen/fixed volume of gas. **M35**

[3]

(iii) State a problem which might be experienced by someone having to carry out these experiments alone.

Starting the reaction and the stopwatch simultaneously is difficult. Accept any reaction starting process in conjunction with starting the clock. Accept closing the apparatus and starting the clock. **M36**

[1]

[Total: 23]

3 Qualitative Analysis

At each stage of any test you are to record details of the following:
- colour changes seen
- the formation of any precipitate
- the solubility of such precipitates in an excess of the reagent added

Where gases are released they should be identified by a test, **described in the appropriate place in your observations.**

You should indicate clearly at which stage of the test a change occurs.
Marks are **not** given for chemical equations.
No additional tests for ions present should be attempted.

If any solution is warmed, a boiling tube MUST be used.

Rinse and reuse test-tubes and boiling tubes where possible.

Where reagents are selected for use in a test, the name or correct formula of the element or compound must be given.

(a) **FA 7** and **FA 8** are mixtures. Each mixture contains one cation and two anions from those listed on pages 18 and 19.

Carry out the following tests and record all your observations in the table below.

FA 7 is $Al_2(SO_4)_3$ + $NaCl$; **FA 8** is $MgCO_3$ + KI; **FA 9** is $(NH_4)_2Fe(SO_4)_2$

Test	Observations	
	FA 7	**FA 8**
(i) Place two spatula measure of **FA 7** into a boiling tube, then add approximately 5 cm^3 of dilute nitric acid using the measuring cylinder. You are to repeat the steps for **FA 8**. Then	**FA 7** dissolves/ A colourless solution is formed. [√]	**FA 8** dissolves and effervescence seen. Gas produced gives a white ppt. with $Ca(OH)_2(aq)$. [√]
add about 5 cm^3 of distilled water and shake to mix the solution. Use a 1 cm depth of the solution obtained in a test-tube for each of tests **(ii)** – **(v)**.	No observation required.	
(ii) Add aqueous sodium hydroxide. Then add dilute nitric acid dropwise until in excess.	White ppt. formed, soluble in excess [√] White ppt. re-forms, soluble in excess $HNO_3(aq)$ [√]	Do not carry out this test.
(iii) Add aqueous ammonia.	White ppt. formed, insoluble in excess [√]	Do not carry out this test.
Test	Observations	
	FA7	**FA8**
(iv) Add aqueous barium nitrate followed by dilute nitric acid.	White ppt. formed, insoluble in dilute HNO_3 [√]	No ppt or no observable change [√]

(v) Add aqueous silver nitrate followed by aqueous ammonia.	White ppt formed, soluble in $NH_3(aq)$ [√]	Yellow ppt formed, insoluble in $NH_3(aq)$ [√]

[4]

2 [√] – [1], max [4] M37, M38, M39, M40

(vi) Use your observations to identify the following ions.
FA 7 contains cation …………………………………

FA 7 contains anions ………………………………… and ………………………………
FA 8 contains anions ……………………………… and ………………………………

State and explain all the evidence for your identification of the cation in **FA 7**.
M41 cation is Al^{3+} and while ppt with $NH_3(aq)$ insoluble in excess, white ppt with NaOH soluble in excess.
M42 FA 7 anions: SO_4^{2-} and Cl^-
M43 FA 8 anions: CO_3^{2-} and I^-

[3]

(b) **FA 9** contains two cations from the list on page 18.

(i) Transfer approximately half of the **FA 9** into a hard-glass test-tube and heat gently at first, and then strongly, until no further change is seen.
Test with litmus papers while you are heating.
Record all your observations below.

Any two observations correct **M44**

- **FA 9** is (pale) green
- steam/ vapour/ condensation/ water liquid
- damp litmus paper turns blue
- yellow/ white/ brown residue formed
- white smoke (produced on strong heating)
- damp litmus turns red on strong heating

[1]

(ii) Carry out further tests that will enable you to identify **both** cations in **FA 9**.
Describe your tests briefly and state your observations.

With NaOH or NH_3, dirty green ppt formed which turns brown on contact with air and Fe^{2+} identified. **M45**
With NaOH(aq) and heat, pungent gas (NH_3) turns damp red litmus paper blue and NH_4^+ identified. **M46**

FA 9 contains cations ……… Fe^{2+}……………….. and ……… NH_4^+ ……………..
[2]

(c) **Planning**

A solder is an alloy of metals which is used to join other metal pieces together.

A specialist solder that can be used to join together pieces of aluminium is made from a mixture by mass of 65% zinc, 20% aluminium and 15% copper.

You are to plan an experimental procedure to confirm the composition of a powdered sample of this solder, by adding reagents and then extracting from the mixture each of the following in sequence;

(i) the copper metal,
(ii) the aluminium as aluminium hydroxide,
(iii) the zinc as zinc hydroxide

You are provided with

- a sample of this solder, with approximate mass 4 g,
- 1.00 mol dm^{-3} sulfuric acid,
- 1.00 mol dm^{-3} ammonia

No other reagents should be used. Standard laboratory equipment is available including a balance, accurate to two decimal places.

(i) Complete the flowchart below to show the order in which the reagents would be added to the solder to allow you to extract and separate the components as copper metal, (**Step 1**), aluminium hydroxide, **(Step 2)**, and zinc hydroxide, **(Step 3)**.
You are reminded that aqueous ammonia contains both the base OH^{-} and the complex-forming molecule NH$_3$.

Step 1	Step 2	Step 3
reagent(s) added	reagent(s) added	reagent(s) added
sulfuric acid **[√]**	(excess, aqueous) ammonia **[√]**	sulfuric acid **[√]**
substance(s) present at the end of the reaction	substance(s) present at the end of the reaction	substance(s) present at the end of the reaction
zinc sulfate **[√]** and aluminium sulfate **[√]** (copper)	zinc (tetra) ammine **[√]** (ions) (aluminium hydroxide)	ammonium sulfate **[√]** (zinc hydroxide)
substance(s) removed by filtration (if any)	substance(s) removed by filtration (if any)	substance(s) removed by filtration (if any)
copper **[√]**	aluminium hydroxide **[√]**	zinc hydroxide **[√]**

Allow: Correct formulae or ions instead of names.
2**[√] – 1 mark; max [5] M47, M48, M49, M50, M51**

Substances present for each step is conditional based on correct reagent added.

[5]

(ii) For some of the steps in the procedure you would need to be careful to add an appropriate quantity of a reagent.
For each step of your procedure explain why particular quantities of reagent should be chosen.

Step 1
Sufficient/ enough/ excess sulfuric acid to dissolve the zinc and aluminium **M52**

Step 2
Sufficient/ enough/ excess aqueous ammonia (to precipitate aluminium hydroxide) and to completely dissolve the zinc hydroxide **M53**

Step 3
Sufficient/ enough sulfuric acid to:
Neutralise ammonia **M54** **OR**
(re)precipitate the zinc hydroxide but not so much that the zinc hydroxide reacts/ dissolves **M54**

[3]

(iii) If the mass of aluminium hydroxide obtained was 1.50 g, calculate the mass of aluminium that was present in the solder.
[A_r: A*l*, 27.0; O, 16.0]

Mass of A*l* in solder = $\frac{27}{27+17\times3}$ x 1.50 g = **<u>0.519 g</u>** **M55**

[1]

[Total: 19]

JURONG JUNIOR COLLEGE
2017 JC 2 PRELIMINARY EXAMINATION
Higher 2

CANDIDATE NAME			
CLASS	**17S**	EXAM INDEX	

CHEMISTRY

9729/01

Paper 1 Multiple Choice

14 September 2017
1 hour

Candidates answer on separate paper.

Additional Materials: Multiple Choice Answer Sheet
Data Booklet

READ THESE INSTRUCTIONS FIRST

Write in soft pencil.
Do not use staples, paper clips, glue or correction fluid.
Write your name, class and exam index number on the Answer Sheet in the spaces provided unless this has been done for you.

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

Read the instructions on the Answer Sheet very carefully.

Each correct answer will score one mark. A mark will not be deducted for a wrong answer.
Any rough working should be done in this booklet.
The use of an approved scientific calculator is expected, where appropriate.

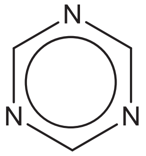
This document consists of **13** printed pages and **1** blank page.

1 When a beam of protons ($^{1}H^{+}$), travelling at the same speed, passes through an electric field of constant strength, the angle of deflection is +12 °.

Assuming an identical set of experimental conditions, which particle would be deflected through an angle of +8 °?

A $^{6}Li^{4-}$ **B** $^{6}Li^{2+}$ **C** $^{3}He^{2+}$ **D** $^{12}C^{3-}$

2 1,3,5–triazine is an aromatic compound and its structure resembles that of benzene.
The structure of 1,3,5–triazine is shown below.



1,3,5-triazine

Which statement about 1,3,5–triazine is correct?

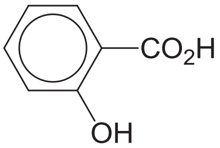
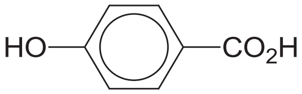
A The empirical formula of 1,3,5–triazine is CN.

B A molecule of 1,3,5–triazine has six σ bonds.

C The π bond between carbon and nitrogen atoms is formed by sp^2–sp^2 overlap.

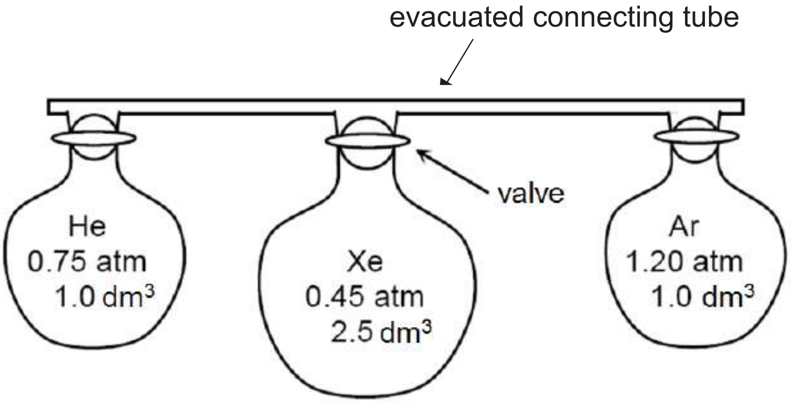
D All the carbon–nitrogen bonds have equal bond lengths.

3 In which pair does the first substance have a higher boiling point than the second?

	First substance	Second substance
A	HF	HC*l*
B	CH_3COCH_3	$(CH_3)_2NH$
C	$(CH_3)_3CH$	$CH_3CH_2CH_2CH_3$
D		

Need a home tutor? Visit smiletutor.sg

4 The following diagram shows the contents of three vessels which are joined together by a connecting tube which is evacuated of air.



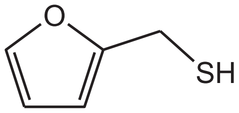
After the valves on the vessels are opened, the final pressure is measured and is found to be 0.675 atm.

Assuming that the temperature of the whole setup is maintained at 30 °C, what is the volume of the connecting tube?

A 0.023 dm^3 **B** 0.040 dm^3 **C** 0.056 dm^3 **D** 0.094 dm^3

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

Furfuryl thiol (M_r = 114) is the key component of the aroma of roasted coffee.



furfuryl thiol

Which statements about furfuryl thiol are correct?

1 On complete combustion, 0.10 g of furfuryl thiol produces 0.23 g of CO_2.

2 On complete combustion, 0.10 g of furfuryl thiol produces 21 cm^3 of SO_2 measured under r.t.p.

3 On complete combustion, 0.10 g of furfuryl thiol produces 0.16 g of H_2O.

4 0.10 g of furfuryl thiol reacts with an excess of bromine to produce 0.38 g of product. Assume that the –SH group in furfuryl thiol does not react with bromine.

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

6 A solution mixture contains both sodium carbonate (M_r = 106) and sodium hydrogen carbonate (M_r = 84.0).

25.0 cm^3 of the solution mixture was titrated against 0.300 mol dm^{-3} hydrochloric acid. 15.0 cm^3 of HCl is required to decolourise the phenolphthalein indicator. A few drops of methyl orange indicator was then added and a further 20 cm^3 of HCl is required for methyl orange indicator to change colour.

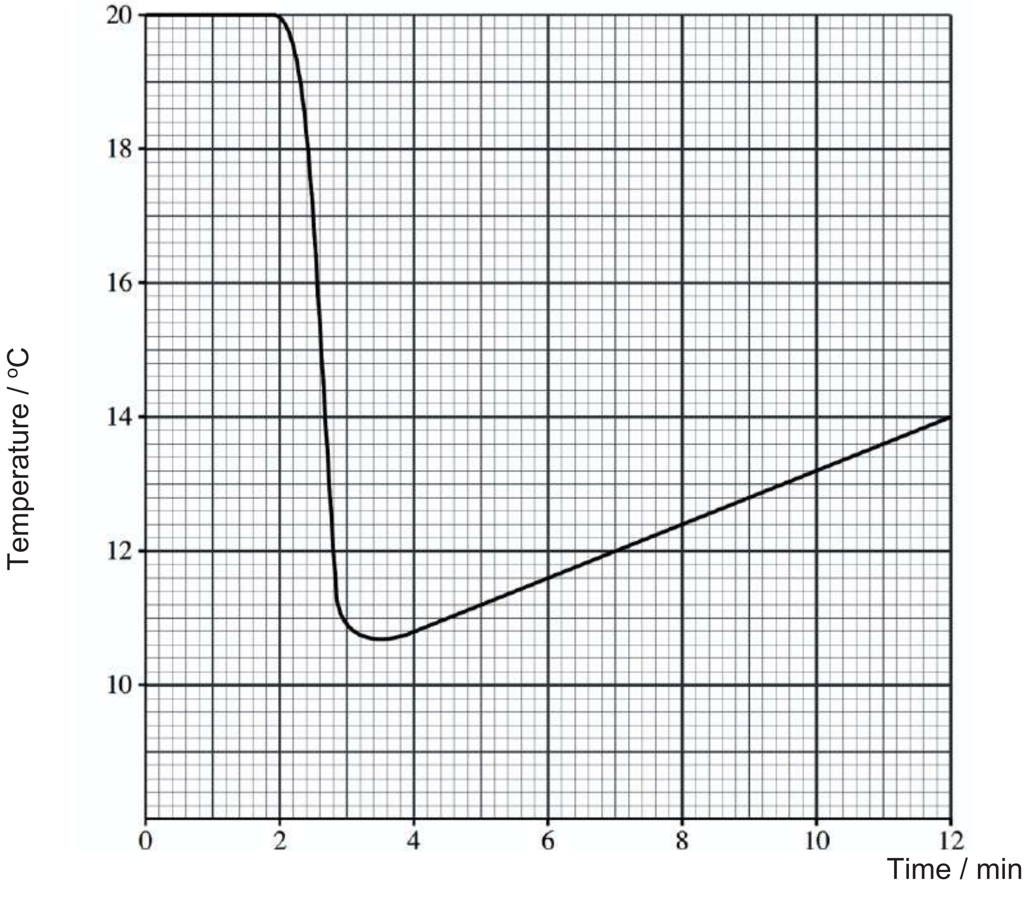
What is the percentage, by mass, of sodium carbonate present in the solution mixture?

A 20.9 % **B** 25.0 % **C** 75.0 % **D** 79.1 %

7 Sodium carbonate reacts with ethanoic acid according to the equation below.

$$Na_2CO_3(s) + 2CH_3COOH(aq) \xrightarrow{\Delta H_r} 2CH_3COONa(aq) + H_2O(l) + CO_2(g)$$

In an experiment to determine the enthalpy change of reaction, ΔH_r, 7.5 g of solid sodium carbonate (M_r = 106) was added to 50 cm^3 of excess aqueous ethanoic acid at the second minute. The temperature of the resultant solution was monitored at various time intervals and the following graph was obtained.



Given that the specific heat capacity of the solution is 4.18 J cm^{-3} K^{-1}, what is the most accurate enthalpy change of reaction, ΔH_r, which can be obtained from this graph?

A +17.7 kJ mol^{-1} **B** +27.5 kJ mol^{-1}

C +29.5 kJ mol^{-1} **D** +31.0 kJ mol^{-1}

8 The kinetic of the following reaction is studied, using a colorimeter, by finding the time taken for the coloured reactant, **E**, to decolourise. The reaction is catalysed by **Y**.

$$\mathbf{E + F \xrightarrow{Y} G + H}$$

The following results are obtained:

Experiment	Volume of solution added / cm^3				Time taken / s
	E	**F**	**Y**	H_2O	
1	10	20	10	10	20
2	10	10	10	20	40
3	10	20	5	15	40
4	5	20	10	15	10

What is the rate equation for the reaction?

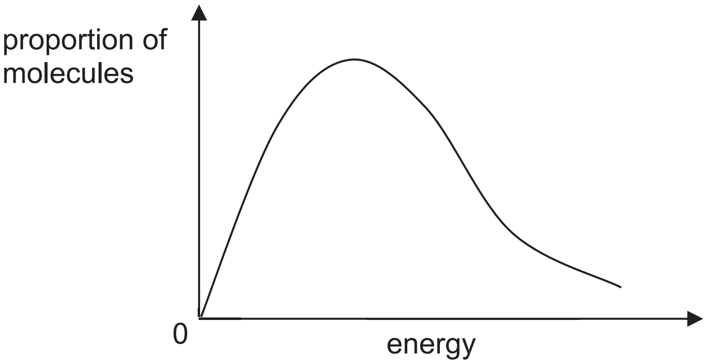
A rate = *k*[**E**][**F**]

B rate = *k*[**E**][**Y**]

C rate = *k*[**F**][**Y**]

D rate = *k*[**E**][**F**][**Y**]

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



As the temperature increases, which statements are correct?

1 The maximum of the curve is displaced to the right.

2 The proportion of molecules with energies above any given value increases.

3 The proportion of molecules with any given energy increases.

A 1 only

B 1 and 2 only

C 2 and 3 only

D 1, 2 and 3

10 The interhalogen compound BrF_3 is a volatile liquid which autoionises.

$$2BrF_3 \rightleftharpoons BrF_2^+ + BrF_4^-$$

The electrical conductivity of BrF_3 decreases with increasing temperature.

Which statement about the autoionisation process is correct?

A The autoionisation process is endothermic and the shape of the cation is linear.

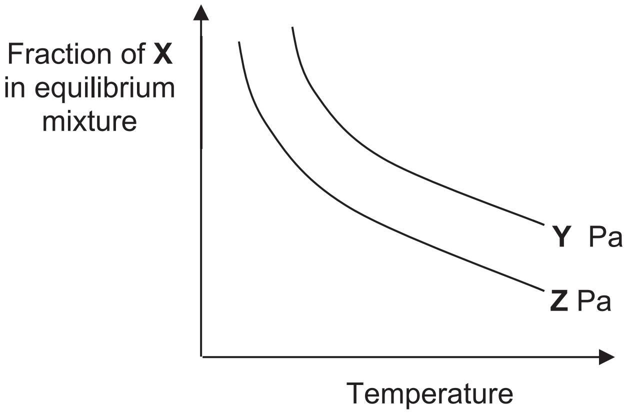
B The autoionisation process is endothermic and the shape of the cation is non–linear.

C The autoionisation process is exothermic and the shape of the cation is linear.

D The autoionisation process is exothermic and the shape of the cation is non–linear.

11 The graph below shows how the fraction of **X**, which represents one of the following compounds in the equilibrium mixture shown below, varies with temperature at pressures of **Y** Pa and **Z** Pa.

$$4NH_3(g) + 3O_2(g) \rightleftharpoons 2N_2(g) + 6H_2O(g) \qquad \Delta H = -1267 \text{ kJ mol}^{-1}$$



Identify **X** and the correct relative magnitudes of **Y** and **Z**.

	X	Pressure
A	N_2	**Z** > **Y**
B	O_2	**Y** > **Z**
C	H_2O	**Y** > **Z**
D	NH_3	**Z** > **Y**

12 What is the pH of an aqueous solution containing 0.1 mol dm^{-3} sodium benzoate and 0.01 mol dm^{-3} benzoic acid? [K_a (benzoic acid) = 6 x 10^{-5} mol dm^{-3}]

A 3.22 **B** 4.22 **C** 4.78 **D** 5.22

13 When 25.0 cm^3 of a 0.100 mol dm^{-3} strong monobasic acid was titrated against 0.200 mol dm^{-3} of a weak base **Q**, 12.50 cm^3 of the base was required to completely neutralise the acid.

Which statements are correct for this experiment?

1 **Q** is a diprotic base.

2 The pH of the solution at the equivalence point is 7.

3 A solution of maximum buffering capacity was formed when 6.25 cm^3 of the base was added.

A 3 only

B 1 and 2 only

C 2 and 3 only

D None of the above

14 The numerical values of the solubility products of three metal sulfides are tabulated below.

Compound	Numerical value of solubility product
CuS	6.3×10^{-36}
ZnS	1.6×10^{-21}
Bi_2S_3	1.1×10^{-73}

Which of the following shows the three metal sulfides arranged in order of increasing molar solubility in water?

	lowest	⟶	highest
A	Bi_2S_3	CuS	ZnS
B	ZnS	CuS	Bi_2S_3
C	ZnS	Bi_2S_3	CuS
D	CuS	Bi_2S_3	ZnS

15 Four compounds of some Period 3 elements are listed below.

Na_2O $SiCl_4$ SO_2 $NaCl$

Which pair of compounds, when mixed in water, could give a resultant solution of pH 7?

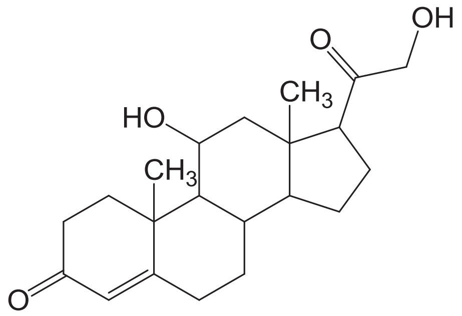
A $NaCl$ and Na_2O

B $NaCl$ and SO_2

C Na_2O and $SiCl_4$

D $SiCl_4$ and SO_2

16 Corticosterone is a hormone involved in the metabolism of carbohydrates and proteins.



corticosterone

How many possible stereoisomers does Corticosterone has?

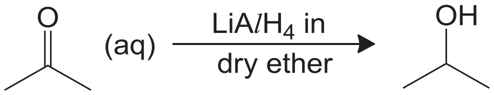
A 2^6 **B** 2^7 **C** 2^8 **D** 2^9

17 Which of the following transformation will occur under the given conditions?

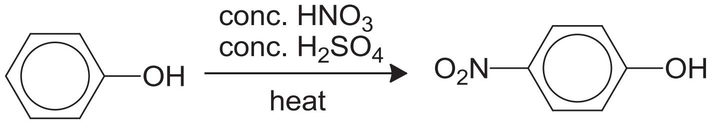
A $CH_3CH_2CH(OH)CH_2I \xrightarrow[\text{heat}]{I_2,\ \text{NaOH}} CH_3CH_2COO^- + CHI_3$

B $CH_3CN(l) \xrightarrow[\text{heat}]{HCl(g)} CH_3COOH + NH_4Cl$

C



D



18 Gem–diols, in which both hydroxyl groups are bonded to the same carbon, can spontaneously eliminate a molecule of water to produce a carbonyl compound.

Which compound, after complete hydrolysis, gives a precipitate when warmed with $[Ag(NH_3)_2]^+$ complex?

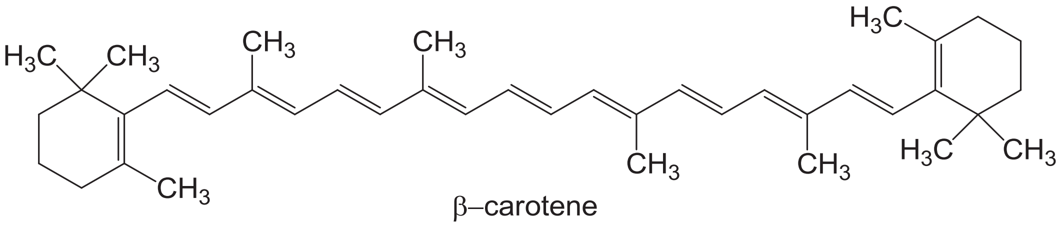
A 1,1–dibromobutane

B 1,2–dibromobutane

C 2,2–dibromobutane

D 2,3–dibromobutane

19 β-carotene is responsible for the orange colour of carrots and its structure is shown below.



β–carotene

When a molecule of β–carotene is oxidised by hot, concentrated acidified $KMnO_4$, many product molecules are formed.

How many of these product molecules contain the ketone functional group?

A 4 **B** 6 **C** 9 **D** 11

20 Lactic acid, $CH_3CH(OH)CO_2H$, causes pain when its concentration builds up in muscles.

Which reagents react with **both** of the –OH groups in lactic acid?

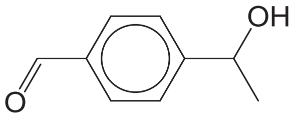
1 hydrogen bromide
2 phosphorus pentachloride
3 sodium
4 sodium hydroxide

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

21 Which of the following represents the correct sequence of increasing pK_a value of the four compounds?

	smallest pK_a	→		largest pK_a
A	CCl_3CO_2H	CH_3CO_2H	C_6H_5OH	C_2H_5OH
B	CCl_3CO_2H	CH_3CO_2H	C_2H_5OH	C_6H_5OH
C	C_6H_5OH	C_2H_5OH	CCl_3CO_2H	CH_3CO_2H
D	C_2H_5OH	C_6H_5OH	CH_3CO_2H	CCl_3CO_2H

22 Consider the following compound **G.**



G is heated with acidified $K_2Cr_2O_7$ to form compound **H**.

Both **G** and **H** are then separately warmed with Fehling's solution and the observations are noted.

What are the observations?

A Both **G** and **H** give a red precipitate.
B Only **G** gives a red precipitate.
C Only **H** gives a red precipitate.
D Neither **G** nor **H** gives a red precipitate.

23 Chloroethane can be used to make sodium propanoate.

chloroethane ⟶ **R** ⟶ sodium propanoate

The intermediate, **R**, is treated with boiling aqueous sodium hydroxide to give sodium propanoate.

Which reagent would produce the intermediate, **R**, from chloroethane?

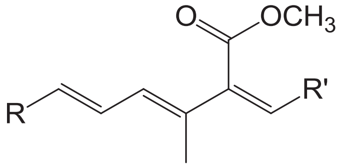
A alkaline $KMnO_4$
B hydrogen cyanide
C sodium hydroxide in ethanol
D potassium cyanide in ethanol

24 Which statements about the formation of a carboxylic acid are correct?

1 A carboxylic acid can be produced by oxidation of a primary alcohol.
2 A carboxylic acid can be produced by reduction of a nitrile.
3 A carboxylic acid can be produced by reduction of an aldehyde.
4 A carboxylic acid can be produced by hydrolysis of an acyl chloride.

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

25 Part of the structure of a fungicide, strobilurin, is shown. R and R’ are inert groups.

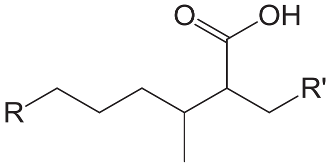


strobilurin

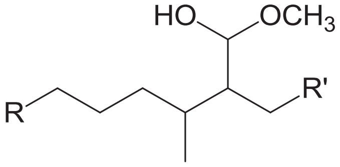
In this reaction, strobilurin is warmed with aqueous sulfuric acid to give compound **X**. Compound **X** is then treated with hydrogen in the presence of a nickel catalyst to give compound **Y.**

What could be the structure of compound **Y**?

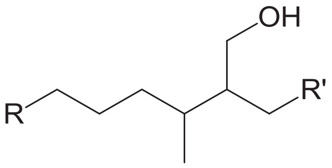
A



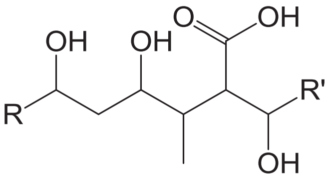
B



C



D



26 Why are amides, $RCONH_2$, less basic than amines, RNH_2?

A Amides form a zwitterion in which the nitrogen atom carries a positive charge.

B Amides have a resonance structure involving the movement of a pair of electrons from the nitrogen atom to the oxygen atom.

C Electrons on the nitrogen atom move on to the C–N bond giving it some double bond character so that it is more difficult to break.

D The amide carbonyl group withdraws electrons from the NH_2 group to make the hydrogen atoms acidic.

27 Which conditions are necessary when an electrode potential is measured using a standard hydrogen electrode as the reference electrode?

1 The use of hydrogen gas at 1 bar and 298 K.
2 Measurement of e.m.f. when the current delivered by the cell is effectively zero.
3 A pH of 1.0 for the solution at the hydrogen electrode.

A 1 and 2 only
B 1 and 3 only
C 2 and 3 only
D 1, 2 and 3

28 *The use of Data Booklet is relevant to this question.*

Peroxodisulfate ions convert iodide ions into iodine slowly.

$$S_2O_8^{2-}(aq) + 2I^-(aq) \rightarrow 2SO_4^{2-}(aq) + I_2(aq)$$

The rate of the reaction can be increased by adding catalysts such as aqueous iron(III) ions.

A possible pathway of a catalyst reaction involves the following steps:

Step 1 $2Fe^{3+}(aq) + 2I^-(aq) \rightarrow 2Fe^{2+}(aq)\ aq) + I_2(aq)$
Step 2 $S_2O_8^{2-}(aq) + 2Fe^{2+}(aq) \rightarrow 2Fe^{3+}(aq) + 2SO_4^{2-}(aq)$

Which statement about the reaction is **incorrect**?

A $S_2O_8^{2-}$ is a stronger oxidising agent than Fe^{3+}.
B The reaction between $S_2O_8^{2-}$ and I^- is slow because the $E^\ominus_{cell}$ value is small.
C The $E^\ominus_{cell}$ for step 2 is more positive than step 1.
D Aqueous cobalt(II) ions can be used as a catalyst for this reaction.

29 The following data refers to iron as a typical transition element and to calcium as an s–block element.

For which property are the data under the correct element?

	Property	*Fe*	*Ca*
A	density	7.87	1.54
B	electrical conductivity	9.6	85
C	melting point	810	1538
D	metallic radius	0.231	0.140

30 When aqueous ammonia is added to a solution containing hexaaquacopper(II) ions, $[Cu(H_2O)_6]^{2+}$, a pale blue precipitate is formed. When excess ammonia is added, blue precipitate dissolves to form a dark blue solution.

What are the roles of the ammonia molecules in the above reactions?

1 Bronsted–Lowry base
2 Ligand
3 Reducing agent

A 1 only
B 2 only
C 1 and 2 only
D 2 and 3 only

BLANK PAGE

JURONG JUNIOR COLLEGE
2017 JC 2 PRELIMINARY EXAMINATION
Higher 2

CANDIDATE NAME			
CLASS	**17S**	EXAM INDEX	

CHEMISTRY — 9729/02

Paper 2 Structured Questions

29 August 2017
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	**10**
2	**18**
3	**11**
4	**10**
5	**12**
6	**14**
Penalty (delete accordingly)	
Lack **3sf** in final ans	**–1 / NA**
Missing/wrong **units** in final ans	**–1 / NA**
Bond linkages	**–1 / NA**
Total	

This document consists of **17** printed pages and **1** blank page.

Answer **all** the questions.

1 **(a)** Draw a fully labelled diagram of the electrochemical cell you would set up in order to measure the standard electrode potential of the Cu^{2+}/Cu half–cell.

[3]

In the Earth's crust, copper often occurs as the sulfide associated with zinc sulfide. Pure copper is extracted from this mixture.

In the first stage of extraction, the copper extracted contains some zinc and silver impurities. Electrolysis was used to purify the extracted copper with impure copper as the anode, and pure copper at the cathode.

(b) Using relevant data from the *Data Booklet*, explain what happens to the impurities at the anode.

....

....

....

....

....

....

....

....

....

....

....

.... [2]

1 **(c)** Using relevant data from the *Data Booklet*, explain what happens at the cathode.

....

....

....

....

....

....

....

....

....

....

....

.... [2]

(d) A similar set up can be used for copper plating, using pure copper electrode as the anode.

Calculate the time taken to coat 0.50 g of copper on the object if a current of 0.20 A was passed through the electrolysis bath.

[3]

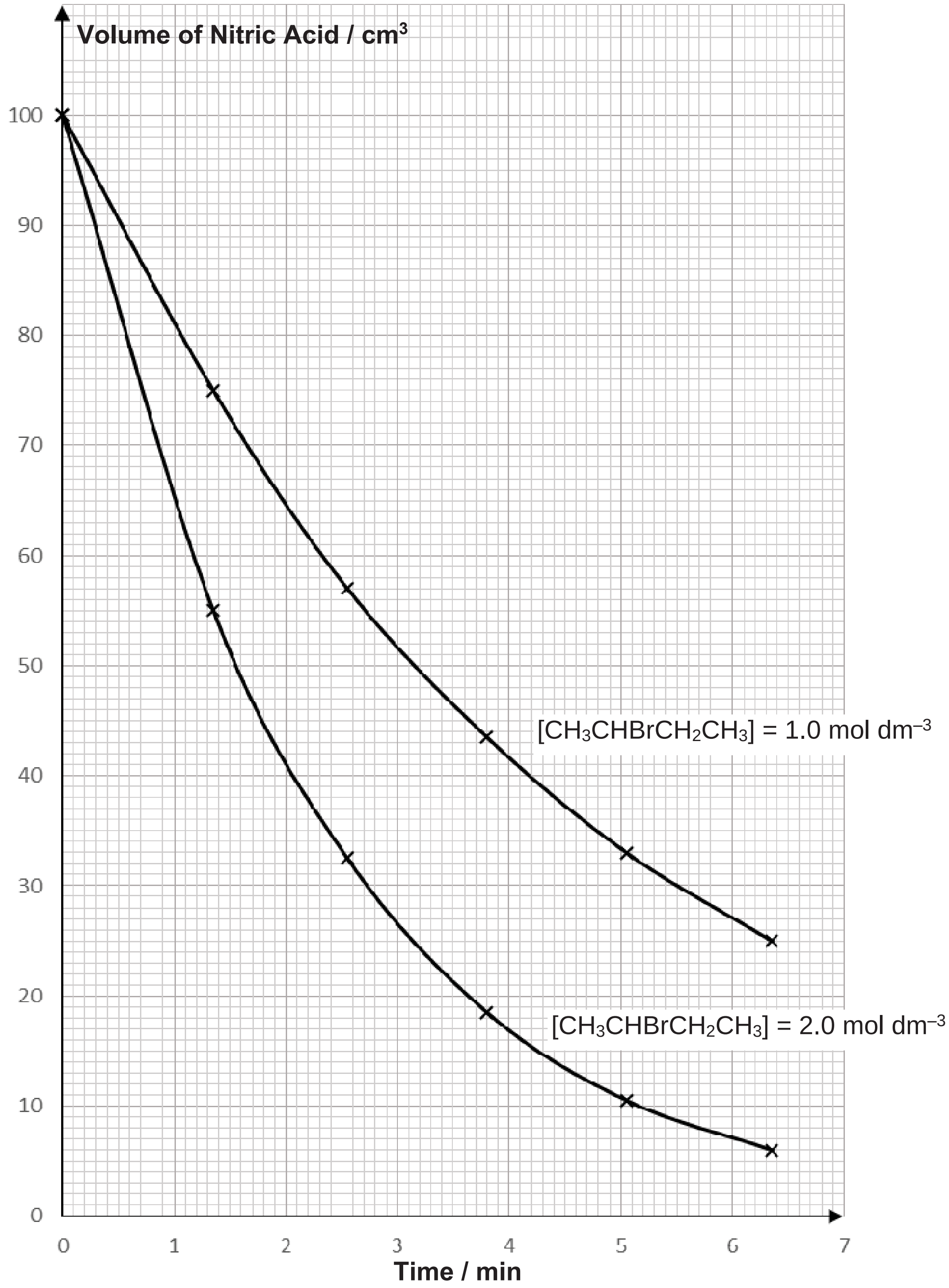
[Total: 10]

2 **(a)** 2–bromobutane, $CH_3CHBrCH_2CH_3$, is hydrolysed by aqueous sodium hydroxide.

The kinetics of the reaction can be monitored by withdrawing samples of the solution at appropriate times and titrating them with aqueous nitric acid after quenching.

Two sets of experiments were performed using different initial concentrations of the 2–bromobutane while the initial concentration of sodium hydroxide was kept at 0.1 mol dm^{-3}.

The results obtained are shown in the graphs below.



2 **(a)** **(i)** Using the graph where [$CH_3CHBrCH_2CH_3$] = 1.0 mol dm^{-3}, find the order of reaction with respect to aqueous sodium hydroxide.

....

....

....

....

....

.... [2]

(ii) Using the graphs above, deduce the order of reaction with respect to 2–bromobutane.

....

....

....

....

....

.... [3]

(iii) Hence, write down the rate equation for this reaction.

.... [1]

(iv) State the half–life of sodium hydroxide when [NaOH] = 0.2 mol dm^{-3} and [$CH_3CHBrCH_2CH_3$] = 1.0 mol dm^{-3}.

.... [1]

(v) Calculate the time taken for [NaOH] to drop to 1 % of its original value when [$CH_3CHBrCH_2CH_3$] = 1.0 mol dm^{-3}.

[1]

For Examiner's Use

2 **(b)** **(i)** With reference to **(a)(iii)**, name and describe the mechanism of this hydrolysis reaction.

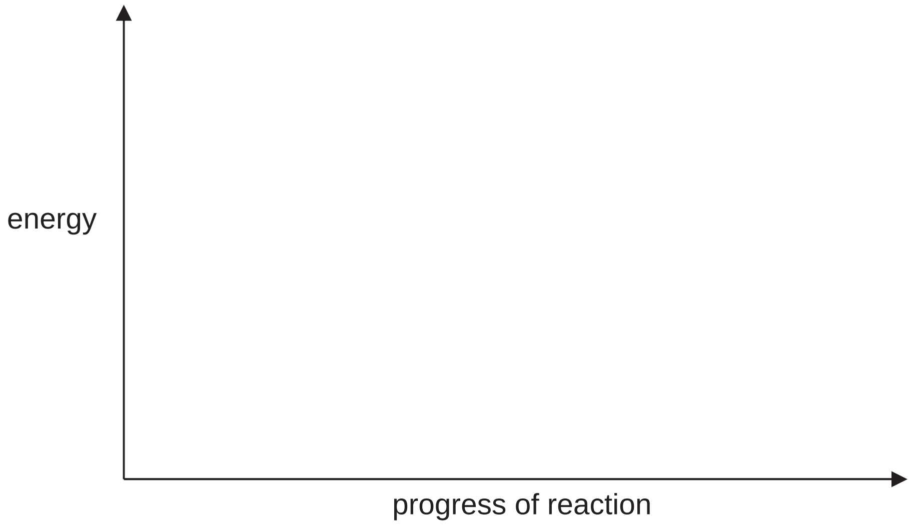
Type of mechanism: ……………………………………………………………

[3]

(ii) Draw the energy profile diagram for the mechanism you have described in **(b)(i)**.

On the diagram, label

- the reactants and products
- the enthalpy change of reaction, ΔH,
- the activation energy, E_a



[3]

(iii) How would the rate change if the experiment is repeated using 2–chlorobutane instead of 2–bromobutane? Explain.

………………………………………………………………………………………………

………………………………………………………………………………………………

………………………………………………………………………………………………

………………………………………………………………………………………………

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

2 **(b)** **(iv)** State and explain if the resultant mixture will be optically active if the reaction started with an optically pure sample of 2–bromobutane.

....

....

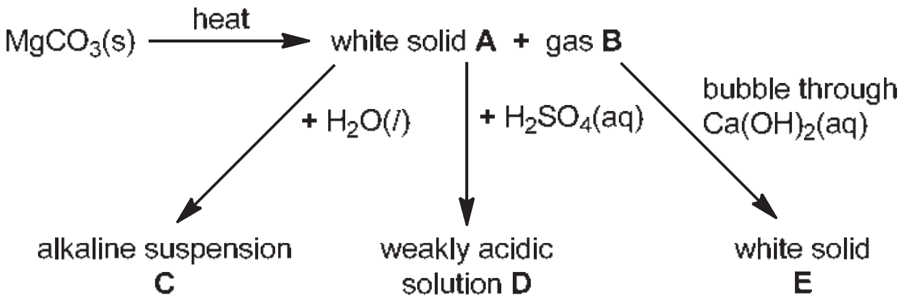
....

.... [2]

[Total: 18]

3 Group 2 elements are ingredients in many important materials from cement to face cream.

A student carried out the following experiments as shown in the reaction scheme below using a sample of magnesium carbonate.



(a) Identify compounds **A** to **E** in the reaction provided.

A: ………. **B:** ………. **C:** ………. **D:** ………. **E:** ………. [5]

(b) Explain, with the aid of an equation, why solution **D** is weakly acidic.

....

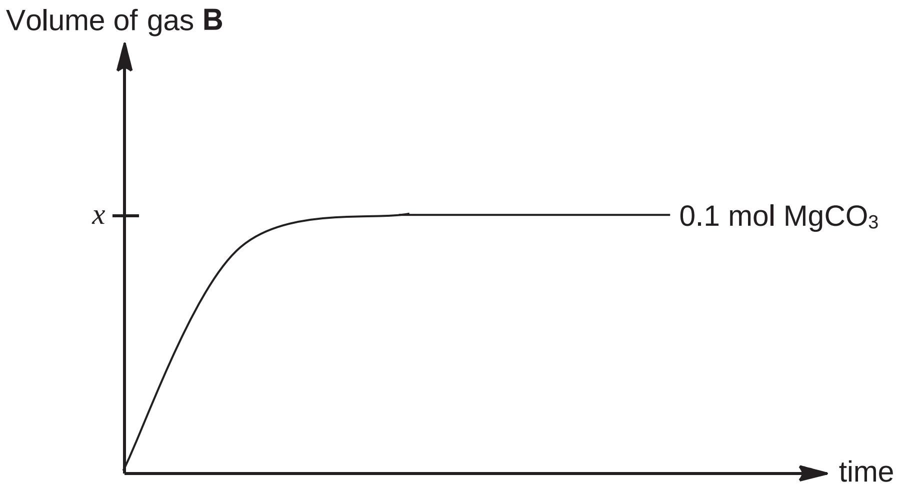
....

....

....

.... [2]

(c) The graph below shows the volume of gas **B** collected over time when 0.1 mol of magnesium carbonate is heated.



(i) Draw, on the same axes above, the graph that would be obtained when 0.1 mol barium carbonate was used and heated until it decomposed completely. [1]

3 **(c)** **(ii)** Explain the shape of the graph that you have drawn for **(c)(i)**.

....

....

....

....

....

....

....

....

.... [3]

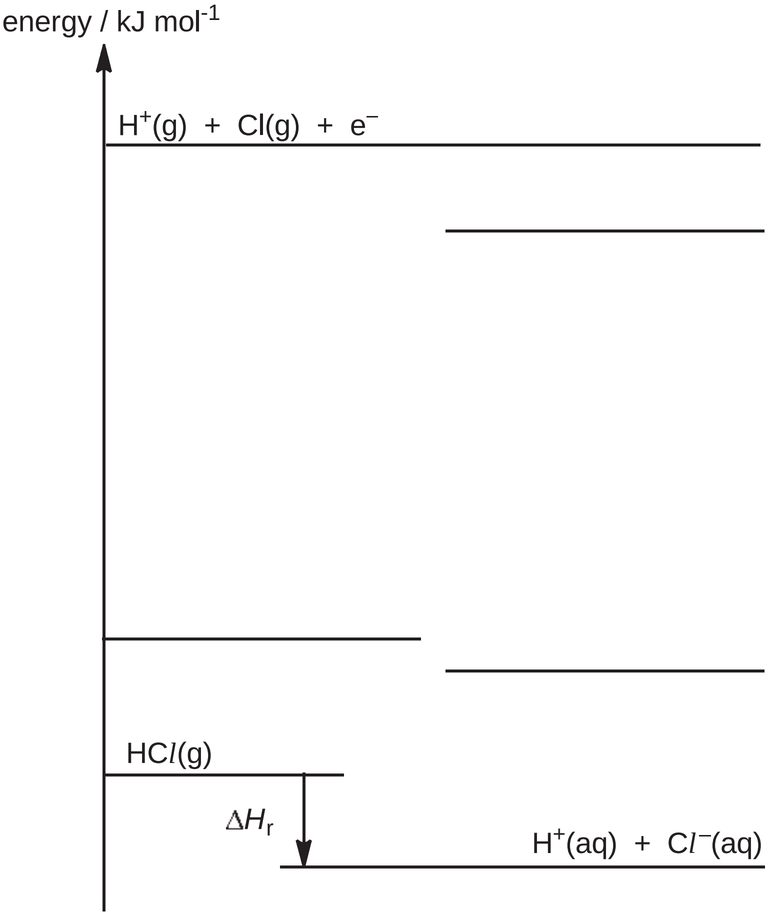
[Total: 11]

4 **(a)** Using relevant data from the *Data Booklet* and the following data, construct a labelled energy level diagram to calculate the enthalpy change of solution for gaseous hydrogen chloride.

Electron affinity of chlorine = –364 kJ mol^{-1}

Enthalpy change of hydration of hydrogen ion = –1071 kJ mol^{-1}

Enthalpy change of hydration of chloride ion = –381 kJ mol^{-1}



[3]

(b) Hence, calculate ΔG_{soln} for hydrogen chloride, given that $T\Delta S_{soln}$ is –18 kJ mol^{-1}.

[1]

4 **(c)** **(i)** Draw a labelled diagram to illustrate the interaction between chloride ion and water. State the type of interaction clearly in your diagram.

[2]

(ii) Explain how the magnitude of enthalpy change of hydration of bromide ions differs from that of chloride ions.

....

....

....

....

.... [2]

(e) *Use of Data Booklet is relevant to this question.*

Both hydrogen chloride and hydrogen bromide dissolve readily in water.

Describe a chemical test, which does not involve silver nitrate, that could distinguish between aqueous solutions of these two gases.

....

....

....

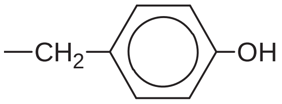
....

.... [2]

[Total: 10]

5 Amino acids are critical to life, and they serve as the building blocks of proteins. Out of the vast variety of amino acids, twenty are termed as essential because they cannot be created by the human body, and therefore must be supplied in the diet.

A peptide **A** was analysed and contained the following amino acids, [RCH(NH_2)CO_2H].

amino acid	**abbreviation**	**formula of R group**	**number of residues**
aspartic acid	asp	$–CH_2COOH$	one
glycine	gly	–H	one
serine	ser	$–CH_2OH$	two
tyrosine	tyr		one
valine	val	$–CH(CH_3)_2$	one

(a) Suggest suitable reagent and conditions for complete hydrolysis of proteins to amino acids non–enzymatically.

.... [1]

(b) **(i)** Given that aspartic acid has pK_a values of 2.0, 3.9 and 9.9, draw the structural formula of aspartic acid in its most stable state at pH 7.

[2]

(ii) Electrophoresis was used to separate the amino acids in the mixture.

Suggest, if any, whether aspartic acid will migrate towards the cathode or the anode.

.... [1]

(c) **(i)** Draw a structure of the dipeptide with the sequence, ser–asp.

[2]

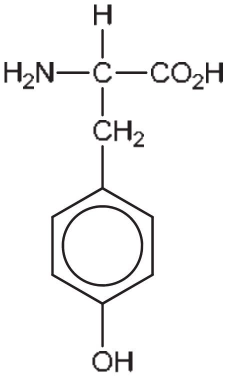
5 (c) (ii) Analysis of peptide **A** gave the following results:

- The N–terminus was shown to be ser.
- On reaction with a special reagent which digests at the carboxylic end of val, two peptides were obtained. One of these two was a dipeptide of sequence gly–ser.
- The enzyme chymotrypsin, which hydrolyses at the carboxylic group of tyr, gave two tripeptides.

Use these results to deduce the amino acid sequence of peptide **A**.

.... [2]

(d) Give the organic product(s) formed when tyrosine is subjected to the following reagents and conditions separately.



tyrosine

Reagent and Conditions	Organic Product(s)
Aqueous Br_2	
Cold aqueous NaOH	
CH_3COOH	

[4]

[Total: 12]

6 This question is about the reactions of Group 17 elements.

(a) 10.0 cm^3 of an aqueous solution containing 0.10 mol dm^{-3} Br_2 was added to 50.00 cm^3 of a 0.10 mol dm^{-3} NaOH solution.

The resulting solution required 30.00 cm^3 of 0.10 mol dm^{-3} HC*l* for complete neutralisation.

(i) Calculate the mole ratio of Br_2 to NaOH.

[3]

(ii) It was observed that during the reaction between Br_2 and NaOH, there is no gas evolved.

Given that the products formed are Br^- and BrO_x^-, write a balanced ionic equation for the reaction and hence deduce the value of x.

Balanced ionic equation: ……………………………………………………….

Value of x: ……….

[1]

6 **(b)** Mass spectrometry is an analytical technique which measures the masses of chemical species present within a sample. A mass spectrum can be used to determine the isotopic composition of a sample, masses of chemical species and to elucidate the chemical structure of a chemical compound.

The mass–to–charge ratio, also known as m/e value, is the M_r of chemical species present in the sample. The peak height ratio gives an indication of the isotopic ratio of elements in the sample.

In two separate experiments, propene was reacted with bromine in inert organic solvent and with aqueous bromine. The organic products were then extracted and analysed using mass spectrometry. The graphs below show the mass spectrum for each experiment.

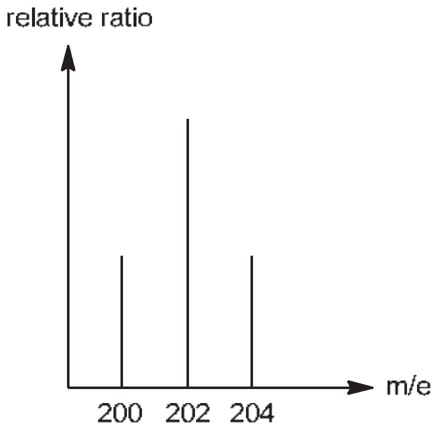


Fig 2.1: reaction with Br_2 in inert solvent

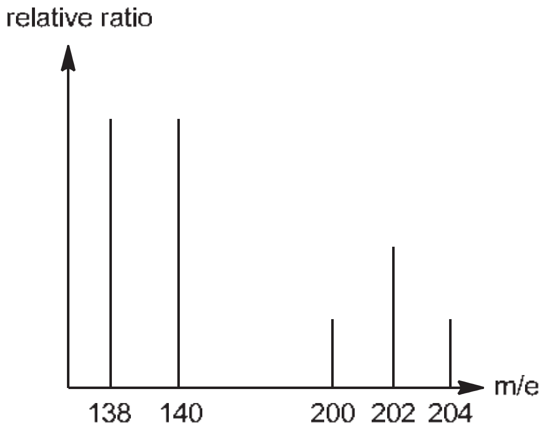


Fig 2.2: reaction with $Br_2(aq)$

(i) Draw the structure of the product formed when propene reacts with bromine in inert organic solvent.

[1]

(ii) Using your answer in **(b)(i)** and Figure 2.1, determine the isotopic composition of bromine.

You may assume that carbon, hydrogen and oxygen only exist in one isotopic form of ^{12}C, ^{1}H and ^{16}O respectively.

....

.... [1]

6 **(b)** **(iii)** Name and outline the mechanism for the reaction between propene and bromine in inert organic solvent.

Name of mechanism: ……………………………………………………………..

[4]

(c) When propene is reacted with aqueous bromine, a different mass spectrum was obtained as shown in Fig 2.2. There are two additional peaks with greater peak height at m/e values of 138 and 140 than those at m/e values of 200 and above.

(i) Explain, with reference to the mechanism you have described in **(b)(iii)**, why the peaks at m/e values of 138 and 140 have greater peak height.

....

....

....

....

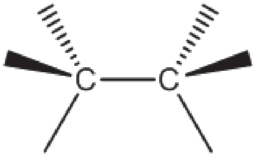
....

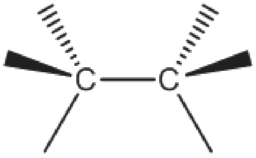
....

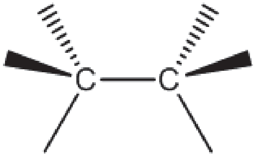
....

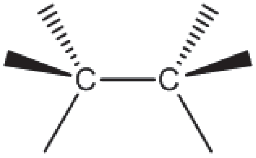
.... [2]

6 **(c)** **(ii)** Draw the four different possible products that are responsible for the peak at m/e value of 138 by completing the diagram below.









[2]

[Total: 14]

BLANK PAGE

JURONG JUNIOR COLLEGE
2017 JC 2 PRELIMINARY EXAMINATION
Higher 2

CANDIDATE NAME	

CLASS	**17S**	EXAM INDEX	

CHEMISTRY

9729/03

Paper 3 Free Response

12 September 2017
2 hours

Candidates answer on separate paper.

Additional Materials: Answer Paper
Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name, class and exam index number on all the work you hand in.
Write in dark blue or black pen on both sides of the paper.
You may use a 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.
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 **11** printed pages and **1** blank page.

Section A

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

1 **(a)** **(i)** Describe the structure and bonding in Group 2 elements. Hence, explain why the melting point of calcium is higher than that of barium. [2]

(ii) Samples of calcium and barium are separately added to beakers of cold water containing a few drops of litmus solution.

Describe one observation you would make

- with calcium and barium
- with calcium only [2]

(b) Explain why the first ionisation energy of calcium is higher than that of potassium and gallium. [2]

(c) Using inert electrodes, electrolysis of two separate solutions containing dilute and concentrated barium chloride respectively gives different products at the anode.

Quote suitable $E^\ominus$ values in the *Data Booklet* and use these values to deduce the product formed at the anode for each case. Explain your answer. [4]

(d) The salts of the Group 2 elements with divalent anions (i.e. those with a charge of 2–) usually show a decreasing trend in solubility down the group. On the other hand, most of their salts with monovalent anions are very soluble.

Magnesium hydroxide, $Mg(OH)_2$, is almost insoluble in water. Stirring a mixture of magnesium hydroxide and aqueous ethanedioic acid, $H_2C_2O_4$, produces a clear colourless solution containing **A**. When a solution of calcium nitrate, $Ca(NO_3)_2$, is added, a white precipitate **B** is formed.

(i) Identify **A** and **B** and hence write balanced equations for the reactions. [2]

The solubility product, K_{sp}, of $Mg(OH)_2$ at 298 K has a numerical value of 2.00×10^{-11}.

(ii) Write an expression for the solubility product, K_{sp}, of $Mg(OH)_2$, stating its units. [2]

(iii) Some $Mg(OH)_2$ solid is added to pure water to obtain a saturated solution. Use the value of K_{sp} to calculate the concentration of $Mg(OH)_2$ in a saturated solution and hence its pH. [2]

(e) The enthalpy change of solution for $Mg(OH)_2$, $\Delta H^{\ominus}_{sol}(Mg(OH)_2(s))$ is represented by the following equation.

$$Mg(OH)_2(s) + aq \rightarrow Mg^{2+}(aq) + 2OH^-(aq)$$

Using relevant data from the *Data Booklet* and the given data in the table below, construct a fully labelled energy cycle to calculate a value for the enthalpy change of solution of $Mg(OH)_2$, $\Delta H^{\ominus}_{sol}(Mg(OH)_2(s))$.

enthalpy change	value / kJ mol^{-1}
$\Delta H^{\ominus}_f(Mg(OH)_2(aq))$	–922
$\Delta H^{\ominus}_f(OH^-(g))$	–133
lattice energy of $Mg(OH)_2$	–2993
enthalpy change of atomisation of Mg(s)	+148

[4]

[Total: 20]

2 **(a)** Chlorine, bromine and iodine all react with hydrogen.

With reference to suitable bond energies data in the *Data Booklet*, state and explain the trend in the reactivities of the halogens with hydrogen. [2]

(b) **(i)** When aqueous bromine is added to aqueous sodium thiosulfate, $Na_2S_2O_3$, a sulfur–containing product is formed. Upon addition of aqueous barium nitrate, a white precipitate appears which is insoluble in excess dilute nitric acid.

Identify the white precipitate. [1]

(ii) However, no white precipitate is formed when the same experiment in **(b)(i)** is repeated with aqueous iodine instead of bromine. The sulfur–containing product formed is sodium tetrathionate, $Na_2S_4O_6$.

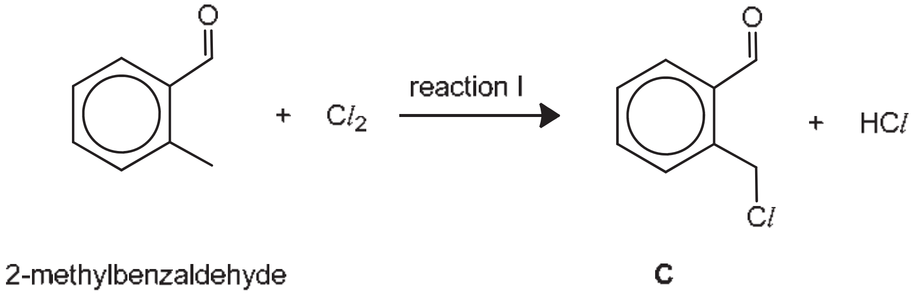
By considering the change in oxidation state of sulfur, explain the difference between the reactions of the two halogens with $S_2O_3^{2-}$. [2]

(c) Silver chloride, AgC*l*, and silver iodide, AgI, are sparingly soluble in water.

$$AgX(s) \rightleftharpoons Ag^+(aq) + X^-(aq) \qquad \text{where X = C}l\text{ or I}$$

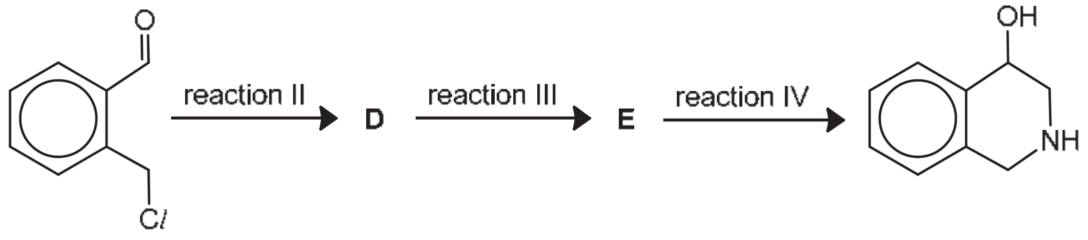
Upon addition of excess aqueous ammonia, AgC*l* dissolves completely but AgI hardly dissolves. Explain these observations. [2]

(d) When reacted with chlorine under suitable conditions, 2-methylbenzaldehyde forms compound **C**.



(i) Name and describe the mechanism for reaction I. You may show all the bonds in the methyl group in your mechanism. [4]

C undergoes further reactions to form compound **F**.



C **F**

(ii) Suggest reagents and conditions for reactions II to IV. [3]

(iii) Draw the structures of **D** and **E**. [2]

(iv) Alkane **G**, C_6H_{14}, undergoes a similar reaction as 2–methylbenzaldehyde with chlorine and produces **only three** monochlorinated constitutional isomers, **H**, **J** and **K**.

H exhibits stereoisomerism whereas **J** and **K** do not.

Suggest the type of stereoisomerism present in **H** and explain what feature is present in **H** that gives rise to this stereoisomerism.

Suggest the structures of **G** and **H**. [4]

[Total: 20]

3 The name of the element, *chromium*, means colour in Greek because many chromium compounds are intensely coloured.

(a) State the full electronic configuration of a chromium atom in its ground state. [1]

(b) Chromium ions tend to form octahedral complexes.

In an octahedral complex, ligands cause the five degenerate *d* orbitals of the chromium ion to be split into two energy levels.

(i) Using Cartesian axes, like those shown in Figure **3.1**, draw **fully–labelled** diagrams of the following.

- One of the *d* orbitals at the lower energy level in an octahedral complex. Label this diagram as "**lower energy**".
- One of the *d* orbitals at the higher energy level in an octahedral complex. Label this diagram as "**higher energy**".

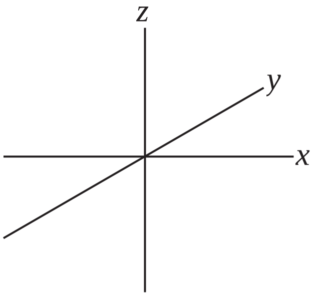


Figure **3.1** [2]

(ii) Hence, explain how the colour of chromium complexes arises. [2]

(c) Due to its ability to vary its oxidation state, chromium compounds tend to undergo redox reaction readily.

$Cr_2O_7^{2-}$ and CrO_4^{2-} ions are the oxoanions of chromium in its highest oxidation state of +6. In aqueous solution, $Cr_2O_7^{2-}$ and CrO_4^{2-} ions are interconvertible since they exist in a chemical equilibrium as shown below.

$$Cr_2O_7^{2-} + H_2O = 2CrO_4^{2-} + 2H^+$$

(i) In acidic medium, the predominant species is $Cr_2O_7^{2-}$ while in alkaline medium, it is CrO_4^{2-}.

Explain why, in alkaline medium, the predominant species is CrO_4^{2-}. [1]

(ii) Both $Cr_2O_7^{2-}$ and CrO_4^{2-} ions are moderately strong oxidising agents. When reduced, green Cr^{3+} solution was formed in acidic medium but in alkaline medium, grey–green $Cr(OH)_3$ precipitate was formed.

Write an ion–electron equation for the reduction of CrO_4^{2-} to $Cr(OH)_3$. [2]

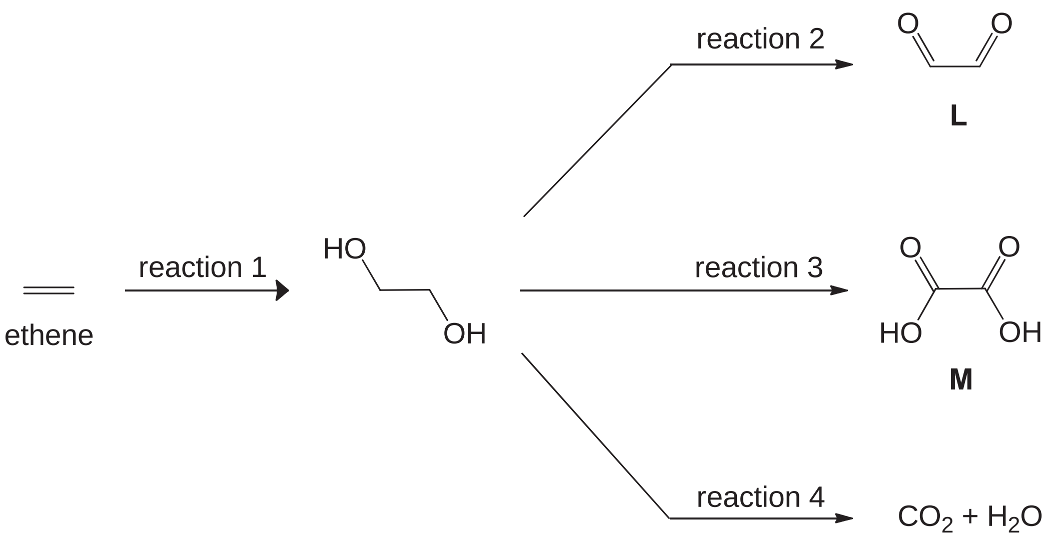
(iii) When a solution of CrO_4^{2-} is reacted with 0.300 mol of an appropriate reducing agent, 0.200 mol of $Cr(OH)_3$ was formed.

Using your answer in **(c)(ii)**, together with the following data, calculate $E^{\ominus}_{cell}$ and standard electrode potential for $CrO_4^{2-}/Cr(OH)_3$.

standard Gibbs free energy change of the reaction, $\Delta G^{\ominus}$ = –365 kJ mol^{-1}
standard electrode potential of the reducing agent = –0.76 V [3]

(iv) Hence, using relevant data from the *Data Booklet,* explain how this value in **(c)(iii)** relates to the relative oxidising power of the two chromium(VI) compounds. [1]

(d) Similar to $Cr_2O_7^{2-}$, compounds containing MnO_4^- ions are commonly used in organic synthesis as good oxidising agents.

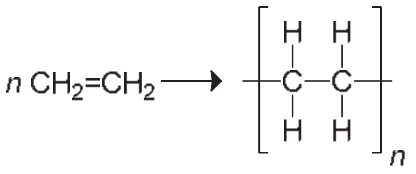


(i) State the necessary reagents and condition for reaction 1 to 4. [4]

(ii) A sodium salt of **M** was added to an aqueous solution of $CrCl_3$, and a six–coordinate complex ion, $[Cr(C_2O_4)_3]^{3-}$, was formed.

Draw the structure of this complex ion, showing clearly the shape around chromium. [1]

(e) In the production of approximately half of the world's polyethylene, a chromium oxide containing catalyst, also known as the Phillips catalyst, was used in the polymerisation of ethene.



$$n\,CH_2{=}CH_2 \longrightarrow \left[\begin{array}{cc} H & H \\ | & | \\ -C & -C- \\ | & | \\ H & H \end{array}\right]_n$$

State the **type** of catalysis involved in this reaction.
Describe how this **type** of catalyst speeds up the reaction. [3]

[Total: 20]

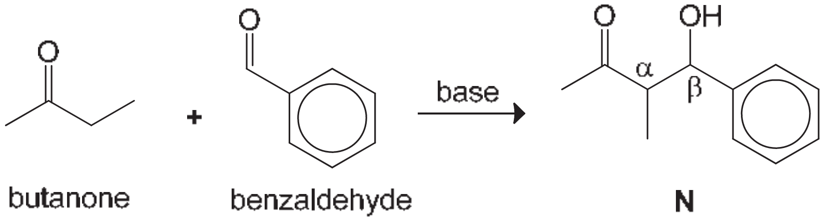
Section B

Answer **one** question from this section.

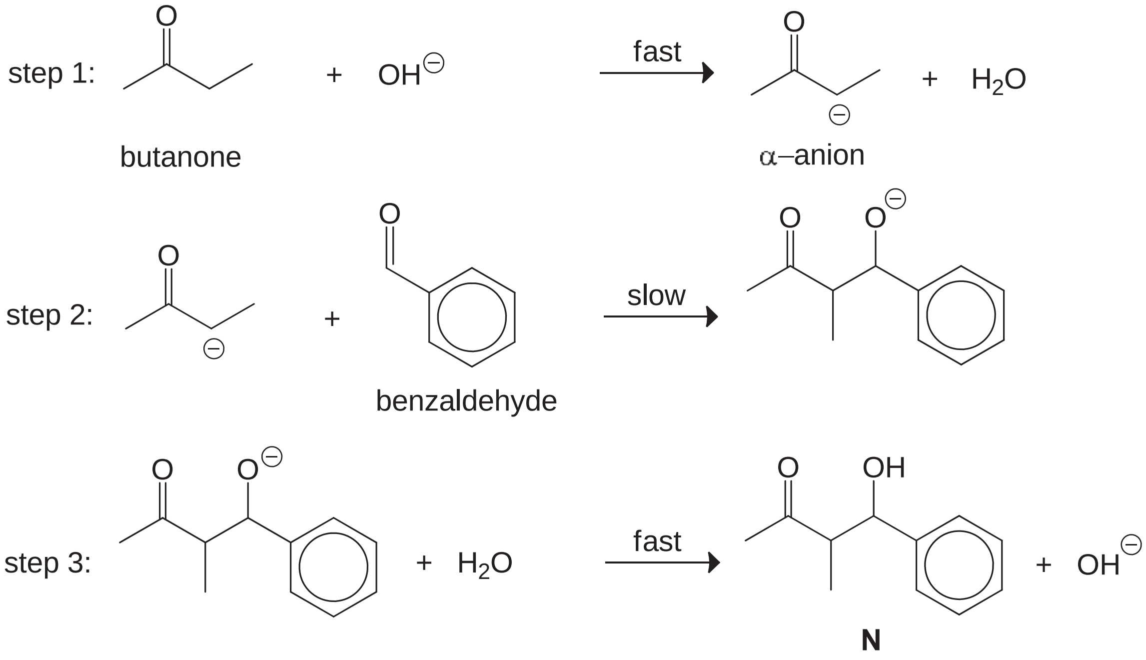
4 The Aldol Addition reaction is important in organic synthesis as it provides a method for linking two smaller molecules by introducing a carbon–carbon bond between them.

The reaction combines two carbonyl compounds to form a new β–hydroxy carbonyl compound, also known as *aldols*, which are commonly found in many important molecules, whether naturally occurring or synthetic.

One example of Aldol Addition reaction is shown in the equation below.

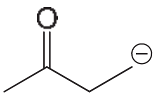


The following shows the mechanism for the Aldol Addition reaction involving butanone and benzaldehyde.



(a) **(i)** State the type of reaction that has occurred during step 1 of the mechanism. [1]

(ii) By considering the stability of the anion, explain why the α–anion is predominantly formed in step 1, instead of the β–anion as shown below.



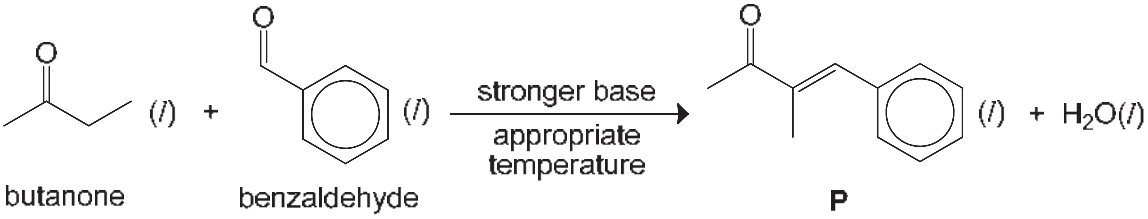
β–anion

[2]

(iii) State the role of the α–anion in step 2 of the mechanism. [1]

(iv) Copy the equations for steps 2 and 3 shown above and complete the mechanism by showing the movement of electron pairs using curly arrows. Indicate all charges and relevant lone pairs. [2]

By either adjusting the reaction temperature or using a stronger base, butanone and benzaldehyde can undergo Aldol Condensation reaction, forming compound **P** as shown below.



(b) **(i)** Using bond energies data in the *Data Booklet*, calculate the enthalpy change for this Aldol Condensation reaction. [2]

(ii) The actual enthalpy change for the Aldol Condensation reaction between butanone and benzaldehyde is **much** more endothermic than that in **(b)(i)**. Suggest **two** reasons to account for this difference in value. [2]

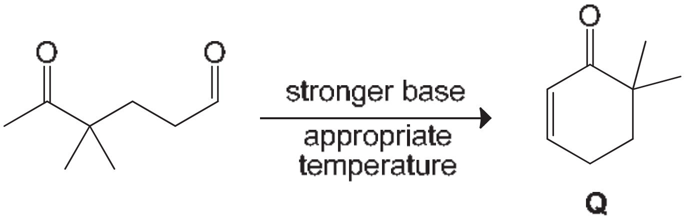
(iii) Given that there is an increase in the entropy of the reaction, state and explain whether the Aldol Condensation reaction is favoured by a low or high reaction temperature. [2]

(iv) Suggest a simple chemical test that could be carried out to see if compound **P** is formed. [2]

(c) **(i)** State the Lewis theory of acids and bases. [1]

(ii) Predict, with reasoning, which base, OH^- or $CH_3CH_2O^-$, would favour the Aldol Condensation reaction. [2]

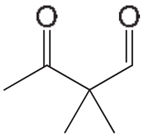
(d) Intramolecular Aldol Condensation reaction can also occur to give a cyclic unsaturated carbonyl compound when a dicarbonyl compound with a sufficiently long carbon chain is used. An example of such a reaction is given below.



Q

(i) State a value for the C=C–C bond angle in **Q**. [1]

(ii) Hence suggest why the expected cyclisation does **not** occur when the following dicarbonyl compound was used.



[1]

(iii) Hence draw the structure of the unsaturated carbonyl product formed when the compound in **(d)(ii)** was used. [1]

[Total: 20]

5 An oxocarbon is a chemical compound consisting of only carbon and oxygen atoms, with carbon monoxide and carbon dioxide being the most common oxocarbons.

(a) Carbon monoxide is one of the most widespread and dangerous industrial hazards due to the formation of carboxyhaemoglobin, $Hb(CO)_4$, which occurs much more readily than the formation of oxyhaemoglobin, $Hb(O_2)_4$.

Reaction 1 $Hb(aq) + 4O_2(aq) \rightleftharpoons Hb(O_2)_4(aq)$

Reaction 2 $Hb(aq) + 4CO(aq) \rightleftharpoons Hb(CO)_4(aq)$

(i) Draw separate dot–and–cross diagrams for carbon monoxide and oxygen.

Hence, explain why the formation of carboxyhaemoglobin occurs much more readily than that of oxyhaemoglobin [3]

(ii) Treatment of severe carbon monoxide poisoning requires oxygen therapy which provides pure oxygen to the patient.

With reference to the equations given above, explain how oxygen therapy works in the treatment of carbon monoxide poisoning [2]

(b) The water–gas shift reaction (WGS) is an industrial method to produce hydrogen gas, by reacting carbon monoxide with water vapour, which is an important reagent in industrial processes such as the production of ammonia gas in Haber process.

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

(i) State two assumptions of the kinetic theory of an ideal gas. [2]

(ii) A 500 cm^3 evacuated vessel was initially filled with 2.0×10^{-4} mol of CO(g) and 4.0×10^{-4} mol of $H_2O(g)$ at 600 K. The vessel was sealed and left to stand. At equilibrium, the percentage yield of H_2 was found to be 97 %.

Using the ideal gas equation, calculate the equilibrium partial pressure of H_2. [1]

(iii) Comment whether the use of the ideal gas equation in **(b)(ii)** is valid. [1]

(iv) Write an expression for the equilibrium constant, K_p, for the WGS reaction and state the units. [2]

(v) Using your answer in **(b)(ii)**, calculate a value of K_p for the WGS reaction that occurred at 600 K, expressing your answer to **two** significant figures. [2]

(c) Phosgene, $COCl_2$, is a valued industrial reagent used in the synthesis of pharmaceuticals and other organic compounds. It can be produced by passing purified carbon monoxide and chlorine gas through a bed of porous activated carbon, which serves as a catalyst.

$$CO(g) + Cl_2(g) \rightarrow COCl_2(g) \qquad \Delta H = -108 \text{ kJ mol}^{-1}$$

Typically, the reaction is conducted between 50 °C and 150 °C. Above 200 °C, phosgene reverts to carbon monoxide and chlorine.

(i) Predict and explain the sign of $\Delta S^{\ominus}$ for the production of phosgene. [1]

(ii) Use your answer in **(c)(i)** and the information given, deduce whether the production of phosgene is enthalpy driven or entropy driven. [1]

(iii) Phosgene is sensitive towards moisture and will give an acidic solution in the presence of moisture. Write an equation to illustrate this reaction. [1]

(d) When reacted with aqueous sodium carbonate, 1 mole of an aromatic compound **R**, $C_{12}H_6O_{12}$, produces 72 dm^3 of carbon dioxide measured at room temperature and pressure.

Heating **R** with appropriate reagent for several hours produces a sweet–smelling compound **S**, $C_{12}O_9$, which is symmetrical.

Deduce the structures for compounds **R** and **S**, explaining the chemistry of the reactions involved. [4]

[Total: 20]

BLANK PAGE

JURONG JUNIOR COLLEGE
2017 JC 2 PRELIMINARY EXAMINATION
Higher 2

CANDIDATE NAME			
CLASS	**17S**	EXAM INDEX	

CHEMISTRY

9729/04

Paper 4 Practical

17 August 2017
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 19 and 20.

Shift
Laboratory

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

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

For Examiner's Use	
1	13
2	16
3	20
4	6
Total	55

This document consists of **20** printed pages and 2 blank pages.

[Turn over

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

1 Determination of the percentage by mass of iron(II) sulfate in mixture

FA 1 is an aqueous solution containing a mixture of iron(II) sulfate, $FeSO_4$ and iron(III) sulfate, $Fe_2(SO_4)_3$.

In the presence of acid, the iron(II) sulfate is oxidised by potassium manganate(VII).

$$2KMnO_4(aq) + 8H_2SO_4(aq) + 10FeSO_4(aq) \rightarrow 5Fe_2(SO_4)_3(aq) + 2MnSO_4(aq) + K_2SO_4(aq) + 8H_2O(l)$$

FA 1 is an aqueous solution containing 215.0 g dm^{-3} of a mixture of iron(II) sulfate, $FeSO_4$ and iron(III) sulfate, $Fe_2(SO_4)_3$.

FA 2 is 2.00 g dm^{-3} potassium manganate(VII), $KMnO_4$.

FA 3 is 1.00 mol dm^{-3} sulfuric acid, H_2SO_4.

In this question, you will perform a dilution followed by a titration. The data from this titration will be used to determine:

- the concentration of $FeSO_4$ in **FA 1**,
- the percentage by mass of $FeSO_4$ in the mixture used to prepare **FA 1**.

(a) (i) Dilution of FA 1

1. Pipette 25.0 cm^3 of **FA 1** into the 250cm^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 iron(II) sulfate and iron(III) sulfate **FA 4**.

Titration of FA 4 against FA 2

1. Fill a burette with **FA 2**.
2. Rinse the pipette thoroughly with deionised water and then with a little **FA 4**.
3. Pipette 25.0 cm^3 of **FA 4** into the conical flask.
4. Using an appropriate measuring cylinder, transfer 10.0 cm^3 of **FA 3** to the same conical flask.
5. Run **FA 2** from the burette into this flask until the first **permanent** pale pink colour is obtained.
6. Record your titration results in the space provided on page **3**. Make certain that your recorded results show the precision of your working.
7. Repeat points **1** to **6** as necessary until consistent results are obtained.

Results

[6]

(ii) 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]

(b) **(i)** Calculate the amount of $KMnO_4$ present in the volume calculated in **(a)(ii)**.

[A_r: O, 16.0; K, 39.1; Mn, 54.9]

Amount of $KMnO_4$ = ………………… [1]

(ii) Calculate the concentration, in mol dm^{-3}, of $FeSO_4$ in **FA 4**.

Concentration of $FeSO_4$ in **FA 4** = ………………… [1]

(iii) Calculate the concentration, in mol dm^{-3}, of $FeSO_4$ in **FA 1**.

Concentration of $FeSO_4$ in **FA 1** = ………………… [1]

(iv) **FA 1** is an aqueous solution containing 215.0 g dm^{-3} of a mixture of $FeSO_4$ and $Fe_2(SO_4)_3$.

Hence, calculate the percentage, by mass, of $FeSO_4$ in this mixture.

[A_r: O, 16.0; S, 32.1; Fe, 55.8]

Percentage by mass of $FeSO_4$ in mixture = ………………… [1]

(c) The maximum error for a 25.0 cm^3 pipette commonly used in schools is ±0.06 cm^3.

The maximum error in any single burette reading is ±0.05 cm^3.

Calculate the maximum percentage error in each of the following.

(i) The volume of **FA 4** pipetted into the conical flask.

Maximum % error = ………………….

(ii) The volume of **FA 2** used in **(a)(ii)**.

Maximum % error = …………………. [2]

[Total: 13]

BLANK PAGE

2 In this experiment you will investigate how the rate of reaction between sodium thiosulfate and sulfuric acid is affected by the concentration of sodium thiosulfate.

When aqueous thiosulfate ions react with hydrogen ions, H^+, in any acid, a pale yellow precipitate of sulfur is formed. The ionic equation for this reaction is given below.

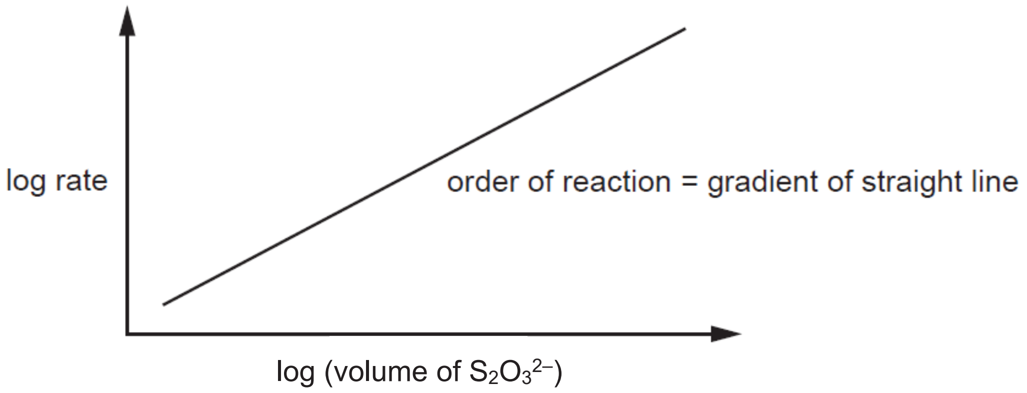
$$S_2O_3^{2-}(aq) + 2H^+(aq) \rightarrow S(s) + SO_2(aq) + H_2O(l)$$

The rate of the reaction can be determined by measuring the time taken to produce a fixed quantity of sulfur.

FA 5 is 37.0 g dm^{-3} hydrated sodium thiosulfate, $Na_2S_2O_3.5H_2O$

You will need access to the **FA 3** solution you used earlier.

The order of reaction with respect to thiosulfate ions can be obtained by plotting a graph of log rate against log (volume of $S_2O_3^{2-}$).



You are advised to read the instructions before starting any practical work.

(a) Method

Experiment 1

- Use an appropriate measuring cylinder, transfer 50.0 cm^3 of **FA 5** into a 250 cm^3 beaker.
- Measure 5.0 cm^3 of **FA 3** in an appropriate measuring cylinder.
- Tip the acid **FA 3** from the measuring cylinder into the beaker and start timing **immediately.**
- Swirl the beaker to mix the reagents and place the beaker on top of the printed insert page provided. (Detach the last page)
- Look down through the solution in the beaker at the print on the insert
- Stop timing as soon as the precipitate of sulfur makes the print on the insert invisible.
- Record the time taken, *t*, to the **nearest second**.
- Empty and rinse the 250 cm^3 beaker.
- Dry the outside of the beaker ready for Experiment 2.

Experiment 2

- Use the measuring cylinder for **FA 5** in Experiment 1 to transfer 10.0 cm^3 of **FA 5** into the rinsed and dried beaker.
- Use the same measuring cylinder for **FA 5** to transfer 40.0 cm^3 of deionised water into the same beaker.
- Measure 5.0 cm^3 of **FA 3** in an appropriate measuring cylinder.
- Tip the acid **FA 3** from the measuring cylinder into the beaker and start timing **immediately.**
- Swirl the beaker to mix the reagents and place the beaker on top of the printed insert page provided.
- Look down through the solution in the beaker at the print on the insert.
- Stop timing as soon as the precipitate of sulfur makes the print on the insert invisible.
- Record the time taken, *t*, to the **nearest second**.
- Empty and rinse the 250 cm^3 beaker.
- Dry the outside of the beaker ready for Experiment 3.

Experiments 3 – 5

Carry out three more experiments to investigate the order of reaction with respect to thiosulfate ions. The volume of **FA 5** should not be less than those in Experiment 2. Deionised water is added to keep the total volume of the final reaction mixture constant.

When you have completed all of your experiments, empty and rinse the beaker.

Prepare a table in the space provided to record, for each experiment

- all volumes
- the value of *t*, to the nearest second
- calculated value of log (1/*t*) and log (volume of **FA 5**) respectively, to 3 significant figures

Results:

[5]

For Examiner's Use

(b) Use the grid below to plot a graph of **log (1/time)** against **log (volume of FA 5)**.

Draw an appropriate straight line through the points plotted.

[3]

(c) Draw construction lines on your graph and obtain data from them to enable you to calculate the gradient of the graph.

Hence, determine the order of reaction with respect to thiosulfate ions.

The reaction is .... order with respect to $S_2O_3^{2-}$. [5]

(d) The experimental method can be modified to enable the rate of reaction with respect to hydrogen ions, H^+, to be investigated.

In the first line of the table below, the volumes of **FA 5**, deionised water and **FA 3** used in **Experiment 2** are recorded.

Complete the following table, suggesting volumes for each of the reagents that could be used in two further experiments to investigate how the rate of reaction varies with a change in volume of sulfuric acid, **FA 3**.

Do not carry out this experiment.

Experiment	Volume of **FA 5**/ cm^3	Volume of deionised water/ cm^3	Volume of **FA 3**/ cm^3
2	10.0	40.0	5.0
(i)			
(ii)			

[1]

(e) A student concluded that the reaction is first order with respect to hydrogen ions, H^+.

Predict how the reaction time measured in **Experiment 2** would have been affected if the following modifications are made to the experiment separately.

For each case, explain your answer.

(i) The experiment had been carried out using 1.0 mol dm^{-3} hydrochloric acid instead of 1.0 mol dm^{-3} sulfuric acid. [1]

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

(ii) The experiment had been carried out in a 100 cm^3 beaker instead of a 250 cm^3 beaker. [1]

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

[Total: 16]

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 precipitate in an excess of the reagent added.

Where gases are released they should be identified by a test, **described in the appropriate place in your observations**.

You should indicate clearly at what stage in a test a change occurs.
No additional tests for ions present should be attempted.

If any solution is warmed, a boiling tube MUST be used.

Rinse and reuse test-tubes and boiling tubes where possible.

Where reagents are selected for use in a test, the name or correct formula of the element or compound must be given.

(a) **FA 6** is a solid and **FA 7** is a solution. **Some** of the ions in **FA 6** and **FA 7** are listed in the Qualitative Analysis notes on pages 19 and 20.

(i) Place a **small** spatula measure of **FA 6** into a **hard–glass** test–tube.

Heat gently at first and then strongly, until no further change is observed.

Test with litmus papers while you are heating.

Record all your observations below.

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

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

(ii) Place two spatula measures of **FA 6** into a boiling–tube. Dissolve the solid in about 5 cm depth of distilled water. Use this **FA 6** solution together with the **FA 7** solution provided for the following tests.

test	*observations*	
	FA 6	**FA 7**
1. To a 0.5 cm depth of solution in a boiling tube add aqueous sodium hydroxide, then		
Warm gently.		
Allow to cool, add a piece of aluminium foil and warm again.	☒	
2. To a 1 cm depth of solution in at test–tube add a 1 cm depth of dilute sulfuric acid followed by a few drops of aqueous potassium manganate(VII).		
3. To a 1 cm depth of solution in at test–tube add a 2 cm depth of hydrogen peroxide and leave to stand.		
4. To a 1 cm depth of solution in at test–tube add a 1 cm depth of dilute hydrochloric acid, then		
Add a 1 cm depth of aqueous barium nitrate.		

[7]

(b) **(i)** Identify as many ions present in **FA 6** and **FA 7** as possible from your observations.

If an ion cannot be identified from the tests, write 'unknown' in the space.

	cation(s)	anion(s)
FA 6		
FA 7		

[2]

(ii) Describe another test you could carry out to confirm the identity of a cation you have identified in **(i)**. Record the reagent(s) and expected observation(s) in the space below.

Do not carry out this test.

…………………………………………………………………………………………

…………………………………………………………………………………………

…………………………………………………………………………………………

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

(iii) Write an ionic equation for the reaction that would occur in **(ii)**. Include state symbols.

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

(c) Planning

Consider the following organic compounds.

benzaldehyde   2–methylpropan–2–ol   propan–2–ol   propanone

Plan an investigation, using test–tube reactions, **other** than using 2,4–dinitrophenylhydrazine reagent 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.

…………………………………………………………………………………………………

…………………………………………………………………………………………………

…………………………………………………………………………………………………

…………………………………………………………………………………………………

…………………………………………………………………………………………………

…………………………………………………………………………………………………

…………………………………………………………………………………………………

…………………………………………………………………………………………………

…………………………………………………………………………………………………

…………………………………………………………………………………………………

…………………………………………………………………………………………………

…………………………………………………………………………………………………

…………………………………………………………………………………………………

…………………………………………………………………………………………………

…………………………………………………………………………………………………

…………………………………………………………………………………………………

…………………………………………………………………………………………………

…………………………………………………………………………………………………

…………………………………………………………………………………………………

For Examiner's Use

[6]

[Total: 20]

4. Planning

Copper has two oxides, Cu_2O and CuO. Copper(II) carbonate, $CuCO_3$, decomposes on heating to form one of these oxides. Separate equations can be written showing the two possible decompositions.

4.1 $2CuCO_3(s) \rightarrow Cu_2O(s) + 2CO_2(g) + \frac{1}{2}O_2(g)$

4.2 $CuCO_3(s) \rightarrow CuO(s) + CO_2(g)$

You are to plan an experiment to investigate the decomposition of copper(II) carbonate on heating and hence decide which of the two equations represents the actual decomposition by collection of gas in the experiment.

(a) Draw a diagram of the apparatus and experimental set up you would use in the experiment.

Your apparatus should use only standard items found in a school or college laboratory and should show clearly

- how the copper(II) carbonate will be heated,
- how the volume of the gas evolved will be collected and measured.

Label each piece of apparatus used, indicating its size or capacity.

[2]

(b) You are required to write a plan to determine which equation represents the actual decomposition of copper(II) carbonate

You may assume that you are provided with a sample of copper(II) carbonate

Your plan should include:

- calculation of the mass of copper(II) carbonate that will produce the maximum volume of gas that can be collected based on the capacity of the apparatus you have indicated in **(a)** for each equation when you are heating the solid.

  (You may assume that the molar gas volume at the temperature in the apparatus used for gas collection stays constant at 25.3 dm^3 throughout the heating process.)
- practical details of how you would
  - determine the mass of copper(II) carbonate used in the experiment;
  - ensure the completion of the decomposition;
  - determine the volume of gas that has been collected.
- brief, but specific, details of how the results would then be used to reach a conclusion.

[Ar : C, 12.0; O, 16.0; Cu, 63.5]

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

For Examiner's Use

[4]

[Total: 6]

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)

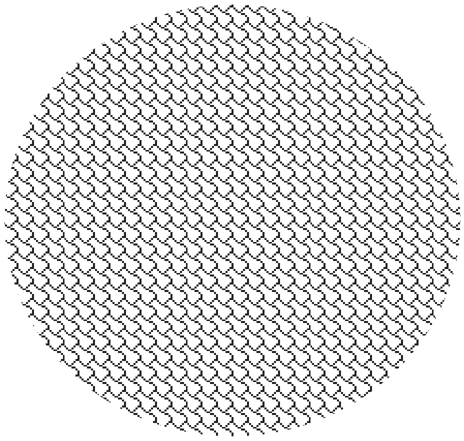
(c) Tests for Gases

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

INSERT



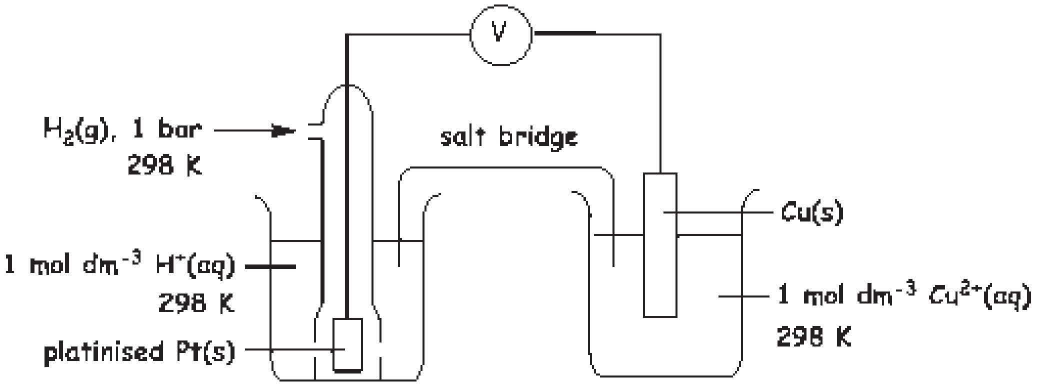
BLANK PAGE

Answers for 2017 JJC Prelim Paper 1 (9729/01)

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

Suggested Mark Scheme for 2017 JJC Prelim Exam Paper 2 (9729/02)

1 **(a)**



(b) From Data Booklet:

$Cu^{2+} + 2e \rightleftharpoons Cu$ +0.34 V

$Ag^+ + e \rightleftharpoons Ag$ +0.80 V

$Zn^{2+} + 2e \rightleftharpoons Zn$ –0.76 V

At the anode, Cu dissolves.

Since $E^\ominus(Zn^{2+}/Zn)$ is less positive than $E^\ominus(Cu^{2+}/Cu)$, zinc impurities dissolve into solution.

Since $E^\ominus(Ag^+/Ag)$ is more positive than $E^\ominus(Cu^{2+}/Cu)$, the silver impurities will not dissolve into solution and will be collected as anode sludge.

(c) At the cathode, Cu is deposited.

Since $E^\ominus(Zn^{2+}/Zn)$ is less positive than $E^\ominus(Cu^{2+}/Cu)$, the zinc impurities will not be oxidise and will thus remain in solution.

(d) amount of Cu to be coated = $0.50 \div 63.5 = 7.87 \times 10^{-3}$ mol

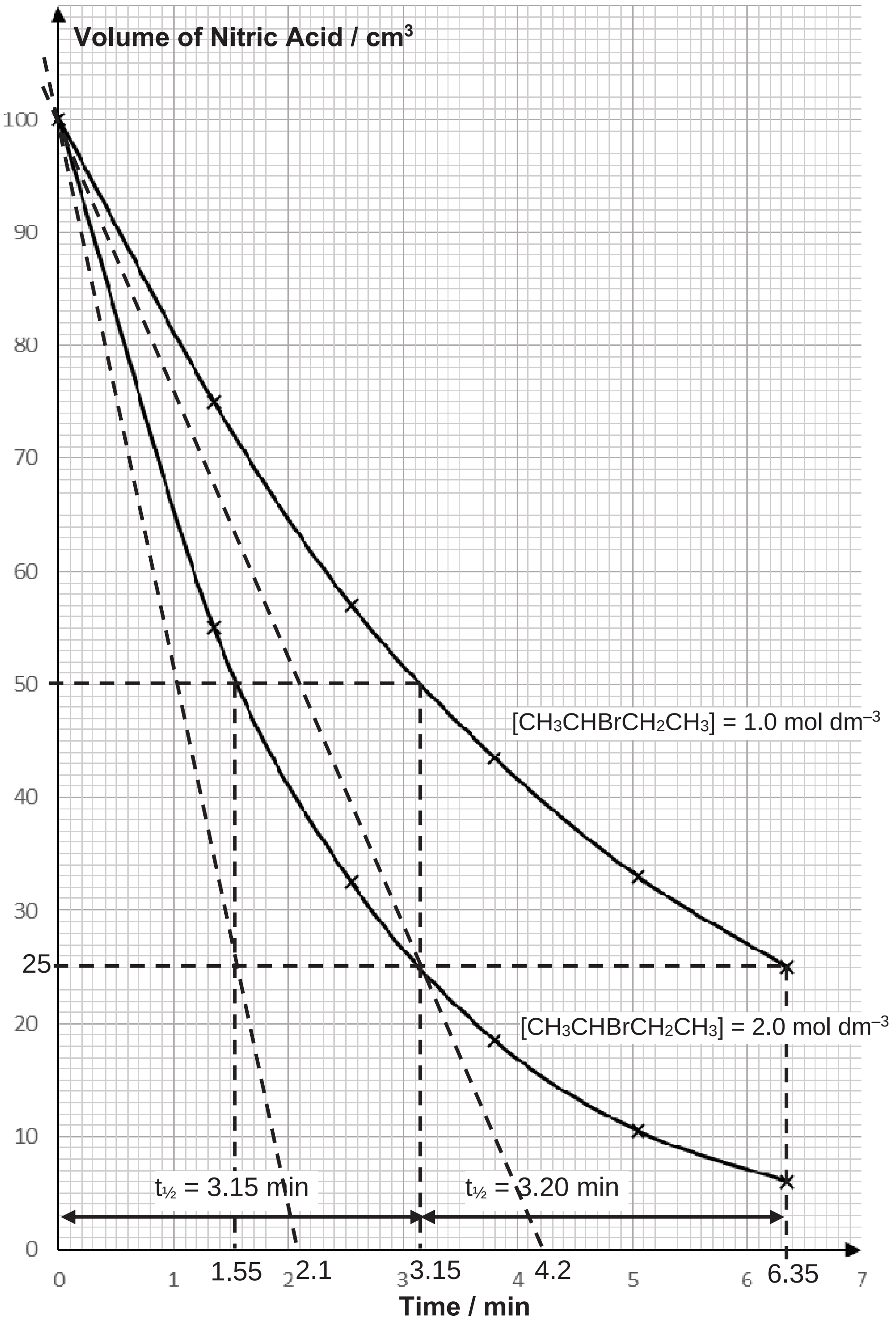
Since $2e^- \equiv 1Cu$,

amount of electrons required = $2 \times (7.87 \times 10^{-3}) = 0.0157$ mol

Using $Q = It = n_eF$,

$$\text{time taken, } t = \frac{0.0157 \times 96500}{0.20} = 7600 \text{ s}$$

2 (a) (i)



average t$_{½}$ = $\dfrac{3.15 + 3.20}{2}$ = 3.18 min

Since half–lives are approximately constant, the reaction is first order w.r.t [NaOH(aq)].

2 (a) (i) When [$CH_3CHBrCH_2CH_3$] = 2.0 mol dm^{-3},

$t_{1/2}$ of NaOH = 1.55 min

When $[CH_3CHBrCH_2CH_3]$ is doubled, half–life of NaOH is (approximately) halved, implying that the rate is (approximately) doubled.

Order of reaction w.r.t $[CH_3CHBrCH_2CH_3]$ is one.

OR

When $[CH_3CHBrCH_2CH_3] = 1.0$ mol dm^{-3},

initial rate = |tangent at t = 0| = $\left|\frac{100-0}{0-4.2}\right| = 23.8$

When $[CH_3CHBrCH_2CH_3] = 2.0$ mol dm^{-3},

initial rate = |tangent at t = 0| = $\left|\frac{100-0}{0-2.1}\right| = 47.6$

When $[CH_3CHBrCH_2CH_3]$ is doubled, initial rate doubles.

Order of reaction w.r.t $[CH_3CHBrCH_2CH_3]$ is one.

(iii) rate = $k[CH_3CHBrCH_2CH_3][OH^-]$

(iv) Since $[CH_3CHBrCH_2CH_3]$ is in large excess as compared to [NaOH], it can be assumed that $[CH_3CHBrCH_2CH_3]$ remains approximately constant throughout.

$\therefore$ rate = k' [NaOH] where $k' = k$[NaOH]

$t_{1/2}$ of NaOH = $\frac{\ln 2}{k'} = \frac{\ln 2}{k[CH_3CHBrCH_2CH_3]}$

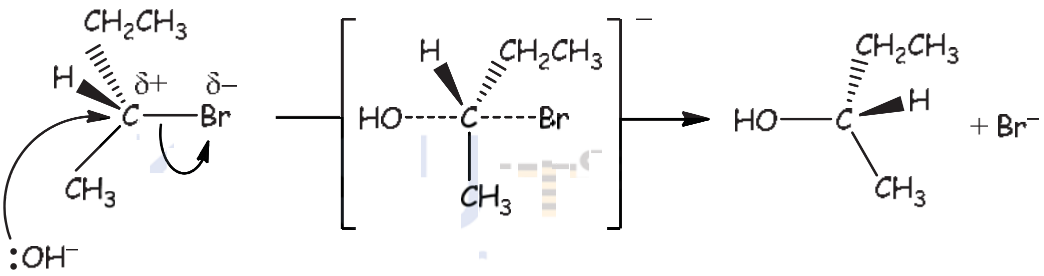
$\therefore$ $t_{1/2}$ of NaOH is independent of [NaOH] and is 3.18 min.

(v) Using $\frac{\text{final amount}}{\text{initial amount}} = \left(\frac{1}{2}\right)^n$ where n is the no. of half–life passed,

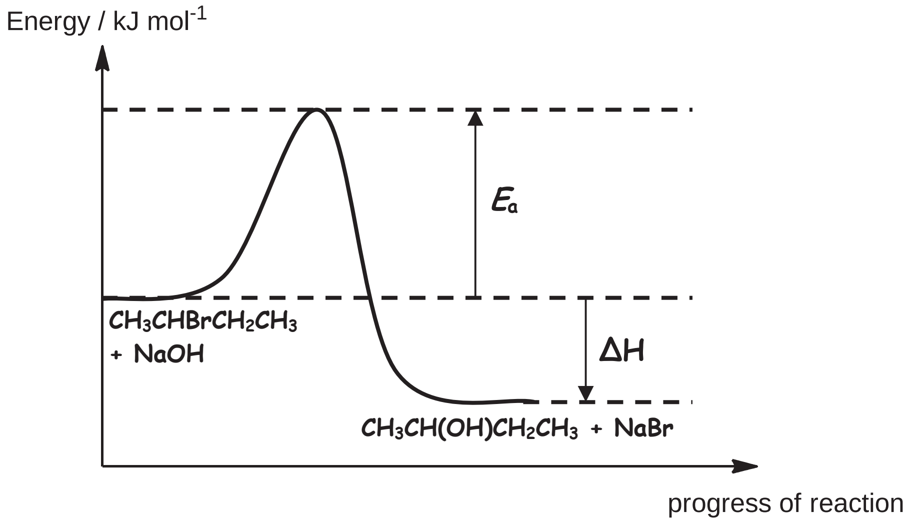
$\frac{1}{100} = \left(\frac{1}{2}\right)^n \Rightarrow n = 6.64$

time taken = 6.64 × 3.18 = 21.1 min

(vi) Type of mechanism: nucleophilic substitution



2 **(b)** **(ii)**



(iii) The rate of reaction will be slower.

Since E(C–C*l*) is larger than E(C–Br), it implies that C–C*l* bond is stronger and harder to break compared C–Br bond.

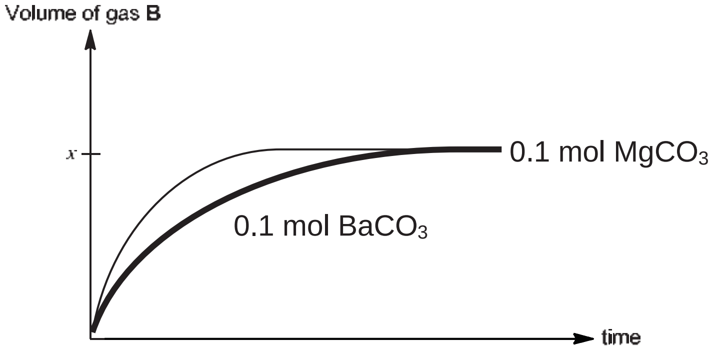
(iv) Yes. Since there is an inversion of stereochemical configuration due to the backside attack of the nucleophile, only one of the enantiomers is produced.

3 **(a)** **A**: MgO **B**: CO_2 **C**: $Mg(OH)_2$ **D**: $MgSO_4$ E: $CaCO_3$

(b) $MgSO_4$ dissolves in water to give $[Mg(H_2O)_6]^{2+}$, which hydrolyses slightly due to slightly higher charge density of Mg^{2+} to give an acidic solution.

$$[Mg(H_2O)_6]^{2+}(aq) \rightleftharpoons [Mg(H_2O)_5OH]^{+}(aq) + H^{+}(aq)$$

(c) **(i)**

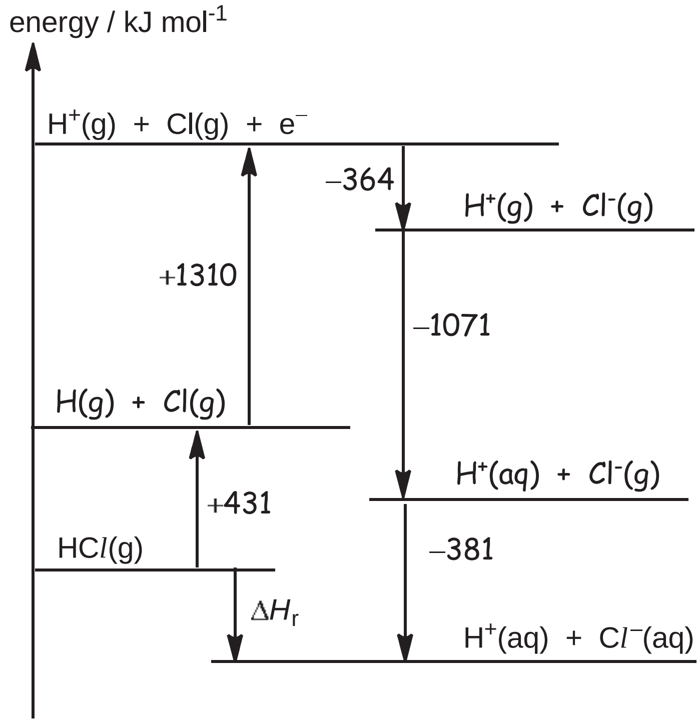


(ii) Since 1 CO_2 ≡ 1MCO_3 and amount of $BaCO_3$ used is the same, the total volume of gas B formed is the same.

Compared to Mg^{2+}, Ba^{2+} has a larger radius and smaller charge density.

Hence, Ba^{2+} is less able to polarise large CO_3^{2-} anion and $BaCO_3$ is more thermally stable and decomposes less readily, resulting in a longer heating time.

4 **(a)**

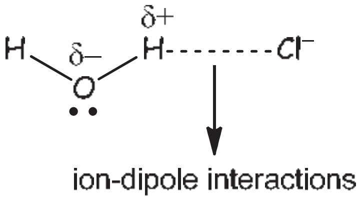


By Hess's Law,

$\Delta H_r = (+431) + (+1310) + (–364) + (–1071) + (–381) = –75.0$ kJ mol$^{–1}$

(b) $\Delta G_{soln} = –75 – (–18) = –57.0$ kJ mol$^{–1}$

(c) **(i)**



(ii) Compared to Cl^-, Br^- has larger radius and lower charge density, resulting in a weaker ion–dipole interactions formed between Br^- and H_2O molecule.

∴ Br^- has a smaller magnitude of ΔH_{hyd}.

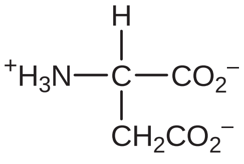
(e) Test : Add $Cl_2(aq)$ to both samples separately.

Observation : For HBr(aq), colourless solution turns orange, due to $Br_2(aq)$.

For HCl(aq), colourless solution remains.

5 **(a)** NaOH(aq) (or KOH(aq) or H_2SO_4(aq) or HCl(aq)), heat for prolonged period.

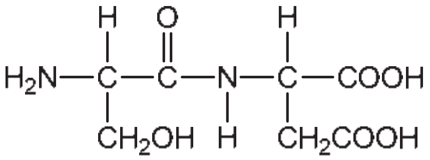
(b) **(i)**



$$^{+}H_3N\text{—}\underset{\displaystyle CH_2CO_2^-}{\overset{\displaystyle H}{C}}\text{—}CO_2^-$$

(ii) anode

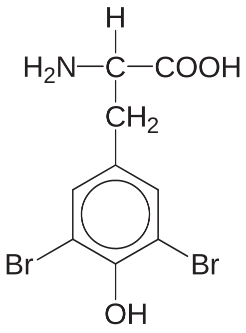
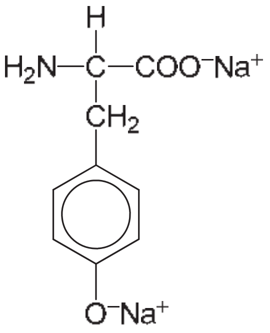
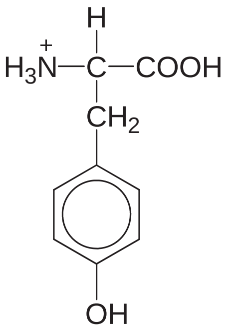
5 **(c)** **(i)**



$H_2N-CH(CH_2OH)-CO-NH-CH(CH_2COOH)-COOH$

(ii) ser–asp–tyr–val–gly–ser

(d)

reagent & condition	Aqueous Br_2	Cold aqueous NaOH	CH_3COOH
product			 CH_3COO^-

6 **(a)** **(i)** amount of HC*l* used = $0.10 \times \frac{30.0}{1000} = 3.00 \times 10^{-3}$ mol

Since 1 HC*l* ≡ 1 NaOH,

amount of NaOH left unreacted = 3.00×10^{-3} mol

total amount of NaOH added initially = $0.10 \times \frac{50.0}{1000} = 5.00 \times 10^{-3}$ mol

amount of NaOH reacted with Br_2 $= (5.00 \times 10^{-3}) - (3.00 \times 10^{-3})$

$= 2.00 \times 10^{-3}$ mol

amount of Br_2 used = $0.10 \times \frac{10.0}{1000} = 1.00 \times 10^{-3}$ mol

∴ Mole ratio of Br_2 : NaOH = $1.00 \times 10^{-3} : 2.00 \times 10^{-3} = 1 : 2$

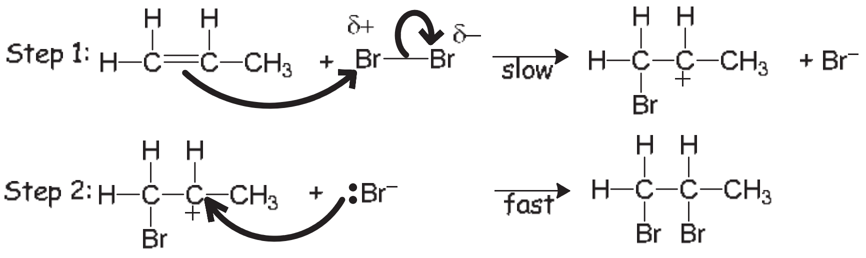
(ii) $Br_2 + 2OH^- \rightarrow Br^- + BrO^- + H_2O$

value of x: 1

(b) **(i)** $CH_2BrCHBrCH_3$

(ii) ^{79}Br and ^{81}Br in the ratio of 1 : 1

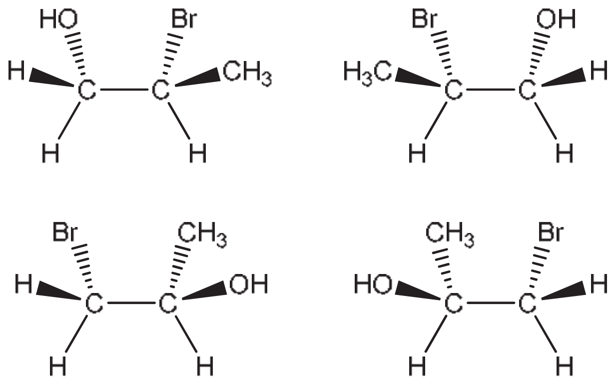
(iii) type of mechanism: electrophilic addition



6 **(c)** **(i)** Since the O atom of H_2O also possesses a lone pair of electrons, the O atom of H_2O can act as a nucleophile to attack the electron–deficient C^+ of carbocation, forming the halohydrin.

Since water is present in large excess compared to Br_2, there will be relatively much more H_2O molecule to act as the nucleophile than the Br^- present in the mixture.

(ii)



Suggested Answers for 2017 H2 Chemistry (9729) Prelim Paper 3

1 **(a)** **(i)** Group 2 elements have giant metallic structures with strong electrostatic attraction between a lattice of positive ions and delocalised electrons.

Since Ca^{2+} has a smaller radius and thus greater charge density than Ba^{2+}, more energy is required to overcome the stronger metallic bonds in Ca than that in Ba. Hence Ca has a higher melting point than Ba.

(ii) Solution turns from purple to blue OR effervescence is observed with calcium and barium. White precipitate is observed with calcium only.

(b) $_{19}K$: [Ar] $4s^1$ $_{20}Ca$: [Ar] $4s^2$ $_{31}Ga$: [Ar] $3d^{10}\ 4s^2\ 4p^1$

Ca has a larger nuclear charge and smaller radius than K while shielding effect by inner shell electrons is relatively similar. Thus the nuclear attraction on the outermost electron is stronger in Ca as compared to that in K. Hence the first ionisation energy of calcium is higher than that of potassium.

The 4s electron to be removed from Ca is nearer to the nucleus and has lower energy than the 4p electron to be removed from Ga. Hence the first ionisation energy of calcium is higher than that of gallium.

(c)

	$E^\ominus$/ V
$O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O$	+1.23
$Cl_2 + 2e^- \rightleftharpoons 2Cl^-$	+1.36

For *dilute* $BaCl_2$(aq),
H_2O is more easily oxidised than Cl^- since $E^\ominus(O_2/H_2O)$ is less positive than $E^\ominus(Cl_2/Cl^-)$. Hence, O_2 gas is produced at the anode.

For *concentrated* $BaCl_2$(aq),
Higher $[Cl^-]$ causes the position of equilibrium of $Cl_2 + 2e^- \rightleftharpoons 2Cl^-$ to shift left, making $E(Cl_2/Cl^-)$ less positive than $E^\ominus(O_2/H_2O)$. Thus, Cl^- becomes more easily oxidised than H_2O and hence, Cl_2 gas is produced at the anode.

(d) **(i)**

$$Mg(OH)_2 + H_2C_2O_4 \rightarrow \underset{\textbf{A}}{MgC_2O_4} + 2H_2O$$

$$MgC_2O_4 + Ca(NO_3)_2 \rightarrow \underset{\textbf{B}}{CaC_2O_4} + Mg(NO_3)_2$$

(ii) $K_{sp} = [Mg^{2+}][OH^-]^2$ units: $mol^3\ dm^{-9}$

(iii)

	$Mg(OH)_2(s)$ $\rightleftharpoons$	$Mg^{2+}(aq)$ +	$2OH^-(aq)$
Eqm conc/ mol dm^{-3}		x	$2x$

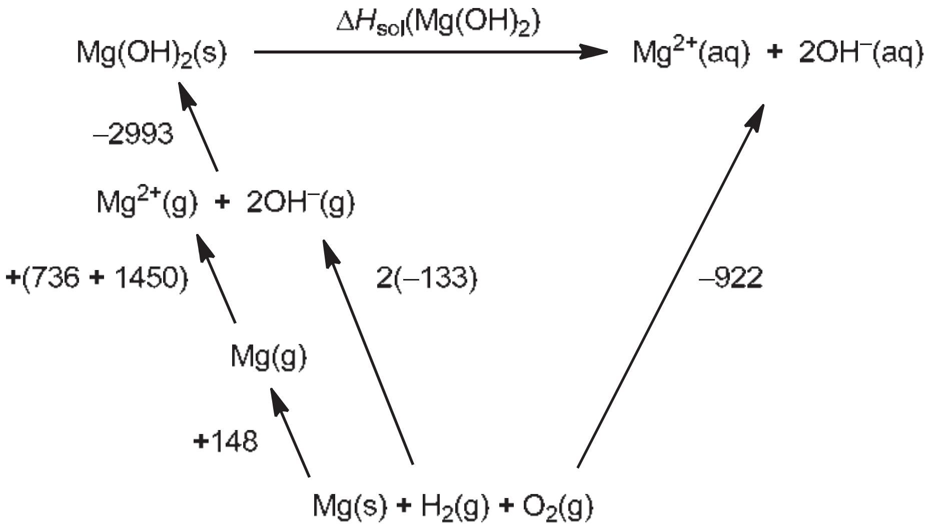
$2.00 \times 10^{-11} = (x)(2x)^2 = 4x^3$

$[Mg(OH)_2(aq)] = x = 1.71 \times 10^{-4}$ mol dm^{-3}

$[OH^-] = 2x = 2 \times 1.71 \times 10^{-4} = 3.42 \times 10^{-4}$ mol dm^{-3}

pH = 14 – (–lg 3.42×10^{-4}) = 10.5

(e)



By Hess' Law,

$\Delta H'_{sol}(Mg(OH)_2(s))$ = –(–2993) – (736+1450) – (148) – 2(–133) + (–922)

= +3 kJ mol^{-1}

2 **(a)** Reactivity decreases down the group.

E(C*l*–C*l*) = +244 kJ mol^{-1}, E(Br–Br) = +193 kJ mol^{-1}; E(I–I) = +151 kJ mol^{-1}

E(H–C*l*) = +431 kJ mol^{-1}, E(H–Br) = +366 kJ mol^{-1}; E(H–I) = +299 kJ mol^{-1}

This is because the decrease in E(H–X) is more significant than the decrease in E(X–X) down the group.

(b) **(i)** $BaSO_4$

(ii) Br_2 causes a larger increase in the oxidation state of S from +2 in $S_2O_3^{2-}$ to +6 in SO_4^{2-}, as compared to I_2 which causes a smaller increase in the oxidation state of S from +2 in $S_2O_3^{2-}$ to +2.5 in $S_4O_6^{2-}$.

Therefore, Br_2 is a stronger oxidising agent than I_2.

(c) When NH_3(aq) is added, $[Ag(NH_3)_2]^+$ complex ion is formed.

$$Ag^+(aq) + 2NH_3(aq) = [Ag(NH_3)_2]^+(aq)$$

Due to the formation of this complex ion, $[Ag^+]$ in the solution decreases and causes the position of equilibrium of AgX(s) = Ag^+(aq) + X^-(aq) to shift to the right, increasing the solubility of both AgX.

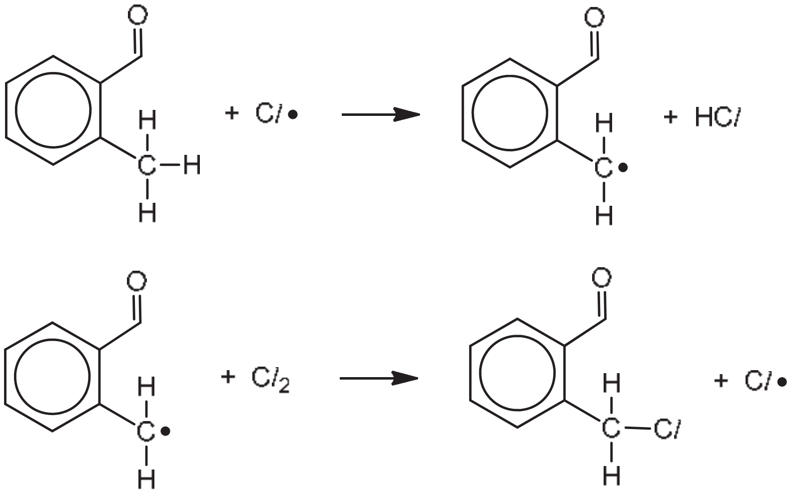
However, AgC*l* has a higher K_{sp} than AgI so AgC*l* dissolves completely but AgI hardly dissolves in NH_3(aq).

(d) **(i)** Name of mechanism: free radical substitution

Initiation step

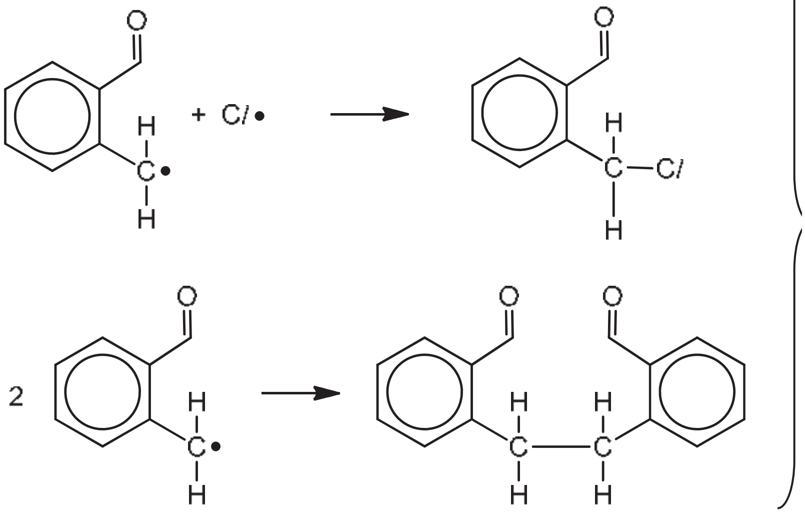
$Cl_2 \xrightarrow{UV} 2Cl\bullet$

Propagation steps



Termination steps

$2Cl\bullet \longrightarrow Cl_2$



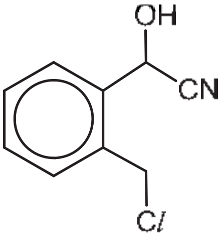
any 2 equations

(ii) II: HCN, trace amount of NaCN or NaOH

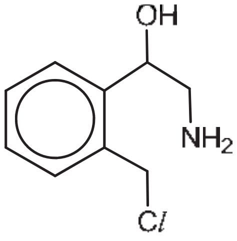
III: $LiAlH_4$, dry ether

IV: ethanol, heat in sealed tube

(iii)

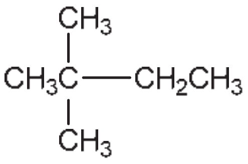


D

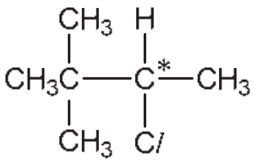


E

(iv)



G

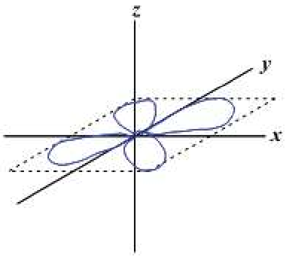


H

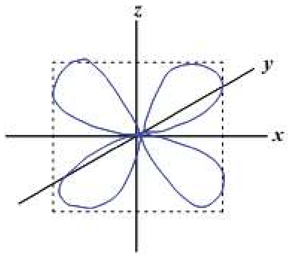
H has a chiral C and thus exhibits enantiomerism.

3 **(a)** $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5\ 4s^1$

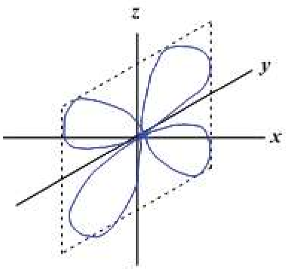
(b) **(i)** Lower energy level:



d_{xy}

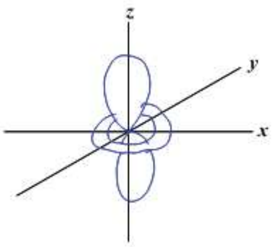


d_{xz}

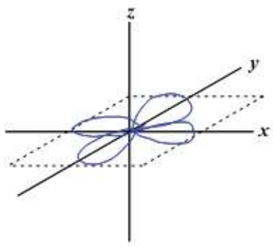


d_{yz}

Upper energy level:



d_{z^2}



$d_{x^2-y^2}$

(ii) Chromium complexes are coloured due to the electron transition between *d*–orbitals.

The presence of ligands causes the *d* orbitals to split into 2 different energy levels.

The energy gap is relatively small such that radiation from the visible light is absorbed when an electron transits from a lower energy *d*–orbital to higher energy *d*–orbital which is partially filled.

Hence, the colour seen is the complement of the colours absorbed.

(c) **(i)** In alkaline medium, OH^- reacts with H^+ which reduces $[H^+]$. This causes the position of equilibrium of $Cr_2O_7^{2-} + H_2O \rightleftharpoons 2CrO_4^{2-} + 2H^+$ to shift right. Hence, there will be more CrO_4^{2-} in the mixture than $Cr_2O_7^{2-}$.

(ii) $CrO_4^{2-} + 4H_2O + 3e^- \rightarrow Cr(OH)_3 + 5OH^-$

(iii)

mole ratio of	$Cr(OH)_3$	:	e^-	:	reducing agent
	0.200	:	3(0.200)		
			3(0.200)	:	0.300
	2	:	6	:	3

Using $\Delta G^\ominus = -n_eFE^\ominus_{cell}$ and $n_e = 6$,

$-365 \times 1000 = -6 \times 96500 \times E^\ominus_{cell}$

$E^\ominus_{cell} = +0.63\ V = E^\ominus(CrO_4^{2-}/Cr(OH)_3) - (-0.76)$

$E^\ominus(CrO_4^{2-}/Cr(OH)_3) = -0.13\ V$

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

Since $E^\ominus(CrO_4^{2-}/X)$ is less positive than $E^\ominus(Cr_2O_7^{2-}/Cr^{3+})$, it implies that CrO_4^{2-} is less readily reduced and thus CrO_4^{2-} is a weaker oxidising agent than $Cr_2O_7^{2-}$.

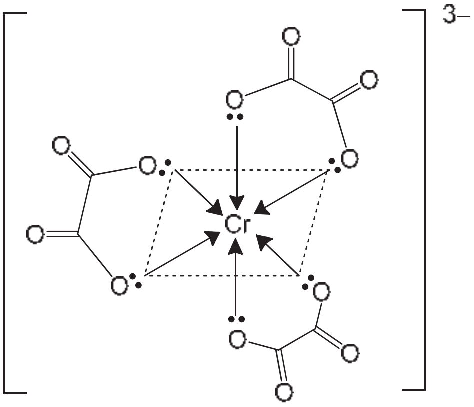
(d) **(i)** reaction 1 : cold alkaline $KMnO_4(aq)$

reaction 2 : acidified $K_2Cr_2O_7(aq)$, heat with immediate distillation

reaction 3 : acidified $K_2Cr_2O_7(aq)$, heat under reflux

reaction 4 : acidified $KMnO_4(aq)$, heat under reflux

(ii)



(e) Heterogeneous catalysis.

When the reactant molecules adsorb on the catalyst surface, the bonds in the molecules are weakened, lowering the activation energy. The surface concentrations of the reactants are increased as well. The product formed then desorbs from the catalyst surface.

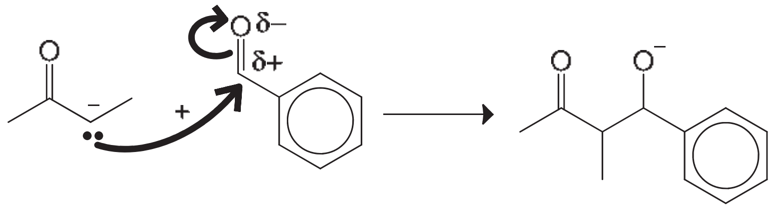
4 **(a)** **(i)** acid–base reaction

(ii) p–p orbital overlap results in the delocalisation of lone pair on α–C⁻ into the adjacent C=O, dispersing the negative charge and thus making α–anion more stable than β–anion. Hence, α–anion is preferentially formed.

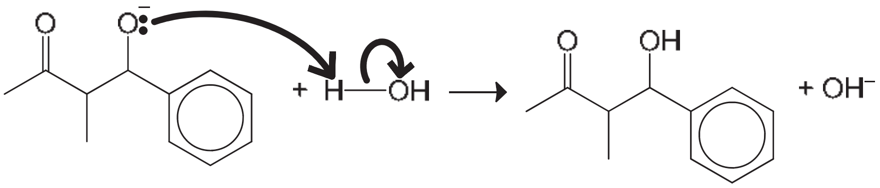
(iii) nucleophile

(iv)

step 2:



step 3:



(b) **(i)**

bonds broken	
1 C=O	+740
2 C–H	2(+410)
Total	+1560

bonds formed	
1 C=C	+610
2 O–H	2(+460)
Total	+1530

ΔH_r = +1560 – (+1530) = +30 kJ mol^{-1}

(ii) Bond energies quoted from *Data Booklet* are average values derived from a full range of molecules that contain the particular bonds.

The bond energies quoted are for gaseous molecules but the reactants and products are in liquid state and hence, the enthalpy changes of vapourisation are not accounted for.

(iii)

$$\Delta G^{\ominus} = \underbrace{\Delta H^{\ominus}}_{+\text{ve}} \underbrace{-\text{T}\,\underbrace{\Delta S^{\ominus}}_{+\text{ve}}}_{-\text{ve}}$$

When temperature increases, $-\text{T}\Delta S^{\ominus}$ becomes more negative.

So at high enough temperature, $\Delta G^{\ominus} < 0$ when $|\Delta H^{\ominus}| < |-\text{T}\Delta S^{\ominus}|$.

Hence, the Aldol Condensation is favoured by a high temperature.

(iv) Test: Add aqueous Br_2 to a small sample of the mixture.

Observation: If **P** is formed, orange $Br_2(aq)$ will decolourise.

(c) **(i)** According to Lewis theory, an acid is an electron pair acceptor while a base is an electron pair donor.

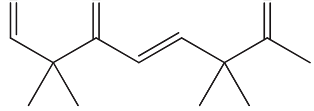
(ii) Electron–donating $-CH_2CH_3$ makes the lone pair on O^- more available for protonation, making $CH_3CH_2O^-$ a stronger base than OH^-.

Hence, $CH_3CH_2O^-$ favour Aldol Condensation reaction.

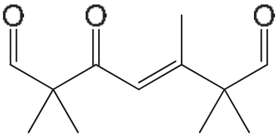
(d) **(i)** 120°

(ii) The cyclisation of the above dicarbonyl compound would form a 4–membered ring and the bond angle of 90° is formed, resulting in angle strain in the ring and thus making the compound unstable.

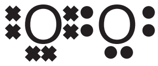
(iii)



or



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



Since C in CO is less electronegative than O in O_2, the lone pair on C in CO is more available for dative bond formation than O in O_2.

Hence, CO is a stronger ligand than O_2 and thus the formation of carboxyhaemoglobin occurs much more readily.

(ii) During oxygen therapy, $[O_2]$ is high and this causes the position of equilibrium 1 to shift right which reduces [Hb].

The reduction of [Hb] causes the position of equilibrium 2 to shift left which reduces $[Hb(CO)_4]$.

Hence, the proportion of $[Hb(O_2)_4]$ in the blood is increased while the proportion of $Hb(CO)_4$ in the blood is reduced, allowing more O_2 to be transported to other parts of the body.

(b) **(i)** Any two of the following:

- Volume of gas molecules is negligible as compared to that of the gas.
- There are no intermolecular forces between the molecules.
- Collisions between molecules are perfectly elastic.
- Molecules move in constant, random motion.
- Kinetic energy of the molecules is directly proportional to the temperature.

(ii) Since the molar ratio of CO : H_2O is 1:1, CO is the limiting reagent.

Equilibrium amount of $H_2 = (2.0 \times 10^{-4}) \times \dfrac{97}{100} = 1.94 \times 10^{-4}$ mol

Using ideal gas equation (*i.e.* pV = nRT),

$$\text{equilibrium partial pressure of } H_2 = \frac{\left(1.94\times10^{-4}\right)\times8.31\times600}{500\times10^{-6}}$$

$$= 1930 \text{ Pa}$$

(iii) It is valid as H_2 tends towards ideal gas behaviour since the H_2 molecule is small (or volume of the container is large due to low pressure) so the volume of the molecules is negligible as compared to that of the gas.

OR

It is valid as H_2 tends towards ideal gas behaviour since the H_2 molecule has few electrons (or volume of the container is large due to low pressure and thus molecules are far apart or the molecules have high kinetic energies to overcome intermolecular forces due to high temperature) so the intermolecular forces in H_2 is negligible.

(iv) $K_p = \dfrac{p_{CO_2} \times p_{H_2}}{p_{CO} \times p_{H_2O}}$ Units of K_p: no units

(v)

	$CO(g)$	+	$H_2O(g)$	$\rightleftharpoons$	$CO_2(g)$	+	$H_2(g)$
Initial pressure / Pa	$\frac{1930}{0.97}$ = 1990		2(1990) = 3990		0		0
Change	–1930		–1930		+1930		+1930
Eqm pressure / Pa	60		2060		1930		1930

$$K_p = \frac{1930 \times 1930}{60 \times 2060} = 30$$

(c) **(i)** $\Delta S^{\ominus}$ is negative because there is a decrease in disorder of the system as the reaction proceeds with a decrease in amount of gaseous particles from 2 mol to 1 mol.

(ii) enthalpy driven

(iii) $COCl_2 + H_2O \rightarrow COCl(OH) + HCl$

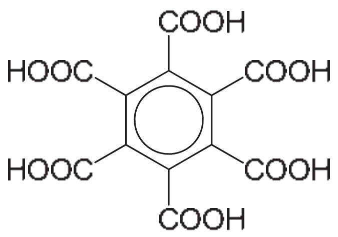
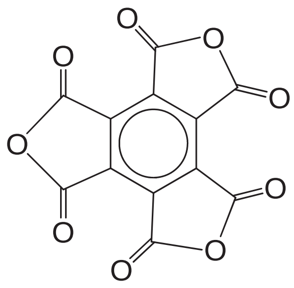
OR $COCl_2 + 2H_2O \rightarrow H_2CO_3 + 2HCl$

OR $COCl_2 + H_2O \rightarrow CO_2 + 2HCl$

(d)

Observation	type of reaction	deduction
W is aromatic.	–	**W** contains benzene ring.
W ($C_{12}H_6O_{12}$) + $Na_2CO_3(aq) \rightarrow CO_2(g)$	acid–carbonate reaction	**W** is a carboxylic acid (or has –COOH).
1 mole of **W** gives 72 dm^3 CO_2 gas	–	$2RCOOH + Na_2CO_3 \rightarrow 2RCOONa + CO_2 + H_2O$ amount of $CO_2 = \frac{72}{24} = 3$ mol Since $2RCOOH \equiv 1CO_2$, ∴ **W** has 6 –COOH.
W + appropriate reagent → sweet smelling **X** ($C_{12}O_9$)	condensation	Recognise that 6 H and 3 O (*i.e.* $3H_2O$) were lost when **W** is converted into **X**. **X** is a cyclic ester.

Combining the deductions, the structure of

W	**X**
	

Suggested Mark Scheme for 2017 JJC Prelim Paper 4 (9729/04)

1 **(a)** **(i)**

Titration number	1	2
final burette reading / cm^3	23.20	33.25
initial burette reading / cm^3	0.00	10.00
volume of FA2 (or $KMnO_4$) used / cm^3	23.20	23.25
	✓	✓

(ii) average volume of **FA2** (or $KMnO_4$) used = $\frac{23.20+23.25}{2}$ = 23.23 cm^3

(b) **(i)** mass of $KMnO_4$ in 23.23 cm^3 = $2.00 \times \frac{23.23}{1000}$ = 0.0465 g

amount of $KMnO_4$ used = $\frac{0.0465}{39.1+54.9+4(16.0)}$ = 2.93×10^{-4} mol

(ii) Since $5FeSO_4 \equiv 1KMnO_4$,
amount of $FeSO_4$ in 25.0 cm^3 of **FA 4** = $5 \times (2.93 \times 10^{-4}) = 1.47 \times 10^{-3}$ mol

$[FeSO_4]$ in **FA 4** = $(1.47 \times 10^{-3}) \div \frac{25.0}{1000}$ = 0.0588 mol dm^{-3}

(iii) amount of $FeSO_4$ in 25.0 cm^3 of **FA 1** = amount of $FeSO_4$ in 250 cm^3 of **FA 4**

= $0.0588 \times \frac{250}{1000}$ = 0.0147 mol

$[FeSO_4]$ in **FA 1** = $0.0147 \div \frac{25.0}{1000}$ = 0.588 mol dm^{-3}

or

Using $c_1V_1 = c_2V_2$,

$[FeSO_4]$ in FA 1 = $0.0588 \times \frac{250}{25.0}$ = 0.588 mol dm^{-3}

(iv) $[FeSO_4]$ in **FA 1** in g dm^{-3} = $0.588 \times [55.8 + 32.1 + 4(16.0)]$ = 89.3 g dm^{-3}

% by mass of $FeSO_4$ in **FA 1** = $\frac{89.3}{215.0} \times 100\ \%$ = 41.5 %

%. error = $\frac{\text{error per reading} \times \text{no. of reading}}{\text{quantity measured}} \times 100\ \%$

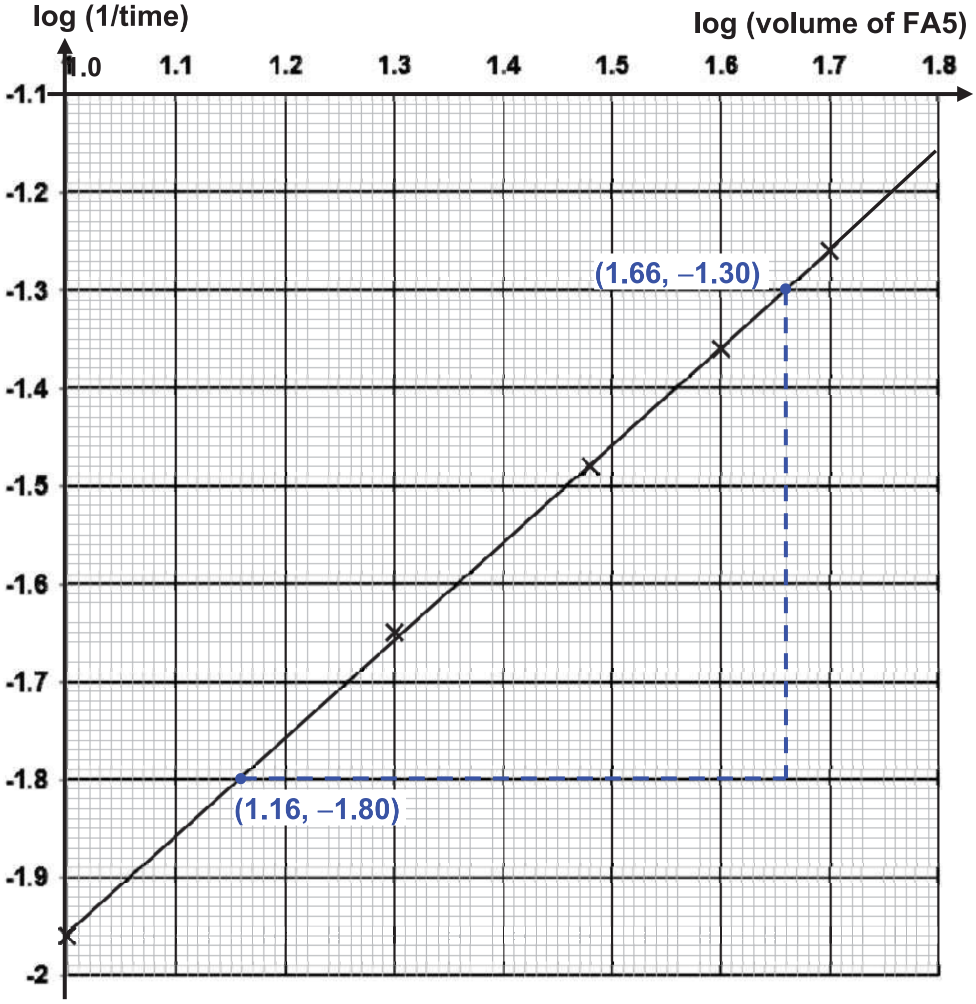
(c) **(i)** % error = $\frac{0.06 \times 1}{25.0} \times 100\ \%$ = 0.240 %

(ii) % error = $\frac{0.05 \times 2}{23.23} \times 100\ \%$ = 0.430 %

2 **(a)**

Experiment	volume of FA 5 / cm^3	volume of FA 3 / cm^3	volume of water / cm^3	t / s	log (1/*t*)	log (volume of FA 5)
1	50.0	5.0	0.0	18	–1.26	1.70
2	10.0	5.0	40.0	93	–1.96	1.00
3	20.0	5.0	30.0	45	–1.65	1.30
4	30.0	5.0	20.0	30	–1.48	1.48
5	40.0	5.0	10.0	23	–1.36	1.60

(b)



(c) gradient = $\frac{(-1.80)-(-1.30)}{1.16-1.66}$ = 1.00 = 1

The reaction is **first** order with respect to thiosulfate ions, $S_2O_3^{2-}$.

(d)

Experiment	Volume of **FA 5**/ cm^3	Volume of deionised water/ cm^3	Volume of **FA 3**/ cm^3
2	10.0	40.0	5.0
(i)	10.0	35.0	10.0
(ii)	10.0	25.0	20.0

2 **(e)** **(i)** Since $2H^+ \equiv 1H_2SO_4$ while $1H^+ \equiv 1HCl$, $[H^+]$ is halved. Since the reaction is first order w.r.t $[H^+]$, when $[H^+]$ is halved, the rate is halved and hence, the reaction time will be doubled.

(ii) Since the total volume of mixture is kept constant (*i.e.* 55 cm^3), the depth of the mixture in a 100 cm^3 beaker is greater and hence, the reaction time will be shorter.

3 **(a)** **(i)** On strong heating, pale green solid turns yellow (or brown) and becomes black eventually. Condensation (or steamy fumes) on test–tube.

Colourless, pungent gas turns damp red litmus blue.

Colourless, pungent gas turns damp blue litmus red.

Colourless, pungent gas decolourised purple $KMnO_4$.

3 **(a)** **(ii)**

test	*observations*	
	FA 6	**FA 7**
1. To a 0.5 cm depth of solution in a boiling tube add aqueous sodium hydroxide, then	Green ppt insoluble in excess NaOH(aq), turning brown on contact with air.	No ppt formed
Warm gently.	Colourless, pungent gas turns damp red litmus paper blue.	No gas evolved.
Allow to cool, add a piece of aluminium foil and warm again.		Effervescence observed. Colourless, pungent gas turns damp red litmus paper blue.
2. To a 1 cm depth of solution in at test-tube add a 1 cm depth of dilute sulfuric acid followed by a few drops of aqueous potassium manganate(VII).	Purple $KMnO_4$ decolourised.	Effervescence observed. Brown, pungent gas formed. Purple $KMnO_4$ decolourised.
3. To a 1 cm depth of solution in at test-tube add a 2 cm depth of hydrogen peroxide and leave to stand.	Effervescence observed. Colourless, odourless gas relights glowing splint. Solution turns yellow.	No gas evolved.
4. To a 1 cm depth of solution in at test-tube add a 1 cm depth of dilute hydrochloric acid, then	No gas evolved.	Effervescence observed. Brown, pungent gas formed.
Add a 1 cm depth of aqueous barium nitrate.	White ppt formed.	No ppt formed.

(b) **(i)**

	cation(s)	anion(s)
FA 6	Fe^{2+} , NH_4^+	SO_4^{2-}
FA 7	unknown	NO_2^-

3 **(b)** **(ii)** To 1 cm depth of the **FA 6** in a test–tube, add 1 cm depth of $NH_3(aq)$.
Green ppt insoluble in excess $NH_3(aq)$, turning brown on contact with air.

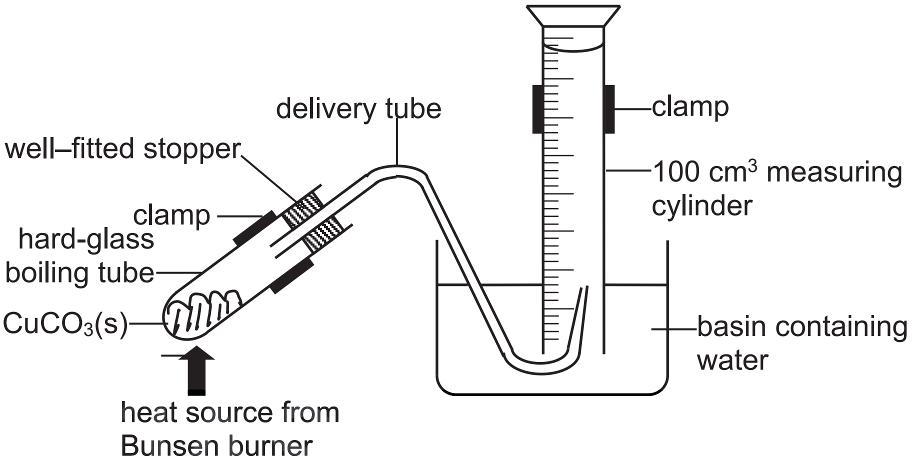
(iii) $Fe^{2+}(aq) + 2OH^-(aq) \rightarrow Fe(OH)_2(s)$
or
$[Fe(H_2O)_6]^{2+}(aq) + 2NH_3(aq) \rightarrow [Fe(OH)_2(H_2O)_4](s) + 2NH_4^+(aq)$

(c)

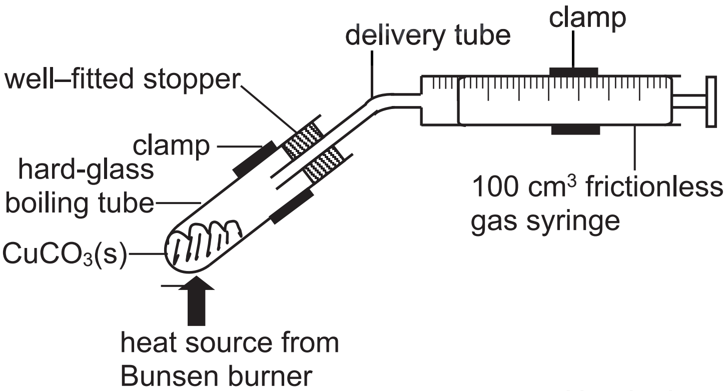
Test	Observation
To 1 cm depth of the 4 samples in separate test–tubes, add 1 cm depth of Tollens' reagent. Warm the mixture in hot water–bath.	For benzaldehyde, silver mirror is formed but not for the other 3 samples.
To 1 cm depth of the remaining 3 samples in separate test–tubes, add a few drops of acidified $KMnO_4(aq)$ (or acidified $K_2Cr_2O_7(aq)$). Warm the mixture in hot water–bath.	For propan–2–ol, purple $KMnO_4$ decolourises (or orange $K_2Cr_2O_7$ turns green) but not for the other 2 samples.
To 1 cm depth of the remaining 2 samples in separate test–tubes, add 1 cm depth of alkaline $I_2(aq)$. Warm the mixture in hot water–bath.	For propanone, pale yellow ppt of CHI_3 is formed but not for the other sample.
To 1 cm depth of the last sample in a test–tube, add 1 small spatula of $PCl_5(s)$.	For 2–methylpropan–2–ol, white fumes of HCl observed.

*The last two steps can be swopped.

4 **(a)** Downward displacement gas collection method:



Gas syringe method:



(b) If a 100 cm^3 capacity apparatus is used,

maximum amount of gas evolved = $\frac{100}{1000} \div 25.3 = 3.95 \times 10^{-3}$ mol

For Equation 4.1, since $2CuCO_3 \equiv 2.5$ gas ($CO_2 + O_2$),

amount of $CuCO_3$ required = $\frac{2}{2.5} \times (3.95 \times 10^{-3}) = 3.16 \times 10^{-3}$ mol

mass of $CuCO_3$ required = $(3.16 \times 10^{-3}) \times 123.5 = 0.391$ g

For Equation 4.2, since $1CuCO_3 \equiv 1\ CO_2$,

mass of $CuCO_3$ required = $(3.95 \times 10^{-3}) \times 123.5 = 0.488$ g

Experimental Procedures:

step 1: Using an electronic weighing balance precise to 3 decimal places, weigh a clean and dry boiling tube and record its mass as m_1.

step 2: Weigh accurately 0.391 g of $CuCO_3$ into the boiling tube and record the total mass as m_2.

$\therefore$ mass of $CuCO_3$ used = $(m_2 - m_1)$ g

step 3: Set up the apparatus as shown in part (a).

step 4: Recording the initial syringe (or burette or measuring cylinder) reading as V_1.

step 5: Light up the Bunsen burner and heat the tube with its content gently then strongly. Decomposition is complete when the syringe piston stops moving (or water level in measuring cylinder/burette stops falling).

step 6: Recording the final syringe (or burette or measuring cylinder) reading as V_2.

$\therefore$ volume of gas collected = $(V_2 - V_1)$ cm^3

amount of $CuCO_3$ used = $\frac{m_2 - m_1}{123.5} = x$ mol

amount of gas collected = $\frac{V_2 - V_1}{1000} \div 25.3 = y$ mol

Then determine the ratio of $x : y$. If the ratio is about 2 : 2.5 (or 4 : 5), Equation 4.1 represent the actual decomposition of $CuCO_3$. If the ratio is about 1 : 1, Equation 4.2 represent the actual decomposition of $CuCO_3$.

Name: ____________________ **Class: 16S**_________ **Reg Number:** ______

MERIDIAN JUNIOR COLLEGE
JC2 Preliminary Examination
Higher 2

Chemistry 9729/01

Paper 1 Multiple–Choice Questions **22 September 2017**

1 hour

Additional Materials: *Data Booklet*
OMR Answer Sheet

INSTRUCTIONS TO CANDIDATES

Write your name, class and register number in the spaces provided at the top of this page.

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

Read very carefully the instructions on the OMR answer sheet.

You are advised to fill in the OMR Answer Sheet as you go along; no additional time will be given for the transfer of answers once the examination has ended.

Use of OMR Answer Sheet

Ensure you have written your name, class register number and class on the OMR Answer Sheet. Use a **2B** pencil to shade your answers on the OMR sheet; erase any mistakes cleanly. Multiple shaded answers to a question will not be accepted.

For shading of class register number on the ***OMR sheet***, please follow the given examples:
If your register number is **1**, then shade **01** in the index number column.
If your register number is **21**, then shade **21** in the index number column.

This document consists of **14** printed pages

1 *The use of Data Booklet is relevant to this question.*

Scientists have been comparing the stability of isotopes using the neutron:proton ratio. Nuclei are considered to be stable if the neutron:proton ratio is between 1:1 to 1.5:1. Stable nuclei within these ratios are known to be in the *'band of stability'*.

Which one of these elements do not lie within the *'band of stability'* ?

A ^{91}Zr **B** ^{133}Cs **C** ^{165}Ho **D** ^{209}Bi

2 The information on two particles, $\mathbf{Q}^+$ and $\mathbf{R}^+$, are given in the table below.

particles	number of electrons	number of neutrons	angle of deflection in an electric field
$\mathbf{Q}^+$	20	25	2.0°
$\mathbf{R}^+$		20	2.3°

Which of the following pairs of particles are isoelectronic?

A **Q** and **R**

B **Q** and $\mathbf{R}^+$

C $\mathbf{Q}^+$ and **R**

D $\mathbf{Q}^+$ and $\mathbf{R}^+$

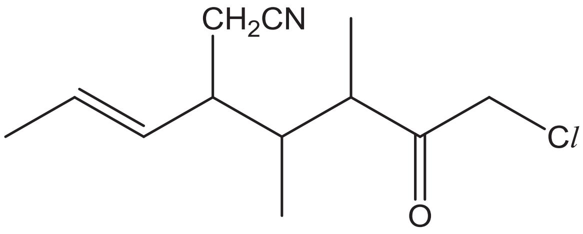
3 Three substances **D**, **E** and **F** have the following physical properties.

substance	melting point / °C	boiling point / °C	electrical conductivity in	
			solid state	liquid state
D	1538	2862	good	good
E	2852	3600	poor	good
F	3550	3825	good	not known

What could be the identities of **D**, **E** and **F**?

	D	E	F
A	Fe	$NaCl$	SiO_2
B	Fe	MgO	C (graphite)
C	$NaCl$	MgO	C (diamond)
D	Fe	SiO_2	C (graphite)

4 What is the number of sp, sp^2 and sp^3 hybridised carbons present in compound **H**?

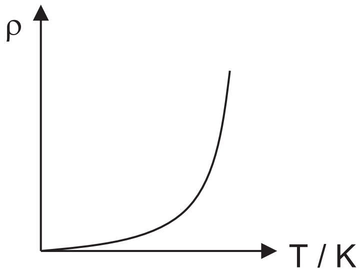


compound **H**

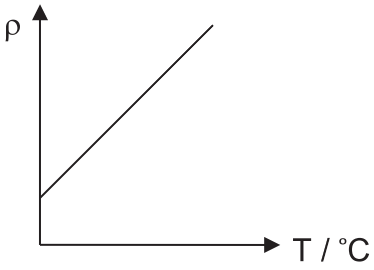
	sp hybridised C	sp^2 hybridised C	sp^3 hybridised C
A	0	3	7
B	1	3	7
C	1	3	8
D	1	4	8

5 Which of the following graphs show the correct relationship for an ideal gas under constant pressure, *P* ?

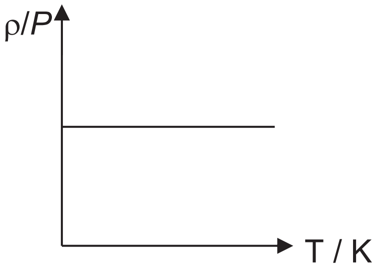
A



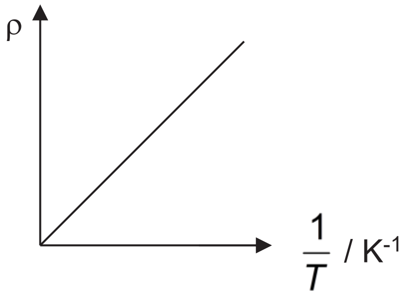
B



C



D



6 In which reaction does ammonia behave as a Lewis base?

1 $HCl + NH_3 \longrightarrow NH_4Cl$

2 $NaH + NH_3 \longrightarrow NaNH_2 + H_2$

3 $Zn^{2+} + 4NH_3 \longrightarrow [Zn(NH_3)_4]^{2+}$

A 1 only

B 3 only

C 1 and 3 only

D 1, 2 and 3

7 A chloride and an oxide of the elements in the third period of the Periodic Table are dissolved in two separate portions of water to form aqueous solutions.

Both of the resulting solutions can be used to dissolve Al_2O_3 but only one of the two can be used to dissolve SiO_2.

Which of the following could be the chloride and the oxide used?

A	$NaCl$	MgO
B	$MgCl_2$	SO_3
C	$SiCl_4$	Na_2O
D	PCl_5	P_4O_{10}

8 Three solutions containing the halogens $\mathbf{X}_2$, $\mathbf{Y}_2$ and $\mathbf{Z}_2$ were added to three aqueous solutions of $\mathbf{X}^-$, $\mathbf{Y}^-$ and $\mathbf{Z}^-$ ions separately. The experimental results are shown in the following table.

	$\mathbf{X}^-$	$\mathbf{Y}^-$	$\mathbf{Z}^-$
$\mathbf{X}_2$	No reaction	No reaction	$\mathbf{X}^-$ formed
$\mathbf{Y}_2$	$\mathbf{Y}^-$ formed	No reaction	$\mathbf{Y}^-$ formed
$\mathbf{Z}_2$	No reaction	No reaction	No reaction

Which of the following statements is correct?

A $\mathbf{Y}_2$ is a stronger oxidising agent than $\mathbf{X}_2$.

B $\mathbf{X}_2$ is a weaker oxidising agent than $\mathbf{Z}_2$.

C $\mathbf{Y}^-$ is a stronger reducing agent than $\mathbf{Z}^-$.

D $\mathbf{Z}^-$ is a weaker reducing agent than $\mathbf{X}^-$.

9 **W** is a compound containing only Fe, C and H. When 1.888 g of **W** was subjected to complete combustion, 4.47 g of CO_2 and 0.914 g of H_2O were formed.

What is the empirical formula of **W**?

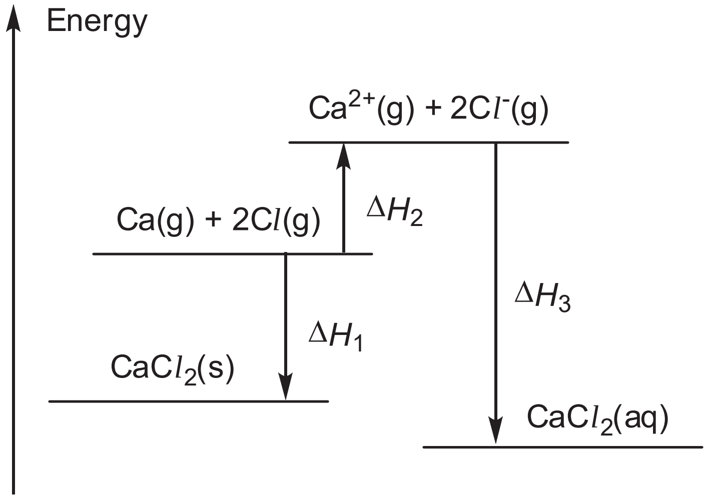
A FeCH

B FeC_2H

C $FeC_{10}H_{10}$

D $Fe_2C_5H_2$

10 The energy level diagram shown represents the dissolution of $CaCl_2$ in water.



Which of the following statements about the diagram is correct?

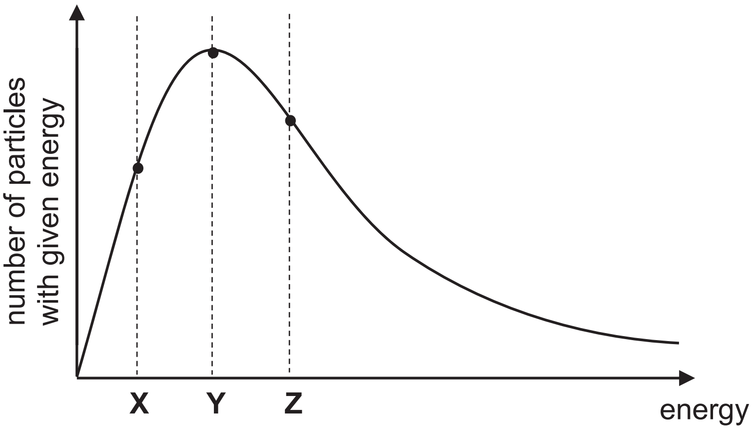
A The enthalpy change of formation of $CaCl_2$ is given by ΔH_1.

B The enthalpy change of dissolving $CaCl_2$ is given by $\Delta H_1+\Delta H_2+\Delta H_3$.

C The sum of the first and second ionisation energies of Ca is given by ΔH_2.

D The sum of the enthalpy change of hydration of Ca^{2+} and Cl^- is given by ΔH_3.

11 The Maxwell–Boltzmann distribution for a gas at constant temperature is shown below.



How would the number of particles change at the kinetic energies **X**, **Y** and **Z** when temperature is lowered by 5 °C.

	X	Y	Z
A	lower	lower	higher
B	lower	higher	higher
C	higher	lower	lower
D	higher	higher	lower

12 The reaction of nitric oxide with hydrogen can be monitored by the initial rate method and the overall kinetics is found to be third order.

$$2NO\,(g) + 2H_2\,(g) \longrightarrow N_2\,(g) + 2H_2O(l)$$

A proposed mechanism of the reaction is given below.

Step 1: $NO + NO \longrightarrow N_2O_2$

Step 2: $N_2O_2 + H_2 \longrightarrow N_2O + H_2O$

Step 3: $N_2O + H_2 \longrightarrow N_2 + H_2O$

What is the slow step in the mechanism?

A Step 1

B Step 2

C Step 3

D No conclusion can be drawn from the mechanism

13 Fe_3O_4 is found naturally in the mineral magnetite. It can be reduced to iron metal using hydrogen according to the following equilibrium.

$$Fe_3O_4\,(s) + 4H_2\,(g) \rightleftharpoons 3Fe\,(s) + 4H_2O\,(g) \qquad \Delta H = +50.4\ \text{kJ mol}^{-1}$$

Which of the following statements are correct about the reaction?

1 A reduction in the total pressure will increase the production of Fe.

2 The numerical values of K_c and K_p are equal.

3 An increase in temperature will increase the value of K_c.

A 1, 2 and 3

B 1 and 2 only

C 2 and 3 only

D 3 only

14 An equal volume of 0.1 mol dm^{-3} $Pb(NO_3)_2$ is added to a mixture containing 0.1 mol dm^{-3} of NaCl and 0.1 mol dm^{-3} NaI.

What is the most probable observation?

K_{sp} of PbCl_2 (white ppt) = 1.7×10^{-4} mol^3 dm^{-9}
K_{sp} of PbI_2 (yellow ppt) = 4.1×10^{-9} mol^3 dm^{-9}

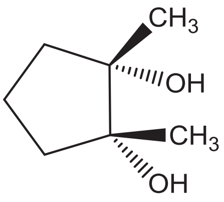
A A white and yellow ppt is formed.

B A yellow ppt is formed.

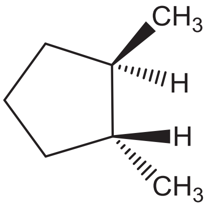
C A white ppt is formed.

D No ppt is formed.

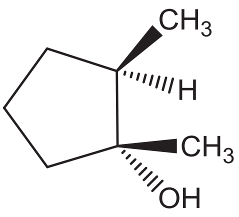
15 Which molecules are optically active?



1



2



3

A 3 only

B 1 and 2 only

C 2 and 3 only

D 1, 2 and 3 only

16 One mole of methylcyclobutane reacts with one mole of halogen in the presence of ultra–violet light.

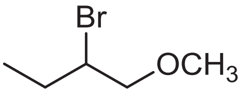
Which statements are true about this reaction?

1 There are only four possible mono–substituted products.
2 Hydrogen is a side product formed in the reaction.
3 Homolytic fission occurs only in the initiation step.

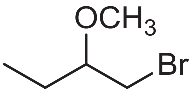
A 1 only
B 1 and 2 only
C 1 and 3 only
D 2 and 3 only

17 Which of the following is the major product when but–1–ene reacts with BrC*l* in pure methanol?

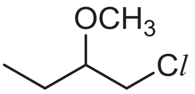
A



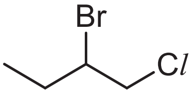
B



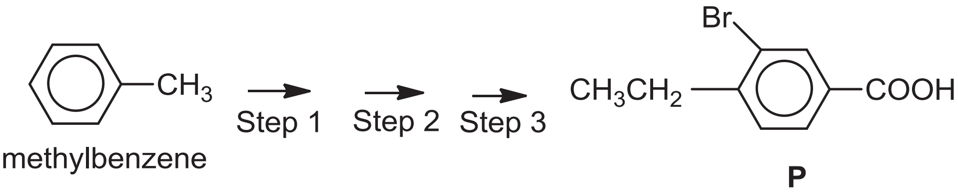
C



D



18 Compound **P** can be synthesised from methylbenzene as shown below.

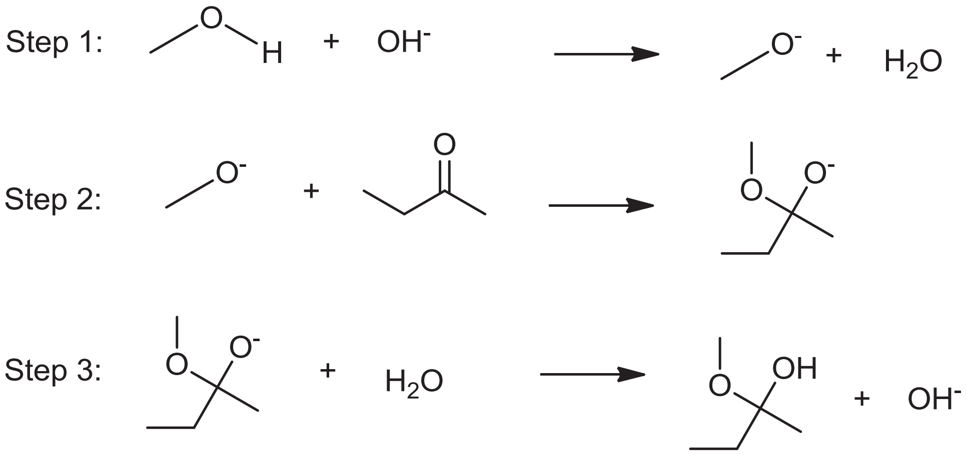


Which of the following could be a sequence for converting methylbenzene to compound **P**?

	step 1	step 2	step 3
A	CH_3CH_2Cl, $AlCl_3$, r.t.p.	Br_2 in $AlBr_3$, in the dark	$KMnO_4$, dilute H_2SO_4, heat
B	$KMnO_4$, dilute H_2SO_4, heat	Br_2 in $AlBr_3$, heat	CH_3CH_2Cl, $AlCl_3$, r.t.p
C	Br_2 in $AlBr_3$, heat	CH_3CH_2Cl, $AlCl_3$, r.t.p	$K_2Cr_2O_7$, dilute H_2SO_4, heat
D	$K_2Cr_2O_7$, dilute H_2SO_4, heat	CH_3CH_2Cl, $AlCl_3$, r.t.p.	Br_2 in $AlBr_3$, in the dark

19 1–methoxybutan–2–ol is an organic compound which has an alcohol and an ether (R–O–R) attached to the same carbon atom. It is formed when butan–2–one reacts with methanol in the presence of a catalyst.

The reaction follows the mechanism below.



1-methoxybutan-2-ol

Which of the following statements about the reaction is **not** correct?

A Methanol acts as a Lewis acid in step 1.

B Step 2 is a nucleophilic addition reaction across the C=O bond.

C Methanol can be used in step 3 instead of water.

D KOH can be used as a catalyst for this reaction.

20 0.5 g of each of the following compounds was heated with NaOH (aq).

$CH_2{=}CHCl$ CH_3CH_2I CH_3COBr C_6H_5Br

Each of the mixtures was then acidified with dilute nitric acid, followed by the subsequent addition of $AgNO_3$ (aq).

Which statement is correct?

A The reaction with C_6H_5Br gave a cream precipitate.

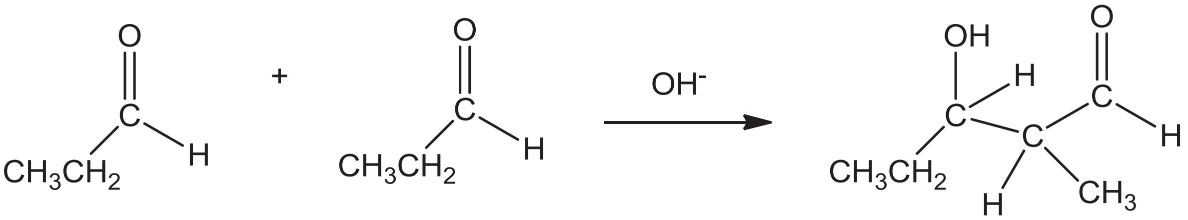
B The reaction with CH_3CH_2I gave a precipitate that dissolved completely in dilute aqueous ammonia.

C The rate of reaction with $CH_2{=}CHCl$ would be the slowest.

D The reaction with CH_3COBr gave the largest mass of precipitate.

21 In the presence of a strong base, aldehydes and ketones may undergo addition reaction to form an *aldo* compound (hydroxycarbonyl).

A reaction of propanal with sodium hydroxide to form an *aldo* compound is as shown below.

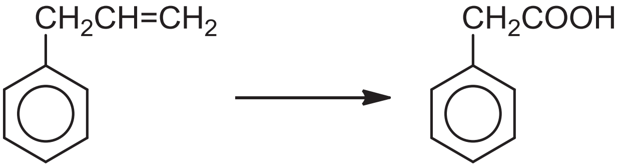


aldol compound

Which product can be formed when sodium hydroxide is added to a mixture of butanal, $CH_3CH_2CH_2CHO$, and propanone, CH_3COCH_3?

A $CH_3CH_2CH_2CH(OH)CH_2CH_2CH_2CHO$
B $(CH_3)_2C(OH)CH_2CH_2CH_2CHO$
C $(CH_3CH_2)_2C(OH)CH_2COCH_3$
D $CH_3CH_2CH_2CH(OH)CH_2COCH_3$

22 Alkenes can undergo oxidation to form carboxylic acids. The following conversion occurs in a multiple–step reaction.



Which of the following reagents is involved in the above conversion?

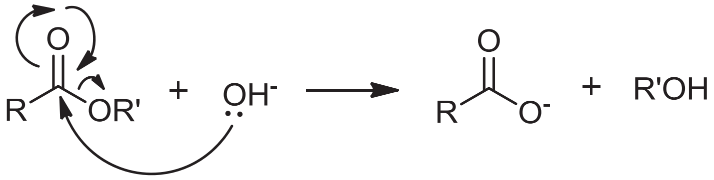
A concentrated H_2SO_4

B acidified $K_2Cr_2O_7$

C acidified $KMnO_4$

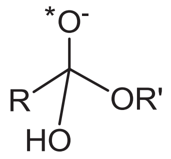
D alkaline I_2

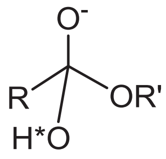
23 Esters can be hydrolysed under basic conditions according to the following mechanism.

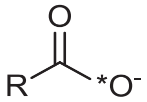


In an isotope labelling experiment, oxygen–18–labeled hydroxide, *OH⁻, is used.

Which of the following are produced as an intermediate or product?

1


2


3


4 R'—O*H

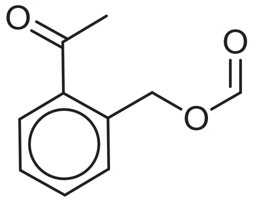
A 1 and 2 only

B 1 and 4 only

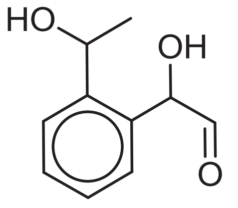
C 2 and 3 only

D 3 and 4 only

24 Compounds **V** and **W** have the following structures.



compound **V**



compound **W**

Which of the following reagents can be used to distinguish between compounds **V** and **W**?

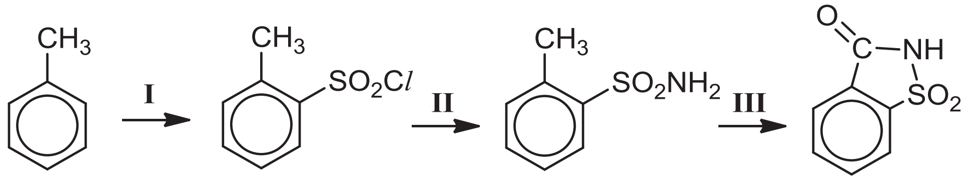
A iodine and aqueous sodium hydroxide

B 2,4–dinitrophenylhydrazine

C acidified aqueous potassium dichromate(VI)

D aqueous silver nitrate and aqueous ammonia

25 Saccharin is an artificial sweetener which can be synthesised from methylbenzene through a series of reactions below.



Which of the following statements is correct about the above synthesis?

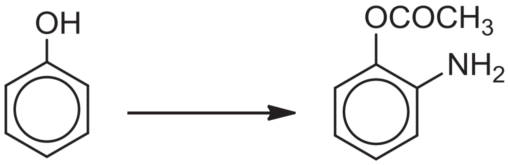
A Reaction **I** involves methylbenzene as an electrophile.

B Reaction **II** is a nucleophilic substitution reaction.

C Reaction **III** does not involve oxidation.

D Reaction **III** does not involve the elimination of water.

26 Phenols are widely used in household products and as intermediates for industrial synthesis. Compound **X** can produced from phenol in three steps.

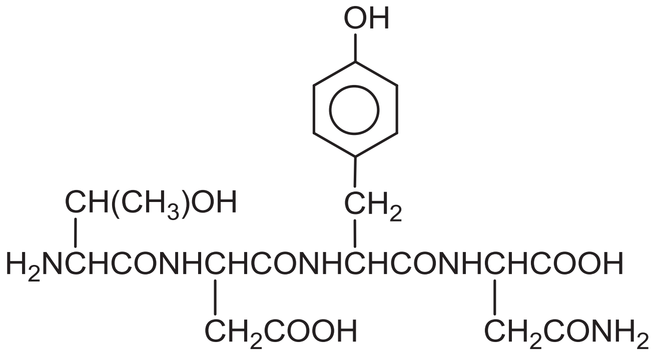


compound **X**

What are the reagents required in this three–step synthesis?

	stage 1	stage 2	stage 3
A	concentrated HNO_3, concentrated H_2SO_4	$NaBH_4$	CH_3COCl
B	aqueous HNO_3	Sn, concentrated HCl followed by NaOH (aq)	CH_3COCl
C	aqueous HNO_3	CH_3COCl	Sn, concentrated HCl, followed by NaOH (aq)
D	aqueous HNO_3	$NaBH_4$	CH_3COCl

27 Compound **Y** is formed from the partial hydrolysis of a hormone molecule.



Compound **Y**

Which of the following statement is **incorrect**?

A Prolonged heating of compound **Y** with dilute NaOH produces three carbon–containing products.

B Prolonged heating of compound **Y** with dilute NaOH liberates an alkaline gas.

C One mole of Na_2CO_3 is needed for complete reaction with one mole of compound **Y**.

D Two moles of Na is needed for complete reaction with one mole of compound **Y**.

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

A galvanic cell consists of a Mg^{2+}/Mg half–cell and a Cu^{2+}/Cu half–cell.

Which of the following statements is correct?

A Reducing the size of the magnesium electrode decreases the e.m.f of the cell.

B Increasing the temperature has no effect on the e.m.f. of the cell.

C Adding aqueous sodium hydroxide to the Cu^{2+}/Cu half–cell increases the e.m.f. of the cell.

D Adding water to the the Mg^{2+}/Mg half–cell increases the e.m.f. of the cell.

29 Methanol can be synthesised according to the reaction below. Cr_2O_3 is used as a catalyst to increase the rate of this reaction.

$$CO\ (g) + 2H_2\ (g) \rightarrow CH_3OH\ (l)$$

Which of the following statements are correct about the synthesis of methanol?

1 Cr_2O_3 is used as a catalyst because Cr can exhibit variable oxidation states in its compounds.

2 Cr_2O_3 lowers the activation energy by using its partially filled 3d orbitals for the adsorption of reactant molecules.

3 There is a decrease in the oxidation number of carbon.

A 1, 2 and 3

B 1 and 2 only

C 2 and 3 only

D 1 only

30 A reaction scheme starting from aqueous copper(II) nitrate solution is shown below.

Both **J** and **K** are copper–containing species.

$$Cu(NO_3)_2(aq) \xrightarrow[\textbf{I}]{NH_3(aq)} \textbf{J} \xrightarrow[\textbf{II}]{\text{excess } NH_3(aq)} \textbf{K} \xrightarrow[\textbf{III}]{KCN(aq)} [Cu(CN)_6]^{4-}(aq)$$

Which of the following statements are correct about the above reaction scheme?

1 One of the reactions involves a redox reaction.

2 CN^- is a stronger ligand than NH_3.

3 Precipitation occurs in step **I**.

A 1, 2 and 3

B 2 and 3 only

C 1 and 2 only

D 2 only

End of Paper 1

2017 MJC H2 Chemistry Prelim Paper 2

1 Concepts of acids and bases are important aspects in Chemistry which can be applied to many areas in our daily life.

(a) There are three theories of acids and bases. In 1887, Svante Arrhenius proposed that acids are substances that produce H^+ in water and bases are those which produce OH^- in water. In 1923, Johannes N Brønsted and Thomas M Lowry proposed another set of definitions for acids and bases. Later in the same year, Gilbert N Lewis defined acids and bases in terms of electron pair acceptors and donors respectively.

(i) State the *Bronsted–Lowry theory* of acids and bases.

[1]

(ii) There are several limitations to Arrhenius' theory of acids and bases. Give an example to illustrate one of its limitations.

[1]

(b) The pK_a values and solubilities of some weak acids in methanol and water at 25 ˚C are given in **Table 1.1**.

Table 1.1

compound	pKa in methanol	pKa in water	solubility/ per 100 g of water
CH_3COOH ethanoic acid	9.71	4.88	100 g
$CH_2(CN)COOH$ 2–cyanoethanoic acid	7.50	2.46	More than 100 g

(i) Two samples of 2–cyanoethanoic acid of identical concentrations were dissolved in water and methanol separately. Calculate the ratio of H^+ ions formed in water and in methanol.

[1]

(ii) Suggest a reason why both acids in **Table 1.1** have lower pK_a in water than in methanol.

[1]

(iii) Explain why 2–cyanoethanoic acid has a higher solubility in water than ethanoic acid.

[1]

(c) The base dissociation constants of some weak bases are given in **Table 1.2**.

Table 1.2

compound	K_b value at 25˚C
methylamine CH_3NH_2	4.6×10^{-4}
dimethylamine $(CH_3)_2NH$	5.4×10^{-4}
trimethylamine $(CH_3)_3N$	6.3×10^{-5}

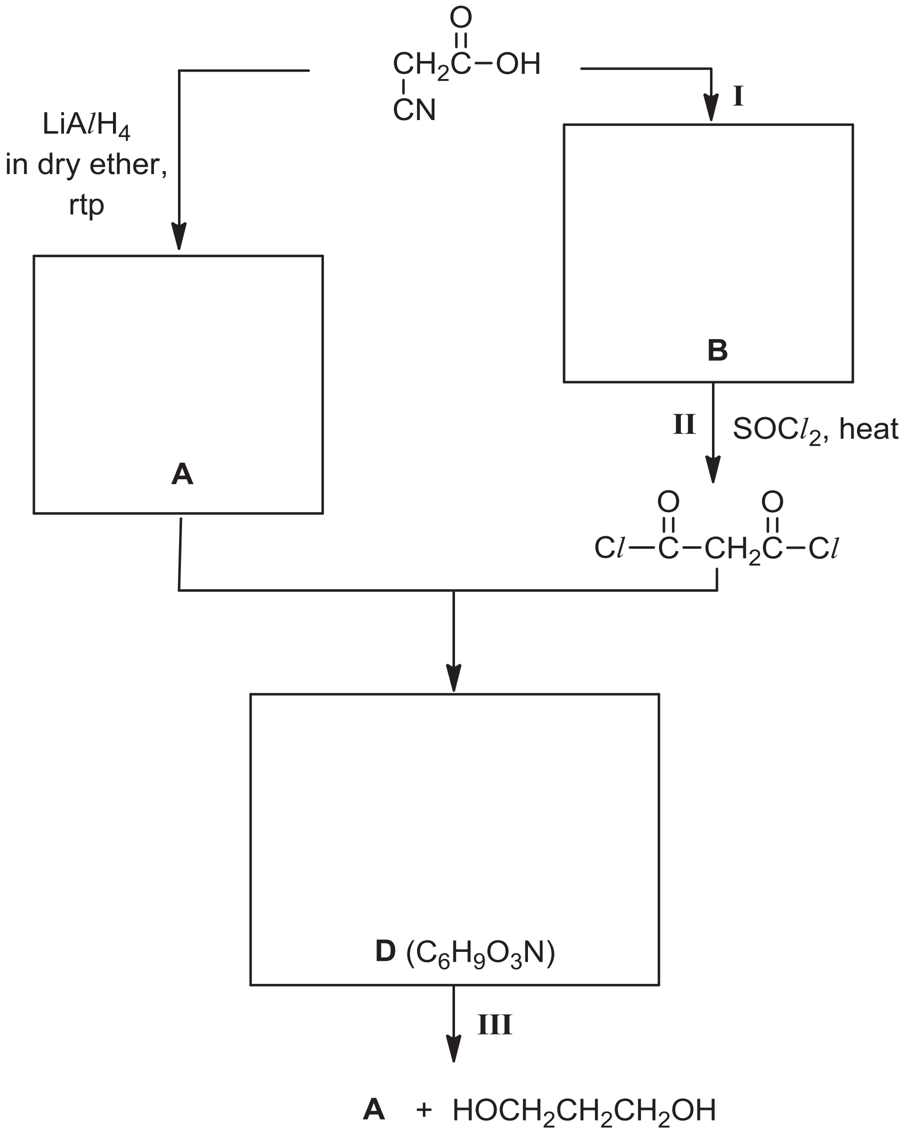
(i) Explain why dimethylamine is more basic than methylamine.

[1]

(ii) Among the three compounds, trimethylamine is the least basic, which is unusual. Suggest a reason for this.

[1]

(d) 2–cyanoethanoic acid can undergo a series of reactions to form a neutral cyclic compound **D**. Compound **D** can further react to produce compound **A** and a diol**.**



(i) Draw the structures of compounds **A**, **B** and **D** in the boxes above.

[3]

(ii) State the types of reaction in step **I** and **II.**

[1]

Step **I**: ……………………………………….

Step **II**: ……………………………………….

(iii) State the reagents and conditions required in Step **I** and **III**.

[2]

Step **I**: ……………………………………….

Step **III**: ……………………………………..

[Total: 13]

2 Vitamins and minerals are essential nutrients that perform many roles in the body. They help to build bones, heal wounds, bolster the immune system and convert food into energy. Young children require many essential minerals such as calcium, magnesium, iodine, iron and zinc to develop and grow.

Table 2.1 shows the recommended daily intake of some essential minerals for children.

Table 2.1

Mineral	**Recommended daily intake for children / mg**	
	Age group	
	1 – 3 years	**4 – 8 years**
Calcium	500	700
Iodine	0.090	0.090
Iron	9	10
Magnesium	80	130
Phosphorus	460	500
Zinc	3	4

Table 2.2 shows part of a nutrition label on a tin of powdered milk formula.

Table 2.2

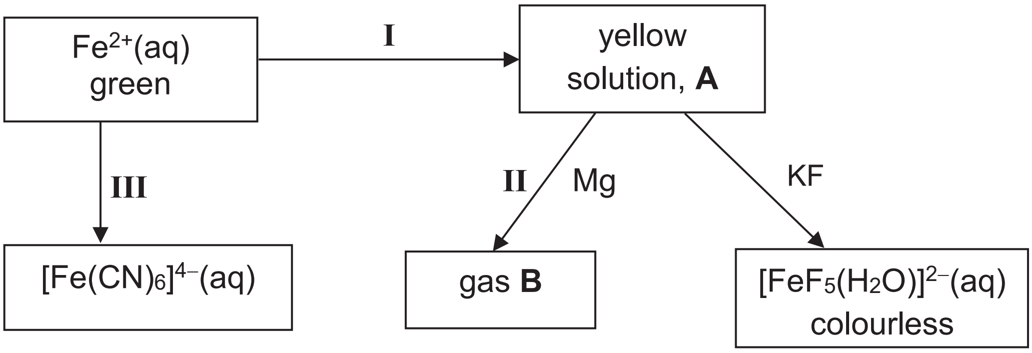
Nutrition Information **Standard Dilution (per 100 ml)**	
Nutrients:	
Protein	2.2 g
Fat	5.1 g
Carbohydrate	11.2 g
Minerals:	
Sodium	39 mg
Potassium	106 mg
Chloride	79 mg
Calcium	119 mg
Phosphorus	69 mg
Magnesium	7.8 mg
Iron	1.03 mg
Zinc	0.7 mg
Copper	0.056 mg
Manganese	0.0094 mg
Iodine	0.011 mg

(a) Zinc helps the immune system fight off invading bacteria and viruses. A 2–year old child takes an average of 3 feeds of milk formula per day, with a quantity of 180 ml per feed.

Using the information provided, determine if the zinc obtained from the milk formula meets the recommended quantity for daily intake. Comment on whether there is a need for the child to supplement his diet with zinc from other sources.

[2]

(b) Iron is an essential mineral used to carry oxygen in the blood.
The following flowchart shows the reactions of iron and its compounds.



(i) Name the types of reactions taking place in **I** and **II**.

[2]

I: ……………………………………….

II: ……………………………………….

(ii) Write the formula of the cation present in **A** and identify gas **B**.
By considering the nature of this cation present, explain fully why gas **B** is formed when Mg is added to **A** in reaction **II**.

[3]

(iii) What is the type of reaction taking place in **III**? Write a balanced equation for the reaction.

[2]

(iv) Fe^{2+}(aq) appears to be green whereas $[FeF_5(H_2O)]^{2-}$(aq) is colourless.

1. Explain why Fe^{2+}(aq) appears to be green.

[3]

2. Write the full electronic configuration of iron in $[FeF_5(H_2O)]^{2-}$.

[1]

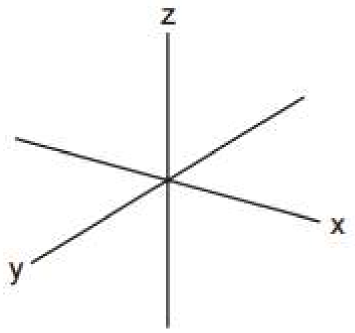
3. Suggest why $[FeF_5(H_2O)]^{2-}$ is colourless.

[1]

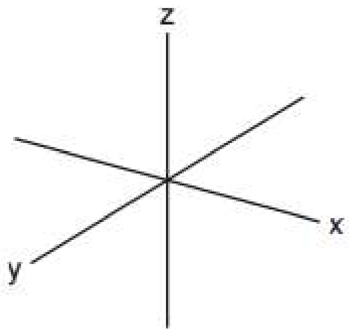
(v) Iron forms many octahedral complexes, of which $[Fe(CN)_6]^{4-}$ is an example. On the axes below, sketch the shapes of a d orbital from the lower energy level and a d orbital from the higher energy level in an octahedral complex.

[2]

lower energy level



higher energy level



(c) Calcium is the most abundant mineral present in milk formula. It is essential for healthy bones and teeth. In the blood, it also helps to regulate the heartbeat, blood pressure and neural transmission.

Table 2.3 gives data about some physical properties of calcium and iron.

Table 2.3

property	calcium	iron
relative atomic mass	40.1	55.8
atomic radius (metallic)/ nm	0.197	0.126
ionic radius (2+)/ nm	0.099	0.076
melting point / °C	839	1538
density / g cm^{-3}	1.54	7.86

(i) Explain why the atomic radius of iron is less than that of calcium.

[2]

(ii) Use relevant data from **Table 2.3** to explain qualitatively why the density of iron is significantly greater than that of calcium.

[1]

(d) Magnesium, phosphorus and chlorides are also minerals found in milk formula.

(i) Write relevant chemical equations to illustrate the reactions of magnesium chloride and phosphorus pentachloride with water. Suggest the approximate pH of any solutions formed.

[2]

(ii) Like magnesium, phosphorus and chlorine, element **Z** is also a Period 3 element. The first six ionisation energies of **Z** are shown in **Figure 2.1** while the 2nd ionisation energies of seven consecutive elements **A – G** (one of which is **Z**) is shown in **Figure 2.2**.

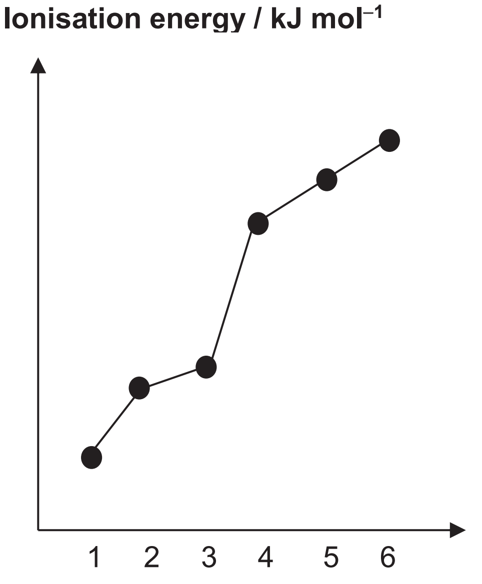


Figure 2.1

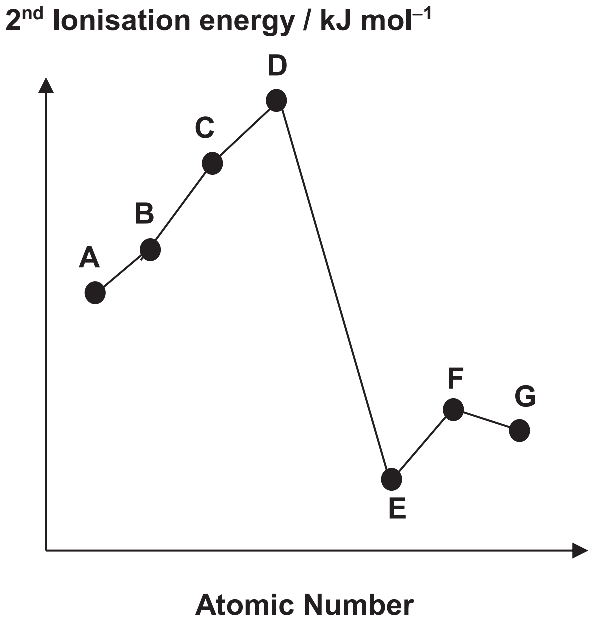


Figure 2.2

Identify element **Z**. Hence, state which element **A – G** in **Figure 2.2**, could be **Z**.

[1]

[Total: 22]

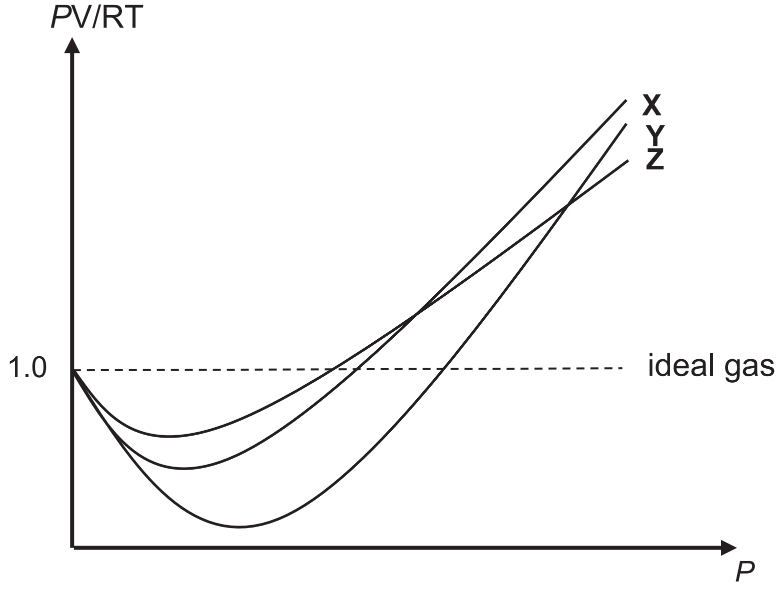
3 Nitrosyl chloride, NOC*l*, is a toxic gas that has caused several industrial accidents.

At 250 °C, NOC*l* readily dissociates into NO and C*l*$_2$.

$$2NOCl\,(g) \rightleftharpoons 2NO\,(g) + Cl_2\,(g)$$

(a) The graphs of *P*V/RT against *P* for 1 mole each of NO, C*l*$_2$ and NOC*l* at room temperature are plotted below.

Figure 3.1



With reference to **Figure 3.1**, deduce which of the graphs is the plot for NOC*l*.

[2]

(b) The dissociation was investigated by adding 5 moles of NOC*l* into a 5.0 dm^3 sealed vessel, and equilibrium was established at 250 °C under a pressure of 5.80 x 10^6 Pa.

(i) Assuming ideal gas behaviour, determine the total amount of gas in moles, at equilibrium.

[1]

(ii) Write the expression for the equilibrium constant, K_p, for the dissociation of $\mathrm{NOC}l$, including units.

[1]

(iii) Calculate a value for K_p under the stated conditions.

[3]

(c) Standard Gibbs free energy change, $\Delta G^\ominus$ is related to K_c by the following equation.

$$\Delta G^\ominus = -RT \ln K_c$$

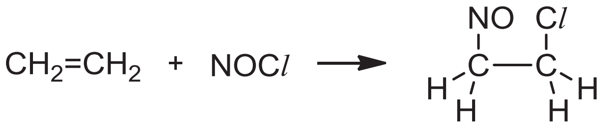
$\Delta G^\ominus$ for the dissociation of $\mathrm{NOC}l$ at 250 °C is –1.47 kJ mol^{-1}.

(i) Using the above information, calculate K_c for the dissociation of $\mathrm{NOC}l$ at 250 °C. [1]

(ii) Suggest how K_c will change when the temperature is raised. [1]

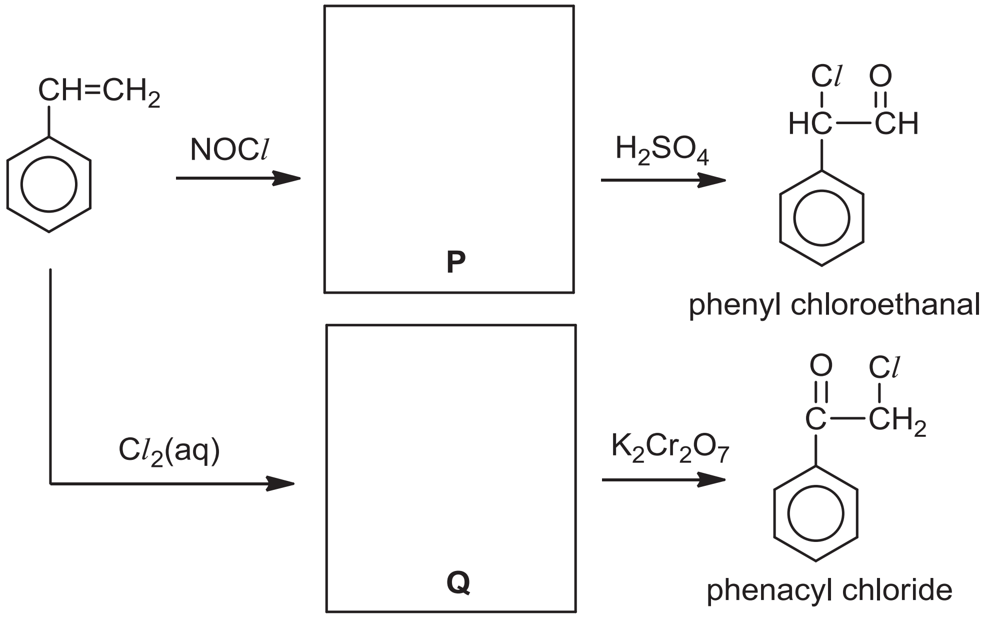
(iii) Hence, using *Le Chatelier's Principle*, deduce whether the dissociation reaction is exothermic or endothermic. [2]

(d) NOC*l* is sometimes used in organic synthesis. It can react with alkenes to form chloro–nitroso compounds according to the following equation.



$$CH_2{=}CH_2 + NOCl \longrightarrow H_2C(NO){-}CH_2(Cl)$$

A reaction scheme involving the use of NOC*l* for the synthesis of phenyl chloroethanal and phenacyl chloride is given below



(i) Draw the structures of compounds **P** and **Q**.

[2]

(ii) State a reagent which can distinguish between phenyl chloroethanal and phenacyl chloride. Write a balanced equation for the reaction.

[2]

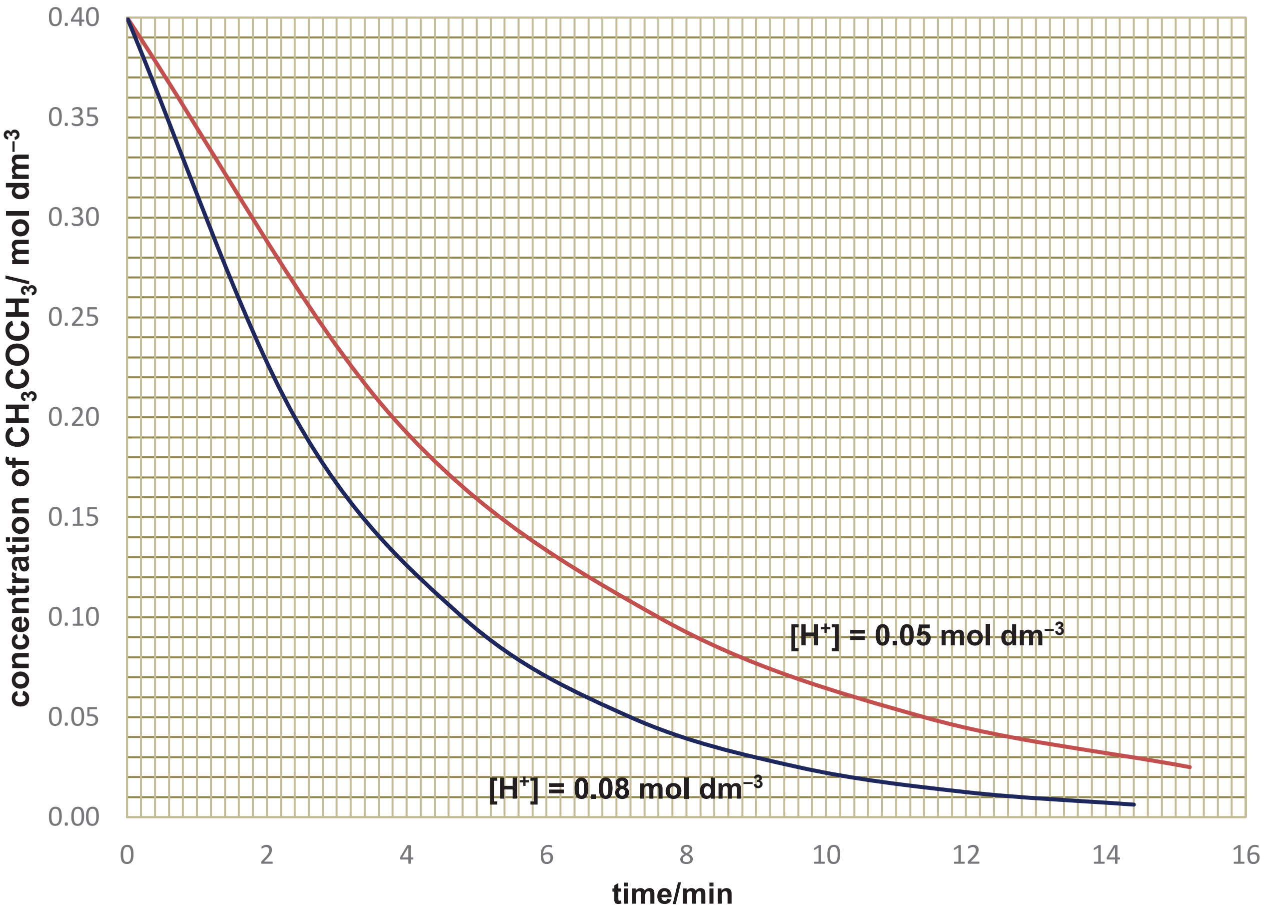
[Total: 15]

4 The bromination of propanone is an acid–catalysed reaction which produces bromopropanone. The equation for the reaction is given below.

$$CH_3COCH_3 + Br_2 \xrightarrow{H^+} CH_2BrCOCH_3 + H^+ + Br^-$$

(a) Two experiments on the kinetics of the reaction are conducted with $[Br_2]$ being kept constant. The $[CH_3COCH_3]$ is monitored and the following graphs are obtained.

Graph of concentration of CH_3COCH_3 with time



(i) Using the information above, deduce the order of reaction with respect to CH_3COCH_3 and H^+. Show your working on the graph.

[3]

(ii) Another experiment was conducted with a different [Br_2]. It was determined that changing [Br_2] has no effect of the rate of reaction. Sketch a graph to show how [Br_2] varies with time.

[1]

(iii) Using your answers from **(a)(i)** and **(a)(ii)**, construct the rate equation for the bromination of CH_3COCH_3.

[1]

(iv) Given that the initial rate of reaction is 7.6 x 10^{-5} mol dm^{-3} min^{-1} when [H^+] is 0.05 mol dm^{-3}, calculate the rate constant, *k*, for the reaction. State its units.

[1]

(b) Bromopropanone, $CH_2BrCOCH_3$, can also be synthesised via organic reactions.

(i) Devise a 3–step synthesis to produce $CH_2BrCOCH_3$ from the allyl alcohol, $CH_2{=}CHCH_2OH$.

[3]

(ii) Other than the use of an oxidising agent, suggest a chemical test to determine if the synthesis reaction in **(b)(i)** is complete.

[2]

(c) $CH_2BrCOCH_3$ undergoes hydrolysis with aqueous NaOH to form $CH_2(OH)COCH_3$. The reaction follows a second order kinetics.

(i) Outline the mechanism for this reaction, showing all the charges and using curly arrows to represent the movement of electron pairs.

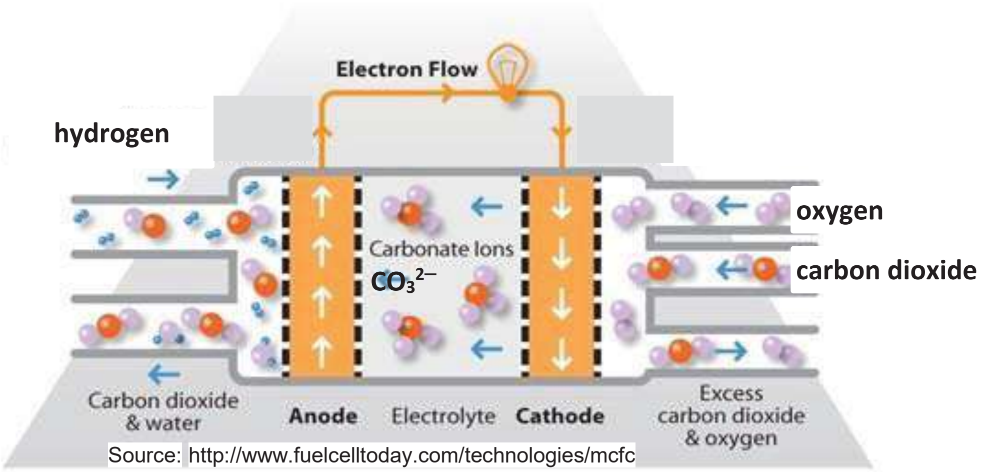
[2]

(ii) CH_3CH_2COBr is an isomer of bromopropanone, $CH_2BrCOCH_3$. The rate of hydrolysis for each of the two compounds is different. State and explain which isomer has a faster rate of hydrolysis.

[2]

[Total: 15]

5 A fuel cell is an electrochemical cell that converts the chemical energy from a fuel into electricity. One example is molten–carbonate fuel cells (MCFCs) developed for natural gas power plants.



Source: http://www.fuelcelltoday.com/technologies/mcfc

(a) At the anode, water and carbon dioxide are formed whereas carbonate ions are formed at the cathode.

(i) Construct the half–equations at the electrodes of this MCFC electrochemical cell. Hence, give the balanced equation for the reaction that occurs during discharge of the MCFC.

[2]

(ii) Draw a fully labelled diagram of the electrochemical cell to determine the standard electrode potential of the $O_2(g)/OH^-(aq)$ electrode system.

[2]

(b) Another example of a fuel cell is direct–formic acid fuel cells (DFAFCs).
It has the overall reaction similar to the combustion of formic acid in oxygen. The following reactions take place at the electrodes.

$CO_2 + 2H^+ + 2e \rightleftharpoons HCOOH \qquad E^\theta = -0.61\ V$

$\frac{1}{2}O_2 + 2H^+ + 2e \rightleftharpoons H_2O \qquad E^\theta = +1.23\ V$

By using one of the phrases *more positive, more negative* or *no change,* deduce the effect of increasing $[OH^-]$ on the electrode potential of the cathode.

[1]

(c) **Table 5.1** shows the different enthalpies of various compounds. The data will be useful for this question.

Table 5.1

	ΔH^θ / kJ mol^{-1}
standard molar enthalpy of formation of CO_2 (g)	−394
standard molar enthalpy of formation of H_2O (*l*)	−286
standard molar enthalpy of formation of CH_3OH (aq)	−246
standard molar enthalpy of formation of HCHO (aq)	−150
standard molar enthalpy of combustion of formic acid, CH_2O_2 (*l*)	−211

(i) Define the term *standard enthalpy change of formation*, ΔH_f^θ of formic acid, CH_2O_2.

[1]

(ii) Using Hess's law and information from **Table 5.1**, construct an energy cycle to calculate the $\Delta H_f^{\ominus}$ of formic acid.

[3]

(iii) Methanol, CH_3OH is toxic because liver enzymes oxidise it to formaldehyde, HCHO.

Using **Table 5.1**, calculate the standard enthalpy change, $\Delta H^{\ominus}$ for the following reaction.

$$CH_3OH\,(aq) + \tfrac{1}{2}O_2\,(g) \longrightarrow HCHO\,(aq) + H_2O\,(l)$$

[1]

[Total: 10]

End of Paper 2

Name ________________________ **Class: 16S**_______ **Reg Number:** _____

MERIDIAN JUNIOR COLLEGE
JC 2 Preliminary Examination
Higher 2

Chemistry 9729/03

Paper 3 Free Response **13 September 2017**

2 hours

Additional Materials: *Data Booklet*
Writing Paper

INSTRUCTIONS TO CANDIDATES

Write your name, class and register number in the spaces provided at the top of this page.

Answer all questions in Section A and one question from Section B.

Begin each question on a fresh page of writing paper.

Fasten the writing papers behind the given **Cover Page for Questions 1 & 2** and **Cover Page for Questions 3 & 4 or 5** respectively.

Hand in Questions **1 & 2** and **3 & 4 or 5** **separately**.

You are advised to spend about 30 minutes per question only.

INFORMATION FOR CANDIDATES

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

You are reminded of the need for good English and clear presentation in your answers.

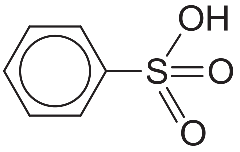
This document consists of **20** printed pages.

Section A

Answer **all** questions in this section.

1 Sulfa drugs are a class of sulfur containing compounds. These drugs have a variety of uses and can be classified as antibiotics and non–antibiotic drugs. They were the "wonder drugs" before penicillin was discovered.

A precursor to synthesising such sulfa drugs is aryl sulfonic acid with the general structure shown below.



Aryl sulfuric acids may be synthesised from the electrophilic substitution reaction between concentrated sulfuric acid and an aromatic compound.

(a) In an experiment to investigate the rate of reaction between concentrated sulfuric acid and benzene to form sulfonic acid, different volumes of sulfuric acid and benzene were used and the time taken for a complete reaction was recorded in **Table 1.1**.

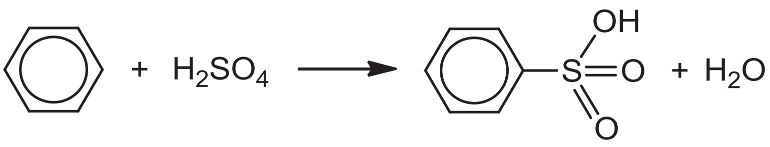
Table 1.1

Experiment	**Volume of concentrated sulfuric acid / cm^3**	**Volume of benzene / cm^3**	**Volume of water / cm^3**	**Time taken for complete reaction / s**
1	10	20	30	60
2	20	20	20	15
3	20	30	10	10

(i) Use the data above to deduce the order of reaction with respect to concentrated sulfuric acid and benzene, showing how you arrive at your answer. [3]

(ii) Hence, construct the rate equation for the reaction. [1]

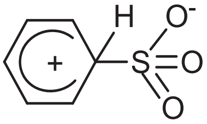
(b) The overall equation for the formation of the aryl sulfonic acid, $C_6H_5SO_3H$, through electrophilic substitution is given below.

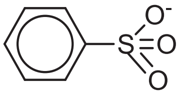


This reaction proceeds via a four–step mechanism.

- **Step 1**: The SO_3 electrophile is first generated from concentrated sulfuric acid given by the following equation.

  $$2H_2SO_4 \rightleftharpoons SO_3 + H_3O^+ + HSO_4^-$$

- **Step 2**: The SO_3 electrophile is then attacked by benzene to form an intermediate  .

- **Step 3**: When the intermediate from **Step 2** is deprotonated, an anion  is formed and the sulfuric acid is regenerated.

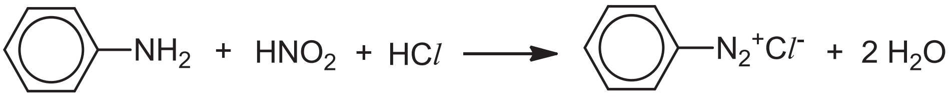
- **Step 4**: The $C_6H_5SO_3^-$ anion is then protonated by a hydronium ion, H_3O^+, to form the products, $C_6H_5SO_3H$ and water.

(i) Use the information given above to outline the mechanism for **Steps 2 to 4**, showing all charges and using curly arrows to show the movement of electron pairs. You are required to show the displayed formulae of all species. [3]

(ii) With reference to your answer in **(a)(ii)**, suggest which step corresponds to the rate determining step of the mechanism. [1]

(c) Another application of aryl sulfonic acid is in coupling with diazonium salts to form useful compounds.

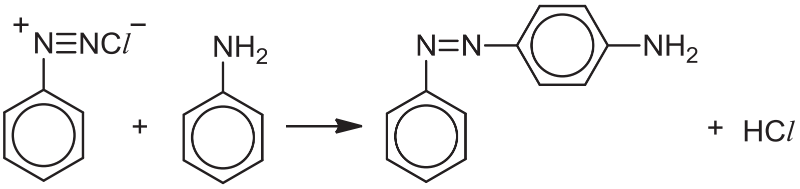
The diazonium salt is first produced by reacting phenylamine with cold nitrous acid and hydrochloric acid. This process is called diazotisation.



diazonium salt

(i) Describe how you will carry out a simple chemical test to distinguish between phenylamine and the diazonium salt. [2]

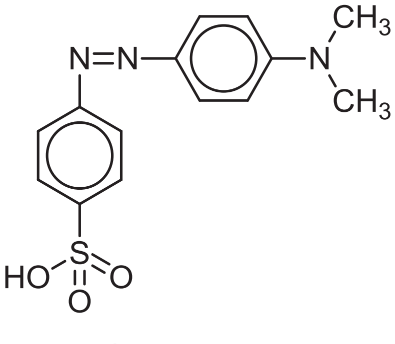
The diazonium salt obtained from the diazotisation can undergo coupling with another phenylamine to form an azo compound, which is a useful dye. An example of a coupling reaction is given below.



diazonium salt

azo compound

Methyl orange, which is used as an acid–base indicator, is formed using coupling reaction between a phenylamine derivative and a sulfonic acid containing diazonium salt.



methyl orange

(ii) Draw the structures of the two reactants used in the coupling reaction to synthesise methyl orange. State which of these two reactants is the electrophile. [3]

(d) Similar to sulfuric acid, concentrated sulfonic acids can be used as a catalyst in the synthesis of esters.

Compound **P**, $C_7H_{13}O_2Br$, is formed from the reaction between compounds **Q** and **R**, using concentrated sulfonic acid as a catalyst. Both compounds **Q** and **R** are able to rotate plane–polarised light.

Upon combustion with excess oxygen, 0.1 mole of compound **Q** produces 0.5 mole of carbon dioxide gas and 0.5 mole of water. Effervescence is observed when two moles of compound **Q** reacts with one mole of sodium carbonate.

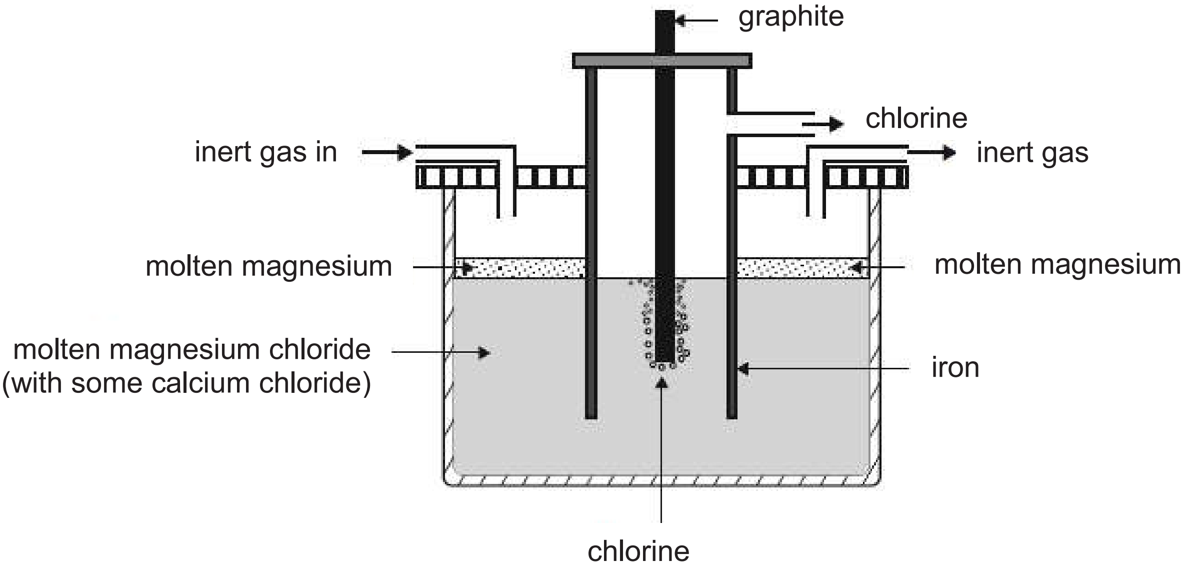
Compound **R** gives a yellow precipitate when heated in an alkaline solution of iodine. Upon heating with sodium hydroxide, followed by the addition of aqueous silver nitrate, a cream precipitate was formed.

Deduce the structures of **P**, **Q** and **R**, explaining the chemistry of the reactions described. [7]

[Total: 20]

2 Magnesium–containing compounds are important substances that have found many applications in our daily life.

(a) Magnesium metal is one of the most abundant elements on Earth. It is produced by the electrolysis of molten magnesium chloride. An example of such an electrolytic cell to form molten magnesium is shown below.



(i) Write the half equations, with state symbols, for the reactions at the graphite and iron electrodes. [2]

(ii) Explain why an inert gas is constantly blown into the compartment. [1]

(iii) Generally, to reduce energy consumption, $CaCl_2$ and $ZnCl_2$ can be added to lower the melting point of $MgCl_2$. However, in this electrolytic cell, only $CaCl_2$ can be used for this purpose.

With reference to $E^\ominus$ values in the *Data Booklet*, explain why only $CaCl_2$ can be used to lower the melting point of $MgCl_2$ in this electrolytic cell and not $ZnCl_2$.
[2]

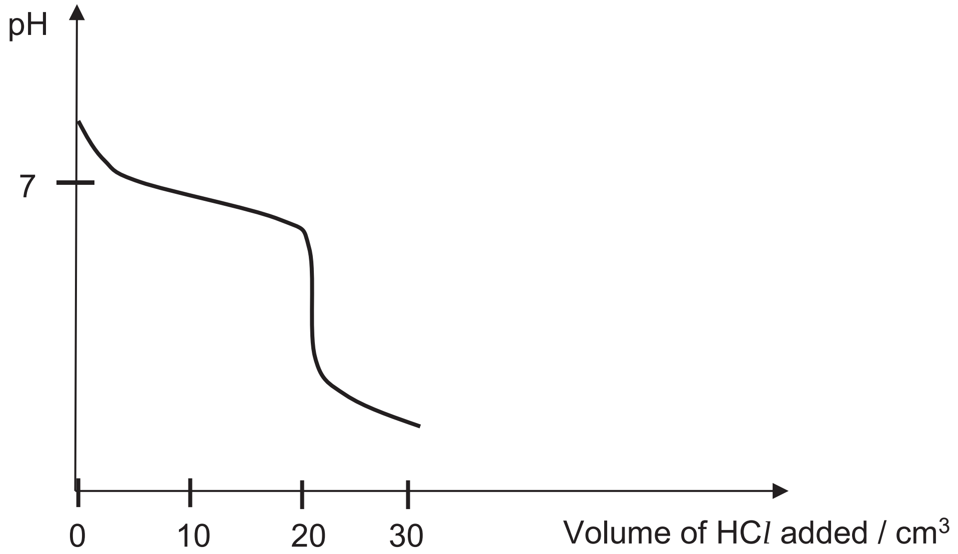
(iv) By quoting relevant $E^\ominus$ values, explain whether an iron electrode is a suitable replacement for the graphite electrode for the above electrolytic cell. [2]

(v) Another metal, **M**, is obtained by using the same electrolytic cell above. During the electrolysis, a current of 1.5 A was applied for 6 hours. The amount of metal **M** obtained was 1.12×10^{-1} mole. Determine the charge of the molten metal ion, $\mathbf{M}^{x+}$. [2]

(b) Magnesium hydrogencarbonate, $Mg(HCO_3)_2$, is a bicarbonate salt of magnesium with $K_b = 2.4 \times 10^{-8}$ mol dm^{-3}.

A sample of 0.10 mol dm^{-3} $Mg(HCO_3)_2$ solution was titrated against a 0.10 mol dm^{-3} solution of hydrochloric acid. The following titration curve was obtained.

Graph 2.1



(i) With the aid of the titration curve, calculate the volume of the sample of $Mg(HCO_3)_2$ solution. [1]

(ii) Calculate the initial pH on the titration curve. [2]

(iii) With the aid of an equation, explain why the pH value obtained at equivalence point is acidic. No calculations are required. [2]

(iv) Given the pH transition ranges of some indicators in **Table 2.1**, suggest with reasoning, an appropriate indicator for the titration between aqueous $Mg(HCO_3)_2$ and hydrochloric acid.

Table 2.1

Name of indicator	pH transition range
bromocresol green	4 – 6
thymolphthalein	9 – 11

[2]

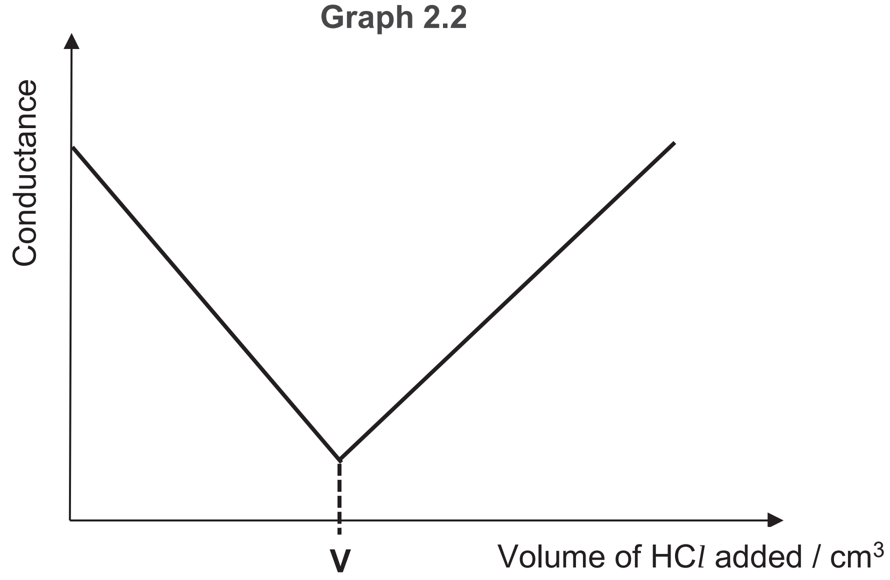
(v) State the volume of hydrochloric acid and calculate the pH at which the buffer operates at its maximum buffer capacity. [2]

(vi) As compared to magnesium hydrogencarbonate, magnesium carbonate has a K_b value of 2.10×10^{-4}. Explain why magnesium carbonate is a stronger base than magnesium hydrogencarbonate. [1]

(c) Instead of monitoring the pH change during the titration, the electrolytic conductivity of the reaction mixture is continuously monitored. The equivalence point is the point at which conductivity undergoes a sudden change.

The conductometric titration curve shown in **Graph 2.2** is obtained when 20 cm^3 of 0.10 mol dm^{-3} aqueous sodium hydroxide was titrated against 0.10 mol dm^{-3} aqueous hydrochloric acid. The change in conductance may be assumed to be only due to the changes in the amount of hydrogen ions and hydroxide ions.

Graph 2.2



Using your understanding of the titration between sodium hydroxide and hydrochloric acid, determine the volume **V** in the above conductometric titration curve. Explain the change in conductance as an increasing volume of HC*l* is added.

[3]

[Total: 22]

3 This question is about the chemistry of oxygen containing compounds.

(a) "Elephant's toothpaste" is a foamy substance caused by the rapid decomposition of hydrogen peroxide as shown by the equation:

$$2H_2O_2 \rightarrow 2H_2O + O_2$$

(i) The decomposition of H_2O_2 results in the formation of a highly reactive species, •OH, with an unpaired electron. With the aid of an equation and the use of curly arrows to represent the movement of electrons, show how this reactive species may be formed from H_2O_2. [1]

(ii) Using data from the *Data Booklet*, calculate $E^{\ominus}_{cell}$ for the decomposition of hydrogen peroxide. [1]

(iii) Hence, calculate $\Delta G^{\ominus}$ for the decomposition of hydrogen peroxide. Explain the significance of your answer. [2]

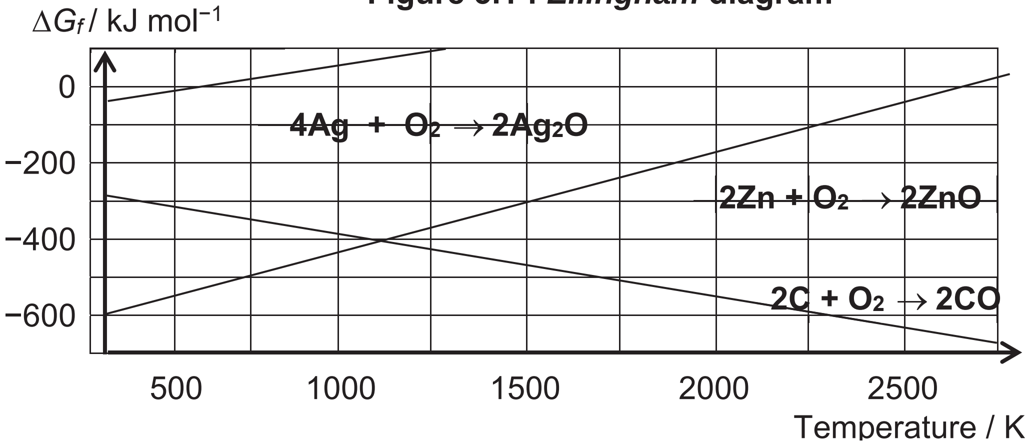
(iv) $Fe^{2+}(aq)$ ions can be used to catalyse the decomposition of hydrogen peroxide. Using relevant data from the *Data Booklet*, describe and explain the role of $Fe^{2+}(aq)$ ions in this reaction. You should support your answers with relevant equations. [3]

(b) ΔG, ΔH and ΔS are related by the following equation.

$$\Delta G = \Delta H - T\Delta S$$

Figure 3.1 is an *Ellingham* diagram, which shows the variation in the Gibbs free energy change of **formation**, ΔG_f, with temperature, T, for some oxides.

Figure 3.1 : *Ellingham* diagram



(i) With reference to the gradient of the graph for the formation of zinc oxide, ZnO, explain with reasoning, the sign of ΔS. [2]

(ii) The *Ellingham* diagram in **Figure 3.1** can also be used to deduce the ease of decomposition of silver oxide and zinc oxide. Suggest which metal oxide is thermally less stable at 1000 K. Explain your answer. [2]

(iii) Similar to enthalpy change of reaction, the Gibbs free energy, ΔG, of a reaction can be calculated using the following expression.

$$\Delta G = \sum \Delta G_f(\text{products}) - \sum \Delta G_f(\text{reactants})$$

Calculate the ΔG value for the reduction of zinc oxide by carbon at 2250 K. Hence, comment on the feasibility of this reaction at 2250 K. [2]

(c) The zinc–air battery is commonly used as small button cells in watches and hearing aids. When a gas permeable and liquid–tight membrane sealing tab in the button cell is removed, oxygen in the air is absorbed into an alkaline electrolyte.

The positive electrode is made of porous carbon and the negative electrode consists of zinc. The zinc electrode slowly dissolves to form a colourless solution. The electrolyte used is a paste of potassium hydroxide.

(i) Write equations, with state symbols, for the reactions that occur at the anode and the cathode respectively. [2]

(ii) The zinc–air battery has a cell potential of +1.59 V. Using relevant data from the *Data Booklet*, calculate the electrode potential for the reaction at the anode. [1]

(iii) The zinc electrode of a new zinc–air button cell weighs 1.85 g. The cell can run until 80% of the zinc is consumed.

Calculate the maximum amount of current that can be drawn from the cell if it is expected to last for 365 days. [1]

(iv) Common alkaline batteries contain zinc and manganese(IV) oxide in a paste of potassium hydroxide. The overall equation is as shown.

$$Zn\,(s) + MnO_2\,(s) + H_2O\,(l) \rightarrow ZnO\,(s) + Mn(OH)_2\,(s)$$

Based on this information, suggest an advantage, other than lower cost that the zinc–air battery has over the common alkaline battery of a similar mass. Explain your answer. [1]

[Total: 18]

Section B

Answer **one** question from this section.

4 Barium hydroxide is a compound that can exist in the anhydrous or hydrated forms. Its main uses are as a precursor for the manufacture of other barium compounds and as a substance to remove sulfates from various products.

(a) **(i)** Draw the dot–and–cross diagram for sulfate(VI) ion. In your diagram, use the symbol 'x' and '•' to distinguish between the electrons from sulfur and oxygen, and the symbol 'Δ' for any additional electrons responsible for the overall negative charge. [1]

(ii) Using the *Valence Shell Electron Pair Repulsion* theory, explain the shape of sulfate(VI) ion. [2]

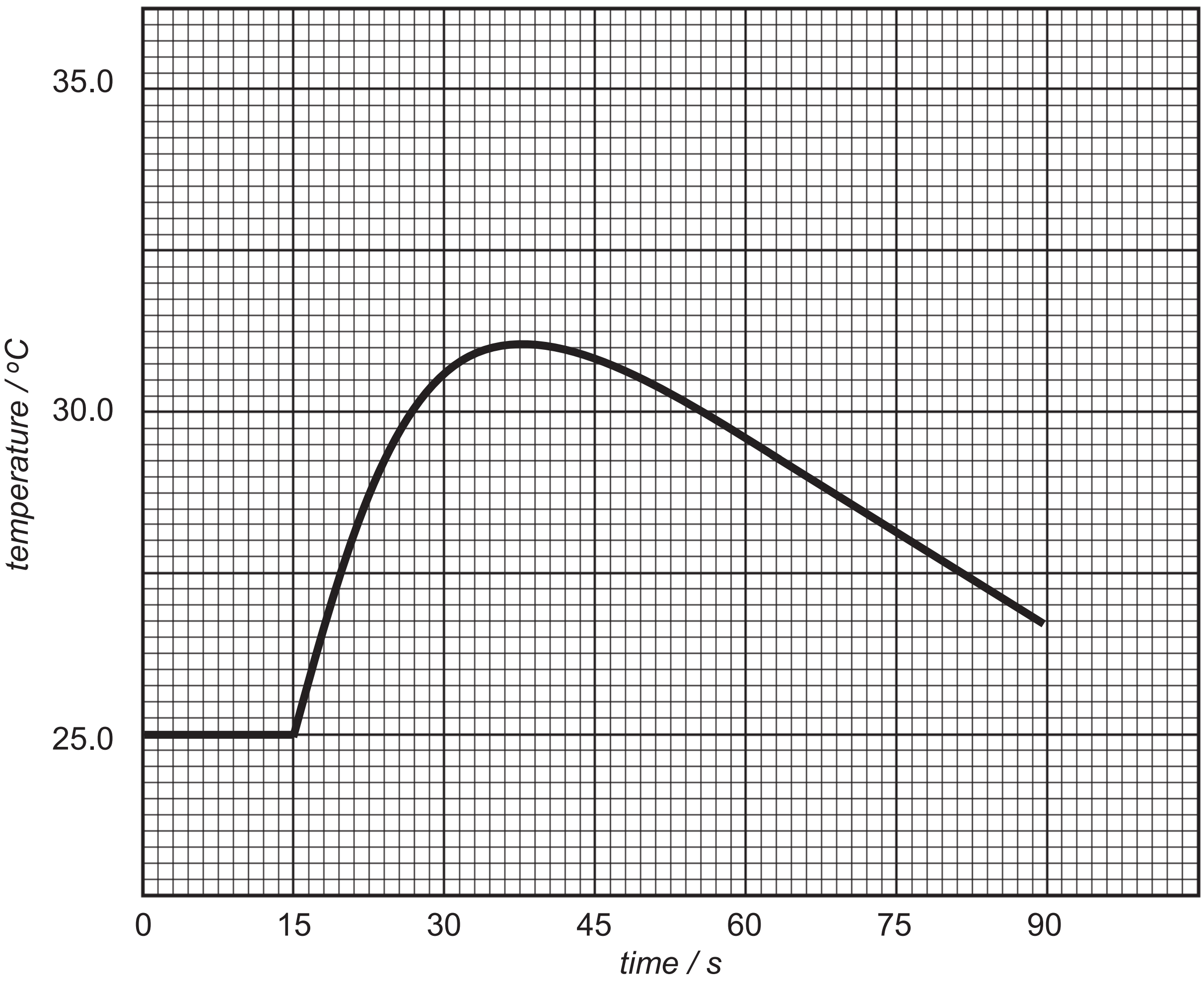
(b) Barium ion most commonly exists in the octahydrate form while magnesium ion usually exists in the hexahydrate form. When a 3.00 g solid sample of $Ba(OH)_2.8H_2O$ is strongly heated, the experimental loss in mass is 1.54 g.

$$Ba(OH)_2.8H_2O\ (s) \rightarrow BaO\ (s) + 9H_2O\ (g)$$

(i) By means of calculations, explain whether the decomposition of the $Ba(OH)_2.8H_2O$ sample is complete. [2]

(ii) Explain whether the thermal decomposition temperature of the anhydrous form of barium hydroxide is higher or lower than that of anhydrous magnesium hydroxide. [2]

(c) A temperature probe is used to measure the temperature of 100 cm^3 of 0.8 mol dm^{-3} barium hydroxide in a polystyrene cup. At 15 seconds, 120 cm^3 of 2.0 mol dm^{-3} hydrochloric acid is added. The temperature readings are recorded using a data logger for 90 seconds. The results are shown below.



(i) Construct appropriate lines on the graph above and determine the temperature rise of the reaction. [1]

(ii) Using your answer in **(c)(i)**, calculate a value for the enthalpy change of neutralisation for the reaction. [2]

(d) Using the following data, calculate a value for the lattice energy of barium hydroxide by means of a *Born–Haber* cycle.

enthalpy change of atomisation of barium = +182 kJ mol^{-1}

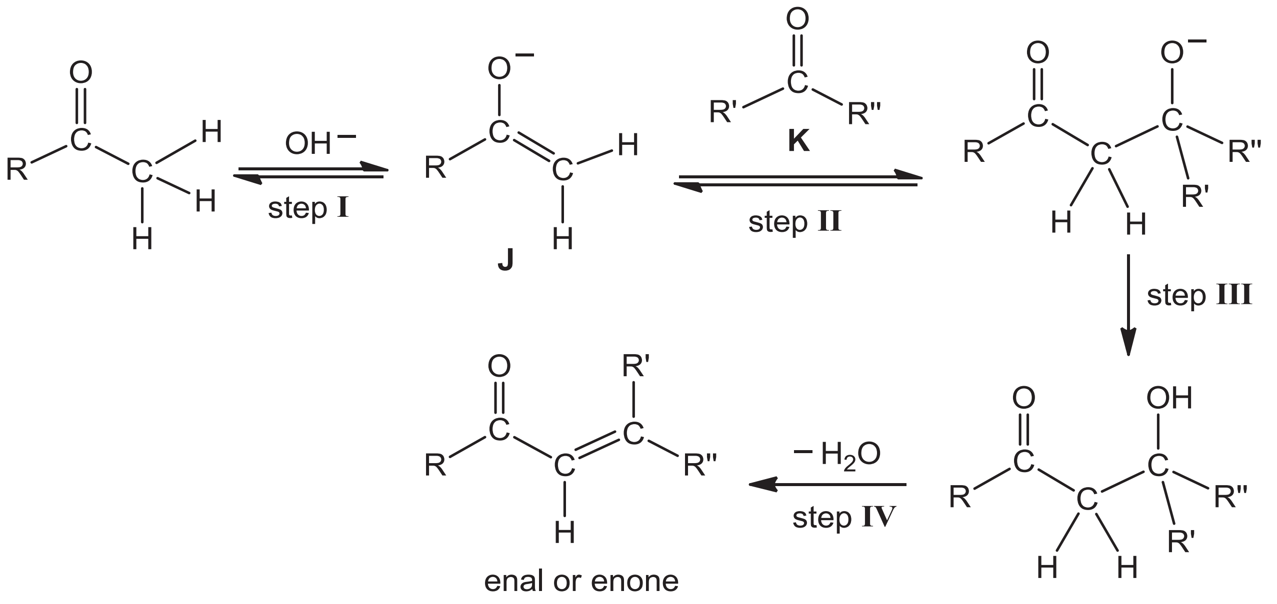
enthalpy change of formation of barium hydroxide = –940 kJ mol^{-1}

$\frac{1}{2}O_2\ (g) + \frac{1}{2}H_2\ (g) + e^- \rightarrow OH^-\ (g)$ = +230 kJ mol^{-1}

[3]

(e) Barium hydroxide may be used as a strong base for the first step of the *aldol condensation* reaction to produce an ‘enal’ or an ‘enone’. An ‘enal’ is a molecule with an alkene group adjacent to an aldehyde group. An ‘enone’ is a molecule with an alkene group adjacent to a ketone group.

The following flowchart shows the *aldol condensation* reaction.

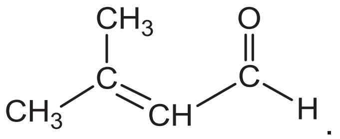


(R, R’ and R’’ = alkyl group or H atom)

(i) State the roles of species **J** and **K** in step **II**. [1]

(ii) State the type of reactions for steps **III** and **IV**. [1]

(iii) Suggest the structures of the two reactants required to synthesise the ‘enal’,



$(CH_3)_2C{=}CHCHO$. [2]

(iv) In certain organic chemistry reactions, concentrated sulfuric acid and concentrated phosphoric acid may be used interchangeably.

Using the above information, propose a two–step synthesis route to convert the enal $(CH_3)_2C=CHCHO$, as the only available organic reactant, to compound **Q**.

Q

State the reagents and conditions required as well as the structures of the intermediates formed. [3]

[Total: 20]

5 Hydrogen cyanide, HCN, is extremely toxic and with sufficient concentrations it leads to rapid death. During the Second World War, a form of hydrogen cyanide known as *Zyklon B* was used in the Nazi gas chambers.

(a) Draw a dot–and–cross diagram to illustrate the bonding in HCN. [1]

(b) The synthesis of HCN was developed in the early 1900s. The most commonly used procedure is the *Andrussow* process. A less common method is the *BMA* process.

Andrussow process: $CH_4\,(g) + NH_3\,(g) + \frac{3}{2}\,O_2\,(g) \rightarrow HCN\,(g) + 3\,H_2O\,(g)$

BMA process: $CH_4\,(g) + NH_3\,(g) \rightarrow HCN\,(g) + 3\,H_2\,(g)$

(i) Using information from the *Data Booklet*, calculate the enthalpy change of reaction for each of the two processes above. [2]

(ii) Hence, comment on why the *Andrussow* process is the preferred procedure. [1]

(c) Other than gaseous HCN, sodium cyanide and potassium cyanide are used in the powder form in many homicide incidents.

It was predicted that salts like zinc cyanide, $Zn(CN)_2$, are harmless. The solubility data of some of these cyanides are given below.

solubility of NaCN at 25 °C = 1.3 mol dm^{-3}
solubility of KCN at 25 °C = 1.1 mol dm^{-3}
K_{sp} of $Zn(CN)_2$ = 8.0×10^{-12} mol^3 dm^{-9}

Using the above information, explain why it was predicted that $Zn(CN)_2$ is harmless. [2]

(d) When cyanide is transported to the body's tissues, it binds irreversibly to an enzyme called *cytochrome c oxidase* and stops cells from being able to use oxygen for respiration. *Cytochrome c oxidase*, which contains Fe^{2+}, converts oxygen to water during respiration.

The United States standard cyanide antidote kit was developed in the last decade as a first aid tool. It comprises of a three step process.

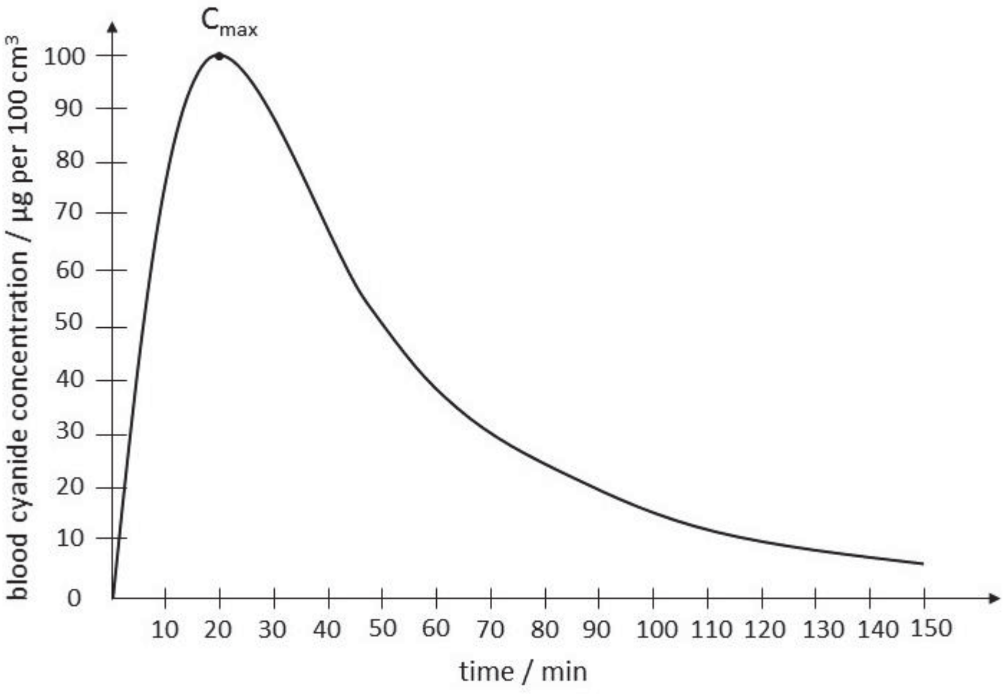
Step 1: Inhalation of a small dosage of amyl nitrite.
Step 2: Intravenous delivery of sodium nitrite, $NaNO_2$.
Step 3: Intravenous delivery of sodium thiosulfate.

(i) The nitrite oxidises some of the Fe^{2+} in haemoglobin in the red blood cells to Fe^{3+}, where Fe^{3+} has a higher affinity for cyanide. Suggest an advantage and a disadvantage of using nitrite as an antidote for cyanide poisoning. [2]

(ii) The sodium thiosulfate converts cyanide into thiocyanate ions, SCN^-, which is relatively harmless to the human body. Suggest, using coordination chemistry, how this conversion serves as an antidote. [1]

The human body has a mechanism which rapidly converts cyanide into the harmless thiocyanate via a first order kinetics when small doses are ingested. The cyanide concentration can be traced and represented by the **Graph 5.1**. **C_{max}** refers to the maximum concentration of cyanide in the body after ingestion. After which, it is eliminated by converting it to thiocyanate.

Graph 5.1



(iii) The safe level of cyanide concentration in blood is 20 μg per 100 cm^3 and below. From 20 to 200 μg per 100 cm^3, it is at a toxic level where the body may develop complications if the level is not brought back to safety after more than 60 minutes. (*Note: 1 μg = 1 x 10^{-6} g.*)

Using the graph and the above information, calculate the maximum cyanide blood concentration a victim can tolerate before complication occurs.

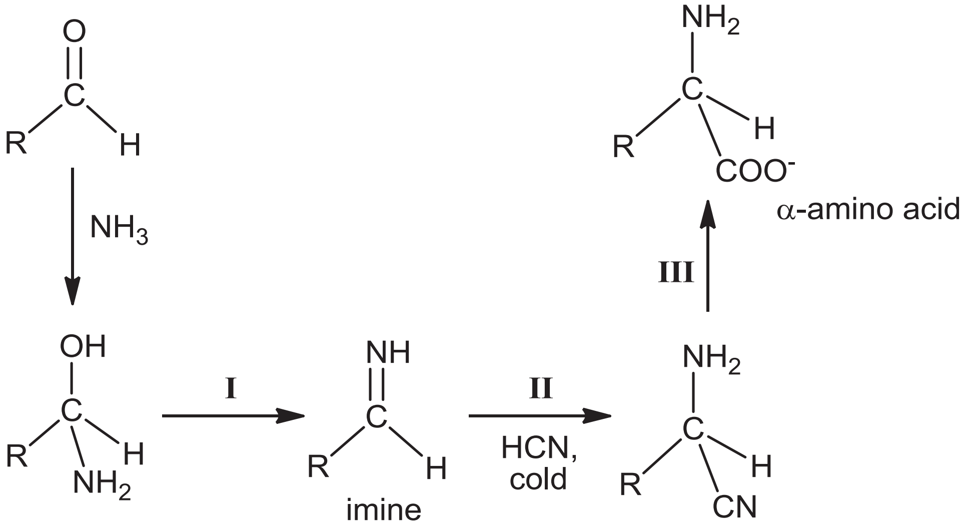
[2]

In the octahedral complex, the d–subshell of the Fe^{3+} ion is split into two energy levels. In a 'high spin' state, the electrons occupy all the d–orbitals singly before pairing up in the lower energy d–orbitals. In a 'low spin' state, the lower energy d–orbitals are filled first, by pairing, before the higher energy d–orbitals are used.

(iv) Explain why splitting of the d–subshell occurs in the octahedral complex. [1]

(v) When cyanide binds with Fe^{3+}, it forms an octahedral complex which is at a 'low spin' state. Draw the electronic distribution of Fe^{3+} ion in its d–orbitals, showing the two energy levels. [1]

(e) Despite its lethal effect, hydrogen cyanide is often used in organic synthesis as a precursor to many important products like amino acids. It was first used by German chemist Adolph Strecker in 1850 to produce α–amino acids.



(i) Name the type of reaction in step **I**. [1]

(ii) Suggest the reagent and condition for step **III**. [1]

(iii) Suggest why a low temperature condition is used in step **II**. [1]

(iv) Step **II** proceeds via 2 stages:

1. acid–base reaction between N in the imine and HCN
2. followed by a nucleophilic attack on C by CN^-

Outline a mechanism for step **II**, showing all charges and using curly arrows to represent the movement of electron pairs. [2]

(v) Suggest why the amino acid synthesised by *Strecker's* method shows no optical activity while that of a naturally occurring amino acid rotates plane polarised light. [2]

[Total: 20]

End of Paper 3

2017 MJC H2 Chemistry Prelim Paper 4

1 Magnesium carbonate is a white solid that is readily found in nature. In this experiment, you will determine the percentage purity of a sample impure magnesium carbonate.

FA 1 is a sample of impure magnesium carbonate. You may assume that only the magnesium carbonate present in the sample will react with the acid. You will first dissolve **FA 1** in excess hydrochloric acid.

$$MgCO_3(s) + 2HCl(aq) \rightarrow MgCl_2(aq) + H_2O(l) + CO_2(g)$$

The resulting solution will then be titrated using sodium hydroxide. You may assume that no compounds present in **FA 1** will react with the sodium hydroxide.

$$NaOH(aq) + HCl(aq) \rightarrow NaCl(aq) + H_2O(l)$$

FA 1 is impure magnesium carbonate.
FA 2 is 2.0 mol dm^{-3} hydrochloric acid, HCl.
FA 4 is 0.20 mol dm^{-3} sodium hydroxide, NaOH.
methyl orange indicator

(a) Procedure

Preparation of standard solution

1. Fill a burette with **FA 2**.
2. Run between 47.50 and 48.50 cm^3 of **FA 2** into a 250 cm^3 beaker.
3. Record your burette readings and the volume of **FA 2** in the space below.

4. Weigh accurately about 2.0 g of **FA 1** in a weighing bottle.
5. Transfer the **FA 1** from the weighing bottle as fully as you can into the beaker containing **FA 2**.
6. Reweigh the weighing bottle and record all masses in the space below.

7. Stir the mixture carefully until all the solid has reacted.
8. Transfer the contents of the beaker into the volumetric flask.
9. Rinse the beaker with distilled water and add it to the volumetric flask. Make the solution up to 250 cm^3 with distilled water and mix thoroughly. Label this solution as **FA 3**.

Titration

1. Fill another burette with **FA 3** from the volumetric flask.
2. Pipette 25.0 cm^3 of **FA 4** into a conical flask.
3. Add a few drops of methyl orange indicator.
4. Titrate **FA 4** with **FA 3** until the end-point is reached.
5. Repeat the titration as many times as you think necessary to obtain consistent results.
6. Record your titration results in the space provided below.

[7]

M1	M2	M3	M4	M5	M6	M7

(b) From your titration results, obtain a suitable volume of **FA 3** to be used in your calculations. Show clearly how you obtained this volume.

volume of **FA 3** = ……………………………… [1]

(c) Calculations

(i) Calculate the amount of hydrochloric acid present in the volume of **FA 3** obtained in **(b)**.

amount of HC*l* = ……………..………………[1]

(ii) Calculate the amount of hydrochloric acid present in 250 cm^3 of **FA 3**.

amount of HC*l* in 250 cm^3 **FA 3** = ……………..………………[1]

(iii) Calculate the amount of hydrochloric acid in **FA 2** that has reacted with magnesium carbonate in **FA 1**.

amount of HC*l* reacted with $MgCO_3$ = ……………………………[1]

(iv) Calculate the percentage purity of magnesium carbonate present in **FA 1**.
[A_r: C, 12.0; O, 16.0; Mg, 24.3]

percentage purity of **FA1** = …………………….. [1]

(d) **(i)** The maximum error in a single burette reading is ±0.05 cm^3.

Student X, carrying out this experiment, recorded that 48.50 cm^3 of **FA 2** was added to **FA 1**.

What are the smallest and largest possible volumes of **FA 2** that were added?

smallest volume used = ……………………………………

largest volume used = ……………………………………

[1]

(ii) Student Y used an identical mass of **FA 1** but added 47.70 cm^3 of **FA 2** instead. How would the percentage purity of **FA 1** calculated by student Y compare to that obtained by student X? Explain your answer.

………………………………………………………………………………………

………………………………………………………………………………………

………………………………………………………………………………………

[1]
[Total: 14]

2 Determination of the enthalpy change of neutralisation, *ΔH_n*

The enthalpy change of neutralisation, ΔH_n, is the enthalpy change when one mole of water is formed during a neutralisation reaction as shown in the equation.

$$H^+(aq) + OH^-(aq) \rightarrow H_2O\,(l)$$

FA 5 is a solution of sulfuric acid, H_2SO_4
FA 6 is 1.50 mol dm^{-3} potassium hydroxide, KOH

You will perform a series of experiments using different volumes of **FA 5** and **FA 6**. The change in temperature, ΔT, for each experiment will be determined and used to plot a graph of ΔT against volume of **FA 5** used.

You will then use data from the graph to determine a value for the enthalpy change of neutralisation, ΔH_n.

(a) Determining the change in temperature for a series of reactions between FA 5 and FA 6

(i) Procedure

1. Support the Styrofoam cup in a 250 cm^3 beaker.
2. Add 10.0 cm^3 of **FA 5** from a measuring cylinder into the Styrofoam cup.
3. Measure the temperature of **FA 5** in the Styrofoam cup. Record the initial temperature of the solution of **FA 5** as $\mathbf{T_{FA5}}$.
4. Wash and dry the thermometer.
5. Measure 40.0 cm^3 of **FA 6** into another measuring cylinder.
6. Measure the temperature of **FA 6** solution using the thermometer and record the initial temperature of the solution of **FA 6** as $\mathbf{T_{FA6}}$.
7. Tip the **FA 6** in the measuring cylinder into the Styrofoam cup, stir and record the maximum temperature obtained in the reaction as $\mathbf{T_{max}}$.
8. Rinse and dry the Styrofoam cup and the thermometer.
9. Repeat steps 2 to 8 using 20.0 cm^3 and 30.0 cm^3 of **FA 5** and appropriate volumes of **FA 6** each time such that the total volume of the reacting mixture is 50 cm^3.

In an appropriate format in the space provided, record:

- all measurements of volumes used,
- all temperatures measured and the change in temperature, Δ**T**.

$$\Delta T = T_{max} - T_{weighted\ initial}$$

$$T_{weighted\ initial} = \frac{(\text{Volume of FA 5} \times T_{\text{FA 5}}) + (\text{Volume of FA 6} \times T_{\text{FA 6}})}{\text{Volume of FA 5} + \text{Volume of FA 6}}$$

These data should be recorded for the experiments described in **(a)(i)**, together with additional experiments described in **(a)(ii)**.

Results

[5]

M1	M2	M3	M4	M5

(a)(ii) On the grid provided, plot a graph of Δ**T** (y–axis) against volume of **FA 5** (x–axis) using the data you obtained in **(a)(i)**.

Consider your plotted plots. Carry out four more experiments which will enable you to identify the volume of **FA 5** which gives the maximum change in temperature, $\Delta \mathbf{T}_{max}$. In each case, the total volume of the reaction mixture must be 50 cm^3.

You may find it useful to consider the results obtained from each experiment before choosing the volumes of solutions for the next experiment.

(iii) Draw a line of best fit through the points where the temperature rise is increasing and another best fit line through the points where the temperature rise is decreasing. Extrapolate these two lines until they cross.

[3]

M1	M2	M3

(iv) Determine from your graph, the maximum change in temperature, $\Delta \mathbf{T}_{max}$, and the volume**,** $\mathbf{V}_{max}$, of **FA 5** required to obtain this value.

$\Delta \mathbf{T}_{max}$ = …………………………

$\mathbf{V}_{max}$ = ………………………… [2]

(b) Using your answers in **(a)(iv)**, calculate

(i) the concentration, in mol dm^{-3}, of H_2SO_4 in **FA 5**.

concentration of H_2SO_4 in **FA 5** = ……….……………………… [1]

(ii) the heat change for the neutralisation reaction at $\Delta \mathbf{T}_{max}$.

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 **(b)(i)** and **(b)(ii)**, calculate a value for the enthalpy change of neutralisation, ΔH_n.

ΔH_n =…………………………..[3]

M1	M2	M3

(d) When the experiment is done in the way described, the results are not very accurate.

Apart from limitations due to the accuracy of the measuring equipment, suggest why the temperature rises are more inaccurate as they approach their maximum value.

....

....

....
[1]

(e) In another experiment, 1.50 mol dm^{-3} aqueous ammonia is used instead of the 1.50 mol dm^{-3} aqueous potassium hydroxide.

Draw on your graph another pair of lines to show the results you would expect to obtain. Explain your answer.

....

....

....

....

....

....

…..
[2]

(f) Planning

Barium carbonate, $BaCO_3$, is widely used in the ceramics industry as an ingredient in glazes. $BaCO_3$ can be formed from the reaction between barium oxide and carbon dioxide as shown in *Reaction 1*.

Reaction 1 : $BaO (s) + CO_2 (g) \rightarrow BaCO_3 (s)$ ΔH_1

Experimentally, it is difficult to measure the enthalpy change of reaction, ΔH_1 directly. Instead, Hess's Law can be used to calculate ΔH_1 using experimentally determined values of ΔH_2 and ΔH_3 for the following reactions as shown below.

Reaction 2 : $BaO (s) + 2HNO_3 (aq) \rightarrow Ba(NO_3)_2(aq) + H_2O(l)$ ΔH_2

Reaction 3 : $BaCO_3 (s) + 2HNO_3 (aq) \rightarrow Ba(NO_3)_2(aq) + H_2O(l) + CO_2 (g)$ ΔH_3

(i) Construct an energy cycle using the information in the question to show how the enthalpy change of reaction, ΔH_1, can be calculated from ΔH_2 and ΔH_3.

[1]

(ii) You are to plan an experiment that will allow you to determine the enthalpy change of *Reaction 2*, ΔH_2. Your plan must enable you to plot a graph that includes data from the experiment. You may assume that all solutions have a density of 1 g cm^{-3} and the specific heat capacity of water is 4.18 J g^{-1} K^{-1}.

You may also assume that the following are provided:

- 3 g solid barium oxide
- 120 cm^3 of 0.500 mol dm^{-3} aqueous nitric acid, HNO_3
- Styrofoam cup
- stop-watch
- thermometer
- apparatus and materials normally found in a school laboratory.

YOU ARE NOT REQUIRED TO PERFORM THIS EXPERIMENT.

In your plan, you should include details of:

- calculations of suitable quantities of reagents used;
- an outline of all essential experimental procedures;
- a sketch of the graph you expect to obtain and
- an outline of the calculations you would perform to find ΔH_2 in kJ mol^{-1}.

[6]
[Total: 25]

…………………………………………………………………………………………………

…………………………………………………………………………………………………

…………………………………………………………………………………………………

…………………………………………………………………………………………………

…………………………………………………………………………………………………

…………………………………………………………………………………………………

…………………………………………………………………………………………………

…………………………………………………………………………………………………

…………………………………………………………………………………………………

…………………………………………………………………………………………………

…………………………………………………………………………………………………

…………………………………………………………………………………………………

3 Inorganic and Organic Analysis

(a) You are provided with **FA 7** and **FA 8**.

In all tests, the reagents should be added gradually until no further change is observed, with shaking after each addition.

At each stage of any test you are to record details of the following.

- colour changes seen
- the formation of any precipitate
- the solubility of such precipitates in an excess of the reagent added

Where gases are released they should be identified by a test, described in the appropriate place in your observations.

Record your observations in the spaces provided. You should indicate clearly at which stage in a test a change occurs.

1. **FA 7** is a sodium compound containing one anion listed on page 20. Dissolve the **FA 7** provided in about 15 cm^3 of distilled water in a boiling tube.

   Carry out the following tests and record your observations in the table below.

Test	Observations
(i) To a 1 cm depth of the solution of **FA 7** in a test-tube, add a few drops of aqueous barium nitrate followed by dilute nitric acid.	
(ii) To a 1 cm depth of the solution of **FA 7** in a test-tube, add an equal volume of aqueous hydrogen peroxide, then	
add a few drops of aqueous barium nitrate, followed by dilute nitric acid.	
(iii) To a 2 cm depth of the solution of **FA 7** in a test tube, add an equal volume of sulfuric acid, then heat the mixture gently and cautiously.	

Test	Observations
(iv) To a 1 cm depth of the solution of **FA 7** in a test-tube, add an equal volume of aqueous sodium hydroxide, then	
add a few drops of aqueous potassium manganate(VII),	
followed by sulfuric acid.	

(v) Identify the anion in **FA 7**, and state the evidences for your identification.

anion ....

evidence ....

....

....

....

....

....

[6]

2. **FA 8** solution contains two cations from those listed in the Qualitative Analysis Notes on page 19. Carry out tests using reagents that will allow you to identify which ions are present.

(i) In the space below, draw a single table to record details of the tests performed and observations made.

[4]

(ii) Identify the cations in **FA 8**, and state the evidences for your identification.

cation ....

evidence ....

....

....

cation ....

evidence ....

....

....

[2]

(b) You are provided with an organic solution **FA 9** which contains one functional group.

FA 9 gives a positive test with 2,4-dinitrophenylhydrazine. Devise two other confirmatory tests using the **bench reagents provided** to identify the functional group present in **FA 9**.

(i) In the space below, draw a single table to record details of the tests performed and observations made.

(ii) Identify the functional group in **FA 9**, and state the evidences for your identification.

Functional group in **FA 9** ....

evidence ....

....

....

....

[4]
[Total : 16]

Answers for 2017 H2 Chemistry P1

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

2017 MJC H2 Chemistry Prelim Suggested Answers

1(a) (i) An acid is a substance that can donate a proton (H^+) to another substance/proton donor.

A base is a substance that can accept a proton (H^+) from another substance/proton acceptor.

(ii) *Arrhenius theory* of acids and bases applies to aqueous system only.
or
Arrhenius theory of acids and bases does not apply to acids/bases that do not dissociate H^+/OH^- from itself.

(b) (i)

$$\frac{[H^+]_{water}}{[H^+]_{methanol}} = \frac{\sqrt{10^{-2.45}}}{\sqrt{10^{-7.50}}} = 331$$

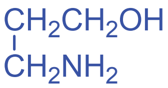
(ii) Water is a more polar solvent than methanol. (hence the both H^+ and conjugates bases can better stabilized through the formation of stronger ion-dipole interations).

(iii) $CH_2(CN)COOH$, can form more extensive hydrogen bonding with water due to its additional –CN group .

(c) (i) In dimethylamine, there are more electron–donating $–CH_3$ groups that increases the electron density of the lone pair on N atom which increases the availability of the lone pair on N to accept H^+.

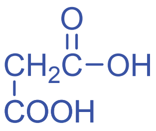
(ii) Trimethylamine have 3 bulky methyl groups that causes steric hindrance. Hence it reduces the availability of lone pair of electron on N atom to accept H^+.

(d) (i)



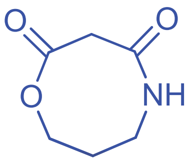
$$\begin{array}{l} CH_2CH_2OH \\ | \\ CH_2NH_2 \end{array}$$

A



$$\begin{array}{l} \quad\;\; O \\ \quad\;\; \| \\ CH_2C-OH \\ | \\ COOH \end{array}$$

B



D

(ii) Step **I**: acidic hydrolysis
Step **II**: Nucleophilic acyl substitution

(iii) Step **I**: dilute sulfuric acid, heat
Step **III**: dilute sulfuric acid, heat followed by $LiAlH_4$, dry ether, rtp

2(a) Zn obtained from daily feed = 0.7 × 180 × 3 / 100 = 3.78 mg

(It meets the recommended quantity for daily intake)

(b) **(i)** **I**: oxidation
II: acid–metal displacement

(ii) Cation in **A**: $[Fe(H_2O)_6]^{3+}$
Gas **B** is H_2.
$[Fe(H_2O)_6]^{3+}$ has very high charge density , it polarises the electron cloud of the surrounding water molecules, weakens and breaks the O–H bond, which results in the release of a proton.

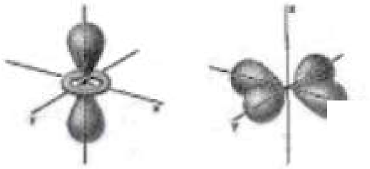
(iii) Ligand exchange
$[Fe(H_2O)_6]^{2+} + 6CN^- \rightarrow [Fe(CN)_6]^{4-} + 6H_2O$

(iv) ***1.*** Fe^{2+} has partially–filled d–orbitals.
In $[Fe(H_2O)_6]^{2+}$, the d orbitals are split into two groups due to the ability of the ligands to split them.
A lower energy d electron undergoes d–d transition and is promoted to a higher energy d orbital. During the transition, the d electron absorbs the red wavelength of light from the visible region of the electromagnetic spectrum and the remaining wavelengths not absorbed appear as the green colour.

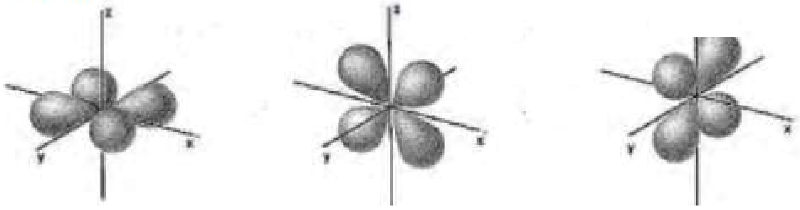
2. $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5$

3. $[FeF_5(H_2O)]^{2-}(aq)$ is colourless because the energy absorbed for d–d transition is out of the range of the visible spectrum.

(v) **correct upper** orbital diagram



correct lower orbital diagram



Any one from each category

(c) **(i)** Fe has more protons and hence has greater nuclear charge than Ca. But there is only slight increase in screening effect as electrons are added to the inner 3d orbitals that provide shielding effect for the 4s electrons from Ca to Fe.

Hence, Fe has greater effective nuclear charge and has increased electrostatic attraction between the nucleus and the valence 4s electrons compared to Ca. Therefore, atomic radius of iron is less than calcium.

(ii) The relative atomic mass of Fe is larger than that of Ca and the atomic radius of Fe (0.126) is smaller than that of Ca (0.197 nm) thus the densities of Fe and Cu is greater than that of Ca.

(d) **(i)** $MgCl_2$ solution: pH = 6.5 PCl_5 solution: pH = 2.0

$MgCl_2\ (s) + 6H_2O\ (l) \longrightarrow [Mg(H_2O)_6]^{2+}\ (aq) + 2Cl^-\ (aq)$

$[Mg(H_2O)_6]^{2+}\ (aq) \rightleftharpoons [Mg(H_2O)_5(OH)]^+\ (aq) + H^+\ (aq)$

$PCl_5\ (s) + 4H_2O\ (l) \rightarrow H_3PO_4\ (aq) + 5HCl\ (aq)$

(ii) Element **Z** belongs to Group 13. => **Z** is A*l*.
Element **F** could be element **Z**.

3(a) **Y** is the plot for NOC*l*. This is because of its permanent dipole–permanent dipole interaction between its molecules which is most significant, hence it deviates most from ideal gas .

(b) (i) $$n = \frac{5.80\times10^{6}\times5.0\times10^{-3}}{8.31\times(250+273)} = 6.67$$

(ii) $$K_p = \frac{(P_{NO})^2(P_{Cl_2})}{(P_{NOCl})^2}\ \textbf{Pa}$$

(iii) Let x be the change in number of moles of gas.
Total number of moles of gases at equilibrium = $5 - 2x + 2x + x$
$x = 1.673$
At equilibrium,
No. of moles of NOC*l* = 1.65
No. of moles of NO = 3.35
No. of moles of Cl_2 = 1.67

$K_p = 5.95 \times 10^6$ Pa

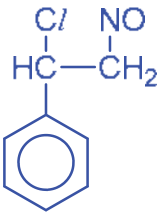
(c) **(i)** $K_c = 1.40$

(ii) When T increases, K_c decreases .

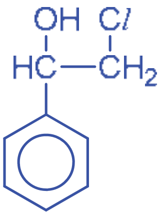
(iii) Since K_c decreases, the amount of reactants will increases and products will decrease .

By *Le Chatelier's* Principle, when temperature is raised and equilibrium position shifts left , the backward reaction is endothermic so as to absorb heat . Therefore the forward reaction is exothermic .

(d) **(i)**

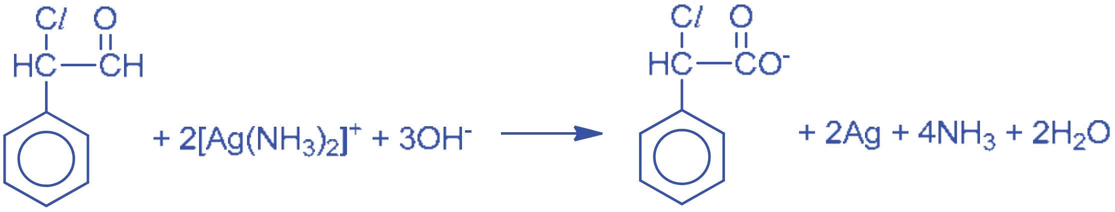


P



Q

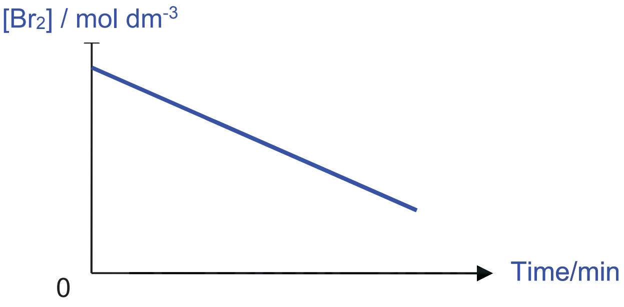
(ii) Tollens' reagent



Accept alternative reagents

4(a) **(i)** Order of reaction w.r.t to CH_3COCH_3 is 1 .
Order of reaction w.r.t to H^+ is 1

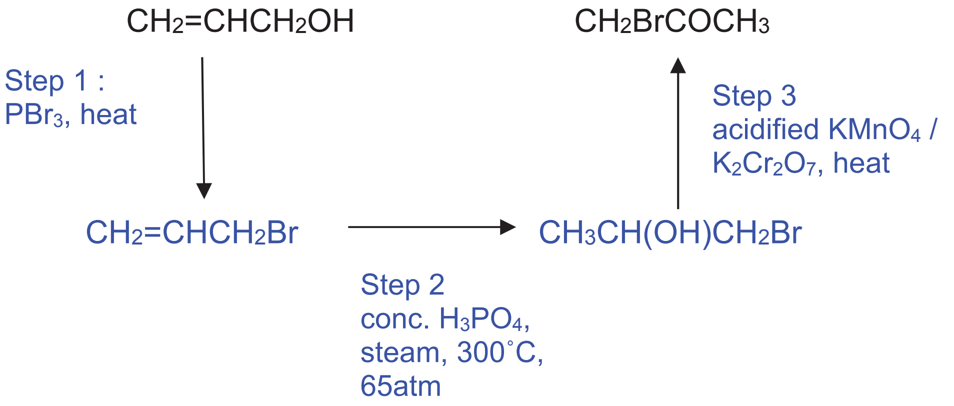
(ii)



(iii) Rate = $k[CH_3COCH_3][H^+]$

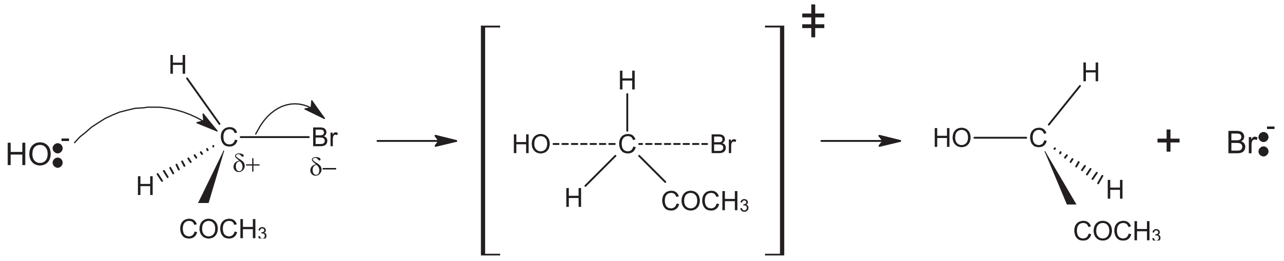
(iv) $k = 3.80 \times 10^{-3}$ $mol^{-1}\ dm^3\ min^{-1}$

(b) **(i)**



(ii) Add aqueous Br_2, r.t.p to the sample.
If the orange Br_2 decolourises, $CH_2{=}CHCH_2OH$ is present, reaction is not complete .

(c) **(i)** Nucleophilic substitution S_N2



(ii) CH_3CH_2COBr has a faster rate of hydrolysis.

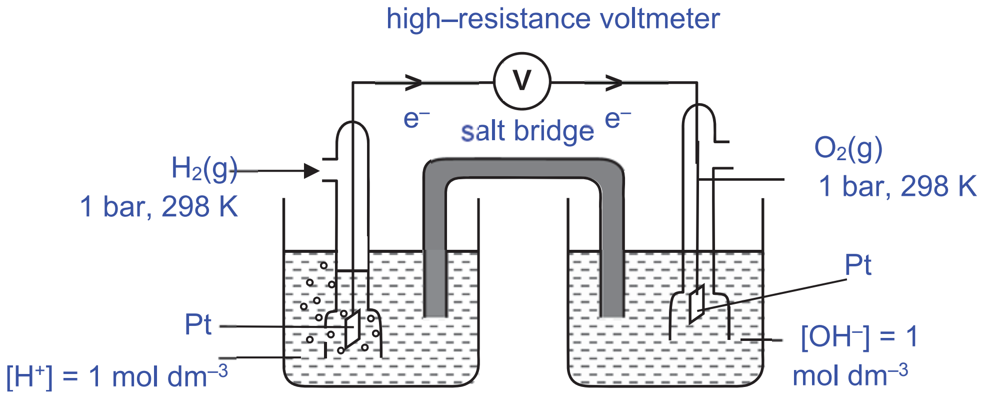
The carbonyl C atom in CH_3CH_2COBr is bonded to two electronegative atoms O and Br which makes the carbonyl C atom highly electron–deficient and is very susceptible to nucleophilic substitution.

5(a) **(i)** Anode: $H_2 + CO_3^{2-} \longrightarrow H_2O + CO_2 + 2e$

Cathode: $\frac{1}{2} O_2 + CO_2 + 2e \longrightarrow CO_3^{2-}$

$H_2 + \frac{1}{2} O_2 \longrightarrow H_2O$

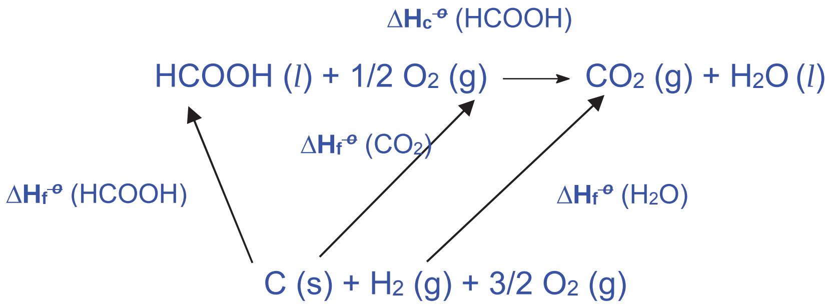
(ii)



(b) more negative

(c) **(i)** $H_f^\ominus$ of formic acid is the energy change when one mole of the formic acid is formed from its elements at standard conditions of 298K and 1 bar.

(ii)



$\Delta H_f^\ominus$ (HCOOH) = –469 kJ mol^{-1}

(iii) $\Delta H_{rxn}^\ominus$ = (–150) + (–286) – (–246) = –190 kJ mol^{-1}

2017 MJC H2 Chemistry Prelim P3 Suggested Answers

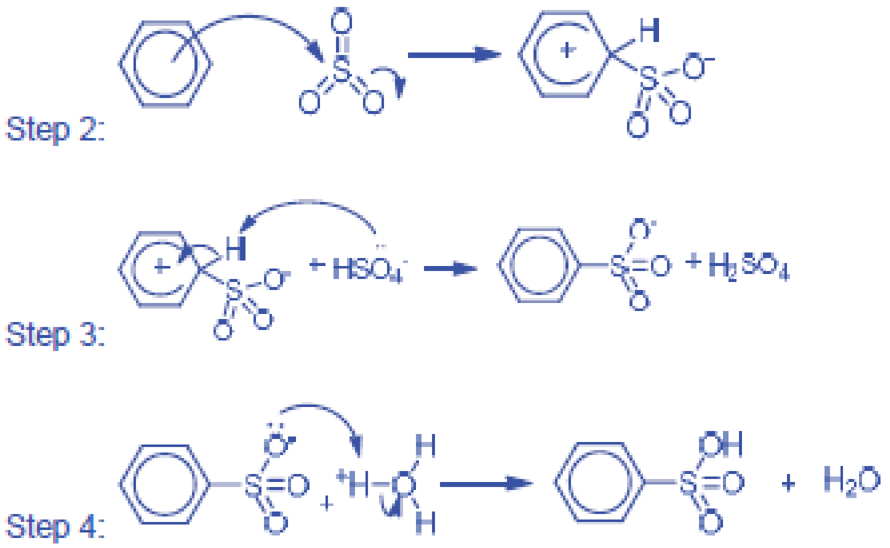
MERIDIAN JUNIOR COLLEGE
JC 2 Preliminary Examination
H2 Chemistry Paper 3

1(a) **(i)** Comparing experiments 1 and 2,
When [H_2SO_4] is doubled and [C_6H_6] is kept constant
Rate of reaction increased 4 times
Order of reaction with respect to H_2SO_4 is 2

Comparing experiments 2 and 3,
When [C_6H_6] is increased 1.5 times and [H_2SO_4] is kept constant
Rate of reaction increased 1.5 times
Order of reaction with respect to C_6H_6 is 1

(ii) Rate = k [C_6H_6] [H_2SO_4]^2

(b) **(i)**

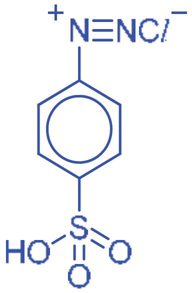


(ii) Step 2

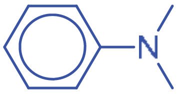
(c) **(i)** Test: Br_2 (aq), r.t.p.

- Phenylamine: Decolourisation of orange bromine solution with the formation of a white precipitate.
- Diazonium salt: No decolourisation of orange bromine solution.

(ii)



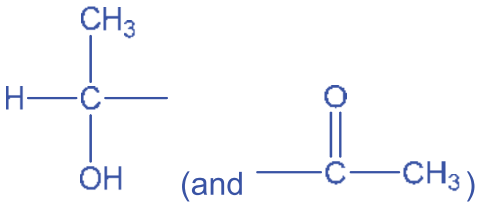
diazonium salt



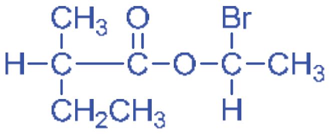
phenylamine derivative

Electrophile is the diazonium salt

(d)

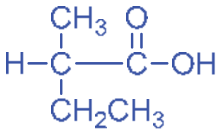
Reaction	Deduction
Q and R can rotate plane–polarized light.	Q and R contains chiral carbon and has no plane of symmetry.
0.1 mol of compound Q produces 0.5 mol of carbon dioxide gas and 0.5 mol of water.	Q contains 5 C atoms and 10 H atoms.
2 mol of Q undergoes acid–base reaction reaction with 1 mol of Na_2CO_3	Q contains 1 carboxylic acid functional group.
R undergoes oxidation when heated in an alkaline solution of iodine to give a yellow precipitate.	Yellow precipitate is CHI_3. R contains structure 
R undergoes nucleophilic substitution when heated with sodium hydroxide, followed by the addition of dilute and aqueous silver nitrate, a cream precipitate was formed.	R contains a bromoalkane / halogenoalkane functional group. Cream precipitate is AgBr.
Q and R undergo nucleophilic acyl substitution to form P.	P contains an ester functional group

Structure of **P**:



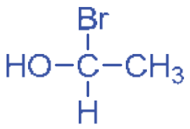
$$H-\underset{CH_2CH_3}{\overset{CH_3}{C}}-\overset{O}{\overset{\|}{C}}-O-\underset{H}{\overset{Br}{C}}-CH_3$$

Structure of **Q**:



$$H-\underset{CH_2CH_3}{\overset{CH_3}{C}}-\overset{O}{\overset{\|}{C}}-OH$$

Structure of **R**:



$$HO-\underset{H}{\overset{Br}{C}}-CH_3$$

2(a) **(i)** Iron electrode: $Mg^{2+}(l) + 2e \rightarrow Mg\ (l)$
Graphite electrode: $2Cl^{-}\ (l) \rightarrow Cl_2\ (g) + 2e$

(ii) To prevent Mg from reaction with oxygen in the air.

(iii) Iron electrode is the cathode in which Mg is formed from molten Mg^{2+}.

As $E^{\ominus}_{Zn2+/Zn}$ is more positive than $E^{\ominus}_{Mg2+/Mg}$, Zn^{2+} is preferentially discharged to form Zn. Thus, the addition of $ZnCl_2$ will interfere with the production of Mg at the cathode.

As $E^{\ominus}_{Ca2+/Ca}$ is less positive than that of Mg^{2+}, Ca^{2+} will not be preferentially discharged to form Mg (or Mg^{2+} will be preferentially discharged instead) . Thus, the addition of $CaCl_2$ will not interfere with the production of Mg at the cathode.

(iv) An iron electrode is not a suitable replacement.

Fe undergoes oxidation to form Fe^{2+}/ Fe^{3+} instead of Cl^{-} oxidising to Cl_2 since $E^{\ominus}_{Fe2+/Fe}$ (-0.44) or $E^{\ominus}_{Fe3+/Fe}$ (-0.04) is less positive than $E^{\ominus}_{Cl2/Cl-}$ (+1.36).

Fe^{2+}/ Fe^{3+} formed could be reduced instead of Mg^{2+} at cathode electrode.

(v) $$1.12 \times 10^{-1} = \frac{1.5 \times 6 \times 60 \times 60}{n_e \times 96500}$$

$n_e = 3$

Therefore, the charge = +3

(b) **(i)** $n_{HCl} = 0.10 \times \frac{20}{1000} = 2 \text{ x } 10^{-3} \text{ mol}$

$n_{Mg(HCO3)2} = \frac{2 \text{ x } 10^{-3}}{2} = 1 \text{ x } 10^{-3} \text{ mol}$

$V_{Mg(HCO3)2} = \frac{1 \times 10^{-3}}{0.10} = 10 \text{ cm}^3$

(ii) $K_b = \frac{[OH^-]^2}{[HCO_3^-]}$

$2.4 \text{ x } 10^{-8} = \frac{[OH^-]^2}{0.10 \times 2}$

$[OH^-] = 6.93 \text{ x } 10^{-5} \text{ mol dm}^{-3}$

pH = 14 – 4.31

pH = 9.84

(iii) $H_2CO_3 \rightleftharpoons HCO_3^- + H^+$ OR $CO_2 + H_2O \rightleftharpoons HCO_3^- + H^+$

H_2CO_3 dissociates (partially) in water or undergoes hydrolysis to produce H^+ and HCO_3^-.

(iv) Bromocresol green.
The pH transition range of the indicator (around 4 – 6) lies within the sharp pH change (around 3 – 6 from graph) over the equivalence point.

(v) 10 cm^3
pOH = pK_b = - lg (2.4 x 10^{-8})
pOH = 7.62
pH = 6.38

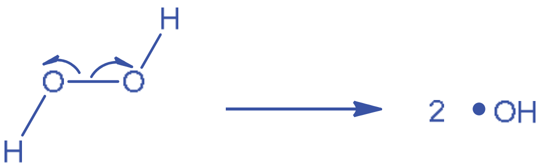
(vi) CO_3^{2-} has higher charge than HCO_3^- hence greater tendency to attract H^+.

(c) Volume V = 20 cm^3

From 0 to V cm^3, the conductance decreases due to the decreasing amount of (OH^-) ions in the solution as H^+ ions react with OH^- ions to form (undissociated) water.

At V cm^3, the conductance is the lowest as all the OH^- ions present have reacted with the added H^+ ions. After V cm^3, as more H^+ ions are present due to the addition of hydrochloric acid, the conductance increases.

3(a) **(i)**



(ii) $E^{\ominus}_{cell} = +1.77 - (+0.68) = +1.09$ V

(iii) $\Delta G^{\ominus} = -(2)(96500)(1.09) = -210$ kJ mol^{-1}

Since $\Delta G < 0$, decomposition is spontaneous.

(iv) Fe^{2+} acts as a homogenous catalyst because of the ability to exist in various oxidation states, thus facilitating the formation of reaction intermediates via alternative pathways of lower E_a.

$H_2O_2 + 2H^+ + 2Fe^{2+} \rightarrow 2Fe^{3+} + 2H_2O$ --- (1)
$E^{\ominus}_{cell} = +1.77 - (+0.77) = +1.00 \text{ V} > 0$

$Fe^{3+} + H_2O_2 \rightarrow Fe^{3+} + O_2 + 2H^+$ --- (2)
$E^{\ominus}_{cell} = +0.77 - (+0.68) = +0.09 \text{ V} > 0$

Overall: $2H_2O_2 \rightarrow 2H_2O + O_2$

- Both steps are spontaneous since their $E^{\ominus} > 0$
- Activation energy is lower and thus reaction is faster.

(b) **(i)** ΔS is negative as there is a decrease in disorder due to decrease in the number of moles of gas molecules from 1 to 0.

(ii) Ag_2O

Since $\Delta G_f > 0$ for formation of Ag_2O, $\Delta G < 0$ for the decomposition of Ag_2O.
$2Ag_2O \rightarrow 4Ag + O_2$
Hence, the decomposition of Ag_2O is spontaneous at 1000 K

(iii) At 2250 K,
(1) $C + O_2 \rightarrow 2CO$ $\Delta G_f = -600$ kJ mol^{-1}
(2) $Zn + O_2 \rightarrow 2ZnO$ $\Delta G_f = -150$ kJ mol^{-1}
(3) $ZnO \rightarrow 2Zn + O_2$ $-\Delta G_f = +150$ kJ mol^{-1}

(1) + (3) : $2ZnO + 2C \rightarrow 2Zn + 2CO$
$\Delta G = -600 + 150 = -450$ kJ mol^{-1}
Since $\Delta G < 0$, the reaction is therefore thermodynamically feasible at 2250 K.

(c) **(i)** $Zn\,(s) + 4OH^-\,(aq) \rightarrow Zn(OH)_4^{2-}\,(aq) + 2e$

$O_2\,(g) + 2H_2O\,(l) + 4e \rightarrow 4OH^-\,(aq)$

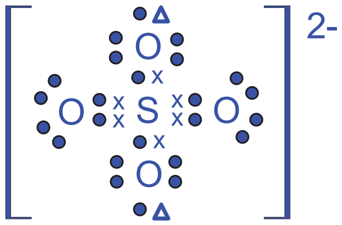
(ii) $1.59 = 0.40 - E^\theta_{oxd}$ hence $E^\theta_{oxd} = -1.19$ V

(iii) $$\frac{80}{100} \times \frac{1.85}{65.4} = \frac{I \times 365 \times 24 \times 60 \times 60}{2 \times 96500}$$

$I = 1.38 \times 10^{-4}$ A

(iv) Zinc-air battery has a higher energy density or power over mass ratio as it uses air as an oxidising agent unlike the heavier oxidising agent MnO_2 used in the alkaline battery.

4(a) **(i)**



(ii) There are 4 bond pairs and 0 lone pair around S. To minimise repulsion, the 4 electron pairs are directed towards corners of a tetrahedron hence tetrahedral shape.

(b) **(i)** Amount $= \dfrac{3.0}{137.3 + 2(16.0 + 1.0) + 8(18.0)} = \dfrac{3.0}{315.3} = 9.515 \text{ x } 10^{-3}$ mol

Amount of H_2O lost = $9.515 \text{ x } 10^{-3} \text{ x } 9 = 8.563 \text{ x } 10^{-2}$ mol
Theoretical mass of H_2O lost = $8.563 \text{ x } 10^{-2} \text{ x } 18.0 = 1.54$ g
Decomposition is complete.

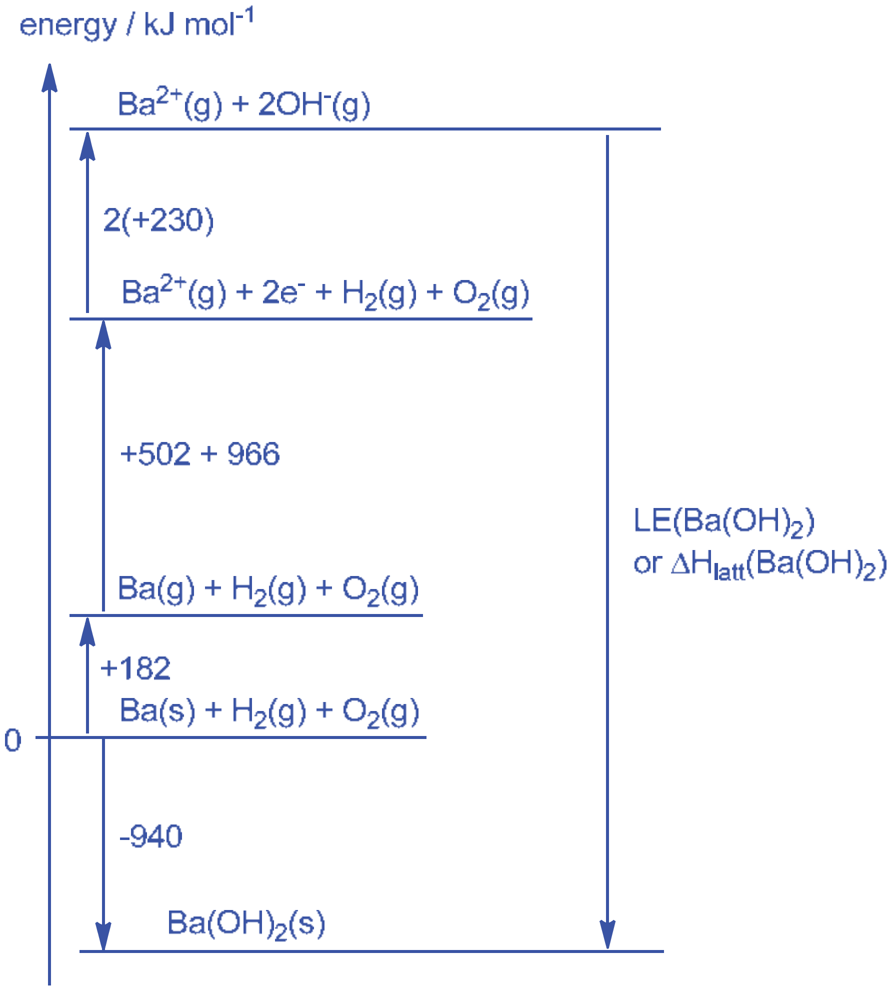
(ii) Ionic radius: $Ba^{2+} > Mg^{2+}$
Charge density and polarising power: $Ba^{2+} < Mg^{2+}$
Ability of cation to polarise, weaken and break O–H bond: $Ba^{2+} < Mg^{2+}$
Thermal stability: $Ba(OH)_2 > Mg(OH)_2$

(c) **(i)** 34.0 – 25.0 = 9.0 °C

(ii) Amount of H_2O formed = $\dfrac{100}{1000}$ 0.8 x 2 = 0.16 mol
Heat absorbed by solution = 220 x 4.18 x 9.0 = 8276.4 J

$$\Delta H_n = -\frac{8276.4}{0.16} = -51.7 \text{ kJ mol}^{-1}$$

(d)



182 + 502 + 966 + 2(230) + LE($Ba(OH)_2$) = –940

ΔH_{latt} ($Ba(OH)_2$) = –3050 kJ mol^{-1}

(e) **(i)** J: nucleophile

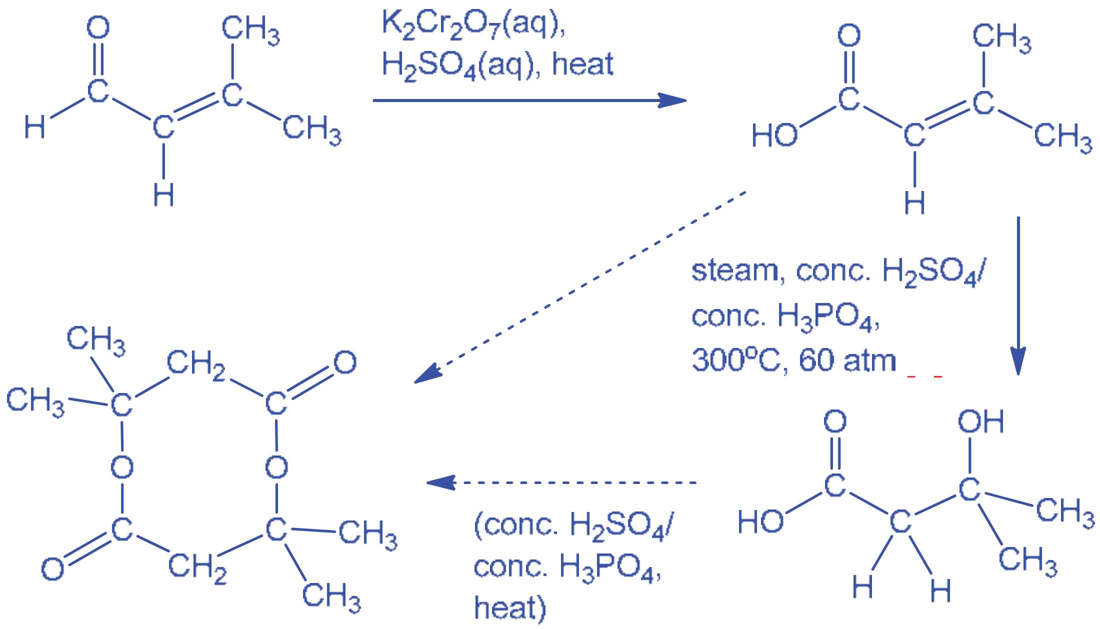
K: electrophile

(ii) III: acid-base / Lewis base

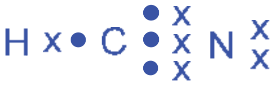
IV: elimination / Lewis acid

(iii) CH_3CHO and CH_3COCH_3

(iv)



5(a)



(b) **(i)** $\Delta H = 4 \times 410 + 3 \times 390 + \frac{3}{2} \times 496 - [410 + 890 + 6 \times 460] = -506\ \text{kJ mol}^{-1}$

ΔH (*BMA process*)
$= 4 \times 410 + 3 \times 390 - [410 + 890 + 3 \times 436]$
$= +202\ \text{kJ mol}^{-1}$

(ii) The Andrussow process is exothermic which is energetically more favourable

(c) Ksp $= s \times (2s)^2$

Solubility $= \sqrt[3]{\dfrac{8.0\times10^{-12}}{4}}$

$= 1.26 \times 10^{-4}$ mol dm^{-3}

$Zn(CN)_2$ has very low solubility in water , hence the CN^- ions will not be dissociated to cause harm.

(d) **(i)** Advantage: nitrite is soluble in water and hence can be transported to the body tissues quickly OR nitrite oxidises Fe^{2+} in haemoglobin to Fe^{3+} which can remove cyanide easily.

Disadvantage: the body will be starved of oxyhaemoglobin that is able to transport oxygen to the cell.

(ii) The SCN^- is a weaker ligandthat will not bind strongly to the Fe^{2+} in cytochrome c oxidase.

(iii) Half-life = 30 min

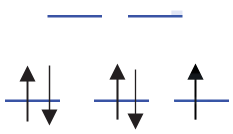
No. of half-lives before complication occurs $= \dfrac{60}{30} = 2$

Maximum blood cyanide concentration = 20 x 2 x 2 = 80 μg per 100 cm^3

(iv) Two orbitals have their lobes pointing at the ligands along the x, y and z axis, hence they experienced greater repulsion from the ligands OR the ligands split the d orbitals into two energy levels.

The other three orbitals experienced less repulsion since their lobes do not point at the ligands along the axes. Hence, there are two energy levels.

(v)

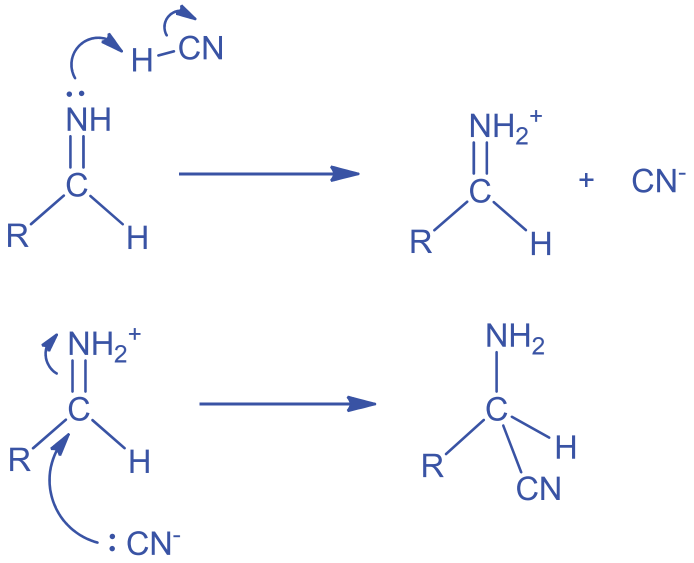


(e) **(i)** Elimination

(ii) NaOH (aq), heat under reflux

(iii) Prevent poisonous HCN from vapourising into the environment.

(iv)



(v) CN^- nucleophile attacks the trigonal planar carbonyl C from either side of the plane with equal probability, producing a racemic mixture.Naturally occurring amino acid is present as one of the enantiomers and will rotate plane polarised light.

MERIDIAN JUNIOR COLLEGE
JC 2 Preliminary Examination
H2 Chemistry Paper 4

---

1 (a) Procedure

Burette readings

Final burette reading / cm^3	48.00
Initial burette reading / cm^3	0.00
Volume of FA 2 / cm^3	48.00

Mass Readings

Mass of weighing bottle and FA 1 / g	6.789
Mass of weighing bottle and residual solid / g	4.789
Mass of FA 1 added / g	2.000

Titration

	1	2
Final burette reading / cm^3	21.30	21.30
Initial burette reading / cm^3	0.00	0.00
Volume of FA 3 / cm^3	21.30	21.30
	✓	✓

(b) Average volume of FA3 used $= \dfrac{21.30 + 21.30}{2} = 21.30\ cm^3$

(c) **(i)**

Amount of HC*l* in FA3 in 21.30 cm^3

$= \dfrac{25.0}{1000} \times 0.2 = 5.00 \times 10^{-3}$ mol

(ii) Amount of HC*l* remaining in FA3 (in 250 cm^3)

$= \dfrac{250}{17.50} \times 5 \times 10^{-3} = 0.0587$ mol

(iii) Initial amount of HC*l* $= \dfrac{48.00}{1000} \times 2.0 = 0.0960$ mol

Amount of HC*l* in FA3 that has reacted = 0.0960 – 0.0587
= 0.0373 mol

(iv) Amount of $MgCO_3 = \dfrac{0.0373}{2}$

$= 0.01865$ mol

Mass of $MgCO_3 = 0.01865 \times (24.3 + 12 + 48) = 1.57$ g

Percentage purity of FA1 $= \dfrac{1.57}{2.00} \times 100\% = 78.6\%$

(d) **(i)**

smallest volume used = 48.40 cm^3

largest volume used = 48.60 cm^3

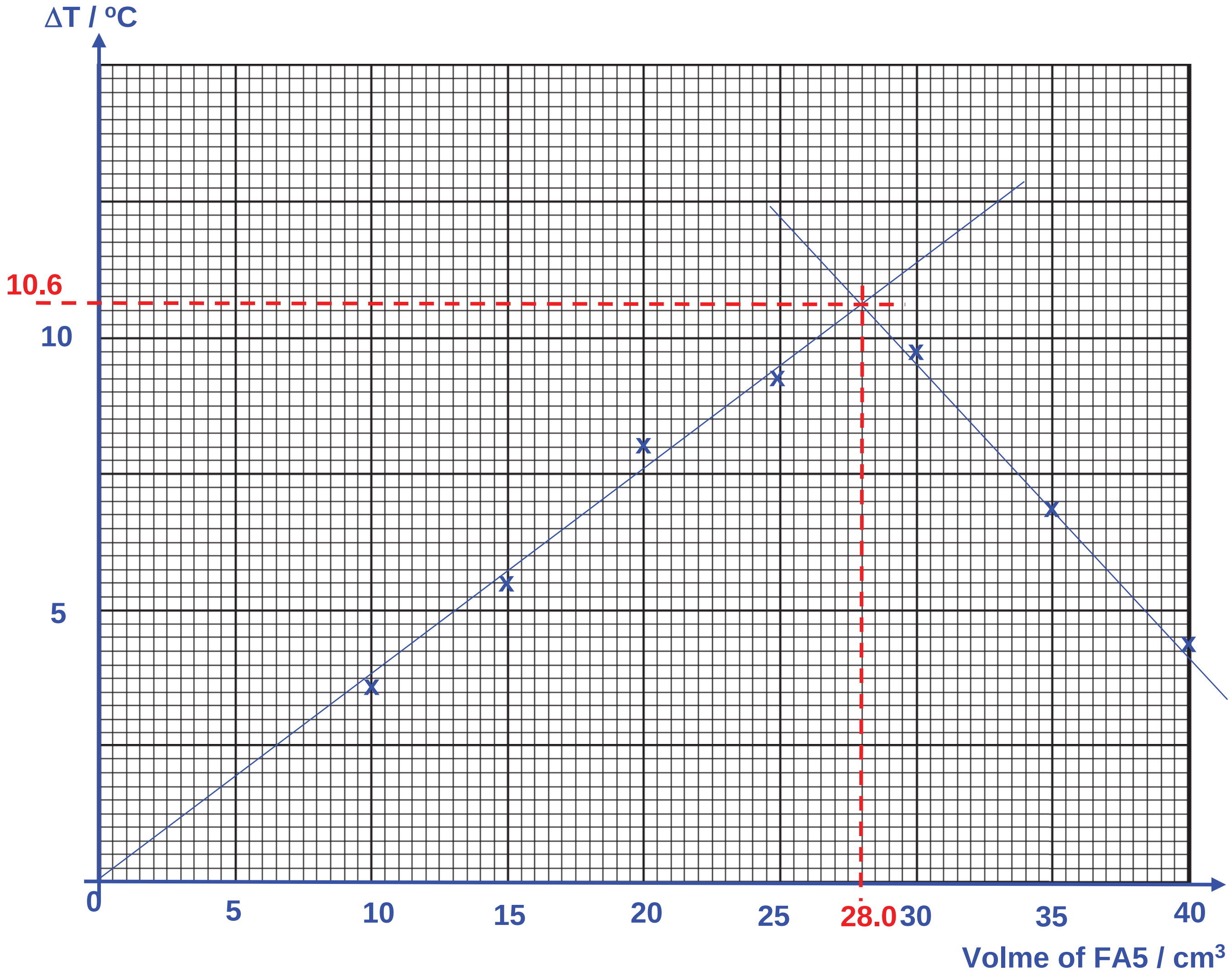
(ii) The percentage purity of FA 1 should be the same for student X and student Y since FA2 (hydrochloric acid) is added in excess to completely react with FA1 (magnesium carbonate).

2 **Results**

Expt	**Volume of FA 5 / cm^3**	**Volume of FA 6 / cm^3**	**T_{FA5} /°C**	**T_{FA6} /°C**	**$T_{weighted\ initial}$ /°C**	**T_{max}/°C**	**ΔT / °C**
1	10.0	40.0	28.0	32.0	31.2	34.5	3.3
2	20.0	30.0	30.0	32.0	31.2	38.0	6.8
3	30.0	20.0	31.0	31.5	31.2	41.0	9.8
4	**40.0**	**10.0**	31.0	31.5	31.1	35.5	4.4
5	**15.0**	**35.0**	29.5	31.5	30.9	36.0	5.1
6	**25.0**	**25.0**	30.5	31.5	31.0	40.0	9.0
7	**35.0**	**15.0**	31.0	31.5	31.2	38.0	6.8

[5]

(ii)



(iv)

ΔT_{max} = 10.6 °C …………………………… V_{max} = 28.0 cm^3 ……………………………

(b **(i)** No of moles of KOH = [(50 – 28) / 1000] x 1.50 = 0.0330 mol

No of moles of H_2SO_4 = 0.0375 × ½ = 0.0165 mol

$[H_2SO_4]$ in FA 5 = $= \dfrac{0.0165}{28.00/1000}$

= 0.589 mol dm^{-3}

(ii) Q = (50) (4.18)(10.6)= 2215 J

(c) $\Delta H_n =$ $= -\dfrac{2215}{2\times[0.589]\times\dfrac{28.00}{1000}} =$ – 67.1 kJ mol^{-1}

(d) As the temperature rises to the maximum value, there is a greater temperature difference between the solution and the surrounding. Hence, there is greater heat loss to the surrounding or there is a greater temperature gradient.

Hence, the temperature is more inaccurate as they approach the maximum value.

(e) **for graph**

Maximum is reached at the same V_{max} of sulfuric acid as the experiment with potassium hydroxide.

for explanation

Lower temperature rise, ΔT_{max}, as some heat that would have been released is used to dissociate the weak base completely. Maximum is reached at the same number of moles of sulfuric acid as the reacting mole ratio remains the same. Hence, V_{max} is the same.

(f) **Planning**

(i)

$$\begin{tikzcd}
BaO\,(s) + CO_2\,(g) \arrow[rr, "\Delta H_1"'] \arrow[dr, "\begin{array}{l}2HNO_3\,(aq)\\ \Delta H_2\end{array}"'] & & BaCO_3\,(s) \arrow[dl, "\begin{array}{l}2HNO_3\,(aq)\\ \Delta H_3\end{array}"] \\
& Ba(NO_3)_2\,(aq) \quad + \quad H_2O(l) \quad + \quad CO_2\,(g) &
\end{tikzcd}$$

By *Hess Law*, $\Delta H_1 = \Delta H_2 - \Delta H_3$

(ii) Pre-calculations

If mass of BaO used is 1.00 g, amount of BaO $= \dfrac{1.00}{137.0+16.0} = 0.006536$ mol

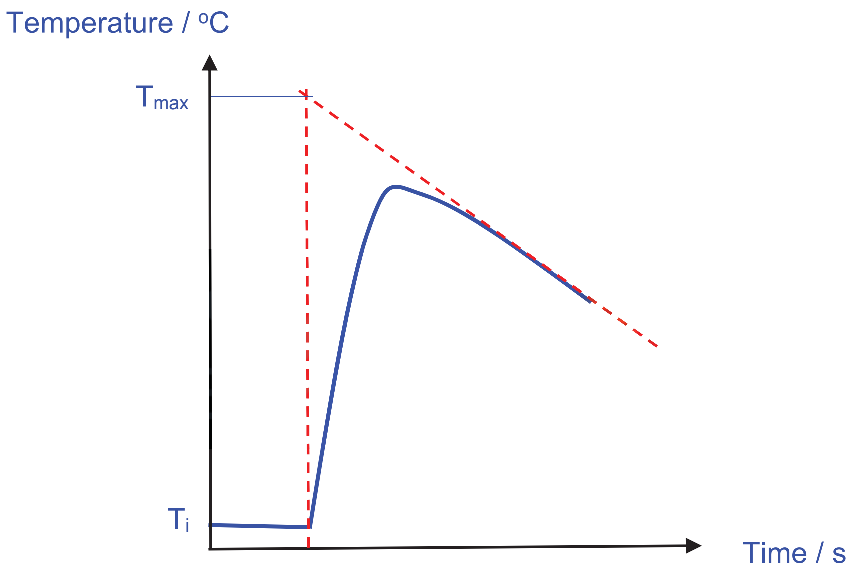
Amount of HNO_3 = 2 x 0.006536 = 0.01307 mol

Minimum volume of HNO_3 required to dissolve the BaO solid $= \dfrac{0.01307}{0.500} = 26.14\ cm^3$

Experimental Procedure

1. Weigh out about 1 g of BaO into a dry weighing bottle. Record the mass readings in a table.
2. Using a 50 cm^3 measuring cylinder, transfer 40 cm^3 of HNO_3 into the styrofoam cup supported in a glass beaker.
3. Measure and record the initial temperature of the HNO_3. Start the stop-watch and stir the solution gently with the thermometer. Record the temperature of the solution every 30 seconds for 2.0 minutes.
4. At 2.0 minutes, transfer the BaO solid into the styrofoam cup. Continuously stir the mixture thoroughly, and read the temperature at 2.5 minutes. Following this, record the temperature every 30 seconds from 3.0 minutes to 8.0 minutes.
5. At the end of the experiment, reweigh the weighing bottle and record the actual mass of BaO used.
6. Plot a graph of temperature against time to obtain a cooling curve. Obtain the maximum temperature change by extrapolation.

Method 1 : Cooling curve



To calculate ΔH_2

Quantity of heat absorbed by solution, Q = $(V_{HNO3}) \times 4.18 \times (T_i - T_{max})$

$= \boldsymbol{x}$ J

$$\Delta H_2 = -X \div \frac{1.00}{137.0+16.0} / 1000$$

$$= -y \text{ kJ mol}^{-1}$$

Other methods possible: *Fixed volume of HNO_3 and change mass of BaO* ***OR*** *Fixed mass of BaO and change volume of HNO_3*

3 Inorganic and Organic Analysis

(a) 1. Test on FA 7

Test	Observations
(i) To a 1 cm depth of the solution of **FA 7** in a test-tube, add a few drops of aqueous barium nitrate followed by dilute nitric acid.	White precipitate formed dissolves in (excess) HNO_3 to form a colourless solution.
(ii) To a 1 cm depth of the solution of **FA 7** in a test-tube, add an equal volume of aqueous hydrogen peroxide, then	No effervescence OR a colourless solution is obtained.
add a few drops of aqueous barium nitrate, followed by dilute nitric acid.	White precipitate formed does not dissolve in (excess) HNO_3.
(iii) To a 2 cm depth of the solution of **FA 7** in a test tube, add an equal volume of sulfuric acid, then heat the mixture gently and cautiously.	When heated, gas produced decolourises purple $KMnO_4$.
(iv) To a 1 cm depth of the solution of **FA 7** in a test-tube, add an equal volume of aqueous sodium hydroxide, then	No ppt formed.
add a few drops of aqueous potassium manganate(VII),	Green solution formed when $KMnO_4$ added.
followed by sulfuric acid.	Green solution (or yellow or brown) turned colourless on adding sulfuric acid.

(v) anion: SO_3^{2-}
evidences (any two):

1. FA 7 reacts with sulfuric acid / in test (iii) to give SO_2 gas which decolourises $KMnO_4$.
2. FA 7 formed white precipitate of $BaSO_3$ formed which dissolves in excess acid.
3. The SO_3^{2-} in FA 7 is oxidised to SO_4^{2-} in test (ii) by H_2O_2 which formed white ppt $BaSO_4$ that is insoluble in excess acid.
4. FA7 reduced purple MnO_4^- to green MnO_4^{2-} under alkaline condition OR to colourless Mn^{2+} under acidic condition.

2. (i) Test on FA 8

Test	Observations
(i) To a 1 cm depth of FA 8 in a test-tube, add aqueous sodium hydroxide drop wise till excess. Heat the mixture.	White ppt is soluble in excess NaOH(aq) to form a colourless solution. Gas evolved turned moist red litmus blue.
(ii) To a 1 cm depth of FA 8 in a test-tube, add aqueous ammonia drop wise till excess.	White ppt is soluble in excess NH_3(aq) to form a colourless solution.

(ii) Cation: Zn^{2+}

Evidence: FA 8 forms a white ppt of $Zn(OH)_2$ which is soluble in excess NaOH to form $Zn(OH)_4^{2-}$. FA 8 forms a white ppt of $Zn(OH)_2$ which is soluble in excess NH_3 to form $Zn(NH_3)_4^{2+}$

Cation: NH_4^+

Evidence: FA 8 evolved NH_3 gas upon heating with NaOH(aq). Hence, NH_4^+ ion is present.

(b) (i) Test on FA 9

Tests	Observation
(i) To a 1 cm depth of FA 9 in a test-tube, add 1 cm^3 of dilute sulfuric acid. Add one drop or 2 drops of aqueous potassium manganate (VII). Place the test-tube in the water bath for several minutes.	Purple $KMnO_4$ decolourised.
(ii) To a 1 cm depth of FA 9 in a test-tube, add 1 cm^3 (or a few drops) of Fehling's solution.	Brick red ppt formed.

Place the test-tube in the water bath for several minutes.	

(ii) Functional group in **FA 9** (aliphatic) aldehyde ....

Evidence: FA 9 undergoes oxidation as it decolorised purple with $KMnO_4$.This shows that it cannot be a ketone.
FA 9 undergoes a positive Fehling's test (or oxidation) as it formed a brick red ppt.
Hence, FA9 is an (aliphatic) aldehyde.

Class Adm No

Candidate Name: ____________________

H

2017 Preliminary Examinations II
Pre-University 3

H2 CHEMISTRY **9647/01**

Paper 1 Multiple Choice **20 Sept 2017**

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 **forty** 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.

This question paper consists of **16** printed pages and **2** blank pages.

Section A

For each question there are four possible answers, **A**, **B**, **C**, and **D**. Choose the **one** you consider to be correct.

1 Dolomite is a carbonate-containing mineral with formula Mg***Z***$(CO_3)_2$ where ***Z*** is a metal ion. It is insoluble in water but reacts with acids.

When 2.00 g of dolomite was completely dissolved in an excess of hydrochloric acid, 0.759 g of carbon dioxide was given off. What is the identity of the metal ***Z***?

A Ba **B** Ca **C** Ra **D** Sr

2 Sulfur dioxide gas is an irritant to the eyes and respiratory system. The maximum safe toleration level of sulfur dioxide in air is 0.014 mg dm^{-3}.

How many molecules of sulfur dioxide gas are present in 1 dm^3 of air at this toleration level?

A $\frac{0.014}{6.02 \times 10^{23}} \times 64.1$

B $\frac{0.014}{1000} \times \frac{1}{64.1} \times 6.02 \times 10^{23}$

C $\frac{0.014}{64.1} \times 6.02 \times 10^{23}$

D $\frac{0.014}{1000} \times 64.1 \times 6.02 \times 10^{23}$

3 The element technetium, Tc (mass number 99; atomic number 43), was discovered in 1937 by two Italian scientists, Segŕe and Perrier.

Under suitable conditions, technetium reacts with fluorine to form TcF_6.

Which of the following options shows the correct number of protons, neutrons and electrons in Tc^{6+}?

	number of protons	**number of neutrons**	**number of electrons**
A	43	43	56
B	43	56	37
C	49	43	37
D	43	56	49

4 Which of the following atoms has three unpaired electrons?

A	Br	**B**	Co	**C**	Ga	**D**	Sc

5 Under standard conditions, water exists in the liquid state but hydrogen sulfide exists in the gaseous state.
Which of the following best explains this phenomenon?

A Water has a higher relative molecular mass than hydrogen sulfide.
B The O-H covalent bond in water is stronger than the S-H covalent bond in hydrogen sulfide.
C The hydrogen bonds between water molecules are stronger than the Van der Waals' forces between hydrogen sulfide molecules.
D Hydrogen sulfide has a more spherical structure compared to water.

6 Antimony, Sb, is in Group V of the Periodic Table. It was proposed that antimony is able to form SbF_4^{n-} anion, the structure of which is of square planar shape.
Which of the following shows the correct value of *n* and the oxidation number of Sb in this anion?

	value of *n*	**oxidation number of Sb**
A	1	+3
B	1	+5
C	3	+1
D	3	+3

[Turn over

7 **X** and **Y** are ideal gases that do not react with one another. The molar mass of **X** is twice that of **Y**.

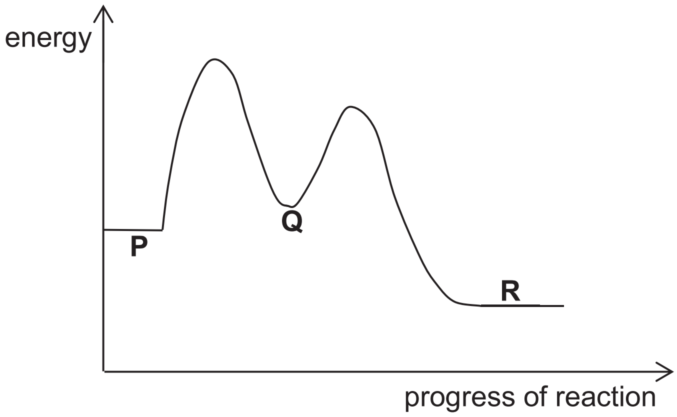
If all measurements are taken at room temperature and pressure, which statement correctly describes **X** and **Y**?

A The volume occupied by 2 g of **X** is half that occupied by 2 g of **Y**.
B The mass of 5 dm^3 of **X** is half that of 5 dm^3 of **Y**.
C The volume occupied by 2.5 g of **X** is equal to the volume occupied by 5 g of **Y**.
D On mixing 1 dm^3 of **X** with 1 dm^3 of **Y**, the partial pressure of **X** is twice that of **Y**.

8 The two steps in the conversion of compound **P** to compound **R** are shown below.

$$\mathbf{P} \rightarrow \mathbf{Q} \quad \text{Step 1}$$
$$\mathbf{Q} \rightarrow \mathbf{R} \quad \text{Step 2}$$

The energy profile of the reaction is shown below.



Which of the following statements about the reaction can be deduced from the information given?

A The enthalpy change for the reaction is endothermic.
B **Q** acts as a catalyst in the reaction.
C Step 1 is the rate determining step.
D **R** is thermodynamically less stable than **P**.

9 When liquid $SOCl_2$ is added to $Ba(OH)_2$, a vigorous reaction occurs and the temperature decreases from 25 °C to 5 °C.

What are the correct signs of ΔH, ΔS and ΔG for this reaction?

	ΔH	**ΔS**	**ΔG**
A	+	+	-
B	+	-	+
C	-	+	-
D	-	-	+

10 A sample of finely ground copper was contaminated with zinc powder.

Treatment of the sample with an excess of hydrochloric acid produced 120 cm^3 of hydrogen gas, measured at room temperature and pressure.

The remaining copper was then reacted with acidified potassium manganate(VII). It was found that 0.00424 mol of potassium manganate(VII) was required for complete oxidation of copper to copper(II) ions.

What is the percentage by mass of copper in the sample?

A 45.2% **B** 65.8% **C** 67.3% **D** 90.4%

11 Zinc(II) reacts with the complex anion hexacyanoferrate(III), $[Fe(CN)_6]^{3-}$, to give a sparingly soluble salt which dissociates in water according to the following equilibrium.

$$Zn_3[Fe(CN)_6]_2(s) \rightleftharpoons 3Zn^{2+}(aq) + 2[Fe(CN)_6]^{3-}(aq)$$

If the solubility product, K_{sp}, of $Zn_3[Fe(CN)_6]_2$ is X, what is the concentration of $Zn^{2+}(aq)$ at equilibrium?

A $\left(\frac{3X}{2}\right)^{\frac{1}{3}}$ **B** $\left(\frac{3X}{2}\right)^{\frac{1}{5}}$ **C** $\left(\frac{9X}{4}\right)^{\frac{1}{3}}$ **D** $\left(\frac{9X}{4}\right)^{\frac{1}{5}}$

[Turn over

12 Which of the following statements about the rate constant, *k*, of chemical reactions is **not** true?

A The rate constant increases when temperature increases.
B The rate constant increases when the concentration of the reactant increases.
C The rate constant decreases when the activation energy increases.
D The units of the rate constant depends on the overall order of reaction.

13 A Period 3 element forms an oxide that is soluble in both water and aqueous sodium hydroxide. Which of the following could be the identity of this element?

A aluminium **B** silicon **C** sodium **D** sulfur

14 In which of the following pairs is the radius of the first species greater than that of the second species?

A Mg, A*l* **B** Ca, Ba **C** Mg^{2+}, Na^{+} **D** K^{+}, Ar

15 Which of the following properties of the Group II elements and their compounds decreases down the group?

A Ease of oxidation of the elements
B Electronegativity of the elements
C Reactivity of elements with chlorine
D Thermal stability of nitrates

16 With reference to the chemistry of Group VII elements and their compounds, which of the following would be a correct prediction for astatine?

A Astatine reacts vigorously with hydrogen at room temperature.
B Astatine exists as a gas at room temperature.
C Astatine reacts with cold aqueous hydroxide to form AtO^- and At^-.
D Molten $AlAt_3$ can conduct electricity.

17 Which of the following products is **least** likely to act as a ligand?

A AlH_3 **B** CO **C** C_2H_5OH **D** CH_3NH_2

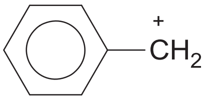
18 The use of *Data Booklet* is relevant to this question.

An element **G** has an atomic number of 23. Which of the following compounds of **G** is **not** likely to exist?

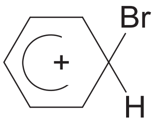
A $K\mathbf{G}O_3$ **B** $\mathbf{G}_2O_5$ **C** $K_2\mathbf{G}O_4$ **D** $\mathbf{G}OCl_2$

19 Which of the following species could be an intermediate in an electrophilic addition reaction?

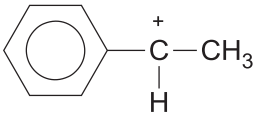
A



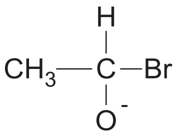
B



C



D



$CH_3-C(H)(Br)-O^-$

20 How many structural isomers with the molecular formula $C_5H_{10}O$ gives an orange precipitate with Brady's reagent and a yellow precipitate with alkaline aqueous iodine?

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

21 In an experiment, it was found that during the free radical substitution of alkanes, primary, secondary and tertiary hydrogen atoms were replaced by bromine atoms at different rates, as shown in the table below.

Reaction	**Relative Rate**
Primary : $RCH_3 \rightarrow RCH_2Br$	1
Secondary : $R_2CH_2 \rightarrow R_2CHBr$	8
Tertiary : $R_3CH \rightarrow R_3CBr$	20

With reference to the information given, which of the following shows the 2 products obtained from the reaction of 2,3-dimethylbutane with bromine gas under UV light and their relative ratio?

A $(CH_3)_2CHCH(CH_3)CH_2Br$: $(CH_3)_2CBrCH(CH_3)_2$ = 3 : 10

B $(CH_3)_2CHCH(CH_3)CH_2Br$: $(CH_3)_2CBrCH(CH_3)_2$ = 1 : 20

C $(CH_3)_3CCH_2CH_2Br$: $(CH_3)_3CCHBrCH_3$ = 3 : 8

D $(CH_3)_3CCH_2CH_2Br$: $(CH_3)_3CCHBrCH_3$ = 3 : 20

22 Concentrated ammonia was heated in a sealed tube with excess bromoethane. Which of the following products will **not** be formed?

A C_2H_7N **B** C_3H_9N **C** $C_4H_{11}N$ **D** $C_8H_{20}NBr$

23 Which of the following statements about phenol is **incorrect**?

A Acidic hydrolysis of phenylethanoate will give ethanoic acid and phenol.

B Phenol reacts with ethanoic acid to give phenylethanoate.

C Phenol gives violet colouration with neutral $FeCl_3$.

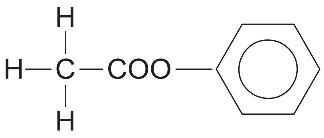
D Phenol gives a white precipitate with aqueous bromine.

24 Several reactions that involve the 'insertion' of carbon monoxide into organic molecules are of industrial importance. One of such reactions is the synthesis of hydroxyethanoic acid from methanal.

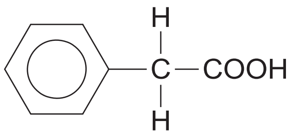
$$CH_2O + CO + H_2O \rightarrow CH_2(OH)CO_2H$$

Which of the following shows the product formed when benzaldehyde undergoes a similar reaction with carbon monoxide in the presence of water?

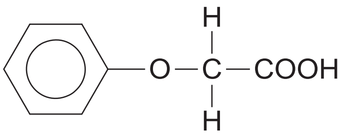
A



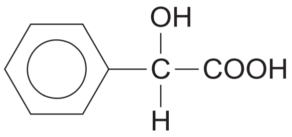
B



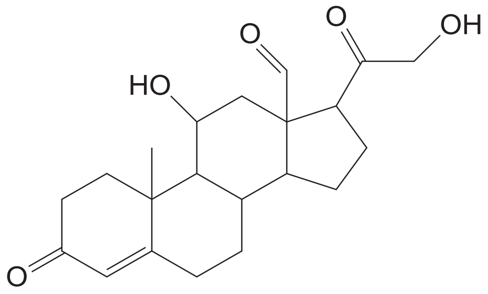
C



D



25 Aldosterone is a hormone essential for sodium conservation in the kidney, salivary glands and colon.

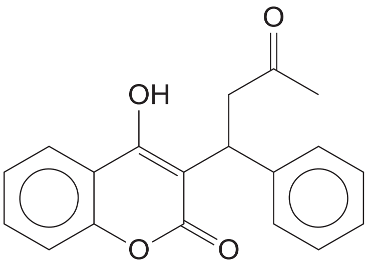


aldosterone

How many chiral carbons are there in the product of the reaction between aldosterone and $LiAlH_4$ in dry ether?

A 7 **B** 8 **C** 9 **D** 10

26 Warfarin is a drug used as an anticoagulant to prevent stroke in people who have heart disease.



warfarin

Which of the following statements is true about warfarin?

A 1 mole of warfarin reacts with 2 moles of 2,4-dinitrophenylhydrazine.

B Warfarin can undergo substitution reaction with $SOCl_2$.

C Warfarin reacts with I_2 and dilute NaOH to give a colourless solution.

D There are 16 sp^2 hybridised carbon atoms in 1 molecule of warfarin.

27 Which of the following amino acids is **not** involved in the formation of proteins in the body?

A $H_2NCH(COOH)CH(CH_3)_2$

B $H_2NCH(CH_3)CH_2COOH$

C $H_2NCH(CH_2SH)COOH$

D $H_2NCH(CH_2C_6H_5)COOH$

28 Why are amides less basic than amines?

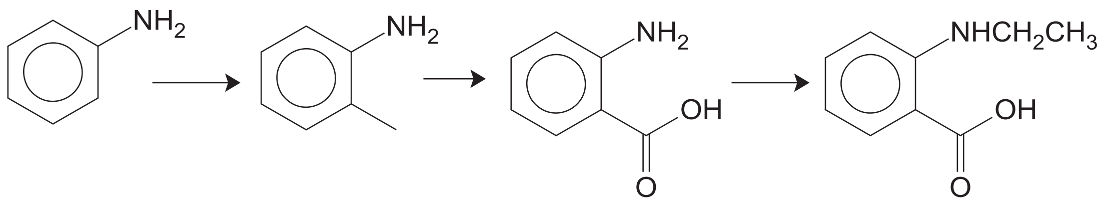
A Amides form a zwitterion, causing its nitrogen atom to carry a positive charge.

B The amide carbonyl group withdraws lone pair of electrons from nitrogen atom, releasing the H atom on NH_2 as proton.

C The C-N bond in amides is stronger than that in amines.

D The resonance structure of amides causes the movement of a pair of electrons from the nitrogen atom to the oxygen atom.

29 The reaction scheme below shows the synthesis of compound **P** from phenylamine.



P

Which of the following types of reaction is **not** involved in the reaction scheme shown?

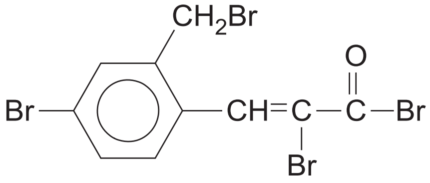
A electrophilic substitution

B nucleophilic addition

C nucleophilic substitution

D oxidation

30 The structure of compound **S** is shown below.



S

0.01 mol of **S** is reacted with excess hot ethanolic silver nitrate. What is the mass of the silver bromide formed from the reaction?

A 1.878 g **B** 3.758 g **C** 5.634 g **D** 7.512 g

Section B

For each of the questions in this section, one or more of the three numbered statements **1** to **3** may be correct.

Decide whether each of the statements is or is not correct (you may find it helpful to put a tick against the statements that you consider to be correct).

The responses **A** to **D** should be selected on the basis of

A	**B**	**C**	**D**
1, **2** and **3** are correct	**1** and **2** only are correct	**2** and **3** only are correct	**1** only is correct

No other combination of statements is used as a correct response.

31 Which of the following types of bonding are present in $[Fe(H_2O)_5(SCN)]Cl_2$?

1 covalent bonding
2 dative bonding
3 ionic bonding

32 Which of the following are **incorrect** assumptions made in the kinetic theory about an ideal gas?

1 The gaseous particles are in constant random motion.
2 The gaseous particles have constant interactions with one another.
3 The volume of the container is negligible.

33 When 290 C of electricity are passed through a molten compound of a metal, 0.001 mol of atoms of the metal is deposited at the cathode.

What could the metal be?

1 aluminium
2 copper
3 silver

34 The following reaction between carbon monoxide and steam occurs in the presence of a suitable catalyst.

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

The standard enthalpy changes of formation of the compounds involved in the reaction are given below.

Compound	**Standard enthalpy change of formation / kJ mol^{-1}**
$CO(g)$	-111
$H_2O(g)$	-242
$CO_2(g)$	-394

Which of the following changes would increase the yield of $H_2(g)$ in the reaction above?

1 decrease in temperature
2 adding sodium hydroxide into the system
3 adding more catalyst into the system

[Turn over

The responses **A** to **D** should be selected on the basis of

A	B	C	D
1, **2** and **3** are correct	**1** and **2** only are correct	**2** and **3** only are correct	**1** only is correct

No other combination of statements is used as a correct response.

35 Which of the following statements are true for the hydrogen halides HCl, HBr and HI?

1 Hydrogen iodide is the strongest acid.
2 Hydrogen iodide has the lowest thermal stability.
3 Hydrogen chloride has the lowest boiling point.

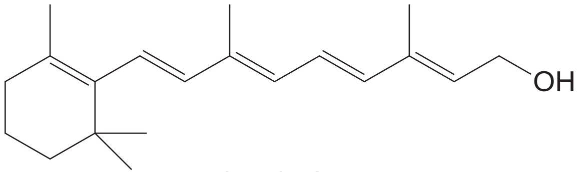
36 Which of the following properties of copper and calcium are likely to differ?

1 density
2 ability to display variable oxidation states
3 reactivity with acid

37 In the catalytic converter in the exhaust system of a car, harmful gases are converted to less harmful ones.
Which of the following processes take place in the catalytic converter?

1 hydrocarbons + oxides of nitrogen → carbon dioxide + water + nitrogen
2 carbon monoxide + oxides of nitrogen → carbon dioxide + nitrogen
3 carbon dioxide + oxides of nitrogen → carbon + nitrogen + water

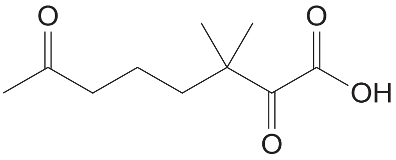
38 The structure of vitamin A is shown below.



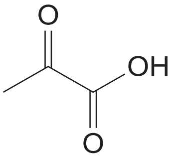
vitamin A

Which of the following are possible products of the reaction of vitamin A with excess hot acidified potassium manganate(VII)?

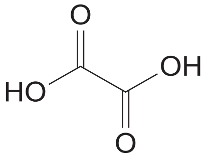
1



2



3



39 Which compounds reacts with an excess of sodium metal to give one mole of H_2(g) per mole of the compound?

1 $CH_3CH(OH)CH_2COOH$

2 $CH_3CH_2COCH(OH)COOH$

3 $CH_3CH(OH)CH_2CHO$

The responses **A** to **D** should be selected on the basis of

A	**B**	**C**	**D**
1, **2** and **3** are correct	**1** and **2** only are correct	**2** and **3** only are correct	**1** only is correct

No other combination of statements is used as a correct response.

40 Hippuric acid can be produced by adding benzoyl chloride to aminoethanoic acid. Which changes in bonding occur during this synthesis?

hippuric acid

1 A carbon-chlorine bond is broken.

2 A carbon-nitrogen bond is formed.

3 A hydrogen-chlorine bond is formed.

END OF PAPER

BLANK PAGE

BLANK PAGE

Class Adm No

Candidate Name: ____________________

H

millennia institute

2017 Preliminary Examination II
Pre-University 3

H2 CHEMISTRY **9647/02**

Paper 2 Structured Questions **12th Sept 2017**

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	**12**	**14**	**15**	**11**	**20**	**72**

1 Planning (P)

Hydrogen peroxide undergoes a redox reaction with acidified $KMnO_4$ as follows:

$$2MnO_4^-(aq) + 5H_2O_2(aq) + 6H^+(aq) \rightarrow 2Mn^{2+}(aq) + 5O_2(aq) + 8H_2O(l)$$

By itself, hydrogen peroxide decomposes slowly in accordance to the following equation:

$$2H_2O_2(aq) \rightarrow 2H_2O(l) + O_2(g)$$

It is found that the decomposition reaction is first order with respect to H_2O_2. The reaction can be accelerated by using solid manganese(IV) oxide as the catalyst.

(a) Write the rate equation for the decomposition of hydrogen peroxide.

.... [1]

(b) Using the information given, you are required to write a plan to determine the rate constant for the decomposition of hydrogen peroxide using the continuous titration method.

You may also assume that you are provided with:

- 250 cm^3 of 0.0100 mol dm^{-3} acidified $KMnO_4$;
- 250 cm^3 of 0.0250 mol dm^{-3} H_2O_2 solution;
- Solid manganese(IV) oxide;
- 25.0 cm^3 pipette;
- Stopwatch;
- the apparatus normally found in a school or college laboratory.

Your plan should include:

- practical details of how you would
  - determine if dilution of the reaction mixture is needed for titration against H_2O_2;
  - ensure the reaction is complete;
  - carry out the titration;
- a sketch of the graph you would expect to obtain;
- brief, but specific, details of how the results would then be used to obtain
  - the initial rate of reaction of decomposition in mol dm^{-3} $min^{-1,}$
  - the rate constant for the reaction

.... [11]

[Total: 12]

2 Hydrogen iodide can undergo decomposition to give a mixture of hydrogen gas and iodine gas.

$$2HI(g) \rightleftharpoons H_2(g) + I_2(g) \qquad \Delta H = +12.0 \text{ kJ mol}^{-1}$$

(a) State Le Chatelier's Principle.

………

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

(b) Predict and explain the effect of the following changes on the position of the above equilibrium, if any.

(i) Increasing the temperature

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

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

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

(ii) Reducing the pressure

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

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

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

(iii) Addition of catalyst

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

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

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

(c) When 1.4 mol of hydrogen iodide is heated in a closed vessel at 550 K, the total pressure at equilibrium was 6 atm.

Given that the mole ratio of hydrogen iodide to iodine gas at equilibrium is 9:4, calculate the equilibrium constant, K_p, at 550 K.

[3]

(d) Hydrogen chloride and hydrogen bromide also undergoes a similar decomposition to give hydrogen gas and its respective halogens.

Describe the trend in the volatility and colours of the halogens.

……

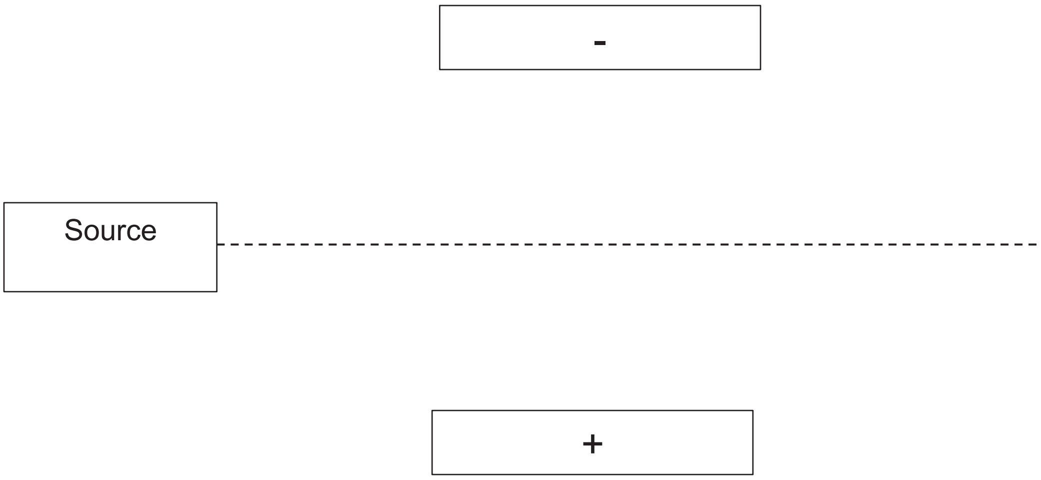
……

……

……[3]

(e) It was observed that a beam of protons gives an angle of 27° in the following electric field.

Indicate on the diagram below how a beam of protons, $^{127}I^-$ and $^{23}Na^+$ ions, travelling at the same speed, behave in the same electric field. Calculate the respective angles of deflection.

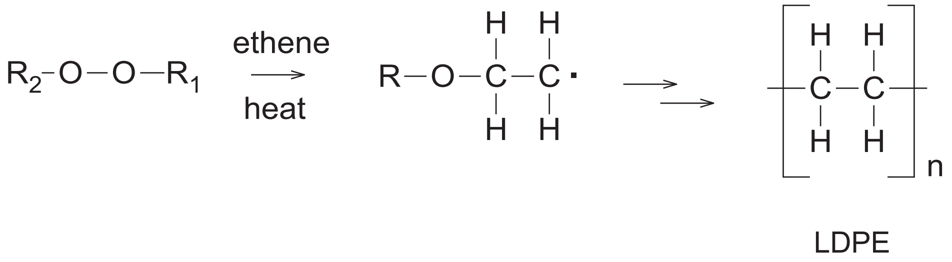


Working:

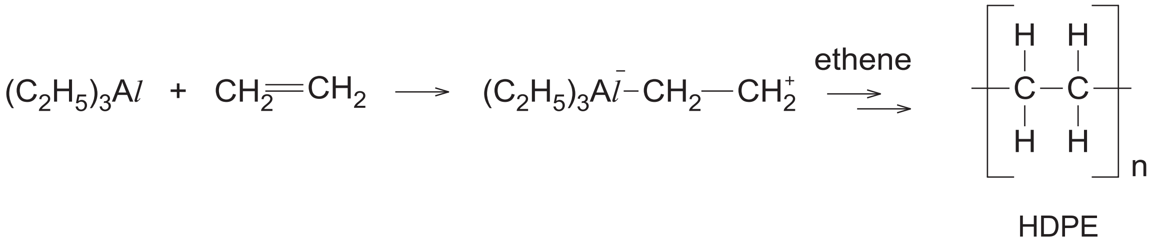
[3]

[Total: 14]

3 In 1933, chemists in Britain discovered that when ethene was subjected to high pressures in the presence of a trace amount of oxygen or organic peroxide, it produced low-density poly(ethene) (LDPE). The radical mechanism using organic peroxides is shown below.



Using triethylaluminium, also known as Ziegler-Natta catalyst, developed by Karl Ziegler and Giulio Natta in 1953, ethene can be polymerised at much lower pressures to produce high-density poly(ethene) (HDPE). In the first step, triethylaluminium can accept the pair of π electrons of ethene to form a carbocation which is very similar to that found in the usual electrophilic addition reactions. This carbocation then undergoes an addition reaction with another ethene molecule. Eventually, long chains of ethene units form.



The major differences between the structures of LDPE and HDPE are that

- the average chain length of LDPE is much shorter than that of HDPE
- the chains of LDPE are branched, while the chains of HDPE are unbranched.

The table below compares the physical properties of LDPE and HDPE.

Property	**Polymer**	
	LDPE	**HDPE**
Density	Low	High
Melting Point	Approximately 130 °C	Approximately 160 °C
Tensile strength	Low	High
Flexibility	Very flexible	Much more rigid

(a) **(i)** Using structure and bonding, explain the difference in melting point between LDPE and HDPE.

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

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

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

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

(ii) Suggest why LDPE has a lower density than HDPE.

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

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

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

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

(b) **(i)** Write an equation to represent the first step in the radical mechanism.

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

(ii) With reference to the mechanism given, explain why the production of LDPE only starts upon heating.

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

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

(iii) Suggest why the chains of LDPE are branched.

……

…… [1]

(c) **(i)** State the role of triethylaluminium in the reaction using Ziegler-Natta catalysts.

…… [1]

(ii) Similar to ethene, propene can be polymerised using the Ziegler-Natta catalysts. Show the structure of the carbocation intermediate formed in the first step.

[1]

(d) **Use the table of characteristics values for the infra-red absorption in the Data Booklet to answer this question.**

Infra-red absorptions can be used to identify functional groups in organic compounds. For example, ethanol shows absorptions at 1000-1300 cm^{-1} and 3230-3550 cm^{-1}.

Use the table to identify the infra-red absorption range that will be shown by

(i) Ethene but not by poly(ethene)

…………………………………………… cm^{-1}

(ii) Propyl ethanoate but not by propene

…………………………………………… cm^{-1}

[3]

(e) The four methods used to dispose polymers are incineration, recycling, depolymerisation and bacterial fermentation.

(i) Combustion of the polymers during incineration can lead to the formation of pollutants such as carbon monoxide which is toxic to humans, if the conditions are not carefully controlled.

In terms of the bonding involved, explain how carbon monoxide prevents oxygen from being transported around the body.

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

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

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

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

(ii) State two advantages of recycling.

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

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

[Total: 15]

4 Iron is a transition element in Period 4 of the Periodic Table.

(a) Explain what is meant by a transition element.

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

(b) Most iron oxide samples have a mole ratio of iron to oxygen in a range between 0.84 : 1 to 0.96 : 1. Suggest why these samples have variable compositions.

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

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

(c) The reaction between peroxodisulfate ions, $S_2O_8^{2-}$ and iodide ions is very slow at room conditions, while addition of iron(III) ions can speed up the reaction rate.

(i) Suggest why the reaction between $S_2O_8^{2-}$ and iodide ions is very slow.

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

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

(ii) Construct ionic equations to outline the catalytic role of iron(III) ions in the reaction.

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

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

(iii) State another iron species that can also act as a catalyst for the reaction.

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

(d) When thiocyanate ligand, SCN^-, is added to the yellow solution of $FeCl_3$, a deep red solution **H** is obtained.

(i) Suggest the formula of the complex responsible for the deep red solution **H**.

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

(ii) State the type of reaction when $FeCl_3$ forms **H**.

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

(iii) Explain why aqueous Fe^{3+} solutions are coloured.

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

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

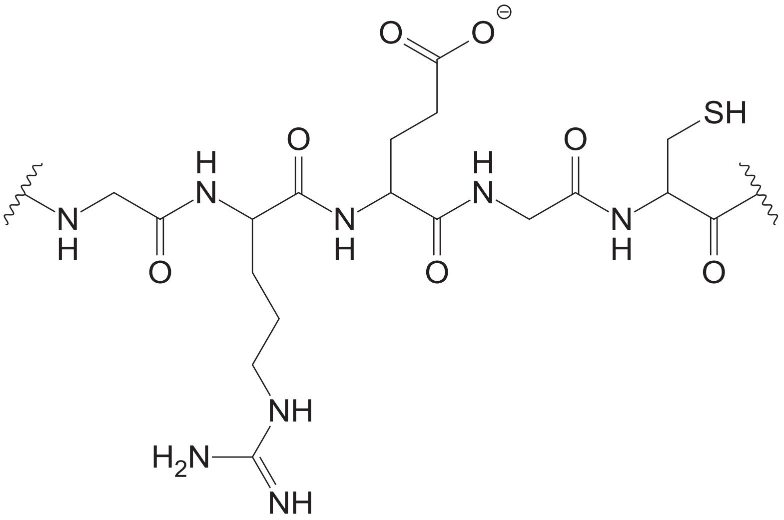
……………………………………………………………………………………………………

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

[Total: 11]

5 The pancreas produces the protein insulin that regulates the metabolism of carbohydrates, fats and proteins.

The structure of a portion of the insulin molecule is shown below. This portion contains a number of amino acids.



(a) Describe the tertiary structure of insulin.

....

....

.... [2]

(b) **(i)** What is meant by the term *denaturation*?

....

.... [1]

(ii) Suggest a brief outline of one method by which insulin may be denatured.

....

....

....

.... [2]

(iii) State the reagent and conditions required for complete hydrolysis of protein in the laboratory.

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

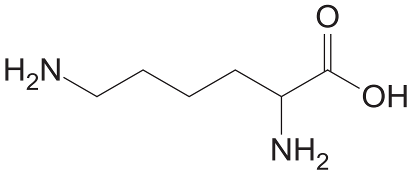
(iv) One of these amino acid residues are present more than once in the above portion of the insulin molecule. Draw a displayed formula for this amino acid residue.

[1]

(v) Explain, with the aid of equations, how the zwitterionic form of the amino acid in **(b)(iv)** act as a buffer.

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

(c) Lysine is a α-amino acid that is used in the biosynthesis of proteins.



(i) Explain what is meant by the term pK_a as applied to a weak acid HA.

…………………………………………………………………………………………………

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

(ii) State the functional groups present in lysine.

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

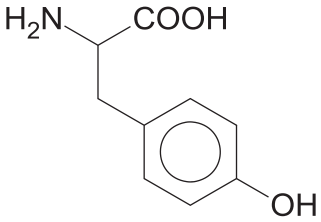
(iii) There are three pK_a values associated with lysine: 2.1, 8.9 and 10.5.

Make use of these pK_a values to suggest the major species present in the solutions of the amino acid with the following pH values.

pH 1	**pH 4**
pH 9	**pH 12**

[4]

(d) Tyrosine is another amino acid present in insulin.



Draw the organic products when tyrosine undergoes reaction with

(i) Br_2(aq)

[1]

(ii) NaOH(aq)

[1]

(iii) excess CH_3CH_2COCl

[1]

(e) State the type of reactions for **reaction with**.

Br_2(aq) …………………………………………………

NaOH(aq) ………………………………………………… [2]

[Total: 20]

END OF PAPER

BLANK PAGE

Candidate Name: ____________________

Class	Adm No

H

millennia institute

2017 Preliminary Examination II
Pre-University 3

H2 CHEMISTRY **9647/03**

Paper 3 Free Response **15th Sept 2017**

2 hours

Candidates answer on separate paper.

Additional materials: Answer Paper
Data Booklet

READ THESE INSTRUCTIONS FIRST

Do not turn over this question paper until you are told to do so

Write your name, class and admission number on all the work you hand in.

Write in dark blue or black pen.

You may use an HB pencil for any diagrams or graphs.

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

Answer any **four** questions.

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	1	2	3	4	5	Total
Marks	20	20	20	20	20	80

This question paper consists of **11** printed pages and **1** blank page.

1 **(a)** Graphite is a naturally-occurring form of crystalline carbon and is found in metamorphic and igneous rocks. Graphite is extremely soft and cleaves with very light pressure yet it is extremely resistant to heat and nearly inert in contact with almost any other material. These extreme properties give it a wide range of uses in metallurgy and manufacturing.

(i) With reference to the structure, account for the following properties of graphite.

- Soft
- Heat resistant and inert [3]

(ii) The following table shows some thermochemistry data.

Reaction	**ΔH / kJ mol^{-1}**
Standard enthalpy change of atomisation of carbon	+715
Enthalpy change of $4H(g) + O(g) + C(g) \rightarrow CH_3OH(l)$	-2069

With the use of relevant data from the *Data Booklet* and the above information, calculate the enthalpy change of formation of methanol. [3]

(b) A butane burner is used to heat the air in a hot air balloon. The hot air balloon has a volume of 2.1 m^3 and its volume does not change when the enclosed air is heated.

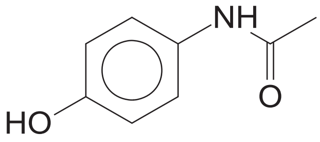
(i) Using the ideal gas equation, calculate the amount of gas molecules the balloon contains at temperature 800 K and a pressure of 1.0×10^6 Pa. [1]

(ii) Hence calculate the mass of air it contains, assuming an average relative molecular mass of 29. [1]

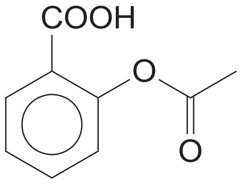
(iii) The standard enthalpy change of combustion of butane is -2877.5 kJ mol^{-1}. It requires 1.0 J of energy to raise the temperature of 1.0 g of air by 1.0 K.
Using your answer in **(b)(ii)**, calculate the mass of butane that needs to be burnt to raise the temperature of the air in the balloon by 20 K. Assume that the hot air balloon is a closed system. [2]

(iv) The actual mass of butane that needs to be burnt to raise the temperature of the air in the balloon by 20 K was found to be 3.81 g.
Suggest why this differs from your answer in (**b)(iii)**. [1]

(c) Paracetamol and aspirin are effective at pain and fever relief due to their ability to dissolve quickly in the blood stream and are soluble in fatty compounds found in cell membrane.



Paracetamol



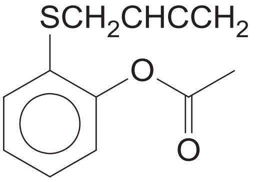
Aspirin

(i) Account for these properties based on the structure and bonding of aspirin. [2]

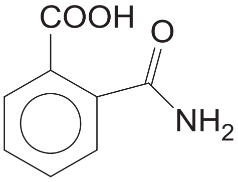
(ii) One of the pain relievers cause more stomach irritation than the other. With reference to the functional groups present, suggest and explain the pain reliever that you will recommend to someone who suffers from gastric bleeding. [2]

(iii) Write the structural formula of the organic product(s) formed when paracetamol tablet is refluxed with sodium hydroxide. [2]

(iv) Extensive research has been made to improve the effectiveness of the pain-relievers. Two proposals were made to modify aspirin.



Drug A



Drug B

Given that the melting points of drugs **A** and **B** are 179 °C and 154 °C respectively, account for the melting point in terms of structure and bonding. [2]

(v) State the relative solubility of drugs **A** and **B** in water. [1]

[Total: 20]

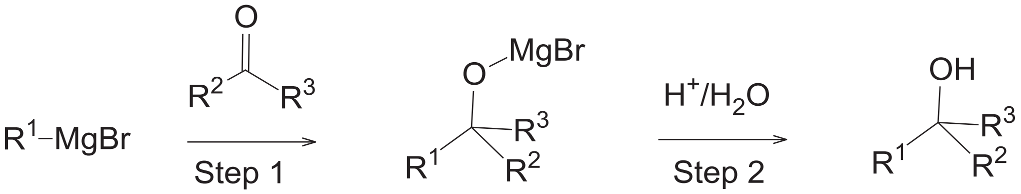
2 Halogens and their compounds can be toxic but some are essential for the human body's functioning and are used in daily products. The oxidising power of chlorine allows it to act as a good disinfectant.

(a) With the use of *Data Booklet*, explain why $FeCl_3$ exists but FeI_3 does not. [4]

(b) Grignard reaction is an important reaction which helps in lengthening the carbon chain. A Grignard reagent has a general formula of R-MgX where R is an alkyl or aryl group and is formed via the reaction of an alkyl or alkyl halide with magnesium powder.

$$\text{R}-\text{X} + \text{Mg} \rightarrow \underset{\text{Grignard reagent}}{\text{R}-\text{MgX}}$$

Carbonyl compounds react with Grignard reagent to increase the carbon chain.



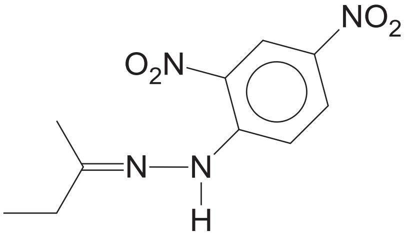
(i) In the formation of Grignard reagent, it is important to carry out the reaction in a dry environment. Suggest a reason. [1]

(ii) It was observed that the reaction to form the Grignard reagent is very slow at the start when magnesium powder is added to the alkyl halide in diethyl ether solvent. Suggest a reason. [1]

(iii) The addition of the Grignard reagent to the carbonyl typically proceeds through a six-membered ring transition state. For the reaction of each molecule of carbonyl compound, two molecules of Grignard reagents are involved in the formation of the transition state.

Suggest the transition state of Step **1** for the reaction between propanone and CH_3MgBr shown above. [1]

(iv) Suggest a four-step synthesis of compound **Q** from a carbonyl compound. State the reagents and conditions for each stage and draw structures of the intermediate organic products. The first two steps should involve the use of Grignard reaction between CH_3MgBr and a relevant carbonyl compound.



Compound Q

[5]

(c) **(i)** Describe what is observed when NaC*l* and NaBr reacts with concentrated sulfuric acid respectively. In each case, suggest the products of the reaction and write equations where appropriate. [2]

(ii) Explain any difference in their reactions with concentrated sulfuric acid. [1]

(d) When cold aqueous sodium hydroxide is added to a yellowish-green solution of chlorine in trichloromethane and shaken together, two immiscible colourless layers (aqueous layer and organic layer) were observed.

(i) State the type of reaction and give an equation, including state symbols, for this reaction.

[2]

(ii) Assuming that the starting reagents were added in stoichiometric ratio, suggest the chemical species found in the two immiscible colourless layers respectively. [2]

(e) One of the compounds that may be formed between chlorine and iodine is iodine tetrachloride, ICl_4^-. Construct a 'dot-and-cross diagram' to show the arrangement of electrons in ICl_4^-. [1]

[Total: 20]

3 **(a)** Hunsdiecker reaction is the organic reaction of silver salts of carboxylic acids with halogens to give organic halides.

The overall reaction is:

$$RCO_2Ag + Br_2 \rightarrow R\text{-}Br + CO_2 + AgBr$$

The reaction mechanism of the Hunsdiecker reaction is believed to involve organic radical intermediates.

The steps involved in the reaction mechanism are as follows:

1. The silver salt of the carboxylic acid quickly reacts with bromine to form the acyl hypohalite intermediate, RCO_2Br.
$$RCO_2Ag + Br_2 \rightarrow RCO_2Br + AgBr$$
2. The initiation step involves the formation of two radicals from the acyl hypohalite intermediate. One of which is bromine radical.
3. The first step of propagation involves the removal of CO_2 from the radical formed in step 2, forming R● and CO_2.
4. R● recombines with the acyl hypohalite intermediate to form the desired organic halide.

(i) Write equations to illustrate the reaction mechanism of Hunsdiecker reaction. [3]

(ii) Draw the structure of the organic product formed when $C_6H_5CH(CH_3)COOAg$ reacts with Br_2. [1]

(iii) The product in **(a)(ii)** displays optical isomerism as it has a chiral centre. Explain the term *chiral centre* and label the chiral centre in **(a)(ii)** with an asterix(*) sign**.** [2]

(iv) Chlorine and iodine can be used in place of bromine to react with silver salts of carboxylic acids.

A student wanted to compare the rate of reaction of iodine reacting with silver salts of carboxylic acids with that of bromine. However, he did not label the apparatus and ended up not able to tell which apparatus has the iodine-containing and bromine-containing organic products.

Describe a chemical test which can allow the student to derive correctly the apparatus with the iodine-containing and bromine-containing organic products respectively. Include the observations, if any. [4]

(b) Write the equations and state the observations of the following reactions, where appropriate.

- Reaction between sodium and oxygen
- Reaction between sulfur and oxygen [4]

(c) **(i)** The following table shows some thermochemistry data.

Reaction	**ΔH / kJ mol^{-1}**
enthalpy change of formation of HC*l*(g)	–92
first electron affinity of C*l*(g)	-364

Using the following data, and relevant data from the *Data Booklet*, construct an energy level diagram to calculate the standard enthalpy change for the following reaction.

$$H^+(g) + Cl^-(g) \rightarrow HCl(g)$$

[4]

(ii) The following reaction is expected to be an endothermic reaction.

$$HCl(g) \rightarrow H(g) + Cl(g)$$

However, the following reaction is an exothermic reaction.

$$HCl(g) + aq \rightarrow H^+(aq) + Cl^-(aq) \qquad \Delta H = -75 \text{ kJ mol}^{-1}$$

Explain the above observations. [2]

[Total: 20]

4 **(a)** **(i)** Heating compound **P**, $C_{10}H_{12}O_3$, with dilute sulfuric acid yields compound **Q**, $C_9H_{12}O_2$, and methanoic acid.

On treatment with dilute nitric acid, compound **Q** forms compound **R** with the formula $C_9H_{11}NO_4$. Compound **Q** also reacts with aqueous bromine to form compound **S**, $C_9H_9O_2Br_3$.

Heating compound **R** with tin in concentrated hydrochloric acid, followed by adding excess aqueous sodium hydroxide to the product gives compound **T**, $C_9H_{12}NO_2Na$.

Compound **T** turns hot acidified potassium dichromate solution green and forms compound **U**, $C_9H_{12}NO_3$. 1 mole of compound **U** reacts with 3 moles of aqueous sodium hydroxide. Compound **T** reacts with hot acidified potassium manganate(VII) and forms compound **V**, $C_8H_8NO_5$.

Suggest structures for compounds **P–V** and give an account of the chemistry involved.

[14]

(ii) Write the equation for the reaction of compound **P** being heated with dilute sulfuric acid. [1]

(b) Ester is an organic molecule which has many uses. Esters with low molecular masses are commonly used as fragrances and are found in essential oils. Phosphoesters form the backbone of DNA molecules.

(i) Given that methyl methanoate and ethyl methanoate are the simplest esters available, suggest a chemical test which can distinguish the two compounds. [3]

(ii) Acyl chlorides and esters are both derivatives of carboxylic acids.
Compare and account for the acidity of methyl methanoate and ethanoyl chloride. [2]

[Total: 20]

5 Vehicle frames are usually made from aluminium as it is lightweight and strong. However, the aluminium frames have to be made more resistant to corrosion as certain parts could be exposed to rainwater and acidic gases in vehicle exhaust.

The industrial process for the anodising of aluminium uses an inert platinum cathode and aqueous sulfuric acid as the electrolyte.

(a) Explain, in terms of the electrode reactions, how a piece of aluminium metal could be anodised to be more resistant to corrosion. [3]

(b) A current of 0.30 mA was switched on for 1 hour to anodise an aluminium frame. Calculate the amount of Al_2O_3 produced from the anodisation. [3]

(c) *Use of the Data Booklet is relevant to this question.*
Explain, stating any observations, how the electrode reactions would be different if

(i) the electrolyte was contaminated with copper(II) sulfate. [2]

(ii) the aluminium electrode was replaced with another platinum electrode. [2]

(d) Infra-red (IR) spectroscopy is a common technique used to identify functional groups in organic compounds and to study how the functional groups are affected by other substances.
When a beam of IR light of varying energies is shone at an organic compound, its functional groups can absorb certain energies characteristic to it. The energy of IR light is measured in wavenumbers, $\tilde{\nu}$, and is expressed as the reciprocal of its wavelength, λ, with units of cm^{-1}.

$$\tilde{\nu} = \frac{1}{\lambda}$$

For example, carbonyl functional groups absorbs IR light at the wavenumber range of 1680 to 1750 cm^{-1}, while alkyl groups absorb IR light at a wavenumber range of 2840 to 3095 cm^{-1}.

The gas-phase kinetics and mechanism of the hydrogenation of propanone using nickel catalyst was studied using IR spectroscopy. Dissociative adsorption of hydrogen gas on solid nickel is known to occur readily (step **I**). The adsorption of propanone gas onto the nickel catalyst was identified by a wavenumber peaking at 1620 cm^{-1}. The shift in wavenumber from 1680 to 1620 cm^{-1} confirms that it is the C=O functional group that is adsorbed onto the nickel catalyst and not the methyl groups (step **II**). However, no wavenumber shift corresponding to the alcohol functional group of the product, propan-2-ol, was found. This indicates that when the product is formed, it immediately desorbed from the catalyst (step **IV**).

Hence, the proposed mechanism for this reaction is as follows.

Step **I**: $2Ni + H_2 \rightleftharpoons 2Ni–H$

Step **II**: $Ni + CH_3COCH_3 \rightleftharpoons NiCH_3COCH_3$

Step **III**: $NiCH_3COCH_3 + NiH \rightleftharpoons NiCH_3COHCH_3 + Ni$

Step **IV**: $NiCH_3COHCH_3 + NiH \rightleftharpoons CH_3CH(OH)CH_3 + 2Ni$

When the experiment was conducted in a closed vessel of fixed volume at a constant temperature of 363 K, the following data was recorded.

Experiment	Partial pressure of hydrogen / kPa	Partial pressure of propanone / kPa	Relative rate
1	0.5	2.5	1
2	1	2.5	2
3	4	5	16
4	10	5	16
5	50	5	16

(i) Nickel is acting as a *heterogeneous* catalyst in this reaction.
Define the term *heterogeneous*. [1]

(ii) Based on experiments **1** to **3**, determine the order of reaction with respect to hydrogen and with respect to propanone.
Hence, deduce the rate equation for the hydrogenation of propanone. [3]

(iii) Based on your answer in **(ii)**, state which step in the proposed mechanism is the rate-determining step. [1]

(iv) Suggest a reason why the catalyst has to be used in the powdered form. [1]

(v) Hence, or otherwise, suggest a reason why the rate of reaction stopped increasing in experiments 4 and 5 when the partial pressure of hydrogen exceeded 4 kPa. [1]

(vi) Sketch an energy distribution diagram to explain how the rate of the reaction would have been different without the use of a catalyst. [3]

[Total: 20]

END OF PAPER 3

BLANK PAGE

Class	Adm No

Candidate Name: ____________________

H

millennia institute

2017 Preliminary Examinations II
Pre-University 3

H2 CHEMISTRY **9647/01**

Paper 1 Multiple Choice **20 Sept 2017**

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 **forty** 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 (40 marks)	

This question paper consists of **16** printed pages and **2** blank pages.

Section A

For each question there are four possible answers, **A**, **B**, **C**, and **D**. Choose the **one** you consider to be correct.

1 Dolomite is a carbonate-containing mineral with formula $Mg\boldsymbol{Z}(CO_3)_2$ where ***Z*** is a metal ion. It is insoluble in water but reacts with acids.

When 2.00 g of dolomite was completely dissolved in an excess of hydrochloric acid, 0.759 g of carbon dioxide was given off. What is the identity of the metal ***Z***?

A Ba **B** Ca **C** Ra **D** Sr

2 Sulfur dioxide gas is an irritant to the eyes and respiratory system. The maximum safe toleration level of sulfur dioxide in air is 0.014 mg dm^{-3}.

How many molecules of sulfur dioxide gas are present in 1 dm^3 of air at this toleration level?

A $\frac{0.014}{6.02 \times 10^{23}} \times 64.1$

B $\frac{0.014}{1000} \times \frac{1}{64.1} \times 6.02 \times 10^{23}$

C $\frac{0.014}{64.1} \times 6.02 \times 10^{23}$

D $\frac{0.014}{1000} \times 64.1 \times 6.02 \times 10^{23}$

3 The element technetium, Tc (mass number 99; atomic number 43), was discovered in 1937 by two Italian scientists, Segŕe and Perrier.

Under suitable conditions, technetium reacts with fluorine to form TcF_6.

Which of the following options shows the correct number of protons, neutrons and electrons in Tc^{6+}?

	number of protons	number of neutrons	number of electrons
A	43	43	56
B	43	56	37
C	49	43	37
D	43	56	49

4 Which of the following atoms has three unpaired electrons?

A Br **B** Co **C** Ga **D** Sc

5 Under standard conditions, water exists in the liquid state but hydrogen sulfide exists in the gaseous state.

Which of the following best explains this phenomenon?

A Water has a higher relative molecular mass than hydrogen sulfide.

B The O-H covalent bond in water is stronger than the S-H covalent bond in hydrogen sulfide.

C The hydrogen bonds between water molecules are stronger than the Van der Waals' forces between hydrogen sulfide molecules.

D Hydrogen sulfide has a more spherical structure compared to water.

6 Antimony, Sb, is in Group V of the Periodic Table. It was proposed that antimony is able to form SbF_4^{n-} anion, the structure of which is of square planar shape.

Which of the following shows the correct value of *n* and the oxidation number of Sb in this anion?

	value of *n*	**oxidation number of Sb**
A	1	+3
B	1	+5
C	3	+1
D	3	+3

7 **X** and **Y** are ideal gases that do not react with one another. The molar mass of **X** is twice that of **Y**.

If all measurements are taken at room temperature and pressure, which statement correctly describes **X** and **Y**?

A The volume occupied by 2 g of **X** is half that occupied by 2 g of **Y**.

B The mass of 5 dm^3 of **X** is half that of 5 dm^3 of **Y**.

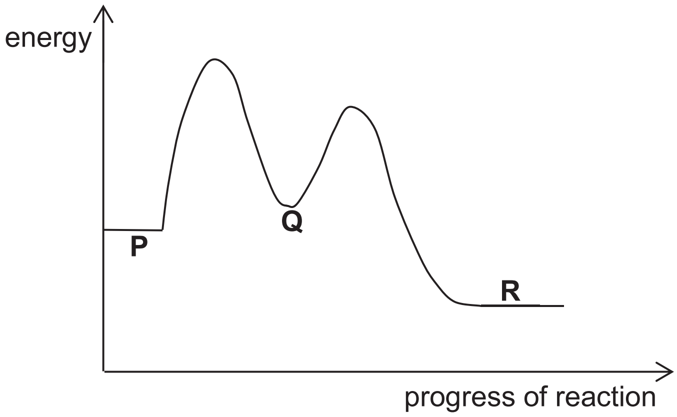
C The volume occupied by 2.5 g of **X** is equal to the volume occupied by 5 g of **Y**.

D On mixing 1 dm^3 of **X** with 1 dm^3 of **Y**, the partial pressure of **X** is twice that of **Y**.

8 The two steps in the conversion of compound **P** to compound **R** are shown below.

P → **Q** Step 1
Q → **R** Step 2

The energy profile of the reaction is shown below.



Which of the following statements about the reaction can be deduced from the information given?

A The enthalpy change for the reaction is endothermic.

B **Q** acts as a catalyst in the reaction.

C Step 1 is the rate determining step.

D **R** is thermodynamically less stable than **P**.

9 When liquid $SOCl_2$ is added to $Ba(OH)_2$, a vigorous reaction occurs and the temperature decreases from 25 °C to 5 °C.

What are the correct signs of ΔH, ΔS and ΔG for this reaction?

	ΔH	ΔS	ΔG
A	+	+	-
B	+	-	+
C	-	+	-
D	-	-	+

10 A sample of finely ground copper was contaminated with zinc powder.

Treatment of the sample with an excess of hydrochloric acid produced 120 cm^3 of hydrogen gas, measured at room temperature and pressure.

The remaining copper was then reacted with acidified potassium manganate(VII). It was found that 0.00424 mol of potassium manganate(VII) was required for complete oxidation of copper to copper(II) ions.

What is the percentage by mass of copper in the sample?

A 45.2% **B** 65.8% **C** 67.3% **D** 90.4%

11 Zinc(II) reacts with the complex anion hexacyanoferrate(III), $[Fe(CN)_6]^{3-}$, to give a sparingly soluble salt which dissociates in water according to the following equilibrium.

$$Zn_3[Fe(CN)_6]_2(s) \rightleftharpoons 3Zn^{2+}(aq) + 2[Fe(CN)_6]^{3-}(aq)$$

If the solubility product, K_{sp}, of $Zn_3[Fe(CN)_6]_2$ is X, what is the concentration of $Zn^{2+}(aq)$ at equilibrium?

A $\left(\frac{3X}{2}\right)^{\frac{1}{3}}$ **B** $\left(\frac{3X}{2}\right)^{\frac{1}{5}}$ **C** $\left(\frac{9X}{4}\right)^{\frac{1}{3}}$ **D** $\left(\frac{9X}{4}\right)^{\frac{1}{5}}$

12 Which of the following statements about the rate constant, *k*, of chemical reactions is **not** true?

A The rate constant increases when temperature increases.
B The rate constant increases when the concentration of the reactant increases.
C The rate constant decreases when the activation energy increases.
D The units of the rate constant depends on the overall order of reaction.

13 A Period 3 element forms an oxide that is soluble in both water and aqueous sodium hydroxide. Which of the following could be the identity of this element?

A aluminium **B** silicon **C** sodium **D** sulfur

14 In which of the following pairs is the radius of the first species greater than that of the second species?

A Mg, A*l* **B** Ca, Ba **C** Mg^{2+}, Na^{+} **D** K^{+}, Ar

15 Which of the following properties of the Group II elements and their compounds decreases down the group?

A Ease of oxidation of the elements
B Electronegativity of the elements
C Reactivity of elements with chlorine
D Thermal stability of nitrates

16 With reference to the chemistry of Group VII elements and their compounds, which of the following would be a correct prediction for astatine?

A Astatine reacts vigorously with hydrogen at room temperature.
B Astatine exists as a gas at room temperature.
C Astatine reacts with cold aqueous hydroxide to form AtO^{-} and At^{-}.
D Molten A*l*At_3 can conduct electricity.

17 Which of the following products is **least** likely to act as a ligand?

A AlH_3 **B** CO **C** C_2H_5OH **D** CH_3NH_2

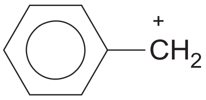
18 The use of *Data Booklet* is relevant to this question.

An element **G** has an atomic number of 23. Which of the following compounds of **G** is **not** likely to exist?

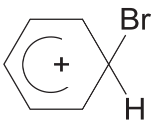
A $K\mathbf{G}O_3$ **B** $\mathbf{G}_2O_5$ **C** $K_2\mathbf{G}O_4$ **D** $\mathbf{G}OCl_2$

19 Which of the following species could be an intermediate in an electrophilic addition reaction?

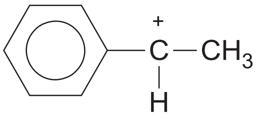
A



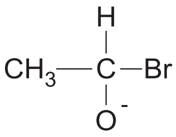
B



C



D



$CH_3CH(Br)O^-$

20 How many structural isomers with the molecular formula $C_5H_{10}O$ gives an orange precipitate with Brady's reagent and a yellow precipitate with alkaline aqueous iodine?

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

21 In an experiment, it was found that during the free radical substitution of alkanes, primary, secondary and tertiary hydrogen atoms were replaced by bromine atoms at different rates, as shown in the table below.

Reaction	**Relative Rate**
Primary : $RCH_3 \rightarrow RCH_2Br$	1
Secondary : $R_2CH_2 \rightarrow R_2CHBr$	8
Tertiary : $R_3CH \rightarrow R_3CBr$	20

With reference to the information given, which of the following shows the 2 products obtained from the reaction of 2,3-dimethylbutane with bromine gas under UV light and their relative ratio?

A $(CH_3)_2CHCH(CH_3)CH_2Br$: $(CH_3)_2CBrCH(CH_3)_2$ = 3 : 10
B $(CH_3)_2CHCH(CH_3)CH_2Br$: $(CH_3)_2CBrCH(CH_3)_2$ = 1 : 20
C $(CH_3)_3CCH_2CH_2Br$: $(CH_3)_3CCHBrCH_3$ = 3 : 8
D $(CH_3)_3CCH_2CH_2Br$: $(CH_3)_3CCHBrCH_3$ = 3 : 20

22 Concentrated ammonia was heated in a sealed tube with excess bromoethane. Which of the following products will **not** be formed?

A C_2H_7N **B** C_3H_9N **C** $C_4H_{11}N$ **D** $C_8H_{20}NBr$

23 Which of the following statements about phenol is **incorrect**?

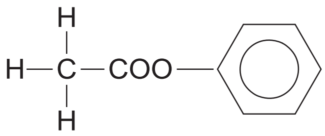
A Acidic hydrolysis of phenylethanoate will give ethanoic acid and phenol.
B Phenol reacts with ethanoic acid to give phenylethanoate.
C Phenol gives violet colouration with neutral $FeCl_3$.
D Phenol gives a white precipitate with aqueous bromine.

24 Several reactions that involve the ‘insertion’ of carbon monoxide into organic molecules are of industrial importance. One of such reactions is the synthesis of hydroxyethanoic acid from methanal.

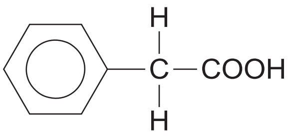
$$CH_2O + CO + H_2O \rightarrow CH_2(OH)CO_2H$$

Which of the following shows the product formed when benzaldehyde undergoes a similar reaction with carbon monoxide in the presence of water?

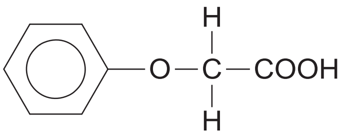
A



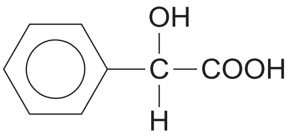
B



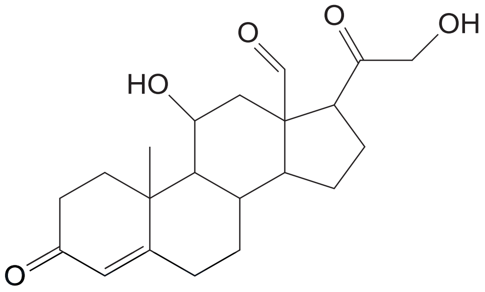
C



D



25 Aldosterone is a hormone essential for sodium conservation in the kidney, salivary glands and colon.



aldosterone

How many chiral carbons are there in the product of the reaction between aldosterone and $LiAlH_4$ in dry ether?

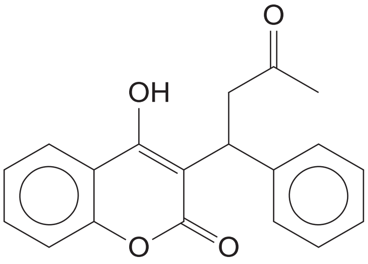
A 7

B 8

C 9

D 10

26 Warfarin is a drug used as an anticoagulant to prevent stroke in people who have heart disease.



warfarin

Which of the following statements is true about warfarin?

A 1 mole of warfarin reacts with 2 moles of 2,4-dinitrophenylhydrazine.

B Warfarin can undergo substitution reaction with $SOCl_2$.

C Warfarin reacts with I_2 and dilute NaOH to give a colourless solution.

D There are 16 sp^2 hybridised carbon atoms in 1 molecule of warfarin.

27 Which of the following amino acids is **not** involved in the formation of proteins in the body?

A $H_2NCH(COOH)CH(CH_3)_2$

B $H_2NCH(CH_3)CH_2COOH$

C $H_2NCH(CH_2SH)COOH$

D $H_2NCH(CH_2C_6H_5)COOH$

28 Why are amides less basic than amines?

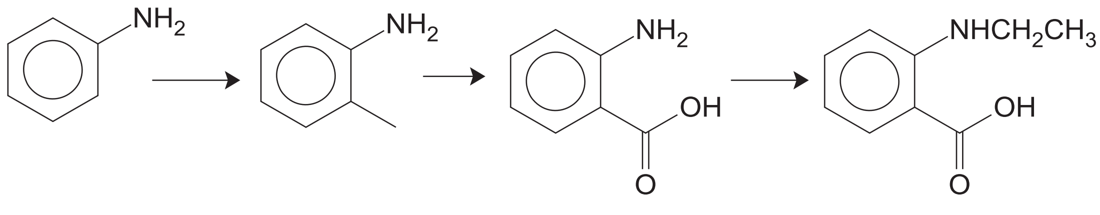
A Amides form a zwitterion, causing its nitrogen atom to carry a positive charge.

B The amide carbonyl group withdraws lone pair of electrons from nitrogen atom, releasing the H atom on NH_2 as proton.

C The C-N bond in amides is stronger than that in amines.

D The resonance structure of amides causes the movement of a pair of electrons from the nitrogen atom to the oxygen atom.

29 The reaction scheme below shows the synthesis of compound **P** from phenylamine.



P

Which of the following types of reaction is **not** involved in the reaction scheme shown?

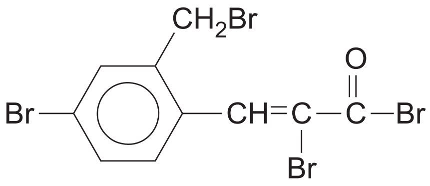
A electrophilic substitution

B nucleophilic addition

C nucleophilic substitution

D oxidation

30 The structure of compound **S** is shown below.



S

0.01 mol of **S** is reacted with excess hot ethanolic silver nitrate. What is the mass of the silver bromide formed from the reaction?

A 1.878 g

B 3.758 g

C 5.634 g

D 7.512 g

Section B

[Turn over

For each of the questions in this section, one or more of the three numbered statements **1** to **3** may be correct.
Decide whether each of the statements is or is not correct (you may find it helpful to put a tick against the statements that you consider to be correct).

The responses **A** to **D** should be selected on the basis of

A	**B**	**C**	**D**
1, **2** and **3** are correct	**1** and **2** only are correct	**2** and **3** only are correct	**1** only is correct

No other combination of statements is used as a correct response.

31 Which of the following types of bonding are present in $[Fe(H_2O)_5(SCN)]Cl_2$?

1 covalent bonding
2 dative bonding
3 ionic bonding

32 Which of the following are **incorrect** assumptions made in the kinetic theory about an ideal gas?

1 The gaseous particles are in constant random motion.
2 The gaseous particles have constant interactions with one another.
3 The volume of the container is negligible.

33 When 290 C of electricity are passed through a molten compound of a metal, 0.001 mol of atoms of the metal is deposited at the cathode.

What could the metal be?

1 aluminium
2 copper
3 silver

34 The following reaction between carbon monoxide and steam occurs in the presence of a suitable catalyst.

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

The standard enthalpy changes of formation of the compounds involved in the reaction are given below.

Compound	**Standard enthalpy change of formation / kJ mol^{-1}**
$CO(g)$	-111
$H_2O(g)$	-242
$CO_2(g)$	-394

Which of the following changes would increase the yield of $H_2(g)$ in the reaction above?

1 decrease in temperature
2 adding sodium hydroxide into the system
3 adding more catalyst into the system

The responses **A** to **D** should be selected on the basis of

A	**B**	**C**	**D**
1, **2** and **3** are correct	**1** and **2** only are correct	**2** and **3** only are correct	**1** only is correct

No other combination of statements is used as a correct response.

35 Which of the following statements are true for the hydrogen halides HCl, HBr and HI?

1 Hydrogen iodide is the strongest acid.
2 Hydrogen iodide has the lowest thermal stability.
3 Hydrogen chloride has the lowest boiling point.

36 Which of the following properties of copper and calcium are likely to differ?

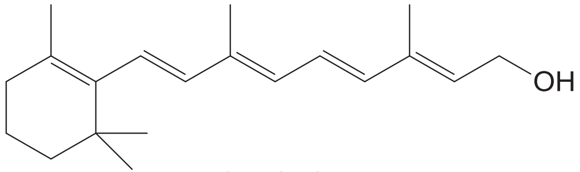
1 density
2 ability to display variable oxidation states
3 reactivity with acid

37 In the catalytic converter in the exhaust system of a car, harmful gases are converted to less harmful ones.

Which of the following processes take place in the catalytic converter?

1 hydrocarbons + oxides of nitrogen → carbon dioxide + water + nitrogen
2 carbon monoxide + oxides of nitrogen → carbon dioxide + nitrogen
3 carbon dioxide + oxides of nitrogen → carbon + nitrogen + water

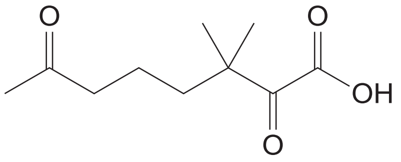
38 The structure of vitamin A is shown below.



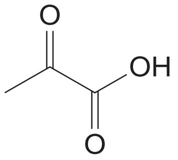
vitamin A

Which of the following are possible products of the reaction of vitamin A with excess hot acidified potassium manganate(VII)?

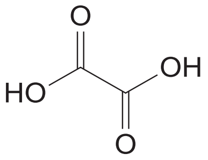
1



2



3



39 Which compounds reacts with an excess of sodium metal to give one mole of H_2(g) per mole of the compound?

1 $CH_3CH(OH)CH_2COOH$

2 $CH_3CH_2COCH(OH)COOH$

3 $CH_3CH(OH)CH_2CHO$

[Turn over

The responses **A** to **D** should be selected on the basis of

A	B	C	D
1, **2** and **3** are correct	**1** and **2** only are correct	**2** and **3** only are correct	**1** only is correct

No other combination of statements is used as a correct response.

40 Hippuric acid can be produced by adding benzoyl chloride to aminoethanoic acid. Which changes in bonding occur during this synthesis?

hippuric acid

1 A carbon-chlorine bond is broken.
2 A carbon-nitrogen bond is formed.
3 A hydrogen-chlorine bond is formed.

END OF PAPER 1

BLANK PAGE

BLANK PAGE

	Class	Adm No
Candidate Name: ____________________		

H

millennia institute

2017 Preliminary Examination II
Pre-university 3

H2 CHEMISTRY **9647/02**

Paper 2 Structured Questions **12th Sept 2017**

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	12	14	15	11	20	72

This question paper consists of 11 printed pages and 1 blank page.

1 Planning (P)

Hydrogen peroxide undergoes a redox reaction with acidified $KMnO_4$ as follows:

$$2MnO_4^-(aq) + 5H_2O_2(aq) + 6H^+(aq) \rightarrow 2Mn^{2+}(aq) + 5O_2(aq) + 8H_2O(l)$$

By itself, hydrogen peroxide decomposes slowly in accordance to the following equation:

$$2H_2O_2(aq) \rightarrow 2H_2O(l) + O_2(g)$$

It is found that the decomposition reaction is first order with respect to H_2O_2. The reaction can be accelerated by using solid manganese(IV) oxide as the catalyst.

(a) Write the rate equation for the decomposition of hydrogen peroxide.

.... [1]

Rate = $k[H_2O_2]$

(b) Using the information given, you are required to write a plan to determine the rate constant for the decomposition of hydrogen peroxide using the continuous titration method.

You may also assume that you are provided with:

- 250 cm^3 of 0.0100 mol dm^{-3} acidified $KMnO_4$;
- 250 cm^3 of 0.0250 mol dm^{-3} H_2O_2 solution;
- Solid manganese(IV) oxide;
- 25.0 cm^3 pipette;
- Stopwatch;
- the apparatus normally found in a school or college laboratory.

Your plan should include:

- practical details of how you would
  - determine if dilution of the reaction mixture is needed for titration against H_2O_2;
  - ensure the reaction is complete;
  - carry out the titration;
- a sketch of the graph you would expect to obtain;
- brief, but specific, details of how the results would then be used to obtain
  - the initial rate of reaction of decomposition in mol dm^{-3} $min^{-1,}$
  - the rate constant for the reaction

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

.... [11]

[Total: 12 marks]

$2MnO_4^-(aq) + 5H_2O_2(aq) + 6H^+(aq) \rightarrow 2Mn^{2+}(aq) + 5O_2(aq) + 8H_2O(l)$

Assuming that 25 cm^3 of 0.0250 mol dm^{-3} of H_2O_2 is used,

Amount of H_2O_2 present = 25/1000 x 0.025 = 0.000625 mol

Amount of MnO_4^- needed = 2/5 x 0.000625 = 0.00025 mol

Vol. of $KMnO_4$ needed = 0.00025/0.01 = 0.025 dm^3 ;

Since two volumes used are within the capacity of the apparatus used, no dilution of the solutions needed;

Procedure:

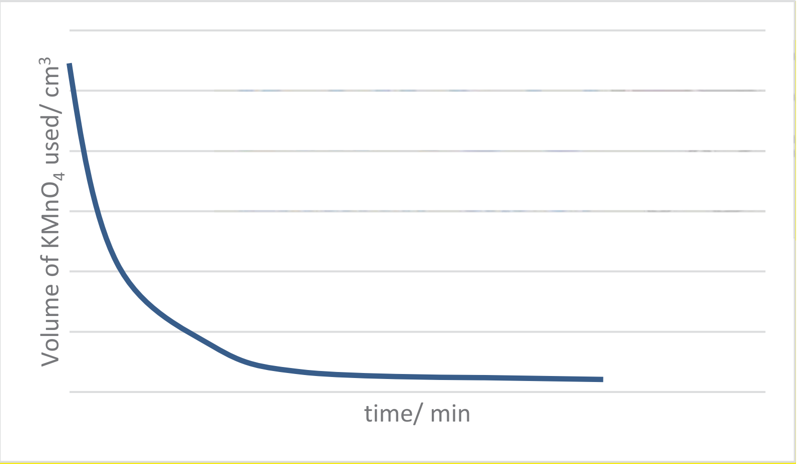
1. From the 250 cm^3 of 0.0250 mol dm^{-3} H_2O_2 solution, pipette 25.0 cm^3 into another conical flask.
2. Fill up the 50.00 cm^3 burette with the standard acidified $KMnO_4$ solution.
3. Take the initial burette reading.
4. Titrate the solution with acidified $KMnO_4$. Swirl continuously during the addition of the titrant.
5. Toward the end-point, add the $KMnO_4$ solution dropwise and swirl. Stop the addition of the titrant when one drop of titrant causes the solution in the conical flask to change from colourless to pale pink.
6. Record the final burette reading. Calculate the volume of acidified $KMnO_4$ solution needed to react with the hydrogen peroxide solution. (This titre volume would give us the concentration of the H_2O_2 solution at that instant of decomposition).

7. Add some solid manganese(IV) oxide into the 500 cm^3 conical flask containing the H_2O_2 solution. Start the stopwatch. Swirl gently.
8. At every 1 min (student can put a range from 30 s to 10 min) interval, pipette 25.0 cm^3 aliquots of the solution containing 20 cm^3 of cold water.
9. Repeat steps 2 to 7 at 1st, 2nd, 3rd, 4th and 5th min.

Table of results

Time/min	**0**	**1**	**2**	**3**	**4**	**5**
Initial burette reading/ cm^3						
Final burette reading/ cm^3						
Titre volume/ cm^3						

Sketch of graph



Since the gradient of the graph at t = 0 is ***x*** cm^3 min^{-1}, Initial rate of reaction = ($\boldsymbol{x}$/1000 x 0.01 x 5/2) ÷ 25/1000 mol dm^{-3} min^{-1}

Since rate = k [H_2O_2],

k = [($\boldsymbol{x}$/1000 x 0.01 x 5/2) ÷ 25/1000] / 0.025

2 Hydrogen iodide can undergo decomposition to give a mixture of hydrogen gas and iodine gas.

$$2HI(g) \rightleftharpoons H_2(g) + I_2(g) \qquad \Delta H = +12.0 \text{ kJ mol}^{-1}$$

(a) State Le Chatelier's Principle.

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

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

Le Chatelier's Principle states that when a system in equilibrium is disturbed, the position of the equilibrium will shift in a direction that tends to reduce that change so as to re-establish the equilibrium.

(b) Predict and explain the effect of the following changes on the position of the above equilibrium, if any.

(i) Increasing the temperature

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

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

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

When temperature of the system is increased, by Le Chatelier's Principle, the equilibrium position shifts to the right towards the endothermic reaction to remove the excess heat

(ii) Reducing the pressure

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

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

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

When pressure is reduced, by Le Chatelier's Principle, the equilibrium position does not shift as the number of gaseous particles on both the reactants and products are the same.

(iii) Addition of catalyst

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

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

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

Catalyst catalyses both forward and backward reactions to the same extent in a reversible reaction, hence there is no shift in equilibrium position.

(c) When 1.4 mol of hydrogen iodide is heated in a closed vessel at 550 K, the total pressure at equilibrium was 6 atm.

Given that the mole ratio of hydrogen iodide to iodine gas at equilibrium is 9:4, calculate the equilibrium constant, K_p, at 550 K.

[3]

$P_{H2} = P_{I2} = (4/17) \times 6 = 1.41$ atm ;

$P_{HI} = (9/17) \times 6 = 3.18$ atm ;

$K_p = (1.411)^2 / (3.176)^2 = 0.198$;

(d) Hydrogen chloride and hydrogen bromide also undergoes a similar decomposition to give hydrogen gas and its respective halogens.

Describe the trend in the volatility and colours of the halogens.

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

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

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

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

Volatility decreases down the group for halogens; colour intensity increases down the group;

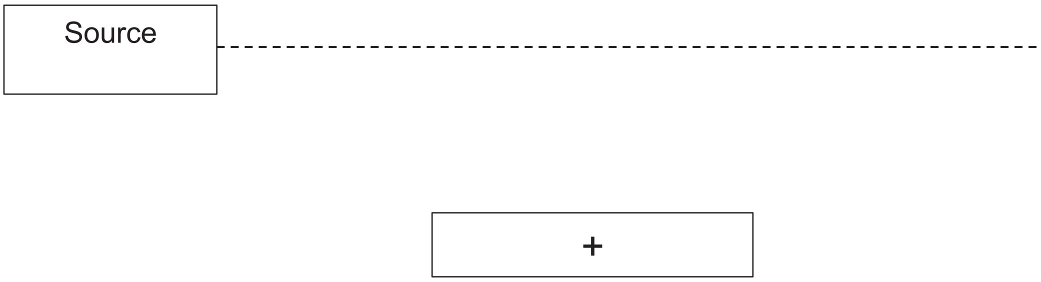
Chlorine: yellowish-green gas

Bromine: reddish-brown liquid

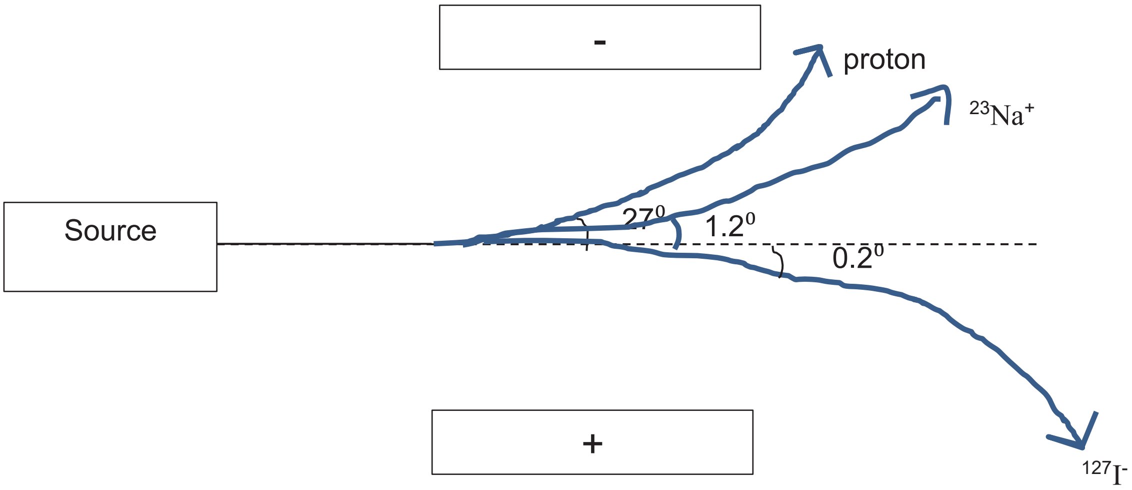
(e) It was observed that a beam of protons gives an angle of 27° in the following electric field.

Indicate on the diagram below how a beam of protons, $^{127}I^-$ and $^{23}Na^+$ ions, travelling at the same speed, behave in the same electric field. Calculate the respective angles of deflection.

-



[3]



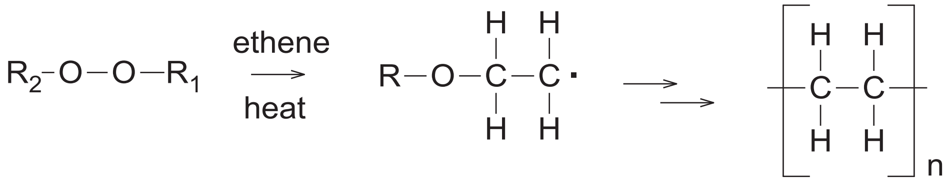
Angle of deflection for H^+ = 1/1 x 27° = 27°

Angle of deflection for Na^+ = 1/23 x 27° = 1.2°

Angle of deflection for I^- = 1/127 x 27° = 0.2°

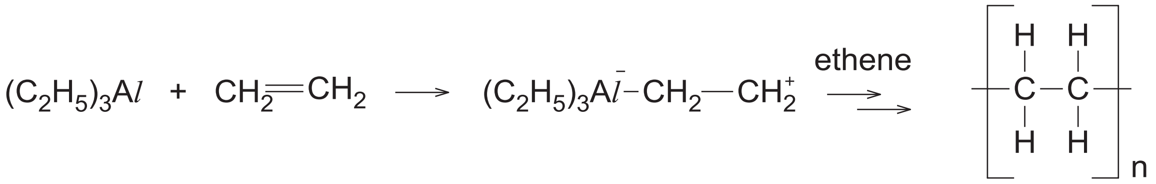
[Total: 14]

3 In 1933, chemists in Britain discovered that when ethene was subjected to high pressures in the presence of a trace amount of oxygen or organic peroxide, it produced low-density poly(ethene) (LDPE). The radical mechanism using organic peroxides is shown below.



LDPE

Using triethylaluminium, also known as Ziegler-Natta catalyst, developed by Karl Ziegler and Giulio Natta in 1953, ethene can be polymerised at much lower pressures to produce high-density poly(ethene) (HDPE). In the first step, triethylaluminium can accept the pair of π electrons of ethene to form a carbocation which is very similar to that found in the usual electrophilic addition reactions. This carbocation then undergoes an addition reaction with another ethene molecule. Eventually, long chains of ethene units form.



HDPE

The major differences between the structures of LDPE and HDPE are that:

- the average chain length of LDPE is much shorter than that of HDPE
- the chains of LDPE are branched, while the chains of HDPE are unbranched.

The table below compares the physical properties of LDPE and HDPE.

Property	**Polymer**	
	LDPE	**HDPE**
Density	Low	High
Melting Point	Approximately 130 °C	Approximately 160 °C
Tensile strength	Low	High
Flexibility	Very flexible	Much more rigid

(a) **(i)** Using structure and bonding, explain the difference in melting point between LDPE and HDPE.

………

……………………………………………………………………………………………

……………………………………………………………………………………………

…………………………………………………………………………………… [2]

Both have simple molecular structures with weak td-id forces of attraction between molecules. HDPE have are straight chain molecules which have **larger** surface area of contact between adjacent molecules than the branched-chain LDPE which is more spherical and packed less closely together. Hence, more energy is needed to break the more extensive td-id forces between HDPE, resulting in higher melting point.

Or

Both have simple molecular structures with weak td-id forces of attraction between molecules. HDPE has a longer chain length as compared to LDPE, thus resulting in a larger electron cloud size. Hence, more energy is needed to break the more extensive td-id forces between HDPE, resulting in higher melting point.

(ii) Suggest why LDPE has a lower density than HDPE.

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

…………………………………………………………………………………… [1]

Since HDPE chains are unbranched, they have a more regular arrangement, thus giving a more compact arrangement.

(b) **(i)** Write an equation to represent the first step in the radical mechanism.

…………………………………………………………………………………… [1]

$$R_2{-}O{-}O{-}R_1 \longrightarrow R_2{-}\dot{O} + \dot{O}{-}R_1$$

(ii) With reference to the mechanism given, explain why the production of LDPE only starts upon heating.

……………………………………………………………………………………………

…………………………………………………………………………………… [1]

Heat is needed to cause homolytic fission of the O-O bond of organic peroxide to produce the alkoxy radicals that will react with the ethene molecules.

(iii) Suggest why the chains of LDPE are branched.

…………………………………………………………………………………………………

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

During propagation step, due to the high reactivity of organic free radicals, the primary radical can abstract the hydrogen from the carbon atom in the middle of the chain.

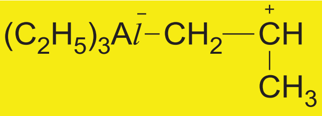
(c) **(i)** State the role of triethylaluminium in the reaction using Ziegler-Natta catalysts.

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

Triethylaluminium acts as an electrophile.

(ii) Similar to ethene, propene can be polymerised using the Ziegler-Natta catalysts. Show the structure of the carbocation intermediate formed in the first step.

[1]



$(C_2H_5)_3\overset{-}{Al}-CH_2-\underset{CH_3}{\overset{+}{C}H}$

(d) **Use the table of characteristics values for the infra-red absorption in the Data Booklet to answer this question.**

Infra-red absorptions can be used to identify functional groups in organic compounds. For example, ethanol shows absorptions at 1000-1300 cm^{-1} and 3230-3550 cm^{-1}.

Use the table to identify the infra-red absorption range that will be shown by

(i) Ethene but not by poly(ethene)

…………………………………………… cm^{-1}

1610-1680 cm^{-1}

(ii) Propyl ethanoate but not by propene

…………………………………………… cm^{-1}

1000-1300 and 1680-1750 cm^{-1}

[3]

(e) The four methods used to dispose polymers are incineration, recycling, depolymerisation and bacterial fermentation.

(i) Combustion of the polymers during incineration can lead to the formation of pollutants such as carbon monoxide which is toxic to humans, if the conditions are not carefully controlled.

In terms of the bonding involved, explain how carbon monoxide prevents oxygen from being transported around the body.

…………………………………………………………………………………………………

…………………………………………………………………………………………………

…………………………………………………………………………………………………

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

Oxygen molecule is reversibly bonded to the haem group.

⇒ the Fe^{2+}-O_2 bond is weak allowing oxygen to be easily given up to the cells.

In the presence of CO, which is a stronger ligand than O_2, ligand exchange takes place and CO is strongly and irreversibly adsorbed at this site, destroying haemoglobin's oxygen carrying capacity.

(ii) State two advantages of recycling.

…………………………………………………………………………………………………

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

Recycling saves energy; recycling conserves the resources needed to process the new polymers; recycling produces less pollution to the air, land and water.

[Total: 15]

4 Iron is a transition element in Period 4 of the Periodic Table.

(a) Explain what is meant by a transition element.

.... [1]

A transition element is a **d-block element** which forms **at least one simple ion**, in compounds, with a **partially filled d-subshell**.

(b) Most iron oxide samples have a mole ratio of iron to oxygen in a range between 0.84 : 1 to 0.96 : 1. Suggest why these samples have variable compositions.

....

.... [1]

Since iron can exist in both +2 and +3 oxidation states, some of the iron (II) ions in iron (II) oxide is oxidised to iron(III) ions.

(c) The reaction between peroxodisulfate ions, $S_2O_8^{2-}$ and iodide ions is very slow at room conditions, while addition of iron(III) ions can speed up the reaction rate.

(i) Suggest why the reaction between $S_2O_8^{2-}$ and iodide ions is very slow.

....

.... [1]

The reaction involves collision of ions of the same charge, $S_2O_8^{2-}$ and I^-, hence the number of effective collisions are small due to electronic repulsion.

(ii) Construct ionic equations to outline the catalytic role of iron(III) ions in the reaction.

....

.... [2]

$2Fe^{3+} + 2I^- \rightarrow 2Fe^{2+} + I_2$

$2Fe^{2+} + S_2O_8^{2-} \rightarrow 2Fe^{3+} + 2SO_4^{2-}$

(iii) State another iron species that can also act as a catalyst for the reaction.

.... [1]

Fe^{2+} ion

(d) When thiocyanate ligand, SCN^-, is added to the yellow solution of $FeCl_3$, a deep red solution **H** is obtained.

(i) Suggest the formula of the complex responsible for the deep red solution **H**.

.... [1]

$[Fe(SCN)(H_2O)_5]^{2+}$

(ii) State the type of reaction when $FeCl_3$ forms **H**.

.... [1]

Ligand exchange reaction

(iii) Explain why aqueous Fe^{3+} solutions are coloured.

....

....

....

.... [3]

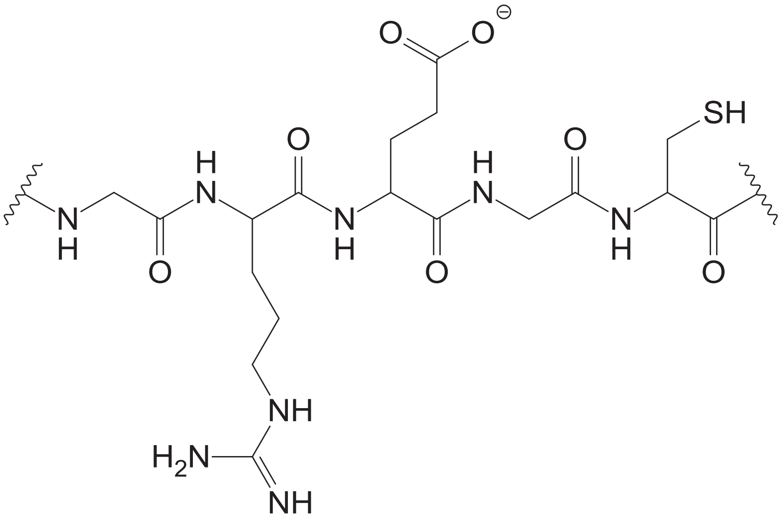
For Fe^{3+}(aq), in the presence of ligands, partially-filled 3d orbitals in vanadium ions are split into two levels (i.e. become non–degenerate) with an energy gap, ΔE, falling within the energy range of the visible spectrum of light.

When light falls on the complex, a particular wavelength of light corresponding to ΔE is absorbed and this causes the electrons from the lower energy d orbitals to be promoted to a vacant higher energy level d orbital; a process known as the d–d electron transition. The colour observed is the complement of the colour absorbed.

[Total: 11]

5 The pancreas produces the protein insulin that regulates the metabolism of carbohydrates, fats and proteins.

The structure of a portion of the insulin molecule is shown below. This portion contains a number of amino acids.



(a) Describe the tertiary structure of insulin.

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

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

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

Tertiary structure refers to the overall 3D conformation of the protein involving folding or coiling of the chains via side-chain (R groups) interactions. Side-chain interactions which hold the tertiary structure in its shape are ionic bonds, disulfide, hydrogen bonding or van der Waals interactions;

(b) **(i)** What is meant by the term *denaturation*?

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

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

Denaturation of proteins involves the disruption of the secondary, tertiary and quarternary structures as these are held together by relatively weak attractions, forming random coil of polypeptide chain.

(ii) Suggest a brief outline of one method by which insulin may be denatured.

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

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

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

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

Addition of H^+ or OH^- protonates or deprotonates the ionic R groups and hence disrupts the polar side chain interactions such as ionic bonds and hydrogen bonds holding the tertiary and quaternary structure of the protein. OR

When heat is applied, weak bonds, such as Van der Waals' forces and hydrogen bonds, holding together the quaternary, tertiary and secondary structures of the protein can be broken.

The increase in temperature increases the vibration of molecules, and the molecules can vibrate so strongly that the intermolecular interactions of the α–amino acid residues are destroyed causing denaturation. OR

Mechanical actions such as beating, whipping, shaking and kneading can also disrupt the intramolecular interactions within the protein molecules, destabilising the protein structure leading to the loss of the tertiary and secondary structures and hence denaturation. OR

The addition of heavy metal ions such as Ag^+, Hg^+, and As^+ which can combine permanently and preferentially with the sulfur atoms in -SH groups, destroying the disulfide (S-S) covalent bonds and thus changing the structure.

Heavy metals form salts or complex ions, hence breaking the ionic interactions

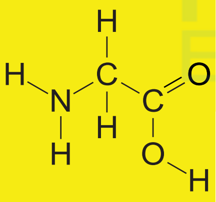
(iii) State the reagent and conditions required for complete hydrolysis of protein in the laboratory.

.... [1]

Heat under reflux with 6 mol dm^{-3} HC*l* for 6 hours

(iv) One of these amino acid residues are present more than once in the above portion of the insulin molecule. Draw a displayed formula for this amino acid residue.

[1]



(v) Explain, with the aid of equations, how the zwitterionic form of the amino acid in **(b)(iv)** act as a buffer.

.... [2]

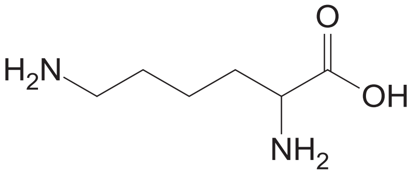
When little amount of acid is added,

$^+H_3NCH_2COO^- + H^+ \rightarrow {}^+H_3NCH_2COOH$

When little amount of base is added,

$^+H_3NCH_2COO^- + OH^- \rightarrow H_2NCH_2COO^- + H_2O$

(c) Lysine is a α-amino acid that is used in the biosynthesis of proteins.



(i) Explain what is meant by the term pK_a as applied to a weak acid H*A*.

....

.... [1]

$pK_a = -\log K_a$

(ii) State the functional groups present in lysine.

.... [1]

Primary amine and carboxylic acid

(iii) There are three pK_a values associated with lysine: 2.1, 8.9 and 10.5.

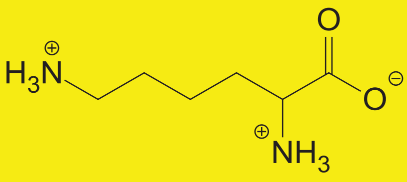
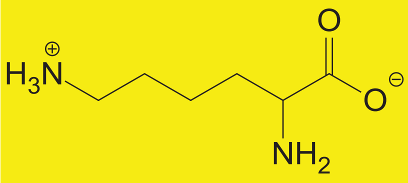
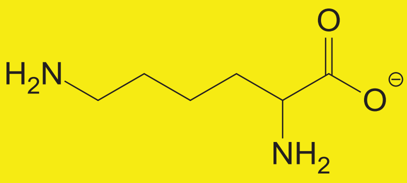
Make use of these pK_a values to suggest the major species present in the solutions of the amino acid with the following pH values.

pH 1	**pH 4**
	Need a home tutor? Visit smiletutor.sg

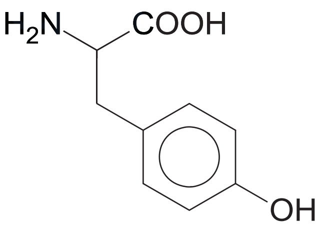
[Turn over

pH 9	pH 12

[4]

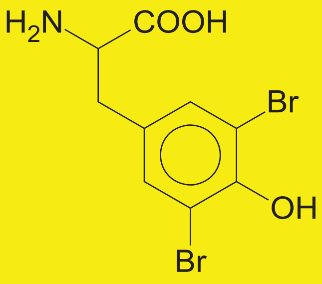
pH 1	pH 4
	
pH 9	**pH 12**
	

(d) Tyrosine is another amino acid present in insulin.



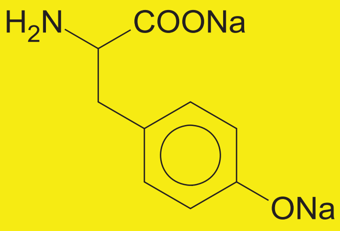
Draw the organic products when tyrosine undergoes reaction with

(i) Br_2(aq)



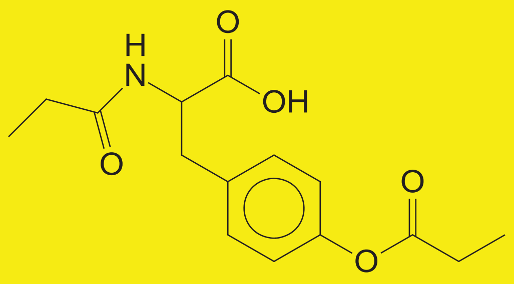
[1]

(ii) NaOH(aq)



[1]

(iii) excess CH_3CH_2COCl



[1]

(e) State the type of reactions for reaction with

Br_2(aq) …………………………………………………

NaOH(aq) ………………………………………………… [2]

Reaction with Br_2(aq): electrophilic substitution

Reaction with NaOH(aq): acid-base reaction

[Total: 20]

BLANK PAGE

BLANK PAGE

Class Adm No

Candidate Name: ____________________

H

millennia institute

2017 Preliminary Examination II

Pre-University 3

H2 CHEMISTRY **9647/03**

Paper 3 Free Response **15th Sept 2017**

2 hours

Candidates answer on separate paper.

Additional materials: Answer Paper
Data Booklet

READ THESE INSTRUCTIONS FIRST

Do not turn over this question paper until you are told to do so

Write your name, class and admission number on all the work you hand in.

Write in dark blue or black pen.

You may use an HB pencil for any diagrams or graphs.

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

Answer any **four** questions.

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	1	2	3	4	5	Total
Marks	20	20	20	20	20	80

1 **(a)** Graphite is a naturally-occurring form of crystalline carbon and is found in metamorphic and igneous rocks. Graphite is extremely soft and cleaves with very light pressure yet it is extremely resistant to heat and nearly inert in contact with almost any other material. These extreme properties give it a wide range of uses in metallurgy and manufacturing.

(i) With reference to the structure, account for the following properties of graphite.

- Soft
- Heat resistant and inert

[3]

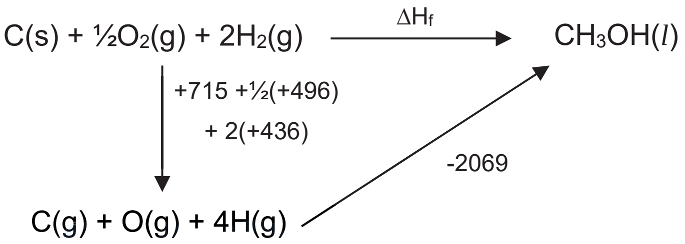
Graphite has a **giant covalent structure**(;). The bonding between the layers is **weak temporary dipole – induced dipole forces(;)** which can be **easily overcomed**, allowing the layers to **slide over** each other easily and thus graphite is soft.

Large amount of thermal energy is required to break the **strong covalent bonds**(;) between the carbon atoms within the layers which account for its resistance to heat.

(ii) The following table shows some thermochemistry data.

Reaction	**Δ*H* / kJ mol^{-1}**
Standard enthalpy change of atomisation of carbon	+715
Enthalpy change of 4H(g) + O(g) + C(g) → $CH_3OH(l)$	-2069

With the use of relevant data from the *Data Booklet* and the above information, calculate the enthalpy change of formation of methanol. [3]



ΔH_f = +715 +½(+496) + 2(+436)+(-2069) = -234 kJ mol^{-1}

(b) A butane burner is used to heat the air in a hot air balloon. The hot air balloon has a volume of 2.1 m^3 and its volume does not change when the enclosed air is heated.

(i) Using the ideal gas equation, calculate the amount of gas molecules the balloon contains at temperature 800 K and a pressure of 1.0 x10^6 Pa. [1]

$pV=nRT$

$1.0 \times 10^6 \times 2.1 = n \times 8.31 \times 800$

n= 316 mol

(ii) Hence calculate the mass of air it contains, assuming an average relative molecular mass of 29. [1]

Mass = 315.9x29 = 9160g

(iii) The standard enthalpy change of combustion of butane is -2877.5 kJ mol^{-1}. It requires 1.0 J of energy to raise the temperature of 1.0 g of air by 1.0 K.

Using your answer in **(b)(ii)**, calculate the mass of butane that needs to be burnt to raise the temperature of the air in the balloon by 20 K. Assume that the hot air balloon is a closed system. [2]

Q=mcΔT=9160x1.0x20=183213 J

$$\Delta H = -\frac{Q}{Amt\ of\ butane} \times coeff$$

$$-2877.5 = -\frac{183212 \div 1000}{amt\ of\ butane} \times 1$$

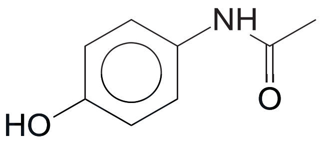
Amount of butane =0.06367 mol

Mass of butane = 0.06367x(4x12.0+1.0x10) = 3.69g

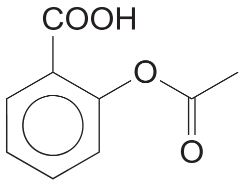
(iv) The actual mass of butane that needs to be burnt to raise the temperature of the air in the balloon by 20 K was found to be 3.81 g. Suggest why this differs from your answer in **(b) (iii).** [1]

More butane needs to be burnt due to heat loss.

(c) Paracetamol and aspirin are effective at pain and fever relief due to their ability to dissolve quickly in the blood stream and are soluble in fatty compounds found in cell membrane.



Paracetamol



Aspirin

(i) Account for these properties based on the structure and bonding of aspirin. [2]

Aspirin has a simple molecular structure. The presence of COOH forms ion-dipole interactions(when hydrolysed to form COO$^-$) / hydrogen bonding with water.

The presence of benzene ring forms favourable van der Waals' forces with the fatty compounds which results in the solubility.

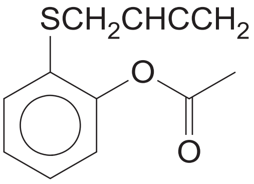
(ii) One of the pain relievers cause more stomach irritation than the other. With reference to the functional groups present, suggest and explain the pain reliever that you will recommend to someone who suffers from gastric bleeding. [2]

Paracetamol causes less stomach irritation and is recommended(;) as the acidic –COOH group of aspirin will attack the lining of the stomach walls, causing irritation.(;)

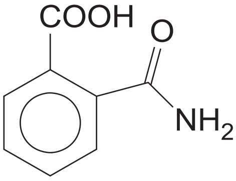
(iii) Write the structural formula of the organic product(s) formed when paracetamol tablet is refluxed with sodium hydroxide. [2]

and $CH_3COO^-Na^+$

(iv) Extensive research has been made to improve the effectiveness of the pain-relievers. Two proposals were made to modify aspirin.



Drug A



Drug B

Given that the melting points of Drugs **A** and **B** are 179 °C and 154 °C respectively, account for the melting point in terms of structure and bonding. [2]

Both drugs have simple molecular structure. Drug A has a higher melting point as the van der Waals' forces of attraction is more extensive and stronger than the hydrogen bonding in Drug B. More energy is needed to overcome the stronger van der Waals' forces of attraction between Drug A.

(v) State the relative solubility of Drugs **A** and **B** in water. [1]

Drug **A** is less soluble in water than drug **B**.

[Total: 20]

2 Halogens and their compounds can be toxic but some are essential for the human body's functioning and are used in daily products. The oxidising power of chlorine allows it to act as a good disinfectant.

(a) With the use of *Data Booklet*, explain why $FeCl_3$ exists but FeI_3 does not. [4]

$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$ $E^\theta = +0.77V$

$Cl_2 + 2e^- \rightleftharpoons 2Cl^-$ $E^\theta = +1.36V$

For $FeCl_3$, initial species present: Fe^{3+} and Cl^-

[O] $2Cl^- \rightarrow Cl_2 + 2e^-$

[R] $Fe^{3+} + e^- \rightarrow Fe^{2+}$

$E^\theta_{cell} = +0.77 - (+1.36) = -0.59V < 0$

Hence, the species cannot undergo further redox. Thus $FeCl_3$ exists.

$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$ $E^\theta = +0.77V$

$I_2 + 2e^- \rightleftharpoons 2I^-$ $E^\theta = +0.54V$

For FeI_3, initial species present: Fe^{3+} and I^-

[O] $2I^- \rightarrow I_2 + 2e^-$

[R] $Fe^{3+} + e^- \rightarrow Fe^{2+}$

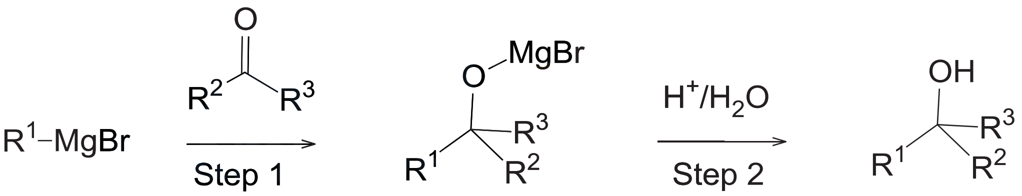
$E^\theta_{cell} = +0.77 - (+0.54) = +0.23V > 0$

Hence, the species can undergo further redox to form Fe^{2+} and I_2. Thus FeI_3 does not exist.

(b) Grignard reaction is an important reaction which helps in lengthening the carbon chain. A Grignard reagent has a general formula of R-MgX where R is an alkyl or aryl group and is formed via the reaction of an alkyl or alkyl halide with magnesium powder.

$$\text{R−X} + \text{Mg} \rightarrow \underset{\text{Grignard reagent}}{\text{R−MgX}}$$

Carbonyl compounds react with Grignard reagent to increase the carbon chain.



(i) In the formation of Grignard reagent, it is important to carry out the reaction in a dry environment. Suggest a reason. [1]

$Mg + 2H_2O \rightleftharpoons Mg(OH)_2 + H_2$

Mg reacts in the presence of water to form magnesium hydroxide and H_2 gas. OR Grignard reagent can react with water to form the respective alkane.

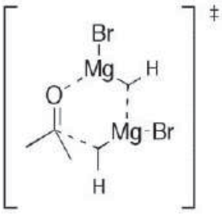
[Turn over

(ii) It was observed that the reaction to form the Grignard reagent is very slow at the start when magnesium powder is added to the alkyl halide in diethyl ether solvent. Suggest a reason. [1]

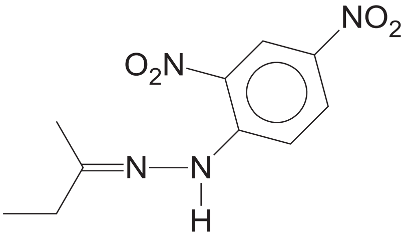
There is an unreactive layer of magnesium oxide coated on the exterior.

(iii) The addition of the Grignard reagent to the carbonyl typically proceeds through a six-membered ring transition state. For the reaction of each molecule of carbonyl compound, two molecules of Grignard reagents are involved in the formation of the transition state.

Suggest the transition state of Step 1 for the reaction between propanone and CH_3MgBr shown above. [1]

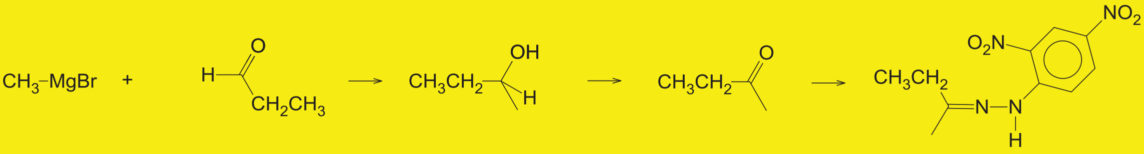


(iv) Suggest a four-step synthesis of compound **Q**. State the reagents and conditions for each stage and draw structures of the intermediate organic products. The first two steps should involve the use of Grignard reaction between CH_3MgBr and a relevant carbonyl compound.



Compound Q

[5]



(c) **(i)** Describe what is observed when NaC*l* and NaBr reacts with concentrated sulfuric acid respectively. In each case, suggest the products of the reaction and write equations where appropriate. [2]

$NaCl + H_2SO_4 \rightarrow HCl + NaHSO_4$

White fumes of HCl (g) produced.(;)

$NaBr + H_2SO_4 \rightarrow HBr + NaHSO_4$

$2HBr + H_2SO_4 \rightarrow Br_2 + SO_2 + 2H_2O$

Orange-brown fumes (mixture of Br_2 and HBr) obtained. (;)

(ii) Explain any difference in their reactions with concentrated sulfuric acid. [1]

The ease of oxidation of halide ions increases from Cl^- to Br^-. Hence, Br^- is oxidised to Br_2 and Cl^- is not oxidised at all.

(d) When cold aqueous sodium hydroxide is added to a yellowish-green solution of chlorine in trichloromethane and shaken together, two immiscible colourless layers (aqueous layer and organic layer) were observed.

(i) State the type of reaction and give an equation, including state symbols, for this reaction. [2]

Type of reaction: disproportionation of chlorine

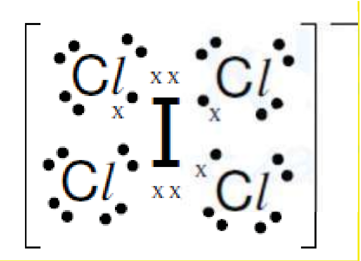
Equation: $Cl_2\,(aq) + 2OH^-\,(aq) \rightarrow Cl^-\,(aq) + ClO^-\,(aq) + H_2O\,(l)$

(ii) Assuming that the starting reagents were added in stoichiometric ratio, suggest the chemical species found in the two immiscible colourless layers respectively. [2]

Aqueous layer: Cl^- (aq) + ClO^- (aq)

Organic Layer: $CHCl_3$

(e) One of the compounds that may be formed between chlorine and iodine is iodine tetrachloride, ICl_4^-. Construct a 'dot-and-cross diagram' to show the arrangement of electrons in ICl_4^-. [1]



[Total: 20]

3 **(a)** Hunsdiecker reaction is the organic reaction of silver salts of carboxylic acids with halogens to give organic halides.

The overall reaction is:

$$RCO_2Ag + Br_2 \rightarrow R\text{-}Br + CO_2 + AgBr$$

The reaction mechanism of the Hunsdiecker reaction is believed to involve organic radical intermediates.

The steps involved in the reaction mechanism are as follows:

1. The silver salt of the carboxylic acid quickly reacts with bromine to form the acyl hypohalite intermediate, RCO_2Br.
$$RCO_2Ag + Br_2 \rightarrow RCO_2Br + AgBr$$
2. The initiation step involves the formation of two radicals from the acyl hypohalite intermediate. One of which is bromine radical.
3. The first step of propagation involves the removal of CO_2 from the radical formed in step 2, forming R● and CO_2.
4. R● recombines with the acyl hypohalite intermediate to form the desired organic halide.

(i) Write equations to illustrate the reaction mechanism of Hunsdiecker reaction. [3]

$$RCO_2Ag + Br_2 \rightarrow RCO_2Br + AgBr$$

Initiation

$$RCO_2Br \rightarrow RCO_2\bullet + Br\bullet$$

Propagation (I)

$$RCO_2\bullet \rightarrow R\bullet + CO_2$$

Propagation (II)

$$R\bullet + RCO_2Br \rightarrow R\text{-}Br + RCO_2\bullet$$

Termination

$$R\bullet + Br\bullet \rightarrow R\text{–}Br$$

$$R\bullet + R\bullet \rightarrow R\text{–}R$$

(ii) Draw the structure of the organic product formed when $C_6H_5CH(CH_3)COOAg$ reacts with Br_2. [1]

$C_6H_5C^*HCH_3Br$

(iii) The product in **(a)(ii)** displays optical isomerism as it has a chiral centre. Explain the term *chiral centre* and label the chiral centre in **(a)(ii)** with an asterix(*) sign**.** [2]

A chiral centre is a **C atom bonded to four different substituents.**

(iv) Chlorine and iodine can be used in place of bromine to react with silver salts of carboxylic acids.

A student wanted to compare the rate of reaction of iodine reacting with silver salts of carboxylic acids with that of bromine. However, he did not label the apparatus and ended up not able to tell which apparatus has the iodine-containing and bromine-containing organic products.

Describe a chemical test which can allow the student to derive correctly the apparatus with the iodine-containing and bromine-containing organic products respectively. Include the observations, if any. [4]

Add NaOH to the respective solutions, followed by HNO_3. Add $AgNO_3(aq)$.
The solution containing a cream precipitate has the bromine-containing product while the solution containing a yellow precipitate has the iodine-containing product.
Add concentrated NH_3 to the respective solutions.
The cream precipitate will dissolve in the concentrated NH_3 while the yellow precipitate will not dissolve in the concentrated NH_3.

(b) Write the equations and state the observations of the following reactions, where appropriate.

- Reaction between sodium and oxygen
- Reaction between sulfur and oxygen

[4]

$2Na + \frac{1}{2}O_2 \rightarrow Na_2O$

Na burns in oxygen with an orange flame.

$\frac{1}{8}S_8 + O_2 \rightarrow SO_2$

S burns with a blue flame to form SO_2.

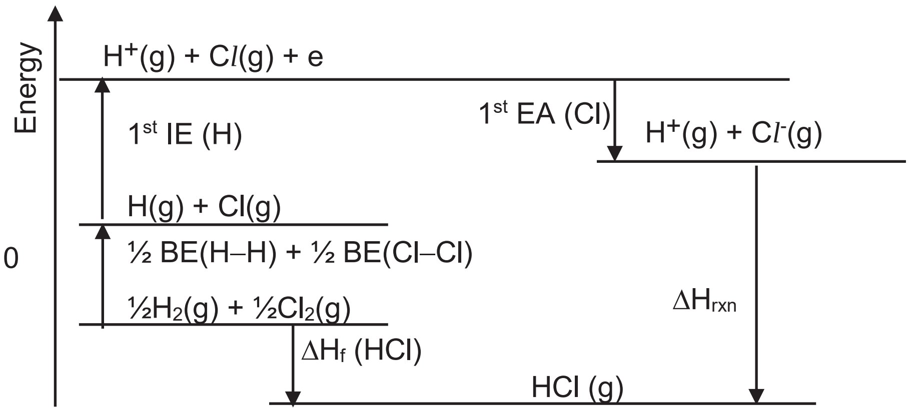
(c) **(i)** The following table shows some thermochemistry data.

Reaction	**ΔH / kJ mol^{-1}**
enthalpy change of formation of HC*l*(g)	–92
first electron affinity of C*l*(g)	-364

Using the following data, and relevant data from the *Data Booklet*, construct an energy level diagram to calculate the standard enthalpy change for the following reaction.

$$H^+(g) + Cl^-(g) \rightarrow HCl(g)$$

[4]



ΔH_{rxn} = ΔH_f (HCl) - ½ BE(H–H) - ½ BE(Cl–Cl) - 1st IE (H) - 1st EA

ΔH_{rxn} = (–92) - ½(436) - ½(244) - 1310 - (–364)

ΔH_{rxn} = - 1378 kJ mol^{-1} = - 1380 kJ mol^{-1}

(ii) The following reaction is expected to be an endothermic reaction.

$$HCl(g) \rightarrow H(g) + Cl(g)$$

However, the following reaction is an exothermic reaction.

$$HCl(g) + aq \rightarrow H^+(aq) + Cl^-(aq) \qquad \Delta H = -75 \text{ kJ mol}^{-1}$$

Explain the above observations. [2]

The first reaction involves bond breaking only while the second reaction involves forming ion-dipole interactions between H^+ and water molecules and Cl^- and water molecules. Energy is evolved in the formation of ion-dipole interactions which can more than compensate the heat absorbed to break the H–Cl bond in the gaseous state and to ionise the H atom, thus resulting in the enthalpy change of reaction is exothermic.

[Total: 20]

4 **(a)** **(i)** Heating compound **P**, $C_{10}H_{12}O_3$, with dilute sulfuric acid yields compound **Q**, $C_9H_{12}O_2$, and methanoic acid.

On treatment with dilute nitric acid, compound **Q** forms compound **R** with the formula $C_9H_{11}NO_4$. Compound **Q** also reacts with aqueous bromine to form compound **S**, $C_9H_9O_2Br_3$.

Heating compound **R** with tin in concentrated hydrochloric acid, followed by adding excess aqueous sodium hydroxide to the product gives compound **T**, $C_9H_{12}NO_2Na$.

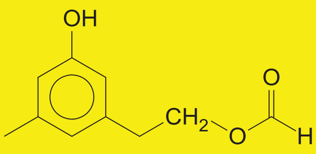
Compound **T** turns hot acidified potassium dichromate solution green and forms compound **U**, $C_9H_{12}NO_3$. 1 mole of compound **U** reacts with 3 moles of aqueous sodium hydroxide. Compound **T** reacts with hot acidified potassium manganate(VII) and forms compound **V**, $C_8H_8NO_5$.

Suggest structures for compounds **P**–**V** and give an account of the chemistry involved.

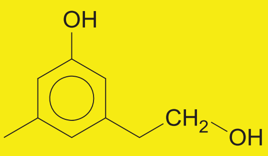
[14]

Observation	Deduction
Heating compound **P** which has the formula, $C_{10}H_{12}O_3$, with dilute sulfuric acid yields compound **Q**, $C_9H_{12}O_2$, and methanoic acid	**P** is an ester **P** undergoes acidic hydrolysis.
On treatment with dilute nitric acid, compound **Q** forms compound **R**	**Q** contains phenol **Q** undergoes electrophilic substitution.
Compound **Q** also reacts with aqueous bromine to form compound **S**, $C_9H_9O_2Br_3$	**Q** contains phenol Br is substituted at 2,4 and 6 position in **S**. **Q** undergoes electrophilic substitution.
Heating compound **R** with tin in concentrated hydrochloric acid	Reduction of nitro group to $-NH_2$ **R** contains $-NO_2$
Adding excess aqueous sodium hydroxide to the product gives compound **T**, $C_9H_{12}NO_2Na$.	Acid-base reaction Phenoxide ion is produced
Compound **T** turns hot acidified potassium dichromate solution green and forms compound **U**, $C_9H_{12}NO_3$.	Oxidation Primary alcohol is present in **T** Phenoxide ion is acidified and revert to phenol in **U**

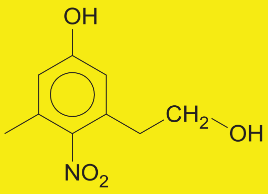
1 mole of compound **U** reacts with 3 moles of aqueous sodium hydroxide.	**U** contains 3 acidic groups(1 phenol,1 ammonium salt group and 1 carboxylic acid group).
Compound **T** reacts with hot acidified potassium manganate(VII) and forms compound **V**, $C_8H_8NO_5$.	Oxidation



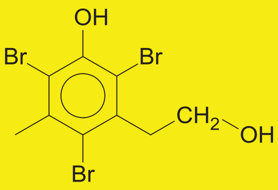
P



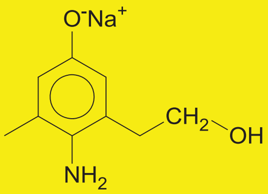
Q



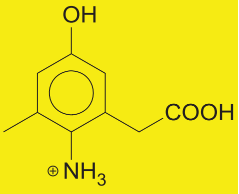
R



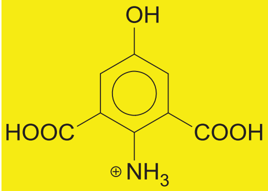
S



T

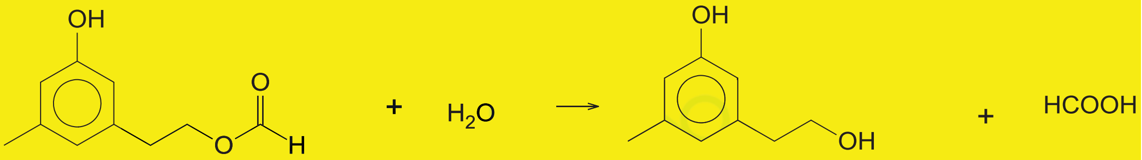


U



V

(ii) Write the equation for the reaction of compound **P** being heated with dilute sulfuric acid.[1]



(b) Ester is an organic molecule which has many uses. Esters with low molecular masses are commonly used as fragrances and are found in essential oils. Phosphoesters form the backbone of DNA molecules.

(i) Given that methyl methanoate and ethyl methanoate are the simplest esters available, suggest a chemical test which can distinguish the two compounds. [3]

To separate solutions of methyl methanoate and ethyl methanoate, add NaOH(aq) and heat it, followed by adding I_2(aq). The solution that forms a yellow precipitate contains ethyl methanoate while the solution that contains methyl methanoate does not form yellow precipitate.

.

(ii) Acyl chlorides and esters are both derivatives of carboxylic acids.
Compare and account for the acidity of methyl methanoate and ethanoyl chloride. [2]

Ethanoyl chloride is more acidic than methyl methanoate(;) as it hydrolyses in water to form HCl which is a strong acid(;).

[Total: 20]

5 Vehicle frames are usually made from aluminium as it is lightweight and strong. However, the aluminium frames have to be made more resistant to corrosion as certain parts could be exposed to rainwater and acidic gases in vehicle exhaust.

The industrial process for the anodising of aluminium uses an inert platinum cathode and aqueous sulfuric acid as the electrolyte.

(a) Explain, in terms of the electrode reactions, how a piece of aluminium metal could be anodised to be more resistant to corrosion. [3]

at the Pt cathode: $2H^+(aq) + 2e^- \rightarrow H_2(g)$

at the A*l* anode:

$2\,H_2O\,(l) \rightarrow 4H^+(aq) + O_2(g) + 4e^-$;

$4Al(s) + 3O_2(g) \rightarrow 2Al_2O_3(s)$;

Overall reaction: $2Al(s) + 3H_2O(l) \rightarrow Al_2O_3(s) + 3H_2(g)$;

(b) A current of 0.30 mA was switched on for 1 hour to anodise an aluminium frame.

Calculate the amount of Al_2O_3 produced from the anodisation. [3]

Q = It

$Q = 0.30 \times 10^{-3} \times 3600 = 1.08$ C

Q= nF

No. of mol of electrons transferred, n = Q / F = 1.08 / 96500 = 1.12×10^{-5} mol ;

$6\ H_2O\ (l) \rightarrow 12H^+(aq) + 3O_2(g) + 12e^-$

$4Al(s) + 3O_2(g) \rightarrow 2Al_2O_3(s)$

For every 12 mol of electron transferred, 2 mol of Al_2O_3 is produced ;

No. of mol of Al oxidised = $1.12 \times 10^{-5} \div 6 = 1.87 \times 10^{-6}$ mol ;

(c) *Use of the Data Booklet is relevant to this question.*

Explain, stating any observations, how the electrode reactions would be different if

(i) the electrolyte was contaminated with copper(II) sulfate. [2]

The cathode reaction will instead be the reduction of Cu^{2+} ions to copper solid.

$2H^+(aq) + 2e^- \rightarrow H_2(g)$ $E^\ominus = 0.00$ V (not req)

$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$; $E^\ominus = +0.34$ V

The platinum cathode will be coated with a pink / orange / brown layer of copper ;

(ii) the aluminium electrode was replaced with another platinum electrode. [2]

Platinum is inert and does not get oxidised. Water is oxidised to oxygen gas.

$2\ H_2O\ (l) \rightarrow 4H^+(aq) + O_2(g) + 4e^-$; $E^\ominus = +1.23$ V

<u>Effervescence</u> of a colourless gas <u>at the anode</u>; (which relights a glowing splint)

(d) Infra-red (IR) spectroscopy is a common technique used to identify functional groups in organic compounds and to study how the functional groups are affected by other substances. When a beam of IR light of varying energies is shone at an organic compound, its functional groups can absorb certain energies characteristic to it. The energy of IR light is measured in wavenumbers, $\tilde{v}$, and is expressed as the reciprocal of its wavelength, λ, with units of cm^{-1}.

$$\tilde{v} = \frac{1}{\lambda}$$

For example, carbonyl functional groups absorbs IR light at the wavenumber range of 1680 to 1750 cm^{-1}, while alkyl groups absorb IR light at a wavenumber range of 2840 to 3095 cm^{-1}.

The gas-phase kinetics and mechanism of the hydrogenation of propanone using nickel catalyst was studied using IR spectroscopy. Dissociative adsorption of hydrogen gas on solid nickel is known to occur readily (step **I**). The adsorption of propanone gas onto the nickel catalyst was identified by a wavenumber peaking at 1620 cm^{-1}. The shift in wavenumber from 1680 to 1620 cm^{-1} confirms that it is the C=O functional group that is adsorbed onto the nickel catalyst and not the methyl groups (step **II**). However, no wavenumber shift corresponding to the alcohol functional group of the product, propan-2-ol, was found. This indicates that when the product is formed, it immediately desorbed from the catalyst (step **IV**).

Hence, the proposed mechanism for this reaction is as follows.

Step **I**: $2Ni + H_2 \rightleftharpoons 2Ni\text{–}H$
Step **II**: $Ni + CH_3COCH_3 \rightleftharpoons NiCH_3COCH_3$
Step **III**: $NiCH_3COCH_3 + NiH \rightleftharpoons NiCH_3COHCH_3 + Ni$
Step **IV**: $NiCH_3COHCH_3 + NiH \rightleftharpoons CH_3CH(OH)CH_3 + 2Ni$

When the experiment was conducted in a closed vessel of fixed volume at a constant temperature of 363 K, the following data was recorded.

Experiment	Partial pressure of hydrogen / kPa	Partial pressure of propanone / kPa	Relative rate
1	0.5	2.5	1
2	1	2.5	2
3	4	5	16
4	10	5	16
5	50	5	16

(i) Nickel is acting as a *heterogeneous* catalyst in this reaction.

Define the term *heterogeneous*. [1]

The catalyst used is in a **different phase / physical state** from the reactants. **;**

(ii) Based on experiments **1** to **3**, determine the order of reaction with respect to hydrogen and with respect to propanone.

Hence, deduce the rate equation for the hydrogenation of propanone. [3]

Rate = $k[H_2]^m[\text{propanone}]^n$
By comparing experiments 1 and 2,
When partial pressure (concentration) of hydrogen doubled and propanone kept constant, rate doubled.
Reaction is first order with respect to hydrogen, m = 1 **;**

By comparing experiments 2 and 3,

$$\frac{\text{rate of expt 3}}{\text{rate of expt 2}} = \frac{k[H_2]^1[\text{propanone}]^n}{k[H_2]^1[\text{propanone}]^n}$$

$$\frac{16}{2} = (4)^1 \times \frac{5}{2.5}^n$$

$2^n = 2$

$n = 1$

Reaction is first order with respect to propanone, n =1 ;

Rate = k[H_2][CH_3COCH_3] or rate=k $p_{H_2}p_{CH_3COCH_3}$;

(iii) Based on your answer in **(ii)**, state which step in the proposed mechanism is the rate-determining step. [1]

Step 4. ;

Explanation (not needed)
If slow step is
step 1: rate = k $[H_2]^1$ X
step 2: rate = k $[CH_3COCH_3]^1$ X
step 3: rate = k $[H_2]^{0.5}$ $[CH_3COCH_3]^1$ X
step 4: rate = k $[H_2]$ $[CH_3COCH_3]^1$ (consistent)

Write the expression for Kc for steps 1 to 3, ignoring Ni as it is in solid state. Re-express the rate equation for step 4 in terms of the actual reactants and not leave it in terms of the intermediates.

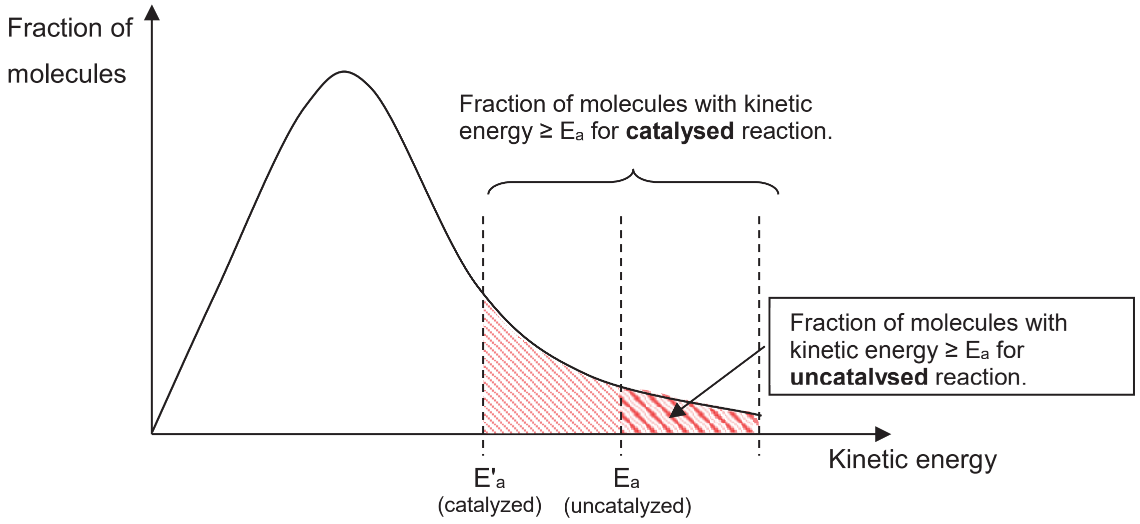
(iv) Suggest a reason why the catalyst has to be used in the powdered form. [1]

The powdered form provides a larger surface area which increases the frequency of effective collisions, speeding up the reaction. ;

(v) Hence, or otherwise, suggest a reason why the rate of reaction stopped increasing in experiments 4 and 5 when the partial pressure of hydrogen exceeded 4 kPa. [1]

The **hydrogen gas concentration (substrate concentration) exceeded the available catalyst surface area** for adsorption / reaction to take place. ;

(vi) Sketch an energy distribution diagram to explain how the rate of the reaction would have been different without the use of a catalyst. [3]



; (1 m for diagram and labels)

- A catalyst provides an **alternative reaction path with lower activation energy (E'_a)** than that for the uncatalysed reaction (E_a).
- Without a catalyst, **fraction of molecules containing energy greater than the activation energy decreases**
- The **frequency of effective collisions is lower without a catalyst**.
- Hence, **rate of reaction decreases**.

;; **(0-1 pt = 0m ; 2-3 pts = 1m, all 4 pts = 2m)**

[Total: 20]

END OF PAPER

BLANK PAGE

NANYANG JUNIOR COLLEGE
JC 2 PRELIMINARY EXAMINATION
Higher 2

CHEMISTRY

9729/01

Paper 1 Multiple Choice

25 SEP 2017

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 **21** printed pages.

1 To determine the mass of arsenic present in a sample of pesticide, all the arsenic was first converted to arsenate ion, AsO_4^{3-}. 1.25×10^{-3} mol of $AgNO_3$ was then added to precipitate AsO_4^{3-} as Ag_3AsO_4. The excess Ag^+ ions needed 3.64 cm^3 of 0.054 mol dm^{-3} KSCN to form silver thiocyanate, AgSCN.

Calculate the mass of arsenic (A_r = 74.9) present in the sample of pesticide.

A 0.015 g **B** 0.026 g **C** 0.079 g **D** 0.488 g

2 How many moles of electrons must be removed from each mole of methylbenzene, $C_6H_5CH_3$, when it is oxidised to benzoic acid, C_6H_5COOH?

A 1 **B** 2 **C** 4 **D** 6

3 Which elements have the same number of unpaired electrons in its orbitals with principal quantum number 2?

1 Beryllium **2** Carbon **3** Nitrogen **4** Oxygen

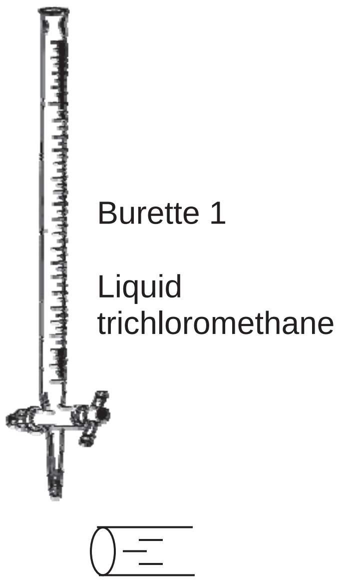
A 1 and 2 only

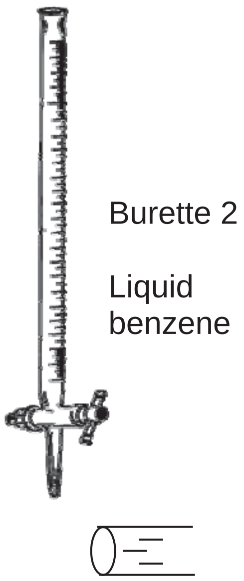
B 2 and 3 only

C 2 and 4 only

D 3 and 4 only

4 The diagram below shows liquid trichloromethane and liquid benzene in burettes 1 and 2 respectively.

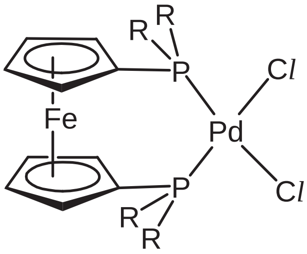




What would happen to the flow of the liquids trichloromethane and benzene when a negatively-charged rod is brought near to each of them?

	Liquid trichloromethane	Liquid benzene
A	Deflected towards the rod	Deflected towards the rod
B	Undeflected	Deflected towards the rod
C	Deflected towards the rod	Undeflected
D	Undeflected	Undeflected

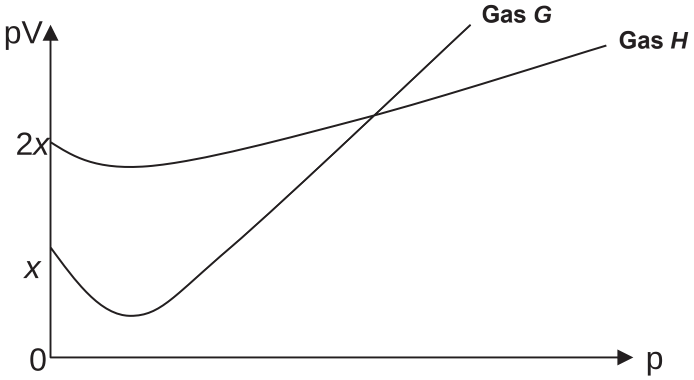
5 Palladium compounds are widely used as catalyst in coupling reactions. One such compound is (dppf)PdCl_2 with its structure shown below.



What does the structure of (dppf)PdCl_2 suggest about the nature of the bonding between Pd and the phosphorus atoms, and the oxidation state of Pd?

	Nature of bonding	Oxidation state
A	Covalent	0
B	Ionic	0
C	Covalent	+2
D	ionic	+2

6 The value of pV is plotted against p for two gases, G and H, 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 G	Gas H
A	0.5 mol of H_2 at 25 ºC	0.5 mol of H_2 at 50 ºC
B	0.5 mol of H_2 at 25 ºC	1 mol of SO_2 at 25 ºC
C	0.5 mol of SO_2 at 25 ºC	0.5 mol of SO_2 at 50 ºC
D	0.5 mol of SO_2 at 25 ºC	1 mol of H_2 at 25 ºC

7 The enthalpy changes involved in the formation of $KCl(aq)$ from $K(s)$ and $Cl_2(g)$ are as follows:

$$\begin{array}{c}K(s)\\+\\\tfrac{1}{2}Cl_2(g)\end{array}\xrightarrow{\Delta H_1}\begin{array}{c}K(g)\\+\\Cl(g)\end{array}\xrightarrow{\Delta H_2}\begin{array}{c}K^+(g)\\+\\Cl^-(g)\end{array}\xrightarrow{\Delta H_3}KCl(s)\xrightarrow{\Delta H_4}\begin{array}{c}K^+(aq)\\+\\Cl^-(aq)\end{array}$$

Which statements are correct?

1 The lattice energy of potassium chloride is ΔH_3.

2 The enthalpy change of solution of potassium chloride is $(\Delta H_3 + \Delta H_4)$.

3 The enthalpy change of formation of solid potassium chloride is $(\Delta H_1 + \Delta H_2 + \Delta H_3)$.

A 3 only

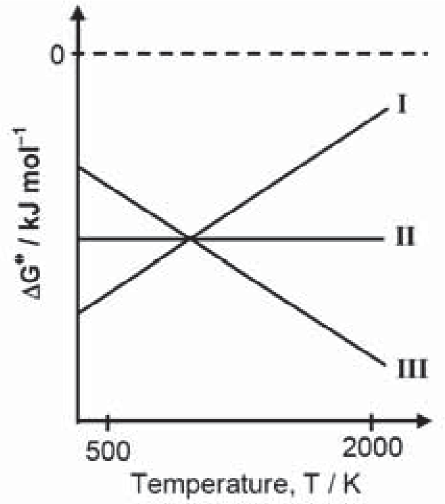
B 1 and 3 only

C 2 and 3 only

D 1, 2 and 3 only

8 In 1944, T. Ellingham published plots of $\Delta G^\ominus$ against temperature T, for a number of reactions. Today, such plots are called Ellingham diagrams.

An Ellingham diagram for three reactions involving the oxidation of C and CO is shown below.



Which of the following shows correctly the three reactions corresponding to **I**, **II** and **III** in the above Ellingham diagram?

	I	II	III
A	$2CO + O_2 \rightarrow 2CO_2$	$C + O_2 \rightarrow CO_2$	$2C + O_2 \rightarrow 2CO$
B	$2C + O_2 \rightarrow 2CO$	$C + O_2 \rightarrow CO_2$	$2CO + O_2 \rightarrow 2CO_2$
C	$C + O_2 \rightarrow CO_2$	$2CO + O_2 \rightarrow 2CO_2$	$2C + O_2 \rightarrow 2CO$
D	$2CO + O_2 \rightarrow 2CO_2$	$2C + O_2 \rightarrow 2CO$	$C + O_2 \rightarrow CO_2$

9 Ozone in the earth's atmosphere decomposes according to the equation:

$$2O_3(g) \rightarrow 3O_2(g)$$

This reaction is thought to occur via a two–step mechanism:

Step 1	$O_3(g) \rightleftharpoons O_2(g) + O(g)$	fast, reversible
Step 2	$O_3(g) + O(g) \rightarrow 2O_2(g)$	slow

With the aid of the K_c expression in Step 1, which rate law is consistent with this mechanism?

A $\text{Rate} = k\dfrac{[O_3]^2}{[O_2]}$

B $\text{Rate} = k\dfrac{[O_3]^2}{[O_2]^3}$

C $\text{Rate} = k[O_3]$

D $\text{Rate} = k[O_3]^2$

10 What does the following pair of values for a reaction system indicate?

	values
ΔG^{θ}	–50.8
K_c	5.80×10^8

A Reaction goes to completion.

B ΔH^{θ} is positive and ΔS^{θ} is negative.

C Rate of the forward reaction is high.

D Position of equilibrium lies to the left.

11 Water dissociates into H^+ and OH^- as shown.

$H_2O \rightleftharpoons H^+ + OH^-$

At 25 °C, the equilibrium $[H^+]$ is 10^{-7} mol dm^{-3}; $[H_2O] = 55.6$ mol dm^{-3}.

What is the order of increasing numerical value of pH, pK_a and pK_w for this equilibrium at this temperature?

	smallest		largest
A	pH	pK_w	pK_a
B	pH	pK_a	pK_w
C	pK_w	pK_a	pH
D	pK_a	pK_w	pH

12 An aqueous solution of sodium carbonate is added very slowly, till excess, to a solution containing 0.2 mol dm^{-3} of zinc nitrate and 0.1 mol dm^{-3} of silver nitrate at 25 °C.

The numerical value of the solubility product of zinc carbonate at 25 °C is 1.4×10^{-11} and that of silver carbonate is 8.1×10^{-12}.

Which statement describes what happens in the solution?

A Only zinc carbonate is precipitated.

B Only silver carbonate is precipitated.

C Zinc carbonate is precipitated first, followed by silver carbonate.

D Silver carbonate is precipitated first, followed by zinc carbonate.

13 J, K and L are elements in the same period of the Periodic Table. The oxide of J is amphoteric, the oxide of K is basic and the oxide of L is acidic.

What is the correct order of trend for these elements?

1 Proton number: K < J < L

2 Atomic radius: L < J < K

3 Melting point: J < L < K

A 1 only

B 2 only

C 1 and 2 only

D 1,2 and 3 only

14 The table below shows the results of experiments in which the halogens, P_2, Q_2 and R_2 were added to separate aqueous solutions containing $P^–$, $Q^–$ and $R^–$ ions.

	$P^–$ (aq)	$Q^–$ (aq)	$R^–$ (aq)
P_2	no reaction	no reaction	R_2 formed
Q_2	P_2 formed	no reaction	R_2 formed
R_2	no reaction	no reaction	no reaction

In which sequence is the solubility of the silver halides in aqueous ammonia arranged in increasing order?

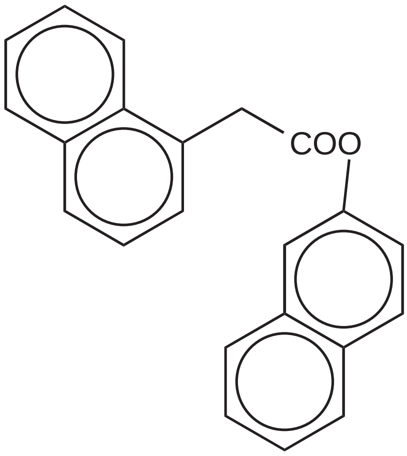
A AgP < AgQ < AgR

B AgQ < AgP < AgR

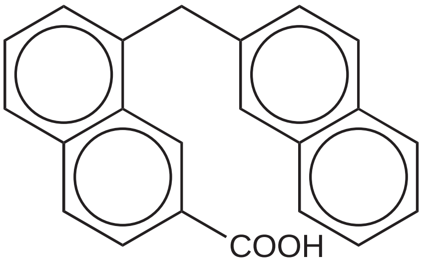
C AgQ < AgR < AgP

D AgR < AgP < AgQ

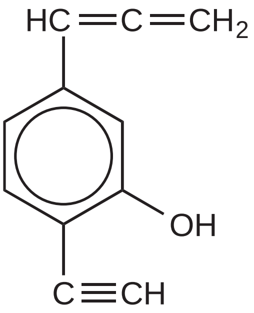
15 The three compounds A, B and C have the following structures.



A



B



C

Which of the following statements about A, B and C are correct?

1 A and C have the same empirical formula.

2 A and B are isomers.

3 The M_r of A is twice that of C.

A 1 and 2 only

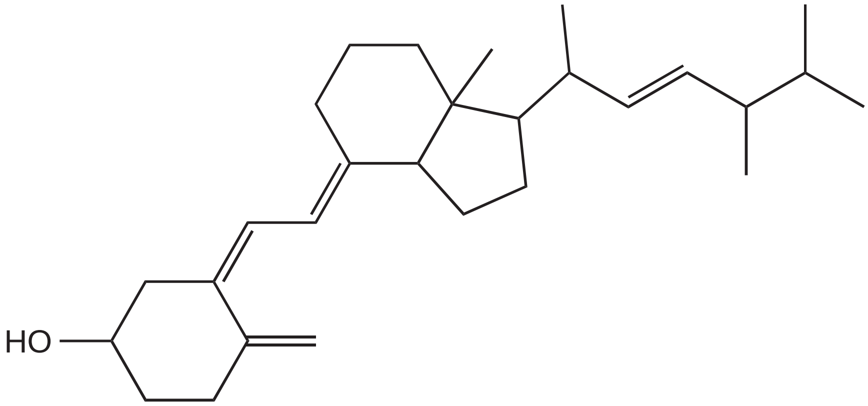
B 1 and 3 only

C 2 and 3 only

D 1, 2 and 3 only

16 Vitamin D has a significant role in calcium homeostasis.

One major form of Vitamin D is ergocalciferol.

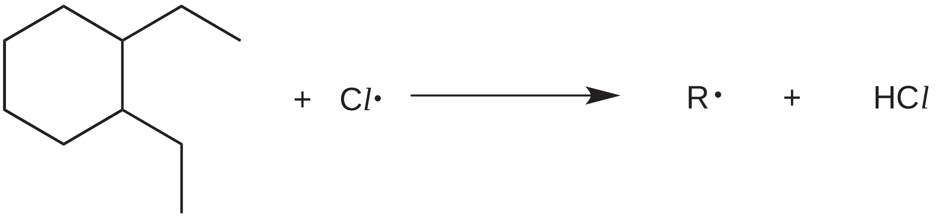


ergocalciferol

How many stereocentres do a molecule of ergocalciferol have?

A 6 **B** 7 **C** 8 **D** 9

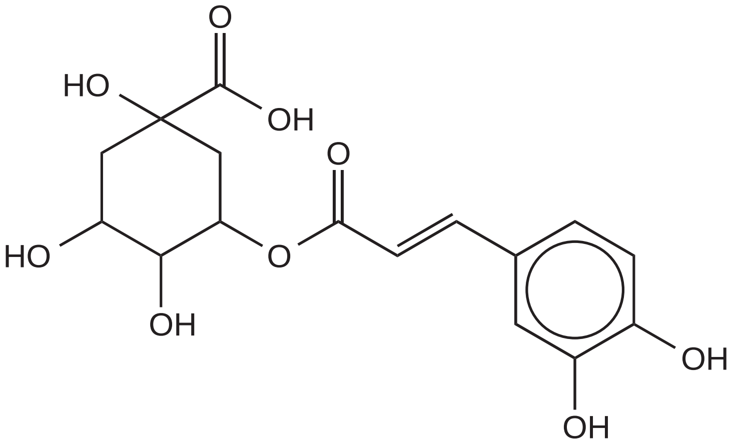
17 When heated with chlorine, the following hydrocarbon undergoes free radical substitution. In the propagation step, the free radical R• is formed from the loss of one hydrogen atom.



How many different forms of R• are theoretically possible?

A 5 **B** 7 **C** 9 **D** 10

18 Chlorogenic acid occurs naturally in coffee.



chlorogenic acid

What is the maximum number of bromine atoms that would be incorporated when gaseous hydrogen bromide reacts with chlorogenic acid?

A 3

B 4

C 5

D 6

19 Deuterium is an isotope of hydrogen, ^{2}H.

Which of the following will not yield a carbon-containing species, which contains deuterium?

A $CH_3COCH_2CH_3$ with warm I_2 and NaOD in D_2O

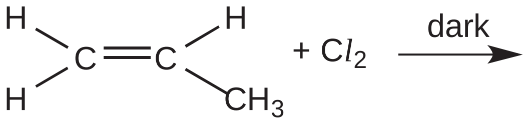
B $CH_3CH_2CH_2COOH$ with $LiAlD_4$ in dry ether

C $CH_3CH_2COCH_3$ with DCN and trace amounts of NaCN

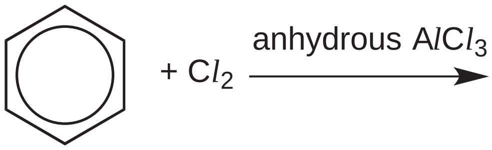
D $CH_3CH_2CH_2CHO$ with hot Ag^+ and ND_3 in D_2O

20 In which reaction does a carbon atom change from being sp^3 hybridised in the intermediate to being sp^2 hybridised in the product?

A



B

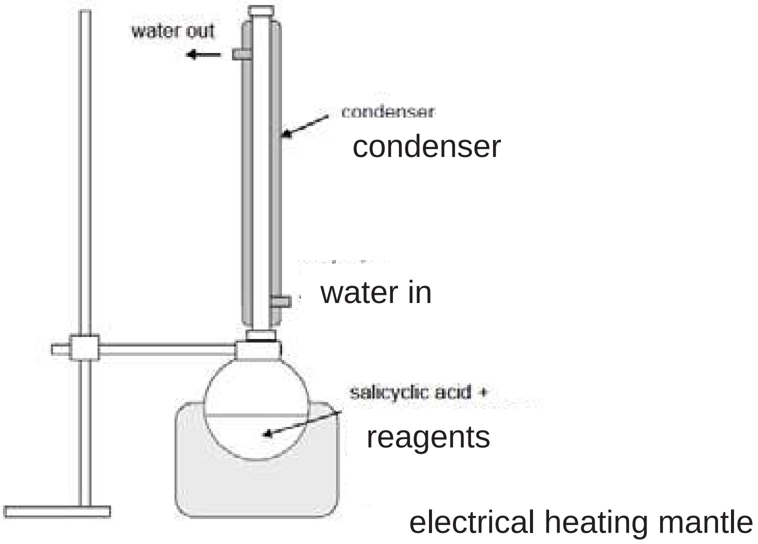


C

$CH_3CH_2CH_3 + Cl_2 \xrightarrow{uv}$

D

21 The setup below is commonly used in the synthesis of organic compounds in the laboratory.



Which of the following reactions requires the above set up for synthesis?

A $CH_3CH_2NH_2 + CH_3COCl \rightarrow CH_3CONHCH_2CH_3 + HCl$

B $CH_3COCl + H_2O \rightarrow CH_3COOH + HCl$

C $CH_3CH_2OH + [O] \rightarrow CH_3CHO + H_2O$

D $CH_3CONH_2 + NaOH \rightarrow CH_3COO^-Na^+ + NH_3$

22 A catalytic converter is part of the exhaust system of many modern cars. Which reactions occur in a catalytic converter?

1 $2CO + 2NO \rightarrow 2CO_2 + N_2$

2 $2SO_2 + 2NO \rightarrow 2SO_3 + N_2$

3 $2CO + O_2 \rightarrow 2CO_2$

4 $CO_2 + NO \rightarrow CO + NO_2$

A 1 and 2 only

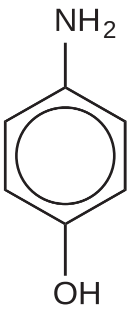
B 1 and 3 only

C 2 and 4 only

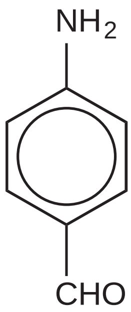
D 3 and 4 only

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

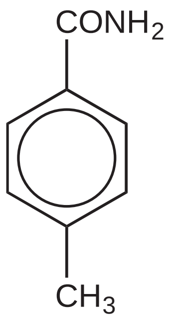
The structures of some nitrogen containing compounds are shown below.



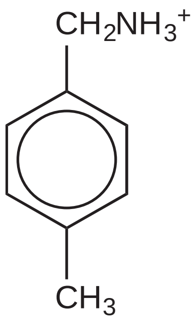
H



I



J

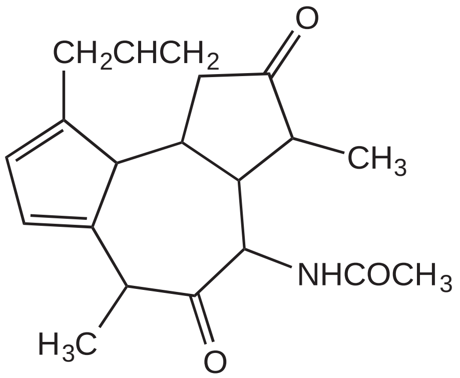


K

What is the order of increasing basicity, least to most basic, of the nitrogen containing compounds?

	increasing basicity →			
A	K	J	I	H
B	K	J	H	I
C	H	I	J	K
D	J	K	I	H

24 The diagram shows the structure of compound L.



compound L

It reacts with LiA*l*H4 in dry ether to give a cyclic compound M.

Which of the following statements about compound M is correct?

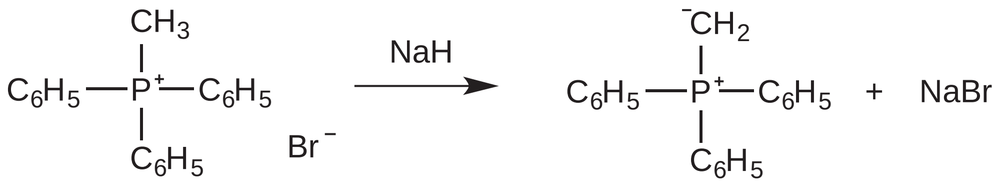
A It reacts with ethanoic acid to form one mole of amide.

B It reacts with two moles of 2,4-dinitrophenylhydrazine.

C It reacts with sodium metal to produce one mole of hydrogen gas.

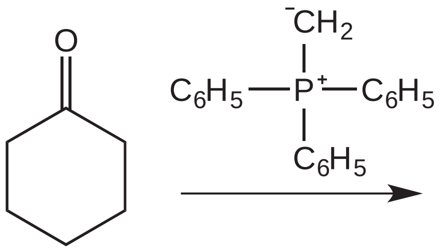
D It reacts with acidified potassium manganate(VII) to form two moles of carbon dioxide gas.

25 Wittig reaction is a popular method to synthesise alkenes from ketones and aldehydes. It involves a reaction between a carbonyl compound and a phosphonium ylid as shown in the following reaction scheme.

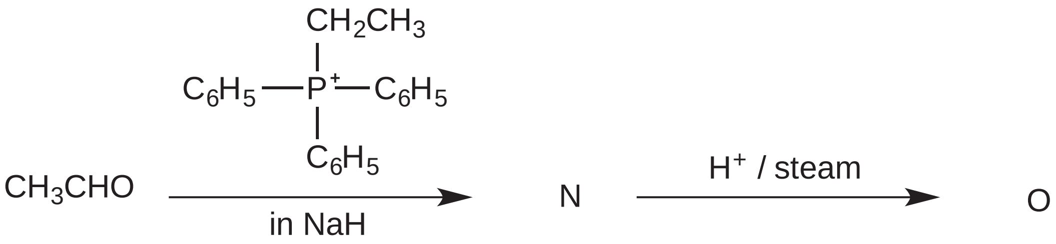


phosphonium salt

phosphonium ylid



The diagram shows a reaction sequence.



Which of the following will give an observation with O?

1 Alkaline aqueous iodine

2 PCl_5

3 2,4-dinitrophenylhydrazine

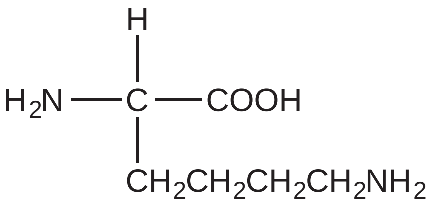
A 1, 2 and 3 only

B 1 and 2 only

C 2 and 3 only

D 1 and 3 only

26 Lysine is an amino acid.

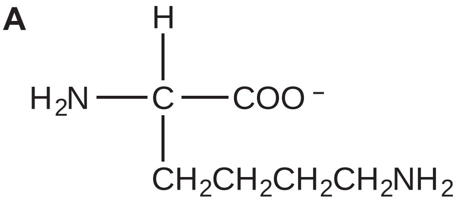


$H_2N-CH(COOH)-CH_2CH_2CH_2CH_2NH_2$

lysine

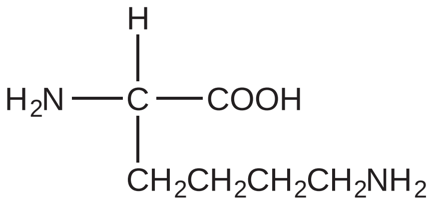
Which structure is predominant when lysine is in aqueous solution at pH = 1?

A



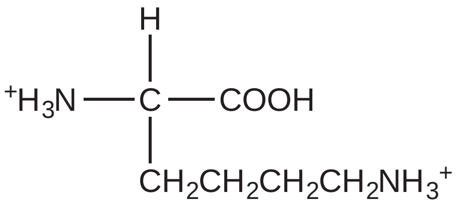
$H_2N-CH(COO^-)-CH_2CH_2CH_2CH_2NH_2$

B



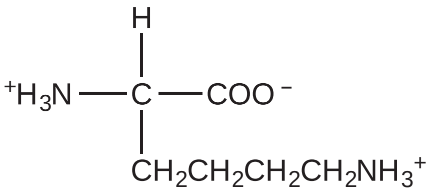
$H_2N-CH(COOH)-CH_2CH_2CH_2CH_2NH_2$

C



$^+H_3N-CH(COOH)-CH_2CH_2CH_2CH_2NH_3^+$

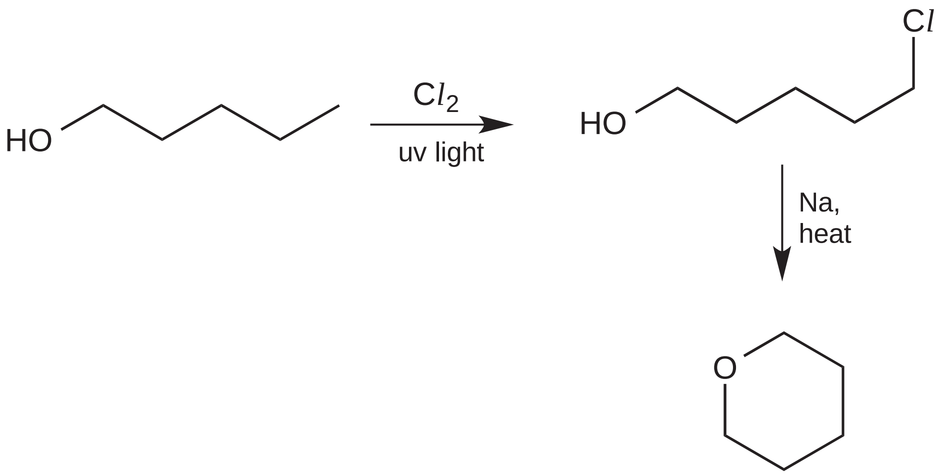
D



$^+H_3N-CH(COO^-)-CH_2CH_2CH_2CH_2NH_3^+$

27 During the synthesis of many organic compounds, by-products are formed.

An ether is produced via the reaction scheme.



What could be the by-products of this reaction?

1 $HO(CH_2)_{10}OH$

2 $Cl(CH_2)_5O(CH_2)_5OH$

3 HCl

A 1, 2 and 3 only

B 1 and 2 only

C 1 and 3 only

D 3 only

28 Which statement correctly defines a transition element?

A Transition elements have partially filled d orbitials.

B Transition elements form many coloured compounds.

C Transition elements or their compounds are widely used as catalysts.

D Transition elements exhibit more than one oxidation sate in their compounds.

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

An electrochemical cell is set up using a Fe^{2+}(aq)|Fe(s) half–cell and a VO_2^+(aq),VO^{2+}(aq)|Pt(s) half–cell.

Which of the following gives a correct effect on the $E^\ominus_{cell}$ and a correct explanation for the effect when each of the changes is made to the cell separately?

	Change	Effect of $E^\ominus_{cell}$	Explanation
1	Add KCN(aq) to the Fe^{2+}(aq)|Fe(s) half–cell	Increases	Concentration of Fe^{2+}(aq) decreases
2	Add water to the VO_2^+(aq),VO^{2+}(aq)|Pt(s) half–cell	Decreases	Concentration of water increases
3	Increase temperature of the Fe^{2+}(aq)|Fe(s) half–cell	No change	Temperature change does not affect $E^\ominus$

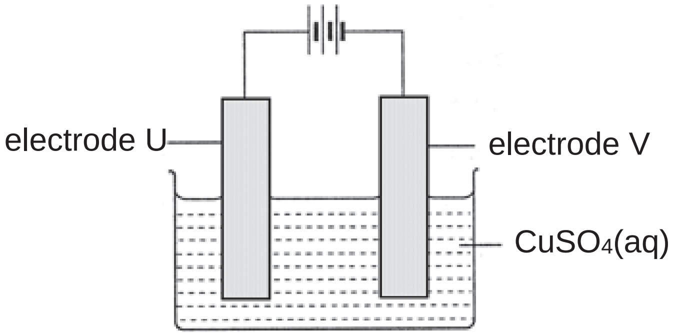
A 1 only

B 2 only

C 1 and 3 only

D 1, 2 and 3 only

30 In an experiment, a cell was set up to obtain pure copper from a copper-silver alloy as shown below.



When a current of 40.0 A flows through the electrolyte for 26.8 minutes, the mass of the anode changes by 26.47 g.

Which of the following statements is correct?

A Electrode U is pure copper and electrode V is the copper-silver alloy.

B The mass of the cathode changes by 26.47 g during the experiment.

C The concentration of $CuSO_4$(aq) decreases during the experiment.

D The copper-silver alloy contains 20% silver by mass.

NANYANG JUNIOR COLLEGE
JC 2 PRELIMINARY EXAMINATION
Higher 2

CANDIDATE NAME	
CLASS	
TUTOR'S NAME	

CHEMISTRY

9729/02

Paper 2 Structured Questions

11 SEP 2017

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	**/13**
2	**/23**
3	**/14**
4	**/11**
5	**/14**
Total	**/75**

This document consists of **22** printed pages.

1 Ammonium salts are commonly used in instant cold packs. The cold pack contains water and an inner pouch containing an ammonium salt. When the pack is squeezed, this inner pouch breaks and releases the salt, which quickly dissolves and lowers the pack's temperature.

To determine whether ammonium chloride or ammonium nitrate is more effective as the ingredient in the cold pack, a student decided to conduct an experiment to find out the enthalpy change of solution of the two salts, starting with ammonium chloride.

He added ammonium chloride to water and found the temperature change by plotting a suitable graph to correct for heat transfer.

In a preliminary investigation, the enthalpy change of solution of ammonium chloride was found to be approximately +15 kJ mol^{-1}.

(a) **(i)** Draw dot-and-cross diagram to illustrate the bonding in ammonium nitrate. Hence state the shape with respect to each nitrogen atom.

[3]

(ii) The student predicted that enthalpy change of solution of ammonium nitrate is more endothermic compared to ammonium chloride. Explain why his prediction is correct.

…………………………………………………………………………………………

…………………………………………………………………………………………

…………………………………………………………………………………………

…………………………………………………………………………………………

…………………………………………………………………………………………

…………………………………………………………………………………………[2]

(b) **(i)** The student was told to use 100 cm^3 of water for conducting the experiment. Suggest a minimum mass of ammonium chloride that could be used. Given that 4.3 J is required to raise the temperature of 1.0 cm^3 of any solution by 1°C. Justify your choice with relevant calculations, stating any other assumptions you made.

[1]

The student carried out the following procedure to find the enthalpy change of solution of ammonium chloride.

1. Weigh accurately 8.00 g of ammonium chloride in a weighing bottle using a weighing balance.
2. Using a 100 cm^3 measuring cylinder, add 100 cm^3 of water into a polystyrene cup.
3. Stir the water gently using the thermometer.
4. Start the stopwatch.
5. Record the temperature of the water in the container, using a 0.1 ^oC thermometer, at 1 min interval.
6. At the 4th min, tip the ammonium chloride into the water. Do not read the temperature at this time.
7. Stir the solution gently and record the temperature of the solution at 4.5 min. Continue to stir and record the temperature at 30 s intervals until 8th min.
8. Reweigh the weighing bottle.

(ii) Draw a sketch of the graph that you expect to obtain from the experiment. Indicate clearly on the graph how the temperature change, ΔT, can be found.

[2]

(iii) Predict and explain the sign of ΔS when ammonium nitrate is dissolved in water.

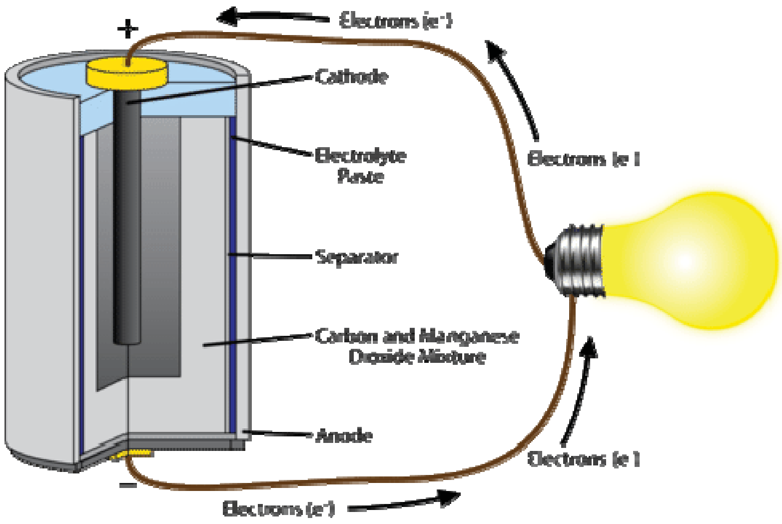
……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

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

(c) Ammonium chloride is also used as electrolyte in zinc–carbon batteries, where the outer zinc container is the negatively charged terminal and is oxidised during discharge.



The following reaction also takes place in the cell.

$$2MnO_2(s) + 2e^- + 2NH_4Cl(aq) \rightarrow Mn_2O_3(s) + 2NH_3(aq) + H_2O(l) + 2Cl^-(aq) \qquad E^\ominus = +0.5\ V$$

Use the table of standard redox potentials given in the *Data Booklet* to answer the questions below.

(i) Write the overall equation for the reaction that occurs in the cell when electrons are discharged.

....[1]

(ii) Calculate the voltage that is generated by this cell.

....[1]

(iii) Calculate a value of $\Delta G^\ominus$ for the cell reaction, and explain the significance of its sign.

....

....

....[2]

[Total: 13]

2 2-iodobutane can be readily converted into 2-aminobutane using ethanolic ammonia.

$$CH_3CHICH_2CH_3 + 2NH_3 \rightarrow CH_3CH(NH_2)CH_2CH_3 + NH_4I$$

In order to determine the rate equation for this reaction, an investigation was carried out at a constant temperature. 4.00 mol dm^{-3} ethanolic ammonia was first prepared by bubbling ammonia gas into ethanol.

Equal volume of 0.20 mol dm^{-3} 2-iodobutane and 4.00 mol dm^{-3} ethanolic ammonia were mixed. At suitable time intervals, 10 cm^3 of the reaction mixture was pipetted into a conical flask and quenched. Chlorine gas was bubbled into the reaction mixture and excess chlorine gas was subsequently removed. The reaction mixture was then titrated with 0.0250 mol dm^{-3} sodium thiosulfate in the presence of an indicator.

(a) Draw a labelled diagram to illustrate the bonding between ammonia and ethanol.

[2]

(b) **(i)** Suggest why the reaction must be quenched and describe how this can be done.

…………………………………………………………………………………

…………………………………………………………………………………

…………………………………………………………………………………

…………………………………………………………………………………[2]

(ii) Write an ionic equation for the reaction when chlorine was bubbled through the reaction mixture.

…………………………………………………………………………………[1]

(iii) Hence, write an ionic equation for the reaction between the reaction mixture and sodium thiosulfate.

…………………………………………………………………………………[1]

(iv) Suggest a suitable indicator for the titration and describe how you would recognise the end-point during the titration.

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

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

(c) The table below shows the results obtained from the titration at different time intervals.

time / min	volume of sodium thiosulfate used / cm^3
5.0	12.00
10.0	20.50
15.0	26.50
20.0	30.50
25.0	33.50
30.0	35.50

(i) To determine the order of reaction with respect to 2-iodobutane, use these data to plot a suitable graph on the grid below.

[2]

(ii) Hence, deduce the order of reaction with respect to 2-iodobutane.

[2]

(iii) The concentration of ethanolic ammonia is halved and a new series of experiments was carried out at the same temperature. When a similar graph was plotted, the gradient at each point was half that obtained from the first graph.

What is the order of reaction with respect to ethanolic ammonia? Explain your answer.

……………………………………………………………………………………

……………………………………………………………………………………

……………………………………………………………………………………

……………………………………………………………………………………[1]

(iv) Hence, construct the rate equation for the reaction between 2-iodobutane and ethanolic ammonia.

……………………………………………………………………………………[1]

(v) Calculate the rate constant, for the reaction between 2-iodobutane and 4.00 mol dm^{-3} of ethanolic ammonia, stating its units.

[3]

(vi) Hence, describe the mechanism between 2-iodobutane and ethanolic ammonia.

[4]

(vii) Suggest and explain the effect on the rate of reaction when

I. 2-iodobutane is replaced with 2-chlorobutane.

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

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

II. ethanolic ammonia is replaced with ethanolic ethylamine.

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

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

[Total: 23]

3 The table below gives data about some physical properties of transition elements chromium, iron and cobalt.

Property	Chromium	Iron	Cobalt
First ionisation energy / kJ mol^{-1}	653	762	757
K_{sp} of $M(OH)_3$ / mol^4 dm^{-12}	6.3×10^{-31}	4×10^{-38}	1.6×10^{-44}

(a) Explain why these three metals have similar first ionisation energies.

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

…………………………………………………………………………………………[2]

(b) Equal volumes of 0.010 mol dm^{-3} chromium(III) solution and 0.010 mol dm^{-3} iron(III) solution were mixed. To separate the two metal ions, solid sodium hydroxide was added to precipitate the maximum amount of $Fe(OH)_3$ from the mixture, without precipitating $Cr(OH)_3$.

(i) Calculate the concentration of hydroxide ion in the mixture when $Cr(OH)_3$ just precipitates.

[2]

(ii) Hence, determine the concentration of iron(III) ions remaining in the solution. Evaluate if the separation is effective.

………………………………………………………………………………………

………………………………………………………………………………………[2]

(iii) Alternatively, sodium hydroxide can be added until in excess to separate iron(III) and chromium(III) ions. Explain how the separation can be achieved, giving a brief procedure and the ionic equations of the reactions involved.

………………………………………………………………………………………

………………………………………………………………………………………

………………………………………………………………………………………

………………………………………………………………………………………

………………………………………………………………………………………

………………………………………………………………………………………

………………………………………………………………………………………

………………………………………………………………………………………[3]

(c) **(i)** In the presence of ligands, the d orbitals of iron(III) complexes split into two groups. Explain how the d orbitals of an octahedral complex, such as $[Fe(H_2O)_6]^{3+}$, are arranged in the presence of ligands. Include a fully labelled diagram in your answer.

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

…………………………………………………………………………………………[2]

(ii) Hence, explain why a solution of $[Fe(H_2O)_6]^{3+}$ is yellow.

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

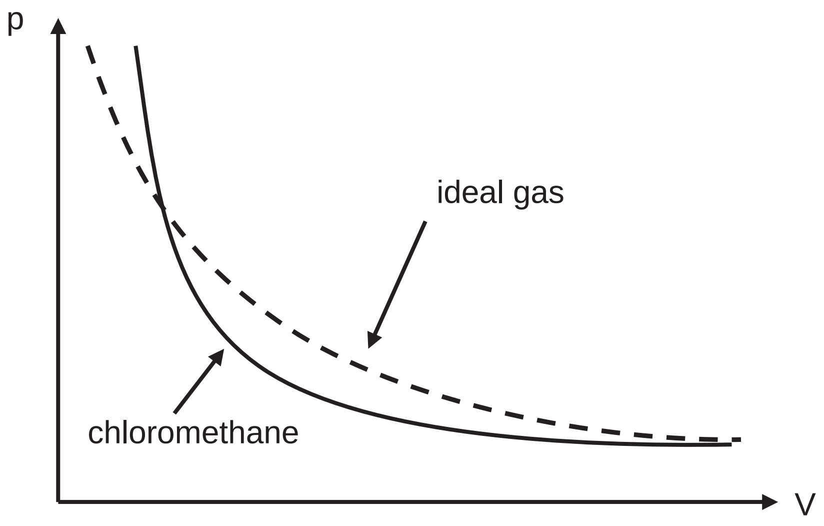
……………………………………………………………………………………………

……………………………………………………………………………………………

…………………………………………………………………………………………[3]

[Total: 14]

4 (a) The following graphs show the pressure–volume relationship for 1 mole of an ideal gas and chloromethane in a syringe at temperature *T* K.



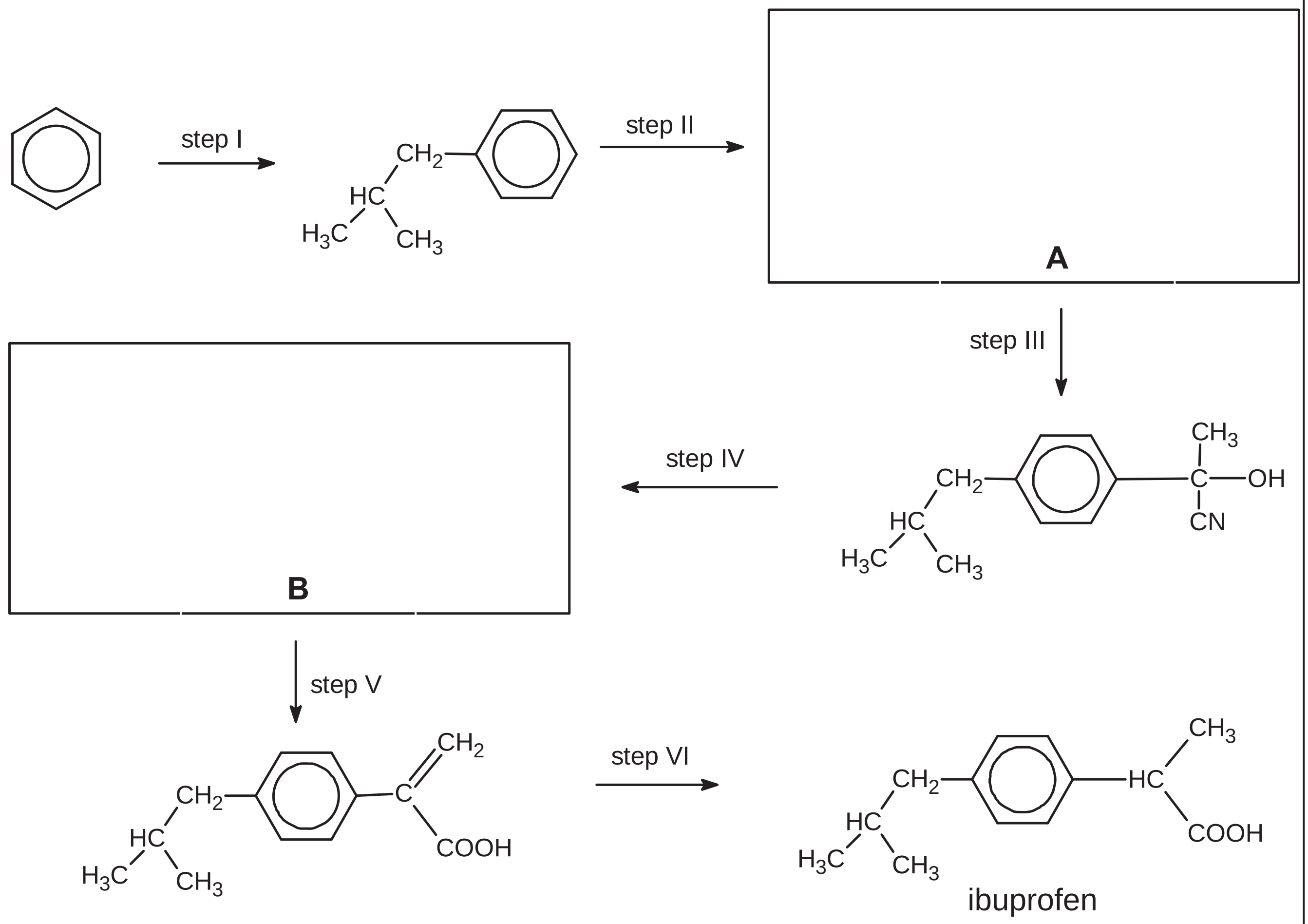
Explain why part of the graph for chloromethane is below that of an ideal gas at low pressure.

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

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

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

(b) Ibuprofen is a common medication that is used to relief pain and fever. Benzene is used as the starting chemical in the production of ibuprofen according to the following synthesis scheme.



(i) State the type of reaction in step I.

……………………………………………………………………………………[1]

(ii) Draw the structures of compounds A and B in the boxes above.

[2]

(iii) Suggest the reagents and conditions for step I, IV and VI.

step I: ……………………………………………………………………………

step IV: ……………………………………………………………………………

step VI: ……………………………………………………………………………

[3]

When approving new medicine for human consumption, food and drug approving agencies require the medicine to contain only one of two enantiomers that is biologically safe.

In the production of ibuprofen, a pair of enantiomers is produced in equal quantities in step III. However, both enantiomers are used to produce ibuprofen.

(iv) Draw the pair of enantiomers and explain why 2 enantiomers are produced is step III. You may use R to represent the phenyl side chain.

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

…………………………………………………………………………………………………

………………………………………………………………………………………[1]

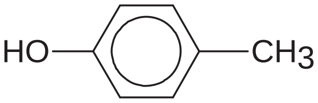
(v) By considering the hybridisation of carbon, explain why both enantiomers can be used to produce ibuprofen?

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

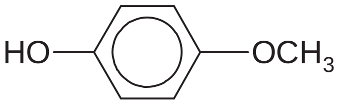
…………………………………………………………………………………………………

………………………………………………………………………………………[1]

(c) The pK_a of two substituted-phenols are given below.



pK_a = 10.26
methylphenol



pK_a = 10.21
methoxyphenol

Suggest a reason for the difference in pK_a values of both compounds.

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

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

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

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

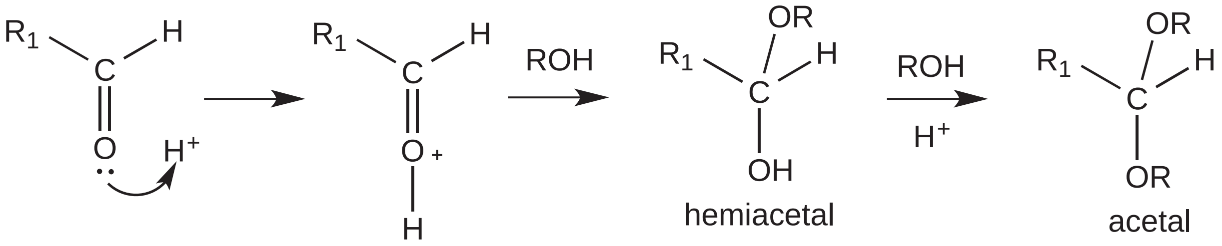
……………………………………………………………………………………………………

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

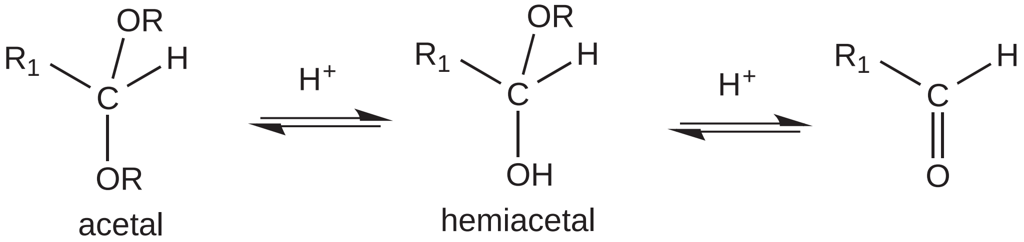
……………………………………………………………………………………………[2]

[Total:11]

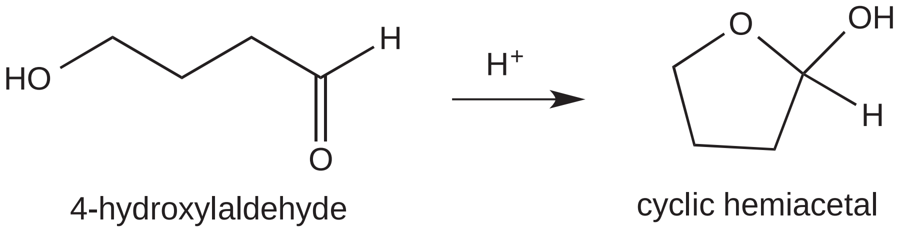
5 The synthesis of hemiacetals and acetals are acid-catalysed as shown.



However, hemiacetal and acetal formation are reversible. In the presence of acid, the acetal and hemiacetal hydrolysed back to form the aldehyde.



(a) **(i)** 4-hydroxyaldehyde undergoes the same mechanism in the presence of acid to form a cyclic hemiacetal, which is more stable towards hydrolysis.



Describe the mechanism for this reaction, including curly arrows showing the movement of electrons, and all charges.

[3]

(ii) Outline a simple chemical test to check if the formation of the cyclic hemiacetal is reversible.

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

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

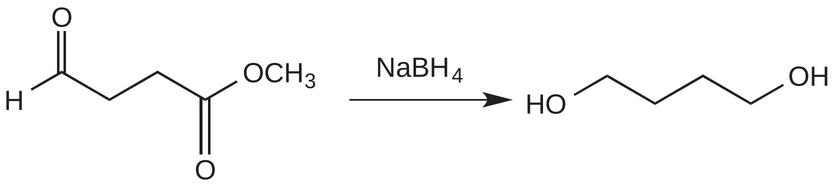
(iii) The product of this reaction, the cyclic hemiacetal, exists as a mixture of stereoisomers. Draw the displayed structure of each stereoisomer of the cyclic hemiacetal.

[2]

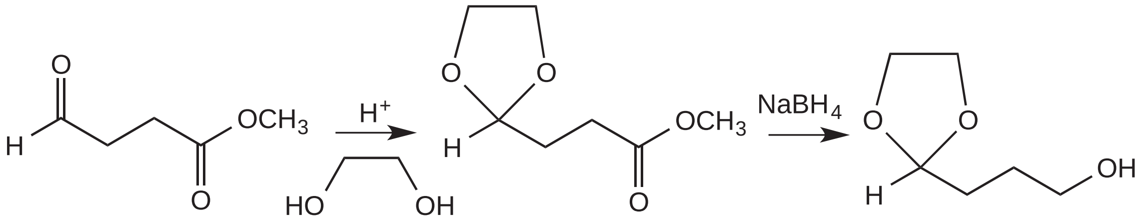
(b) Protecting groups are introduced in reactions involving complex molecules with different functional groups. This is to prevent the interfering functional groups from reacting. These functional groups in a molecule must be protected in order for reaction to proceed the desired way.

For instance, aldehyde undergoes reduction readily. The aldehyde could be converted to form acetal to protect the aldehyde against the reduction reaction.

Without protecting group:



With protecting group:



(i) Explain why sodium boron hydride, NaBH4 reduces ester slowly to form primary alcohol while it reduces aldehyde more readily.

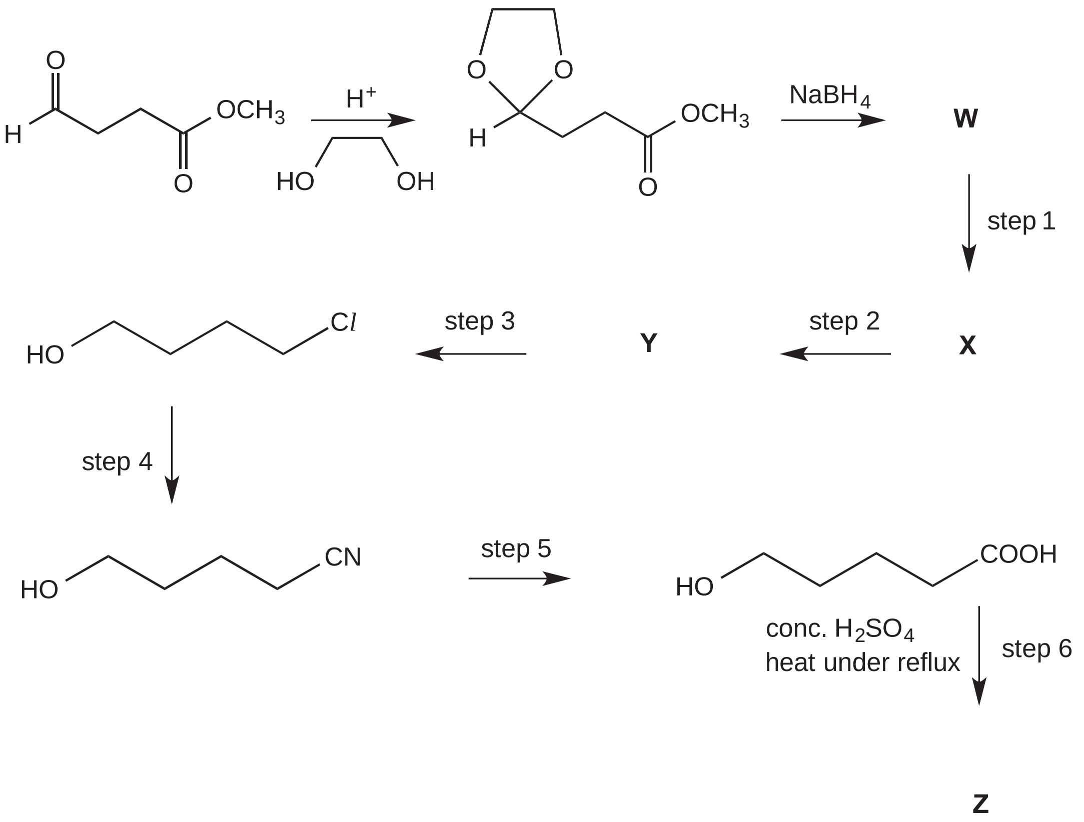
……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

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

Compound Z can be made from the following reaction scheme, where the first step involves the protection of aldehyde.



(ii) Suggest the structural formulae of W, X, Y and Z.

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

[2]

(iii) State the reagents and conditions needed for step 1, 2 and 3.

step 1: ……………………………………………………………………………………

step 2: ……………………………………………………………………………………

step 3: ……………………………………………………………………………………

[3]

(iv) State the type of reaction for step 4 and 5.

step 4: ……………………………………………………………………………………

step 5: ……………………………………………………………………………………

[1]

[Total:14]

NANYANG JUNIOR COLLEGE
JC 2 PRELIMINARY EXAMINATION
Higher 2

CHEMISTRY **9729/03**
Paper 3 Free Response **19 SEP 2017**
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 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

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 **13** printed pages.

Section A

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

1 **(a)** **(i)** Suggest why the melting point of MgO, Al_2O_3 and SO_3 is decreasing in the following order

$$MgO > Al_2O_3 > SO_3$$ [2]

(ii) Explain how the electronegativity of the elements in the oxides determine the type of bonding and hence the acid-base nature in MgO and P_4O_{10}. [2]

(b) A student was given 3 unknown oxides A, B and C containing Na_2O, Al_2O_3, and P_4O_{10}, The labels A to C do not correspond to the identities of the oxides.

He was given 2 packets of sample mixture, each containing different mole ratios of oxides A to C given in the table.

The student dissolved each sample mixture in half a beaker of water and recorded the observations of the resulting solution.

Sample	A	B	C	Observation of resulting solution
1	1	1	7	Neutral solution
2	1	1	1	Highly acidic solution

(i) Write a balanced equation when NaOH reacts with

- Al_2O_3
- P_4O_{10}

[2]

(ii) By considering the reactions of the oxides with water and the stoichiometric ratios obtained in **(i)**, account for the observations for samples 1 and 2. Hence deduce the identities of A, B and C. [4]

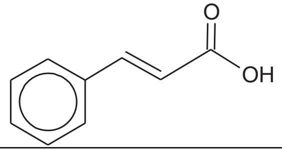
(c) The mineral dolomite is a double carbonate of magnesium and calcium, with the formula of $CaMg(CO_3)_2$. When a sample of impure dolomite was heated at 315 °C, $\boldsymbol{x}$ cm^3 of gas was collected which gave white ppt with lime water. When another sample of the same mass was heated at 530 °C, $\mathbf{2}\boldsymbol{x}$ cm^3 of gas was collected. When 1.000g of dolomite was reacted with excess hydrochloric acid, 0.450 g of gas was collected.

(i) Write an equation to account for the reaction that took place at 315 °C. [1]

(ii) Account for the different volumes of gases collected at 315 °C and 530 °C. [3]

(iii) Determine the percentage purity of the impure dolomite sample. [2]

(d) The following are some of the commonly used acids in food and beverage industries for various purposes like flavouring, preservatives and improving the texture of food. Their pK_a values are given below.

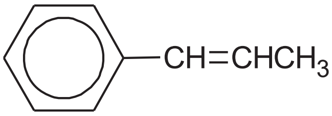
Name	Structure	pK_a
Carbonic acid	H_2CO_3	3.61
Ethanoic acid	CH_3CO_2H	4.72
Cinnamic acid		4.44

(i) By considering the structure of both acids, suggest and explain if ethanoic acid or cinnamic acid will react with NaOH(aq) first. [2]

(ii) Explain, using appropriate equations, what would happen when carbon dioxide is bubbled into a solution containing the salt formed in **(i)**. [2]

[Total: 20]

2 Phenylpropenes, for instance, 1−phenylpropene, has been used as precursors for a variety of effective insecticides.



1-phenylpropene

(a) Draw a labelled diagram to show the orbitals that form the C=C bond in 1−phenylpropene, and state the type of hybridisation involved. [2]

(b) 1−phenylpropene reacts with iodine monochloride, I*Cl*, in the presence of an inert organic solvent.

(i) Describe the mechanism of this reaction, showing curly arrows, charges, dipoles and any relevant lone pairs. [2]

(ii) Suggest the structure of another carbocation that can be formed from the mechanism drawn in **(i)**. Hence, explain which is the preferred carbocation formed. [2]

(iii) 1−phenylpropene also reacts with aqueous iodine monochloride. When water is present, a different organic compound can be formed.

Suggest the structure of this organic compound, and explain how it is formed with reference to the mechanism you have described in **(i)**. [2]

(c) Hydroformylation is an industrial process for the production of aldehydes from alkenes. This chemical reaction entails the net addition of –CHO and a hydrogen atom to a carbon-carbon double bond.

When an equimolar mixture of $C_6H_5CH_2CH=CH_2$, CO and H_2 at an initial total pressure of 120 atm is allowed to reach equilibrium at 500 K, the partial pressure of $C_6H_5CH_2CH_2CH_2CHO$ is found to be 39.6 atm.

Write the K_p expression for this process and hence calculate a value for K_p at 500 K, stating its units. [3]

(d) Alcohol D, C_xH_yOH, is an alarm pheromones emitted by the Koschevnikov gland of honey bees.

When 0.10 cm^3 of liquid D was dissolved in an inert solvent and an excess of sodium metal added, 10.9 cm^3 of gas was produced.

When 0.10 cm^3 of liquid D was combusted in excess oxygen in an enclosed vessel, the volume of gas was reduced by 65 cm^3. The addition of excess KOH(aq) caused a further reduction in gas volume of 131 cm^3.

All gases were measured at 273 K.

(i) Use these data to calculate values for x and y in the molecular formula C_xH_yOH for D. [3]

Alcohol D reacts with acidified $K_2Cr_2O_7$, and can be dehydrated to alkene E. On treating E with an excess of hot acidified concentrated $KMnO_4$, an equimolar mixture of ethanoic acid and butanone is produced.

(ii) Use this information to deduce the skeletal formulae of D and E, explaining your reasoning. [2]

(iii) State and explain with two reasons whether E can show cis-trans isomerism. [1]

(e) Dinitrogen pentoxide, N_2O_5, has been used as a reagent to introduce the nitro group in arenes. It exists as a white solid of N_2O_5, with the structure $O_2N{-}O{-}NO_2$.

N_2O_5 can be produced by the following sequence.

I: $N_2(g) + O_2(g) \rightarrow 2NO(g)$ $\Delta H = +180\ kJ\ mol^{-1}$
II: $NO(g) + ½\ O_2(g) \rightarrow NO_2(g)$ $\Delta H = -57\ kJ\ mol^{-1}$
III: $2NO_2(g) + ½\ O_2(g) \rightarrow N_2O_5\ (g)$ $\Delta H = -55\ kJ\ mol^{-1}$

(i) Draw the dot-and-cross diagram of N_2O_5. [1]

(ii) Given that the bond energy of N−O bond is 210 $kJ\ mol^{-1}$ and using relevant data from the Data Booklet, estimate the average bond energy of the N=O bond. [2]

(iii) The standard enthalpy change of formation of solid N_2O_5 is +11.3 $kJ\ mol^{-1}$. Using the relevant enthalpies given, construct an energy cycle to calculate the enthalpy change of sublimation of N_2O_5. [2]

[Total: 22]

3 Proteins are macromolecules, consisting of one or more long chains of amino acid residues. Proteins perform a vast array of functions in the human body such as the transport of oxygen in the blood by haemoglobin, an iron-containing protein.

(a) Glycine, NH_2CH_2COOH is an amino acid. It is electrically neutral at pH 5.97. When placed in a solution of low pH, it exists as a dibasic acid, $^{+}NH_3CH_2COOH$. The two corresponding acid dissociation values are:

$K_{a\,(1)}$ = 4.57×10^{-3} mol dm^{-3} for the −COOH
$K_{a\,(2)}$ = 2.51×10^{-10} mol dm^{-3} for the $-NH_3^{+}$

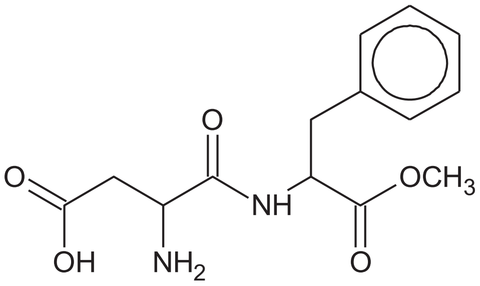
The acidic properties of glycine was studied when 25.0 cm^3 of 0.0500 mol dm^{-3} $^{+}NH_3CH_2COOH$ was titrated with 40.00 cm^3 of 0.100 mol dm^{-3} NaOH.

(i) Calculate the initial pH of a solution of $^{+}NH_3CH_2COOH$. [1]

(ii) Calculate the pH of the solution when $^{+}NH_3CH_2COOH$ is completely neutralised. [2]

(iii) Hence, sketch the pH-volume curve you would expect to obtain for the titration. Label the key points based on your calculations in **(i)** and **(ii)**, stating the maximum buffering capacity. You may assume that the final pH of the solution is 12.4. [3]

(b) Apart from having many biological functions, amino acids are used in a variety of applications in the food industry. Aspartame, an amino acid derivative is used as an artificial sweetener in many foods and beverages. However, it is not commonly used as a baking sweetener as it breaks down easily at high pH when heated.

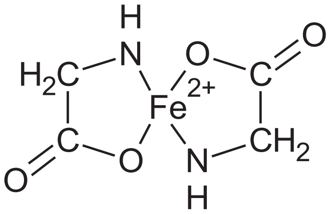


aspartame

Predict the products of aspartame when it is heated at high pH. [2]

(c) Amino acids are also widely applied in the health industry. They form chelates with metals ions by acting as ligands.

The following is an example of a chelated metal ion.



For the uptake of essential metal ions into the body, chelated metal ions are believed to be the preferred choice as health supplements because their complex structures better survive passage through the acidic environment of the stomach and subsequently absorbed into the body. On the other hand, free metal ions are typically flushed through the intestine without being absorbed into the bloodstream.

(i) The following equilibrium is established when iron(II) sulfate dissolves in acid.

$$FeSO_4(s) + 2H^+(aq) \rightleftharpoons H_2SO_4(aq) + Fe^{2+}(aq)$$

By considering the above equilibrium, suggest why non-chelated compounds such as iron (II) sulfate are not well absorbed by the body. [1]

The formation constant, K_f, is an indication of the stability of a complex ion. The K_f values of amino acid complexes of many health supplements are in the 10^4 to 10^5 range and are highly absorbed. For formation constants above 10^6, there will be minimal metal released and such compounds are essentially useless in biological systems.

The table below lists the K_f values of some iron and mercury complexes with amino acids and common ligands.

Ligand	Metal ions	
	Fe^{2+}	Hg^{2+}
cysteine	10^6	10^{14}
CN^-	10^{35}	10^{41}
$edta^{4-}$	10^{14}	10^{21}

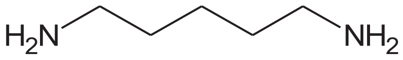
(ii) Given the equilibrium concentration of a solution of $[Fe(CN)_6]^{4-}$ is 0.65 mol dm^{-3}, calculate the concentration of cyanide ion present in equilibrium with the complex ion. [2]

(iii) In other cases, amino acids in the body such as cysteine are capable of forming a tightly bound complex with mercury, hence when taken in small amounts, mercury is not as toxic. However, exposure to high level of mercury will require chelation therapy, a medical procedure which involves injecting suitable ligands into the bloodstream to remove mercury ions from the body.

By using the K_f values, suggest an explanation whether the following ligands can be injected into the bloodstream for the chelation therapy.

- CN^-
- $edta^{4-}$ [2]

(d) Upon death, the proteins in body starts to decompose and produce ammonia in the lungs soon after death, and the ammonia diffuses outward through the nose and mouth. Within a few hours, the body starts to produce heavier amines such as 1,5-diaminopentane in its tissues, giving rise to the foul smell.



1,5-diaminopentane

(i) Suggest how the basicity of 1,5-diaminopentane and phenylamine might compare to that of ammonia. Explain your reasoning. [2]

(ii) Phenoxyethanol is used in embalming to disinfect and temporarily preserve human and animal remains. It can be made from phenol in two steps.

phenoxyethanol

State reagents and conditions for each of the two steps, and give the structure of the intermediate formed. [3]

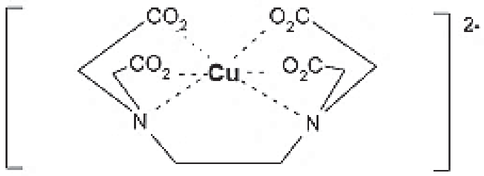
[Total: 18]

Section B

Answer **one** question from this section.

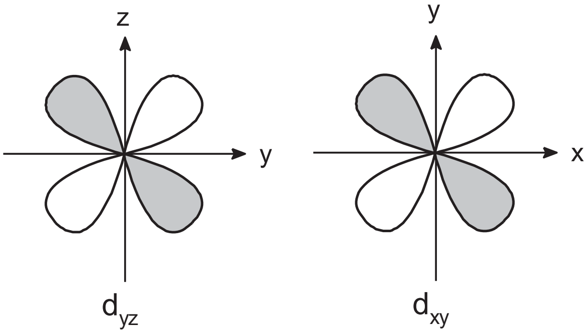
4 **(a)** Copper and the compounds it forms have a wide variety of uses.
Copper-EDTA complexes are commonly used in cosmetics and it gives the blue colour in many shampoos.

The structure of the copper-EDTA complex is given below.



(i) State the electronic configuration of this copper ion. [1]

(ii) Two of the d orbitals are given below. Sketch the shape of the other three d orbitals present in copper. [2]



(b) Copper produced from ore undergoes an electrolytic treatment at some stage via electrorefining. In the electrorefining of impure anodes, unwanted impurities are eliminated, yielding copper with high purity at the cathode.

When a particular ore was reduced, an alloy was obtained. It mainly consists of copper, but with silver and lead as minor impurities.

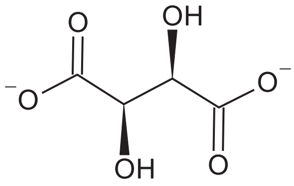
(i) Explain, with reference to relevant $E^\ominus$ values, and the information given above, what happens to the silver and lead impurities during the purification process. [3]

(ii) A current of I A was passed through the cell described in **(b)** for t min. It was found that the mass of the cathode increased from m_o g to m_x g. Using the information provided, deduce an expression for Avogadro's constant, L. [2]

(c) Tartrate and citrate salts are used with copper(II) ions in the preparation of Fehling's and Benedict's solutions that are used to test for presence of aldehydes and reducing sugars.

(i) Copper(II) ions can form a salt of formula $Cu_x(C_yH_zO_7)_2$ with citrate ions. The composition of this salt by mass is Cu: 33.55 %; C: 25.30 %; O: 39.40 %. Determine x, y and z. [2]

The structure of tartrate ion that is used in the preparation of Fehling's reagent is given below.



Tartrate ion

(ii) Explain why the tartrate ion is a
- Bronsted-Lowry base
- Lewis base [3]

(iii) Ethanedioic acid, HO_2CCO_2H, is another dibasic acid like tartaric acid, $HO_2CCH(OH)CH(OH)CO_2H$. Explain why pK_1 of ethanedioic acid is lower than pK_1 of tartaric acid. [1]

(d) Compound J, $C_9H_8O_4$, forms a non-chiral molecule K, $C_9H_{12}O_3$, when reacted with $LiAlH_4$ in dry ether. However, when J was reacted with $NaBH_4$ instead, a product of molecular formula $C_9H_{10}O_4$ was formed.
J gives an orange precipitate with 2,4-dinitrophenylhydrazine but does not give any precipitate when warmed with Fehling's reagent. K reacts with bromine water to form L, $C_9H_9O_3Br_3$.

(i) Suggest the structures of J, K and L. [3]

(ii) Write a balanced equation for the reaction of J with $LiAlH_4$. [1]

(iii) State two observations that you would expect to see when K reacts with bromine water to form L. [1]

(iv) $LiAlH_4$ reactions must be done in the absence of water as it will react spontaneously with water. Write a balanced equation for this reaction. [1]

[Total: 20]

5 The Kolbe electrolysis is an electrochemical method used to synthesise alkanes. Hermann Kolbe discovered the method in 1849 when he demonstrated the existence of carbon dioxide and ethane produced during the electrolysis of an aqueous solution of potassium ethanoate. The method has several advantages, for example the possibility to control the potential of the electrode and the simplicity of the reaction because no reducing or oxidizing agents are required.

The reaction mechanism is thought to involve a three-stage process.

In step I, the ethanoate ion CH_3COO^- is first converted into an ethoxy radical intermediate $CH_3COO\bullet$.

This intermediate then undergoes decarboxylation to form a methyl radical intermediate.

step II $CH_3COO\bullet \rightarrow \bullet CH_3 + CO_2$

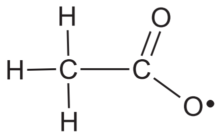
Finally two methyl radical intermediates dimerises to form the alkane product.

step III $2\ \bullet CH_3 \rightarrow CH_3\text{-}CH_3$

(a) **(i)** Suggest and explain, in terms of change in oxidation number, the electrode where step I took place in the electrolysis process. Hence, write a half-equation for step I. [2]

(ii) A gas is obtained at the other electrode. Write the half-equation to explain how the gas is formed. Calculate the volume of gas produced at room temperature and pressure when a current of 500 mA is passed for 20 minutes through a solution of potassium ethanoate. [3]

(iii) Use information given above to draw out the full mechanism for steps II and III of the Kolbe Reaction. You are advised to use structural formulae for all species, such as



for $CH_3COO\bullet$ as well as appropriate curly arrows so that it is clear which bonds are broken and which are formed. Indicate any unpaired electrons by a dot (•). [2]

(b) Kolbe electrolysis of a single acid salt gives a symmetrical alkane. However, when a mixture of two mono-carboxylic acid salts is used, all probable alkanes are formed.

$$R'CO_2^- + RCO_2^- \Rightarrow R\text{–}R + R\text{–}R' + R'\text{–}R'$$

Electrolysing a mixture of ethanoate salt and the salt of another mono-carboxylic acid W produced three different alkanes: ethane, X and Y, which could be separated by fractional distillation.

(i) A gaseous sample of 0.30 g of X occupied 168 cm^3 at 300 K and 1 atm. Calculate the M_r of X and hence deduce its molecular formula. [2]

(ii) State 2 assumptions you have made in your calculation in **(i)**. [2]

(iii) Use information given above and your answer in **(i)** to suggest possible structures for the alkane Y and the acid W. [2]

(c) In another separate experiment, a new alkane Z, C_5H_{12}, was formed. When reacted with chlorine under ultraviolet light, Z produced only four monochloro compounds with the formula $C_5H_{11}Cl$. Some of the products is/are chiral. Suggest the structure of Z as well as that of the chiral product(s) formed. Explain your reasoning. [3]

(d) Red cabbage juice contains a pigment molecule called flavin that changes colours according to the pH of the solution as shown below.

pH	2	4	6	8	10	12
colour	red	pink	violet	blue	green	yellow

Suggest and explain, with the aid of equations, what would be observed if a few drops of red cabbage juice was added separately to the following solutions.

(i) Silicon chloride [2]

(ii) Ammonium chloride [2]

[Total: 20]

[Turn over

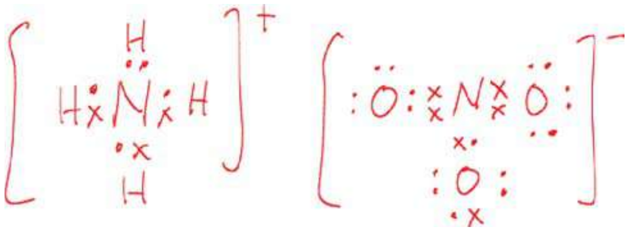
2017 H2 Chemistry Prelim Answers

Paper 1 Answer Key

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

Paper 2 Answers

1 **(a)** **(i)**



Shape of ammonium ion: tetrahedral
Shape of nitrate ion: trigonal planar

(ii) $\Delta H_{sol} = -(\text{-Lattice Energies}) + (-\Delta H_{hyd}) = |\text{L.E.}| - |\Delta H_{hyd}|$

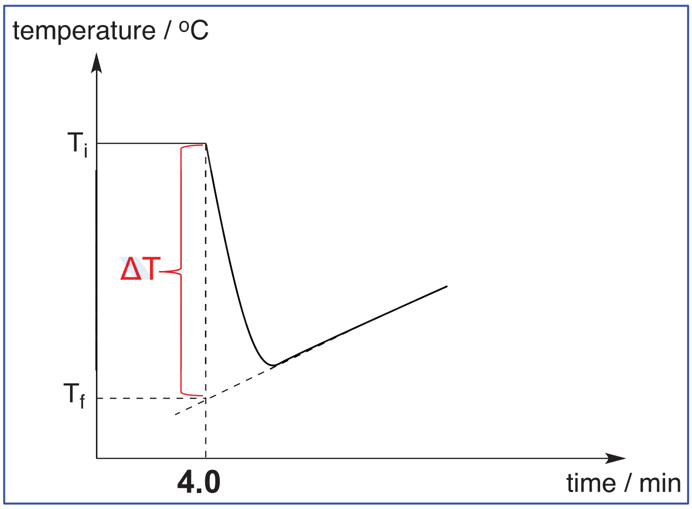
$|\text{L.E.}| \propto \dfrac{|q^{+}q^{-}|}{r^{+}+r^{-}}$

$|\Delta H_{hyd}| \propto \dfrac{|q|}{r}$

Anionic radius of nitrate ion is larger than chloride, therefore the decrease in $|\Delta H_{hyd}|$ of nitrate ion is larger than the decrease in |L.E.|. ΔH_{sol} is expected to be more endothermic.

(b) **(i)** Assuming a temperature change of 5 °C and no heat loss to surroundings,
n(salt) x 15 000 = 100 x 4.3 x 5
n(salt) = 0.1433 mol
minimum mass = 0.1433 x 53.5 = 7.67 g

(ii)



(iii) $\Delta G^o = \Delta H^o - T\Delta S^o$

ΔG^o is negative since reaction is spontaneous and ΔH^o is positive since reaction is endothermic. Therefore sign of ΔS^o is positive as there are more ways to arrange the particles when the solid dissolves in water.

(c) **(i)** Since Zn is oxidised, $Zn(s) \rightarrow Zn^{2+}(aq) + 2\ e^-$

Overall equation:

$Zn(s) + 2\ MnO_2(s) + 2\ NH_4Cl(aq) \rightarrow Mn_2O_3(s) + ZnCl_2(aq) + 2NH_3(aq) + H_2O(l)$

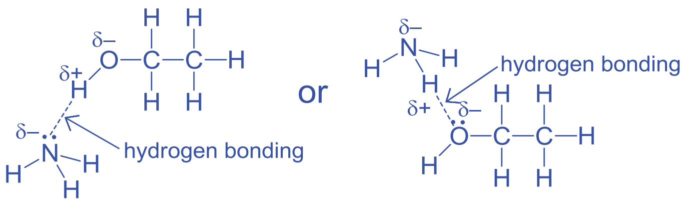
(ii) $E^\circ_{cell} = (+0.5) - (-0.76) = +1.26V$

(iii) $\Delta G^o = -\ nFE^o = -\ 2 \times 96500 \times 1.26 = -\ 243\ 000\ J\ mol^{-1}$

$= -\ 243\ kJ\ mol^{-1}$

The sign of ΔG^o is negative and hence the reaction is spontaneous.

2 **(a)**



(b) **(i)** Quenching is required to stop or slow down the reaction so as to achieve a more accurate titre value at that time or to find the concentration at that instance.

Quenching agent: large volume of cold water / add large volume of acid to remove the NH_3 (in this question).

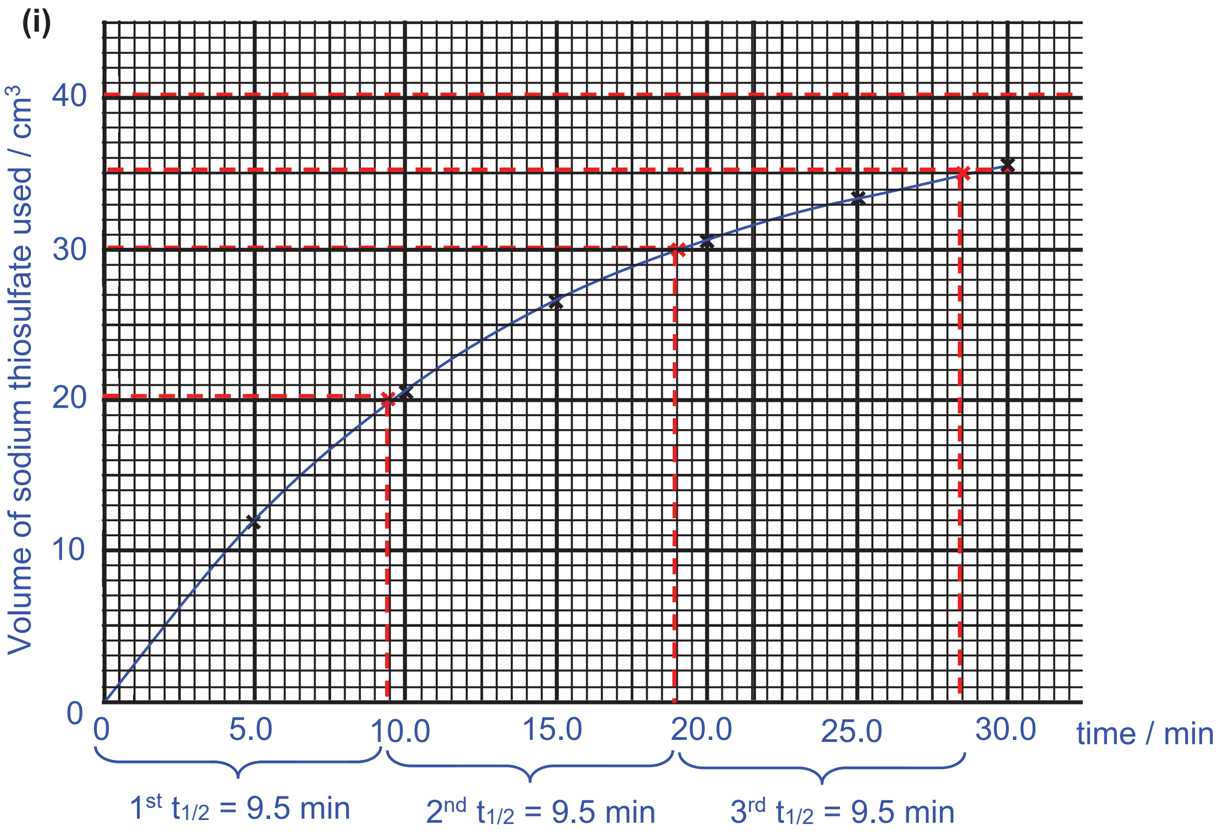
(ii) $Cl_2 + 2I^- \rightarrow 2Cl^- + I_2$

(iii) $I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-}$

(iv) Starch indicator is added when the solution turns pale yellow.

The end-point can be recognised when one drop of sodium thiosulfate added cause the dark blue solution to permanently turn colourless.

(c) (i)



(ii) [2-iodobutane] = 0.20 / 2 = 0.10 mol dm^{-3}

n(2-iodobutane) : n(I^-) : n($S_2O_3^{2-}$) = 1 : 1 : 1

n(2-iodobutane) = n($S_2O_3^{2-}$) = $\frac{10}{1000}$ × 0.10 = 0.001000 mol

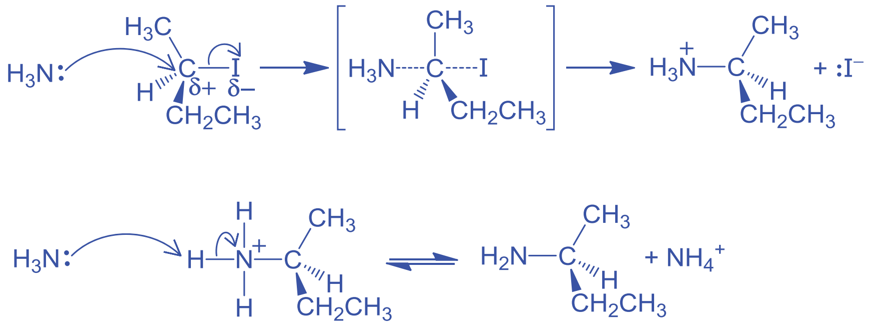
V($S_2O_3^{2-}$) required when all 2-iodobutane reacted = $\frac{0.001000}{0.0250}$ = 0.04000 dm^3 = 40.00 cm^3

When volume of sodium thiosulfate increases from 0 to 20 cm^3,
1st $t_{1/2}$ = 9.5 min .
When volume of sodium thiosulfate increases from 20 to 30 cm^3
2nd $t_{1/2}$ = 9.5 min.
Since the 1st $t_{1/2}$ is approximately equal to 2nd $t_{1/2}$, it is 1st order with respect to 2-iodobutane.

(iii) Since the rate for 2.00 mol dm^{-3} of ethanolic ammonia reaction is half the rate for 4.00 mol dm^{-3} of ethanolic ammonia reaction, it is 1st order with respect to ethanolic ammonia.

(iv) rate = k [2-iodobutane][ethanolic ammonia]

(v) Nucleophilic Substitution (S_N2)



(vi) After mixing equal volume of 0.20 mol dm^{-3} 2-iodobutane and 4.00 mol dm^{-3} ethanolic ammonia, [2-iodobutane] = 0.10 mol dm^{-3} and [ethanolic ammonia] = 2.00 mol dm^{-3}.

Since [ethanolic ammonia] is in large excess,
rate = k' [2-iodobutane], where k' = k [ethanolic ammonia]

$$t_{1/2} = \frac{\ln 2}{k'} = \frac{\ln 2}{k\text{ [ethanolic ammonia]}}$$

$$9.5 = \frac{\ln 2}{k\ (2.00)}$$

k = 0.0365 [1] mol^{-1} dm^{3} min^{-1}

(vii) I. 2-iodobutane is replaced with 2-chlorobutane.

BE(C−C*l*) = 340 kJ mol^{-1} BE(C−I) = 240 kJ mol^{-1}

As more energy is required to overcome the stronger C−C*l* bond, the rate of reaction decreases.

II. ethanolic ammonia is replaced with ethanolic ethylamine.

Electron donating ethyl group increases the electron density around the nitrogen atom of ethylamine, making the lone pair of electrons more available (or make the nitrogen more nucleophilic) to attack the electrophilic carbon. Hence, rate of reaction increases.

3 **(a)** From Cr to Co,

- number of protons increases, nuclear charge increases
- additional electron is added to the penultimate 3d subshell.
- Hence, screening/shielding effect also increases as presence of the 3d orbital shields the 4s electrons from the nuclear attraction.
- The effective nuclear charge experience by the outer 4s electrons increases only very gradually.
- Energy required to remove the 4s electron is relatively invariant.

(b) **(i)** $K_{sp} = [Cr^{3+}][OH^-]^3$

$6.3 \times 10^{-31} = (0.010/2)[OH^-]^3$

$[OH^-] = 5.013 \times 10^{-10}$ mol dm^{-3}

(ii) $K_{sp} = [Fe^{3+}][OH^-]^3$

$4 \times 10^{-38} = [Fe^{3+}](5.013 \times 10^{-10})^3$

$[Fe^{3+}] = 3.174 \times 10^{-10}$ mol dm^{-3} << 0.005 mol dm^{-3} hence effective

(iii) To the solution of Cr^{3+} and Fe^{3+} ions, add sodium hydroxide until excess. $Cr(OH)_3$ ppt forms and is soluble in excess.

$Cr^{3+} + OH^- \rightarrow Cr(OH)_3$

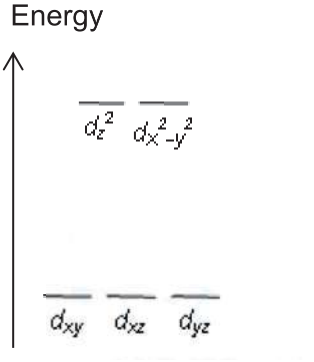
$Cr(OH)_3 + 3OH^- \rightarrow [Cr(OH)_6]^{3-}$

$Fe(OH)_3$ ppt is insoluble in excess sodium hydroxide.

$Fe^{3+} + OH^- \rightarrow Fe(OH)_3$

Filter the mixture and $Fe(OH)_3$ is the residue and $[Cr(OH)_6]^{3-}$ is the filtrate.

(c) **(i)** The electrons in orbitals that lie along the same axes as the ligands experiences greater repulsion, hence the energy is raised.



(ii) In the presence of ligands, the 3d orbitals split into 2 groups with an energy gap. When visible light passes through the iron complex, the violet wavelength of light corresponding to the energy gap is absorbed by the 3d electron in the lower energy level. This electron is promoted to a vacant 3d orbital at the higher energy level. The complementary colour, corresponding to unabsorbed wavelengths is observed.

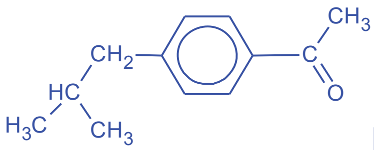
4 **(a)** At low pressure, when volume increases, pressure of chloromethane falls more than that of ideal gas as permanent dipole-permanent dipole interaction between CH_3Cl molecules hold the particles closer together, hence they strike the walls of the container with less force, resulting in lower pressure.

OR

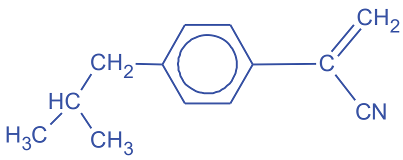
At low pressure, volume of chloromethane gas is lower/decreases more than ideal gas for a given pressure as permanent dipole-permanent dipole interaction between molecules is significant and the molecules are attracted closer to each other.

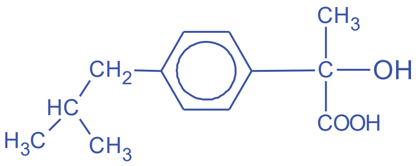
(b) **(i)** Electrophilic Substitution.

(ii)

A: 

[1]

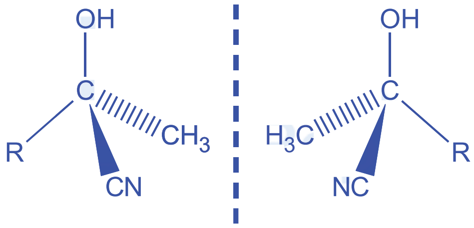
B: 

or 

(iii)

	Reagents and conditions	
Step I	anhydrous $AlCl_3$,$(CH_3)_2CHCH_2Cl$, room temperature	
Step IV	Al_2O_3, heat at 350 °C (OR conc H_2SO , 170 °C less preferred as hydrolysis of nitrile may occur)	Any dilute acid, heat under reflux
Step VI	H_2, Ni catalyst, heat **OR** H_2, Pt / Pd catalyst, room temp.	

(iv)



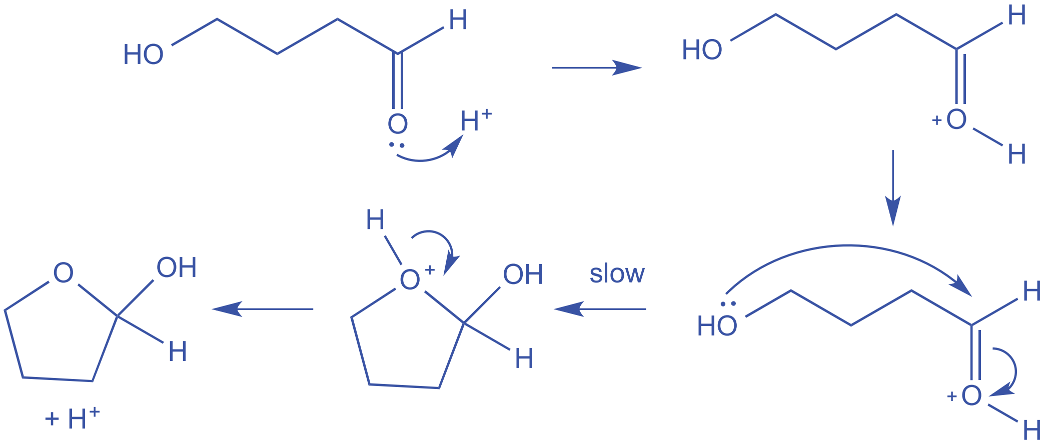
The CN^- nucleophile can approach the trigonal planar carbonyl carbon from the top or bottom of the plane **with equal probability** to give the 2 enantiomers **in equal amounts**.

(v) The sp^3 chiral carbon formed in step III eventually became sp^2 hybridised after elimination in step V (or IV) hence the two enatiomers will form the same alkene (which doesn't exhibit cis-trans isomerism).

(c) The relative strength of an acid depends on the stability of its conjugate base formed. Methoxyphenol has a lower pK_a, thus has a higher K_a value and is a stronger acid than methylphenol.
The $-OCH_3$ group is slightly more electronegative than CH_3 group [1] thus decreases the electron density of the conjugate base and disperses the negative charge on the phenoxide O atom to the OCH_3 group [1] hence has greater stability than the methylphenoxide.

Alternatively:
The relative strength of an acid depends on the stability of its conjugate base formed. Methoxyphenol has a lower pK_a, thus has a higher K_a value and is a stronger acid than methylphenol.
The p orbital of O in OCH_3 group overlaps with the π orbital of the phenoxide ion, thus there is greater dispersion of the negative charge over a larger volume [1] hence methoxyphenol has greater stability than the methylphenoxide.

5 **(a)** **(i)** Nucleophilic Addition

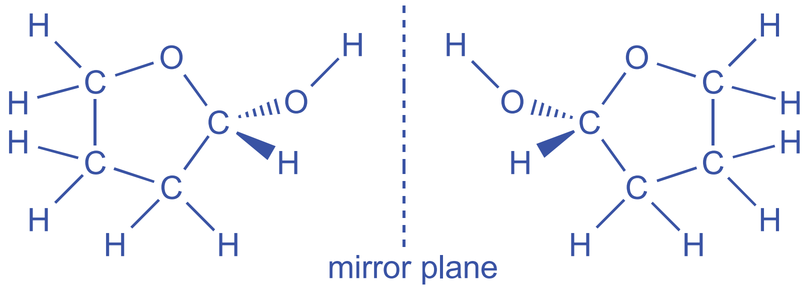


(ii) Add 2,4-DNPH, warm (Accept Fehling's solution OR Tollens' reagent)

When an orange precipitate seen, 4-hydroxyaldehyde is present. The formation of the cyclic hemiacetal is reversible.

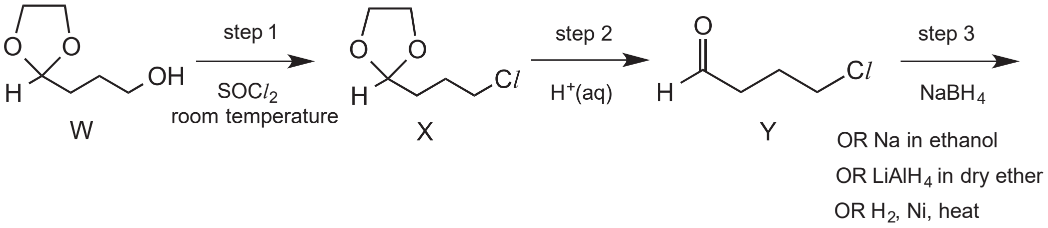
No orange precipitate seen, 4-hydroxyaldehyde is absent. The formation of cyclic hemiacetal is irreversible.

(iii)

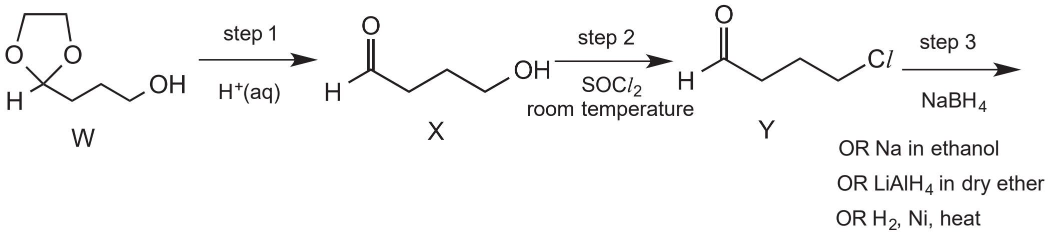


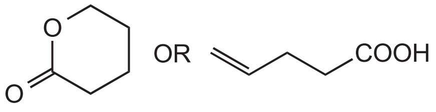
(b) **(i)** The electron donating –OCH_3 in ester disperses the partial positive charge on the carbonyl carbon, making it less electrophilic. Hence less susceptible to attack by hydride.

(ii)
(iii) Possible Synthetic route 1:



Possible Synthetic route 2:





Z

(iv) step 4: nucleophilic substitution
step 5: acid hydrolysis or hydrolysis

Paper 3 Answers

1 (a) (i) MgO and Al_2O_3 have giant ionic structures consisting of cations and anions held together by strong ionic bonds, requiring large amount of energy to break the strong bonds.

Al^{3+} in Al_2O_3 has a smaller ionic radius than Mg^{2+} but has a higher ionic charge of 3+ thus have a high charge density and high polarising power.

It is able to cause some polarisation of the O^{2-} ion electron cloud, giving rise to some covalent character / weakening the ionic bond.

SO_3 has a simple molecular structure consisting of SO_3 molecules held together by weak dispersion forces thus require small amount of energy to break the bonds.

(ii) Large electronegativity difference in Mg and O cause the bonds in MgO to be ionic and a basic oxide is obtained.

Smaller electronegativity difference in P and O causes the bond in P_4O_{10} to be covalent hence acidic oxide is obtained.

(b) (i) $Al_2O_3\ (s) + 2OH^- (aq) + 3H_2O\ (l) \rightarrow 2[Al(OH)_4]^- (aq)$

$P_4O_{10}\ (s) + 12OH^- (aq) \rightarrow 4PO_4^{3-} (aq) + 6H_2O\ (l)$

(ii) In Sample 1: 7 moles of **C** (Na_2O) (in Sample 1) dissolved in water to produce 14 mol of OH^- ions which reacted with 12 mol of H^+ from dissolution of 1 mol of P_4O_{10} and 1 mol of Al_2O_3 to give a neutral solution.

In Sample 2: 1 mol of **A** (P_4O_{10}) reacts with water to produce 12 mol of H^+, 6 mol of which reacted with 1 mol of Al_2O_3 and 2 mol with 2 mol NaOH formed, with 4 mol of H^+ still remaining in solution.

A & B: Al_2O_3 & P_4O_{10} **C**: Na_2O

(c) (i) $CaMg(CO_3)_2\ (s) \rightarrow CaCO_3(s) + MgO(s) + CO_2(g)$

(ii) Mg^{2+} has a smaller ionic radius than Ca^{2+} while their ionic charges are the same. Charge density of Mg^{2+} is higher and hence has higher polarising power than Ca^{2+}. Mg^{2+} is able to polarise / distort the electron cloud of CO_3^{2-} causing $MgCO_3$ to be less thermally stable and decompose at 315 °C. Both carbonates will decompose at a higher temperature of 530 °C hence volume of CO_2 evolved is doubled.

(iii)

$$n_{\text{pure dolomite}}\ \text{present} = \frac{0.450/44.0}{2} = 5.11 \times 10^{-3}\ \text{mol} \qquad [1]$$

$$\%\ \text{purity of dolomite} = \frac{5.11 \times 10^{-3} \times (40.0 + 24.0 + 2(12.0 + 3\times16.0))}{1.000} \times 100$$

$$= 94.09 \approx 94.1\% \qquad [1]$$

(d) **(i)** Cinnamic acid will react with aq NaOH first. The p orbital of O atom in cinnamate ion overlaps with the pi orbital of the –C=O, C=C and benzene to form a delocalised electron cloud. The negative charge on O of cinnamate ion is dispersed into the delocalised cloud, stabilising the ion hence is more acidic.

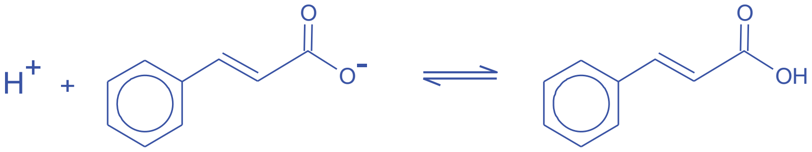
The ethanoate ion has an electron donating methyl group that increases the electron density of the $CH_3CO_2^-$ ion hence destabilising it.

(ii) CO_2 will dissolve in water to form carbonic acid.

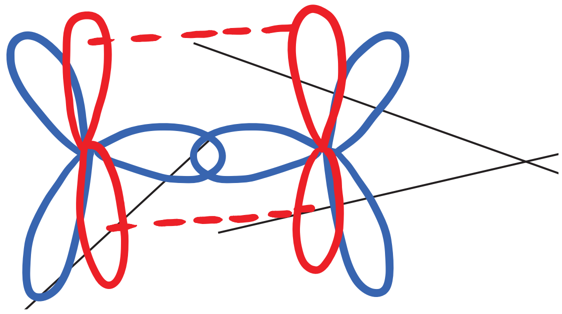
$CO_2 + H_2O \rightleftharpoons H_2CO_3$

The carbonic acid is a stronger acid than cinnamic acid thus will dissociate in water to and protonate the cinnamate ion to form back cinnamic acid.

$H_2CO_3 \rightleftharpoons HCO_3^- + H^+$



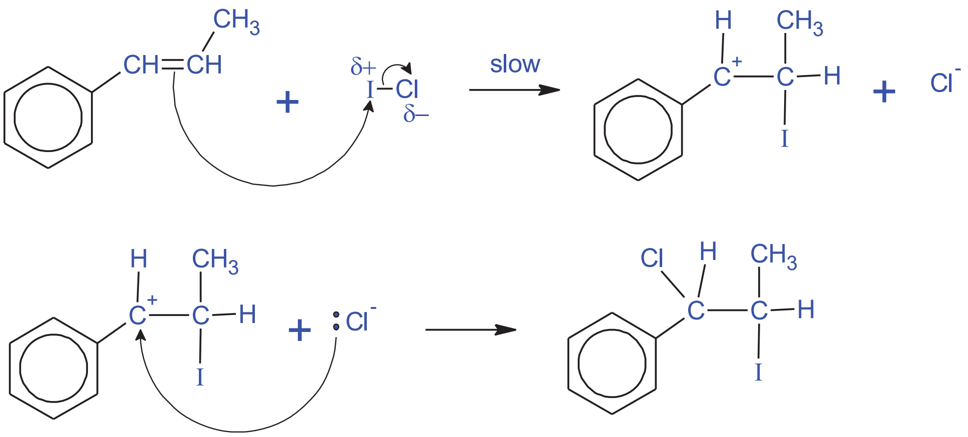
2 **(a)**



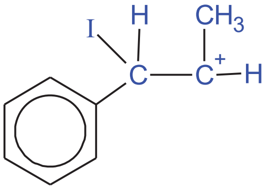
The unhybridised p-orbital overlap sideways to form π bond.

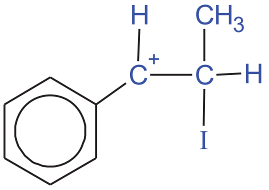
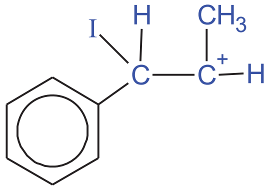
The sp^2 hybrid orbital overlap head on to form σ bond.

(b) **(i)** Electrophilic Addition

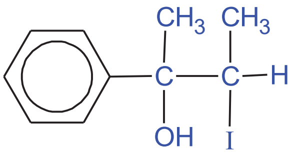


(ii)



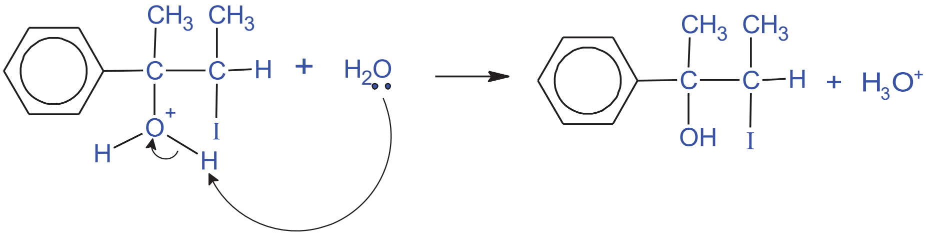
 is more stable than  and hence is the preferred carbocation formed. The p orbital of the carbocation centre overlaps with the delocalised π electron cloud of the benzene ring, electrons from the benzene ring delocalises to the carbocation centre. Hence the positive charge can be dispersed into the benzene ring, stabilizing it further.

(iii)



The lone pairs of electrons on O in H_2O acts as competing **nucleophile** in the 2nd step of the mechanism to attack the carbocation intermediate.

Note: A proton will be lost subsequently to form the organic compound as shown in the structure above.



(c)

	$C_6H_5CH_2CH=CH_2$	CO	H_2	⇌	$C_6H_5(CH_2)_3CHO$
Initial pressure / atm	40	40	40		0
Change in pressure / atm	−39.6	−39.6	−39.6		+39.6
Equilibrium pressure / atm	0.4	0.4	0.4		39.6

$$K_p = \frac{(P_{C6H5CH2CH=CH2})}{(P_{C6H5(CH2)3CHO})(P_{CO})(P_{H2})} = \frac{39.6}{(0.4)(0.4)(0.4)} = 619 \text{ atm}^{-2}$$

(d) **(i)** $C_xH_yOH + Na \downarrow C_xH_yO^{-}Na^{+} + \frac{1}{2} H_2$

amount of H_2, n_{H_2}

$= \dfrac{10.9 \times 10^{-3}}{22.7}$ = 4.80×10^{-4} mol

amount of C_xH_yOH = 2 x n_{H_2}

= 2 x 4.80×10^{-3} = 9.60×10^{-4} mol

Contraction = initial total volume – final total volume

65 = ($V_{O2\ total}$) – ($V_{O2\ excess}$ + V_{CO2})

$V_{O2\ total}$ – $V_{O2\ excess}$ = 65 + V_{CO2}

$V_{O2\ reacted}$ = 65 + V_{CO2} = 65 + 131 = 195 cm^3

OR

Let initial V_{O2} be z cm^3.

<table>
<tr><th></th><th>C_xH_yOH (l)</th><th>$(\frac{4x+y-1}{4})$ O_2 (g)</th><th>xCO_2 (g)</th><th>$(\frac{y+1}{2})$ H_2O (l)</th></tr>
<tr><td>Initial volume/ cm^3</td><td>–</td><td>z</td><td>0</td><td></td></tr>
<tr><td>After combustion and cooling/ cm^3</td><td>0</td><td colspan="2">z – 65</td><td></td></tr>
<tr><td>After reaction with NaOH/ cm^3</td><td>0</td><td>z – 131 – 65 (leftover O_2)</td><td>131 (formed)</td><td></td></tr>
</table>

Volume of O_2 used = z – (z– 131 – 65) = 196 cm^3

Amount of O_2 used = $\dfrac{196 \times 10^{-3}}{22.7}$ = 8.63×10^{-3} mol

Volume of CO_2 formed = 131 cm^3

Amount of CO_2 formed = $\dfrac{131 \times 10^{-3}}{22.7}$ = 5.78×10^{-3} mol

<u>Comparing ratio:</u>

Mole ratio of $C_xH_yOH : CO_2$ is $1:x$.

Hence $\dfrac{1}{9.60\times10^{-4}} = \dfrac{x}{5.78\times10^{-3}} \quad \therefore x = \dfrac{5.78\times10^{-3}}{9.60\times10^{-4}} = 6$

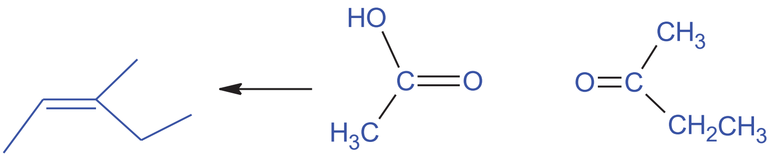
Comparing mole ratio of C_xH_yOH and O_2 = 1 : $\dfrac{4x+y-1}{4}$

Since x=6, $\dfrac{1}{9.60\times10^{-4}} = \dfrac{\frac{4(6)+y-1}{4}}{8.63\times10^{-3}} \qquad \therefore y \approx 13$

Hence **D** is <u>$C_6H_{13}OH$</u>.

(ii)

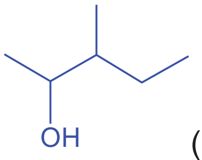
E is



Alkene **E** is oxidised (•) by hot acidified conc. $KMnO_4$ to give ethanoic acid and butanone.

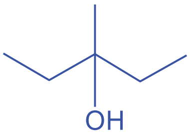
Note: Working backwards, **E** ↓ **D** (via addition of H−OH across the double bond)

D can be



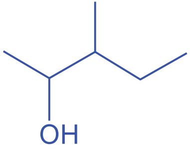
(secondary alcohol)

or



(tertiary alcohol)

D has to be

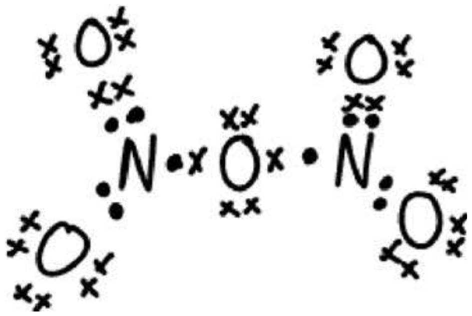


Since **D** can be oxidised (•) by $K_2Cr_2O_7$ it has to be a secondary alcohol.
Alkene **E** can be obtained by the elimination (•) of alcohol **D**.

(iii) Yes. **E** can exhibit cis trans.

There is restricted rotation about the C=C due to the presence of π bonding and there are 2 different groups attached to each of the carbon atom in the C=C.

(e) **(i)**



(ii) $N_2(g) + 5/2\ O_2(g) \downarrow N_2O_5(g)$

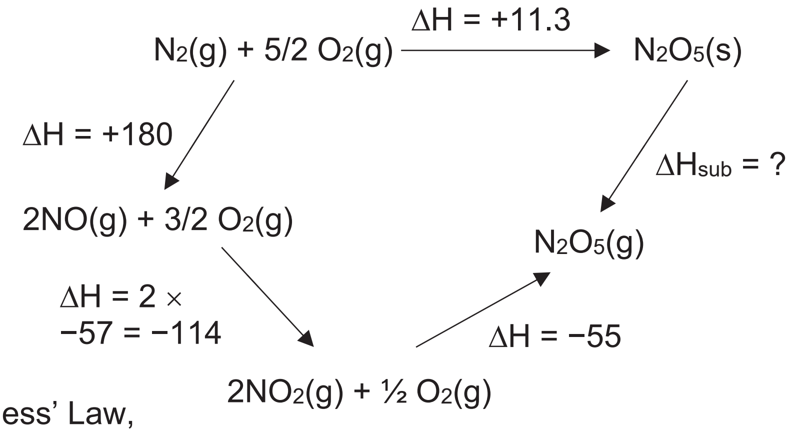
$\Delta H_f\ (N_2O_5) = 180 + 2(-57) - 55 = 11.0$ kJ mol^{-1}

$\Delta H_f\ (N_2O_5) = BE(N{\equiv}N) + 5/2\ BE(O{=}O) - 2BE(N{=}O) - 4BE(N{-}O)$

$+11.0 = 944 + 5/2\ (496) - 2BE(N{=}O) - 4(210)$

$BE(N{=}O) = +666$ kJ mol^{-1}

(iii)



By Hess' Law,

$\Delta H_{sub} = -11.3 + 180 + (-114) + (-55) = -0.300$ kJ mol^{-1}

3 **(a)** **(i)** $[H^+] = \sqrt{4.57 \times 10^{-3} \times 0.0500} = 0.01511$ mol dm^{-3}

$pH = -\lg 0.01511 = 1.82$

(ii) $K_{b(2)} = \dfrac{1.0x10^{-14}}{2.51x10^{-10}} = 3.984 \times 10^{-5}$ mol dm^{-3}

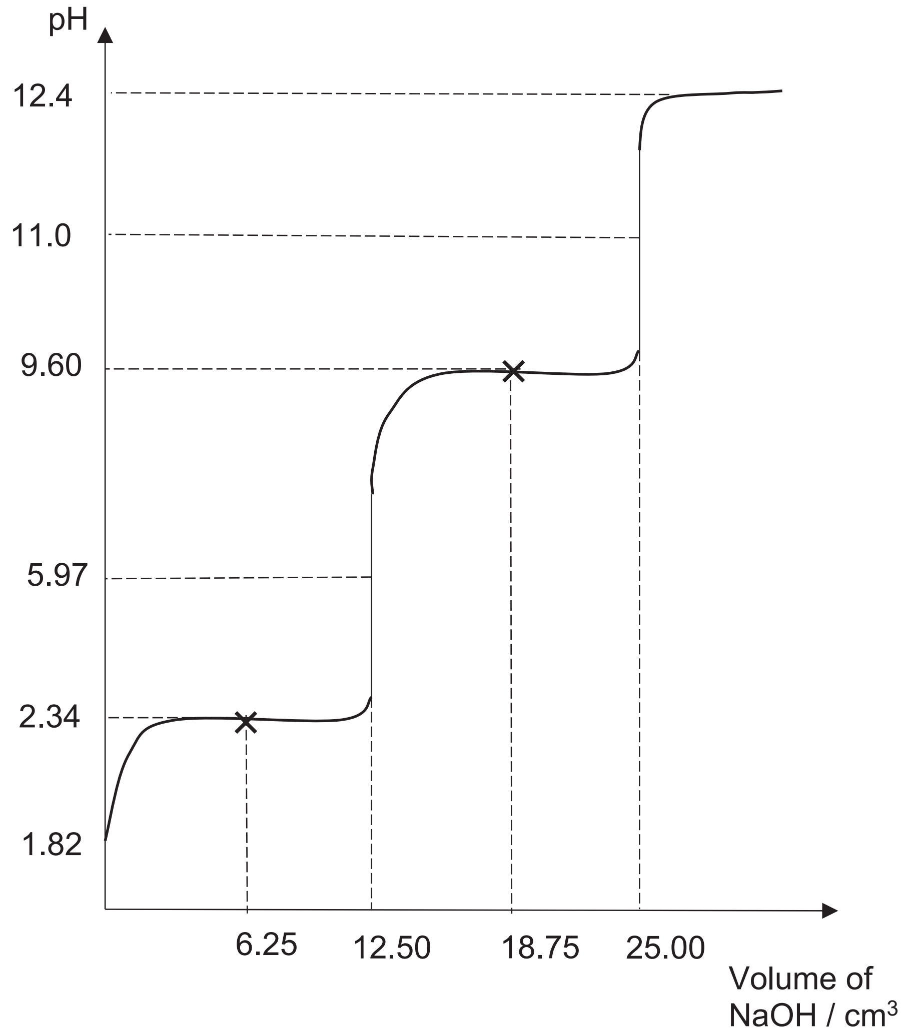
$[NH_2CH_2COO^-] = \dfrac{\frac{25}{1000}x0.0500}{\frac{50}{1000}} = 0.0250$ mol dm^{-3}

$[OH^-] = \sqrt{3.984 \times 10^{-5} \times 0.02500} = 9.980 \times 10^{-4}$ mol dm^{-3}

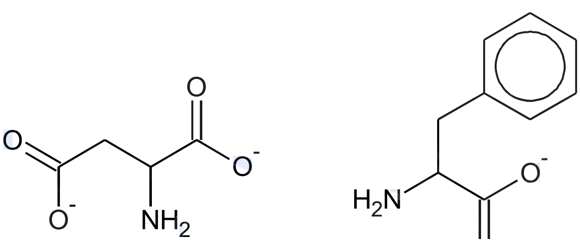
$pOH = -\lg 9.980 \times 10^{-4} = 3.0$

$pH = 14 - 3.0 = 11.0$

(iii) pH at 1st M.B.C. = p$K_{a(1)}$ = 2.34
pH at 2nd M.B. C. = p$K_{a(2)}$ = 9.60



(b)



CH$_3$OH

(c) **(i)** By Le Chatelier's principle, in the presence of high concentration of H$^+$, the position of equilibrium shifts left to decrease the concentration of H$^+$. Iron (II) sulfate dissolves, releasing free Fe^{2+} ions which are mobile and flushed through the intestine without being absorbed into the bloodstream.

(ii) $Fe^{2+} + 6CN^- \rightleftharpoons [Fe(CN)_6]^{4-}$

$$K_f = \frac{[Fe(CN_6)^{4-}]}{[Fe^{2+}][CN^-]^6}$$

Let the concentration of Fe^{2+} be a mol dm^{-3}

$$10^{35} = \frac{0.65}{(a)(6a)^6}$$

a = 2.024 × 10^{-6} mol dm^{-3}

$[CN^-] = 6 \times 2.024 \times 10^{-6} = 1.21 \times 10^{-5}$ mol dm^{-3}

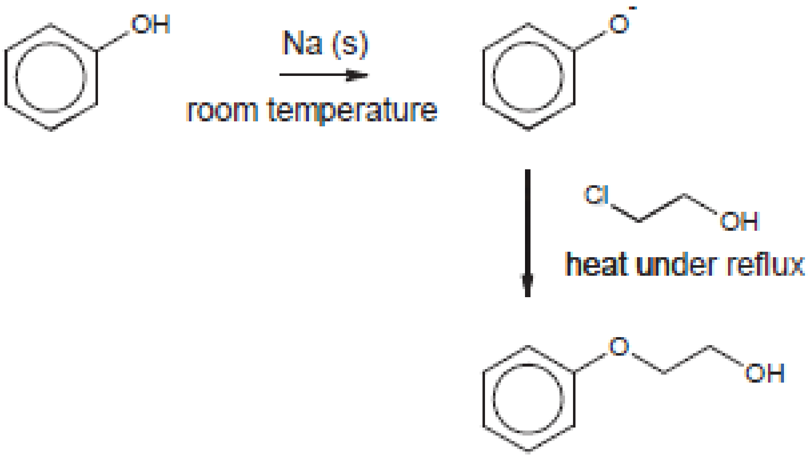
(iii) K_f of complex formed between Fe^{2+} and CN^- is 10^{35} and CN^- binds strongly and reversibly with iron in haemoglobin. They are not easily released and prevent the haemoglobin from carrying oxygen. CN^- cannot be used as a ligand.

Since K_f of complex formed between Hg^{2+} and $edta^{4-}$ is greater than that of complex formed between Hg^{2+} and cysteine ($10^{21} > 10^{14}$), $edta^{4-}$ is able to displace Hg^{2+} from cysteine and forms a more stable complex.

(d) **(i)** 1,5-diaminopentane contain electron donating alkyl groups that increase the electron density on the N atom. This increases the availability of the lone pair of electrons on N atom for bonding with a proton. Hence, 1,5-diaminopentane is a stronger base than ammonia.

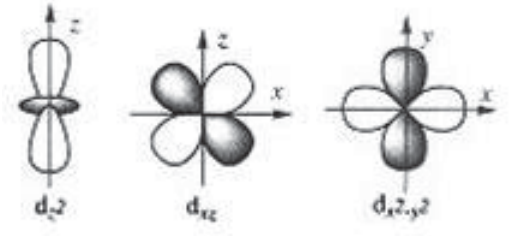
The p-orbital of N atom overlaps with the π-electron cloud of the benzene ring, causing the lone pair on N atom to be delocalised into the benzene ring. This decreases the availability of the lone pair of electrons on N atom for bonding with a proton. Hence, phenylamine is a weaker base than ammonia.

(ii)



4 (a) (i) $1s^22s^22p^63s^23p^63d^9$

(ii)



(b) (i)

			$E^\ominus$/V
(1)	$Ag^+ + e^- \rightleftharpoons$	Ag	+0.80
(2)	$Cu^{2+} + 2e^- \rightleftharpoons$	Cu	+0.34
(3)	$Pb^{2+} + 2e^- \rightleftharpoons$	Pb	–0.13

Reactions at anode:
(The operating voltage is carefully regulated so that it is sufficient for Cu to be oxidised.)

- Since $E^\ominus(Cu^{2+}/Cu)$ is more positive than $E^\ominus(Pb^{2+}/Pb)$, Pb will also be oxidised.
- Both Cu and Pb dissolve into the solution as cations and migrate to the cathode.
- Since $E^\ominus(Ag^+/Ag)$ is more positive than $E^\ominus(Cu^{2+}/Cu)$, Ag will not be oxidised.
- Ag drops off the electrode as the copper around dissolves, and fall to the bottom of the electrolytic tank to form anode sludge.

Reactions at cathode:

- Since $E^\ominus(Cu^{2+}/Cu)$ is more positive than $E^\ominus(Ni^{2+}/Ni)$ for (4), Cu^{2+} is preferentially reduced.
- Pb^{2+} remains in the solution.

(ii) Q = It C

$I(t\text{x}60) = \frac{m_x - m_o}{63.5}(2)\ F$ [1]

$F = Le = \frac{63.5I(60t)}{2(m_x - m_0)}$

$L = \frac{63.5I(60t)}{2(m_x - m_0)\times 1.6\times 10^{-19}}$

$= \frac{3810It}{3.2\times 10^{-19}(m_x - m_0)} = \frac{1.19\times 10^{22}\ It}{(m_x - m_0)}$ [1]

(c)

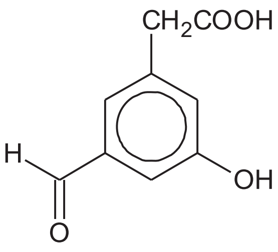
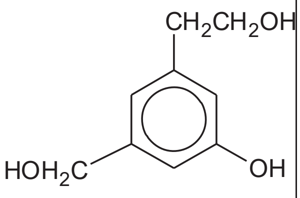
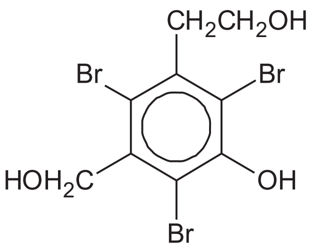
Element	Cu	C	H	O
Mass /g	33.55	25.30	1.75	39.40
Amount /mol	0.5283	2.108	1.75	2.462
Ratio	1	3.990	3.31	4.660
Simplest ratio	3	12	10	14

$Cu_3(C_6H_5O_7)_2$
$x = 3, y = 6, z = 5$

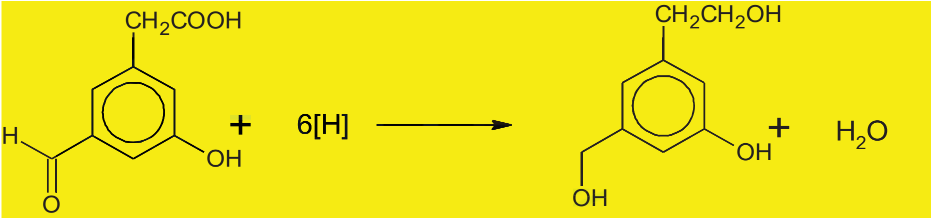
(d) **(i)** It can accept protons.
It can share/donate its lone pair of electrons on O^-.

(ii) $HO_2CCO_2H \rightleftharpoons HO_2CCO_2^- + H^+$
$HO_2CCH(OH)CH(OH)CO_2H \rightleftharpoons HO_2CCH(OH)CH(OH)CO_2^- + H^+$
$HO_2CCO_2^-$ is more stable than $HO_2CCH(OH)CH(OH)CO_2^-$ as the negative charge on the O atom can be more effectively dispersed due to 2 electronegative O atoms are beside that carboxylate ion where there is only 1 O atom in the conjugate base of tartaric acid. Dissociation of ethanedioic is more favoured.

(e) **(i)**

J	**K**	**L**
		

(ii)



(iii) **2** observations: Orange bromine water decolourises, white ppt forms.

(iv) $LiAlH_4 + 4H_2O \rightarrow LiOH + Al(OH)_3 + 4H_2$

5 **(a)** **(i)** The oxidation state of oxygen increases from –2 in CH_3COO^- to –1 in $CH_3COO\bullet$ hence the oxidation reaction took place at the anode.

$CH_3COO^- \rightarrow CH_3COO\bullet + e^-$

(ii) $H_2O + 2e^- \rightarrow H_2 + 2OH^-$

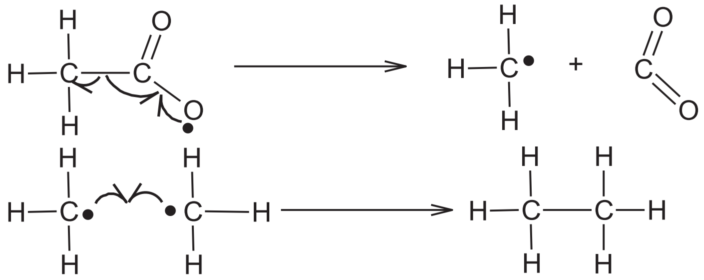
$Q=It = 500 \times 10^{-3} \times 20 \times 60 = 600$ C

$Q=nzF \Rightarrow 600 = n\,(2)(96500)$

$n(H_2) = 3.108 \times 10^{-3}$ mol

$v(H_2) = 3.108 \times 10^{-3} \times 24 = 0.0746\ dm^3\ (= 74.6\ cm^3)$

(iii)



(b) **(i)**

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

$$M = \frac{mRT}{PV}$$

$$= \frac{(0.30)(8.31)(300)}{(101325) \times (168 \times 10^{-6})}$$

$$= 43.9\ g\ mol^{-1} \Rightarrow M_r = 43.9$$

Let molecular formula of X be C_nH_{2n+2} do include this line to introduce what's n.

$12(n) + 2n + 2 = 44$

$n = 3 \Rightarrow$ X is C_3H_8

(ii) Intermolecular forces between the gas particles is negligible/insignificant.

The volume of gas particles is insignificant/negligible compared to volume of container.

(iii) X is C_3H_8 hence its structural formula is $CH_3CH_2CH_3$. Since it is unsymmetrical R–R', it is formed by two different alkyl radicals ($CH_3\bullet$ from ethanoate and another R• from salt of acid A).

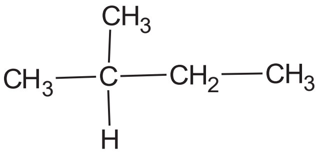
Hence, salt of acid W produced $CH_3CH_2\bullet$ in step III.

Alkane **Y** (R'–R') is $CH_3CH_2CH_2CH_3$

Acid **W** contains an additional COOH (lost during step II decarboxylation) attached to $CH_3CH_2\bullet$ hence it is CH_3CH_2COOH

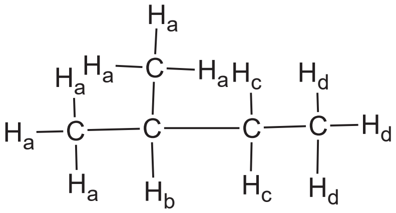
(c)

D is

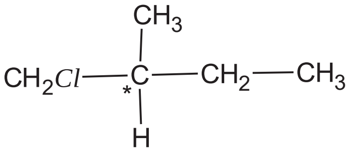


$CH_3-\overset{CH_3}{\underset{H}{C}}-CH_2-CH_3$

There are four different types of H in different chemical environment in D as shown below.

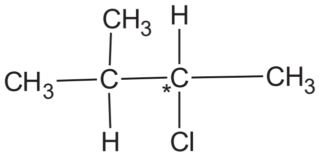


The 2 chiral products are



$CH_2Cl-\overset{CH_3}{\underset{H}{\overset{*}{C}}}-CH_2-CH_3$

and



$CH_3-\overset{CH_3}{\underset{H}{C}}-\overset{H}{\underset{Cl}{\overset{*}{C}}}-CH_3$

(d) **(i)** $SiCl_4 + 2H_2O \rightarrow SiO_2\ (s) + HCl\ (g)$

$SiCl_4$ undergoes hydrolysis to form a strongly acidic solution of pH 1-2. The solution turns red.

(ii) $NH_4^+\ (aq) + H_2O\ (l) \rightleftharpoons NH_3\ (aq) + H_3O^+\ (aq)$

Ammonium chloride is an acidic salt. The conjugate acid NH_4^+ hydrolyses in water to form a weakly acidic solution of pH 5 (approx. mid-way of pH change at eq pt for WB-SA titration pH3-7). The solution turns purple/pink.

Paper 4 Answers

1 **(a)**

Final burette reading / cm^3	
Initial burette reading / cm^3	
Volume of **FA 1** used / cm^3	**V_{FA1}**

(b) **(i)**

Titration	1	2
Final burette reading / cm^3		
Initial burette reading / cm^3		
Volume of **FA 2** used / cm^3	V1	V2

(ii) $V_{FA2} = \frac{V1 + V2}{2}$ cm^3 (2 d.p)

Correct choices and correct evaluation average titre, correct d.p.

(c) $[FA\ 2] = \frac{3.16}{158.0} = \mathbf{0.0200}$ mol dm^{-3} (3 s.f.)

(d) n_{KMnO_4} reacted during titrtation = $\frac{V_{FA\,2}}{1000}$ x **0.0200** = **Ans 2** mol (3 s.f.)

(e) $H_2O_2(aq) \rightarrow 2e + O_2(g) + 2H^+(aq)$

$MnO_4^-(aq) + 8H^+(aq) + 5e \rightarrow Mn^{2+}(aq) + 4H_2O(l)$

$2MnO_4^- + 5H_2O_2 + 6H^+ \rightarrow 5O_2 + 2Mn^{2+} + 8H_2O$

$[H_2O_2]$ in **FA 4** = $\frac{\textbf{Ans 2} \times \frac{5}{2}}{\frac{25.0}{1000}}$ = **Ans 3** mol dm^{-3} (3.sf.)

(f) $[H_2O_2]$ in **FA 1** = **Ans 3** x $\frac{250}{V_{FA\,1}}$ = **Ans 4** mol dm^{-3}

(g) % error in measurement made by student **A** = $\frac{0.5}{20.90}$ x 100 = 2.39 %

correct working [1]

% error in measurement in original expt = $\frac{0.05 \times 2}{20.90}$ x 100 = 0.478 %

Ratio of percentage error = $\frac{2.39}{0.478}$ = 5 Correct answer [1]

(h) Since volume of H_2SO_4 used is in excess, the use of a burette does not affect / increase the reliability of the results.

2 **(a)**

Expt	$V_{FA\,5}$ / cm^3	V_{H_2O} / cm^3	$V_{FA\,6}$ / cm^3	time / s	$\left(\frac{1000}{\text{time}}\right)$ / s^{-1} x 10^3	lg $\left(\frac{1000}{\text{time}}\right)$	lg ($V_{FA\,5}$)
1	60.0	0.0	5.0				
2	50.0	10.0	5.0				
3	40.0	20.0	5.0				
4	30.0	30.0	5.0				
5	20.0	40.0	5.0				

(b) Axes labels + choice of scales to occupy at least half graph paper.

Correctly plotted points to half a square.

Best–fit line (minimal deviation and approx. equal deviation above and below the line)

(c) Points chosen to calculate gradient should be at least half the size of best–fit line.
Constructions lines for gradient shown, read off points accurately to half a square.
Gradient correctly evaluated to whole number with working shown.

(d) Rate of reaction is given by rate= $\frac{\text{amount of sulfur produced}}{\text{time taken}}$.

Since a constant amount of sulfur is produced for every experiment, rate is inversely proportional to time.

(e) 5 cm^3 of **FA 6** was used for every experiment and total volume of solution was kept constant at 65 cm^3 by adding deionised water.

The volume of **FA 5** measured out would be proportional to the concentration of **FA 5** used for each experiment.

(f) Relative rates and concentrations of $S_2O_3^{2-}$ were used in the experiment thus the proportionality constants are not available.
The student should use actual rate and concentrations of $S_2O_3^{2-}$ for the experiment to plot the graph.

(g) Expt 1 (60 cm^3 **FA 5**).
Time taken for the reaction to obscure the printed insert is the smallest leading to a largest percentage error in time measurement.

$$\text{percentage error in time measurement} = \frac{\text{uncertainty in time measurement}}{\text{time taken}} \times 100$$

OR

Expt 5 (20 cm^3 of **FA 6**)
The rate of producing sulfur is the slowest, leading to difficulty in estimating when the printed insert is obscured.

(h) **Plan**

1. Using a 25 cm^3 measuring cylinder, measure 20 cm^3 of **FA 5** and place it in a boiling tube.
2. Using another 25 cm^3 measuring cylinder, measure 10 cm^3 of **FA 6** into a second boiling tube.
3. Fill a large beaker with some water and warm it to about 75 °C
4. Place a 0.2 °C division thermometer into each boiling tube and warm the boiling tubes in the water bath (beaker of hot water).
5. Note the exact temperature of each solution and pour both contents into a 100 cm^3 beaker.
6. Start timing and swirl the solution to ensure even mixing before placing it on a printer insert.
7. Note the time taken for the mixture to just obscure the printed insert.
8. Discard the solution and rinse the beaker immediately. Wipe the external wall of the beaker dry.
9. Repeat steps 1 to 8 to obtain 3 other experiments at temperatures of 60, 45, and 30 °C.

Table – Temperature and Time

Expt	$T_{FA\,5}$ / °C	$T_{FA\,6}$ / °C	Ave Temp / °C	Time taken / s
1				
2				
3				
4				

3

	Test	*Observations*
(a)	Add sodium hydrogencarbonate to **FA 7**.	• Orange / Yellow-brown / brown ppt formed. • Effervescence. Gas evolved gives white ppt with lime water.
(b)	Add, with shaking, aqueous ammonia to **FA 7**, until the aqueous ammonia is in excess. Filter the mixture and add dilute sulfuric acid dropwise to the filtrate.	• Orange / Yellow-brown / brown ppt formed, insoluble in excess aq NH_3. • Colourless filtrate obtained. • White ppt formed, soluble in excess acid to give a colourless solution.
(c)	Add dilute sulfuric acid followed by aqueous potassium iodide to **FA 7**. Add starch solution.	• Orange / Yellow-brown / brown solution fades in acid. • Orange / brown solution formed with KI. • Dark blue / black / blue-black solution formed with starch
(d)	Add aqueous barium chloride to **FA 7**. Add dilute hydrochloric acid.	• White ppt formed, • insoluble in excess acid.
(e)	Add aqueous sodium hydroxide to **FA 7** until the alkali is in excess. Filter the mixture, add a little aluminium powder to the filtrate. Warm cautiously.	• Orange / Yellow-brown / brown ppt formed, insoluble in excess alkali. • Red litmus remained unchanged.

(f)	Add aqueous silver nitrate to **FA 7**. Filter the mixture, discarding the filtrate. Wash the residue by pouring distilled water through it. Discard the washings and then pour aqueous ammonia through the residue. Collect the filtrate produced. Add dilute nitric acid dropwise to the filtrate.	• White ppt formed with $AgNO_3$. • Pale yellow filtrate obtained. • White ppt soluble in aq NH_3. • White ppt reformed, insoluble in excess acid.

(g) Possible cation(s): Fe^{3+} and Zn^{2+}

Reason(s)
• Fe^{3+} forms brown ppt of $Fe(OH)_3$ with NaOH and aq NH_3 and ppt is insoluble in excess NaOH and aq NH_3
• sulfuric acid neutralises NH_3 in filtrate to give the zinc ppt ($Zn(OH)_2$) and dissolves in excess acid to form Zn^{2+}

Possible anion(s): Cl^- and SO_4^{2-}

Reason(s)
• Cl^- form white ppt with $AgNO_3$ and is soluble in aq NH_3
• SO_4^{2-} forms white ppt with Ba^{2+} which is insoluble in acid.

(h) **FA 7** behaves as acid

Fe^{3+} has a small size and high charge hence highly polarising. It undergoes hydrolysis with water to produce H^+ ions.

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

(i)

Test No.	Reagent added	Butanal	Phenyl propan–2–ol	Propanol	Propanone
1	2,4–DNPH		✓		✓
2	aq I_2, NaOH	✓			✓
Other possible tests					
3	Fehling's	✓			
4	Sodium		✓	✓	
5	Tollens'	✓			
6	$KMnO_4$ / H^+	✓	✓	✓	

Plan

1. To 4 separate test–tubes, place 1 cm depth of each unknown solution followed by 2,4–DNPH, shake the mixture and warm. Record the observation.

2. To another set of 4 test–tubes, add 1 cm depth of each unknown solution followed by 1 cm depth of aq I_2. Add NaOH(aq) dropwise to each test–tube till the yellow colour is almost discharged. Warm the test–tubes. Record the observation.

Deduction

- Solution that gives orange ppt with 2,4–DNPH and yellow ppt with alkaline aq I_2 is methyl propapone.
- Solution that gives orange ppt with 2,4–DNPH but does not give yellow ppt with alkaline aq I_2 is butanal.
- Solution that gives yellow ppt with alkaline aq I_2. but does not give orange ppt with 2,4–DNPH is phenylpropan–2–ol.
- Solution that does not give orange ppt with 2,4–DNPH nor yellow ppt with alkaline aq I_2 is propanol

NATIONAL JUNIOR COLLEGE
SH2 PRELIMINARY EXAMINATION

Higher 2

CANDIDATE NAME

SUBJECT CLASS

REGISTRATION NUMBER

CHEMISTRY

9729/01

Paper 1 Multiple Choice

Thursday 14 Sept 2017
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, subject class and registration number on the Answer Sheet in the spaces provided unless this has been done for you.

There are **30** questions on this paper. Answer **all** questions. For each question there are four possible answers **A**, **B**, **C** and **D**.
Choose the **one** you consider correct and record your choice in **soft pencil** on the separate Answer Sheet.

Read the instructions on the Answer Sheet very carefully.

Each correct answer will score one mark. A mark will not be deducted for a wrong answer.
Any rough working should be done in this booklet.
The use of an approved scientific calculator is expected, where appropriate.

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

Instructions on how to fill in the Optical Mark Sheet

1. Enter your NAME (as in NRIC). TAN AH TECK
2. Enter the SUBJECT TITLE. CHEMISTRY
3. Enter the TEST NAME. SH2 Prelim
4. Enter the CLASS. cm2P

RUB OUT ERRORS THOROUGHLY

USE PENCIL ONLY
FOR ALL ENTRIES ON THIS SHEET

0	1	2 ●	3	4	5	6
0	1 ●	2	3	4	5	6
0 ●	1	2	3	4	5	6

Example:

Shade the index number in a 5 digit format on the optical mark sheet:
2^{nd} digit and the last 4 digits of the Registration Number.

Student	Examples of Registration No.	Shade:
	1605648	65648

For each question there are four possible answers, **A**, **B**, **C**, and **D**. Choose the **one** you consider to be correct.

1 A mixture of two sulfur-containing gases, H_2S and CS_2, was burned in an excess of oxygen.

$$H_2S + \frac{3}{2}O_2 \rightarrow H_2O + SO_2$$

$$CS_2 + 3O_2 \rightarrow CO_2 + 2SO_2$$

Upon complete combustion followed by cooling back to room temperature, the gaseous mixture was first passed through acidified $KMnO_4$. The volume contracted by 10.0 cm^3.

After which, the resulting gas was passed through aqueous sodium hydroxide, a further contraction of 2.0 cm^3 occurred. All volumes are measured under the same conditions.

What was the mole fraction of H_2S in the mixture?

A 0.333

B 0.500

C 0.750

D 0.833

2 Chromium has an oxidation state of +3 in its metal ore, chromite, $FeCr_2O_4$. Pure chromium is extracted from chromite in several steps show below.

$$FeCr_2O_4 \xrightarrow{\text{Step I}} Na_2CrO_4 \xrightarrow[H^+]{\text{Step II}} Na_2Cr_2O_7 \xrightarrow{\text{Step III}} Cr_2O_3 \xrightarrow[Al]{} Cr$$

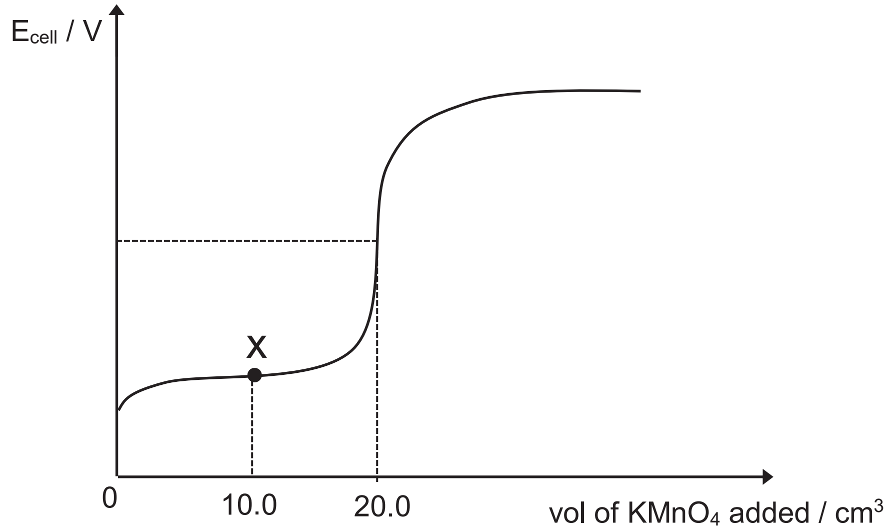
Which shows the correct type of reaction involving chromium in steps **I**, **II** and **III**?

	Step I	**Step II**	**Step III**
A	displacement	acid–base	displacement
B	oxidation	oxidation	reduction
C	displacement	oxidation	oxidation
D	oxidation	acid–base	reduction

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

The amount of iron in a pill that contain iron(II) salts can be estimated by titration with $KMnO_4$(aq).

When a pill is dissolved in 10 cm^3 of dilute sulfuric acid and titrated against 0.40 mol dm^{-3} $KMnO_4$, the E_{cell} was measured against a standard hydrogen electrode and plotted as shown:



Which statements are correct?

1 The number of moles of Fe^{2+} in the pill is 4.0×10^{-2} mol.

2 The value of E_{cell} at point **X** is 0.77 V.

3 The colour change at end point is from pink to pale green.

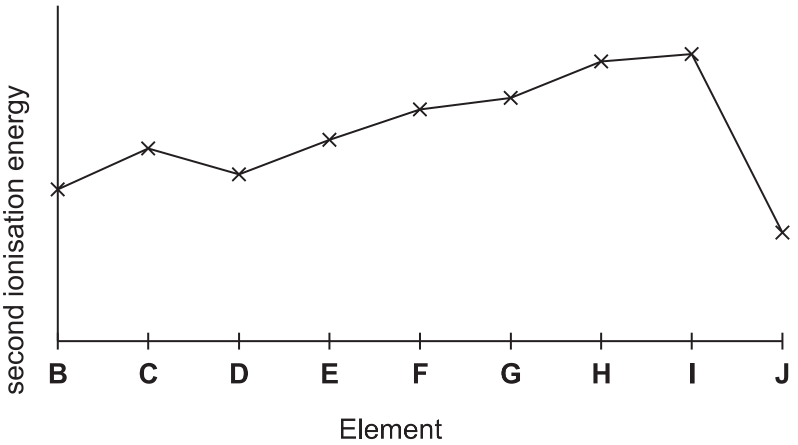
A **1** and **2** only

B **1** and **3** only

C **2** and **3** only

D **1** only

4 The following graph represents the second ionisation energy trend of 9 consecutive elements in Periods 3 and 4.



Which statement is correct?

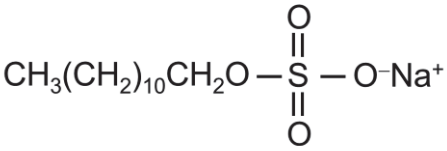
A Element **C** is in Group 3.

B Element **F** has the lowest boiling point.

C The ionic radius of ion of **E** is greater than that of ion of **J**.

D The formula of the compound formed between elements **D** and **G** is $\mathbf{D_2G_3}$.

5 Long-chain alkanes are converted on an industrial scale into alkylsulfates for use as detergents. One example is sodium lauryl sulfate shown below.



$$CH_3(CH_2)_{10}CH_2O-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\|}}{S}}-O^-Na^+$$

Which statements can be deduced from the structure given?

1 The compound can dissolve in both polar and non-polar solvents.

2 The shape about the sulfur atom is square planar.

3 All the C–C–C bond angles are 109.5°.

A **1**, **2** and **3**

B **1** and **2** only

C **1** and **3** only

D **2** and **3** only

6 Which statement is true for a fixed amount of an ideal gas when temperature increases at constant pressure?
(V = volume, p = pressure and T = temperature in K)

A V remains constant.

B $\frac{pV}{T}$ remains constant.

C Density of the gas remains constant.

D pV remains constant.

7 The reduction of iron ore, Fe_2O_3, by carbon monoxide is an exothermic reaction which occurs in the upper part of the furnace.

$$Fe_2O_3(s) + 3CO(g) \rightarrow 2Fe(s) + 3CO_2(g) \qquad \Delta H = -27 \text{ kJ mol}^{-1}$$

Given that ΔH_f^θ for CO_2 (g) = −394 kJ mol^{-1} and ΔH_f^θ for CO (g) = −110 kJ mol^{-1}, what is the standard enthalpy change of formation of Fe_2O_3(s)?

A +257 kJ mol^{-1}

B +825 kJ mol^{-1}

C −257 kJ mol^{-1}

D −825 kJ mol^{-1}

8 Which value would be required to calculate the lattice energy for the hypothetical ionic compound BaF_3 using Born-Haber cycle?

A Third electron affinity of fluorine

B Third ionisation energy of fluorine

C Ba–F bond energy

D F–F bond energy

9 A sample of X(g) with initial pressure of p atm is allowed to reach equilibrium at constant pressure.

$$X(g) \rightleftharpoons Y(g) + 2Z(g)$$

The equilibrium partial pressure of X is 0.25p atm.

What is the value of K_p?

A $0.5p$ **B** $4.5p$ **C** $0.25p^2$ **D** $6.75p^2$

10 Which indicator is suitable for use in a titration of 0.1 mol dm^{-3} H_2SO_4 with 0.1 mol dm^{-3} of NH_3?

A Methyl orange (pH range 3.3 – 4.4)

B Bromothymol blue (pH range 6.0 – 7.6)

C Phenolphthalein (pH range 8.3 – 10.0)

D None of the above

11 Magnesium hydroxide is extracted from the seawater as follows.

Aqueous calcium hydroxide is added to seawater. Magnesium hydroxide is then filtered off.

$$Ca(OH)_2(aq) + MgCl_2(aq) \rightarrow Mg(OH)_2(s) + CaCl_2(aq)$$

Which statement best explains why magnesium hydroxide is formed in the above reaction?

A Magnesium is less electropositive than calcium.

B The solubility product for $Mg(OH)_2$ is lower than that for $Ca(OH)_2$.

C The enthalpy change of hydration for Mg^{2+} is less exothermic than for Ca^{2+}.

D The magnitude of the lattice energy of $Mg(OH)_2$ is less than that of $Ca(OH)_2$.

12 **P**, **Q** and **R** react in aqueous solution according to the following equation:

$$\mathbf{P} + 3\mathbf{Q} + 2\mathbf{R} \rightarrow \mathbf{T} + \mathbf{U}$$

The kinetics of the above reaction was studied and the experimental results obtained are shown in the table below.

Expt	Volume of **P** /cm^3	Volume of **Q** /cm^3	Volume of **R** /cm^3	Volume of water /cm^3	Relative initial rate
1	10	10	10	20	16
2	10	5	20	15	32
3	5	5	10	30	4
4	10	5	10	25	8

What is the rate equation for the above reaction?

A Rate = k[**P**][**Q**]

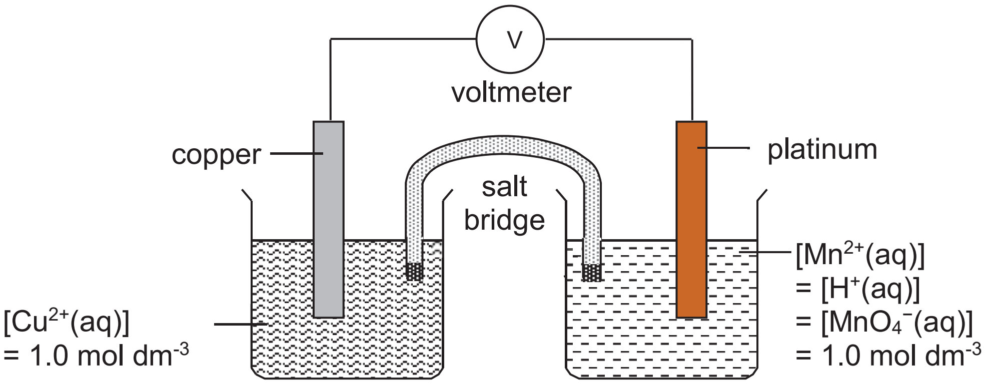
B Rate = k[**P**][**Q**][**R**]

C Rate = k[**P**][**Q**]^2[**R**]

D Rate = k[**P**][**Q**][**R**]^2

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

A cell is set up by connecting a Cu^{2+}/Cu half-cell and an acidified MnO_4^-/Mn^{2+} half-cell.



Which change in the set up will cause the corresponding effect on the e.m.f (potential difference) of the cell?

	Change	**Effect on e.m.f of cell**
A	Addition of excess NH_3 (aq) into oxidation half-cell	Increases
B	Addition of concentrated H_2SO_4 into reduction half-cell	Decreases
C	Increase the size of the copper electrode	Increases
D	Replace copper with an alloy of copper and zinc	Remains the same

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

The AgC*l* / Ag reference electrode is based on the following reaction:

$$AgCl + e^- \rightleftharpoons Ag + Cl^-$$

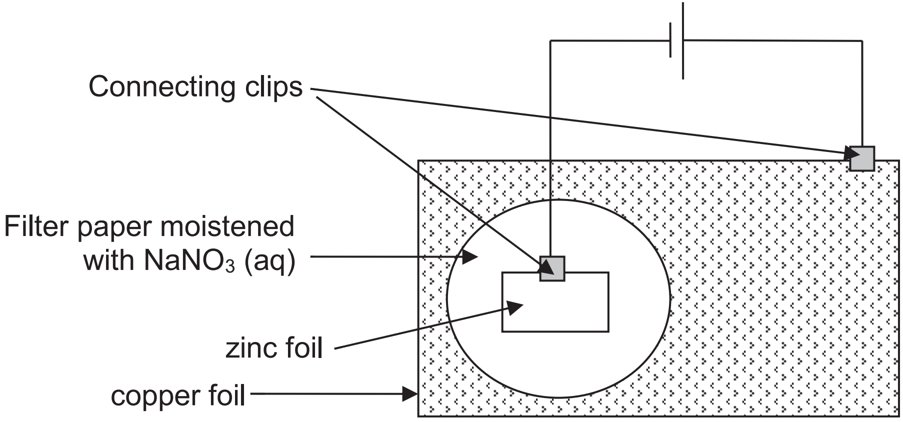
The reduction potential of the Fe^{2+} / Fe half−cell was found to be −0.64 V when measured using the AgC*l* / Ag reference electrode.

What is the reduction potential of the AgC*l* / Ag electrode with respect to the standard hydrogen electrode?

A −1.10 V **B** −0.20 V **C** +0.20 V **D** +1.10 V

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

A current is passed through a simple cell as shown below:



What could be an expected observation?

A Sodium metal was deposited on the filter paper.

B The size of the zinc foil reduced with time.

C The filter paper turned blue.

D A brown gas was observed.

16 Consider the sequence of oxides Na_2O, SiO_2, P_4O_{10}.

Which factor decreases in the order Na_2O, SiO_2, P_4O_{10}?

A melting point

B covalent character

C pH when mixed with water

D solubility with aqueous alkali

17 Anhydrous barium nitrate and anhydrous magnesium nitrate decompose on heating, nitrogen dioxide and oxygen are evolved and an oxide is formed.

Which statements concerning these decompositions are correct?

1 Nitrogen dioxide is evolved at a lower temperature from magnesium nitrate than from barium nitrate.

2 For both nitrates, the volume of nitrogen dioxide evolved is four times greater than the volume of oxygen.

3 The numerical value of the lattice energy of magnesium nitrate is smaller than that of barium nitrate.

A **1**, **2** and **3**

B **1** and **2** only

C **2** and **3** only

D **1** only

18 Element **Y** forms a chloride, **Y**Cl_n, which has a melting point of 3 °C. When treated with an excess of acidified silver nitrate, 0.50 g of the chloride produced 1.20 g of AgCl.

Another 0.50 g sample of the chloride was heated strongly. Chlorine gas was evolved and the residue gave 0.72 g of AgCl when treated with an excess of acidified silver nitrate.

What is the value of ***n*** and the identity of element **Y**?

	value of *n*	**identity of element Y**
A	5	Sb
B	5	P
C	4	Ge
D	4	Si

19 Which statements are correct for the compounds in the following sequence?

hydrogen chloride, hydrogen bromide, hydrogen iodide

1 The thermal stability increases.

2 The enthalpy change of formation becomes less exothermic.

3 The ease of oxidation increases.

A **1**, **2** and **3**

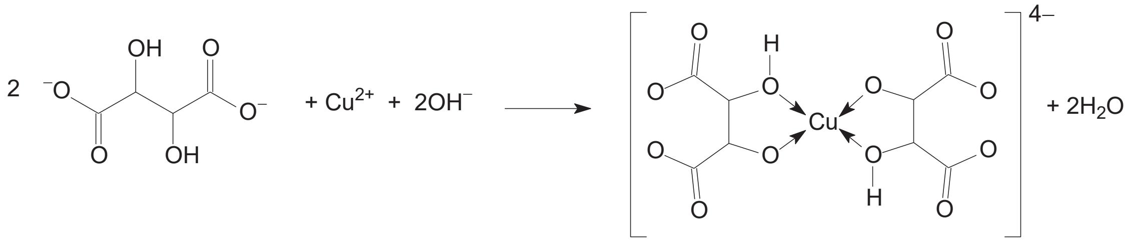
B **1** and **2** only

C **1** and **3** only

D **2** and **3** only

20 Fehling's solution is a common reagent used to identify aldehyde functional group in organic compound. It can be prepared by mixing aqueous copper(II) sulfate with tartrate ions in presence of strong alkalis.

The formation of copper tartrate complex is shown in the following equation.



tartrate ion

copper tartrate complex

Which statement is correct for the above reaction?

A The tartrate ion acts as a Lewis acid.

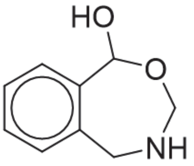
B The tartrate ion can exist as 3 stereoisomers.

C The coordination number of the complex ion is 2.

D The oxidation number of Cu in the complex ion is 0.

21 Hybridisation of orbitals can be observed for central atoms such as C, N and O.

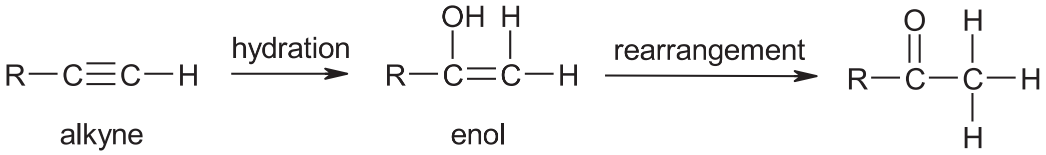
How many atoms in the following molecule are sp^3 hybridised?



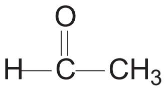
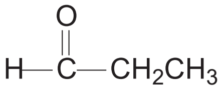
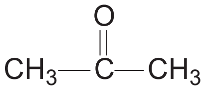
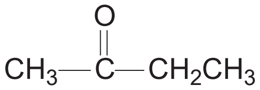
A 3 **B** 4 **C** 5 **D** 6

22 An alkyne, a hydrocarbon with C≡C bond, undergoes hydration in a similar mechanism as an alkene. However, the formation of an enol is unstable and would undergo rearrangement to form a carbonyl compound.

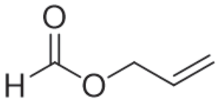
One example of the reaction is shown below.



Which product is **not** the major product when the corresponding alkyne undergoes hydration?

	alkyne	product
A	$H-C\equiv C-H$	 $H-\overset{\overset{O}{\|}}{C}-CH_3$
B	$H-C\equiv C-CH_3$	 $H-\overset{\overset{O}{\|}}{C}-CH_2CH_3$
C	$CH_3-C\equiv C-H$	 $CH_3-\overset{\overset{O}{\|}}{C}-CH_3$
D	$CH_3-C\equiv C-CH_3$	 $CH_3-\overset{\overset{O}{\|}}{C}-CH_2CH_3$

23 When compound **A** was heated with excess acidified $KMnO_4$, carbon dioxide gas was produced.



Compound **A**

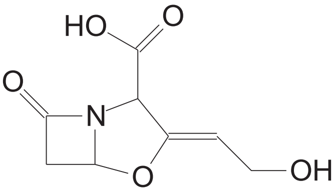
Carbon dioxide gas reacts with excess calcium hydroxide according to the following equation.

$$Ca(OH)_2(aq) + CO_2(g) \rightarrow CaCO_3(s) + H_2O(l)$$

What is the mass of calcium carbonate ($M_r = 100.1$) that can be obtained when 1 mole of compound **A** is treated with hot excess acidified $KMnO_4$?

A 100.1 g **B** 200.2 g **C** 300.3 g **D** 400.4 g

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



compound **X**

Which statements regarding compound **X** are correct?

1 Its molecular formula is $C_8H_8NO_5$.

2 It has 2^3 stereoisomers.

3 2 mol of Br atoms are added when 1 mol of compound **X** reacts with excess HBr(g).

4 6 mol of H atoms are added when 1 mol of compound **X** reacts with $LiAlH_4$ in dry ether.

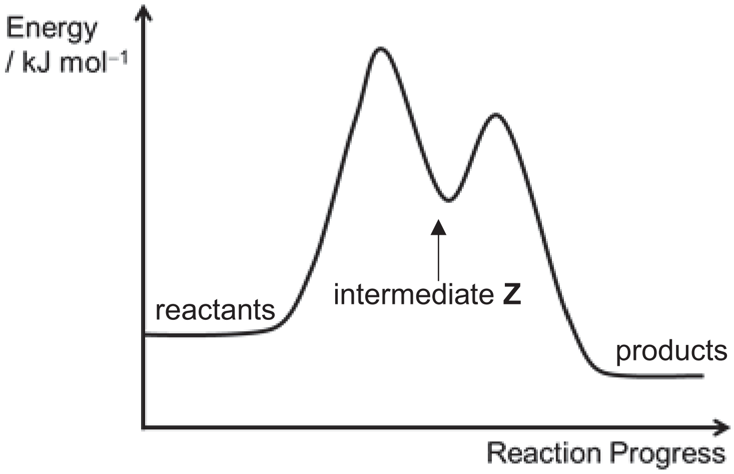
A **1** and **2** only

B **1** and **3** only

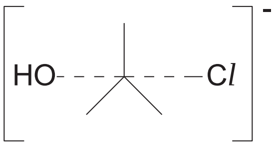
C **2** and **3** only

D **2** and **4** only

25 The energy profile diagram for the nucleophilic substitution reaction between hydroxide ions and 2–chloro–2–methylpropane is shown below.



Which statements can be inferred from the information given above?

1 The intermediate **Z** is 

2 This reaction has an overall order of reaction of 1.

3 Removal of 2−methylpropan−2−ol product does not affect the yield of the reaction.

4 Increasing the concentration of hydroxide ions reduces the time taken for reaction to complete.

A **1** and **2** only

B **1** and **4** only

C **2** and **3** only

D **3** and **4** only

26 Which compound will **not** react with $NaBH_4$, but react with H_2 when heated with nickel catalyst?

1 CH_3CH_2COOH

2 CH_3CH_2CHO

3 CH_3CH_2CN

4 $CH_3CH=CH_2$

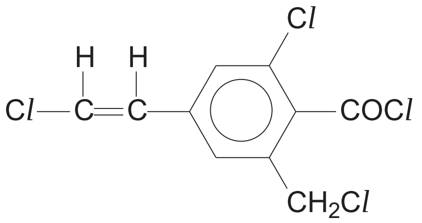
A **1** and **3** only

B **1** and **4** only

C **2** and **3** only

D **3** and **4** only

27



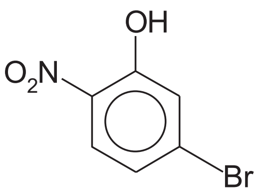
1 mole of the above molecule is treated with NaOH(aq) and warmed, followed by adding excess dilute nitric acid.

How many moles of silver chloride will be formed when excess aqueous silver nitrate is added?

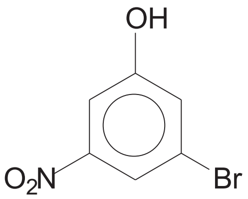
A 1 **B** 2 **C** 3 **D** 4

28 3-bromophenol is a versatile starting material for the synthesis of medicinal compounds. Which compound is likely to be the major product of the reaction between dilute nitric acid and 3-bromophenol?

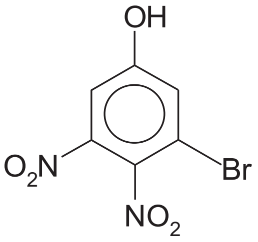
A



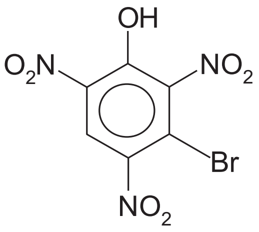
B



C



D



29 Cyanohydrins are useful intermediates in organic syntheses. They can be made by reacting carbonyl compounds with hydrogen cyanide.

Which statements are correct about the reaction of propanone and hydrogen cyanide?

1 Propanone reacts with HCN to give a racemic mixture.

2 Propanal reacts with HCN at a faster rate than propanone.

3 The cyanohydrin obtained from the reaction can be distinguished from propanone by warming with NaOH(aq).

A **1**, **2** and **3**

B **1** and **2** only

C **2** and **3** only

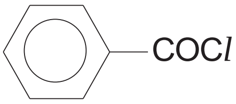
D **1** only

30 Deuterium, D, is an isotope of hydrogen, ${}^{2}_{1}H$.

Which reaction will **not** yield an organic compound containing deuterium, D?

A $CH_3CH_2CN \xrightarrow[DCl,\ heat]{D_2O}$

B $CH_3COCHI_2 \xrightarrow[D_2O,\ warm]{I_2,\ NaOD}$

C  $\xrightarrow[KOD]{D_2O}$

D $CH_3CH_2CONHCH_3 \xrightarrow{LiAlD_4}$

NATIONAL JUNIOR COLLEGE
SH2 PRELIMINARY EXAMINATION
Higher 2

CANDIDATE NAME			
SUBJECT CLASS		REGISTRATION NUMBER	

CHEMISTRY

Paper 2 Structured Questions

9729/02

Thursday
24 August 2017
2 hours

Candidates answer on Question Paper.
Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your subject class, registration number and name on all the work you hand in.
Write in dark blue or black pen.
You may use a soft pencil for any diagrams or graphs.
Do not use staples, paper clips, glue or correction fluid/tape.

Answers **all** questions.
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.

Appropriate significant figures and units are expected for final numerical answers.

For Examiner's Use	
1	/14
2	/16
3	/11
4	/16
5	/18
Paper 2 Total	/75

This document consists of **19** printed pages and **1** blank page.

1 Nitrous oxide, N_2O and nitrogen dioxide, NO_2, are atmospheric pollutants. Nitrous oxide has an atmospheric residence time as long as 20 to 30 years but nitrogen dioxide has a residence time of only approximately 4 days.

(a) Suggest how NO_2 is formed in a car engine and how it may be removed from car exhaust gases.

[2]

(b) **(i)** Draw the dot-and-cross diagrams of N_2O and NO_2, given that nitrogen is the central atom in both species.

[2]

(ii) Hence, explain for the difference in residence times between N_2O and NO_2.

[1]

(c) In the gaseous state, NO_2 can dimerise as follows.

$$2NO_2(g) \rightleftharpoons N_2O_4(g)$$

The following data are for $NO_2(g)$ and $N_2O_4(g)$ at 298 K.

	$\Delta H_f^\ominus$ / kJ mol^{-1}	$\Delta S_f^\ominus$ / J mol^{-1}K^{-1}
$NO_2(g)$	+33.2	+240
$N_2O_4(g)$	+9.2	+304

(i) Calculate $\Delta H^\ominus$ and $\Delta S^\ominus$ for the above reaction.

[2]

(ii) Explain the signs of your calculated $\Delta H^\ominus$ and $\Delta S^\ominus$.

[2]

(iii) The two gases in the above reaction can co-exist in an equilibrium. Calculate the temperature at which a dynamic equilibrium is established.

[2]

(iv) At 294 K, N_2O_4 liquefies. Given that the molar entropy change of vaporisation of N_2O_4 is +88 J mol^{-1}K^{-1}, calculate the molar enthalpy change of vaporisation of N_2O_4.

[1]

(v) With reference to your answers in **(c)(i)** and **(iv)**, calculate ΔH and ΔS for the reaction below.

$$2NO_2(g) \rightarrow N_2O_4(l)$$

[2]

[Total: 14]

2 This question is about the reactions of iodine and its compounds.

(a) In the 18th and 19th centuries, iodine was industrially produced from kelp, a large seaweed. Combustion of kelp converts the organic substances to ash, and sodium halides (mainly sodium iodide) are obtained.

In the laboratory, a similar process can be done according to the following procedure.

1. Fill a large crucible on a tripod with the seaweed. Heat with a strong Bunsen flame until all the seaweed has been turned to ash.

2. Boil the ash with about 20 cm^3 of purified water in a beaker, and filter while hot. Collect the filtrate in a second beaker and allow to cool.

3. Add about 2 cm^3 of dilute sulfuric acid to the filtrate, followed by hydrogen peroxide solution.

4. Transfer the mixture to a separating funnel and add 10−20 cm^3 of a suitable ***organic solvent***. Stopper the separating funnel and shake vigorously for about 30 s. With the separating funnel inverted, release any pressure that has built by opening the tap briefly.

5. Clamp the funnel and allow the layers to separate.

6. Run off the aqueous layer into a 250 cm^3 conical flask.

7. Run the organic layer into an evaporating basin, and set aside to evaporate in the fume cupboard to obtain the iodine crystals.

(i) State and explain, with the aid of a relevant equation, what you would observe during procedure **3**.

[2]

(ii) With reference to the *Data Booklet*, explain why hydrochloric acid is **not** used in the acidification process in procedure **3**.

[2]

(iii) Suggest a suitable organic solvent for the extraction of iodine in procedure **4** and state what you would observe.

[2]

(iv) Suggest a reason why in procedure **7**, evaporation is employed instead of direct heating over a strong Bunsen flame.

[1]

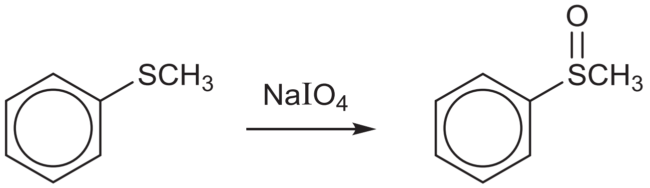
(v) In order to check if the kelp contained significant amount of chloride anions, a student transferred 1 cm^3 of the filtrate obtained in procedure **2** into a test tube and added acidified silver nitrate solution. A cream precipitate was obtained.

State and explain what reagent should be added to verify if there was a significant amount of chloride mixed with iodide.

[2]

(b) Sodium iodate, $NaIO_4$ (M_r = 214.0), is a powerful oxidising agent that can be used to oxidise thioethers into sulfoxides.

Thioanisole (M_r = 124.1), $C_6H_5SCH_3$, is a thioether. In a reaction between thioanisole and sodium iodate, it was found that 0.9 cm^3 of thioanisole (density = 1.06 g cm^{-3}) reacts completely with 15.40 cm^3 of 107 g dm^{-3} solution of sodium iodate to give methyl phenyl sulfoxide, $C_6H_5SOCH_3$.



thioanisole methyl phenyl sulfoxide

(i) Deduce the stoichiometry ratio for the reaction between thioanisole and sodium iodate.

[2]

(ii) Hence, write the balanced chemical equation for the reaction.

.... [1]

(iii) Thiophenol, C_6H_5SH, has similar reactions as phenol. Suggest how thioanisole can be synthesized from thiophenol in two steps.

[2]

(c) Hydrogen peroxide, H_2O_2, is another common redox reagent which can act as either an oxidising agent or reducing agent. H_2O_2 is a weak acid that dissociates according to the following equilibrium.

$$H_2O_2 \rightleftharpoons HO_2^- + H^+$$

With reference to the *Data Booklet*, deduce whether H_2O_2 is a better reducing agent in acidic or alkaline condition.

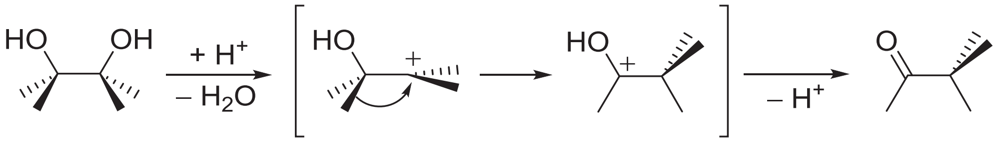
....

....

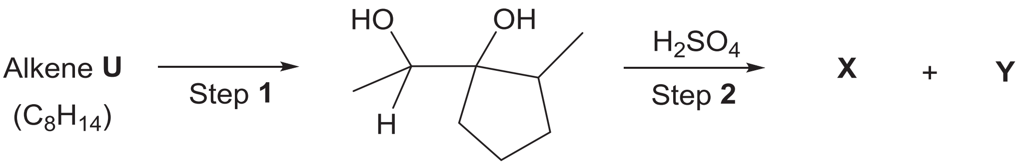
.... [2]

[Total: 16]

3 The pinacol rearrangement is a 1,2–rearrangement procedure which converts 1,2–diol to a carbonyl compound. This rearrangement process occurs under acidic condition (e.g. H_2SO_4). The diagram below shows the key steps in the mechanism, with movement of electrons pairs represented by curly arrows, needed to generate the carbonyl from 1,2–diol.



In a particular synthetic route, an alkene **U**, of molecular formula of C_8H_{14}, was first converted into a diol **W**. Compound **W** then reacted with H_2SO_4 to form two carbonyls **X** and **Y** as major products, in a reaction similar to pinacol rearrangement.



W

Compound **X** produces a yellow precipitate when heated with alkaline I_2 solution but not for compound **Y**. Compound **Y** gives a silver mirror when warmed with ammonical solution of silver nitrate.

(a) Suggest the structure of alkene **U**.

[1]

(b) State the reagents and conditions required for Step **1**.

Reagents : ....

Conditions : .... [1]

(c) Draw the structure of the most stable carbocation intermediate involved in Step **2** which resulted in the formation of the major products **X** and **Y**. Explain your answer.

Structure of carbocation intermediate

....

....

.... [2]

(d) Deduce the structures of compounds **X** and **Y.**

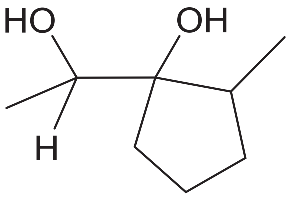
X

Y

[2]

(e) Compound **W** exhibits optical isomerism.

(i) Indicate each chiral atom(s) of compound **W** on the structure given below with an asterisk (*).



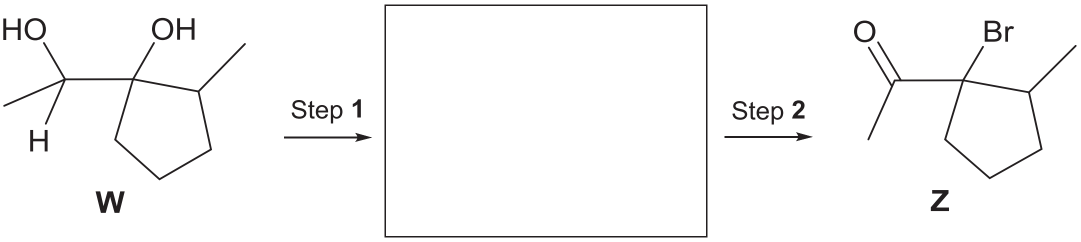
W

[1]

(ii) State the number of possible stereoisomers of compound **W**.

[1]

(f) State the reagents and conditions needed to convert diol **W** into compound **Z** shown below in 2 steps. Show the structure of the intermediate organic compound.



Reagents and Conditions

Step **1** ....

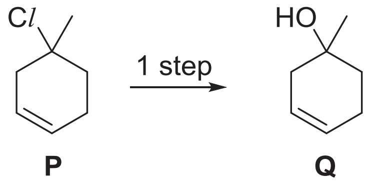
Step **2** ....

[3]

[Total: 11]

4 Chlorine, bromine and iodine are group 17 elements which are commonly found in organic material and used extensively in organic synthesis.

(a) Halogenoalkane is an example of such organic compounds and it can be converted into alcohol. For instance, 4–chloro–4–methylcyclohexene can be converted into an alcohol as shown below.

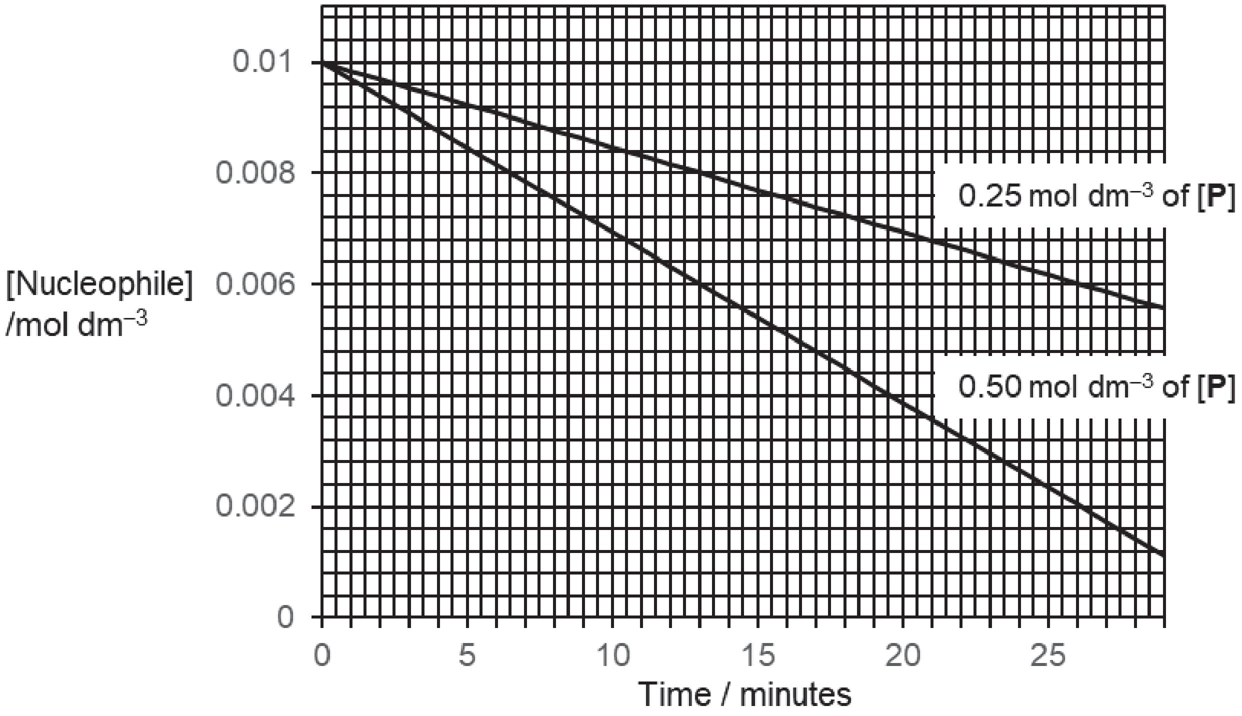


P **Q**

(i) State the reagents and conditions for the formation of compound **Q** from compound **P**.

.... [1]

(ii) Two experiments with different initial concentrations of **P** were used to study the kinetics of the reaction. A [nucleophile]–time graph was plotted using the results obtained from the experiments.



Deduce the order of reaction with respect to compound **P** and the nucleophile. Hence, state the rate equation.

Rate Equation : [3]

(iii) Using the nucleophile you have suggested in **(i)**, suggest the mechanism for this reaction.

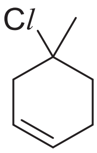
Show any relevant lone pairs, dipoles and charges, and indicate the movement of electron pairs with curly arrows.

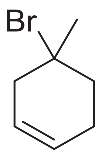
[3]

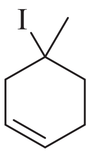
(iv) Suggest if any optical activity is present in the products of this reaction. Explain your answer.

[3]

(v) Bromoalkane and iodoalkane can undergo the same substitution reaction as chloroalkane to give alcohols but with different rates of reaction.







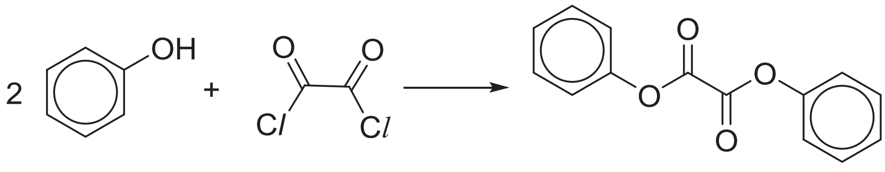
Rank the compounds, in increasing order of the time taken to undergo complete reaction with a nucleophile. Explain your answer, with reference to the *Data Booklet*.

You may use R to represent the hydrocarbon chain.

[2]

(b) Acyl chloride is an alternative for carboxylic acid in making esters.

Diphenylethandioate (M_r = 242.0), is an ester which produces the light in glow sticks when oxidised. It can be made from phenol (M_r = 94.0) and ethanedioyl dichloride (M_r =127.0).



Diphenylethandioate

(i) Given that this reaction has an average experimental yield of 75% and ethanedioyl dichloride is used in excess, calculate the mass of phenol needed to obtain 20 g of diphenylethandioate.

[2]

(ii) With reference to **(b)(i)**, suggest a simple chemical test that could be carried out to check if the reaction is completed.

....

....

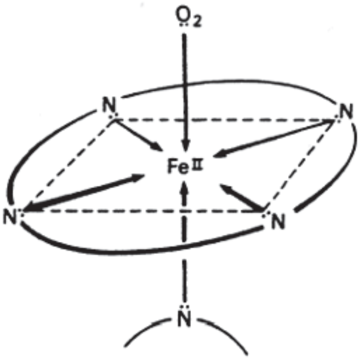
.... [2]

[Total: 16]

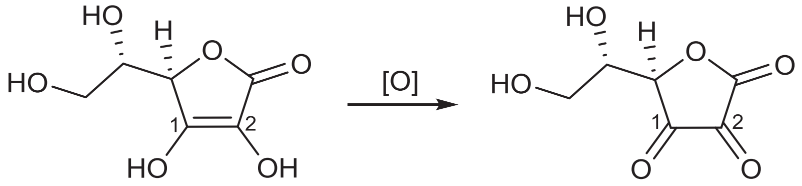
5 Haemoglobin reacts with oxygen to form oxyhaemoglobin as follows.

$$Hb + O_2 \rightleftharpoons HbO_2$$

In order for haemoglobin to absorb oxygen, iron must be present. The structure of the iron containing haem group is shown below.



In the presence of vitamin C, iron taken into the body in the diet as Fe^{3+} is converted into Fe^{2+} and incorporated in the haemoglobin structure. Vitamin C itself is oxidized in the process as follows.



Vitamin C

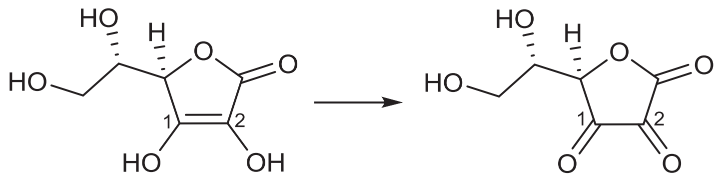
Approximately 10,000 million new blood cells are formed in the bone marrow daily. Red blood cells have a lifespan of 120 days. Each person should have about 150 mg of haemoglobin per cm^3 of their blood and a blood count of 5 million red blood cells per cm^3. Iron makes up 4% by mass of the haemoglobin molecule.

(a) **(i)** State the oxidation state of C_1 of vitamin C before and after oxidation.

Oxidation state of C_1 in vitamin C : ....

Oxidation state of C_1 after oxidation : .... [1]

(ii) Hence or otherwise, complete the half equation for the oxidation of vitamin C below.



\+ ....

[1]

(b) **(i)** Calculate the amount of iron, in moles, that needs to be available each day within the bone marrow for the production of new red blood cells.

[3]

(ii) The recommended dietary allowance of iron is 20 mg per day which is lower than the value calculated in **(b)(i)**. Suggest a reason for this.

....

.... [1]

(c) **(i)** In the space provided below, draw the shapes of all the 3d orbitals. Label the axes clearly.

d_{z^2} **$d_{x^2-y^2}$**

d_{xy} **d_{xz}** **d_{yz}**

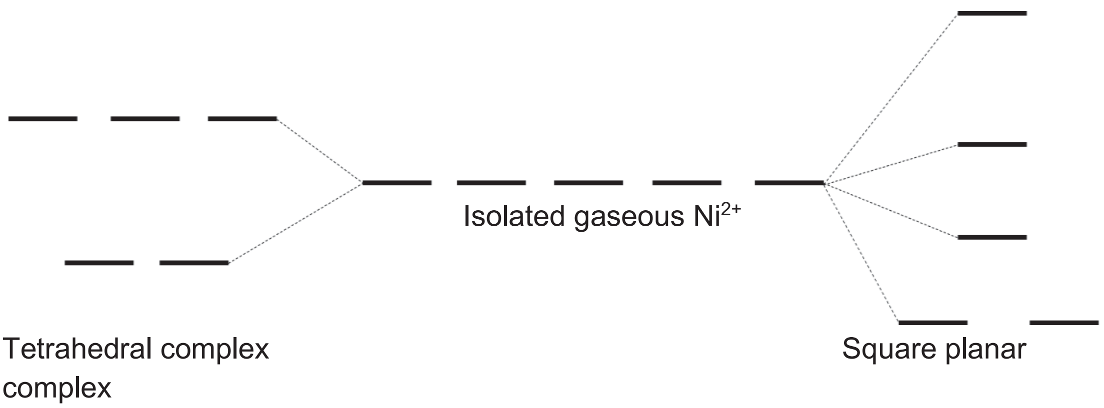
[2]

(ii) Account for the red colouration of blood.

[3]

(d) Complexes of Ni^{2+} are commonly found to have coordination number of 4, and exist either as tetrahedral or square planar complexes.

The splitting of the energy levels of d orbitals for tetrahedral and square planar complexes are different from that of an octahedral complex.



(i) Complete the electronic configuration for Ni^{2+}.

$1s^2\ 2s^2\ 2p^6$ [1]

(ii) The Aufbau principle states that in the ground state of an atom or ion, electrons fill atomic orbitals of the lowest available energy levels before occupying higher levels.

On the energy levels provided in **(d)**, show the electronic arrangement of the 3d electrons of Ni^{2+} in the tetrahedral and square planar complex.

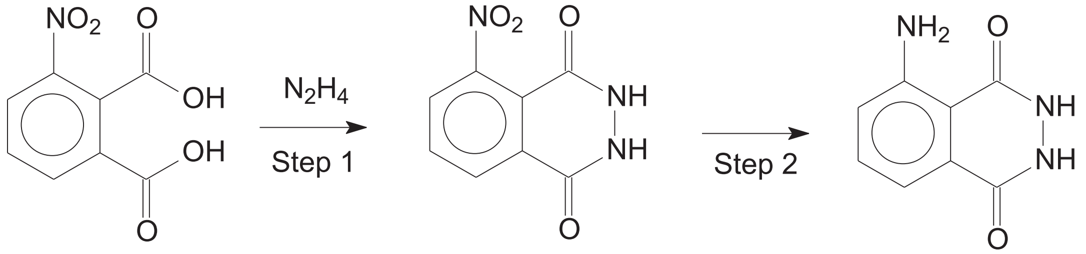
[1]

(iii) Complex ions with only paired electrons are considered to be diamagnetic while those with at least one unpaired electron are considered to be paramagnetic.

A Ni^{2+} complex $[NiX_4]^{2-}$ is found to be diamagnetic, with reference to your answer in **(ii)**, state the shape of this complex ion.

[1]

(e) Forensic investigators use luminol to detect traces of blood at crime scenes, as it reacts with the iron in haemoglobin. Luminol can be synthesized using the following route.



luminol

(i) State the type of reaction for Step 1.

[1]

(ii) A research student used the following reagent for Step 2.

Sn, conc HCl, heat under reflux, followed by excess NaOH(aq)

Suggest a reason why his method will not give luminol as the product.

[1]

(iii) Suggest and explain the relative basicity of N_2H_4 as compared to luminol.

[2]

[Total: 18]

End of Paper

Blank Page

NATIONAL JUNIOR COLLEGE

SH2 PRELIMINARY EXAMINATION

Higher 2

CANDIDATE NAME

SUBJECT CLASS

REGISTRATION NUMBER

CHEMISTRY

9729/03

Paper 3 Free Response

Monday 11 Sep 2017
2 hours

Candidates answer on separate paper.

Additional Materials: Data Booklet
Answer Paper

READ THESE INSTRUCTIONS FIRST

Write your subject class, registration number and name on all the work you hand in.
Write in dark blue or black pen.

You may use a soft pencil for any diagrams or graphs.
Do not use paper clips, highlighters, glue or correction fluid/tape.

Section A
Answers **all** questions.

Section B
Answers **one** question.

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

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

This document consists of **11** printed pages and **1** blank page.

Section A

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

1 **(a)** **(i)** Write an equation for the thermal decomposition of barium carbonate. [1]

(ii) Describe and explain the trend observed in the ease of thermal decomposition of the carbonates of the Group 2 elements. [2]

(b) Monuments made of marble or limestone, such as the Taj Mahal in India and the Mayan temples in Mexico, are eroded by acid rain containing sulfuric acid. The carbonate stone is converted into sulfate by acid rain.

$$CaCO_3(s) + H_2SO_4(aq) \rightarrow CaSO_4(s) + H_2O(l) + CO_2(g)$$

The life of such monuments is now being extended by treating them with a mixture of urea, $(NH_2)_2CO$, and barium hydroxide solutions.

reaction 1: After soaking in the pores of the carbonate stone containing water, urea reacts gradually to give ammonia and carbon dioxide.

reaction 2: Carbon dioxide produced then reacts with barium hydroxide to form barium carbonate.

(i) State the shape and bond angle around the C atom of $(NH_2)_2CO$. [2]

(ii) Write balanced equations for **reactions 1** and **2**. [2]

(c) When carbon dioxide gas dissolves in water, carbonic acid, H_2CO_3, is formed.

$$CO_2(g) \rightleftharpoons CO_2(aq)$$
$$CO_2(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq)$$

In a school laboratory, a student was instructed to titrate 25.0 cm^3 of 0.100 mol dm^{-3} carbonic acid with 0.125 mol dm^{-3} NaOH using phenolphthalein indicator. (K_{a1} of $H_2CO_3 = 4.3 \times 10^{-7}$ mol dm^{-3})

(i) Calculate the pH of 0.100 mol dm^{-3} H_2CO_3. [1]

(ii) Calculate the volume of NaOH needed to completely react with 25.0 cm^3 of 0.100 mol dm^{-3} H_2CO_3. [1]

(iii) Calculate the pH of the solution when H_2CO_3 and HCO_3^- are in equal concentrations. [1]

(iv) Calculate the pH of the resulting solution when 20.0 cm^3 of NaOH is added to 25.0 cm^3 of H_2CO_3. [2]

(v) Using your answers in **(i)** to **(iv)**, sketch the shape of the pH curve during the titration. [2]

(d) Barium compounds also have other uses and soluble barium salts are highly poisonous. For example, barium sulfate is used as a 'barium meal' in X-ray diagnostic work for patients with digestive tract problems. On the other hand, barium carbonate is used in rat poison.

The solubility products of $BaCO_3$ and $BaSO_4$ at 25 °C are given in the table below.

	Numerical value of K_{sp}
$BaCO_3$	5.5×10^{-10}
$BaSO_4$	1.3×10^{-10}

(i) Calculate the solubility of barium carbonate in mol dm^{-3} at 25 °C. [1]

(ii) When the concentration of Ba^{2+} ions exceeds 0.100 mol dm^{-3}, it is lethal. Suggest a reason why barium carbonate is poisonous when ingested by mouth whereas barium sulfate is safe. [2]

(e) The values of lattice energy of $CaSO_4$ and $BaSO_4$ are −2374 kJ mol^{-1} and −2480 kJ mol^{-1} respectively.

Some standard enthalpy changes of hydration are listed below.

	$\Delta H_{hyd}^{\ominus}$ / kJ mol^{-1}
Ca^{2+}	−1577
Ba^{2+}	−1305
SO_4^{2-}	−1099

Determine the enthalpy change of solution, $\Delta H_{sol}^{\ominus}$, for these two salts. Hence, comment on the difference in the solubilities of the two salts. [3]

[Total: 20 marks]

2 This question is about the chemistry of aluminium, iron and ruthenium, Ru.

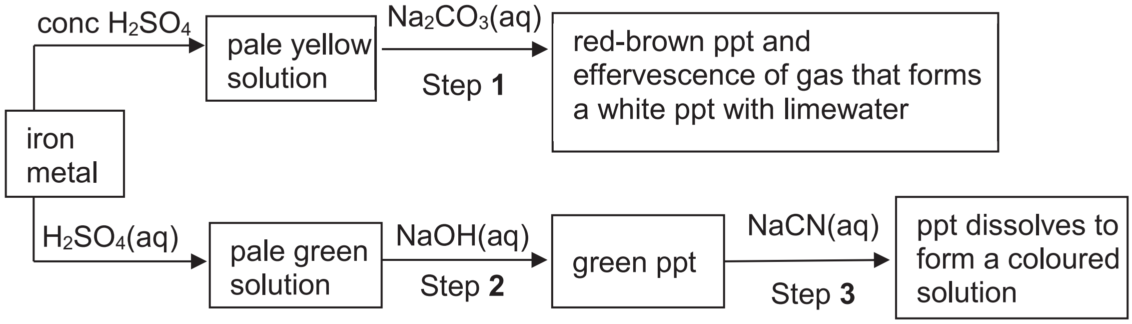
(a) Anodising is a process used to increase the thickness of the natural oxide on the surface of metal parts. Aluminium is a common metal which can be anodised as aluminium is a reactive metal that is readily oxidised by oxygen. This forms a layer of aluminium oxide, Al_2O_3, making it resistant to corrosion.

(i) Using H_2SO_4(aq) as the electrolyte and an inert electrode, draw an electrolysis set-up to show how an iPhone 7®, which is made of Al, can be anodised. [2]

(ii) Write chemical equations to show the reactions at the anode during anodising. [2]

(iii) The iPhone 7® has a surface area of 93.0 cm^2 to be anodised. Calculate the time needed to form a 0.2 mm protective layer of Al_2O_3 on the iPhone 7® if a current of 2.0 A is passed through the set-up. [2]
(Density of Al_2O_3 is 3.95 g cm^{-3})

(b) Iron metal is dissolved in limited amounts of dilute and concentrated sulfuric acid solutions and the resultant solutions undergo a series of reactions as shown below.



(i) Account for the observations seen in step **1**. [2]

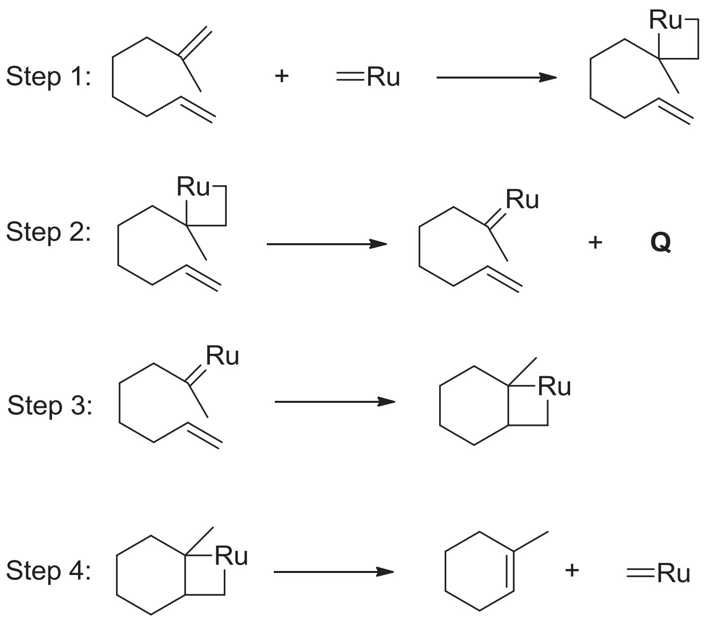
(ii) Write equations with state symbols to account for the observations in steps **2** and **3**. [2]

(c) When aqueous ruthenium(III) chloride is treated with zinc and aqueous ammonia, an orange compound is formed. The orange compound contains 36.9% ruthenium, 30.7% nitrogen, 25.8% chlorine and a certain percentage of hydrogen by mass. When aqueous silver nitrate is added, 1 mol of the orange compound forms 2 mol of $AgCl$ precipitate.

Given that 1 mol of the orange compound contains only 1 mol of Ru, determine the molecular formula of the orange compound. Draw a diagram of the structure of the complex ion in the orange compound. [3]

(d) Robert H. Grubbs used catalysts containing ruthenium for ring-closing reactions involving dienes.

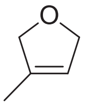
An example of such reactions is as shown.
(Note: =Ru represents CH_2=Ru)



(i) Formation of **Q** thermodynamically drives this reaction forward.
State the identity of **Q**. [1]

(ii) Copy step **4** onto your writing paper. Draw 2 full-headed curly arrows showing the movement of electrons to form the products. [1]

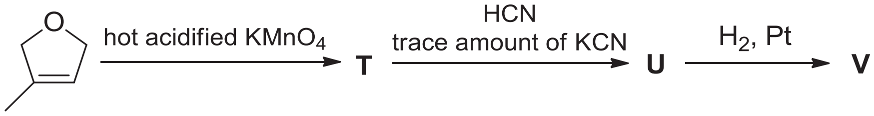
(iii) Suggest suitable reactants to synthesize **S** using the above method.



S

[2]

(e)



S

The ether functional group, $–CH_2–O–CH_2–$, in compound **S** is inert.
V exists as a crystalline solid at 300 °C.
Draw the structures of **T**, **U** and **V**. [3]

[Total: 20]

3 **(a)** The colour of blackberries is due to a compound known as cyanidin. At certain pH, cyanidin (Cy) exist as CyH^+, which is red, and at higher pH as Cy, which is purple.

$$\underset{\text{red}}{CyH^+} \rightleftharpoons \underset{\text{purple}}{Cy + H^+}$$

(i) Write an expression for the acid dissociation constant, K_a of CyH^+. [1]

(ii) Given the K_a value of CyH^+ is 5×10^{-5}, calculate the ratio of $\frac{[CyH^+]}{[Cy]}$ in the blackberries fruit juice buffered at pH = 5.3 and hence predict the colour of the solution at pH = 5.3. [2]

(b) Fruit juices are often preserved by adding small quantities of sulfur dioxide, but SO_2 also reacts with both forms of cyanidin to give colourless compounds. For the red form, the reaction can be represented as follows:

$$CyH^+(aq) + SO_2(aq) + H_2O(l) \rightleftharpoons CySO_3H_2(aq) + H^+(aq) \quad \text{Equilibrium (1)}$$

When sufficient sulfur dioxide is added to a fruit juice buffered at pH = 3.0 to reach an equilibrium SO_2 concentration of 1.0×10^{-2} mol dm^{-3}, the intensity of the red colour decreases to **one tenth** of its original value.

(i) Write an expression for the equilibrium constant for equilibrium (1) and use the data to calculate its value. [2]

(ii) Would this decolourisation of the preserved fruit juice be more or less severe at pH = 4.0 compared to pH = 3.0? Explain your answer. [2]

(c) Primary fermentation of blackberries produces wine and carbon dioxide. It undergoes a secondary fermentation to convert compound **J** (M_r =134) to compound **K** (M_r =90) to decrease the acidity of the wine.

Compounds **J** and **K** undergo the following reactions.

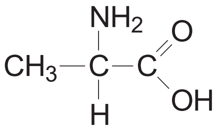
- Both **J** and **K** react with sodium carbonate and hot acidified $K_2Cr_2O_7$, but not with 2,4–dinitrophenylhydrazine.
- Both **J** and **K** react with excess hot concentrated H_2SO_4, but only **J** gives a mixture with a pair of cis-trans isomers.
- 0.234 g sample of **J** reacts completely with 35 cm^3 of 0.10 mol dm^{-3} NaOH(aq).
- **K** give a yellow precipitate with alkaline aqueous iodine.
- 7.5×10^{-4} mol of **K** produces 18 cm^3 H_2 gas at r.t.p. when excess Na is added.

Use the information above to deduce the structures of compounds **J** and **K**. Explain all the reactions involved. [5]

(d) Pyruvic acid, CH_3COCO_2H, can be produced from compound **K**. Explain why pyruvic acid is more acidic than benzoic acid. [2]

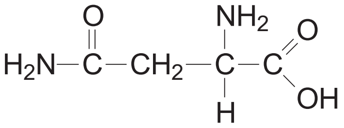
(e) Trace amount of amino acids could be found in fruits.

One of the amino acids, alanine, has the following structure.



(i) Suggest suitable reagents and conditions, and the structures of intermediate compounds formed, in the 3-steps synthesis of alanine from pyruvic acid. [4]

(ii) Describe a simple chemical test that you would carry out to distinguish alanine from asparagine.



asparagine

State the expected observations. [2]

[Total: 20]

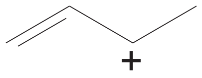
Section B

Answer **one** question from this section.

4 **(a)** Alkenes are commonly used as a precursor to make halogenalkanes.

(i) Describe the mechanism for the reaction of 1 mol of buta−1,3−diene with 1 mol of HBr. Show any relevant lone pairs, dipoles and charges, and indicate the movement of electron pairs with curly arrows.

The intermediate of the mechanism is shown below.

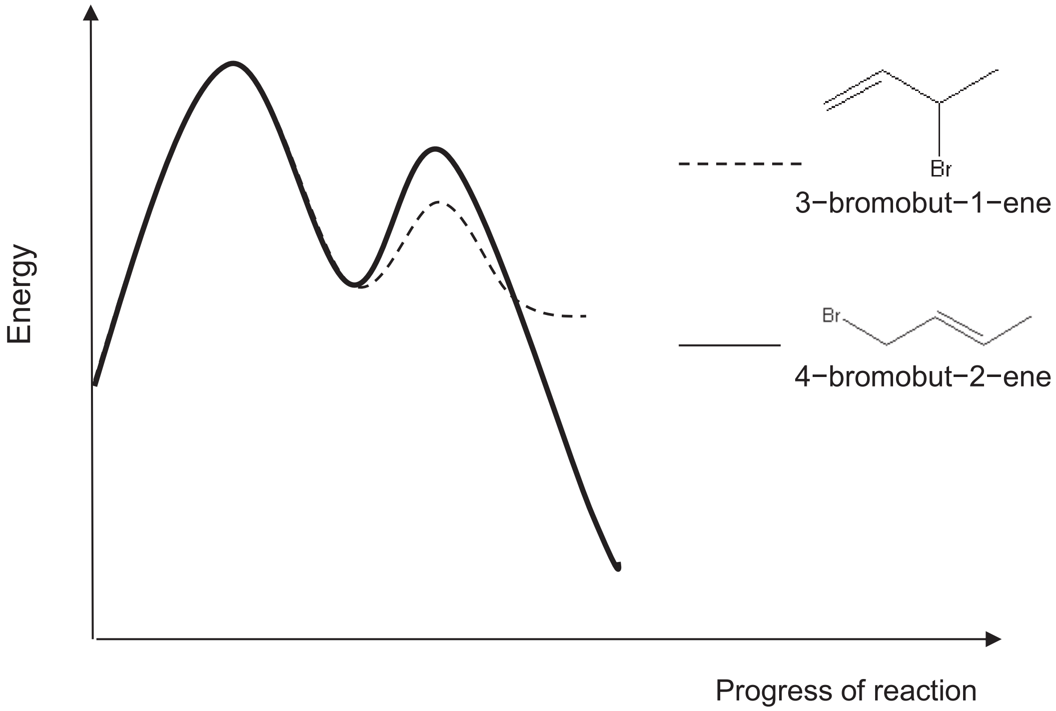


[3]

(ii) The intermediate in the above reaction in **(i)** can undergo a rearrangement to give a **primary** carbocation.

Draw the structure for the primary carbocation formed and show, with arrows, how the intermediate can be rearranged. [2]

(b) The diagram below shows the energy profile diagram for the formation of the products of the reaction of 1 mol of buta−1,3−diene with 1 mol of HBr.

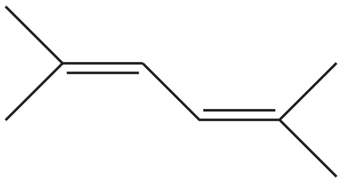


(i) Draw the Boltzmann distribution curve for the step 2 of the above reaction. Indicate their difference in activation energies that resulted in the two products formed. [2]

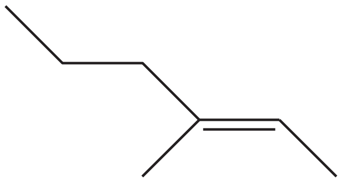
(ii) With reference to the Boltzmann distribution curve for the reaction, explain why 3−bromobut−1−ene is formed faster. [3]

(iii) With respect to the number of substituents on the C=C bond, suggest why 4−bromobut−2−ene is more stable than 3−bromobut−1−ene. [1]

(c) Separate bottles containing the following alkenes were mixed up.



compound **L**



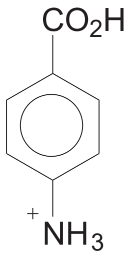
compound **M**

(i) Suggest a distinguishing test to determine the identity of the compounds and give the balanced equation for any reaction that occurs. [4]

(d) Arenes consist of 3 C=C bonds separated by C–C bonds, yet they exhibit different properties from alkenes.

(i) Explain why arenes cannot undergo electrophilic addition, unlike alkenes. [1]

(ii) Suggest suitable reagents and conditions, and the structures of intermediate compounds formed, for the synthesis of compound **N** from benzene.



compound **N** [4]

[Total: 20]

5 **(a)** Calcium chloride, $CaCl_2$, is commonly used as a desiccant to reduce humidity level of an enclosed space to allow the storage of articles that are prone to damage in high humidity. The lattice energy of $CaCl_2$ can be calculated from a Born–Haber cycle using the relevant data in the *Data Booklet* and the following data.

Enthalpy change of atomisation of calcium	= +177 kJ mol^{-1}
Enthalpy change of formation of calcium chloride, $CaCl_2$(s)	= −795 kJ mol^{-1}
First electron affinity of chlorine	= −364 kJ mol^{-1}

(i) Explain, with the aid of an equation, what is meant by *lattice energy* of $CaCl_2$. [1]

(ii) Construct a Born-Haber cycle for the formation of $CaCl_2$ and use it to calculate the lattice energy of $CaCl_2$. [4]

(iii) Explain how you would expect the magnitude of the lattice energy of aluminium oxide, Al_2O_3 (s) might compare to that of $CaCl_2$(s). [2]

(iv) Calcium chloride can be prepared by the reaction of calcium oxide and chlorine gas.

$$2CaO(s) + 2Cl_2(g) \rightarrow 2CaCl_2(s) + O_2(g)$$

Using the data above and given that the enthalpy change of formation of calcium oxide is −635 kJ mol^{-1}, construct an energy cycle and use it to calculate the enthalpy change of reaction for the equation above. [2]

(b) Calcium chloride, $CaCl_2$ is a solid with a high melting point (775 °C) whereas aluminium chloride, $AlCl_3$, sublimes at 178 °C.

(i) Explain the difference in melting points between these two chlorides in terms of their structure and bonding. [3]

(ii) Aluminium chloride is a halogen carrier where it reacts with chloromethane gas to generate the electrophile in the electrophilic substitution of hydrogen atoms in benzene:

$$AlCl_3 + CH_3Cl \rightarrow AlCl_4^- + CH_3^+$$

Explain why aluminium chloride can react with chlorine gas. Draw a diagram to illustrate the bonding in $AlCl_4^-$ [2]

(iii) The reaction in **(ii)** is an important step in the synthesis of 3–methylbenzoic acid, a precursor used to make DEET, a well-known insect repellent.

Suggest suitable reagents and conditions for a 3-steps synthesis of 3–methylbenzoic acid from benzene. [3]

(c) A 0.505 g sample of gaseous aluminium chloride takes up a volume of 90 cm^3 at 300 °C and 10^5 Pa.

(i) Under what conditions of temperature and pressure would you expect the behaviour of gaseous aluminium chloride to be most like that of an ideal gas? [1]

(ii) Calculate the M_r of the vapour at this temperature. [1]

(iii) With reference to your answer in **(ii)**, draw a displayed formula to show the type of bonding in the molecules of the vapour. [1]

[Total: 20]

BLANK PAGE

NATIONAL JUNIOR COLLEGE

SH2 Year-End Practical Examination

Higher 2

CANDIDATE NAME	

SUBJECT CLASS		REGISTRATION NUMBER	

CHEMISTRY **9729/04**

Paper 4 Practical

17 August 2017

Candidates answer on the Question paper

2 hours 30 minutes

Additional Materials: As listed in the Confidential Instructions

---

READ THESE INSTRUCTIONS FIRST

Write your identification number and name.
Give details of the practical shift and laboratory where appropriate, in the boxes provided.
Write in blue or black pen.
You may use an HB pencil for any diagrams or graphs.
Do not use staples, paper clips, glue or correction fluid.

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

The use of an approved scientific calculator is expected, where appropriate. You may lose marks if you do not show your working or if you do not use appropriate units.
Qualitative Analysis Notes are printed on pages 19 and 20.

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	/ 12
2	/ 16
3	/ 10
4	/ 17
Total	/ 55

This document consists of **20** printed pages including this cover page.

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

1 Determination of x in the formula of hydrated magnesium carbonate, $MgCO_3.xH_2O$.

Magnesium carbonate is a white, powdery compound that occurs naturally as anhydrous and several hydrated forms. Due to its non-toxicity, it is widely marketed in common products such as cosmetics and toothpaste.

A sample of a hydrated magnesium carbonate mineral is analysed to find out the number of moles of water per mole of magnesium carbonate.

You are given the following:

FA 1 is $MgCO_3.\mathbf{x}H_2O$ solid.

FA 2 is 2.00 mol dm^{-3} nitric acid, HNO_3.

FA 4 is 9.10 g dm^{-3} sodium hydroxide, NaOH.

Indicator: methyl orange

In this question, you will perform a back titration. The data from this titration will be used to determine the *M*r of $MgCO_3.\mathbf{x}H_2O$ and hence the value of **x**.

(a) In this titration, you will react $MgCO_3.\mathbf{x}H_2O$ with an accurately measured amount of excess **FA 2**. The reaction mixture was then used to prepare bulk solution **FA 3**. The amount of unreacted **FA 2** in **FA 3** is then determined *via* titration with **FA 4**. The end-point is reached when the colour of the solution changes from pink to yellow.

(i) Preparation of FA 3 by reacting FA 1 with excess FA 2

Record all the mass measurements in the space provided on page **3**.

1. Weigh out accurately about 0.20 g of **FA 1** in a clean and dry weighing bottle.
2. Transfer **FA 1** to a clean and dry small beaker. Measure and record the mass of weighing bottle and residual solid. Calculate the actual mass of **FA 1** transferred.
3. Pipette 25.0 cm^3 of **FA 2** to dissolve ALL solid **FA 1.**
4. Transfer the resultant solution to a 250 cm^3 volumetric flask.
5. Use a small volume of deionised water to rinse the inner wall of the small beaker and the glass rod. Transfer ALL washings to the volumetric flask.
6. Add more deionised water to make up the volume to the mark. Stopper and shake to ensure complete reaction and to obtain a uniform solution.
7. Label this solution as **FA 3**.

(ii) **Titration of FA 3 against FA 4**

8. Fill the burette with **FA 4**.

9. Using a pipette, transfer 25.0 cm^3 of **FA 3** into a conical flask and titrate the unreacted HNO_3 with **FA 4**, using methyl orange as indicator.

10. Run **FA 4** from the burette into this flask until solution changes from pink to yellow.

11. Record your titration results in the spaces provided below. Make certain that your recorded results show the precision of your instrument used.

12. Repeat steps **9** to **11** until your results are within ± 0.10 cm^3.

Results

[5]

(iii) From your titrations, obtain a suitable volume of **FA 4** to be used in your calculations. Show clearly how you obtained this volume.

Volume of **FA 4** = …………………… [1]

(b) **(i)** Using your titration results, calculate the amount of unreacted HNO_3 in 25.0 cm^3 of **FA 3**. Hence calculate the total amount of unreacted HNO_3 in 250 cm^3 of **FA 3**.
[*A*r: H, 1.0; O, 16.0; Na, 23.0]

Amount of unreacted HNO_3 in 250cm^3 of **FA 3** = ………………. [1]

(ii) Determine the total amount of HNO_3 in 25.0 cm^3 of **FA 2** before reacting with $MgCO_3$.**x**H_2O.

Amount of HNO_3 in 25.0 cm^3 of **FA 2** = ………………...

(iii) Hence calculate the amount of HNO_3 used to react with $MgCO_3$.**x**H_2O.

Amount of HNO_3 reacted with $MgCO_3$.**x**H_2O = ………………. [1]

(iv) Determine the relative molecular mass of $MgCO_3.\mathbf{x}H_2O$.

M_r of $MgCO_3.\mathbf{x}H_2O$ = ……………………

Hence calculate the value of **x** in $MgCO_3.\mathbf{x}H_2O$. Give your answer to the nearest whole number.
[*A*r: H, 1.0; C, 12.0; O, 16.0; Mg, 24.3]

x is ………..……….[2]

(c) Another student repeated the experiment using the procedure in **(a)**, however in **step 6**, he made up the solution to the 250 cm^3 mark by adding **FA 2** instead of deionised water. Explain the effect on his titre value and why it is unsuitable to do so.

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

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

[Total:12]

2 **Determination of the enthalpy change for the formation of hydrated magnesium carbonate, $\Delta H_{reaction1}$.**

In this experiment, you are to determine $\Delta H_{reaction3}$.
$\Delta H_{reaction1}$ will be determined using Hess's law.

$Mg(s) + C(s) + (3+\mathbf{x})/2\ O_2(g) + \mathbf{x}H_2(g) \rightarrow MgCO_3.\mathbf{x}H_2O(s)$ $\Delta H_{reaction1}$

$Mg(s) + 2HNO_3(aq) \rightarrow Mg(NO_3)_2(aq) + H_2(g)$ $\Delta H_{reaction\ 2} = -490\ kJ\ mol^{-1}$

$MgCO_3.\mathbf{x}H_2O(s) + 2HNO_3(aq) \rightarrow Mg(NO_3)_2(aq) + CO_2(g) + (\mathbf{x}+1)H_2O(l)$ $\Delta H_{reaction3}$

FA 1 is $MgCO_3.\mathbf{x}H_2O$ solid.

FA 2 is 2.00 mol dm^{-3} nitric acid, HNO_3.

(a) You are to perform the experiment below.

Determination of $\Delta H_{reaction3}$

1. Place a Styrofoam cup with lid inside a second Styrofoam cup which is held in a glass beaker to prevent it from tipping over.
2. Using a measuring cylinder, place 40.0 cm^3 of **FA 2** into the first Styrofoam cup. Measure and record its initial temperature, T_i.
3. Measure accurately about 1.00 g of **FA 1** in a weighing bottle.
4. Transfer **FA 1** into the Styrofoam cup containing **FA 2** and quickly replace the lid. Stir and measure the highest/lowest temperature obtained. Record this temperature, T_f.
5. Reweigh the weighing bottle.
6. Wash and dry the Styrofoam cups.
7. Record your data in the space provided below. Make certain that the recorded results show the precision of the instrument used.

Results

[3]

(i) Using your results, calculate the amount of heat change, $\Delta q_{reaction3}$, by reaction 3:

[$c = 4.18\ Jg^{-1}K^{-1}$, density of water = $1.00\ g\ cm^{-3}$]

$$MgCO_3.\mathbf{x}H_2O(s) + 2HNO_3(aq) \xrightarrow{\Delta H_{reaction3}} Mg(NO_3)_2(aq) + CO_2(g) + (\mathbf{x}+1)H_2O(l)$$

$\Delta q_{reaction3}$ = …………….[1]

(ii) Calculate the $\Delta H_{reaction3}$.

(If you were unable to calculate **x** in **1(b)(iv)**, you may assume that **x** = 3 for the calculation here and in part **(b)**. Note: this is a hypothetical value.)

$\Delta H_{reaction3}$ = …………….[1]

(b) Determination of $\Delta H_{reaction1}$

It is given that ΔH_f^{θ} of $CO_2(g)$ and $H_2O(l)$ is −393.5 kJ mol^{-1} and −285.8 kJ mol^{-1} respectively. Using these values together with $\Delta H_{reaction2}$ and $\Delta H_{reaction3}$, construct an energy cycle and calculate a value for $\Delta H_{reaction1}$.

$\Delta H_{reaction1}$ = ………………….[2]

(c) **(i)** Calculate the percentage error in the measurement of ΔT in the experiment.

percentage error = ………………….[1]

(ii) Apart from errors associated with the thermometer, suggest one **significant** source of error in the procedure used in this experiment. Suggest an improvement that could be made to reduce this error.

………………………………………………………………………………………..

………………………………………………………………………………………..

………………………………………………………………………………………..

……………………………………………………………………………………….[2]

(d) **Planning**

In another experiment, you are to plan an experiment to determine the identities of 3 unknown solutions using experimental techniques from thermochemistry.

You are provided with the following:

- solutions of **FB 1**, **FB 2** and **FB 3**, which can be any of the following:
  - 1 mol dm^{-3} aqueous ammonia
  - 1 mol dm^{-3} potassium hydroxide
  - 2 mol dm^{-3} hydrochloric acid
- the apparatus normally found in a school laboratory

In your plan, you should include

- appropriate quantities of solution used,
- the apparatus you would use and the procedure you would follow,
- the measurements you would take,
- an outline of how you would use your results to identify the 3 solutions. (Note: the use of indicator and litmus paper is not allowed)

…………………………………………………………………………………………

…………………………………………………………………………………………

…………………………………………………………………………………………

…………………………………………………………………………………………

…………………………………………………………………………………………

…………………………………………………………………………………………

……………………………………………………………………………………………[6]

[Total: 16]

3 Determination of the order with respect to Fe^{3+} of the reaction between iron(III) and iodide in acidified medium.

Iodide ions are oxidised by iron(III) ions in the presence of acid.

$$2Fe^{3+}(aq) + 2I^{-}(aq) \rightarrow 2Fe^{2+}(aq) + I_2(aq)$$

The rate of this reaction can be measured by adding thiosulfate ions, $S_2O_3^{2-}$, and some starch indicator to the mixture. As the iodine is produced, it reacts immediately with the thiosulfate ions and is reduced back to iodide ions.

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

When all the thiosulfate ions have reacted, the iodine which continues to be produced then turns the starch indicator blue-black. The rate of reaction may be determined by timing how long it takes for the reaction mixture to turn blue-black.

You are to investigate how the rate of reaction is affected by changing the concentration of iron(III) chloride.

The general rate equation can be expressed as rate = $k\,[Fe^{3+}]^n[I^-]^p$

As the concentration of iodide is present in high concentration, its concentration stays relatively constant during the course of reaction.

Rate equation thus can be rewritten as: rate = $k'\,[Fe^{3+}]^n$

Taking the logarithm function of the whole equation gives:

$$\lg \text{rate} = \lg k' + n\lg[Fe^{3+}]$$

By plotting a suitable graph, the gradient gives the order of reaction with respect to Fe^{3+}.

You are provided with the following

FA 5 is 0.0500 mol dm^{-3} aqueous sodium thiosulfate, $Na_2S_2O_3$.

FA 6 is 0.500 mol dm^{-3} aqueous potassium iodide, KI.

FA 7 is 1.00 mol dm^{-3} sulfuric acid, H_2SO_4.

FA 8 is 0.0500 mol dm^{-3} aqueous iron(III) chloride, $FeCl_3$.

Starch solution

(a) Procedure

Experiment 1

1. Fill a burette with **FA 5** and another burette with **FA 8**.
2. Run 20.00 cm^3 of **FA 8** from the burette into a 250 cm^3 conical flask.
3. Use a suitable measuring cylinder to add 20 cm^3 of **FA 7** to the flask.
4. Place a magnetic stir bar into the flask and set it stirring at a constant speed of 600 rpm.
5. Using another suitable measuring cylinder, transfer 20 cm^3 of **FA 6** into a 100 cm^3 beaker.
6. Add to the beaker from the burette 1.00 cm^3 of **FA 5**.
7. Add 1 cm^3 of starch indicator to the mixture in the beaker.
8. Tip the contents of the beaker into the conical flask and immediately start a stopwatch.
9. Observe the solution and stop the time when the solution turns blue-black.
10. Record the time taken to the nearest second.

Experiment 2

Repeat step 1 – 10 **except in step 2**, run 10.00 cm^3 of **FA 8** into the flask and using a suitable measuring cylinder to transfer 10 cm^3 deionised water into the flask.

Experiment 3 – 5

Carry out three further experiments to investigate how the reaction time changes with different volumes of iron(III) chloride.

Do not use a volume of **FA 8** that is less than 6.00 cm^3.

Record all your results in a single table. You should include the volume of **FA 8**, the volume of deionised water and the reaction time. Your recorded results should also include calculated values to enable you to plot

lg (1/time) against **lg (volume of FA 8)**

[5]

(b) **(i)** Use the grid below to plot a graph of **lg (1/time)** against **lg (volume of FA 8)**.

[3]

(ii) From your results, deduce the order of reaction with respect to Fe^{3+}.

order with respect to Fe^{3+} = ………………[2]

[Total: 10]

4 **Qualitative analysis**

In this question, you will deduce the two anions in solution **X** and a cation and an anion in solution **Y**. You will also work with an organic compound **Z**.

You will perform a series of test-tube reactions and use the observations to help you identify the unknown.

Test	**Procedure**	**Observations**
(a)	To 6 cm^3 of **X**, add barium nitrate solution until in excess.	
(b)	Filter the mixture from **(a).** Wash and retain the residue for test **(c)**. Collect the filtrate for test **(d)** and **(e)**.	
(c)	To separate portions of the residue **(i)** add 2 cm^3 of hydrochloric acid	
	(ii) add 2 cm^3 of organic compound **Z** [You are to test for any gas evolved]	
(d)	To 1 cm depth of the filtrate from **(b)** in a test-tube **(i)** Add a few drops of organic compound **Z** and warm in a water bath **(ii)** followed by 1 cm^3 of nitric acid and 5 drops of silver nitrate. Add excess ammonia solution.	

(e)	To separate 1 cm depth of **Y** **(i)** add filtrate from **(b)** dropwise until in excess	
	(ii) add NaOH(aq), followed by one spatula of zinc powder and warm (CARE!)	

[5]

(f) **(i)** From the observation in part **(c)(i)** and **(e)(i)**, identify the anion in the residue and the filtrate.

……………………………………………………………………………………..[2]

(ii) Suggest two functional groups present in organic compound **Z**. Justify your answer by quoting relevant evidence from the tests carried out.

……………………………………………………………………………………..

……………………………………………………………………………………..

……………………………………………………………………………………..

……………………………………………………………………………………..[2]

(g) Suggest 1 possible identity for the cation and anion present in solution **Y**.

cation: ……………………………….. [1]

anion: ……………………………….. [1]

(h) **Planning**

Consider the following organic compounds.

benzaldehyde 2-methylpropan-2-ol butan-1-ol propanal

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 results. 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]

[Total: 17]

GO TO NEXT PAGE FOR QUALITATIVE ANALYSIS NOTES

Qualitative Analysis Notes
[*ppt. = precipitate*]

(a) Reactions of aqueous cations

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

(b) Reactions of anions

anions	*reaction*
carbonate, CO_3^{2-}	CO_2 liberated by dilute acids
chloride, Cl^-(aq)	gives white ppt. with Ag^+(aq) (soluble in NH_3(aq))
bromide, Br^-(aq)	gives pale cream ppt. with Ag^+(aq) (partially soluble in NH_3(aq))
iodide, I^-(aq)	gives yellow ppt. with Ag^+(aq) (insoluble in NH_3(aq))
nitrate, NO_3^-(aq)	NH_3 liberated on heating with OH^-(aq) and 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 by dilute acids; gives white ppt. with Ba^{2+}(aq) (soluble in dilute strong acids)

(c) Tests for gases

gas	*test and test result*
ammonia, NH_3	turns damp red litmus paper blue
carbon dioxide, CO_2	gives white ppt. with limewater (ppt. dissolves with excess CO_2)
chlorine, Cl_2	bleaches damp litmus paper
hydrogen, H_2	“pops” with a lighted splint
oxygen, O_2	relights a glowing splint
sulfur dioxide, SO_2	turns aqueous potassium manganite(VII) from purple to colourless

(d) Colour of halogens

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

NJC H2 Chemistry Prelim Paper 1 Suggested Answers

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

1 Ans: **C**

SO_2 reacts with acidified $KMnO_4$
Total vol of SO_2 = 10 cm^3

Left over CO_2 reacts with NaOH(aq)
Vol of CO_2 = 2 cm^3

Vol of SO_2 produced from CS_2 = 4 cm^3
Vol of SO_2 produced from H_2S = 10 – 4 = 6 cm^3
Vol of CS_2 : Vol of H_2S = 2 : 6
mole fraction of H_2S in the mixture = $\frac{6}{8}$ = 0.750

2 Ans: **D**

Step I: Oxidation state of Cr increases from +3 in $Cr_2O_4^{2-}$ to +6 in CrO_4^{2-}.
Step II: Oxidation state of Cr remains as +6 in both CrO_4^{2-} and $Cr_2O_7^{2-}$.

$$2CrO_4^{2-} + 2H^+ \rightarrow Cr_2O_7^{2-} + H_2O$$

Step III: Oxidation state of Cr decreases from +6 in $Cr_2O_7^{2-}$ to +3 in Cr_2O_3.

3 Ans: **A**

$5Fe^{2+} + MnO_4^- + 8H^+ \rightarrow 5Fe^{3+} + Mn^{2+} + 4H_2O$
Amount of MnO_4^- required = $\frac{20}{1000} \times 0.40 = 0.008$ mol
Amount of $Fe^{2+} = 5 \times 0.008 = 0.040$ mol

At point X, the reaction is only half completed, $[Fe^{2+}] = [Fe^{3+}]$.

E_{cell} when connected to standard hydrogen electrode = +0.77 V

The colour change at end point is from yellow to first permanent pink.

Vol $KMnO_4$ added	Species present in conical flask	Colour of solution
0	Fe^{2+}(aq)	Pale green
Before eqv pt	Fe^{2+}(aq), Fe^{3+}(aq), Mn^{2+}(aq)	Yellow-green
At eqv pt	Fe^{3+}(aq), Mn^{2+}(aq)	Yellow
Just after eqv pt	Fe^{3+}(aq), Mn^{2+}(aq), small amt of MnO_4^-(aq)	Pink
In excess	Fe^{3+}(aq), Mn^{2+}(aq), large amt of MnO_4^-(aq)	Purple

4 Ans: **C**

Making reference to the I.E. values from Data Booklet, we can conclude that **I** is potassium.

Element **C** is A*l*, it is in Group 13.

Element **F** is S and it exists as S_8 molecules. The lowest boiling point is Ar gas (element **H**).

Ion of **E** (P^{3-}, 0.212 nm) is larger than that of **J** (Ca^{2+}, 0.099nm)

Element **D** and **G** are Si and C*l* respectively. The compound formed is $SiCl_4$.

5 Ans: **C**

The ionic compound can form strong ion-dipole interaction with polar solvent, making it soluble in polar solvents. The long chain hydrocarbon can also form strong temporary dipole-induced dipole interaction with non-polar organic solvents, making it soluble in organic solvents.

Around S atom, there are 4 bond pair regions and 0 lone pair, the shape is tetrahedral.

All the C atoms are sp^3 hybridised with tetrahedral shape and bond angle of 109.5°

6 Ans: **B**

pV = nRT, with n and p kept constant.
As T increases,

Option **A**: V increases. [$V = \frac{nR}{p} \times T$]

Option **B**: $\frac{pV}{T}$ remains constant. [$\frac{pV}{T} = nR$]

Option **C**: Density of the gas deceases [$\frac{m}{V} = \frac{pM_r}{RT}$]

Option **D**: pV increases. [pV = nRT]

7 Ans: **D**

$\Delta H_{rxn} = \Sigma\ \Delta H_f^{\ominus}\text{ (products)} - \Sigma\ \Delta H_f^{\ominus}\text{ (reactants)}$
$-27 = 3\times(-394) - [\Delta H_f^{\ominus}\ Fe_2O_3 + 3\times(-110)]$
$\Delta H_f^{\ominus}\ Fe_2O_3 = -825\ kJ\ mol^{-1}$

8 Ans: **D**

The following processes are involved in the Born-Haber cycle for ionic compounds:

1) Enthalpy change of formation of $BaF_3(s)$
2) Enthalpy change of atomisation of Ba(s)
3) Bond energy of F−F
4) 1st + 2nd + 3rd ionisation energies of Ba(g)
5) First electron affinity of F(g)

Ba^{3+} and F^- forms ionic compounds and would not have Ba−F bond energy.

9 Ans: **C**

Note since pressure is kept constant, ICE table **should NOT** be about change in pressure.

	X(g)	$\rightleftharpoons$	Y(g)	+ 2Z(g)
Initial / mol	x		0	0
Change / mol	–y		+y	+2y
Eqm / mol	x–y		y	2y

$P_Y + P_Z = p - 0.25p = 0.75p$
Since Y and Z are in a mol ratio of 1:2, $P_Y = 0.25p$, $P_Z = 0.5p$

$$K_p = \frac{(0.25p)(0.5p)^2}{0.25p} = 0.25p^2$$

10 Ans: **A**

Titration of a strong acid (H_2SO_4) with a weak base (NH_3). Equivalent point pH is less than 7 as NH_4^+ is a weakly acidic cation.

Methyl orange will be a suitable indicator as the working pH range of methyl orange coincides with the region of sharp pH change at equivalent point of this titration.

11 Ans: **B**

Since $Ca(OH)_2$ exist as aq and $Mg(OH)_2$ exist as a solid, K_{sp} of $Mg(OH)_2$ must be lower than $Ca(OH)_2$.
$|\Delta H_{hyd}| \propto$ charge density of ion, Mg^{2+} has a more exothermic ΔH_{hyd}.
$|L.E.| \propto \frac{q_+ \times q_-}{r_+ + r_-}$, magnitude of L.E. for $Mg(OH)_2$ is greater.

12 Ans: **D**

Since V_{total} is kept constant, volume of reactant used is proportional to its concentration in the final reaction mixture.
Comparing expt 3 and 4, when [P] × 2, initial rate also × 2. It is first order w.r.t **P**.
Comparing expt 4 and 2, when [R] × 2, initial rate × 4. It is second order w.r.t **R**.
Comparing expt 1 and 3, let rate = $k[P][Q]^y[R]^2$

$$\frac{\text{rate 1}}{\text{rate 3}} = \frac{k(10)(10)^y(10)^2}{k(5)(5)^y(10)^2}$$

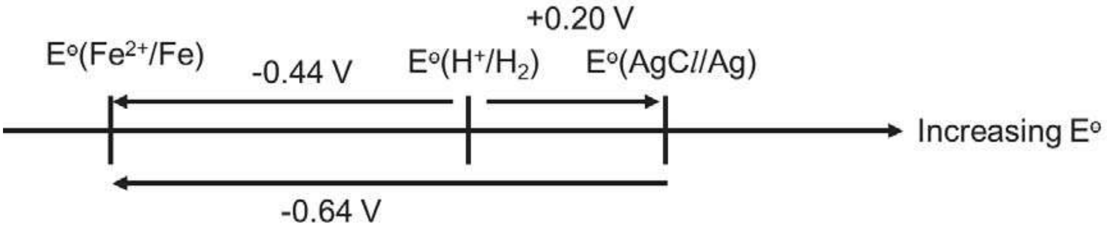
$4 = (2)(2)^y$
$(2)^y = 2$
It is first order w.r.t **Q**

13 Ans: **A**

Since $E^\ominus(MnO_4^-,H^+/Mn^{2+}) = +1.52$ V is greater than $E^\ominus(Cu^{2+}/Cu) = +0.34$ V, the reduction half-cell is $MnO_4^-,H^+/Mn^{2+}$ and oxidation half-cell is Cu^{2+}/Cu.
$E^\ominus_{cell} = E^\ominus(MnO_4^-,H^+/Mn^{2+}) - E^\ominus(Cu^{2+}/Cu)$

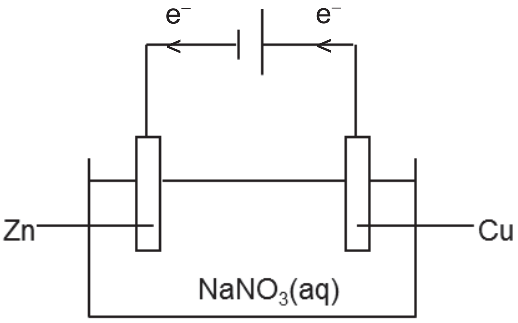
A	When excess NH_3 is added to Cu^{2+}/Cu half-cell, the half-cell become $[Cu(NH_3)_4]^{2+}/Cu$, $E^\ominus = -0.05$ V and $E^\ominus_{cell}$ increases.
B	When additional H^+ is added into $MnO_4^-,H^+/Mn^{2+}$ half-cell, the position of equilibrium for $MnO_4^- + 8H^+ + 5e^- \rightleftharpoons Mn^{2+} + 4H_2O$ shifts to the right, $E^\ominus(MnO_4^-,H^+/Mn^{2+})$ increases and $E^\ominus_{cell}$ increases.
C	Size of electrode does not affect $E^\ominus(Cu^{2+}/Cu)$ as solids does not affect position of equilibrium.
D	When alloy of copper and zinc is present, Zn reacts with Cu^{2+} to give Zn^{2+} and Cu(s). The concentration of Cu^{2+} decreases and position of equilibrium for $Cu^{2+} + 2e^- \rightleftharpoons Cu$ shifts to the left, $E^\ominus(Cu^{2+}/Cu)$ decreases and $E^\ominus_{cell}$ increases.

14 Ans: **C**



15 Ans: **C**

This is the simplified electrolytic cell.



Species present: Na^+ (aq), NO_3^- (aq), H_2O, Zn cathode, Cu anode
At cathode: $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$
At anode: $Cu \rightarrow Cu^{2+} + 2e^-$
The filter paper will turn blue due to the formation of Cu^{2+}(aq)
Note: this is not a litmus paper.

16 Ans: **C**

A	Melting point: $SiO_2 > Na_2O > P_4O_{10}$ SiO_2 (covalent lattice with strong covalent bond) Na_2O (ionic lattice with strong ionic bond) P_4O_{10} (simple molecular with weak IMF)
B	Covalent character: $P_4O_{10} = SiO_2 > Na_2O$
C	pH when mixed with water: Na_2O (pH = 14) > SiO_2 (pH = 7) > P_4O_{10} (pH = 3)
D	Na_2O is soluble in aq alkali due to reaction of Na_2O with H_2O to give NaOH. SiO_2 is insoluble in aq alkali due to strong covalent bond in the covalent lattice. P_4O_{10} is soluble in aq alkali due to reaction of P_4O_{10} with NaOH to give Na_3PO_4.

17 Ans: **B**

$M(NO_3)_2(s) \rightarrow MO(s) + 2NO_2(g) + ½\ O_2(g)$ (option 2 is correct)

Ionic radius of Mg^{2+} is smaller than Ba^{2+}. Mg^{2+} has a higher charge density and stronger polarising power. Mg^{2+} is able to distort electron cloud of NO_3^- to a larger extent and N–O covalent bond in $Mg(NO_3)_2$ is weakened significantly. Hence $Mg(NO_3)_2$ decompose at a lower temperature. (option 1 is correct).

$|L.E.| \propto \dfrac{q_+ \times q_-}{r_+ + r_-}$, magnitude of L.E. for $Mg(NO_3)_2$ is greater. However, N–O covalent bond is broken during thermal decomposition and hence we should not even be comparing the lattice energy.

18 Ans: **A**

Before heating, YCl_n reacts with $AgNO_3$ to produce 8.368×10^{-3} mol of AgC*l*.
After heating, the product reacts with $AgNO_3$ to produce 5.021×10^{-3} mol of AgC*l*.

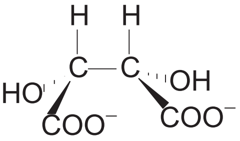
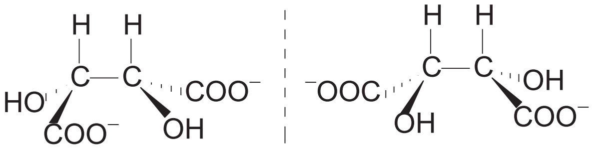
This shows that Y can form two chlorides with different oxidation state.
Y must be from Group 15 (e.g. PCl_5 and PCl_3)

1 mol of YCl_5 gives 5 mol of Cl^-
Amount of $YCl_5 = (8.368 \times 10^{-3}) \div 5 = 1.674 \times 10^{-3}$ mol
M_r of $YCl_5 = 0.50 \div 1.674 \times 10^{-3} = 298.8$
A_r of $Y = 298.8 - 5 \times 35.5 = 121.3$
Y is Sb

19 Ans: **D**

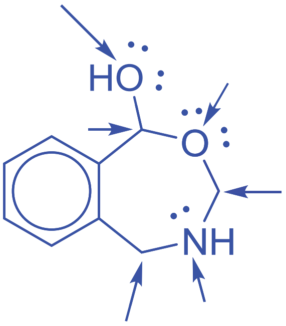
Down Group 17,
- Thermal stability of HX decreases due to weaker bond energy
- Enthalpy change of formation becomes less exothermic (calculate using BE values)
- The ease of oxidation increases as $E^\ominus(X_2/X^-)$ decreases down the group.

20 Ans: **B**

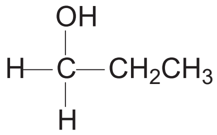
A	The tartrate ion acts as a Bronsted acid, it donates 2 H^+ to react with 2 OH^- and form the new ligand.
B	There are 2 chiral carbons for tartrate ion with 4 possible stereoisomers. However due to internal line of symmetry, 2 of the isomers are identical (they are known as the meso compound). Hence there are only 3 stereoisomers.  
C	The coordination number of the complex ion is 4. (4 dative bonds)
D	The oxidation number of Cu in the complex ion is +2. The ligands each have a charge of –3 after losing a H^+ from the tartrate ion.

21 Ans: **D**

There are a total of 6 central atoms with tetrahedral electron geometry. Hence, these 6 atoms are sp^3 hybridised. Take note that for the case of O and N in the molecule, the lone pair sits in the sp^3 orbital.



22 Ans: **B**

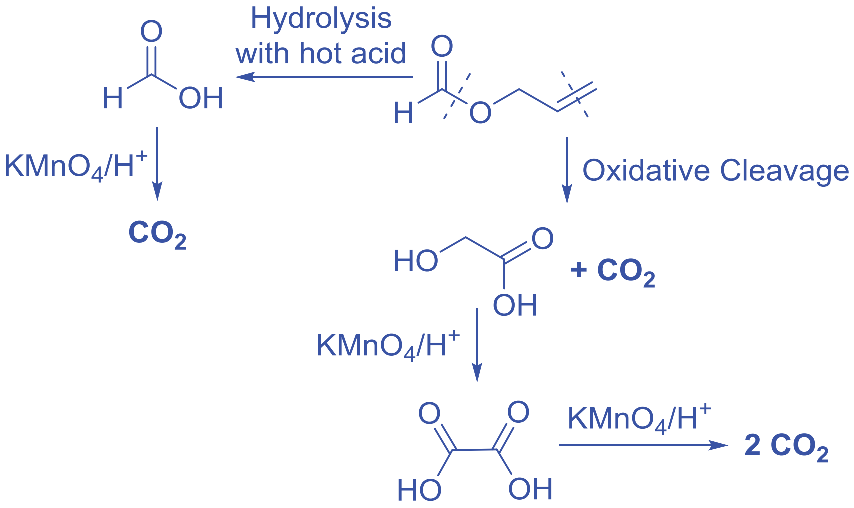


$$H-\overset{OH}{\underset{H}{C}}-CH_2CH_3$$

is the minor product from the addition reaction due to the lower stability of the carbocation intermediate.

23 Ans: **D**

4 moles of CO_2 can be obtained from the reaction of compound **A** with hot excess acidified $KMnO_4$.



Since 1 mole of $CaCO_3$ can be obtained from every mole of CO_2 produced,
Mass of $CaCO_3$ = 4 x 100.1 = **400.4** g

24 Ans: **C**

The molecular formula is $C_8H_9NO_5$. **(option 1 is wrong)**

There are 2 chiral carbons with 1 C=C bond capable of cis-trans isomerism. Hence total number of stereoisomer = 2^3 **(option 2 is correct)**

HBr(g) reacts with alkene and alcohol groups, 2 Br atoms are found in the product. **(option 3 is correct)**

$LiAlH_4$ reduces carboxylic acid and amide but not alkene. Only 4 H atoms are found in the product. **(option 4 is wrong)**

25 Ans: **C**

The energy profile diagram suggests the substitution proceeds in 2 steps, meaning it is an S_N1 reaction. This would mean that the rate = k [$(CH_3)_3CCl$]. Overall order of reaction would be 1 (**option 2 is correct**). [OH^-] would not affect the rate of reaction (**option 4 is wrong**).Intermediate Z is the carbocation (**option 1 is wrong**).

Rate of reaction is also not based on products. There is also no equilibrium established in this question. Le Chatelier's Principle does not apply in this question. Removal of product does not cause any increase in the yield (**Option 3 is correct**).

26 Ans: **D**

$NaBH_4$ only reacts with carbonyl groups. H_2(g), Ni(s) can react with alkene, carbonyl and nitrile group.

27 Ans: **B**

Acyl chloride reacts readily with water to give Cl^-.
Alkyl halide reacts with hot OH^-(aq) to give Cl^-.
C–C*l* bond in chlorobenzene and C*l* bonded directly to C=C has a partial double bond character due to delocalisation of lone pair electron of C*l* into the neighbouring π electron cloud. These C–C*l* bond will not break upon heating with OH^-(aq)

28 Ans: **A**

–OH in phenol is 2, 4 directing w.r.t the –OH group, dilute HNO_3 will only lead to mono nitration.

29 Ans: **C**

The cyanohydrin product from propanone does not contain a chiral centre, only one product $CH_3C(OH)(CN)CH_3$ is formed. Hence it cannot be considered as racemic mixture

$\delta+$ C atom in propanal experiences less steric hindrance and is able to react with the nucleophile CN^- at a faster rate. Furthermore, there are 2 electron donating alkyl groups bonded directly to the $\delta+$ C atom in propanone, decreasing the magnitude of $\delta+$ on the C atom. Hence propanone reacts with the nucleophile CN^- at a slower rate.

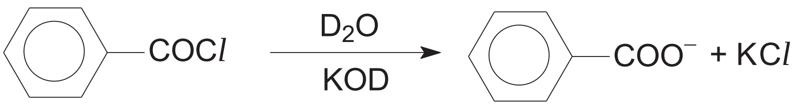
The cyanohydrin product $CH_3C(OH)(CN)CH_3$ reacts with hot NaOH(aq) to give pungent NH_3 gas which turns moist red litmus paper blue.

30 Ans: **C**

A $CH_3CH_2CN \xrightarrow[DCl\text{, heat}]{D_2O} CH_3CH_2COOD + NH_4^+$

B $CH_3COCHI_2 \xrightarrow[D_2O\text{, warm}]{I_2\text{, NaOD}} CH_3COO^- + CDI_3$

C



D $CH_3CH_2CONHCH_3 \xrightarrow{LiAlD_4} CH_3CH_2CD_2NHCH_3 + D_2O$

NJC H2 Chemistry Prelim Paper 2 Suggested Answers

1 **(a)** Due to **high temperature in the car engine**, **N_2 and O_2 from the air** can react to form NO_2.

NO$_2$ can be removed from the exhaust gas with the use of a **catalytic converter**, it can be **reduced by CO** to form harmless N_2.

(b) **(i)**

(ii) NO_2, being a **radical**, is **very reactive** and reacts with other gases in the air and gets destroyed more readily, hence a shorter atmospheric residence time

(c) **(i)** $\Delta H^\ominus = +9.2 - 2(+33.2) = -57.2 \text{ kJ mol}^{-1}$

$\Delta S^\ominus = +304 - 2(+240) = -176 \text{ J mol}^{-1}\text{ K}^{-1}$

(ii) $\Delta H^\ominus$ has a negative sign since the dimerization is a **bond formation process**, hence heat is given out / reaction is exothermic.

$\Delta S^\ominus$ has a negative sign since the dimerization results in **fewer gas particles**, hence there is a decrease in the disorderliness of the system.

(iii) At equilibrium,

$\Delta G = 0$
$\Delta H^\ominus - T\Delta S^\ominus = 0$
$-57.2 - T(-176/1000) = 0$

$T = 325 \text{ K}$

(iv) When N_2O_4 liquefies,
$\Delta G = 0$
$\Delta H_{vap} - T\Delta S_{vap} = 0$
$\Delta H_{vap} = T\Delta S_{vap} = 294 \times 88 = +25.9 \text{ kJ mol}^{-1}$

(iv) Using Hess's law,

$$\begin{tikzcd}
 & N_2O_4\,(l) \arrow[d, "②"] \\
NO_2\,(g) \arrow[ur, "③"] \arrow[r, "①"'] & N_2O_4\,(g)
\end{tikzcd}$$

② = ① – ③
For $\Delta H_{rxn} = -57.2 - {+25.9} = -83.1 \text{ kJ mol}^{-1}$
For $\Delta S_{rxn} = -176 - 88 = -264 \text{ J mol}^{-1}\text{ K}^{-1}$

2 **(a)** **(i)** H_2O_2 oxidises the I^-, to aqueous I_2, so a **brown solution** / **black solid** would be obtained.
$H_2O_2 + 2I^- + 2H^+ \rightarrow I_2 + 2H_2O$

(ii) $E^{\theta}_{Cl_2/Cl^-} = +1.36\ V$
$E^{\theta}_{H_2O_2/H_2O} = +1.77\ V$
$E^{\theta}_{cell} = +0.41\ V > 0$

Since E^{θ}_{cell} is positive, reaction is spontaneous, H_2O_2 can oxidise chloride to chlorine while it itself is reduced to H_2O.

Hence, the oxidation of iodide may not be complete.

(iii) hexane / cyclohexane

The aqueous layer will **decrease in brown intensity** and the colourless organic layer will turn **purple / violet**.

(iv) Organic solvent is **flammable**, and can **cause a fire to break out**.

With higher temperature, iodine may **sublime** and escape.

(v) **Excess aqueous NH_3** should be added.

AgC*l* is soluble in excess NH_3(aq) but AgI is not. If there was significant amount of silver chloride in the precipitate obtained, most of the precipitate dissolved upon adding excess aqueous NH_3

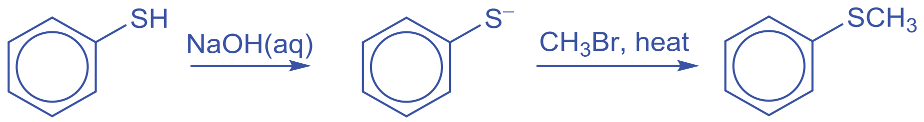
(b) **(i)** Amount of thioanisole used = $\frac{0.9\times1.06}{124.1}$ = 0.007687 mol

Amount of $NaIO_4$ used = $\frac{107\times{}^{15.40}/_{1000}}{214.0}$ = 0.0077 mol

∴ $NaIO_4$ reacts with thioanisole in a 1:1 mol ratio.

(ii) $C_6H_5SCH_3 + NaIO_4 \rightarrow C_6H_5SOCH_3 + NaIO_3$

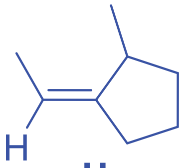
(iii)



(c) As a reducing agent, H_2O_2 will be oxidized.
Quote both eqns and $E^{\ominus}$
(In acidic) $O_2 + 2H^+ + 2e^- \rightleftharpoons H_2O_2$ $E^{\ominus} = +0.68\ V$
(In alkaline) $O_2 + H_2O + 2e^- \rightleftharpoons HO_2^- + OH^-$ $E^{\ominus} = -0.08\ V$

Due to a more negative $E^{\ominus}$ value, HO_2^- is more likely to be oxidised than H_2O_2. H_2O_2 is a better reducing agent in alkaline condition.

3 **(a)**

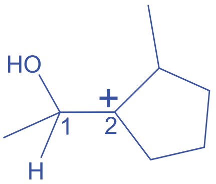


U

(b) Reagents : Dilute $KMnO_4$, NaOH(aq)

Conditions : cold

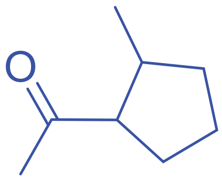
(c) Structure of carbocation intermediate



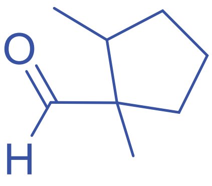
The carbocation ion would be formed at C_2 as it will form a more highly substituted carbocation than if the C+ is formed on C_1. OR

The carbocation would be formed at C_2 as it will have **more** electron donating alkyl group attached to C_2 than if the C+ is formed at C_1

(d)

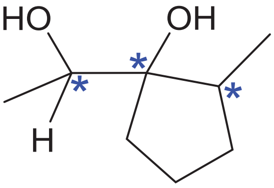


X



Y

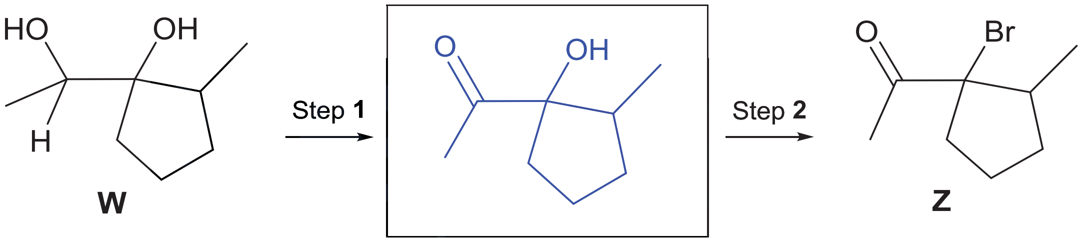
(e) **(i)**



W

(ii) $2^3 = 8$

(f)



Reagents and Conditions

Step **1** $KMnO_4$, H_2SO_4(aq), heat (or $K_2Cr_2O_7$, H_2SO_4, Heat [under reflux])

Step **2** Anhydrous PBr_3 (or $SOBr_2$ or HBr(g))

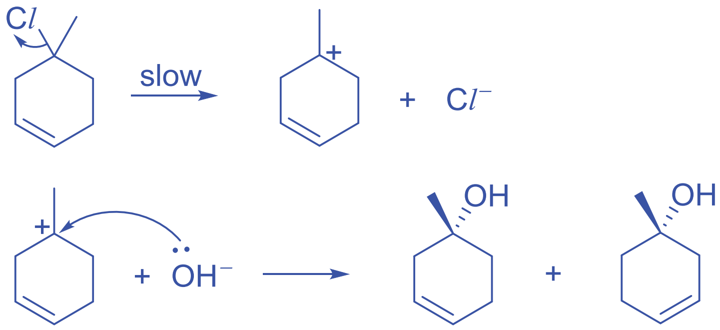
4 **(a)** **(i)** NaOH(aq), heat

(ii) Since the $[OH^-]$ decreases linearly over time with fixed gradient, rate of reaction remains the same throughout the whole experiment, the order or reaction with respect to OH^- is 0.

Comparing the time taken for 0.4 mol dm^{-3} of OH^- being reacted, it takes a half the time for sample with 0.5 mol dm^{-3} of **P** (13 mins) than that of 0.25 mol dm^{-3} of **P** (26.5 mins). This means when the [**P**] is doubled, the rate is also doubled. The order of reaction with respect to **P** is 1.

Rate Equation : Rate = k [Compound **P**]

(iii) Nucleophilic Substitution (S$_N$1)



(iv) There is no optical activity present in the products.

Trigonal planar carbocation intermediate allows nucleophile to approach from top and bottom of the plane at equal probability producing equimolar of enantiomers forming a racemic mixture. The effect of rotation of plane polarised light by one enantiomer is <u>completely cancel</u> by the other enantiomer resulting in lack of optical activity.

(v) Trend: R–I, R–Br, R–C*l*

Rate of this nucleophilic reaction depends on the breaking of the C–X bond. C–I bond (240 kJ mol^{-1}) is the weakest as compared to C–Br (280 kJ mol^{-1}) and C–C*l* (340 kJ mol^{-1}). C–I bond is the easiest to be broken and hence would take the shortest time to complete the substitution (highest rate). C–Br bond is weaker than C–C*l*, so C–Br would be easier to break and take shorter time than C–C*l*.

(b) **(i)** 75% yield = 20 g
100% yield = 20 x 4/3 = 26.67g
Amount of diphenylethandioate = 26.67 ÷ 242 = 0.11021 mol
Amount of phenol = 0.11021 x 2 = 0.22042 mol
Mass of phenol used = 0.22042 x 94 = 20.7 g

(ii) Add neutral $FeCl_3$ (aq). Reaction is completed when there is no formation of violet complex, indicating that all phenol have been reacted.

OR

Add aqueous Br_2. Reaction is completed when orange aqueous Br_2 do not decolourise upon addition, indicating all phenol have been reacted. Reaction is incomplete when orange aqueous Br_2 decolorised and white precipitate formed.

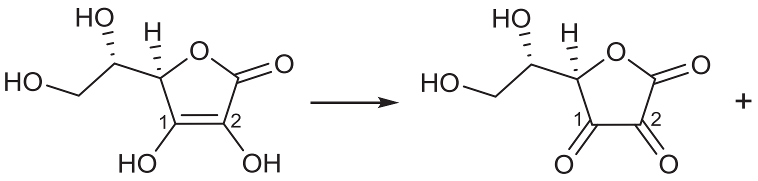
OR

Add Br_2 in CCl_4. Reaction is completed when orange-red Br_2 do not decolourise upon addition, indicating all phenol have been reacted. Reaction is incomplete when orange-red Br_2 decolorised.

5 (a) (i) Oxidation state of C_1 in vitamin C : +1

Oxidation state of C_1 after oxidation : +2

(ii)



$2H^+ + 2e^-$

(b) (i) 5 million red blood cells contain 150 mg of haemoglobin.

Mass of haemoglobin in 10000 million red blood cells

$= \frac{10000}{5} \times 150 = 300000$ mg

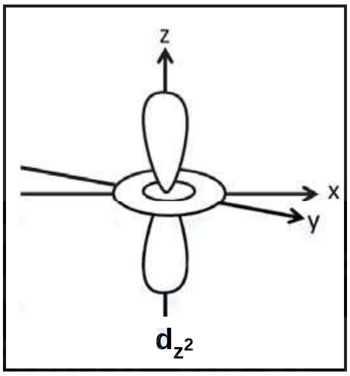
Mass of iron in 10000 million red blood cells

$= \frac{4}{100} \times 300000$ mg $= 12000$ mg $= 12$ g

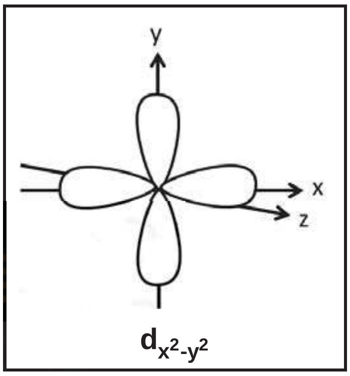
Amount of iron required $= \frac{12}{55.8} = 0.215$ mol

(ii) Red blood cell has a lifespan of 120 days. However, even when the red blood cells dies, some of the **iron still remains in the body for further use.**

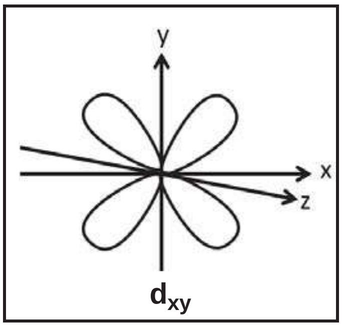
(c) (i)



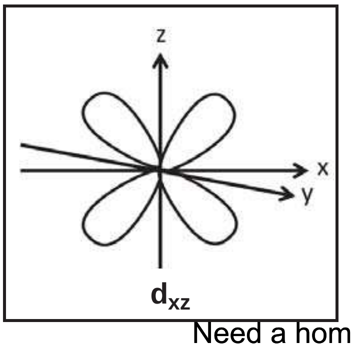
d_{z^2}



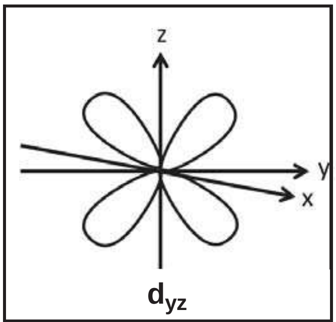
$d_{x^2-y^2}$



d_{xy}



d_{xz}



d_{yz}

(ii) In the presence of ligands, the d-orbitals of the transition element ion are split into two different energy levels with a small energy gap, ∆E**.**

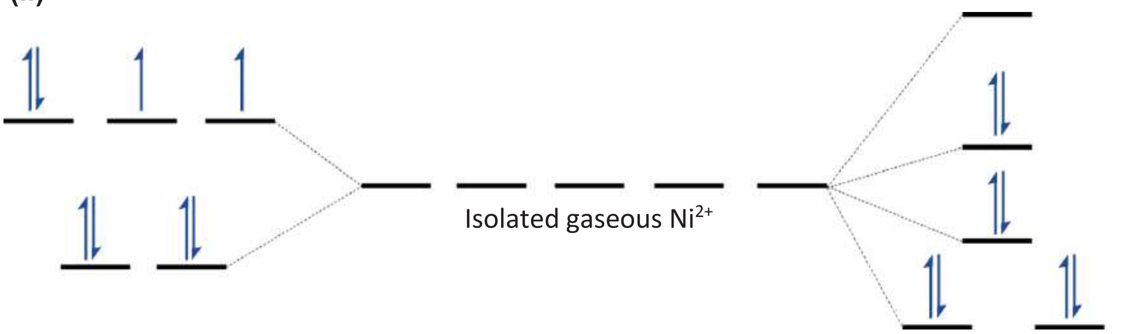
Electrons in the lower energy d-orbitals can absorb light of a certain wavelength with energy corresponding to the energy gap, ∆E, and be promoted to the higher energy d-orbitals **(d-d transition).**

The light not absorbed would be reflected and the colour of the complex is the **complementary** of the wavelength absorbed.

(d)

(i) $1s^2\ 2s^2\ 2p^6\ \ 3s^2\ 3p^6\ 3d^8$

(ii)



Tetrahedral complex

Square planar complex

(iii) Square planar [only contains paired electrons in the d orbitals]

(e) **(i)** Condensation (also accept nucleophilic substitution or nucleophilic acyl substitution)

(ii) Heating under reflux with conc HC*l* will cause the hydrolysis of the amide group in luminol.

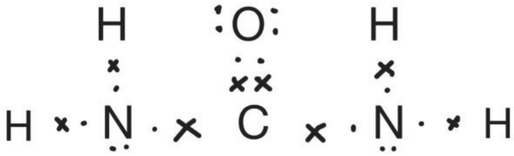
(iii) Luminol is less basic as compared to N_2H_4.
The lone pair on all N of luminol are involved in delocalization with the neighbouring benzene and C=O groups. As such, they are less available for donation to H^+ and act as a base. The lone pair on N of N_2H_4 do not undergo such delocalization and is more available for donation to H^+.

NJC H2 Chemistry Prelim Paper 3 Suggested Answers

1 (a) (i) $BaCO_3(s) \rightarrow BaO(s) + CO_2(g)$

(ii)
- Down the group, cations of Group 2 metals have the same charge but their size increases. The $\frac{charge}{size}$ ratio of the cation decreases. This leads to a decrease in polarising power.
- The electron clouds in the carbonate anion is being distorted to a smaller extent down the group and the weakening of C–O bond is less significant down the group.
- More energy is required to break the C–O bonds in the carbonate anion down the group.
- Therefore, the ease of thermal decomposition of the carbonates decreases down the group.

(b) (i)



Shape: trigonal planar
Bond angle: 120 °

(ii) Reaction 1: $(NH_2)_2CO + H_2O \rightarrow 2NH_3 + CO_2$

Reaction 2: $Ba(OH)_2 + CO_2 \rightarrow BaCO_3 + H_2O$

(c) (i) $K_a = \frac{[HCO_3^-][H_3O^+]}{[H_2CO_3]}$

$K_a = \frac{(x)^2}{0.100-x} = 4.3 \times 10^{-7}$ mol dm^{-3}

$[H^+] = \sqrt{4.3 \times 10^{-7} \times 0.1} = 2.074 \times 10^{-4}$ mol dm^{-3}

pH = 3.68

(ii) $H_2CO_3 + 2NaOH \rightarrow Na_2CO_3 + 2H_2O$

Amount of H_2CO_3 = $\frac{25}{1000} \times 0.1$ = 0.0025 mol

Amount of NaOH required = 0.005 mol
Volume of NaOH required = $\frac{0.005}{0.125}$ = 0.04dm^3 = 40.0 cm^3

(iii) At maximum buffering capacity,
$pH = pK_{a1}$
$= 6.37$

(iv) From part (ii), 40 cm³ of NaOH is required to completely neutralise the 2 H^+ from H_2CO_3.

When 20 cm³ of NaOH is added, only 1 H^+ from H_2CO_3 will react with NaOH

	OH^-	$+ H_2CO_3$	$\rightarrow$	HCO_3^-	$+ H_2O$
Initial / mol	0.0025	0.0025		0	-
Change / mol	–0.0025	–0.0025		+0.0025	-
Final / mol	0	0		0.0025	-

$[HCO_3^-]$ = $2.50 \times 10^{-3}/(0.02 + 0.025) = 0.05556$ mol dm^{-3}

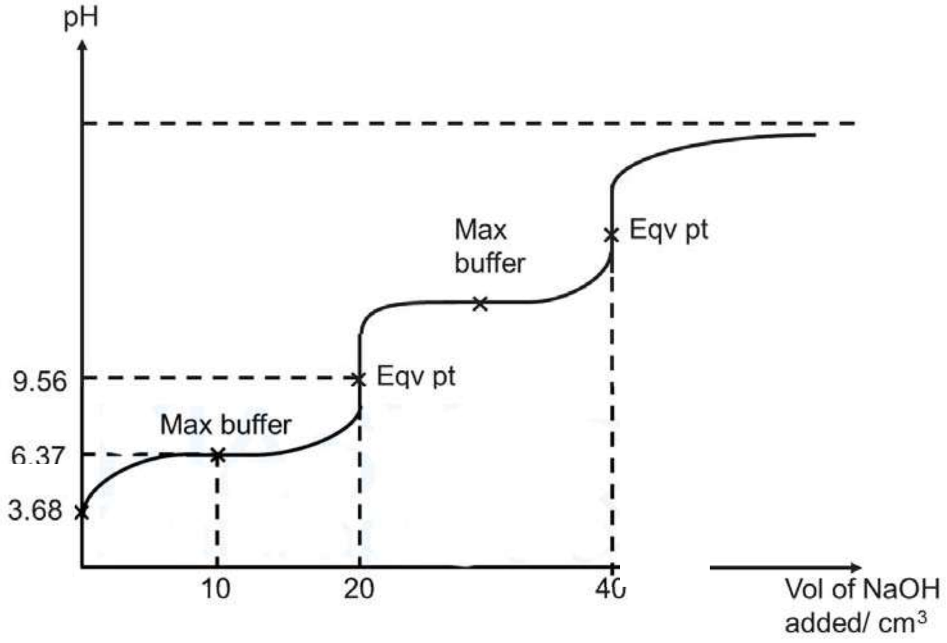
HCO_3^- acts as a weak base that dissociates partially.
$HCO_3^- + H_2O \rightleftharpoons H_2CO_3 + OH^-$

$K_b = \frac{[H_2CO_3][OH^-]}{[HCO_3^-]}$

$K_b = \frac{(x)^2}{0.05556-x} = \frac{1\times10^{-14}}{4.3\times10^{-7}} = 2.325 \times 10^{-8}$ mol dm^{-3}

$x = [OH^-] = 3.595 \times 10^{-5}$
$pOH = -\lg[OH^-] = 4.44$
$pH = 9.56$

(v)



(d) **(i)** $BaCO_3(s) \rightleftharpoons Ba^{2+}(aq) + CO_3^{2-}(aq)$

Let solubility of $BaCO_3(s)$ be s
$K_{sp} = [Ba^{2+}][CO_3^{2-}] = s^2 = 5.5 \times 10^{-10}$
$s = 2.35 \times 10^{-5}$ mol dm^{-3}

(ii) $BaCO_3(s) \rightleftharpoons Ba^{2+}(aq) + CO_3^{2-}(aq)$ --- eqm (1)

When ingested by mouth, the H^+ in stomach will react with CO_3^{2-} to form H_2CO_3 or CO_2. $[CO_3^{2-}]$ will decrease and equilibrium (1) will shift right. $BaCO_3$ will be more soluble in presence of H^+ and produces more Ba^{2+}, resulting in concentration of Ba^{2+} to exceed 0.100 mol dm^{-3}.

$BaSO_4(s) \rightleftharpoons Ba^{2+}(aq) + SO_4^{2-}(aq)$ --- eqm (2)

$[SO_4^{2-}]$ remains unchanged as SO_4^{2-} does not react with H^+. Hence, there is no shift in the position of equilibrium in (2). Concentration of Ba^{2+} is not affected and will not exceed the lethal level of 0.100 mol dm^{-3}

(e) $\Delta H_{sol}^{\ominus} = \Sigma\Delta H_{hyd}^{\ominus} - LE$

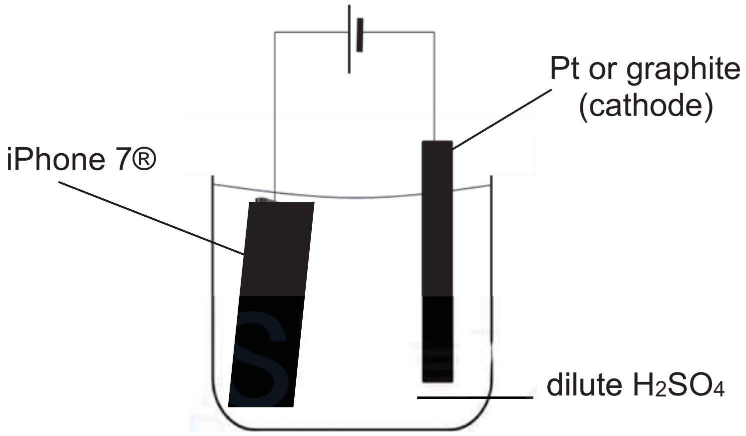
$\Delta H_{sol}^{\ominus}$ of $CaSO_4 = -1577 - 1099 + 2374$
$= -302$ kJ mol^{-1} [1]

$\Delta H_{sol}^{\ominus}$ of $BaSO_4 = -1305 - 1099 + 2480$
$= +76$ kJ mol^{-1} [1]

The $\Delta H_{sol}^{\ominus}$ of $CaSO_4$ is more negative compared to $BaSO_4$. $CaSO_4$ is more soluble than $BaSO_4$.

A negative $\Delta H_{sol}^{\ominus}$ shows that the aq ions of $CaSO_4$ are more stable than the ionic solid. Linking to $\Delta G = \Delta H - T\Delta S$, a more negative ΔH value will give a more negative ΔG value. Hence the reaction is more likely to be energetically feasible.

2 **(a)** **(i)**



Item to be anodised placed at anode

Correct inert metal / graphite used as cathode

Clear and labelled diagram

Use of battery

(ii) $2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$
$2Al(s) + {}^3/_2O_2(g) \rightarrow Al_2O_3(s)$

(iii) Volume of Al_2O_3 required = 93.0 × 0.02 = 1.86 cm^3
Mass of Al_2O_3 = 3.95 × 1.86 = 7.347 g
No. of moles of O_2 $= {}^3/_2 \times$ No of moles of Al_2O_3
$= {}^3/_2 \times \frac{7.347}{102} = 0.1080$ mol

No of moles of electrons passed = 0.1080 × 4 = 0.4322 mol
Q = 0.4322 × 96500 = 41705 C

Time needed = 41705 ÷ 2.0 = 20853 = 2.09×10^4 s (3 s.f.)

(b) **(i)** Fe^{3+} has high charge/size and is able to distort the electron cloud of water molecules, breaking the O-H bonds and release H^+
OR $[Fe(H_2O)_6]^{3+} \rightleftharpoons [Fe(H_2O)_5(OH)]^{2+} + H^+$
H^+ reacts with carbonate to form CO_2. $Fe(OH)_3$ is the red-brown ppt.

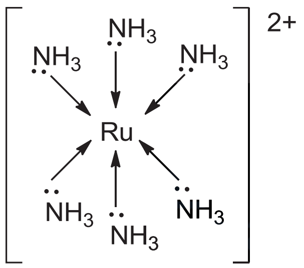
(ii) $Fe^{2+}(aq) + 2OH^-(aq) \rightleftharpoons Fe(OH)_2(s)$ green ppt
$[Fe(H_2O)_6]^{2+}(aq) + 6CN^-(aq) \rightleftharpoons [Fe(CN)_6]^{4-}(aq) + 6H_2O(l)$ formation of coloured solution
OR $Fe(OH)_2(s) + 6CN^-(aq) \rightleftharpoons [Fe(CN)_6]^{4-}(aq) + 2\,OH^-(aq)$

(c)

	Ru	N	C*l*	H
Mass in 100 g	36.9	30.7	25.8	6.6
Amount	36.9 / 101.1 = 0.365	30.7 / 14 = 2.193	25.8 / 35.5 = 0.7268	6.6 / 1.0 = 6.6
Simplest ratio	0.365 / 0.365 = 1	2.193 / 0.365 = 6	0.7268 / 0.365 = 2	6.6 / 0.365 = 18

There are 2 moles of free Cl^- ions. The remaining N and H must be from 6 NH_3 ligands.

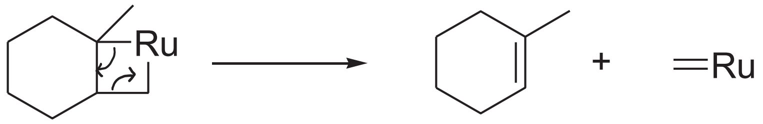
Hence, molecular formula of orange compound is $[Ru(NH_3)_6]Cl_2$.
accept $RuN_6H_{18}Cl_2$



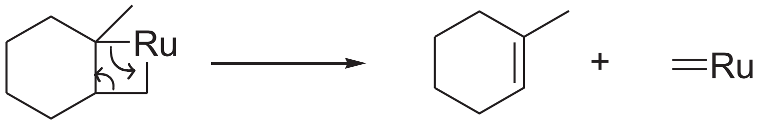
(d) **(i)** Ethene

(ii) Two possible answers:

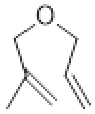
Step 4:



Step 4:



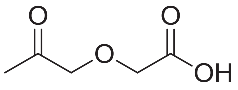
(iii)



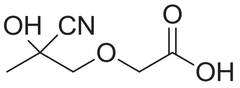
and =Ru

(e)

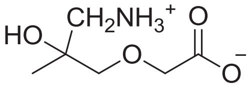
T:

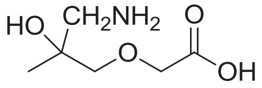


U:



V:





undergoes internal acid-base reaction to give V

3 (a) (i)

$$K_a = \frac{[Cy][H^+]}{[CyH^+]}$$

(ii)

$[H^+] = 10^{-5.3}$

$$K_a = \frac{[Cy][H^+]}{[CyH^+]}$$

$$5 \times 10^{-5} = \frac{[Cy][10^{-5.3}]}{[CyH^+]}$$

$$\frac{[CyH^+]}{[Cy]} = \frac{[10^{-5.3}]}{[5 \times 10^{-5}]}$$

$$= 0.100$$

OR $pH = pK_a + \lg \frac{[Cy]}{[CyH^+]}$

$$5.3 = -\lg(5 \times 10^{-5}) + \lg\frac{[\mathrm{Cy}]}{[\mathrm{CyH^+}]}$$

$$\lg\frac{[\mathrm{Cy}]}{[\mathrm{CyH^+}]} = 0.9990$$

$$\frac{[\mathrm{Cy}]}{[\mathrm{CyH^+}]} = 10^{0.9990} = 9.976$$

$$\frac{[Cy\mathrm{H^+}]}{[Cy]} = (1 \div 9.976) = 0.100 \text{ (3sf)}$$

Since concentration of C*y* is much greater than C*y*H⁺, the dominant species is Cy. Hence, the colour of the solution will be purple colour.

(b) **(i)**

$$K_c = \frac{[CySO_3H_2][\mathrm{H^+}]}{[Cy\mathrm{H^+}][SO_2]}$$

$[\mathrm{H^+}] = 10^{-3.0}$ mol dm^{-3}

Let initial concentration of C*y*H⁺ be x mol dm^{-3}

$[\mathrm{C}y\mathrm{H^+}]_{eqm} = \frac{1}{10}x$ mol dm^{-3}

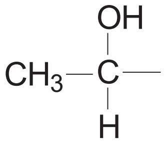
$[\mathrm{C}y\mathrm{SO_3H_2}]_{eqm} = \frac{9}{10}x$ mol dm^{-3}

$$K_c = \frac{[CySO_3H_2][\mathrm{H^+}]}{[Cy\mathrm{H^+}][SO_2]} = \frac{[(9/10)x][10^{-3.0}]}{[(1/10)x][1\times10^{-2}]} = 0.9$$

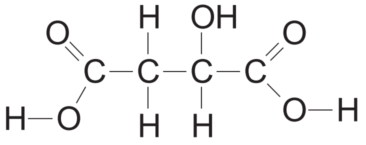
(ii) The decolourisation of the preserved fruit juice will be more severe at pH = 4.0.
At higher pH, [H⁺] is lower. According to Le Chatelier's principle, position of equilibrium (I) will shift to the right to increase [H⁺], thereby reducing the amount of cyanidin to a greater extent.

(c)

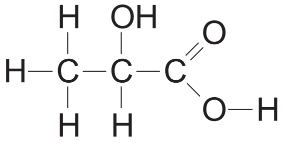
Information	Deduction
Both **J** and **K** react with sodium carbonate	**J** and **K** undergoes acid base reaction with sodium carbonate. ➔ Both compounds contain – carboxyl (COOH) group.
Both **J** and **K** react with acidified $K_2Cr_2O_7$, but not with 2,4–dinitrophenylhydrazine.	**J** and **K** undergoes oxidation reaction with $K_2Cr_2O_7$. ➔ Both compounds are not carbonyl compound and contain 1°/2°alcohol.

Both **J** and **K** react with excess hot concentrated H_2SO_4, but only **J** gives a mixture with a pair of cis-trans isomers.	**J** and **K** undergoes elimination of H_2O to form alkene. Alkenes obtained from **J** exhibited cis-trans isomerism, but not that of **K** (terminal alkene).
A 0.234 g sample of **J** reacts completely with 35 cm^3 of 0.10 mol dm^{-3} NaOH.	J undergoes neutralisation/acid base reaction with NaOH. Amt of **J**= $\frac{0.234}{134}$ =1.746 x10^{-3} mol Amt of NaOH = 3.5 x 10^{-3} mol Mole ratio of **J**: NaOH is 1:2 **J** is dibasic acid which contains two COOH groups. Given M_r of **J** = 134, $2xM_r(COOH)+M_r(OH)+M_r(C_xH_y)$ = 134 2(45) + (17) + x(12) + y(1) = 134 107 + x(12) + y(1) = 134 x(12) + y(1) = 27 x = 2 and y = 3
K give a yellow precipitate with alkaline aqueous iodine.	**K** undergoes mild oxidation with alkaline aqueous iodine. **K** contains the following structure $CH_3-\underset{H}{\overset{OH}{C}}-$
A 7.5 x 10^{-4} mol of **K** produces 18 cm^3 H_2 gas at r.t.p. when excess Na is added.	**K** undergoes redox/ acid metal reaction with Na. Amt of H_2 liberated = 18/24000 =7.5 x 10^{-4} mol Mole ratio of **K**:H_2 is 1:1 **K** contains two OH groups (make up of 1 COOH and 1 OH group). Given M_r of **K** = 90, $1xM_r(COOH)+M_r(CH_3CH(OH))=90$

J:



K:



(d) In conjugate base of pyruvic acid, the negative charge on O of COO^- can delocalise over **3** oxygen atoms which disperse the negative charge to greater extent as compared to the delocalisation of the negative charge of O of COO^- between **2** oxygen atoms and the benzene ring in the benzoate ion.

or Presence of the additional electron withdrawing C=O group in conjugate base pyruvic acid disperses the negative charge on O of COO^- to greater extent compared to the carboxylate group and benzene ring in the benzoate ions.

Hence, $CH_3COCO_2^-$ is more stabilised as compared to $C_6H_5COO^-$ and position of equilibrium shifts to right favouring the dissociation of the pyruvic acid into H^+.

e) (i)

Step 1:	H_2, Pt *or* H_2, Ni, heat or $NaBH_4$, ethanol
Step 2:	If X = Br, HBr(g) *or* KBr, conc H_2SO_4, heat If X = C*l*, HC*l*(g) with anhydrous ZnC*l*$_2$ catalyst
Step 3:	excess NH_3 in ethanol, heat in sealed tube

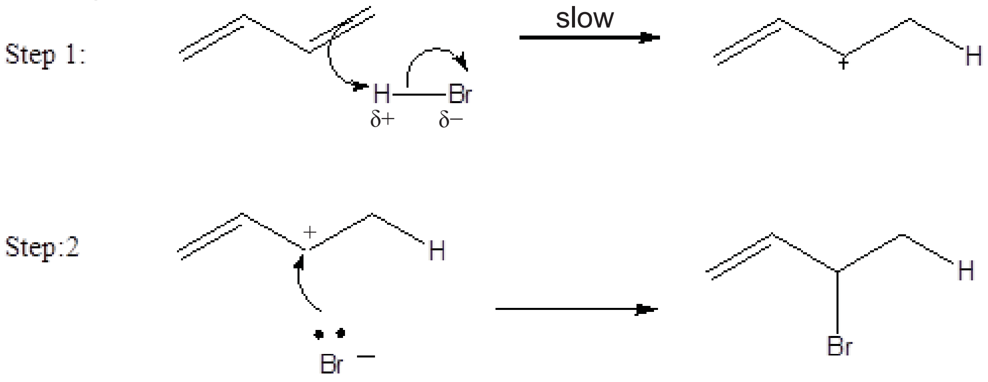
(ii) Add NaOH(aq) and heat

Observation:

alanine: **No alkaline gas evolved. Moist** red litmus paper remains red.

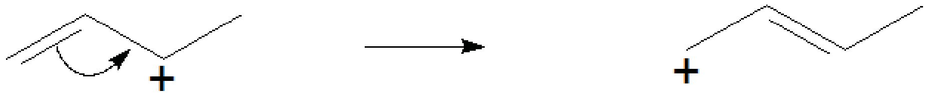
asparagine: Pungent **alkaline** gas evolved which turn **moist** red litmus paper blue

4 **(a)** **(i)** Electrophilic Addition



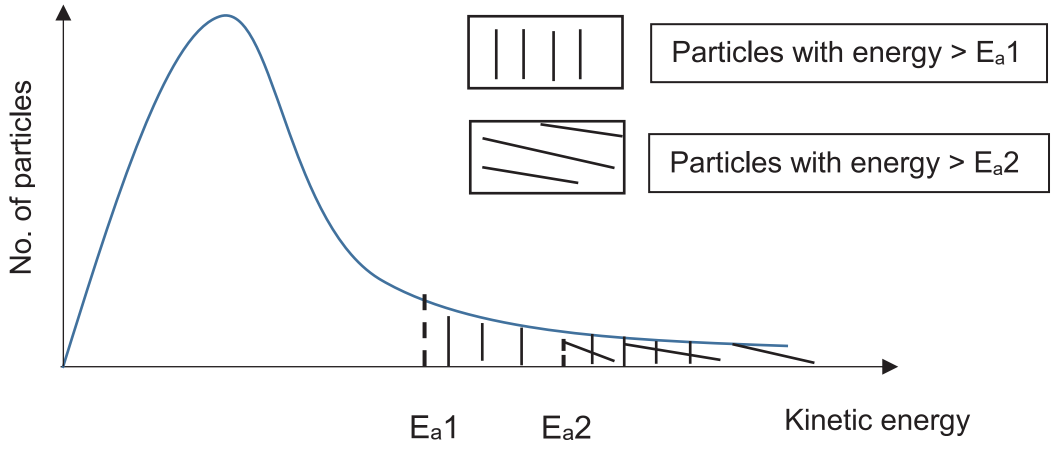
Correct product
Correct Partial charges and arrows

(ii)



Correct arrow
Correct product

b **(i)**



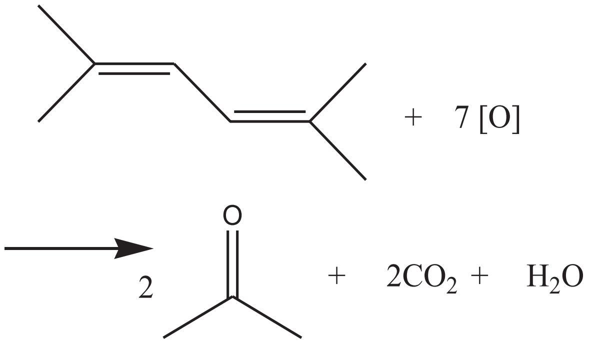
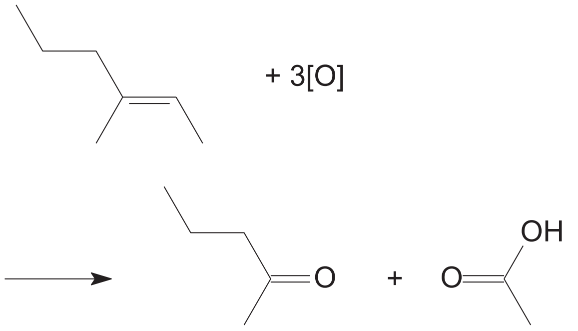
E_a1 is the E_a for the formation of 3–bromobut–1–ene
E_a2 is the E_a for the formation of 4–bromobut–2–ene
Axis labelled
Peak of graph should be before plateau off
Graph plateau off
Graph starts from origin
Legend for shaded area

(ii) The activation energy for the formation of the 3−bromobut−1−ene is lower, hence there are more particles with energy larger than the activation energy. This leads to an increase in the frequency of effective collision and hence the rate of forming 3−bromobut−1−ene is faster.

(iii) 4−bromobut−2−ene is a more substituted alkene hence it is more stable.

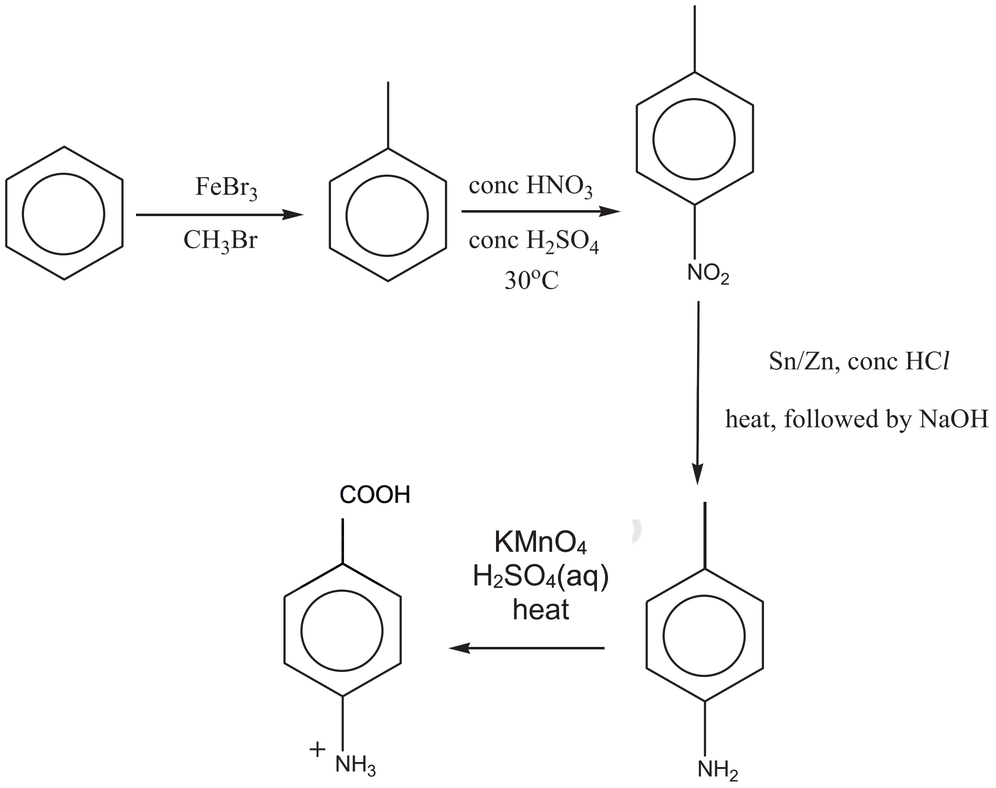
(c)

$KMnO_4$ (aq), H_2SO_4 (aq), heat

Compound L	Purple KMnO4 decolourises Effervescence observed. The gas forms white ppt in limewater	
Compound M	Purple KMnO4 decolourises	

d) **(i)** Electrophilic addition to an arene will disrupt the resonance stability as the p orbitals cannot form a continuous overlap.

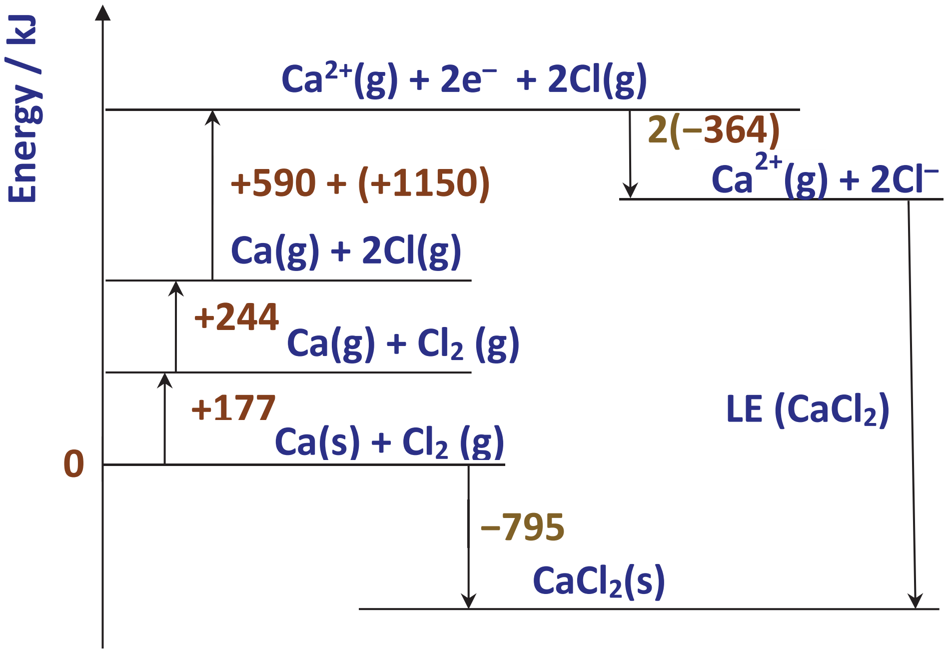
(ii)



5 a) (i) Lattice energy of $CaCl_2$ is the heat evolved when one mole of solid $CaCl_2$ is formed from isolated gaseous Ca^{2+} and Cl^-.

$Ca^{2+}(g) + 2Cl^-(g) \rightarrow CaCl_2(s)$ L.E = negative, <0

(ii)



L.E. = −795 − 177 − 244 − 590 − 1150 − 2(−364) = −2228 kJ mol⁻¹ ≈ −2230 kJ mol⁻¹

(iii)

$$|\text{L.E.}| \propto \frac{q_+ \times q_-}{r_+ + r_-}$$

Al_2O_3 has larger $q^+ \times q^-$ than $CaCl_2$
Al_2O_3 has smaller interionic distance than $CaCl_2$

Hence, magnitude of LE of Al_2O_3 > magnitude of LE of $CaCl_2$

(iv)

$$\begin{tikzcd}
2CaO\,(s) + 2Cl_2\,(g) \arrow[rr, "\Delta H_{rxn}"] & & 2CaCl_2\,(s) + O_2\,(g) \\
& 2Ca\,(s) + O_2\,(g) + Cl_2\,(g) \arrow[ul, "2 \times (-635)"] \arrow[ur, "2 \times (-795)"'] &
\end{tikzcd}$$

correct energy cycle that is balanced and labelling of relevant enthalpy change symbol or value.

$$2 \times (-635) + \Delta H_{rxn} = 2 \times (-795)$$

$$\Delta H_{rxn} = 2 \times (-795) - 2 \times (-635)$$

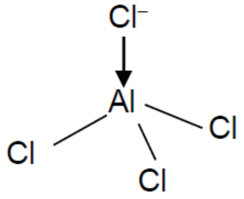
$$= -320 \text{ kJ mol}^{-1}$$

b) **(i)** $CaCl_2$ has giant ionic structure. Large amount of energy required to overcome strong ionic bonds between Ca^{2+} and Cl^- ions.

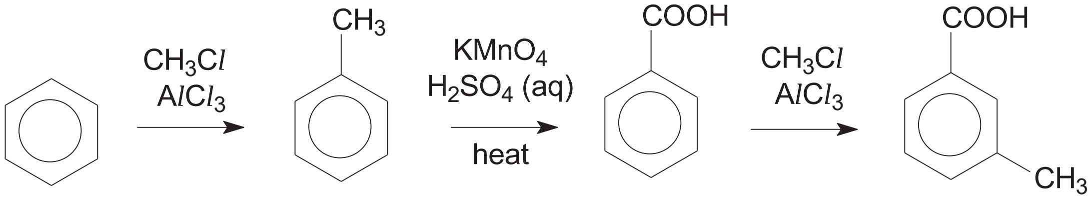
$AlCl_3$ has simple molecular structure. Small amount of energy required to overcome weak intermolecular temporary dipole – induced dipole interactions.

Hence melting point of $CaCl_2$ is higher than $AlCl_3$.

(ii) Al does not have a full octet structure in $AlCl_3$ (or Al is electron deficient) so it is able to accept another pair of electrons from Cl^-.



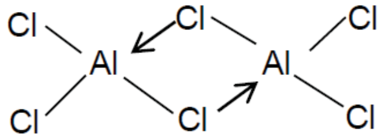
(iii)



c) **(i)** High temperature and low pressure.

(ii) $M_r = \frac{\text{mass} \times RT}{PV} = \frac{0.505 \times 8.31 \times (273+300)}{10^5 \times 90 \times 10^{-6}} = 267.2$

(iii)



Suggested solution for 2017 SH 2 Prelim Practical

1 (a) (ii) **Table 1: Weighings of FA1**

Mass of weighing bottle and **FA1** / g	**3.696**
Mass of weighing bottle and residual **FA1** / g	**3.497**
Mass of **FA1** transferred / g	**0.199**

Table 2: Titration of FA3 with FA4 using screened methyl orange as indicator

	1	**2**
Final burette reading / cm^3	**30.00**	**36.90**
Initial burette reading / cm^3	**9.00**	**16.00**
Volume of **FA4** used / cm^3	**21.00**	**20.90**

(iii) average volume = $\frac{21.00 + 20.90}{2}$ = 20.95 cm^3

(b) (i) amount of HNO_3 in 25.0 cm^3 = amount of NaOH = 20.95 / 1000 x (9.10/40.0) = 4.77 x 10^{-3}

amount of HNO_3 in 250.0 cm^3 = 4.77 x 10^{-2}

(ii) amount of HNO_3 in 25.0 cm^3 = 25/1000 x 2 = 0.05 mol

(iii) amount of HNO_3 = 0.05 – 4.77 x 10^{-2} = 2.34 x 10^{-3}

(iv) amount of $MgCO_3.xH_2O$ = 2.34 x 10^{-3} / 2 = 1.17 x 10^{-3}

M_r = 0.208 / 1.15 x 10^{-3} = 170.2

x = [180.7 – (24.3 + 12.0 + 16.0 x 3)] / 18 = 4.77 ≈ 5

(c) The acid **will not be diluted** and close to 2.00 mol dm^{-3}, the titre value required to neutralise 25 cm^3 of FA 3 will be **about 250 cm^3 / more than 10 times greater**. Since this **exceeds the capacity of burette**, it is unsuitable.

2 **(a)** **Table 1: Weighings of FA1**

Mass of weighing bottle and **FA1** / g	4.495
Mass of weighing bottle and residual **FA1** / g	3.478
Mass of **FA1** transferred / g	1.017

Table 2: Measurement of temperature

T_i / °C	30.3
T_i / °C	33.3
ΔT / °C	3.0

(i) $\Delta q_{reaction3} = -mc\Delta T = -\ 40 \times 4.18 \times 3.0 = -502\ J$

(iii)

$$\begin{tikzcd}
Mg(s) + C(s) + (3+\mathbf{x})/2\ O_2(g) + \mathbf{x}H_2(g) \arrow[r, "\Delta H_{reaction1}"] \arrow[d, "+\ 2HNO_3(aq)"', "-490"] & MgCO_3.\mathbf{x}H_2O(s) \arrow[d, "-86.0"', "+\ 2HNO_3(aq)"] \\
Mg(NO_3)_2(aq) + C(s) + (3+\mathbf{x})/2\ O_2(g) + (\mathbf{x}+1)H_2(g) \arrow[r, "-393.5 + 6 \times -285.5"] & Mg(NO_3)_2(aq) + CO_2(g) + (\mathbf{x}+1)H_2O(l)
\end{tikzcd}$$

By Hess's law,

$\Delta H_{reaction1} = -490 - 393.5 + 6 \times -285.5 - (-86.0) = -2510\ kJ\ mol^{-1}$

OR

If they use $\mathbf{x} = 3$

By Hess's law,

$\Delta H_{reaction1} = -490 - 393.5 + 4 \times -285.5 - (-68.3) = -1957.2\ kJ\ mol^{-1}$
$= -1960\ kJ\ mol^{-1}$

(c) **(i)** percentage error = $(\pm\ 0.1 \times 2) / 3.0 \times 100 = \pm\ 6.67\ \%$

(ii) $\Delta H_{reaction3}$ = −502 / (1.017 / 174.3) = −86.0 kJmol^{-1}

OR

If they use ***x*** *= 3*

$\Delta H_{reaction3}$ = −502 / (1.017 / 138.3) = −68.3 kJmol^{-1}

(ii) **Error:**

The experiment did not take into account **heat exchange with surrounding** / **calorimeter / heat loss to surrounding / calorimeter**.

Improvement 1:

Use **cooling curve method** where **temperature changes after mixing are measured at 30s intervals** for about 3 min, then **max temperature is extrapolated to time of mixing**. This accounts for heat exchange with surrounding, hence a more accurate ∆T is obtained.

Improvement 2:

Calibration of the calorimeter by **making use of reaction with accurately known enthalpy change**. The calibrated heat capacity, C of the calorimeter takes into account heat exchange with surrounding, hence a more accurate ∆T is obtained.

OR

Error:

The experiment did not **repeat experiment to ensure consistent results**.

Improvement:

Repeat experiment until **∆T/m between a pair of experiments is within 5%**.

(d) **Suggested solution:**

Procedure:

1. Using three **10.0 cm³ measuring cylinders**, measure 5.0 cm³ of **FB 1**, **FB 2** and **FB 3**.
2. Mix separately, 5.0 cm³ of **FB 1** to 5.0 cm³ of **FB 2** and 5.0 cm³ of **FB 1** to 5 cm³ of **FB 3**, into 2 **test-tubes**
3. Measure for the rise in temperature using a **0.2 °C division thermometer**

Deduction:

- If both reaction mixture gives a temperature rise, **FB 1** is **HC*l***.
- If one of the 2 reaction mixture does not give a temperature rise, then this pair of solutions must be NH_3(aq) and KOH(aq). **HC*l*** can be identified.

Upon identifying **HC*l***,

4. Using a 10.0 cm³ measuring cylinder, add 10.0 cm³ of **HC*l*** to a **Styrofoam cup** and measure the initial temperature, T_1, using a a **0.2 °C division thermometer**.

5. Using another 10.0 cm^3 measuring cylinder, transfer 10 cm^3 of **one of the bases** into another Styrofoam cup.
6. Wash and dry the thermometer
7. Measure the initial temperature, T_2, of the **base** solution.
8. Add **HC*l*** to **base** and stir with the thermometer and note the highest temperature reached, T_f and determine ΔT.
9. Wash and dry the Styrofoam cup.
10. Repeat steps 4 – 9 but replace base with the other base solution.

Assuming if **FB 1** is **HC*l***

	FB 2	**FB 3**
T_i / °C		
T_f / °C		
ΔT / °C		

Deduction of results:

Since **HC*l*** is 2 mol dm^{-3}, the limiting reagent is the base and the same amount of base is used / same amount of H_2O is produced in each reaction.

When total volume of reaction mixture is kept constant and the no of moles of water formed in the reaction is the same, ΔT depends only on the strength of the base used.

As weak acid dissociates partially, a portion of the energy released from neutralisation is used to complete the dissociation of the weak acid. Therefore less energy is released compared to a neutralisation between a strong acid and a strong base.

The reaction mixture that gives a lower ΔT must contain 1 mol dm^{-3} aqueous ammonia.

Alternative solution

Procedure:

1. To 1 **test-tube**, add 5.0 cm^3 of **FB 1** using a **10.0 cm^3 measuring cylinder** and measure the initial temperature, T_1, using a **0.2 °C division thermometer**.
2. Using another 10.0 cm^3 measuring cylinder, measure 5.0 cm^3 of **FB 2**.
3. Wash and dry the thermometer.
4. Measure the initial temperature, T_2, of **FB 2**.
5. Transfer **FB 2** into the test-tube. Stir with the thermometer and note the highest temperature reached, T_f and determine ΔT.
6. Wash and dry the test-tube.
7. Repeat steps 1 – 6 but by mixing 5.0 cm^3 of **FB 1** to 5 cm^3 of **FB 3** and 5.0 cm^3 of **FB 2** to 5 cm^3 of **FB 3** respectively.

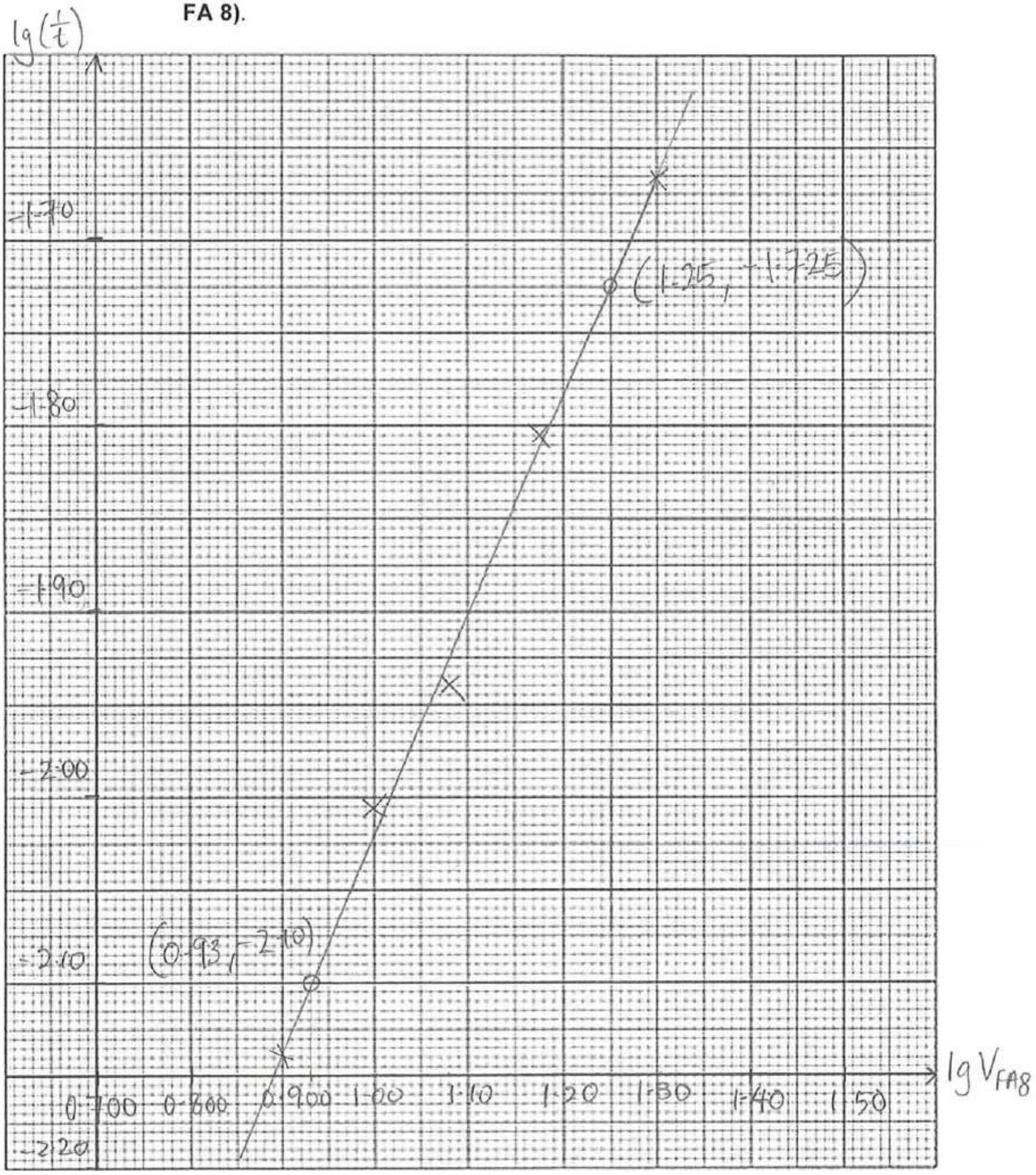
	FB 1	**FB 2**	**FB 3**
FB 1		**T_1 =** **T_2 =** **T_f =** **ΔT =**	**T_1 =** **T_2 =** **T_f =** **ΔT =**
FB 2			**T_1 =** **T_2 =** **T_f =** **ΔT =**

Results analysis: similar to first solution of using ΔT to identify the 3 solutions.

3 **(a)**

Expt	**Vol of FA 8 / cm^3**	**Vol of DI / cm^3**	**time / sec**	**lg $V_{FA\,8}$**	**lg 1/t**
1	20.00	0.0	46	1.30	-1.66
2	10.00	10.0	116	1.00	-2.06
3	15.00	5.0	64	1.18	-1.81
4	12.00	8.0	87	1.08	-1.94
5	8.00	12.0	251	0.903	-2.40

3 (b) (i) Use the grid below to plot a graph of **lg (1/time)** against **lg (volume of FA 8)**.



(ii) Order of reaction wrt Fe^{3+} = gradient of graph
= (-1.725 – -2.10) / (1.25 – 0.93) = 1.17 ≈ 1

4

Test	**Procedure**	**Observations**
(a)	To 6 cm^3 of **X**, add barium nitrate solution until in excess.	**White ppt.** formed, insoluble in excess.
(b)	Filter the mixture from **(a).** Wash and retain the residue for test **(c)**. Collect the filtrate for test **(d)** and **(e)**.	
(c)	To separate portions of the residue **(i)** add 2 cm^3 of hydrochloric acid	A **colourless and odourless gas** evolved, which forms a **white ppt with $Ca(OH)_2$**
	(ii) add 2 cm^3 of organic compound **Z** [You are to test for any gas evolved]	A **colourless and odourless gas** evolved, which forms a **white ppt with $Ca(OH)_2$**
(d)	To 1 cm depth of the filtrate from **(b)** in a test-tube **(i)** add a few drops of organic compound **Z** and warm in a water bath for 5 minutes **(ii)** followed by 1 cm^3 of nitric acid and 5 drops of silver nitrate. Add excess ammonia solution.	Solution remains colourless. **white ppt.** formed, **soluble in excess NH_3**
(e)	To separate 1 cm depth of **Y** **(i)** add filtrate from **(b)** dropwise until in excess	Pale **blue ppt**. formed, **insoluble in excess**
	(ii) add NaOH(aq), followed by one spatula of zinc powder and warm. (CARE!)	Pale **blue ppt.** formed upon adding NaOH(aq). Vigourous effervescence, **colourless and pungent gas evolved**, which **turns damp red litmus paper blue**

(f) **(i)** carbonate / CO_3^{2-} in residue

hydroxide / OH^- in filtrate

(ii) **Carboxylic acid** is present.

From test (c)(ii), **CO_2 is produced from the reaction of Z with carbonate** in the residue from **(b)**, which suggests an acidic group is present.

Halogenoalkane / **chlorine-containing** organic compound / **alkyl halides** / is present.

From test (d)(i), a white ppt. is produced upon heating with OH^- and adding nitric acid and $AgNO_3$, which dissolves in excess NH_3, which suggests that the **white ppt. is AgC*l***. Hence C*l* is present in **Z**.

(g) cation: Cu^{2+}

anion: NO_3^- / NO_2^-

(h) Possible solution:

Step	**Procedure**	**Observations and conclusions**
1	Add Cu^{2+} complex in NaOH(aq) to each sample in a test-tube, warm	For **propanal**, **brick-red ppt** is formed due to the presence of aliphatic aldehyde. For other compounds, **blue solution remains**.
2	Add 2,4-dinitrophenylhydrazine to a new sample of the remaining 3 unknowns, warm	For **benzaldehyde**, **orange ppt.** is formed due to the presence of carbonyl group. For remaining compounds, **no orange ppt. form**.
3	Add $KMnO_4$, dil H_2SO_4 to a new sample of the remaining 2 unknowns, heat	For **butanol**, **purple $KMnO_4$ decolourises** due to oxidation of primary alcohol. For the last compound, purple $KMnO_4$ remains.
4	Add PCl_5(s) to a new sample of the last unknown	For **2-methylpropan-2-ol**, **white fumes of HC*l*** observed due to presence of OH / alcohol group.

PIONEER JUNIOR COLLEGE

JC2 PRELIMINARY EXAMINATION
HIGHER 2

CANDIDATE NAME

CT GROUP 1 6 S

INDEX NUMBER

CHEMISTRY

9729/01

Paper 1 Multiple Choice

22 September 2017

1 hour

Additional Materials: Multiple Choice Answer Sheet
Data Booklet

READ THESE INSTRUCTIONS FIRST

Write in soft pencil.
Do not use staples, paper clips, highlighters, glue or correction fluid.
Write your name, Centre number and index number on the Answer Sheet in the spaces provided unless this has been done for you.

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

Read the instructions on the Answer Sheet very carefully.

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

Section A

For each question, there are four possible answers labelled **A**, **B**, **C** and **D**. Choose the **one** you consider to be correct.

1 Equal volumes of 1 mol dm^{-3} hydrogen sulfide and sulfur dioxide (each containing a different isotope of sulfur) are mixed to precipitate sulfur according to the equations shown below:

$$H_2{}^{32}S(aq) \rightarrow {}^{32}S(s) + 2H^+(aq) + 2e^-$$
$${}^{34}SO_2(aq) + 4H^+(aq) + 4e^- \rightarrow {}^{34}S(s) + 2H_2O(l)$$

What is the relative atomic mass of the sulfur precipitated?

A 32.1

B 32.7

C 33.0

D 33.3

2 50 cm^3 of a 0.0400 mol dm^{-3} solution of acidified Fe^{2+} was oxidised to Fe^{3+} by 100 cm^3 of 0.0100 mol dm^{-3} of an oxidising agent, XO_3^-.

What is the final product of **X**?

A $\mathbf{X}O_2$

B $\mathbf{X}O^-$

C $\mathbf{X}O_2^-$

D $\mathbf{X}^-$

3 Paramagnetism refers to the magnetic state of an atom with one or more unpaired electrons. The greater the number of unpaired electrons in an atom, the greater the paramagnetism.

Which atom has the greatest paramagnetism?

A Oxygen

B Chlorine

C Scandium

D Vanadium

4 Which of the following statements about the nitrate(V) ion, NO_3^-, are correct?

1 The hybridisation of the nitrogen atom is sp^2.

2 All the nitrogen–oxygen bond lengths in NO_3^- are equal in length.

3 NO_3^- has a total of twenty-four valence electrons.

A 1, 2 and 3

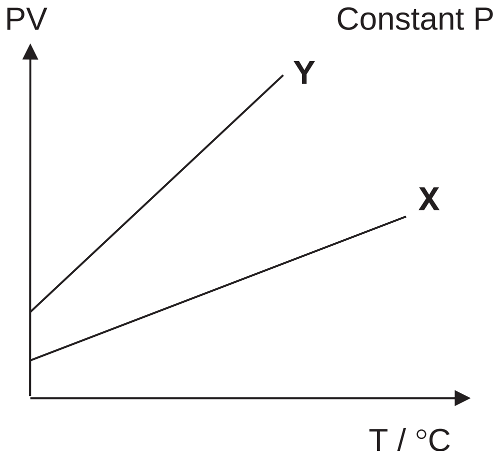
B 1 and 2 only

C 1 and 3 only

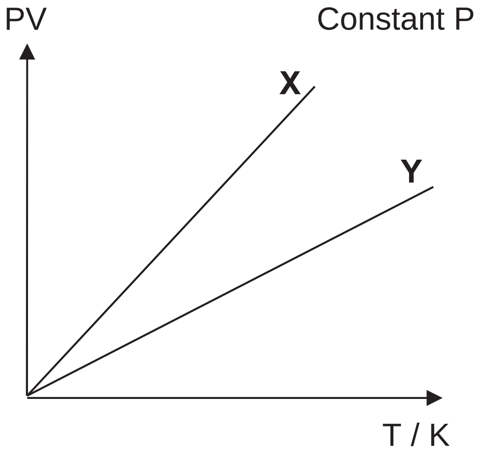
D 2 and 3 only

5 Which graph correctly describes the behaviour of fixed masses of the ideal gases **X** and **Y**, where **X** has a higher M_r than **Y**?

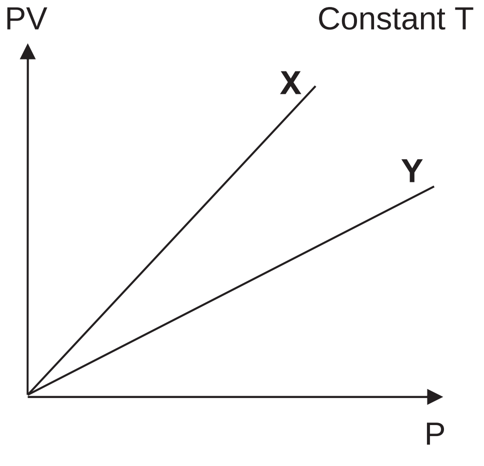
A



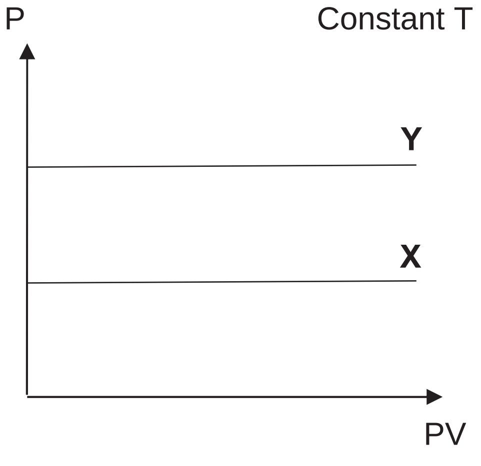
B



C



D



6 A student dissolved 10.5 g of sodium fluoride, NaF, in 250 g of water. The following data is obtained:

Lattice energy of NaF	−918 kJ mol^{-1}
Enthalpy change of hydration of F$^-$	−457 kJ mol^{-1}
Enthalpy change of hydration of Na$^+$	−390 kJ mol^{-1}

Given that the specific heat capacity of water is 4.2 J g^{-1} K^{-1}, what would be the final temperature of the solution, if the initial temperature of water is 30^{o}C?

A 6.5^{o}C **B** 13.1^{o}C **C** 16.9^{o}C **D** 46.9^{o}C

7 The kinetics of the reaction between iodide and peroxodisulfate can be investigated by varying the volume of the reactants used. The two reactants are mixed in the presence of a known amount of $Na_2S_2O_3$ and a little starch.

$$S_2O_8^{2-}(aq) + 2I^-(aq) \rightarrow 2SO_4^{2-}(aq) + I_2(aq)$$

The time taken for an intense blue colour to be observed is then determined.

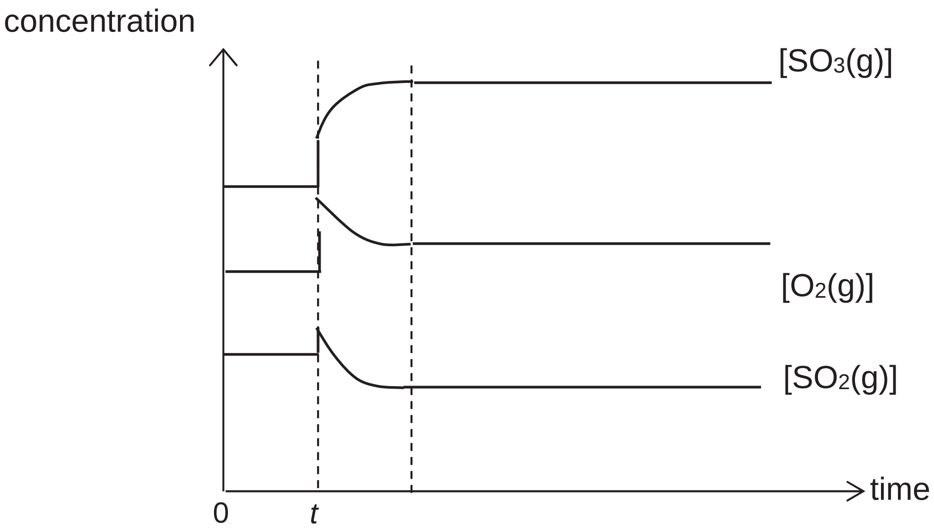
Experiment	Volume used / cm^3			Time / s
	1.0 mol dm^{-3} KI	0.040 mol dm^{-3} $Na_2S_2O_8$	H_2O	
1	10.0	5.0	25.0	170
2	15.0	5.0	20.0	113
3	15.0	10.0	15.0	56.5
4	20.0	***x***	***y***	21.3

What are the values of ***x*** and ***y*** in Experiment 4?

	x	***y***
A	5.0	15.0
B	10.0	10.0
C	15.0	5.0
D	20.0	0.0

8 An equilibrium mixture containing gaseous SO_2, O_2 and SO_3 is subjected to a change at time *t*. The mixture is allowed to reach equilibrium again. The variation of the concentrations of SO_2, O_2 and SO_3 with time is given below.

$$SO_3(g) \rightleftharpoons SO_2(g) + \tfrac{1}{2}O_2(g) \qquad \Delta H > 0$$



Which of the following changes made at time *t* would result in the above variation of the concentrations of the gases?

A Increasing the temperature.

B Decreasing the temperature.

C Adding a catalyst.

D Reducing the volume of the vessel.

9 Poly(tetrafluoroethene) is a polymer used as a coating in non-stick kitchen utensils and for replacement bone joints. One of the stages in the manufacture of the polymer is

$$2CHClF_2(g) \rightleftharpoons C_2F_4(g) + 2HCl(g) \qquad \Delta H = +128 \text{ kJ mol}^{-1}$$

Which of the following changes will increase the amount of tetrafluoroethene, C_2F_4, present at equilibrium?

1 decrease pressure

2 increase temperature

3 use a catalyst

A 1 only

B 1 and 2 only

C 2 and 3 only

D 1, 2 and 3

10 Three unknown solutions **P**, **Q** and **R** contain a strong monobasic acid, a weak monobasic acid and a strong monoacidic base, but not necessarily in this same order. The concentration and pH of each solution are shown below.

P	**Q**	**R**
1.000 mol dm^{-3} pH = 2.4	0.010 mol dm^{-3} pH = 12.0	0.001 mol dm^{-3} pH = 3.0

Which of the following statements **are** correct?

1 **Q** contains a strong base.

2 **P** contains a weak acid.

3 Mixing 100 cm^3 of **P** and 100 cm^3 of **R** produces a buffer solution.

A 1 only is correct.

B 1 and 2 only are correct.

C 2 and 3 only are correct.

D 1, 2 and 3 are correct.

11 The numerical values of the solubility product of AgBr, $AgIO_3$ and Ag_2CO_3 are given in the table below.

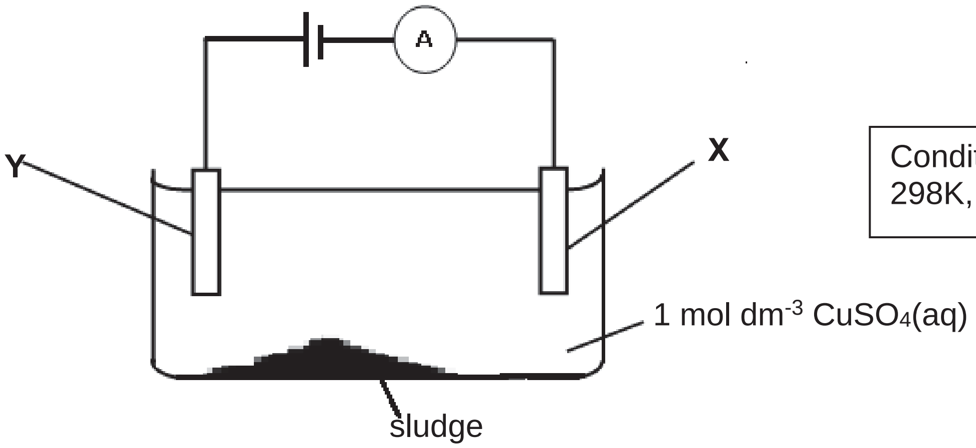
compound	solubility product
AgBr	5 x 10^{-13}
$AgIO_3$	2 x 10^{-8}
Ag_2CO_3	5 x 10^{-12}

An aqueous solution of $AgNO_3$ was added slowly, until in excess, to a solution containing 1.5 mol dm^{-3} of NaBr, 1.5 mol dm^{-3} of KIO_3 and 1.5 mol dm^{-3} of Na_2CO_3.

What is the correct order of precipitation of the three silver salts?

	first to precipitate	⟶	last to precipitate
A	AgBr	$AgIO_3$	Ag_2CO_3
B	AgBr	Ag_2CO_3	$AgIO_3$
C	Ag_2CO_3	AgBr	$AgIO_3$
D	$AgIO_3$	Ag_2CO_3	AgBr

12 *Use of the Data Booklet is relevant to this question.* The circuit shown in the diagram was set up to purify impure Cu, which contains Ag and Fe impurities.
(In the diagram below, A represents ammeter)



Conditions:
298K, 1 bar

What of the following represents the substance used as electrode **X**, the products formed at the anode and cathode, and the substance present in the sludge after some time?

	Electrode X	**Products at anode**	**Products at cathode**	**sludge**
A	Impure Cu	Cu^{2+}	Cu	Ag
B	Impure Cu	Fe^{2+}	Cu^{2+}	Ag
C	Pure Cu	Ag^{+}, Fe^{2+}	Cu^{2+}	Zn
D	Pure Cu	Cu^{2+}, Fe^{2+}	Cu	Ag

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

An electrochemical cell is set up using a $Fe^{2+}(aq)|Fe(s)$ half–cell and a $VO_2^{+}(aq),VO^{2+}(aq)|Pt(s)$ half–cell.

Which of the following gives a correct effect on the E_{cell} and a correct explanation for the effect when each of the changes is made to the cell separately?

	Change	Effect on E_{cell}	Explanation
1	Add KCN(aq) to the $Fe^{2+}(aq)|Fe(s)$ half–cell	Increases	Concentration of $Fe^{2+}(aq)$ decreases
2	Add water to the $VO_2^{+}(aq),VO^{2+}(aq)|Pt(s)$ half–cell	Decreases	Concentration of water increases
3	Add NaOH(aq) to $Fe^{2+}(aq)|Fe(s)$ half–cell	No change	pH has no effect on E_{cell}

A 1 only

B 1 and 3 only

C 2 and 3 only

D 1, 2 and 3

14 These information relates to element **S**.

- **S** is in Period 3 of the Periodic Table.
- **S** forms an acidic oxide on exposure to air.
- **S** atom has a half-filled subshell in its ground state.

What is the identity of **S**?

A Na

B Si

C P

D S

15 Coloured glass, as used in church windows, requires three oxides; one of a transition metal, and two other oxides: one macromolecular and one ionic.

Which combination is likely to produce a coloured glass?

A	Al_2O_3	MgO	SnO
B	P_4O_{10}	CaO	CuO
C	SiO_2	CaO	CuO
D	SiO_2	PbO	ZnO

16 The carbonates of Group 2 decompose according to the following equation.

$MCO_3(s) \longrightarrow MO(s) + CO_2(g)$

For this reaction, ΔH value increases down the group.

Carbonate	Mg	Ca	Sr	Ba
ΔH / kJ mol^{-1}	+ 101	+ 178	+ 235	+ 269

Which property best explains this trend?

A The first and second ionisation energy of the metal

B The lattice energy of the metal carbonate

C The ionic radius of the metal ion

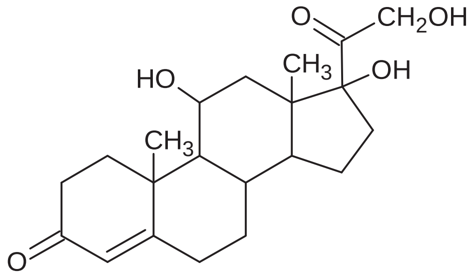
D The proton number of the metal

17 A yellow-green solution is formed when concentrated hydrochloric acid is added to blue aqueous copper(II) chloride solution. Addition of potassium iodide to the mixture results in the formation of a brown solution and a white precipitate.

Which process does **not** occur in this sequence?

A dative bond formation
B complex ion formation
C precipitation of copper(II) iodide
D reduction of Cu^{2+} ions

18 Hydrocortisone is the active ingredient in some anti-inflammatory skin cream.



hydrocortisone

How many sp^3 hybridised carbon atoms and chiral centres are present in a hydrocortisone molecule?

	sp^3 carbon atoms	**chiral centres**
A	16	6
B	16	7
C	17	6
D	17	7

19 Ethane reacts with chlorine gas in the presence of ultraviolet light to form a mixture of products via free radical substitution.

Which statements about this reaction are correct?

1 Homolytic fission occurs only in the initiation step.

2 Chloroethane is formed in the propagation and termination steps.

3 Bond formation occurs only in the termination step.

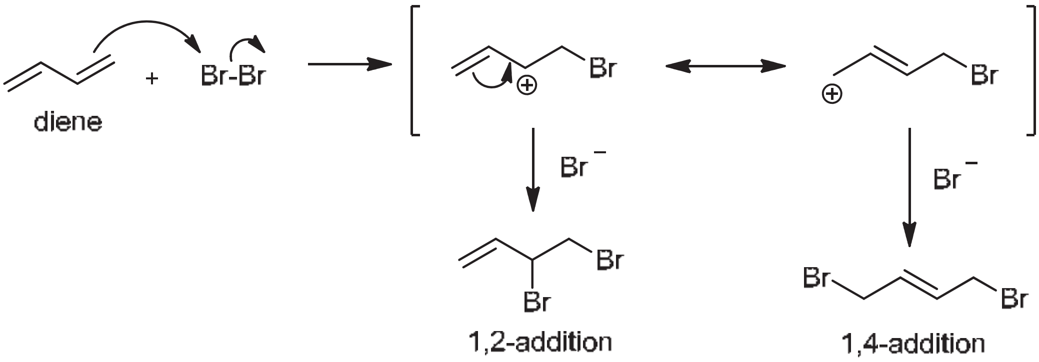
A 2 only

B 2 and 3 only

C 1 and 3 only

D 1, 2 and 3

20 When a conjugated diene undergoes electrophilic addition with Br_2, it forms two products through the 1,2–addition and the 1,4–addition, which is shown in the mechanism below.

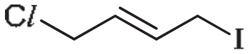


Which of the following statements is **not** correct?

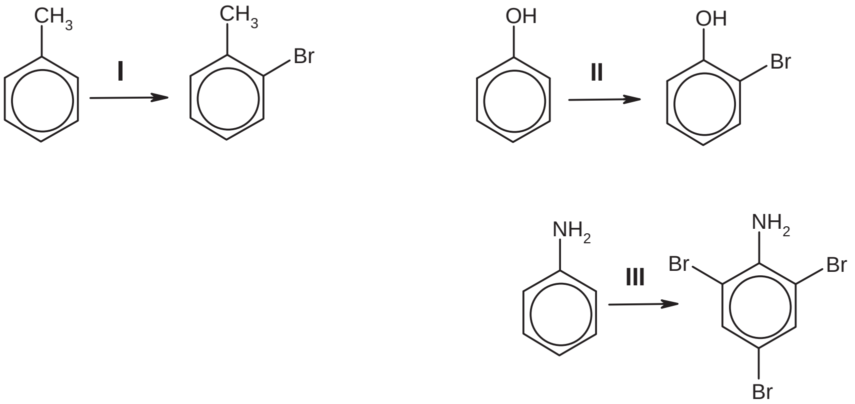
A The overall rate law is second order.

B The carbocation intermediates are resonance stabilised.

C The 1,2–addition product formed when HCl is used is .

D The 1,4–addition product formed when ICl is used is .

21 Methylbenzene, phenol and phenylamine all undergo electrophilic substitution with suitable reagents.



Which of the following could the reagents be for steps **I** to **III**?

	I	**II**	**III**
A	Br_2, Fe	Br_2 in CCl_4	$Br_2(aq)$
B	Br_2, $FeBr_3$	$Br_2(aq)$	Br_2 in CCl_4
C	$Br_2(aq)$	Br_2 in CCl_4	Br_2, Fe
D	Br_2 in CCl_4	Br_2, $FeBr_3$	$Br_2(aq)$

22 2–methylpropanoic acid can be synthesised from 1–chloropropane through a series of reactions. Which set of reagents, used in sequential order, would be the most suitable for this synthesis?

A step I: aqueous HCN with trace KCN
step II: dilute NaOH

B step I: ethanolic KCN
step II: dilute HC*l*

C step I: aqueous KOH
step II: gaseous HC*l*
step III: ethanolic KCN
step IV: dilute HC*l*

D step I: ethanolic KOH
step II: gaseous HBr
step III: ethanolic KCN
step IV: dilute H_2SO_4

23 Which of the following statements on the nucleophilic substitution of 3-bromo-3-methylhexane with aqueous sodium hydroxide is **not** true?

A The product has a chiral centre.

B The intermediate is a carbocation.

C The reaction produces an optically inactive mixture.

D The OH^- nucleophile attacks 3-bromo-3-methylhexane just as the Br^- leaves.

24 Lactic acid (2-hydroxypropanoic acid), **E**, occurs in soured milk. It can be synthesised from ethanol by the following series of reactions.

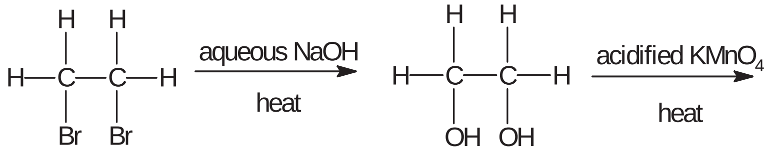
$$C_2H_5OH \xrightarrow{\textbf{I}} \textbf{C} \xrightarrow[\text{HCN + trace NaCN}]{\textbf{II}} \textbf{D} \xrightarrow{\textbf{III}} \underset{\textbf{E}}{CH_3CH(OH)CO_2H}$$

Which of the following correctly represent the reagents and conditions for step **I**, and the structures of compounds **C** and **D**?

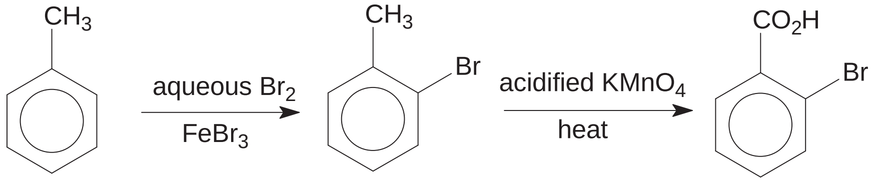
	step **I**	**C**	**D**
A	$KMnO_4$(aq), H_2SO_4(aq), heat	CH_3COOH	CH_3COCN
B	$KMnO_4$(aq), H_2SO_4(aq), distil	CH_3CHO	$CH_3CH(CN)OH$
C	$K_2Cr_2O_7$(aq), H_2SO_4(aq), heat	CH_3COOH	CH_3COCN
D	$K_2Cr_2O_7$(aq), H_2SO_4(aq), distil	CH_3CHO	$CH_3CH(CN)OH$

25 Which is the most feasible synthesis route?

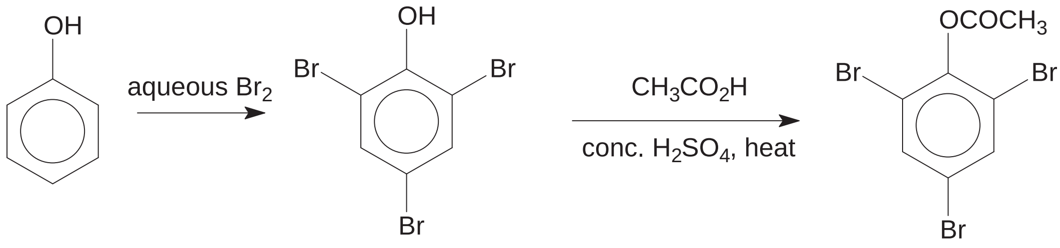
A



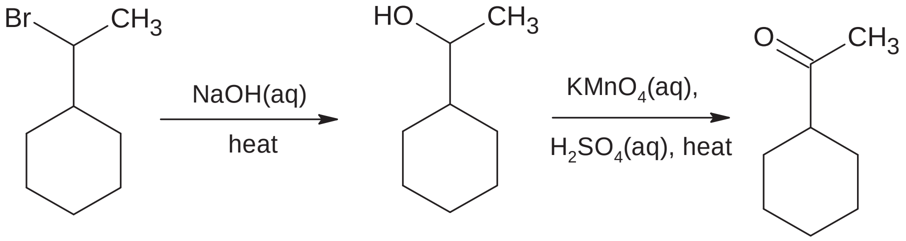
B



C

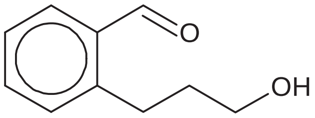


D

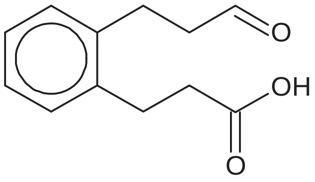


26 Compound **X** gives a positive result when treated with $[Ag(NH_3)_2]^+$ and PCl_5 but a negative result when treated with alkaline Cu(II) complex.
What could **X** be?

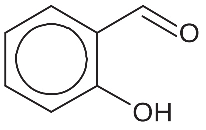
A



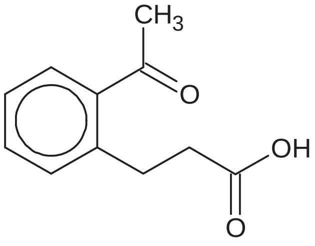
B



C



D

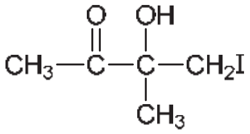


27 Compound **Y** has the following properties.

- It changes the colour of acidified sodium dichromate(VI) from orange to green.
- It gives yellow precipitate with warm, alkaline aqueous iodine.

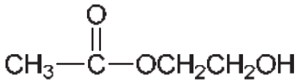
Which compound could be **Y**?

A



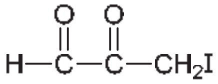
$CH_3-\overset{\overset{O}{\|}}{C}-\underset{\underset{CH_3}{|}}{\overset{\overset{OH}{|}}{C}}-CH_2I$

B



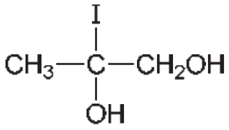
$CH_3-\overset{\overset{O}{\|}}{C}-OCH_2CH_2OH$

C



$H-\overset{\overset{O}{\|}}{C}-\overset{\overset{O}{\|}}{C}-CH_2I$

D



$CH_3-\underset{\underset{OH}{|}}{\overset{\overset{I}{|}}{C}}-CH_2OH$

28 An ester **Z** was heated with aqueous NaOH and the resulting mixture was then distilled. The distillate obtained decolourised hot, acidified potassium manganate(VII), giving effervescence that forms white precipitate with aqueous $Ca(OH)_2$. The residue in the distillation flask, after acidification, gave a white precipitate insoluble in water.

Which of these could be **Z**?

A $C_6H_5CO_2CH_3$

B $CH_3CO_2C_6H_5$

C $CH_3CO_2CH_2C_6H_5$

D $CH_3CH_2CO_2CH_2C_6H_5$

29 Which reaction produces a carbon compound incorporating deuterium, D? (D= ^2_1H, an isotope of hydrogen)

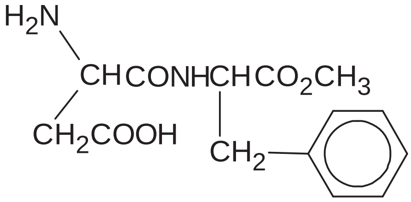
A $CH_3CH_2CN \xrightarrow[D_2O]{NaOD}$

B $CH_3CD_2OH \xrightarrow[\text{heat}]{\text{acidified } KMnO_4}$

C $CH_3COCI_3 \xrightarrow[D_2O]{NaOD}$

D $(CH_3)_3COH \xrightarrow[\text{heat}]{\text{conc. } D_2SO_4}$

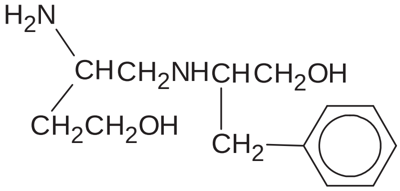
30 *Aspartame* is widely used as a sweetener in canned drinks.



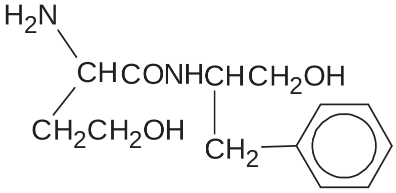
Aspartame

When *Aspartame* is treated with $LiAlH_4$ in dry ether, what is the final product obtained?

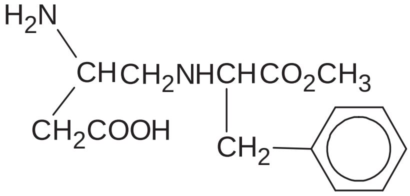
A



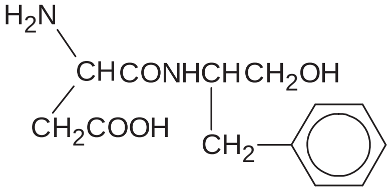
B



C



D



End of Paper

PIONEER JUNIOR COLLEGE

JC2 PRELIMINARY EXAMINATION
HIGHER 2

CANDIDATE NAME	
CT GROUP	1 6
INDEX NUMBER	

CHEMISTRY **9729/02**

Paper 2 Structured **12 September 2017**

2 hours

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

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

Answer **all** questions.

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

FOR EXAMINER'S USE			
Paper 1			**/ 30**
Paper 2			
1	/ 14	4	/ 12
2	/ 8	5	/ 13
3	/ 11	6	/ 17
Penalty		sf	unit
Paper 2			**/ 75**
Paper 3			**/ 80**
Paper 4			**/ 55**
Total			

This document consists of 19 printed pages.

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

1 **(a)** Carbon dioxide, produced mainly from the burning of fossil fuels, is a greenhouse gas which trapped heat within the Earth's atmosphere, causing global warming and potentially catastrophic global climate change. One major source of carbon dioxide produced worldwide is from the rapidly expanding aviation industry.

(i) Commercial passenger jet-liners combust kerosene as fuel. The formula of kerosene may be taken as $C_{14}H_{30}$. Write a balanced equation, with state symbols, for the complete combustion of kerosene.

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

In 2017, Singapore Airlines announced that it will be launching the world's longest commercial non-stop passenger flight from Singapore to New York, with a flight distance of 15,000 km. The ultra-long range Airbus A350 aircraft used on this route burns 7.5 kg of kerosene per km.

(ii) Calculate the mass of carbon dioxide produced, in tonnes, during this flight. [1 tonne = 1000kg]

[3]

(iii) Apart from carbon dioxide, nitrogen dioxide is another air pollutant found in the flue gases from the jet engine of aircrafts. Explain how nitrogen dioxide is produced in the jet engine.

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

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

(iv) Why is it important to remove nitrogen dioxide from the flue gases?

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

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

(b) Scientists have been studying the idea of carbon capture and storage technologies to try to remove atmospheric carbon dioxide on an industrial scale. One promising technology is called *calcium looping*. This process involved using calcium oxide to react with the atmospheric carbon dioxide to form calcium carbonate (i.e. limestone) which can then be stored away in abandoned mines.

$$CaO(s) + CO_2(g) \rightarrow CaCO_3(s) \qquad \Delta H_1$$

(i) Using the space below, construct a fully labelled energy cycle diagram to calculate ΔH_1 using the following data.

standard enthalpy change of formation of CaO(s)	-635 kJ mol^{-1}
standard enthalpy change of formation of $CaCO_3(s)$	-1207 kJ mol^{-1}
standard enthalpy change of combustion of C(s)	-394 kJ mol^{-1}

[3]

(ii) Like calcium carbonate, aluminum oxide is a major components of naturally occurring rocks. Explain clearly, in terms of bonding and structure, why aluminum oxide is insoluble in water.

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

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

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

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

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

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

(c) Carbonate buffers are widely used for biochemical purposes.

A student wishes to form a CO_3^{2-}/ HCO_3^- buffer in the laboratory.

Given that the carbonate ion has a K_b of 1.8 x 10^{-4} mol dm^{-3}, calculate the volume of 0.10 mol dm^{-3} of hydrochloric acid that he has to add to 25.0 cm^3 of 0.12 mol dm^{-3} of Na_2CO_3, to form a resulting buffer solution of pH 9.50.

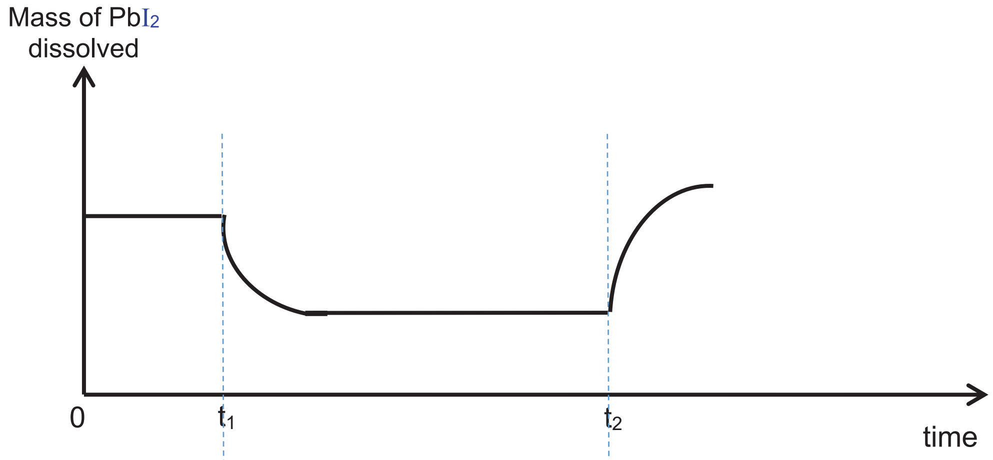
[2]

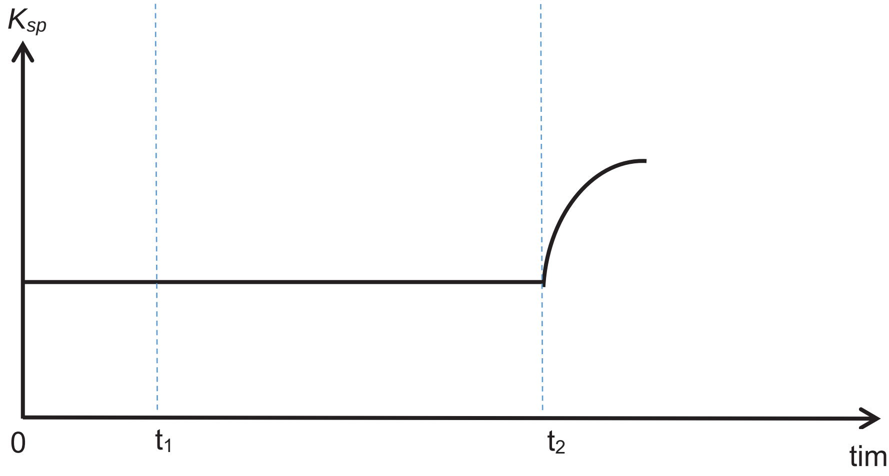
[Total:14]

2 **(a)** This question is about lead(II) halides. PbI_2 is a sparingly soluble salt:

$$PbI_2(s) + aq \rightleftharpoons Pb^{2+}(aq) + 2\,I^-(aq) \qquad \Delta H>0$$

A student aimed to investigate the solubility product and solubility of PbI_2 under different conditions. He first added some solid PbI_2 into 100 cm^3 of water at 15°C, and subsequently made two changes at t_1 and t_2. The graphs below show the mass of PbI_2 dissolved and solubility product of PbI_2 against time.





Some possible changes listed below were made by the student at t_1 and t_2.

1. Cool reaction mixture to 10°C in water bath
2. Heat reaction mixture to 50°C in water bath
3. Add $AgNO_3$(s)
4. Pump in $Pb(NO_3)_2$(aq)

With reference to **both** graphs, suggest and explain which of the above changes (1)-(4), was made at t_1 and t_2 respectively.

change made at t_1: ……………………………………………………………………………………

explanation:………………………………………………………………………………………………

……[2]

change made at t_2: ……………………………………………………………………………………

explanation:..

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

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

………[2]

(b) The values of the solubility products of two salts, lead(II) iodide, PbI_2, and silver (I) iodide, AgI are given below.

$$K_{sp}\,(PbI_2) = 3.97 \times 10^{-9}\ mol^3\ dm^{-9}$$
$$K_{sp}\,(AgI) = 8.3 \times 10^{-17}\ mol^2\ dm^{-6}$$

A lab technician added solid PbI_2 into water, shaking it thoroughly. He filtered off the remaining solid, leaving a saturated solution **H**.

He added drops of aqueous silver nitrate to **H**, until AgI just precipitates. Determine the concentration of Ag^+ when AgI just precipitates.

[2]

(c) When a precipitate is formed, $\Delta G^{\ominus}_{ppt}$, in J mol^{-1}, is given by the following expression.

$$\Delta G^{\ominus}_{ppt} = 2.303\ RT \log K_{sp}$$

Given that for lead(II) chloride, $PbCl_2$, $K_{sp} = 1.70 \times 10^{-5}$ mol^3 dm^{-9} at 298 K, calculate $\Delta^{\ominus}G_{ppt}$ for $PbCl_2$ at 298K. Thus explain if $PbCl_2$ is soluble at 298K.

[2]
[Total:8]

3 **(a)** Chlorine has been extensively used in the manufacture of many compounds.

One such compound is household bleach, which contains sodium chlorate(I), NaC*l*O.

The chlorate(I) ion acts as a powerful oxidising agent in acidic solution:

$$2ClO^-(aq) + 4H^+(aq) + 2e^- \rightleftharpoons Cl_2(g) + 2H_2O(l) \qquad E^\ominus = +1.64\ V$$

(i) Define the term *standard electrode potential*.

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

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

(ii) Draw a fully labelled diagram, to show how the standard electrode potential, $E^\ominus(ClO^-/Cl_2)$, could be measured.

[3]

(b) Use the *Data booklet* to predict the reaction, if any, that would occur when the following pairs of reagents are mixed in acidified aqueous solution. If a reaction occurs, write a balanced equation and calculate $E^\ominus_{cell}$.

(i) $NaClO(aq)$ and $H_2O_2(aq)$

[2]

(ii) $NaClO(aq)$ and $Cr(NO_3)_3(aq)$

[2]

(c) When a few drops of aqueous sodium carbonate was added to chromium(III) nitrate, carbon dioxide gas and a grey-green precipitate, **R**, were obtained.

With the aid of equation(s), explain why CO_2 is given off in the above reaction, and identify precipitate **R**.

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

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

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

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

……………………………………………………………………………………………

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

[Total:11]

4 Manganese is a first row d-block element in the Periodic table with a melting point of 1246°C. Like many other d-block elements, manganese shows properties that are atypical from other s-block metals, such as potassium and calcium.

Its minerals are widely distributed, with manganese dioxide and manganese carbonate being the most common. Manganese is also an essential element in living organisms, where many types of enzymes make use of the variable oxidation states of manganese to take part in the various redox reactions.

(a) **(i)** Explain why manganese has a much higher melting point than calcium, which is found in the same period.

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

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

(ii) Explain briefly why the density of manganese is significantly greater than that of calcium.

……………………………………………………………………………………………

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

(b) Heating a mixture of KOH and MnO_2 in air gives potassium manganite, K_2MnO_4, which is an important precursor to potassium permanganate, $KMnO_4$, a common oxidising agent.

(i) State the oxidation state of manganese and hence, write the electronic configuration of the manganese ion in each of the following compounds:

MnO_2 :
Oxidation state: ………………………………

Electronic configuration: ………………………………

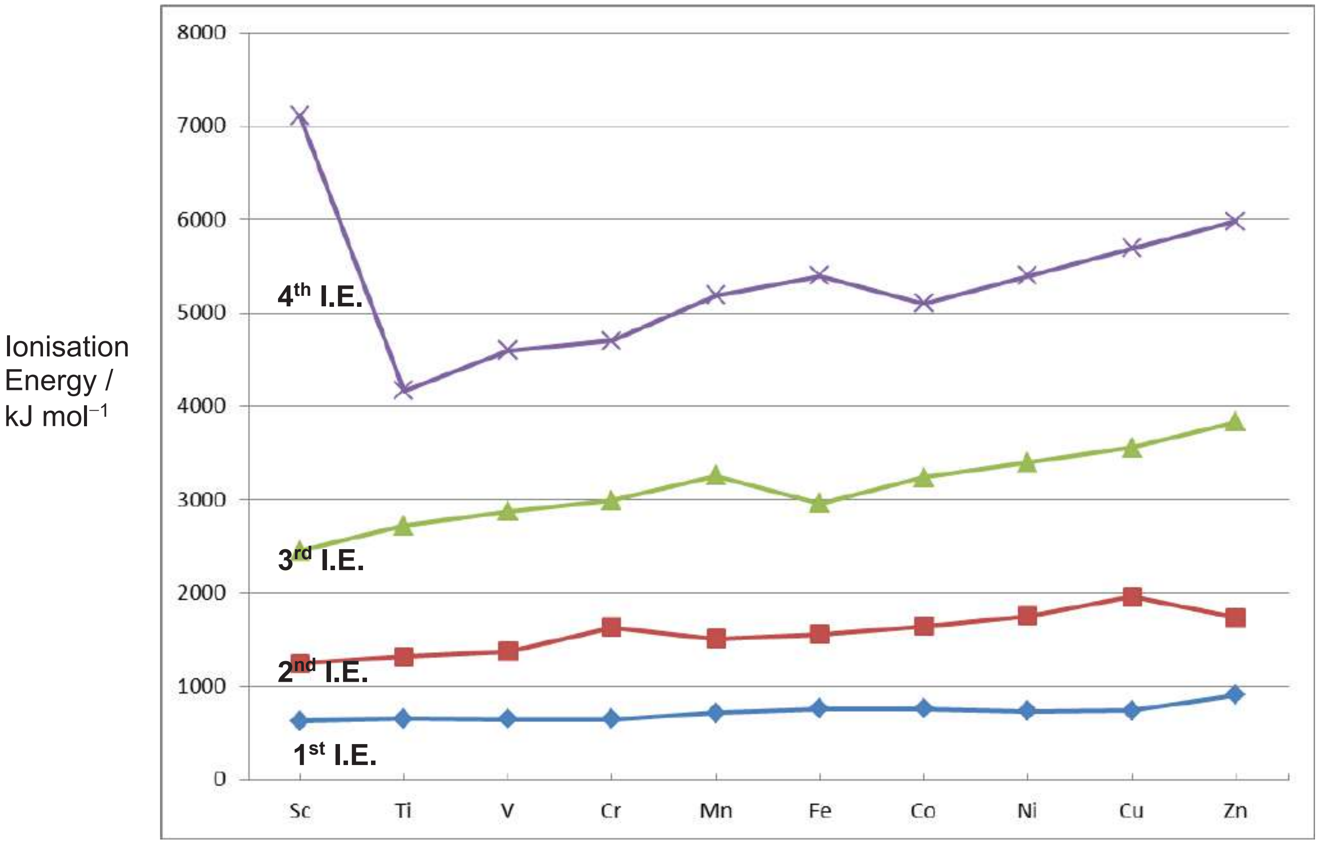
K_2MnO_4:
Oxidation state: ………………………………

Electronic configuration: ……………………………… [2]

(ii) Write a balanced equation for the redox reaction between MnO_2, KOH and air.

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

(c) The graph below shows the variation of the first to fourth ionisation energies for the first row d–block elements scandium to zinc.



(i) Give an equation that represents the second ionisation energy of manganese.

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

(ii) Explain why the first ionisation energies of the elements Ti to Cu, are relatively invariant across the Period.

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

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

(iii) Explain why the fourth ionisation energy of cobalt is lower than that of iron.

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

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

[Total:12]

5 **(a)** Structure elucidation is an important skill that chemists must acquire to help them determine the chemical structures of organic compounds.

A novice chemist requires your assistance in determining the structure of an aromatic organic compound **P**, that she found in the laboratory. The molecular formula of compound **P** is $C_9H_{11}ON$, and **P** contains two functional groups.

(i) An orange precipitate is observed when **P** is reacted with 2,4-dinitrophenylhydrazine. Name the type of reaction that occured. From this observation only, name two different functional groups that could be present in **P**.

Type of reaction: ……………………………………………………….…………………

Functional groups: ………………………… and …………………….………………

[2]

(ii) No silver mirror is formed when **P** is warmed with hot ammoniacal silver nitrate (mixture of aqueous ammonia and aqueous silver nitrate). Which of the functional groups you named in **(a)(i)**, is confirmed by this observation?

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

(iii) When compound **P** is reacted with bromine water in excess, a white solid which has M_r = 385.7, is formed. Deduce the molecular formula of the white solid that is formed.

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

(iv) Compound **P** reacts with hot potassium manganate(VII) in aqueous sodium hydroxide. A product with the molecular fomula, $C_8H_5NO_4Na_2$, is formed.
Draw the structure of the product.

[1]

(v) You now have enough information to determine the structural formula of compound **P**. Draw the structure for **P**, explaining clearly why you have placed each of the two functional groups in their respective positions.

……………………………………………………………………………………………

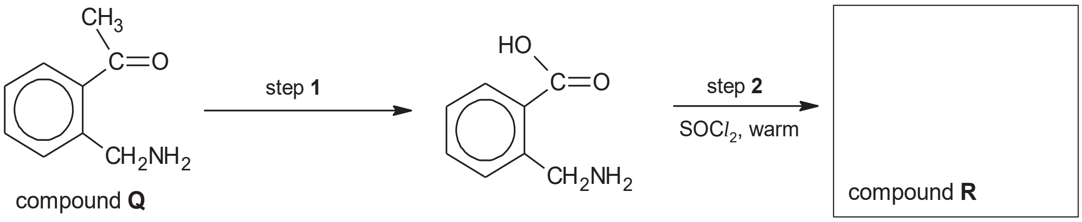
……………………………………………………………………………………………

…………………………………………………………………………………………[2]

(b) Compound **Q**, $C_9H_{11}ON$, is a structural isomer of compound **P**.

The diagram below shows a possible reaction scheme for converting compound **Q** to **R,** C_8H_7NO.

(i) Complete the diagram by suggesting the reagents and conditions for step **1**, and give the structural formula of compound **R**.



[2]

(ii) It was found that the yield of **R** was low. Suggest a reason for this.

……………………………………………………………………………………………

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

(c) The table below shows the pK_b values of two organic nitrogen compounds in aqueous solutions.

Compound	pK_b
methylamine, CH_3NH_2	3.36
trimethylamine, $(CH_3)_3N$	4.19

Using the data provided in the table above, suggest an explanation on the relative basicities of these two compounds.

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

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

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

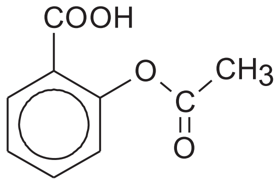
……………………………………………………………………………………………………

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

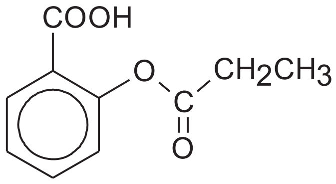
…………………………………………………………………………………………………… [3]

[Total:13]

6 **(a)** Acetylsalicylic acid (ASA), which is extracted from the leaves of the willow tree, has been used for its health effects for at least 2,400 years. It is an important medication that is used to treat pain, fever, and inflammation.

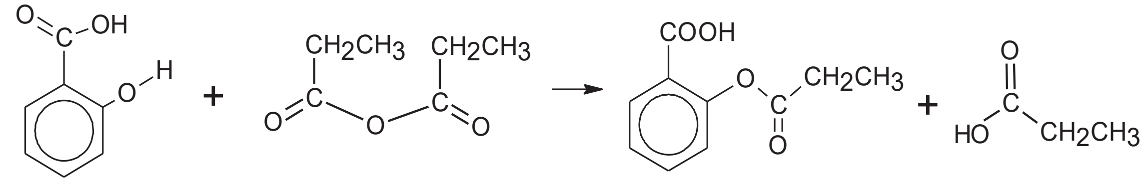

Acetylsalicylic acid

A chemist wanted to form a derivative of ASA, compound **T** below:


Compound **T**

One method to form compound **T** was to react 2-hydroxybenzoic acid and propanoic anhydride in reaction **1** below.

Reaction **1**


2-hydroxybenzoic acid propanoic anhydride compound **T**

(i) State the type of reaction that has occurred in reaction **1**.

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

The mechanism of reaction **1** consists of four steps and is described below:
Step **1**:
The phenol group on 2-hydroxybenzoic acid acts as a nucleophile and attacks one of the reactive carbons in propanoic anhydride to form only one intermediate **W**. The intermediate **W** contains both a cationic oxygen and an anionic oxygen.

Step **2**:
A proton is released from intermediate **W** to form intermediate **X**.

Step **3**:
From intermediate **X**, a carboxylate anion is expelled as a leaving group, and an ester **Y** is formed as the other product.

Step **4**:
Protonation of the carboxylate anion formed in step **3** produces a carboxylic acid.

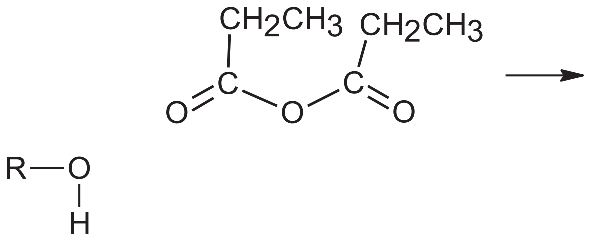
(ii) Draw all four steps in the full mechanism for the reaction between 2-hydroxybenzoic acid and propanoic anhydride.

(you may use ROH to represent 2-hydroxybenzoic acid in your answer.)

For the first step of the mechanism, *complete* the diagram shown below and draw the remaining three steps of the mechanism in the space given below. Show all intermediates, relevant charges, lone pairs of electrons and indicate the movement of electron pairs with curly arrows in **all** the steps.

Step **1**

Let R–O–H represents 2-hydroxybenzoic acid.



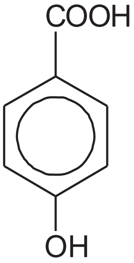
Step **2**

Step **3**

Step **4**

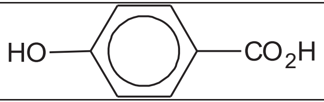
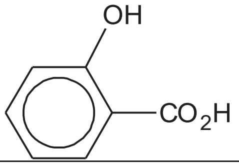
[4]

(iii) An isomer of 2-hydroxybenzoic acid is shown below:



4-hydroxybenzoic acid

Both 2-hydroxybenzoic acid and 4-hydroxybenzoic acid are dibasic acids that ionises in two stages. The acid dissociation constant, pK_1, for the first stage of dissociation is given below.

	pK_1
	4.54
	2.97

With the aid of a diagram, explain why 2-hydroxybenzoic acid has a lower pK_1.

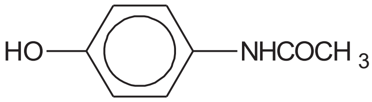
……………………………………………………………………………………………..

……………………………………………………………………………………………..

……………………………………………………………………………………………..

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

(b) Another medicine that is used widely to treat fever and pain is paracetamol, or commonly known as panadol.



Paracetamol

Some information on paracetamol is provided in Table 1 below.

Data on paracetamol	
Molecular Formula	$C_8H_9NO_2$
Density	1.263 g/cm^3
Melting Point	169^{o}C
Boiling Point	420^{o}C
Solubility in water	14 mg/ml
Bioavailability*	75% (oral) 100% (intravenous)
Biological half-life**	2 hours

Table 1

**Bioavailability refers to the percentage of a drug which enters the blood circulation when introduced into the body and hence able to have an active and effective effect.*

***Biological half-life of a drug is the time taken for the drug to reduce to half its original amount in the body.*

(i) Paracetamol can be produced from the reaction between 4-aminophenol and ethanoic anhydride as shown below.

C_6H_7NO +	$C_4H_6O_3$ →	$C_8H_9NO_2$	+ $C_2H_4O_2$
4-aminophenol	ethanoic anhydride	paracetamol	
(M_r : 109)	(M_r : 102)	(M_r : 151)	

It is known that the yield of this reaction is only 60%.

Calculate the minimum masses of the reactants that are required to produce 10 g of paracetamol.

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

(ii) A doctor wishes to prescribe oral medication for one of his patients suffering from headache. In order for the medicine to be effective, the patient requires a recommended dosage of 560 mg of paracetamol in her body.

How many 250 mg paracetamol tablets should the patient take each time?

[2]

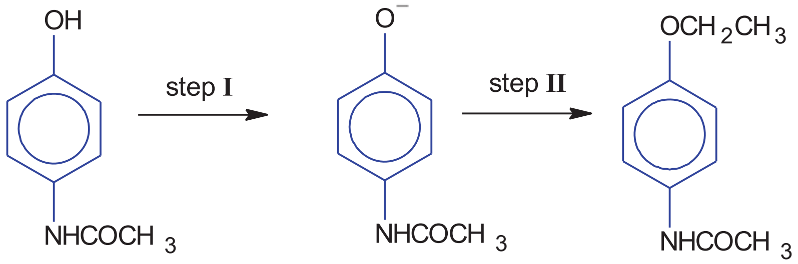
(iii) A patient suffering from acute dental pain is advised to consume orally, four 250 mg paracetamol tablets.

To effectively alleviate his pain, at any point of time, the amount of paracetamol in his body **must not** drop below 93 mg.

With reference to relevant data from Table 1, and the use of suitable calculations, determine the maximum number of hours that the oral medication prescribed above remains effective, and show clearly whether the doctor should advise the patient to take four tablets of paracetamol once in every 4 hours, 6 hours, or 8 hours.

[2]

(c) **(i)** Phenacetin was once used as an analgesic (pain killing drug). It can be synthesised from paracetamol below.



paracetamol phenacetin

Suggest reagents and conditions for step **I** and **II**.

step **I:** ……………………………………………………………………………………

step **II**: ……………………………………………………………………………………

[2]

(ii) A student added aqueous sulfuric acid to paracetamol and heated it. Give the structures of the products obtained.

[2]

[Total:17]

End of paper

PIONEER JUNIOR COLLEGE

JC2 PRELIMINARY EXAMINATION
HIGHER 2

CANDIDATE NAME

CT GROUP 1 6

INDEX NUMBER

CHEMISTRY

9729/03

Paper 3 Free Response

15 September 2017

2 hours

Candidates answer on separate paper.

Additional Materials: Answer Paper
Data Booklet
Cover Page

READ THESE INSTRUCTIONS FIRST

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

Section A
Answer **all** questions.

Section B
Answer **one** question.

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

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

This document consists of **17** printed pages.

Section A

Answer **all** questions in this section.

1 Compounds containing halogens form a large class of chemicals, which are of industrial importance and are synthesised in huge quantities worldwide.

(a) Phosgene, $COCl_2$, is a gas which was produced during World War I, and was used as a chemical weapon. One method to produce phosgene from trichloromethane is as shown below.

$$2CHCl_3(g) + O_2(g) \rightarrow 2COCl_2(g) + 2HCl(g) \qquad \Delta H = -346 \text{ kJ mol}^{-1}$$

Using the data below, calculate the standard enthalpy change of formation of $HCl(g)$.

standard enthalpy change of formation of $CHCl_3(g)$	-103 kJ mol^{-1}
standard enthalpy change of formation of $COCl_2(g)$	-184 kJ mol^{-1}

[1]

(b) Aqueous hydrochloric acid is another chemical with many industrial uses. It can be obtained by reacting hydrogen gas and chlorine gas in the presence of UV light, followed by dissolving the hydrogen chloride gas in water.

The equation for this reaction is shown below.

$$\tfrac{1}{2}H_2(g) + \tfrac{1}{2}Cl_2(g) \rightarrow H^+(aq) + Cl^-(aq) \qquad \Delta H_r$$

Using the Data Booklet, the data in the table below, and your answer in **(a)**, construct an appropriate energy-level diagram to calculate ΔH_r.

	$\Delta H^\ominus$/ kJ mol^{-1}
First ionisation energy of H(g)	+1310
First electron affinity of Cl(g)	– 364
Standard enthalpy change of hydration of $Cl^-(g)$	– 381
Standard enthalpy change of hydration of $H^+(g)$	– 1130

[4]

(c) When heated, Group 17 hydrides, HX, undergo thermal decomposition.

$$HX \longrightarrow \tfrac{1}{2} H_2 + \tfrac{1}{2} X_2$$

Using the data on bond energies of the various H-X bonds given below, predict and explain how the thermal stability of the hydrides varies down Group 17.

Bonds	**Bond energies/ kJ mol^{-1}**
H-Cl	+431
H-Br	+366
H-I	+299

[2]

(d) Seawater is an important source of ionic halides like sodium chloride, sodium bromide and sodium iodide.

When silver nitrate is added to separate test-tubes containing aqueous sodium chloride, sodium bromide and sodium iodide, the various AgX (X = Cl, Br and I) precipitates were observed. The solubilities of these precipitates upon addition of dilute NH_3 and concentrated aqueous NH_3, are recorded below.

	NaCl	**NaBr**	**NaI**
To NaX(aq), add $AgNO_3$(aq)	white ppt observed	cream ppt observed	yellow ppt observed
To the resulting mixture, add dilute NH_3(aq)	soluble	insoluble	Insoluble
To the resulting mixture, add excess concentrated aqueous NH_3(aq)	soluble	soluble	Insoluble

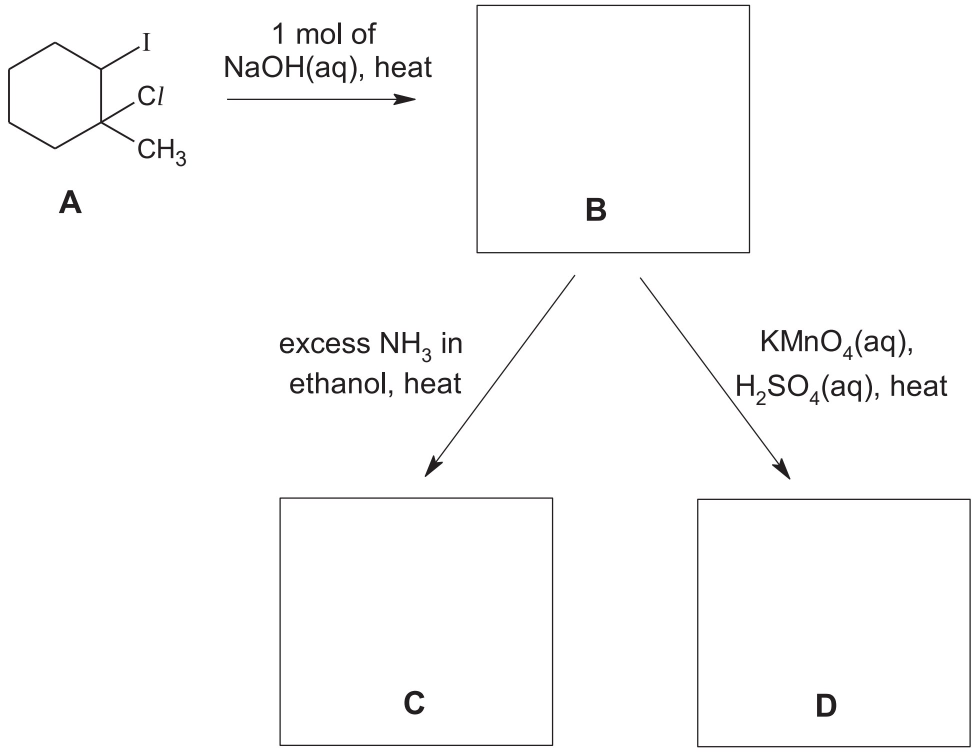
(i) Write the balanced ionic equation for the formation of the cream precipitate from adding silver nitrate to sodium bromide. [1]

(ii) Explain the effect of adding aqueous ammonia to each of the resulting mixture and clearly account for any difference in the observation. [3]

(e) Halogenoalkanes are widely synthesised by reacting halogens with alkenes. In turn, halogenoalkanes can undergo nucleophilic substitution using aqueous sodium hydroxide to form alcohols commercially.

(i) Give one reason why iodoalkanes are more reactive towards nucleophilic substitution with aqueous NaOH than the corresponding chloroalkanes. [1]

(ii) A sequence of reactions, starting from compound **A**, a dihalogeno compound, is shown on the next page.

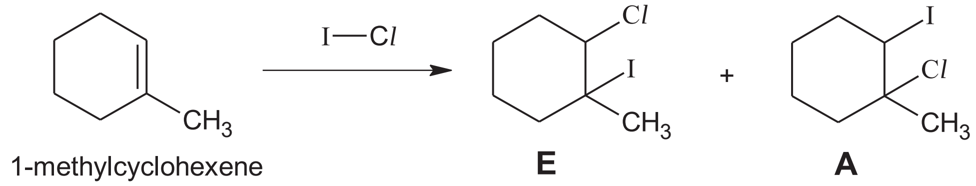


Draw the structures of compounds **B**, **C** and **D**.

[3]

(iii) The halogens form many interhalogen compounds, one such example is ICl, commonly known as Wijs' reagent.

Wijs' reagent can react with 1-methylcyclohexene to form a mixture of compound **E** and **A**. Explain why **A** is the major product for this reaction.



[2]

(f) **(i)** Below outlines a reaction scheme of phosgene with NaOH(aq).

$$\mathrm{COCl_2} \xrightarrow[\text{stage 1}]{\mathrm{OH^-}} \mathrm{COCl(OH)} \xrightarrow[\text{stage 2}]{} \mathrm{CO_2 + HCl}$$

State the types of reaction occurring in stage 1, and stage 2. [2]

(ii) To remove any phosgene present in chloroform, a small amount of methanol is added. Use the information in **(f)(i),** suggest the structure of the organic compound formed when phosgene reacts with methanol. [1]

[Total:20]

2 **(a)** Carbon monoxide reacts with steam over a copper / zinc catalyst, to form a mixture of carbon dioxide and hydrogen gas.

Reaction 1: $CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$

When an equimolar mixture of hydrogen and carbon dioxide at an initial total pressure of 4 atm is allowed to reach equilibrium at 1000 K, the percentage of steam in the mixture of gases is found to be 15%.

(i) Calculate K_p of the system in **reaction 1** at 1000 K. [2]

(ii) Suggest, with a reason, whether a higher pressure will favour the formation of steam. [1]

(b) Sodium ethanoate can be used to prepare ethane by an electrochemical reaction, which is known as the Kolbe electrolysis reaction.

Ethane is formed at the anode by the following reaction:

$$2CH_3CO_2^- \rightarrow C_2H_6 + 2CO_2 + 2e^-$$

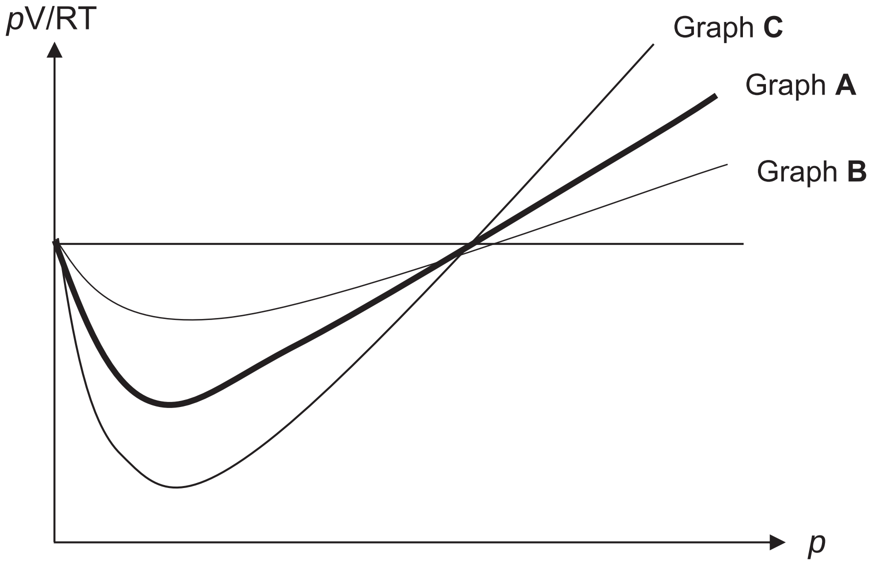
A student investigated the electrolysis of an aqueous solution of sodium ethanoate, using graphite electrodes in a litmus solution.

(i) Give the equation for the reaction occurring at the cathode, and state the final colour expected at the cathode.

Construct an equation for the **overall** reaction. [2]

(ii) Calculate the time, in minutes, needed by the student to pass a current of 5.0 A through a solution of sodium ethanoate, to produce 1.50 g of ethane. [2]

(c) **(i)** The value of pV/RT is plotted against p for the following three gases, where p is the pressure and V is the volume of the gas.
Given that graph **A** represents 1 mol of CO_2 at 298 K, identify which of the following graphs, **B** or **C,** represent 1 mol of CO_2 at 500 K. Explain your answer.



[2]

(ii) Sulfur dioxide is used by the Romans in winemaking, when they discovered that burning sulfur candles inside empty wine vessels keeps them fresh and free from vinegar smell.

One such cylinder of sulfur dioxide has an internal volume of 2.5 dm^3, and a mass of 2.3 kg.

Calculate the pressure (in pascals) that the sulfur dioxide would exert inside the cylinder at room temperature. [1]

(d) Sulfuric acid is used in many industrial processes of major importance.

The process used to produce sulfuric acid involves a three–stage process. The first stage is to pass air over burning sulfur. The emerging gas is then passed over a catalyst, V_2O_5, which is maintained at 450-550ºC in the reaction chamber.

Stage **I**: $S(s) + O_2(g) \rightarrow SO_2(g)$
Stage **II**: $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$
Stage **III**: $SO_3(g) + H_2O(l) \rightarrow H_2SO_4(l)$

(i) Draw dot-and-cross diagrams to show the bonding in SO_2 and H_2SO_4.
State the bond angle, with respect to sulfur atom, in each of them. [4]

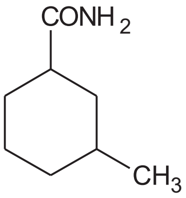
(ii) The boiling points of sulfur trioxide and sulfur dioxide are 45°C and -10°C respectively. Account for the difference in boiling points for both compounds, in terms of structure and bonding. [2]

(e) For each of the following pairs of compounds, suggest **one** simple chemical test to distinguish them from each other. State the reagents and conditions needed and give the expected observations for each compound.

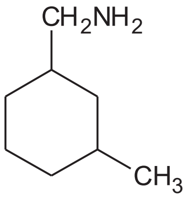
(i) $CH_2{=}CHCH_2CH(CH_3)OH$ **J** $CH_2{=}CHC(CH_3)_2OH$ **K**

[2]

(ii)



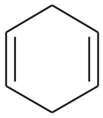
L



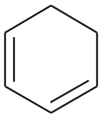
M

[2]

(iii)



P



Q

[2]

[Total:22]

3 Nitrous oxide, N_2O, is commonly known as laughing gas due to the euphoric effects of inhaling it. At a temperature of 1000 K, in the presence of chlorine catalyst, N_2O decomposes to its elements according to the following equation:

$$2N_2O(g) \rightarrow 2N_2(g) + O_2(g)$$

The experimental rate equation for this reaction is:

$$\text{Rate} = kP_{N_2O}^{a}\, P_{Cl_2}^{b}\,,$$

where P_{N_2O} and P_{Cl_2} are the partial pressures of N_2O and Cl_2 respectively, and a and b are non-zero constants.

The rate of decomposition of pure N_2O may be followed at constant temperature, by measuring the total pressure of the system with time.

The data below refers to a reaction in which pure N_2O decomposes in the presence of chlorine catalyst, Cl_2, (at partial pressure of 47 kPa).

Experiment 1:

time / s	0	40	80	140	240
P_{total} / kPa	87.0	91.3	93.0	98.0	102.2
P_{N_2O}	40	31. 4	25	18	9.6

(a) **(i)** Show that the partial pressure of N_2O at any instant is given by $P_{N_2O} = 214 - 2P_{total}$ [2]

(ii) Use the given data provided in the table above to plot a graph of P_{N_2O} against time on suitable axes.

Showing all your working and drawing clearly any construction lines on your graph, use your graph to determine the value of a, the order of reaction with respect to N_2O. [4]

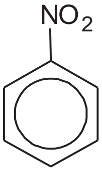
(iii) Two additional experiments, experiments 2 and 3 were carried out and the following results were obtained.

	P_{N_2O} / kPa	P_{Cl_2} / kPa	Initial rate/ kPa s^{-1}
experiment 2	70	35	0.306
experiment 3	70	70	0.613

Determine b, the order of reaction with respect to chlorine. Explain your reasoning. [1]

(iv) Hence write the rate equation for the reaction. [1]

(b) Nitrobenzene is an organic compound used to mask unpleasant odors in shoe and leather dressings.



(i) Suggest the type of hybridisation of N in nitrobenzene. [1]

(ii) Nitrobenzene can be formed from reacting benzene with concentrated nitric acid and sulfuric acid. Name and outline the mechanism of the nitration of benzene. Indicate the rate-determining step and draw the formula of the organic intermediate. [3]

(iii) Given that the nitration of benzene is exothermic, sketch the reaction pathway diagram of the reaction, labelling clearly the reactant, intermediate and product on your diagram. [2]

(c) To investigate the mechanism of nitration of benzene, every hydrogen atom on benzene is replaced by its isotope, deuterium, to form C_6D_6.

Carbon–deuterium (C-D) bond has higher bond energy than a carbon–hydrogen (C-H) bond.

If the rate-determining step involves the breaking of a C–H bond, replacing the C–H bond with a C–D bond will change the rate constant, k, of the reaction. This is known as the deuterium isotope effect.

Deuterium isotope effect = $\frac{k_H}{k_D}$

k_H = rate constant for nitration of C_6H_6

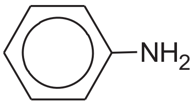
k_D = rate constant for nitration of C_6D_6

If $\frac{k_H}{k_D} = 1$, it is said that the deuterium isotope effect is absent.

If $\frac{k_H}{k_D} >> 1$, it is said that the deuterium isotope effect is present.

Predict with reasoning, if the deuterium isotope effect would be present in the nitration of benzene. [1]

(d) **(i)** Nitrobenzene can be converted to phenylamine, which is used in the synthesis of polyurethane, a polymer used in making tyres.



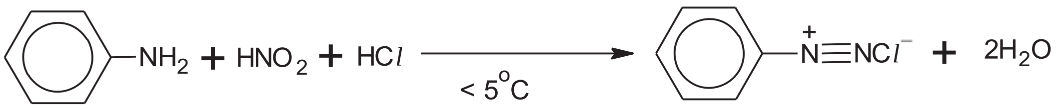
phenylamine

Suggest the reagents and conditions to convert nitrobenzene to phenylamine. [1]

(ii) The following equations illustrate the formation of phenol from phenylamine, in two steps:

In step **1**, phenylamine reacts with cold nitrous acid, HNO_2, and hydrochloric acid, HC*l*, to form phenyldiazonium chloride.

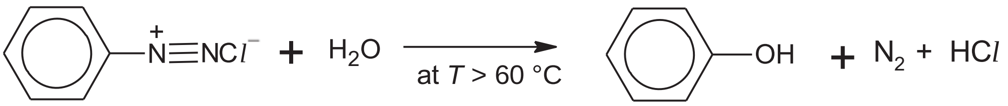
<u>step **1**</u>



phenyldiazonium chloride

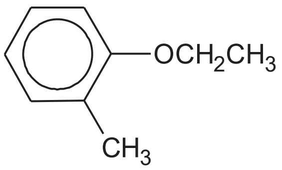
In step **2**, phenyldiazonium chloride can react with water upon heating to give phenol.

<u>step **2**</u>



phenyldiazonium chloride

Propose a two-step synthetic pathway for the conversion of 2-methylphenylamine to compound **S** below.



Compound **S**

[2]

[Total:18]

Blank Page

Section **B**

Answer **one** question from this section.

4 **(a)** A blood test can detect abnormally high levels of an amino acid which is one of the signs of the disease phenylketonuria, a rare condition in which a person is unable to properly break down amino acids such as phenylalanine.

In acidic solution, phenylalanine is completely protonated and exists as $H_3N^+CHRCO_2H$, where R is $–CH_2C_6H_5$.

Protonated phenylalanine, $H_3N^+CHRCO_2H$, acts as a dibasic acid that ionises in stages.

$$H_3N^+CHRCO_2H \rightleftharpoons H_3N^+CHRCO_2^- + H^+ \qquad pK_1 = 1.83$$

$$H_3N^+CHRCO_2^- \rightleftharpoons H_2NCHRCO_2^- + H^+ \qquad pK_2 = 9.13$$

(i) Calculate the pH of a 0.80 mol dm^{-3} solution of protonated phenylalanine (ignore the effect of pK_2 on the pH). [1]

(ii) An amphiprotic species is one that can act as a Bronsted-Lowry acid or base. The pH of a solution containing an amphiprotic species is given by the following expression.

$pH = ½(pK_1 + pK_2)$

In the titration of protonated phenylalanine with NaOH, an amphiprotic species is formed.

Identify the amphiprotic species formed and calculate the pH of the solution.

[2]

(iii) Sketch the titration curve when 25.0 cm^3 of the protonated form of phenylalanine is being titrated with 70 cm^3 of NaOH(aq) of the same concentration. On your sketch, clearly mark the two pK_a values and the points you have calculated in **(i)** and **(ii)**. [3]

(iv) Suggest a suitable indicator from the following table to be used to detect the first equivalence point and state the colour change of the solution at this equivalence point.

indicator	**pH range**	**acid solution**	**basic solution**
Thymol Blue	1 – 3	red	yellow
Methyl Red	5 – 6	red	yellow
Phenol red	7 – 8	yellow	red
Phenolphthalein	8 - 10	colourless	red

[2]

(b) "Acidity regulators" are food additives that have a buffering action on the pH of food. A mixture of citric acid, $C_5H_7O_4CO_2H$, and its sodium salt is often used for this purpose.
You may assume that citric acid behaves as a monobasic weak acid.

$C_5H_7O_4CO_2H \rightleftharpoons C_5H_7O_4CO_2^- + H^+$; $K_a = 7.4 \times 10^{-4}$ mol dm^{-3}

(i) A citric acid / sodium citrate buffer mixture is prepared by mixing 40.0 cm^3 of 0.100 mol dm^{-3} citric acid and 60.0 cm^3 of 0.200 mol dm^{-3} sodium citrate.

Calculate the pH of the buffer solution. [1]

(ii) Write equations to show how this mixture of citric acid and sodium citrate regulates the acidity on addition of H^+ ions and OH^- ions. [2]

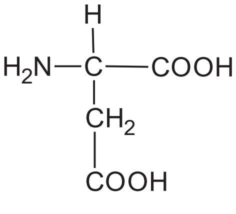
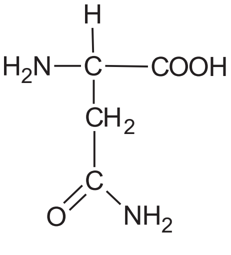
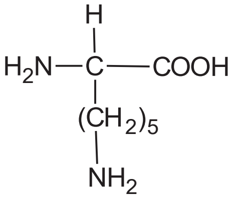
(c) **(i)** Describe the conditions needed to hydrolyse a protein non-enzymatically. [1]

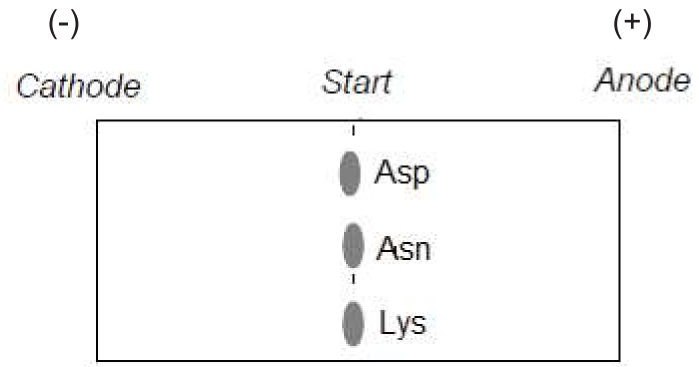
(ii) Histidine decarboxylase undergoes enzymatic hydrolysis. Upon hydrolysis, the polypeptide fragments of the enzyme's active site are isolated as shown below.

- Ala-Cys-Phe
- Gly-Gly
- Lys-Asp-Asp-Gly-Gly
- Phe-Arg-Lys

Deduce the sequence of the 9 amino acid residues of the enzyme's active site. [2]

(iii) A different segment of tripeptide, Asp-Asn-Lys, was subjected briefly to acidic hydrolysis which produced individual amino acids as well as various peptides. The resulting mixture buffered at pH 13 was separated in an electric field using electrophoresis.

Amino acid			
Abbreviation	Asp	Asn	Lys



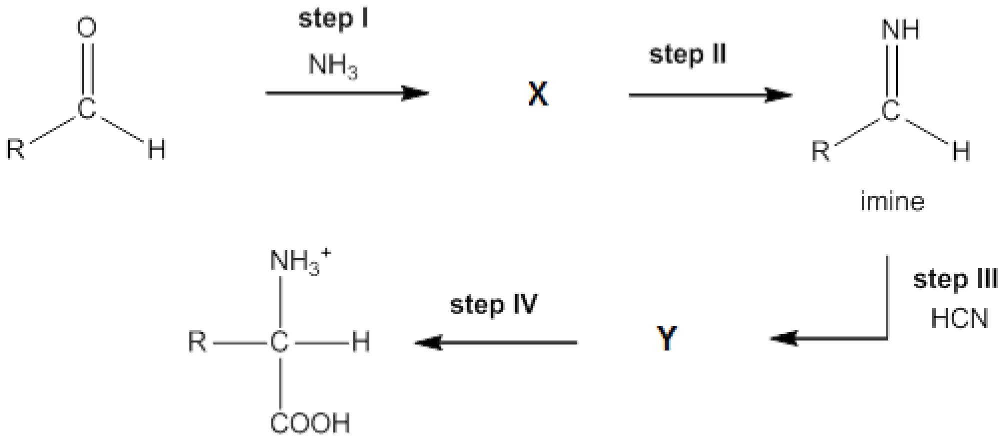
Using the above template, sketch and label the position of the three amino acids after the separation. State one factor that affects the rate at which the charged particles move during electrophoresis.

[3]

(d) The Strecker synthesis assembles an α-amino acid from the amine precursor and an aldehyde.

- Step **I** is a nucleophilic addition reaction.
- Step **II** involves the elimination of water from **X** to form an imine**.**
- Step **III** is similar to the formation of cyanohydrin when the imine undergoes nucleophilic addition with HCN and forms an α-amino nitrile, **Y**.
- Step **IV** is the hydrolysis of **Y** to form the carboxylic acid functional group.

In the following reaction flow scheme, draw the intermediate compounds **X** and **Y** and suggest the reagent and condition for step **IV** in the scheme.



[3]
[Total:20]

5 Copper is an important transition element that can readily form complex ions with *ligands*. Copper forms a large variety of compounds, usually with variable oxidation states. Copper compounds also act as useful *homogeneous catalysts*, commonly used in many industrial operations.

(a) Define the terms *ligand* and *homogeneous catalyst*. [2]

(b) In recent years, horseshoe crabs have generated great interest amongst scientists due to its blood with remarkable antibacterial properties. An unusual aspect of the blood is that it is bright blue, a consequence of using copper-based complexes, haemocyanin, to transport oxygen.

Two Haemocyanin (Hc) reversibly bind a single oxygen molecule, O_2, to form oxyhaemocyanin, HcO_2, according to the following equilibrium:

$$2Hc(aq) + O_2(aq) \rightleftharpoons 2HcO_2(aq) \qquad \textit{equilibrium 1}$$

Oxygenation causes a color change between Cu(I) deoxygenated form and the Cu(II) oxygenated form.

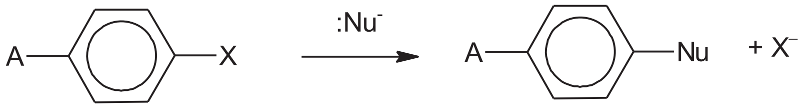
(i) By considering *equilibrium 1* and the level of oxygen in both the lungs and body cells, comment on how the crab cells receive oxygen from the air in the lungs.

[2]

(ii) Indicate the color change from Cu(II) oxygenated form to Cu(I) deoxygenated form. Hence explain why both copper complex ions exhibit different colours.

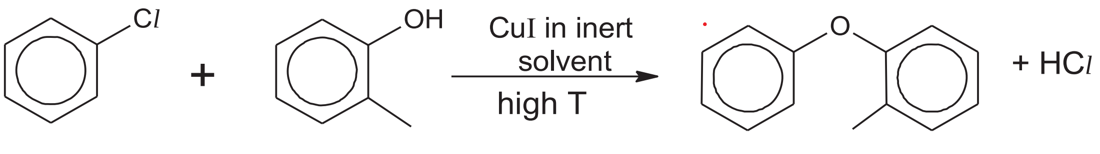
[5]

(c) Most aromatic compounds undergo electrophilic substitution. However it is possible for aryl halides to undergo a limited number of nucleophilic substitution reactions with strong nucleophiles. An example of a reaction is as follows:



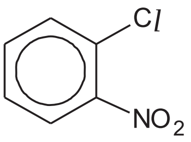
An example of an aryl nucleophilic substitution is the *Ullmann coupling* reaction where hydrocarbons fragments are coupled, using copper compounds as a catalyst.

An example is indicated in reaction **1** below.

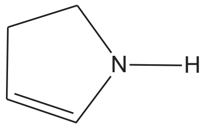


reaction **1**

(i) The conditions for the *Ullmann coupling* reactions are usually harsh conditions, and yet give low yield. In a similar reaction under the same temperature and pressure, the two compounds below were reacted together:



and



.

Deduce and draw the structure of the product for the above reaction. [1]

(ii) Predict, with reasoning, if the above reaction in **(c)(i)** will result in a higher or lower yield compared to reaction **1**. [2]

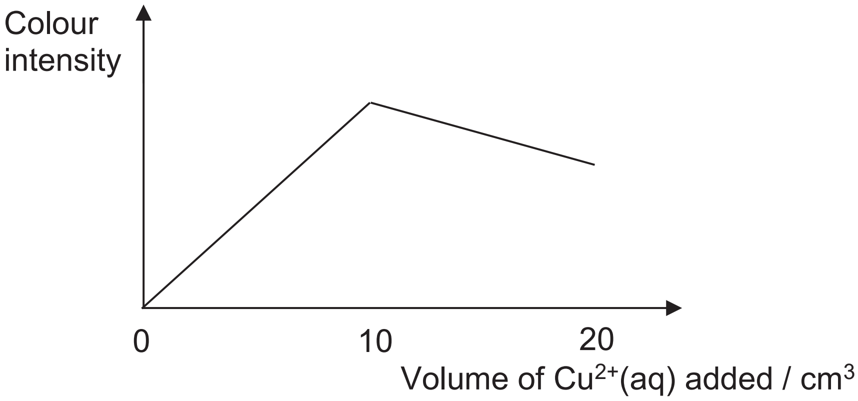
(iii) Like copper(I) iodide, aqueous Fe^{2+} is a good homogeneous catalyst used in the decomposition of aqueous hydrogen peroxide as indicated below.

$$2H_2O_2(aq) \rightarrow 2H_2O(l) + O_2(g)$$

With reference to relevant data in the *Data Booklet*, suggest a mechanism for the catalysis of the above reaction by aqueous Fe^{2+}. [3]

(d) Copper(II) species can have various coordination numbers.

The formula of a methylamine-copper complex ion, $[Cu(CH_3NH_2)_x(H_2O)_2]^{2+}$, can be determined using a colorimeter. In an experiment, a solution of 0.050 mol dm^{-3} of $Cu^{2+}(aq)$ was added 1 cm^3 at a time to 20 cm^3 of 0.100 mol dm^{-3} of aqueous CH_3NH_2. The colour intensity of the resultant solution after each addition was measured using a colorimeter. The following graph was obtained.



(i) Using the graph, determine the value of ***x.*** [2]

(ii) Draw the structure of the methylamine-copper complex ion. [1]

(e) Mercury is poisonous as it can cause many health problems ranging from neurological, respiratory to cardiovascular problems. One possible treatment for mercury poisoning involves administering a solution of $EDTA^{4-}$, a common hexadentate ligand which forms complexes with many metal ions.

Copper and calcium ions are essential minerals required by the body. Using relevant data from below, comment on the use of $EDTA^{4-}$ as a treatment for mercury poisoning and comment on its effect on the concentrations of copper and calcium ions in the body.

Equilibrium	K_c / $mol^{-1}\ dm^3$
$Ca^{2+} + EDTA^{4-} \rightleftharpoons [Ca(EDTA)]^{2-}$	6×10^{10}
$Cu^{2+} + EDTA^{4-} \rightleftharpoons [Cu(EDTA)]^{2-}$	5×10^{18}
$Hg^{2+} + EDTA^{4-} \rightleftharpoons [Hg(EDTA)]^{2-}$	6.3×10^{21}

[2]

[Total:20]

End of Paper

H

PIONEER JUNIOR COLLEGE

JC2 Preliminary Practical Examination
HIGHER 2

CANDIDATE NAME	
CT GROUP	1 6
INDEX NUMBER	

CHEMISTRY **9729/04**

Paper 4 Practical **28 August 2017**
2 hours 30 min

Candidates answer on the Question Paper

Additional Materials: As listed in your apparatus list

READ THESE INSTRUCTIONS FIRST

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

Answer **all** questions.

The use of an approved scientific calculator is expected, where appropriate.
You may lose marks if you do not show your working or if you do not use appropriate units.

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

Shift: _______________

Lab: _______________

For Examiner's Use	
Q1	/22
Q2	/15
Q3	/18
Total	/55

This document consists of **22** printed pages.

1 **Experiment to investigate the behaviour of acids and bases in aqueous solution**

FA 1 is 1.00 mol dm^{-3} sodium hydrogen carbonate, $NaHCO_3$
FA 2 is sodium hydroxide, NaOH, of concentration between 1.5 mol dm^{-3} to 2.0 mol dm^{-3}
FA 3 is 2.00 mol dm^{-3} sulfuric acid, H_2SO_4

An acid-base neutralisation reaction involves reacting the two solutions, to produce water molecules. The equation for this neutralisation reaction is given below.

$$H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$$

The reaction between $H^+(aq)$ and $OH^-(aq)$ is an exothermic reaction and is used to perform a thermometric titration.

This task involves **two** different acid-base reactions.

The first reaction is between **FA 1**, $NaHCO_3$, and **FA 2**, NaOH.

Reaction 1 $NaHCO_3(aq) + NaOH(aq) \rightarrow Na_2CO_3(aq) + H_2O(l)$ $\Delta H_{reaction1}$

The molar enthalpy change for **reaction 1**, $\Delta H_{reaction1}$ is the enthalpy change when 1.00 mol of $NaHCO_3$ reacts completely with NaOH.

You will perform a thermometric titration to determine the equivalence point of the reaction. The equivalence point is the point where the $OH^-(aq)$ from the base completely neutralises the $H^+(aq)$ from the acid.

The second reaction is between **FA 1**, $NaHCO_3$, and **FA 3,** H_2SO_4,.

Reaction 2 $NaHCO_3(aq) + ½H_2SO_4(aq) \rightarrow ½Na_2SO_4(aq) + H_2O(l) + CO_2(g)$ $\Delta H_{reaction2}$

The molar enthalpy change for **reaction 2**, $\Delta H_{reaction\ 2}$, is the enthalpy change when 1.00 mol of $NaHCO_3$ reacts completely with H_2SO_4.

In the 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 record the temperature of the mixture after each addition of **FA 2**.

You will then analyse your results graphically in order to determine the

- volume of **FA 2** at the equivalence point, $V_{equivalence}$,
- maximum temperature change, ΔT_{max1},
- molar enthalpy change for the reaction, $\Delta H_{reaction1}$, for **reaction 1.**

In your second experiment, you will mix together given volumes of **FA 1** and **FA 3**.

You will then determine the

- maximum temperature change, $\Delta T_{\text{max 2}}$,
- molar enthalpy change, $\Delta H_{\text{reaction 2}}$, for **reaction 2**.

Part 1: The 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.*

Procedure for the reaction between FA 1 and FA 2

1 Fill a burette with **FA 2**.

2 Place a Styrofoam cup inside a second Styrofoam cup which is held in a beaker to prevent it from 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.

Note: If you overshoot on an addition, record the **actual** total volume of **FA 2** added up to that point.

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 in the table provided.

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.

Results

Initial temperature of **FA 1** : _____________

[2]

(ii) On the grid on below, plot a graph of maximum temperature, T (*y-axis*) against volume of **FA 2** added (*x-axis*).

(iii) Draw **two** smooth lines of best fit.

- The first best-fit line should be drawn using the plotted points where the temperature is **rising**.
- The second best-fit line should be drawn using the plotted points where the temperature is **falling**.
- Extrapolate these lines until they cross.

Note: Each line should have a shape best suited to its plotted points. [3]

(iv) Determine from your graph

- the maximum temperature reached, T_{max},
- the maximum temperature change ΔT_{max1},
- the volume, $V_{equivalence}$, of **FA 2** needed to completely react with 25.0 cm^3 of **FA 1**.

Record these values in the spaces provided below.

maximum temperature reached, T_{max} = _______ °C

maximum temperature change, ΔT_{max} = _______ °C

volume of **FA 2** used, $V_{equivalence}$ = _______ cm^3

[3]

Part 2: The reaction between FA 1 and FA 3

(b) The molar enthalpy change for reaction 2, $\Delta H_{reaction2}$, 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, $\Delta H_{reaction2}$. To do this you will need to calculate the maximum temperature change produced when 40 cm^3 of **FA 1**, $NaHCO_3$ and 15 cm^3 of **FA 3**, H_2SO_4 are mixed.

You should be aware that the reaction mixture will produce considerable frothing.

In this experiment, you will select a suitable apparatus to measure **FA1** and **FA 3**.

(i) Calculate the maximum percentage errors in 40 cm^3 of **FA 1** when using

- measuring cylinder

- burette

[1]

(ii) Explain your choice of apparatus for measuring **FA 1**.

……………………………………………………………………………..

……………………………………………………………………………..

[1]

(iii) **Procedure for the reaction between FA 1 and FA 3**

1. Label one Styrofoam cup, **A**. Label a second Styrofoam cup, **B.**

2. Place the cup **A** inside a Styrofoam cup which is held in a beaker to prevent it from tipping over.

3. Transfer 40 cm^3 of **FA 1** into cup **A** using your chosen apparatus.

4. Stir the **FA 1** solution in cup **A** with the thermometer. Read and record its temperature, T_{FA1}**.** This is the initial temperature of **FA 1**.

5. Wash and dry the thermometer.

6. Transfer 15.0 cm^3 of **FA 3** into cup **B**. Stir the **FA 3** solution with the thermometer. Read and record its temperature of the mixture, T_{FA3}. 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.

In an appropriate format in the space provided below, record all values of measured temperatures for this experiment.

Results

[1]

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 specific heat capacity, c, of 4.18 J g^{-1} K^{-1}. Use your results from **(a)(iv)** to calculate the following.

(i) The concentration of sodium hydroxide, [NaOH], in **FA 2**.

[NaOH] in **FA 2** = ______________________________

[1]

(ii) The heat change, q, for the reaction occurring in **(a)(i)**, and hence determine a value for the molar enthalpy change for **reaction 1**, $\Delta H_{\text{reaction1}}$.

q = ______________________________

$\Delta H_{\text{reaction1}}$ = ______________________________

[2]

(d) Use your results from **(b)** to calculate a value for the molar enthalpy change for **reaction 2**, $\Delta H_{\text{reaction2}}$.

For the experiment in **(b)**, the weighted average initial temperature, $\Delta T_{average,}$ of **FA 1** and **FA 3** may be calculated using the formula given below:

$$T_{\text{average}} = \frac{(V_{FA1} x T_{FA1}) + (V_{FA3} x T_{FA3})}{(V_{FA1} + V_{FA3})}$$

q = ______________________________

$\Delta H_{\text{reaction2}}$ = ______________________________

[5]

(e) Ionic equations for neutralisation, reaction **1**, and reaction **2** are shown below.

$H^+(aq) + OH^-(aq) \longrightarrow H_2O(l)$	ΔH_{neu}= -57.1 kJ mol^{-1}
$HCO_3^-(aq) + OH^-(aq) \rightarrow CO_3^{2-}(aq) + H_2O(l)$	$\Delta H_{reaction1}$
$HCO_3^-(aq) + H^+(aq) \rightarrow H_2O(l) + CO_2(g)$	$\Delta H_{reaction2}$

Carbon dioxide reacts with solutions of carbonate ions according to the following equation.

reaction 3 $CO_2(g) + H_2O(l) + CO_3^{2-}(aq) \longrightarrow 2HCO_3^-(aq)$ $\Delta H_{reaction3}$

Using your calculated answers in **(c)(ii)** and **(d)**, together with the given value of enthalpy change of neutralisation, ΔH_{neu}, determine a value for the enthalpy change for this reaction, $\Delta H_{reaction3}$.

[3]

[Total: 22]

2 To investigate the kinetics of reaction in an iodine clock reaction

FA 4 is 0.100 mol dm^{-3} aqueous potassium iodide, KI.
FA 5 is 1.00 mol dm^{-3} dilute sulfuric acid, H_2SO_4 .
FA 6 is 0.100 mol dm^{-3} aqueous potassium bromate(V), $KBrO_3$
FA 7 is 5.00 x 10^{-3} mol dm^{-3} aqueous sodium thiosulfate, $Na_2S_2O_3$

You are also provided with starch indicator and deionised water.

This reaction starts from a solution containing potassium bromate(V), sulfuric acid, sodium thiosulfate and starch. To this, a solution of potassium iodide is added.

There are two reactions occurring in the solution. In the first slow reaction, iodine is formed.

Reaction **I** $6I^-(aq) + BrO_3^-(aq) + 6H^+(aq) \rightarrow 3I_2(aq) + Br^-(aq) + 3H_2O(l)$

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

Since there is a small but constant amount of sodium thiosulfate added to the reaction mixture, the iodine being slowly produced by Reaction **I** will immediately react in Reaction **II** until all the sodium thiosulfate has been used up. At that point, free iodine will be present in the solution, which will cause a sudden appearance of a deep blue colour as starch is present.

You will perform a series of **three** experiments, by varying the volume of **FA 6** added, with each solution being made up to the same total volume with water. For each experiment, you will note the volume of **FA 6** added, V_{FA6}, and the time taken, **t**, for the solution to turn blue. Using your results, determine the order of reaction with respect to BrO_3^-.

(a) Experiment 1

1 Use appropriate measuring cylinders, add 10.0 cm^3 of **FA 5**, 20.0 cm^3 of **FA 7** and 1 cm^3 of starch indicator into the conical flask labelled reaction mixture. Note: 10 drops is approximately 1 cm^3.

2 Using a measuring cylinder, add 30.0 cm^3 of **FA 6** into the conical flask.

3 Swirl the contents of the flask.

4 Measure 10 cm^3 of **FA 4** using measuring cylinder. Add **FA 4** quickly into the conical flask. Start the stopwatch during this addition.

5 Mix the contents thoroughly by swirling the flask.

6 Stop the stopwatch when the blue colouration is observed.

7 Record the time, **t**, to the nearest 0.1 s.

8 Wash the conical flask thoroughly with water. Stand it upside down on a paper towel to drain.

Experiments 2 and 3

Carry out two more experiments by repeating steps 1 to 8, and varying the volumes of **FA 6**, so that you can determine the order of reaction with respect to BrO_3^-.

The volume of **FA 6** should **<u>not</u>** be more than that in experiment **1**. In each experiment, deionised water is added to keep the **total volume** of the final reaction mixture **constant**.

Prepare a table in the space provided to record, for each experiment:

- volumes of **FA 6**, V_{FA6}, and deionised water used,
- all values of t, to the nearest 0.1 s,

and

- calculated values of **(V_{FA6}) x t** and **(V_{FA6})^2× t** (to 3 significant figures)

*Note: As the volumes of **FA 4, FA5, FA 7** and starch indicator are constant for each experiment, you do not need to record these volumes in your table.*

Results

[3]

The rate of reaction is given by the equation:

$$\text{rate} \propto [\text{reactant}]^{n}$$

where n is the order of reaction with respect to the reactant investigated. The value of n can be 0, 1 or 2.

In this experiment, the rate of reaction $\propto \left(\frac{1}{\text{time}}\right)$,

and
[reactant] $\propto$ volume of reactant used.
Hence, $\left(\frac{1}{\text{time}}\right) \propto (\text{volume of reactant})^{n}$

Rewriting, $(\text{volume of reactant})^{n} \times \text{time} = \text{constant}$

(b) **(i)** Explain why $\left(\frac{1}{\text{time}}\right)$ is a measure of the rate of reaction, in this experiment.

………………………………………………………………………………..

……………………………………………………………………………….. [1]

(ii) From your results using Vt or V^2t values, deduce the order of the reaction with respect to bromate(V) ions.

………………………………………………………………………………..

……………………………………………………………………………….. [1]

(c) In an attempt to find the order of reaction with respect to H^+ ions, a student carried out experiments **4** and **5**, by varying volume of **FA 5, V_{FA5}**.

Only the numerical values of $V_{FA5} \times t$ and $(V_{FA5})^2 \times t$ are tabulated below.

Experiment	**V_{FA5} / cm^3**	**$V_{FA5} \times t$**	**$(V_{FA5})^2 \times t$**
4	**5.0**	**225**	**1130**
5	**15.0**	**75.0**	**1130**

From the above calculated values of $V_{FA5} \times t$ and $(V_{FA5})^2 \times t$, deduce the order of reaction with respect to H^+ ions.

……………………………………………………………………………………

…………………………………………………………………………………… [1]

(d) The order of reaction with respect to iodide ions, I^-, is given to be one.

The rate equation is written as;

$$\text{rate} = k\,[I^-]\,[BrO_3^-]^m\,[H^+]^n$$

where *m* and *n* are the order of reaction with respect to BrO_3^- and H^+ respectively.

In order to find half-life of the reaction, a student proposed that the rate equation can be rewritten as:

$$\text{rate} = k'[I^-],\ \textit{where } k' = k\,[BrO_3^-]^m\,[H^+]^n \quad \textit{equation 1}$$

From his *equation 1*, the student then proposed that the half-life of reaction can be calculated using $\frac{\ln 2}{k'}$.

Comment on the validity of his statement.

……………………………………………………………………………………………

……………………………………………………………………………………………

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

(e) Instead of washing and draining the conical flask as required in **step 8** of **(a)**, another student simply just poured away the reaction mixture. There was some leftover reaction mixture in the flask when he performed the subsequent experiment.

State and explain the effect on time, **t**, in his subsequent experiment.

……………………………………………………………………………………………

……………………………………………………………………………………………

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

(f) Plan

In **(a)** and **(c)**, the orders of reaction with respect to bromate(V) ions and H^+ were investigated using the initial rate method.

The order of reaction with respect to iodide ion was not investigated but was given as 1 in **(d)**.

Instead of doing a number of initial rate experiments, the order of reaction with respect to iodide ion, I^-, can be determined by following **one** reaction from the start to the end, in what is known as the *continuous method*.

To do so, the reacting mixture is prepared with a known concentration of I^-, and known concentrations of H^+ and BrO_3^-, both of which must be in **excess**. Over time, the amount of, and concentration of I_2 increases. The appearance of I_2 is noted by the colour of the mixture turning yellow-orange. (Due to the low concentrations of I_2 used in this experiment, I_2 appears yellow-orange)

An investigation is planned to allow you to determine the order of reaction with respect to iodide ion, I^-.

You may assume you are provided with the following.

- 0.5 mol dm^{-3} H_2SO_4, 1.0 mol dm^{-3} KI and 1.0 mol dm^{-3} $KBrO_3$,
- standard iodine solutions of various concentrations,
- deionised water

(i) Suggest with reasoning, the volumes of H_2SO_4, KI, $KBrO_3$ and deionised water you would mix to obtain 250 cm^3 of the reaction mixture.

Reagent	Volume used/ cm^3
H_2SO_4	
KI	
$KBrO_3$	
Deionised water	

……………………………………………………………………………….....

……………………………………………………………………………….....

……………………………………………………………………………….....

……………………………………………………………………………….....

……………………………………………………………………………….....

……………………………………………………………………………… [2]

(ii) It is possible to determine the concentration of a solution of a coloured solute using a colorimeter.

A few cm^3 of the solution is placed inside a machine, known as a colorimeter. This machine measures the amount of light that is absorbed when a specific wavelength of visible light is shone through a coloured solution. It does this by comparing the amount of light passing through the sample with the amount of light passing through the pure solvent. The amount of light absorbed is expressed as an absorbance value.

According to Beer-Lambert's Law, the higher the concentration of the coloured substance, the higher the absorbance value. Using this relationship, it is possible to determine the progress of the reaction.

A colorimeter was first used to measure the absorbance of a standard solution of iodine, I_2, of concentration equal to that of the highest concentration of I_2 the reaction mixture can produce.

Then, the reaction mixture is prepared and placed in a 1 cm^3 cuvette. The cuvette is placed into the colorimeter and the absorbance of the solution is measured and recorded at regular time intervals.

The experiment is stopped when the absorbance reading reaches about 80% of that of the standard solution of iodine.

To determine the order of reaction with respect to iodide ion, a product time graph of absorbance against time is plotted and the order of reaction with respect to iodide ion can be determined.
The colorimeter is set to use the wavelength of light that is absorbed most strongly by iodine.

Suggest a colour in the visible spectrum from which a suitable wavelength of light might be chosen. Explain your answer.

Colour: ………………………………………………………………………

Explanation: ………………………………………………………………

[2]

(iii) Sketch the shape of the plot of absorbance of I_2 against time graph that you expect to obtain, in the space provided below.

Explain clearly, how it can be used to determine the order of reaction with respect to iodide ion.

[3]

[Total: 15]

3 Qualitative Analysis

(a) (i) **Before starting this analysis, ensure your Bunsen burner is turned off.**

In this question you will deduce the functional groups of two organic compounds, **FA 8** and **FA 9**.

FA 8 and **FA 9** each has only **one** functional group, and contains only carbon, hydrogen, and **one** oxygen atom.

You will perform a series of test-tube reactions and use the observations to help you deduce the functional groups present.

You are provided with liquid samples **FA 8** and **FA 9**. Perform the following tests described in Table **3.1**, on **FA 8** and **FA 9**, and record your observations in the table. If it appears that no reaction has taken place, this should be clearly recorded.

Use a fresh sample of each liquid in each test.

Samples FA 8 and FA 9 are provided in sample tubes. It is essential that you replace the lid as soon as you have removed the sample for each test.

You should also prepare a fresh solution of Tollens' reagent in **Test 1** of **Table 3.1**.

One test has already been carried out and the observation is recorded in **Table 3.1**.

Preparation of Tollens' reagent

To a 3 cm depth of aqueous silver nitrate in a test-tube, add 6 drops of aqueous sodium hydroxide.

To this mixture add aqueous ammonia dropwise. Stir with a glass rod until the brown solid just dissolves.

Keep this solution for use as Tollens' reagent in the question.

Table 3.1		
Test	**Observations with**	
	FA 8	**FA 9**
1. Label a test-tube **FA 8**. To this test-tube, add 2 cm^3 of Tollens' reagent, followed by 5 drops of **FA 8**. Prepare a hot water bath using hot water provided. Warm the mixture in the water bath for five minutes. **Repeat using FA 9, in place of FA 8.**		
2. Label a test-tube **FA 9**. To this test-tube, add 5 drops of **FA 9** and 6 drops of aqueous sodium hydroxide. Now add iodine solution, dropwise, until a permanent yellow / orange colour is present. Warm the mixture in the water bath for two minutes.	**Pale Yellow precipitate**	
3. Label a test-tube **FA 8**. To this test-tube, add 1 cm^3 of Fehling's solution A and 1 cm^3 Fehling's solution B. To this test-tube, add 1 cm^3 of **FA 8**. Warm the mixture in the water bath (at 80°C) for 15 minutes. **Repeat using FA 9 in place of FA 8.**		
4. Label a test-tube **FA 8**. Place about 2 cm depth of aqueous sodium hydroxide in this test-tube. To this test tube, add 5 drops of **FA 8**, followed by 5 drops of aqueous potassium manganate (VII) solution. Warm the mixture in the water bath for five minutes. **Repeat using FA 9 in place of FA 8.**		[3]

		(ii)	Complete **Table 3.2** below, using observations in **Table 3.1**, to identify the functional groups present in **FA 8** and **FA 9**. In each case, give evidence to support your conclusion. [2]

Table 3.2

	Functional group present	**Evidence**
FA 8		
FA 9		

(b) **(i)** State the feature(s) present in the structure in the compounds which gave a positive result for **Test 2**.

[1]

(ii) Based on the results in **Table 3.1**, identify one of the compounds, **FA8** or **FA9**, and give its structural formula.

[1]

(c) Solid **FA 10** contains an unknown cation. The cation is **not** NH_4^+ or Pb^{2+}.

Dissolve 1 spatula full of **FA 10** into 10 cm^3 of deionised water in a test-tube. This stock solution will be required for the subsequent tests to identify the cation present.

Cation analysis

You are provided with the following bench reagents to identify the cation in **FA 10**.

- $HNO_3(aq)$
- $H_2SO_4(aq)$
- $Ca(OH)_2(aq)$
- $NaOH(aq)$
- $NH_3(aq)$

(i) Based on the colour of the solution, identify the possible cations in **FA 10**.

………………………………………………………………………………..

………………………………………………………………………………..

[1]

(ii) You are required to choose reagents that will allow you to carry out tests to identify the cation present in **FA 10**.

Indicate in the space below, the reagents selected and the observations of the tests. Hence, identify the cation in **FA10**.

………………………………………………………………………………..

………………………………………………………………………………..

………………………………………………………………………………..

………………………………………………………………………………..

………………………………………………………………………………..

………………………………………………………………………………..

………………………………………………………………………………..

[4]

(d) **Plan**

Consider the following organic compounds.

pent-1-ene 1-chloropropane ethyl ethanoate ethanoyl chloride

Plan an investigation, using test-tube reactions, **other** than those used in **(a)** 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.
DO NOT carry out the experiment.

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

…………………………………………………………………………………………… [6]

[Total: 18]

[End of paper]

Answers

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

H

PIONEER JUNIOR COLLEGE

JC2 PRELIMINARY EXAMINATION
HIGHER 2

CANDIDATE NAME	

CT GROUP	1	6				INDEX NUMBER					

CHEMISTRY **9729/02**

Paper 2 Structured **12 September 2017**

2 hours

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

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

Answer **all** questions.

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

FOR EXAMINER'S USE			
Paper 1			**/ 30**
Paper 2			
1	/ 14	4	/ 12
2	/ 8	5	/ 13
3	/ 11	6	/ 17
Penalty		sf	unit
Paper 2			**/ 75**
Paper 3			**/ 80**
Paper 4			**/ 55**
Total			

This document consists of **19** printed pages.

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

1 **(a)** Carbon dioxide, produced mainly from the burning of fossil fuels, is a greenhouse gas which trapped heat within the Earth's atmosphere, causing global warming and potentially catastrophic global climate change. One major source of carbon dioxide produced worldwide is from the rapidly expanding aviation industry.

(i) Commercial passenger jet-liners combust kerosene as fuel. The formula of kerosene may be taken as $C_{14}H_{30}$. Write a balanced equation, **with state symbols**, for the complete combustion of kerosene.

[1]

$C_{14}H_{30}(l) + 43/2\ O_2(g) \rightarrow 14CO_2(g) + 15H_2O(l)$

In 2017, Singapore Airlines announced that it will be launching the world's longest commercial non-stop passenger flight from Singapore to New York, with a flight distance of 15,000 km. The ultra-long range Airbus A350 aircraft used on this route burns 7.5 kg of kerosene per km.

(ii) Calculate the mass of carbon dioxide produced, in tonnes, during this flight.
[1 tonne = 1000kg]

[3]

Mass of $C_{14}H_{30}$ used in the flight = (7500 g) × 15,000 = 1.125×10^8 g

Amount of $C_{14}H_{30}$ = $(1.125 \times 10^8) \div [14(12.0) + 30(1.0)]$ = 5.682×10^5 mol

Since 1 mol of $C_{14}H_{30}$ ≡ 14 mol of CO_2,

Therefore, 5.682×10^5 mol ≡ 7.954×10^6 mol CO_2.

Mass of CO_2 produced = $(7.954 \times 10^6) \times (12.0 + 32.0) = 3.50 \times 10^8$g
= **350 tonnes**

(iii) Apart from carbon dioxide, nitrogen dioxide is another air pollutant found in the flue gases from the jet engine of aircrafts. Explain how nitrogen dioxide is produced in the jet engine. [1]

Atmospheric nitrogen gas and oxygen gas react under the high temperature and pressure of the jet engine to produce nitrogen dioxide.

(iv) Why is it important to remove nitrogen dioxide from the flue gases? [1]

Nitrogen dioxide is (covalent oxide) acidic oxide and dissolve in water to form acid rain which is corrosive.

(b) Scientists have been studying the idea of carbon capture and storage technologies to try to remove atmospheric carbon dioxide on an industrial scale. One possible technology is called *calcium looping*. This process involved using calcium oxide to react with the atmospheric carbon dioxide to form calcium carbonate (i.e. limestone) which can then be stored away in abandoned mines.

$$CaO(s) + CO_2(g) \rightarrow CaCO_3(s) \qquad \Delta H_1$$

(i) Using the space below, construct a energy cycle diagram to calculate ΔH_1 using the following data.

standard enthalpy change of formation of CaO(s)	-635 kJ mol^{-1}
standard enthalpy change of formation of $CaCO_3$(s)	-1207 kJ mol^{-1}
standard enthalpy change of combustion of C(s)	-394 kJ mol^{-1}

[3]

$$\begin{tikzcd}
Ca(s) + C(s) + 3/2\ O_2(g) \arrow[r, "\Delta H_f(CaCO_3(s))"] \arrow[d, "\Delta H_f(CaO\ (s))"'] & CaCO_3(s) \\
CaO(s) + C(s) + O_2(g) \arrow[r, "\Delta H_c(C(s))"] & CaO(s) + CO_2(g) \arrow[u, "\Delta H_1"']
\end{tikzcd}$$

By Hess' Law,
$\Delta H_f(CaCO_3(s)) = \Delta H_f(CaO_3(s)) + \Delta H_c(C(s)) + \Delta H_1$
$(-1207) = (-635) + (-394) + \Delta H_1$
$\Delta H_1 =$ **-178 kJ mol^{-1}**

(ii) Like calcium carbonate, aluminum oxide is a major components of naturally occurring rocks. Explain clearly, in terms of chemical bonding and structure, why aluminum oxide is insoluble in water.

[3]

Aluminum oxide has a giant ionic lattice structure with its Al^{3+} cations and O^{2-} anions held by strong ionic bonds. Energy released during the formation of the ion-dipole interactions between water and the ions in aluminum oxide is insufficient to overcome the strong ionic bonds between the Al^{3+} cations and O^{2-} anions. Hence, aluminum oxide is insoluble in water.

(c) Carbonate buffers are widely used for biochemical purposes.

A student wishes to form a CO_3^{2-}/ HCO_3^- buffer in the laboratory.

Given that the carbonate ion has a K_b of 1.8×10^{-4} mol dm^{-3}, calculate the volume of 0.10 mol dm^{-3} of hydrochloric acid that he has to add to 25.0 cm^3 of 0.12 mol dm^{-3} of Na_2CO_3, to form a resulting buffer solution of pH 9.50. [2]

$pOH = pK_b + \log[HCO_3^-]/ [CO_3^{2-}]$

$14- 9.5 = - (-3.745) + \log[HCO_3^-]/ [CO_3^{2-}]$
$[HCO_3^-]/ [CO_3^{2-}] = \underline{5.69}$

	CO_3^{2-} +	H^+ →	HCO_3^-
Initial amount	0.003	+x	0
Change in amount	-x	- x	+ x
Final amount	0.003 –x	0	x

$[HCO_3^-]/ [CO_3^{2-}] = 5.69 = x/V \div (0.003-x)/V$
Solving, $x = 2.55 \times 10^{-3}$, volume of HCl = $\underline{25.5 \text{ cm}^3}$

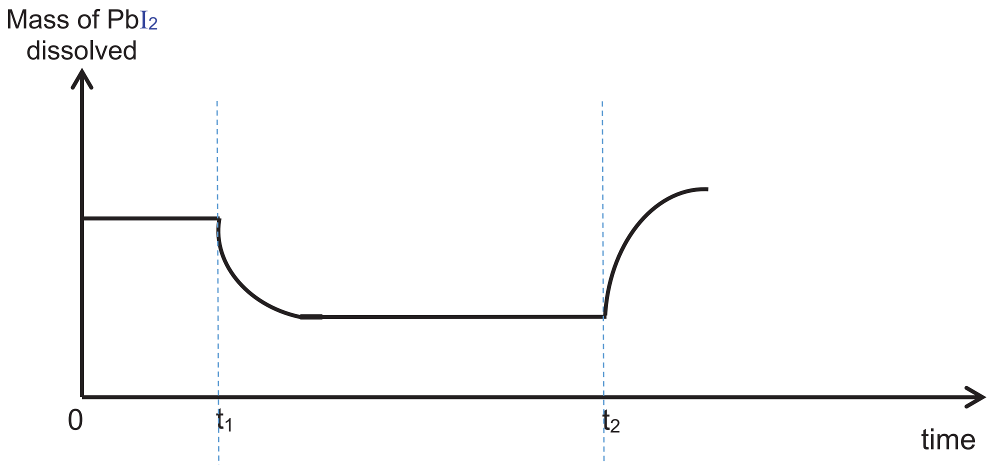
[Total:14]

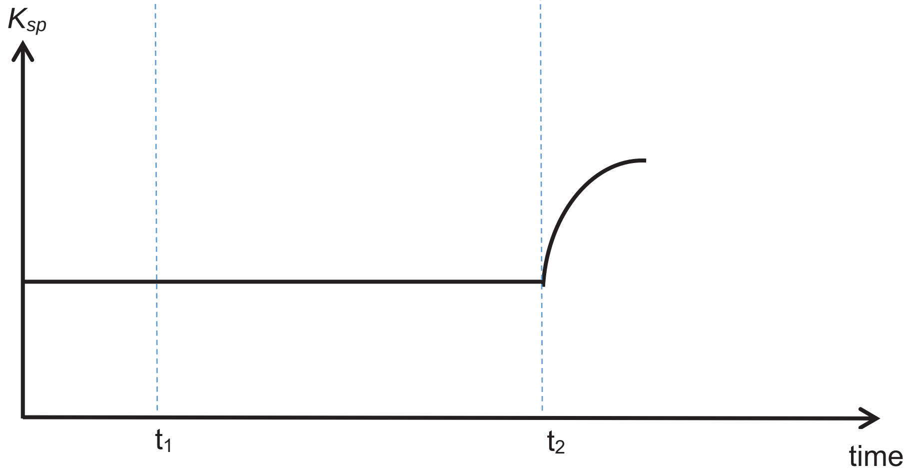
2 This question is about lead (II) halides.

(a) $PbI_2\,(s) + aq \rightleftharpoons Pb^{2+}(aq) + 2\,I^{-}\,(aq)$ $\quad \Delta H > 0$

A student wanted to investigate the solubility product and solubility of PbI_2, a sparingly soluble salt, under different conditions. He first added some solid PbI_2 into 100 cm^3 water at 15°C, and subsequently made two changes at t_1 and t_2.

The graphs below show the mass of PbI_2 dissolved and solubility product of PbI_2 against time.





Some possible changes listed below were made by the student at t_1 and t_2.

1. Cool reaction mixture to 10°C in water bath
2. Heat reaction mixture to 50°C in water bath
3. Add $AgNO_3(s)$
4. Pump in $Pb(NO_3)_2(aq)$

With reference to **both** graphs, suggest and explain which of the above changes (1)-(4), was made at t_1 and t_2 respectively.

change made at t_1:

explanation:.. [2]

change made at t_2:

explanation:.. [2]

Change made at t_1: (4). Addition of $Pb(NO_3)_2(aq)$
$PbI_2(s) + aq \rightleftharpoons Pb^{2+}(aq) + 2I^-(aq)$ eqm

Explanation: Addition of $Pb(NO_3)_2(aq)$, hence $[Pb^{2+}]$ increases, according to Le Chatelier's Principle, position of equilibrium shifts left to decrease $[Pb^{2+}]$. Thus, less PbI_2 dissolve and K_{sp} remain constant as K_{sp} is temperature dependent.

change made at t_2 : Heat reaction mixture to 50 °C in water bath
explanation: According to Le Chatelier's Principle, as temperature increase, the position of equilibrium shifts right to favour the forward endothermic reaction, to absorb heat and decrease temperature.
Hence, $[Pb^{2+}]$ and $[I^-]$ increase. The mass of PbI_2 dissolved and K_{sp} increase.

(b) The values of the solubility products of two salts, lead (II) iodide, PbI_2, and silver (I) iodide, AgI are given below.

$$K_{sp}(PbI_2) = 3.97 \times 10^{-9}\ mol^3\ dm^{-9}$$
$$K_{sp}(AgI) = 8.3 \times 10^{-17}\ mol^2\ dm^{-6}$$

A lab technician added solid PbI_2 into water, shaking it thoroughly. He filtered off the remaining solid, leaving a saturated solution **H**.

He added drops of aqueous silver nitrate to **H**, until AgI just precipitates.

Determine the concentration of Ag^+ when AgI just precipitates. [2]

	$PbI_2(s)$	+ aq	$\rightleftharpoons$	$Pb^{2+}(aq)$	+ $2I^-(aq)$
Eqm conc / mol dm^{-3}				s	$2s$

$[Pb^{2+}][I^-]^2 = 3.97 \times 10^{-9} = (s)(2s)^2 = 4s^3$
$s = 9.975 \times 10^{-4}$ mol dm^{-3}

In X, $[I^-] = 2s = 2 \times 9.975 \times 10^{-4} = 1.996 \times 10^{-3}$ mol dm^{-3}
When AgI just precipitates; IP (AgI) = K_{sp} (AgI)
$[Ag^+][I^-] = 8.3 \times 10^{-17}$
$[Ag^+](1.996 \times 10^{-3}) = 8.3 \times 10^{-17}$
$[Ag^+] = 4.16 \times 10^{-14}$ mol dm^{-3} (3.s.f)

(c) When a precipitate is formed, $\Delta G^{\ominus}_{ppt}$, in J mol^{-1}, is given by the following expression.

$$\Delta G^{\ominus}_{ppt} = 2.303\ RT \log K_{sp}$$

Given that for lead(II) chloride, $PbCl_2$, K_{sp} = 1.70 x 10^{-5} mol^3 dm^{-9} at 298 K, calculate $\Delta^{\ominus}G_{ppt}$ for $PbCl_2$ at 298K.

Hence explain if lead(II) chloride is soluble at 298K. [2]

$\Delta G^{\theta}_{ppt}(PbCl_2)$ = 2.303 RT log $K_{sp}(PbCl_2)$
= 2.303 x 8.31 x (298) log (1.70 x 10^{-5})
= **<u>- 27200 J mol^{-1}</u>** <0, hence energetically feasible to ppt out so it is **<u>not soluble.</u>**

[Total:8]

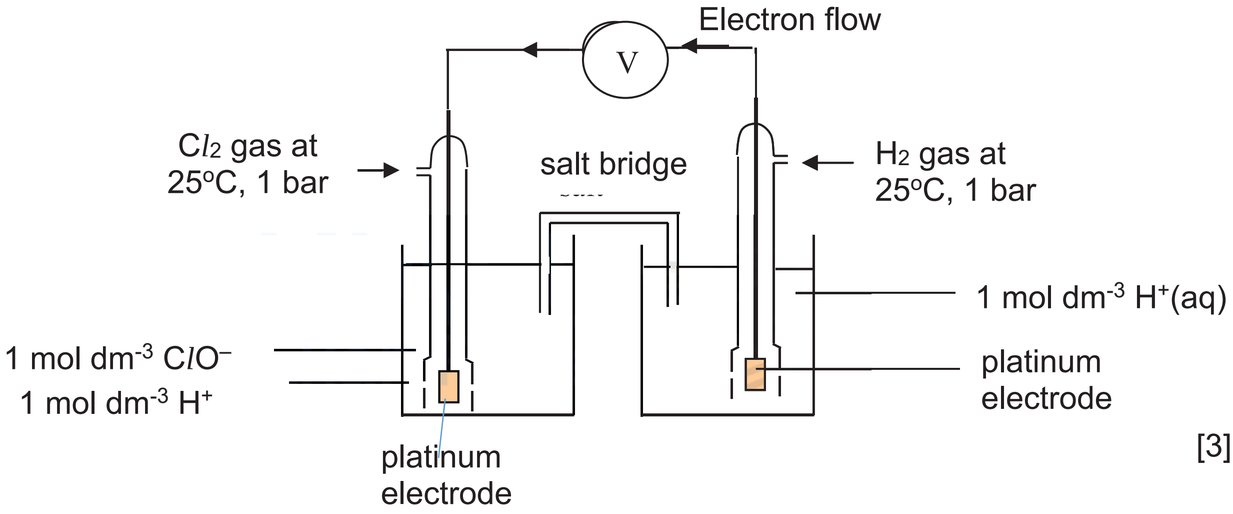
3 **(a)** Chlorine has been extensively used in the manufacture of many compounds. One such compound is household bleach, which contains sodium chlorate(I), NaClO.

The chlorate(I) ion acts as a powerful oxidising agent in acidic solution:

$$2ClO^-(aq) + 4H^+(aq) + 2e^- \rightleftharpoons Cl_2(g) + 2H_2O(l) \qquad E^{\ominus} = +1.64\ V$$

(i) Define the term *standard electrode potential*.
It is the **<u>potential difference between a standard hydrogen electrode and a half cell</u>** under standard conditions of **<u>25°C</u>**, **<u>1 bar</u>** and <u>concentration of all ions involved is **1 mol dm^{-3}**</u>.

(ii) Draw a fully labelled diagram, to show how the standard electrode potential, $E^{\ominus}(ClO^-/Cl_2)$, could be measured.



[3]

(iii) Draw a fully labelled diagram to show how the $E^{\ominus}$cell of the cell in **(a)(ii)** could be measured.
…………………………………………………………………………………………[3]

(b) Use the *Data booklet* to predict the reaction, if any, that would occur when the following pairs of reagents are mixed in acidified aqueous solution. If a reaction occurs, write a balanced equation and calculate $E^\ominus_{cell}$.

(i) $NaClO(aq)$ and $H_2O_2(aq)$

$2ClO^-(aq) + 4H^+(aq) + 2e^- \rightleftharpoons Cl_2(g) + 2H_2O(l)$ $E^\ominus = +1.64$ V

$H_2O_2 \rightleftharpoons O_2(g) + 2H^+(aq) + 2e^-$ $E^\ominus_{ox} = -0.68$ V

$E^\ominus_{cell} = +1.64 + -0.68 =$ **+0.96V>0 (3 s.f)**

$H_2O_2 + 2ClO^- + 2H^+ \rightarrow O_2 + Cl_2 + 2H_2O$ [2]

(ii) $NaClO(aq)$ and $Cr(NO_3)_3(aq)$

$2ClO^-(aq) + 4H^+(aq) + 2e^- \rightleftharpoons Cl_2(g) + 2H_2O(l)$ $E^\ominus = +1.64$ V

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

$E^\ominus_{cell} = +1.64 - 1.33 = +0.31V > 0$

$2Cr^{3+} + 1H_2O + 6ClO^-(aq) \rightarrow 3Cl_2 + Cr_2O_7^{2-} + 2H^+$ [2]

(c) When a few drops of aqueous sodium carbonate was added to chromium(III) nitrate, carbon dioxide gas and a grey-green precipitate, **R**, were obtained.

Explain why CO_2 is given off in the above reaction, and identify precipitate **R**.

Cr^{3+} has a high charge density. Hence $[Cr(H_2O)_6]^{3+}$ can undergo partial hydrolysis in water to produce H^+ ions, forming CO_2 with carbonate ions.

$Cr(OH)_3$

$[Cr(H_2O)_6]^{3+} \rightleftharpoons [Cr(H_2O)_5(OH)]^{2+} + H^+$

$2H^+ + CO_3^{2-} \rightarrow H_2O + CO_2$ [3]

[Total:11]

4 Manganese is a first row d-block element in the Periodic table with a melting point of 1246°C. Like many other d-block elements, manganese shows properties that are atypical from other s-block metals, such as potassium and calcium.

Its minerals are widely distributed, with manganese dioxide and manganese carbonate being the most common. Manganese is also an essential element in living organisms, where many types of enzymes make use of the variable oxidation states of manganese to take part in the various redox reactions.

(a) **(i)** Explain why manganese has a much higher melting point than calcium, which is found in the same period.

Both Mn and Ca are metals with strong metallic bonds/ electrostatic force of attraction between the positive metal ions and this sea of delocalized electrons.

- The small difference in energy between the 4d and 5s orbitals allows for the number of **delocalised** electrons in the metallic lattice to be increased.
- The ionic radius of manganese is smaller than that of calcium, hence increasing the charge density of manganese ions.
- With a bigger number of delocalised electrons and a higher charge density of manganese ions, more energy is required to break these stronger metallic bonds in manganese. Thus manganese has a much higher melting point than calcium.

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

(ii) Explain why the density of manganese is significantly greater than that of calcium.

- Manganese has a greater atomic mass than calcium and has a smaller atomic radii than calcium.

- This results in manganese having higher density than calcium.

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

(b) Heating a mixture of KOH and MnO_2 in air gives potassium manganite, K_2MnO_4, which is an important precursor to potassium permanganate, $KMnO_4$, a common oxidising agent.

(i) State the oxidation state of manganese and hence, write the electronic configuration of the manganese ion in each of the following compounds:

MnO_2 :

Oxidation state: +4
Electronic configuration: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^3$

K_2MnO_4:

Oxidation state: +6
Electronic configuration: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^1$

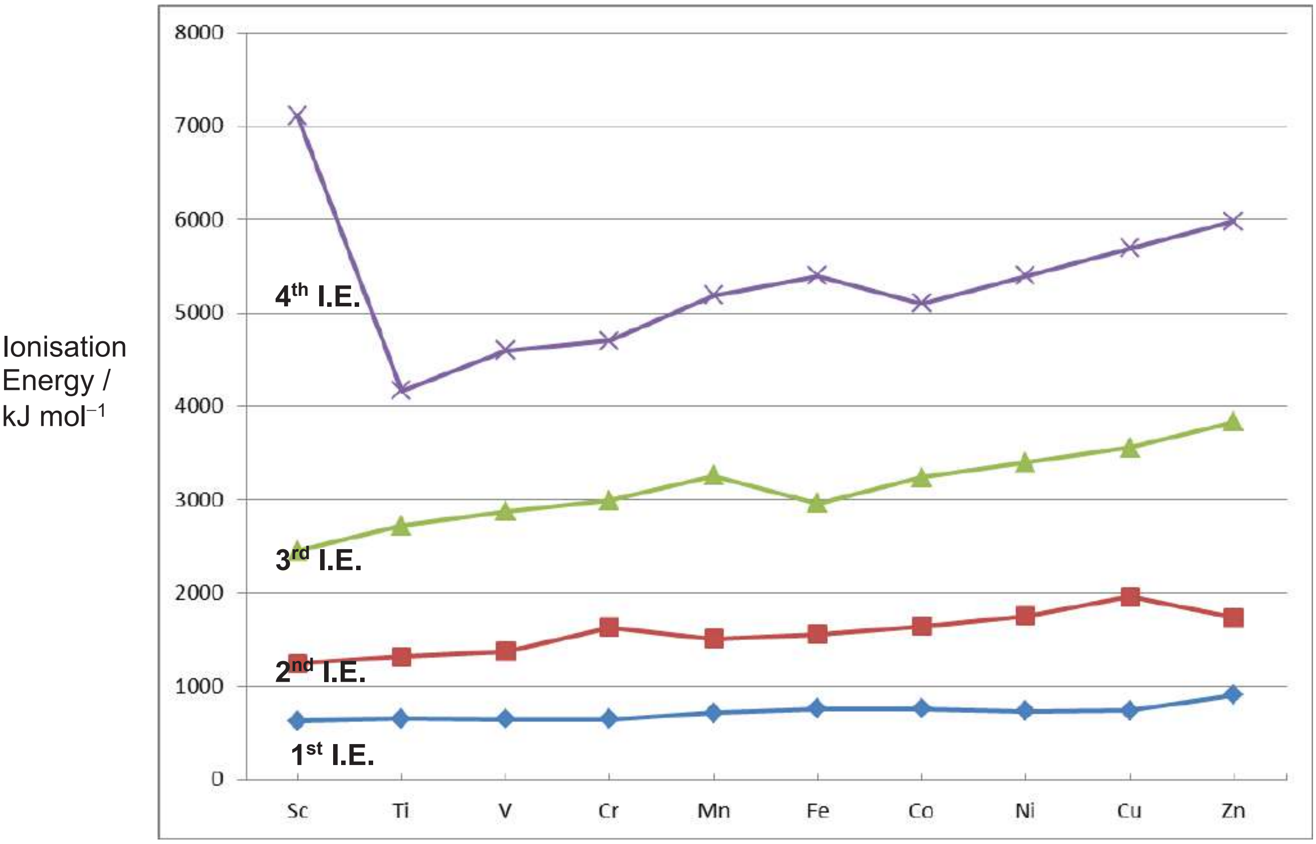
……………………………………………………………………………………….....[2]

(ii) Write a balanced equation for the redox reaction between MnO_2, KOH and air.

$2MnO_2 + 4KOH + O_2 \rightarrow 2K_2MnO_4 + 2H_2O$

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

(c) The graph below shows the variation of the first to fourth ionisation energies for the first row d–block elements scandium to zinc.



(i) Give an equation that represents the second ionisation energy of manganese.

$Mn^+(g) \longrightarrow Mn^{2+}(g) + e^-$

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

(ii) Explain why the first ionisation energies of the elements Ti to Cu, are relatively invariant across the Period. [2]

- Across the period from Ti to Cu, there is an increase in number of protons, hence nuclear charge increases.
- However, electrons are added to the penultimate shell (inner 3d sub-shell), resulting in an increase of shielding effect too.
- These 3d orbital electrons shielded the outer 4s orbital electrons from the increased nuclear charge. As a result, the effective nuclear charge is almost

constant (only increases very slightly) thus IE is almost constant.

(iii) Explain why the fourth ionisation energy of cobalt is lower than that of iron.

Fe: : [Ar]$3d^6 4s^2$
Co: [Ar]$3d^7 4s^2$

- Electronic configuration of
  Fe^{3+} : [Ar]$3d^5$
  Co^{3+} : [Ar]$3d^6$
  OR
- The 4th electron from Co is removed from 3d orbital containing a pair of electrons while the 4th electron from Fe is removed from a singly occupied 3d orbital.

Due to inter-electron repulsion between the paired 3d electrons in Co^{3+}, the energy required to remove the 4th electron in Co is lower than in Fe.

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

[Total:12]

5 **(a)** Structure elucidation is an important skill that chemists must acquire to help them determine the chemical structures of organic compounds.

A novice chemist requires your assistance in determining the structure of an aromatic organic compound **P**, that she found in the laboratory.

The molecular formula of compound **P** is $C_9H_{11}ON$, and **P** contains two functional groups.

(i) An orange precipitate is observed when compound **P** is reacted with 2,4-dinitrophenylhydrazine. Name the type of reaction that has taken place. From this observation, deduce the functional groups that could be present in compound **P**.

Condensation.

Aldehyde or Ketone (reject carbonyl)

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

(ii) No silver mirror is formed when compound **P** is heated with hot ammoniacal silver nitrate (mixture of aqueous ammonia and aqueous silver nitrate).
Which of the functional groups you named in **(a)(i)**, is confirmed by this observation?

Ketone.

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

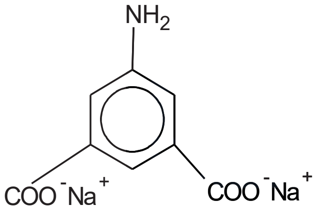
(iii) When compound **P** is reacted with bromine water in excess, a white solid which has $M_r = 385.7$, is formed.
Deduce the molecular formula of the white solid that is formed.

$C_9H_8NOBr_3$

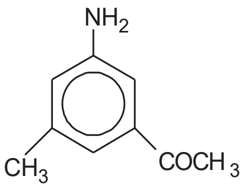
Phenylamine reacts with the aqueous bromine to form the white solid, which is a tribrominated substituted product in which 3 hydrogen atoms on the benzene ring are being substituted with bromine atoms.

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

(iv) Compound **P** reacts with hot potassium manganate(VII) in aqueous sodium hydroxide. A product with the molecular fomula, $C_8H_5NO_4Na_2$, is formed.
Draw the structure of the product.



(v) You now have enough information to determine the structural formula of compound **P**. Draw the structure for **P**, explaining clearly why you have placed each of the two functional groups in their respective positions.



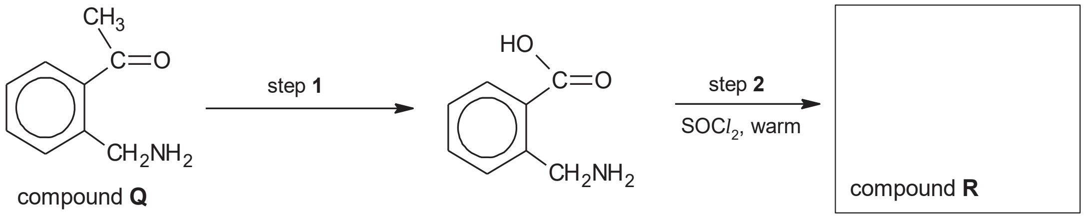
The phenylamine group in compound **P** is 2,4-directing.
Hence in **(a)(iv)**, 3 bromine atoms are substituted for 3 hydrogen atoms at 2, 4, and 6 position wrt to -NH_2 group attached to benzene ring.
Thus, the -CH_3 and the -$COCH_3$ groups will be at positions 3 or 5.

…………………………………………………………………………………………[2]

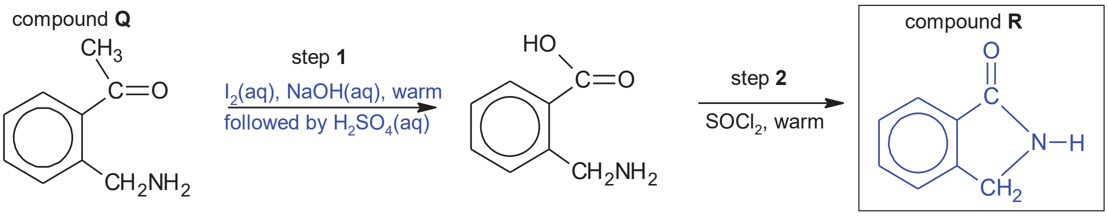
(b) Compound **Q**, $C_9H_{11}ON$, is a structural isomer of compound **P**.

The diagram below shows a possible reaction scheme for converting compound **Q** to form compound **R,** C_8H_7NO.

(i) Complete the diagram by suggesting the reagents and conditions for step **1**, and give the structural formula of compound **R**.



[2]



(ii) It was found that the yield of compound **R** was low. Suggest a reason for this. [1]

Acid in step 1 protonates basic amine OR
Intramolecular acid base reaction between acidic –COOH and basic –CH_2NH_2 group in intermediate compound formed in step 1

(c) The table below shows the pK_b values of two organic nitrogen compounds in aqueous solutions.

Compound	***p*K$_b$**
methylamine, CH_3NH_2	3.36
trimethylamine, $(CH_3)_3N$	4.19

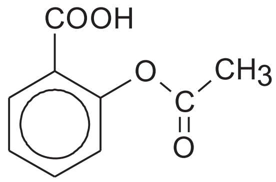
Using the data provided in the table above, suggest an explanation on the relative basicities of these two compounds.

[3]

Methylamine is more basic than trimethylamine.
The basicity of an organic nitrogen compound depends on the availability of the lone pair of electrons on the nitrogen atom to accept a proton.
Either explanation is acceptable:
1) Steric Factor:
The presence of 3 alkyl groups in trimethylamine (compared to 1 alkyl group in methylamine) results in steric hindrance, which hinders/makes it more difficult for the lone pair on nitrogen to accept the proton.
OR
2) Hydration Factor:
Hydration effect refers to the stabilisation of the protonated amine by water molecules. The water molecules form hydrogen bonds with the protonated amine and release energy called hydration energy, stabilising the protonated alkylamine.
Hydration due to hydrogen bonding is greater in protonated methylamine, and hence it is the most basic.

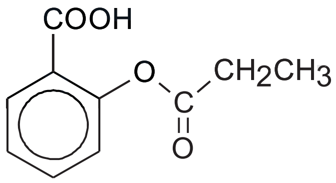
[Total:13]

6 **(a)** Acetylsalicylic acid (ASA), which is extracted from the leaves of the willow tree, has been used for its health effects for at least 2,400 years. It is an important medication that is used to treat pain, fever, and inflammation.



Acetylsalicylic acid

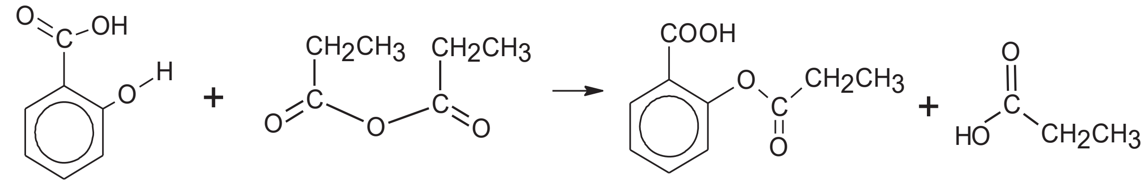
A chemist wanted to form a derivative of ASA, compound **T** below:



Compound **T**

One method to form compound **T** was to react 2-hydroxybenzoic acid and propanoic anhydride in reaction **1** below.

Reaction **1**


2-hydroxybenzoic acid propanoic anhydride compound **T**

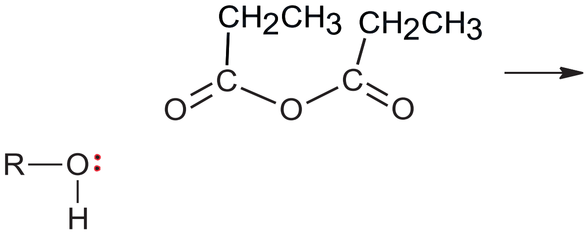
(i) State the type of reaction that has occurred in the formation of compound **T** in reaction **1**.
Nucleophilic acyl substitution

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

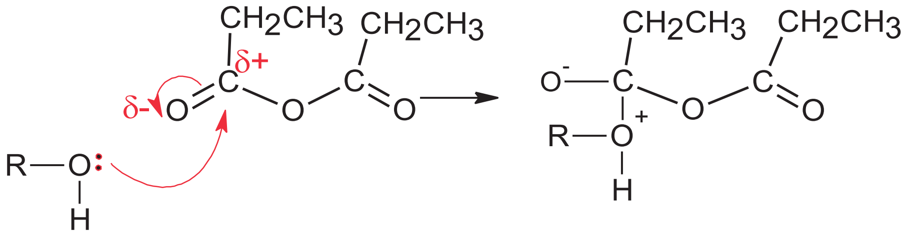
The mechanism of reaction **1** consists of three steps and is described below:
Step 1:
The phenol group on 2-hydroxybenzoic acid acts as a nucleophile and attacks one of the reactive carbons in propanoic anhydride to form only one intermediate **W**. The intermediate **W** contains both a cationic oxygen and an anionic oxygen.
Step 2:
A proton is released from intermediate **W** to form intermediate **X**.
Step 3:
From intermediate **X**, a carboxylate anion is expelled as a leaving group, and an ester **Y** is formed as the other product.
Step 4:
Protonation of the carboxylate anion formed in step 3 produces a carboxylic acid.

(ii) Draw all four steps in the full mechanism for the reaction between 2-hydroxybenzoic acid and propanoic anhydride.
(you may use ROH to represent 2-hydroxybenzoic acid in your answer.)

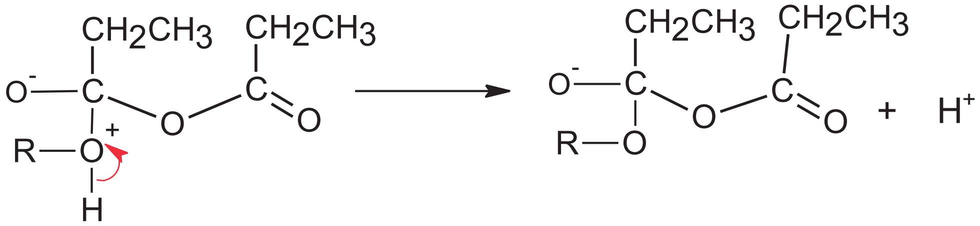
For the first step of the mechanism, *complete* the diagram shown below and draw the remaining three steps of the mechanism in the space given below each step. Show all intermediates, relevant charges, lone pairs of electrons and indicate the movement of electron pairs with curly arrows in all the steps.
<u>Step 1</u>
Let R–O–H represents 2-hydroxybenzoic acid.



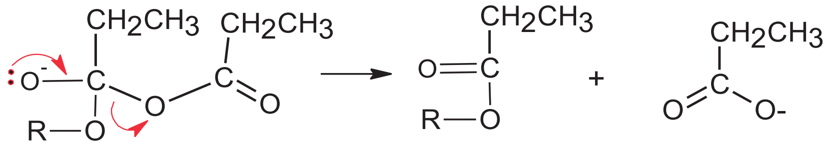
Step 1



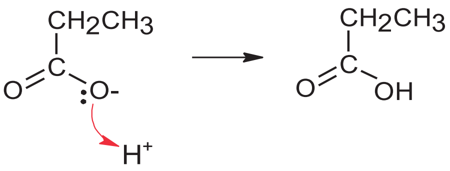
Step 2



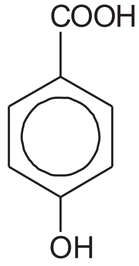
Step 3



Step 4

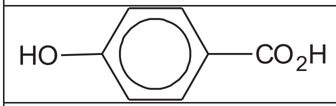
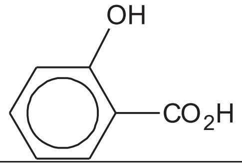


(iii) An isomer of 2-hydroxybenzoic acid is shown below:



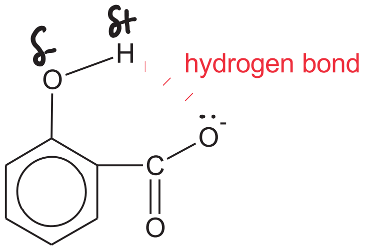
4-hydroxybenzoic acid

Both 2-hydroxybenzoic acid and 4-hydroxybenzoic acid are dibasic acids that ionises in two stages. The acid dissociation constant, pK_1, for the first stage of dissociation is given below.

	pK_1
	4.54
	2.97

With the aid of a diagram, explain why 2-hydroxybenzoic acid has a lower pK_1.

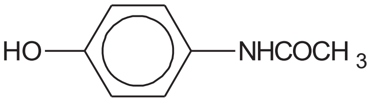
2-hydroxybenzoic acid has lower pK_1 thus it is a stronger acid than 4-hydroxybenzoic acid.



Due to the close proximity of the –COO⁻ and -OH groups in 2-hydroxybenzoate ion, the anion is stabilised by intramolecular hydrogen bonding.
As such, the equilibrium position for the dissociation of 2-hydroxybenzoic acid will lie more towards the right, releasing more H^+, and hence, stronger acid.

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

(b) Another medicine that is used widely to treat fever and pain is paracetamol, or commonly known as panadol.



Paracetamol

Some information on paracetamol is provided in Table 1 below.

Data on paracetamol	
Molecular Formula	$C_8H_9NO_2$
Density	1.263 g/cm^3
Melting Point	169°C
Boiling Point	420°C
Solubility in water	14 mg/ml
Bioavailability*	75% (oral) 100% (intravenous)
Biological half-life**	2 hours

Table 1

**Bioavailability refers to the percentage of a drug which enters the blood circulation when introduced into the body and hence able to have an active and effective effect.*

***Biological half-life of a drug is the time taken for the drug to reduce to half its original amount in the body.*

(i) Paracetamol can be produced from the reaction between 4-aminophenol and ethanoic anhydride as shown below.

C_6H_7NO	+	$C_4H_6O_3$	→	$C_8H_9NO_2$	+	$C_2H_4O_2$
4-aminophenol		ethanoic anhydride		paracetamol		
(M_r : 109)		(M_r : 102)		(M_r : 151)		

It is known that the yield of this reaction is only 60%. Calculate the minimum masses of the reactants that are required to produce 10 g of paracetamol.

Mass of 4-aminophenol required = $\frac{10}{151}\times\frac{100}{60}\times 109$ = 12.0 g

Mass of ethanoic anhydride required = $\frac{10}{151}\times\frac{100}{60}\times 102$ = 11.3 g

(ii) A doctor wishes to prescribe oral medication for one of his patients suffering from headache. In order for the medicine to be effective, the patient requires a recommended dosage of 560 mg of paracetamol in her body.

How many 250 mg paracetamol tablets should the patient take each time?

Mass of paracetamol that must be in the patient's body = 560 mg
Mass of paracetamol that must be taken orally by patient
= 560 / (75 /100)
= 747 mg
Number of 250 mg paracetamol tablets that the patient should take
= 747 / 250 = 2.99 ≈ 3 tablets

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

(iii) A patient suffering from acute dental pain is advised to consume orally, four 250 mg paracetamol tablets.

To effectively alleviate his pain, at any point of time, the amount of paracetamol in his body **must not** drop below 93 mg.

With reference to relevant data from Table 1, and the use of suitable calculations, determine the maximum number of hours that the oral medication prescribed above remains effective, and show clearly whether the doctor should advise the patient to take four tablets of paracetamol once in every 4 hours, 6 hours, or 8 hours. [2]

Mass of paracetamol in 4 x 250 mg tablets = 1000 mg
Mass of paracetamol that will be useful and effective = 75% x 1000 = 750 mg
Since biological half-life of paracetamol is 2 hours,

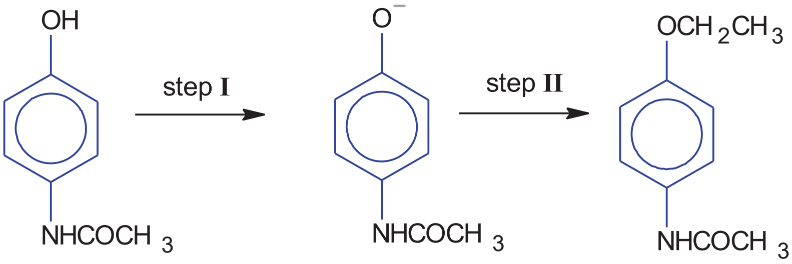
$$750\text{ mg} \xrightarrow{\text{2 hours}} 375\text{ mg} \xrightarrow{\text{2 hours}} 187.5\text{ mg} \xrightarrow{\text{2 hours}} 93.75\text{ mg}$$

It takes 2x3 = 6 hours for oral medication to remain effective, for the amount of paracetamol in his body to be at least **must not** drop below 93 mg

From the above calculation, it can be seen that the patient should take 4 tablets of paracetamol once every 6 hours.

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

(c) **(i)** Phenacetin was once used as an analgesic (pain killing drug). It can be synthesised from paracetamol below.



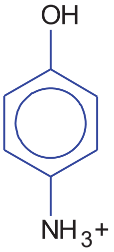
paracetamol

phenacetin

Suggest reagents and conditions for step **I** and **II**.

step **I** : NaOH(aq) (reject heat) or Na
step **II**: CH_3CH_2Br, heat

(ii) A student added aqueous sulfuric acid to paracetamol and heated it. Suggest the products obtained.



+ CH_3COOH

[Total:17]

End of paper

H

PIONEER JUNIOR COLLEGE

JC2 PRELIMINARY EXAMINATION
HIGHER 2

CANDIDATE NAME	

CT GROUP

1	6			

INDEX NUMBER

CHEMISTRY

9729/03

Paper 3 Free Response

15 September 2017

2 hours

Candidates answer on separate paper.

Additional Materials: Answer Paper
Data Booklet
Cover Page

READ THESE INSTRUCTIONS FIRST

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

Section A
Answer **all** questions.

Section B
Answer **one** question.

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

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

This document consists of **17** printed pages.

Section A

Answer all questions in this section.

1 Compounds containing halogens form a large class of chemicals, which are of industrial importance and are synthesised in huge quantities worldwide.

(a) Phosgene, $COCl_2$, is a gas which was produced during World War I, and was used as a chemical weapon. One method to produce phosgene from trichloromethane is as shown below.

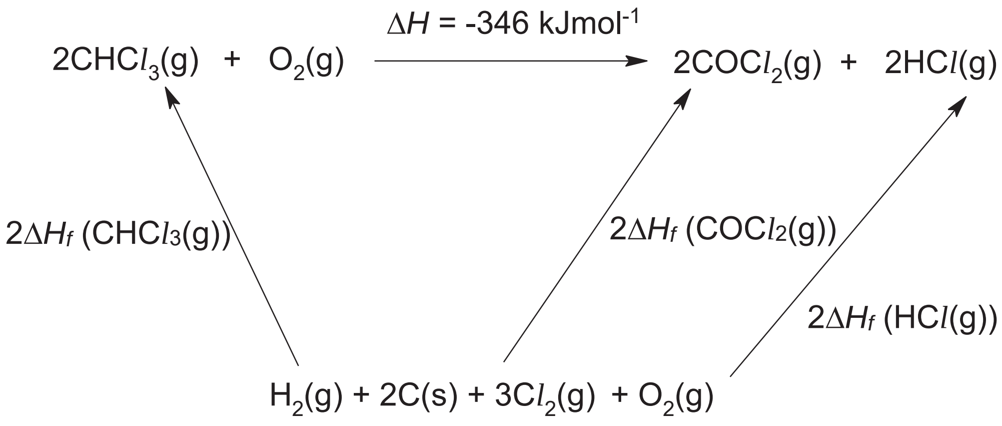
$$2CHCl_3(g) + O_2(g) \rightarrow 2COCl_2(g) + 2HCl(g) \qquad \Delta H = -346 \text{ kJ mol}^{-1}$$

Using the data below, calculate the standard enthalpy change of formation of $HCl(g)$.

standard enthalpy change of formation of $CHCl_3(g)$	-103 kJ mol^{-1}
standard enthalpy change of formation of $COCl_2(g)$	-184 kJ mol^{-1}

[1]

no need cycle



By Hess' Law,

$2\Delta H_f (CHCl_3(g)) + \Delta H = 2\Delta H_f (COCl_2(g)) + 2\Delta H_f (HCl(g))$

$2(-103) + (-346) = 2(-184) + 2\Delta H_f (HCl(g))$

$\Delta H_f (HCl(g))=$ **-92.0 kJ mol^{-1}**

(b) Aqueous hydrochloric acid is another chemical with many industrial uses. It can be obtained by reacting hydrogen gas and chlorine gas in the presence of UV light, followed by dissolving the hydrogen chloride gas in water.

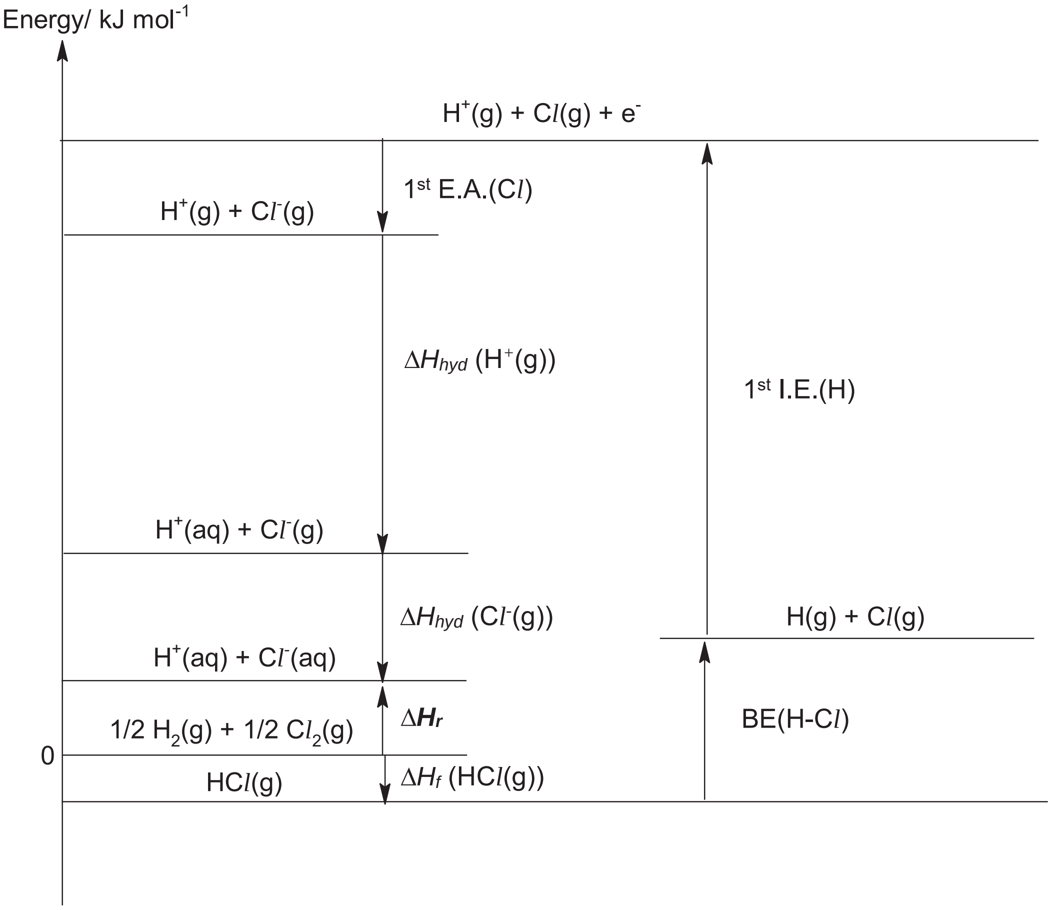
The equation for this reaction is as shown below.

$$\tfrac{1}{2}H_2(g) + \tfrac{1}{2}Cl_2(g) \rightarrow H^+(aq) + Cl^-(aq) \qquad \Delta H_r$$

Using the Data Booklet, the data in the table below, and your answer in **(a)**, construct an appropriate energy-level diagram to calculate ΔH_r.

	$\Delta H^{\ominus}$/ kJ mol^{-1}
First ionisation energy of H(g)	+1310
First electron affinity of C*l*(g)	– 364
Standard enthalpy change of hydration of Cl^- (g)	– 381
Standard enthalpy change of hydration of H^+(g)	– 1130

[4]



By Hess' Law,

$\boldsymbol{\Delta H_r}$ = ΔH_f (HC*l*(g)) + BE(H-C*l*) + 1st I.E.(H) + 1st E.A.(C*l*) + ΔH_{hyd} (H^+(g)) + ΔH_{hyd} (Cl^-(g))

$\boldsymbol{\Delta H_r}$ = (-92) + 431 + (+1310) + (– 364) + (– 1130) + (– 381)

BE(H-C*l*) = **-226 kJ mol^{-1}**

Elements should be clearly placed at ground state of energy = 0.

(c) When heated, Group 17 hydrides, HX, undergo thermal decomposition.

$$HX \longrightarrow \tfrac{1}{2} H_2 + \tfrac{1}{2} X_2$$

Using the data on bond energies of the various H-X bonds given below, predict and explain how the thermal stability of the hydrides varies down the Group 17.

Bonds	**Bond energies/ kJ mol^{-1}**
H-C*l*	+431
H-Br	+366
H-I	+299

[2]

The thermal stability of Group 17 hydrides **decreases** down the group.

Down the group, the **atomic radii of the halogen increases**, which resulted in the less effective overlap due to the bigger orbitals involved. The **H-X bond length increases,** resulting in decreasing bond energy and lesser energy is required to break the weaker H-X bond for decomposition and the thermal stability decreases.

(d) Seawater is an important source of ionic halides like sodium chloride, sodium bromide and sodium iodide.

When silver nitrate is added to separate test-tubes containing aqueous sodium chloride, sodium bromide and sodium iodide, the various AgX (X = C*l*, Br and I) precipitates were observed. The solubilities of these precipitates upon addition of dilute NH_3 and concentrated aqueous NH_3, are recorded below.

	NaC*l*	**NaBr**	**NaI**
To NaX(aq), add $AgNO_3$(aq)	white ppt observed	cream ppt observed	yellow ppt observed
To the resulting mixture, add dilute NH_3(aq)	soluble	insoluble	Insoluble
To the resulting mixture, add excess concentrated NH_3(aq)	soluble	soluble	Insoluble

(i) Write the balanced ionic equation for the formation of the cream precipitate from adding silver nitrate to sodium bromide.

[1]

$Br^-(aq) + Ag^+(aq) \rightarrow AgBr(s)$

State symbols must be given as it is ionic equation.

(ii) Explain the effect of adding aqueous ammonia to each of the resulting mixture and clearly account for any difference in the observation. [3]

$AgX(s) \rightleftharpoons Ag^+(aq) + X^-(aq)$

$Ag^+(aq) + 2NH_3(aq) \rightleftharpoons [Ag(NH_3)_2]^+(aq)$ **reaction 2**

The **solubility product, K_{sp}, of the silver halides decreases down Group 17** (i.e. K_{sp} of AgC*l* > AgBr > AgI).

When aqueous ammonia solution is added, based on reaction **(2)**, the small amount of $Ag^+(aq)$ ions present in the resulting mixture is used up to form $[Ag(NH_3)_2]^+(aq)$ complex. This **decreases the concentration of $Ag^+(aq)$ ions** as a result and **the ionic product of the silver halide decreases** .

Since silver chloride has the largest K_{sp}, the **ionic product** drops below **K_{sp} of AgC*l*** and hence silver chloride dissolves when NH_3(aq) solution is added.

In contrast, silver bromide and sodium iodide has smaller K_{sp}. Hence, even though ionic product decreases, the **ionic products of both silver bromide and silver iodide are still larger than their respective K_{sp} values** and the precipitates remained insoluble when dilute NH_3(aq) solution is added.

However, with concentrated aqueous ammonia, the formation of diamminesilver(I) complex is sufficient to decrease the [Ag^+], thus causing the ionic product of AgBr to fall below its K_{sp} value thus ppt dissolves. This explains why AgBr(s) is soluble in concentrated NH_3(aq) but insoluble in dilute NH_3(aq).

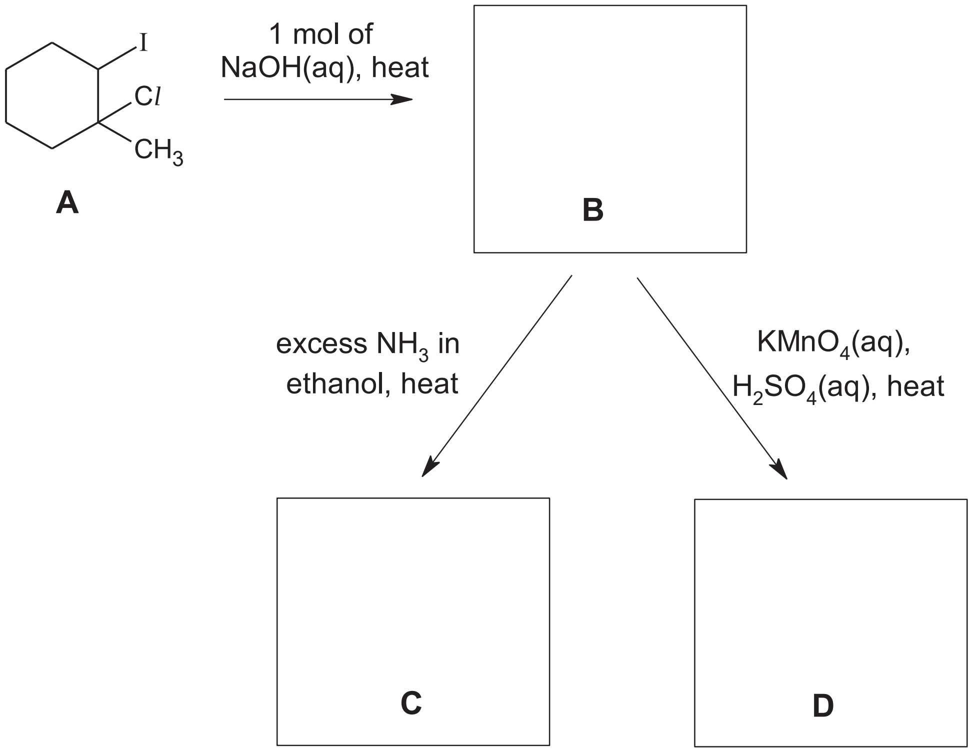
For AgI:
The formation of diamminesilver(I) complex in both dilute and concentrated aqueous ammonia is not sufficient to cause the ionic product of AgI to fall below its K_{sp} value (as the K_{sp} value of AgI is extremely low). Therefore, AgI(s) is insoluble in both dilute and concentrated NH_3(aq).

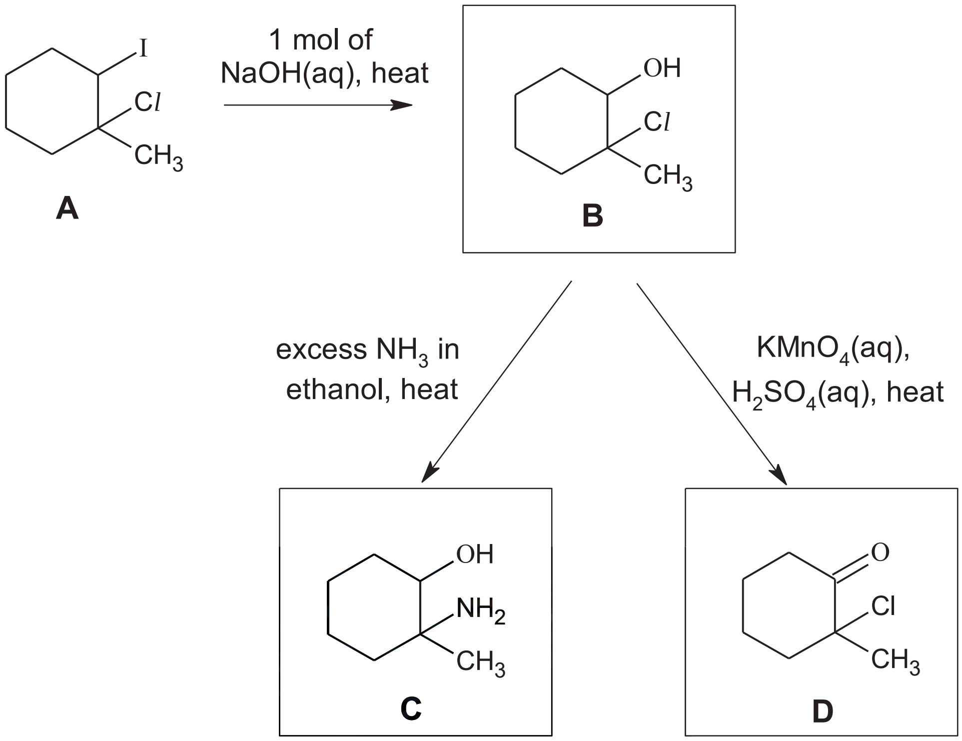
(e) Halogenoalkanes are widely synthesised by reacting halogens with alkenes. In turn, halogenoalkanes can undergo nucleophilic substitution using sodium hydroxide to form alcohols commercially.

(i) Give one reason why iodoalkanes are more reactive towards nucleophilic substitution with aqueous NaOH than the corresponding chloroalkanes. [1]

The bond energy of C–I is lower / C–I bond weaker than C– C*l*. C–I bond is more easily broken.
OR
C*l*$^-$ is also a weaker leaving group than I^- as C*l*$^-$ is a stronger base than I^-.

(ii) A sequence of reactions, starting from compound **A**, a dihalogeno compound, is shown below.



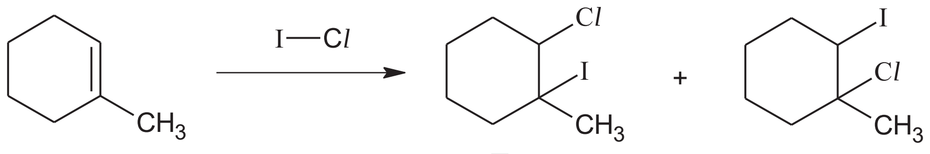


Draw the structures of compounds **B**, **C** and **D**.

[3]

(iii) The halogens form many interhalogen compounds, one such example is ICl, commonly known as Wijs' reagent.

Wijs' reagent can react with 1-methylcyclohexene to form a mixture of compound **E** and **A**. Explain why **A** is the major product for this reaction.



1-methylcyclohexene **E** **A**

[2]

The alkene functional group of 1-methylcyclohexene will **attack the iodine atom** of the ICl molecule **first as iodine atoms are more delta positive** than Cl, to form a new C- I bond. The major product will have the new ICl bond formed on the carbon number 2, as this will result in a **more stable carbocation with the positive charge on the first carbon** which had an additional **electron-donating methyl group**. OR form more stable carbocation

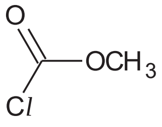
(f) (i) Below outlines a reaction scheme of phosgene with NaOH(aq) in two stages.

$$COCl_2 \xrightarrow[\text{stage 1}]{OH^-} COCl(OH) \xrightarrow[\text{stage 2}]{} CO_2 + HCl$$

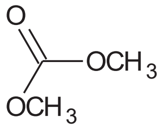
State the types of reaction occurring in stage 1, and stage 2. [2]

Stage 1: Nucleophilic acyl substitution (*for carboxylic acids and derivatives*)
Stage 2: Elimination

(ii) In order to remove any phosgene present in a bottle of chloroform, a small amount of methanol is added. use the information in **(f)(i)** to suggest the structural formula of the organic compound formed when phosgene reacts with methanol. [1]



or



[Total:20]

2 (a) Carbon monoxide reacts with steam over a copper / zinc catalyst, to form a mixture of carbon dioxide and hydrogen gas.

Reaction 1: $CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$

When an equimolar mixture of hydrogen and carbon dioxide at an initial total pressure of 4 atm is allowed to reach equilibrium at 1000 K, the percentage of steam in the mixture of gases is found to be 15%.

(i) Calculate K_p of the system in **reaction 1** at 1000 K. [2]

	$CO(g)$	$H_2O(g)$	$\rightleftharpoons$	$CO_2(g)$	+	$H_2(g)$
Initial pressure / atm	0	0		2		2
Change in pressure / atm	+x	+x		-x		-x
Eqm pressure / atm	x	x		2-x		2-x

$P_{H2O} = x / 4 = 0.15$
Thus, $x = P_{H2O} = P_{CO} = 0.60$ atm
$P_{CO2} = P_{H2} = 1.40$ atm
$K_p = (1.40)^2 / (0.60)^2 = 5.44$

(ii) Suggest, with a reason, whether or not a higher pressure would favour the formation of steam. [1]

<u>No</u> because <u>same number of moles of gas on right and left side</u>

(b) Sodium ethanoate can be used to prepare ethane by an electrochemical reaction, which is known as the Kolbe electrolysis reaction. Ethane is formed at the anode by the following reaction:

$$2CH_3CO_2^- \rightarrow C_2H_6 + 2CO_2 + 2e^-$$

A student investigated the electrolysis of aqueous solution of sodium ethanoate, using graphite electrodes in a litmus solution.

(i) Give the equation for the reaction occurring at the cathode, and state the final colour expected at the cathode.

Construct an equation for the **overall** reaction. [2]

At the cathode:

- Equation at cathode: $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$
- The product OH^- turns the litmus solution <u>blue</u>.

- Overall reaction:

$$2\ CH_3CO_2^- + 2H_2O \rightarrow C_2H_6 + 2CO_2 + H_2 + 2OH^-$$

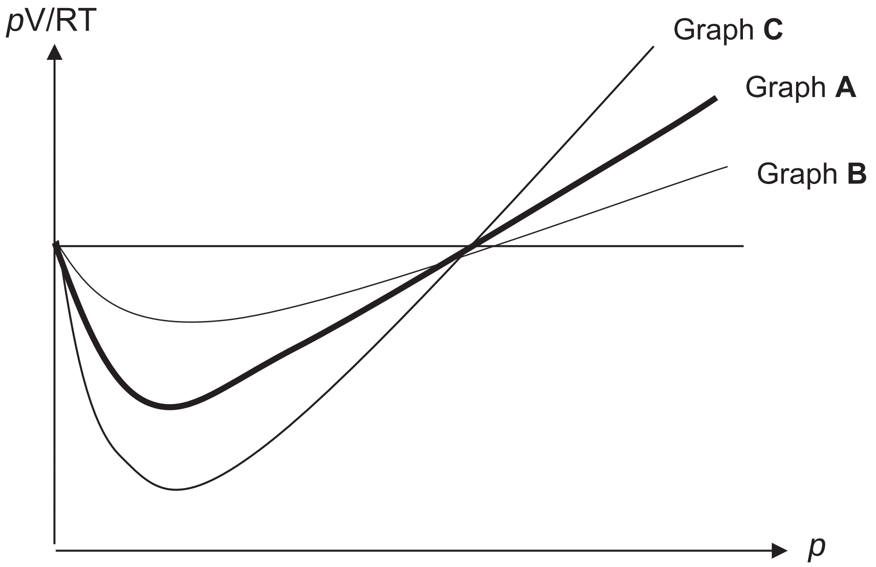
(ii) Calculate the time, in minutes, needed by the student to pass a current of 5.0 A through a solution of sodium ethanoate, to produce 1.50 g of ethane. [2]

No of moles of ethane = 1.5/30 = 0.0500 mol
No of moles of electrons = 0.05 x 2 = 0.100 mol

time = Q/I = $\frac{0.1\times96500}{5\times60}$ = 32.2 min

(c) **(i)** The value of pV/RT is plotted against p for the following three gases, where p is the pressure and V is the volume of the gas.
Given that graph **A** represents 1 mol of CO_2 at 298 K.

Identify which of the following graphs, **B** or **C,** represent 1 mol of CO_2 at 500 K.



[2]

Graph **B** is <u>CO_2 at 500 K</u>
CO_2 at 500 K deviates less than CO_2 at 298 K. At higher temperature, CO_2 <u>molecules possess higher average kinetic energy</u> and are more able to <u>overcome forces of attraction</u> between the molecules.

(ii) Sulfur dioxide is used by the Romans in winemaking, when they discovered that burning sulfur candles inside empty wine vessels keeps them fresh and free from vinegar smell.

One such cylinder of sulfur dioxide has an internal volume of 2.5 dm^3, and a mass of 2.3 kg.

Calculate the pressure (in pascals) that the sulfur dioxide would exert inside the cylinder at room temperature. [1]

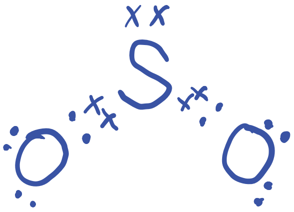
Pls take note: Room temperature is now 293K!
pV = nRT
$p = (2.3 \times 10^3 / 64.1)(8.31)(293) / (2.5 \times 10^{-3})$
$= 3.49 \times 10^4$ kPa

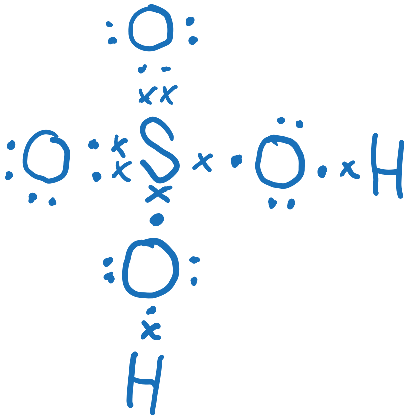
(d) Sulfuric acid is used in many industrial processes of major importance.

The process used to produce sulfuric acid involves a three–stage process. The first stage is to pass air over burning sulfur. The emerging gas is then passed over a catalyst, V_2O_5, which is maintained at 450-550ºC in the reaction chamber.

Stage **I**: $S(s) + O_2(g) \rightarrow SO_2(g)$
Stage **II**: $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$
Stage **III**: $SO_3(g) + H_2O(l) \rightarrow H_2SO_4(l)$

(i) Draw dot-and-cross diagrams to show the bonding in SO_2 and H_2SO_4. State the bond angle, with respect to sulfur atom, in each of them. [4]





Accept between 110° and 120°   109.5°

(ii) The boiling points of sulfur trioxide and sulfur dioxide are 45°C and -10°C respectively.

Account for the difference in boiling points for both compounds, in terms of structure and bonding. [2]

- Both compounds have **simple covalent structures/ simple molecular structures**.
- However, SO_3 has a higher boiling point than SO_2 because SO_3 has **stronger (intermolecular) instantaneous dipole-induced dipole attractions** due to its
- **larger electron cloud size / more electrons being polarised.**

(SO_2 has weaker intermolecular permanent dipole-dipole attractions.)

- Hence, **more energy** is required to overcome the bonding in SO_3.

(e) For each of the following pairs of compounds, suggest **one** simple chemical test to distinguish them from each other. State the reagents and conditions needed and give the expected observations for each compound.

(i) $CH_2{=}CHCH_2CH(CH_3)OH$ **J** $CH_2{=}CHC(CH_3)_2OH$ **K**

Test: Add **$K_2Cr_2O_7$(aq), H_2SO_4(aq) and heat** to both compounds.

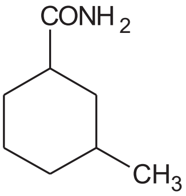
Observation: The solution of **A** will change from **orange to green** while the solution of **B** will **remain orange**.

OR

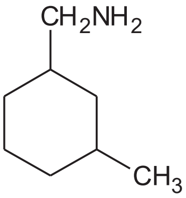
Test: Add **I_2(aq), NaOH(aq) and warm** to both compounds.

Observation: The solution of **J** will decolourise brown iodine and give a **yellow ppt** while solution of **K will not**.

(ii)



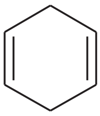
L



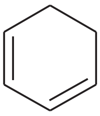
M

Test: Add NaOH(aq) and heat to both compounds.
Observation: **L** will give pungent gas (NH_3) that turns **moist red paper blue** while **M will not**.

(iii)



P



Q

Add $KMnO_4$(aq), H_2SO_4(aq) and heat to both compounds.
Observation: The solution of **P and Q** will change from **purple to colourless** but the solution of **Q** will **produce** bubbles of CO_2 that form white ppt with limewater

[Total:22]

3 Nitrous oxide, N_2O, is commonly known as laughing gas due to the euphoric effects of inhaling it. At a temperature of 1000 K, in the presence of chlorine catalyst, N_2O decomposes to its elements according to the following equation:

$$2N_2O(g) \rightarrow 2N_2(g) + O_2(g)$$

The experimental rate equation for this reaction is Rate = $kP_{N_2O}^{a}\,P_{Cl_2}^{b}$

where P_{N_2O} and P_{Cl_2} are the partial pressures of N_2O and Cl_2 respectively and a and b are non-zero constants.

The rate of decomposition of pure N_2O may be followed at constant temperature, by measuring the total pressure of the system with time.

The data below refers to a reaction in which pure N_2O decomposes in the presence of chlorine catalyst, Cl_2, (at partial pressure of 47 kPa).

Experiment 1:

time / s	0	40	80	140	240
P_{total} / kPa	87.0	91.3	93.0	98.0	102.2
P_{N_2O}	40	31. 4	25	18	9.6

(a) **(i)** Show that the partial pressure of N_2O at any instant is given by
$P_{N_2O} = 214 - 2P_{total}$ [2]

Let x = pressure of N_2O that dissociated

	$2N_2O(g)$	$\rightarrow 2N_2(g)$	$+ O_2(g)$

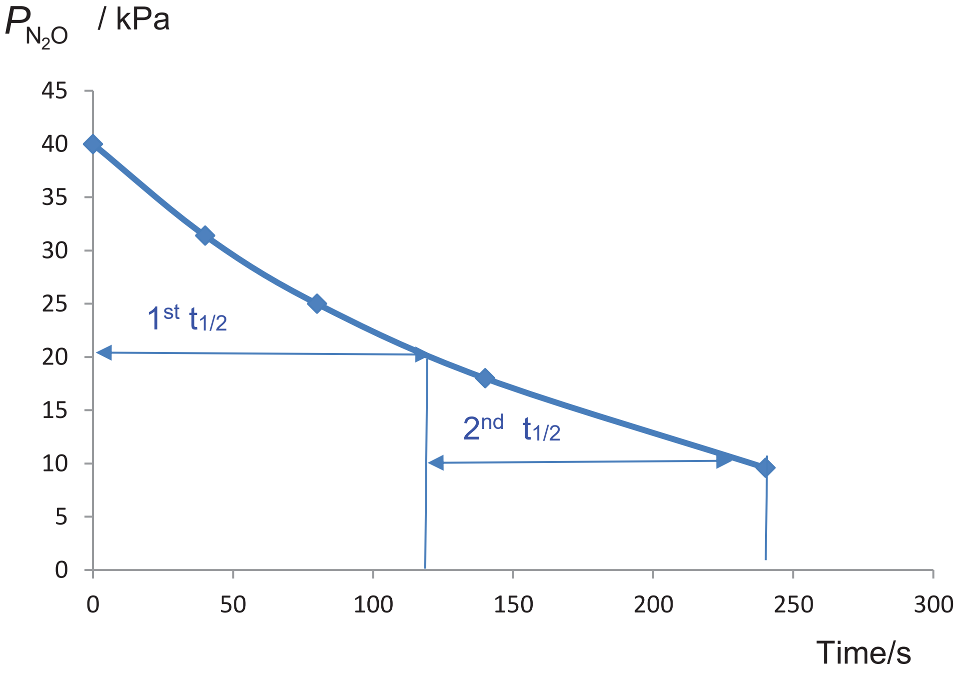
Initial P / kPa	40	0	0
Change in P/ kPa	-2x	+2x	+1x
Final P / kPa	40-2x	2x	X

P_{total} = 40-2x + 2x + x +47 = 87+x

X = P_{total} - 87

P_{N_2O} = 40-2x = 40 -2(P_{total} – 87) = 214 -2P_{tot} (shown)

(ii) Use the given data provided in the table above to plot a graph of P_{N_2O} against time on suitable axes. Showing all your working and drawing clearly any construction lines on your graph, use your graph to determine the value of a, the order of reaction with respect to N_2O.



-Axes, correct labelled (with units)
-Correct plotting of points
-Correctly draw grid lines to show the two $t_{1/2}$ (range of half-life ±10%)
$t_{1/2}$ is about 121s
-Conclude first order from constant half lives construction lines for the 2 half-lives [4]

(iii) Two additional experiments, experiments 2 and 3 were carried out and the following results were obtained.

	P_{N_2O} / kPa	P_{Cl_2} / kPa	Initial rate/ kPa s^{-1}
experiment 2	70	35	0.306
experiment 3	70	70	0.613

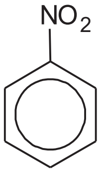
Determine b, the order of reaction with respect to chlorine. Explain your reasoning. [1]

Compare experiments 2 and 3, keeping P_{N_2O} constant, when P_{Cl_2} doubled, initial rate doubled. Order with respect to chlorine =1

(iv) Hence write the rate equation for the reaction. [1]

Rate = $kP_{N_2O}\,P_{Cl_2}$ give ecf based on students' orders from (e)(ii) and (iii)

(b) Nitrobenzene is an organic compound used to mask unpleasant odors in shoe and leather dressings.



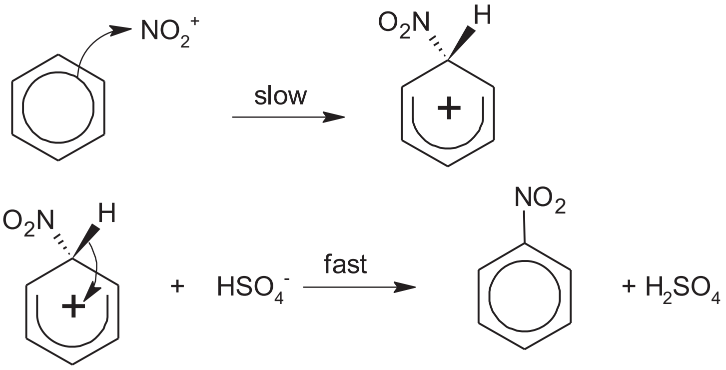
(i) Suggest the type of hybridisation of N in nitrobenzene. [1]

sp^2 hybridisation

(ii) Nitrobenzene can be formed from reacting benzene with concentrated nitric acid and sulfuric acid. Name and outline the mechanism of the nitration of benzene. Indicate the rate-determining step and draw the formula of the organic intermediate. [3]

Electrophilic substitution

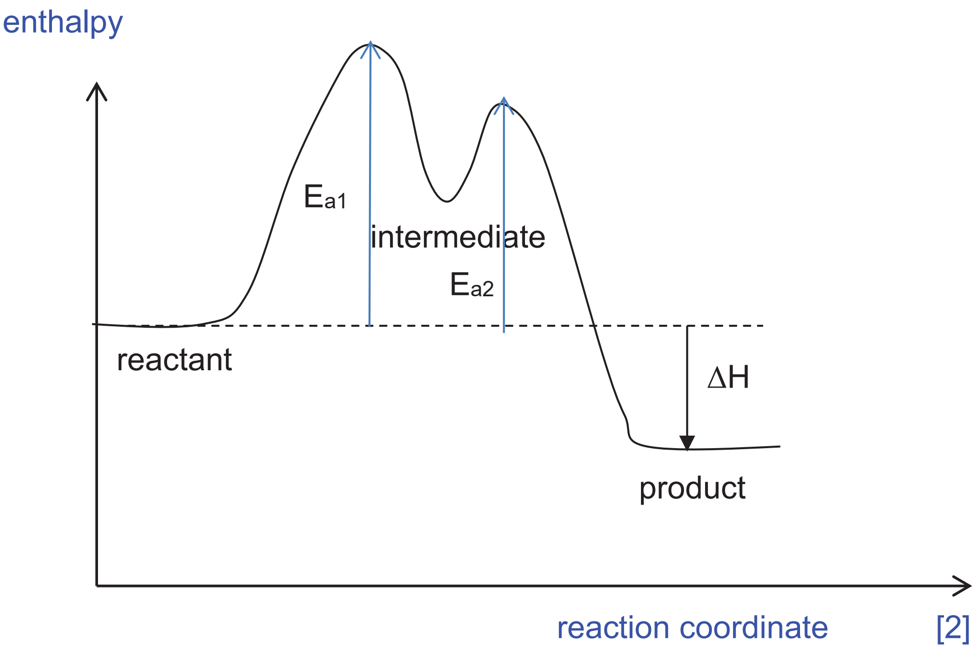
$2H_2SO_4 + HNO_3 \rightleftharpoons 2HSO_4^- + NO_2^+ + H_3O^+$



Deduct one mark if any of these are missing below

- Correctly drawn curly arrows for step 1
- Correctly drawn curly arrows for step 2
- Label **slow (rate-determining)** step
- correct intermediate (no need to show dashed and bold lines)
- Regeneration of catalyst, **H_2SO_4**

(iii) Given that the nitration of benzene is exothermic, sketch the reaction pathway diagram of the reaction, labelling clearly the reactant, intermediate and product on your diagram.



[2]

- Axes clearly labelled
- Relative energy level of reactants and product (lower)
- Show 2 'humps', and Ea1 > Ea2
- Label reactant,
- Label intermediate and
- Label product

(c) To investigate the mechanism of nitration of benzene, every hydrogen atom on benzene is replaced by its isotope, deuterium, to form C_6D_6.

Carbon–deuterium (C-D) bond has higher bond energy than a carbon–hydrogen (C-H) bond.

If the rate-determining step involves the breaking of a C–H bond, replacing the C–H bond with a C–D bond will change the rate constant, k, of the reaction. This is known as the deuterium isotope effect.

Deuterium isotope effect = $\dfrac{k_H}{k_D}$

k_H = rate constant for nitration of C_6H_6

k_D = rate constant for nitration of C_6D_6

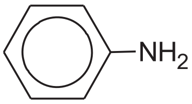
If $\dfrac{k_H}{k_D} = 1$, it is said that the deuterium isotope effect is absent.

If $\dfrac{k_H}{k_D} >> 1$, it is said that the deuterium isotope effect is present.

Predict with reasoning, if the deuterium isotope effect would be present in the nitration of benzene. [1]

As the rate-determining step does not involve the breaking of a C-H bond / the C-H bond is only broken in the fast step of the mechanism, there is no deuterium isotope effect present in nitration of benzene.

(d) **(i)** Nitrobenzene can be converted to phenylamine, which is used in the synthesis of polyurethane, a polymer used in making tyres.



phenylamine

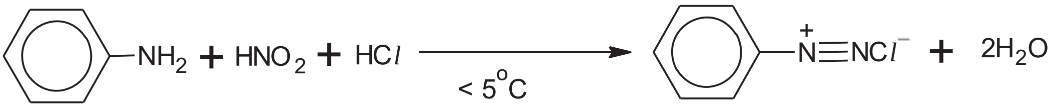
Suggest the reagents and conditions to convert nitrobenzene to phenylamine. [1]

Sn, concentrated HCl, heat
Followed by NaOH(aq)

(ii) The following equations illustrate the formation of phenol from phenylamine, in two steps:

In step 1, phenylamine reacts with cold nitrous acid, HNO_2, and hydrochloric acid, HC*l*, to form phenyldiazonium chloride.

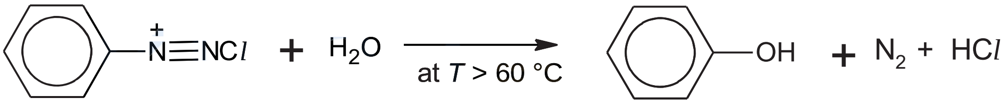
Step **1**



phenyldiazonium chloride

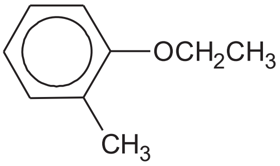
In step 2, phenyldiazonium chloride can react with water upon heating to give phenol.

Step **2**



phenyldiazonium chloride

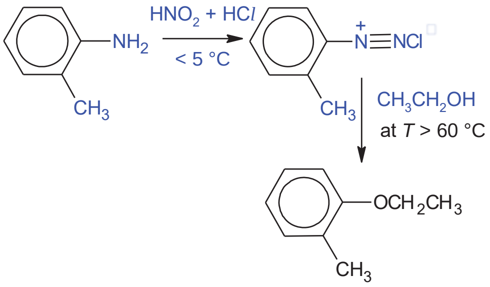
Propose a two-step synthetic pathway for the conversion of 2-methylphenylamine to compound **S** below.



Compound **S**

[2]

Answers:



[Total:18]

Section **B**

Answer **one** question from this section.

4 **(a)** A blood test can detect abnormally high levels of an amino acid which is one of the signs of the disease phenylketonuria, a rare condition in which a person is unable to properly break down amino acids such as phenylalanine.

In acidic solution, phenylalanine is completely protonated and exists as $H_3N^+CHRCO_2H$, where R is $–CH_2C_6H_5$.

Protonated phenylalanine, $H_3N^+CHRCO_2H$, acts as a dibasic acid that ionises in stages.

$H_3N^+CHRCO_2H \rightleftharpoons H_3N^+CHRCO_2^- + H^+$ $\quad pK_1 = 1.83$

$H_3N^+CHRCO_2^- \rightleftharpoons H_2NCHRCO_2^- + H^+$ $\quad pK_2 = 9.13$

(i) Calculate the pH of a 0.80 mol dm^{-3} solution of protonated phenlyalanine (ignore the effect of pK_2 on the pH).

Let $[H_3O^+] = [H_3N^+CHRCO_2^-] = x$ mol dm^{-3} at equilibrium

	$H_3N^+CHRCO_2H$	+	H_2O	$\rightleftharpoons$	H_3O^+	+ $H_3N^+CHRCO_2^-$
Initial conc	0.80				-	-
Change in conc	-x				+x	+x
Eqm conc	0.80-x				x	x

$$K_a = \frac{[H_3O^+][H_3N^+CHRCO_2^-]}{[H_3N^+CHRCO_2H]} = \frac{x^2}{0.80 - x}$$

Since protonated phenylalanine is a weak acid, extent of dissociation is small.

$\Rightarrow$ Hence x is negligible compared to 0.80 mol dm^{-3}.

Therefore, $(0.80 – x) \approx 0.80$

$$K_a = \frac{x^2}{0.80} = 10^{-1.83}$$

Solving, x =0.10878 mol dm^{-3}

Hence, initial pH = −lg [H^+ (aq)] = 0.963 (3sf)

(ii) An amphiprotic species is one that can act as a Bronsted-Lowry acid or base. The pH of a solution containing an amphiprotic species is given by the following expression.

pH = ½(pK_1 + pK_2)

In the titration of protonated phenylalanine with NaOH, an amphiprotic species is formed.

Identify the amphiprotic species formed and calculate the pH of the solution.

Amphiprotic species formed = $H_3N^+CHRCO_2^-$

pH at 1st equivalence point= (1.83 + 9.13)/2 = 5.48

(iii) Sketch the titration curve when 25.0 cm^3 of protonated form of phenylalanine is being titrated with 70 cm^3 of NaOH(aq) of the same concentration. On your sketch, clearly mark the two pK_a values and the points you have calculated in **(i)** and **(ii)**.

- Label both axes
- Label initial pH = 0.963
- Sketch shape correctly 2 sharp changes in pH at correct equivalence volumes 25.0 cm^3 & 50.0 cm^3
- Label pK_1 = 1.83 at 12.5 cm^3
- Label pK_2 = 9.13 at 27.5 cm^3
- pH at 1st equivalence point = 5.48

(iv) Suggest a suitable indicator from the following table to be used to detect the first equivalence point and state the colour change of the solution at this equivalence point.

indicator	**pH range**	**acid solution**	**basic solution**
Thymol Blue	1 – 3	Red	yellow
Methyl Red	5 – 6	yellow	Red
Phenol red	7 – 8	yellow	Red
Phenolphthalein	8 – 10	colourless	red

1st equivalence point pH = 5.48 (region of sharp pH change), methyl red is a suitable indicator.
The colour will change **from yellow to orange**.

(b) "Acidity regulators" are food additives that have a buffering action on the pH of food. A mixture of citric acid, $C_5H_7O_4CO_2H$, and its sodium salt is often used for this purpose.

You may assume that citric acid behaves as a monobasic weak acid.

$$C_5H_7O_4CO_2H \rightleftharpoons C_5H_7O_4CO_2^- + H^+; \qquad K_a = 7.4 \times 10^{-4} \text{ mol dm}^{-3}$$

(i) A citric acid / sodium citrate buffer mixture is prepared by mixing 40.0 cm^3 of 0.100 mol dm^{-3} citric acid and 60.0 cm^3 of 0.200 mol dm^{-3} sodium citrate.

Calculate the pH of the buffer solution. [1]

Amount of HA = 4 x10^{-3} mol
Amount of A^- 0.012 mol

pH = pKa + log [A^-]/[HA]

= 3.13 + log (3) = 3.63

(ii) Write equations to show how this mixture of citric acid and sodium citrate regulates the acidity on addition of H^+ ions and OH^- ions. [2]

On addition of H^+,

$C_5H_7O_4CO_2^- + H^+ \longrightarrow C_5H_7O_4CO_2H$

On addition of OH^-,

$C_5H_7O_4CO_2H + OH^- \longrightarrow C_5H_7O_4CO_2^- + H_2O$

Full forward arrows

(c) **(i)** Describe the conditions needed to hydrolyse a protein non-enzymatically. [1]

Heat under reflux with $H_2SO_4(aq)$ or NaOH(aq) for several hours.

(ii) Histidine decarboxylase undergoes enzymatic hydrolysis. Upon hydrolysis, the polypeptide fragments of the enzyme's active site are isolated as shown below.

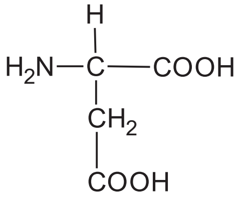
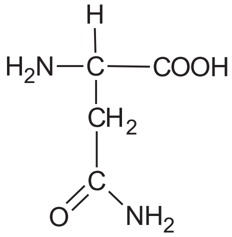
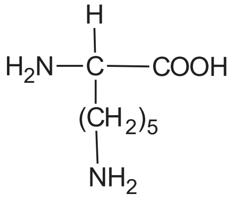
- Ala-Cys-Phe
- Gly-Gly
- Lys-Asp-Asp-Gly-Gly
- Phe-Arg-Lys

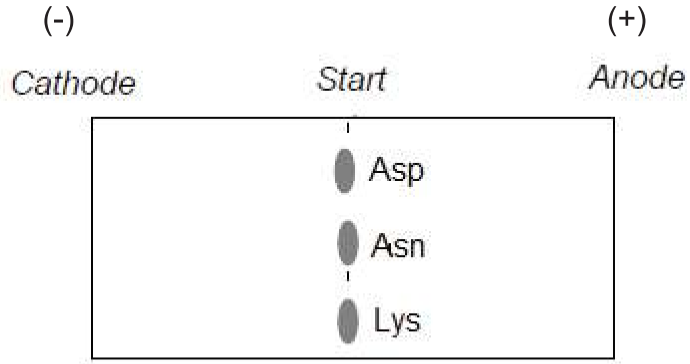
Deduce the sequence of the 9 amino acid residues of the enzyme's active site. [2]

Working
Ala-Cys-Phe
Phe-Arg-Lys
Lys-Asp-Asp-Gly-Gly
Gly-Gly must show working for stacking

Ala-Cys-Phe-Arg-Lys-Asp-Asp-Gly-Gly

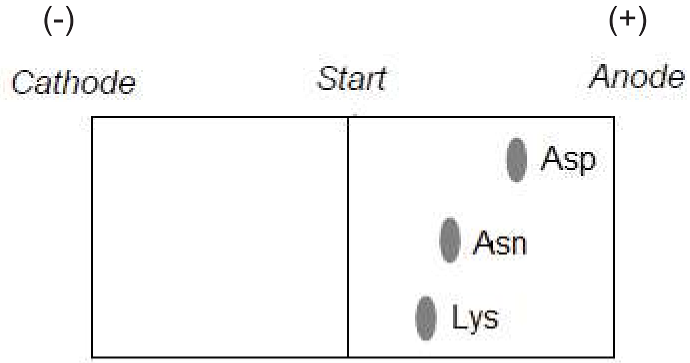
(iii) A different segment of tripeptide, Asp-Asn-Lys, was subjected briefly to acidic hydrolysis which produced individual amino acids as well as various peptides. The resulting mixture buffered at pH 13 was separated in an electric field using electrophoresis.

Amino acid			
Abbreviation	Asp	Asn	Lys



Using the above template sketch and label the position of the three amino acids after the separation. State one factor that affect the rate at which the charged particles move during electrophoresis.

[3]

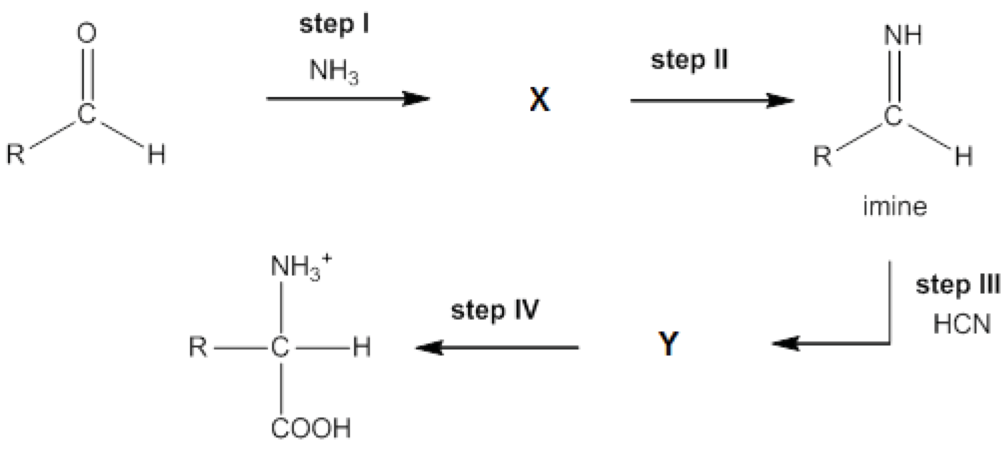


One factor: Mass or charge density of species

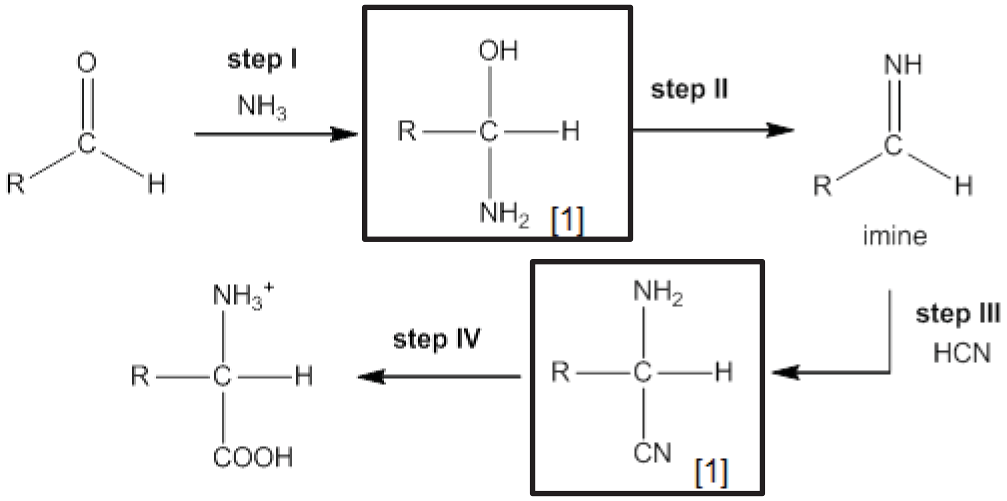
(d) The Strecker synthesis assembles an α-amino acid from the amine precursor and an aldehyde.

- Step **I** is a nucleophilic addition reaction.
- Step **II** involves the elimination of water from **X** to form an imine**.**
- Step **III** is similar to the formation of cyanohydrin when the imine undergoes nucleophilic addition with HCN and forms an α-amino nitrile, **Y**.
- Step **IV** is the hydrolysis of **Y** to form the carboxylic acid functional group.

In the following reaction flow scheme, draw the intermediate compounds **X** and **Y** and suggest the reagent and condition for the step **IV** in the scheme.



[3]



Step IV: H_2SO_4 (aq) heat or HC*l* (aq) heat (accept dilute in place of aq)

[Total:20]

5 Copper is an important transition element that can readily form complex ions with *ligands*. Copper forms a large variety of compounds, usually with variable oxidation states. Copper compounds also act as useful *homogeneous catalysts*, commonly used in many industrial operations.

(a) Define the terms *ligand* and *homogeneous catalyst*. [2]

Ligand is a neutral molecule or anion which contains at least **1 lone pair of electrons** available for forming **dative bonds** with the available **empty orbitals** on the central metal ion/atom.

Homogeneous catalysts **increase the rate of reaction** by providing an alternative pathway with **lower activation energy**. *Homogeneous catalysts* are in the **same phase as the reactants** in the reaction.

(b) In recent years, horseshoe crabs have generated great interest amongst scientists due to its blood with remarkable antibacterial properties. An unusual aspect of the blood is that it is bright blue, a consequence of using copper-based haemocyanin to transport oxygen.

Haemocyanin (Hc) contains two copper atoms that reversibly bind a single oxygen molecule, O_2, to form oxyhaemocyanin, HcO_2, according to the following equation:

$$2Hc(aq) + O_2(aq) \rightleftharpoons 2HcO_2(aq) \quad \textit{equilibrium 1}$$

Oxygenation causes a color change between Cu(I) deoxygenated form and the Cu(II) oxygenated form.

(i) By considering *equilibrium 1*, comment on how the crab cells receive oxygen from the air in the lungs. Check TYS haemoglobin
Hint: Consider the level of oxygen in the lungs

[2]

In the lungs, $[O_2]$ is high. This results in the **position of equilibrium shifting to the right**, favouring the formation of the oxyhaemocyanin HcO_2.

In the cells, $[O_2]$ is low. The position of equilibrium will hence **shift to the left**, favouring the release of O_2.

(ii) Indicate the color change from Cu(II) oxygenated form to Cu(I) deoxygenated form. Hence explain why both copper complex ions exhibit different colours.

[5]

From blue to colourless

oxyhaemocyanin contains Cu^{2+}: [Ar] $3d^9$
Cu(II) has partially filled 3d-orbitals.
In presence of ligands, the originally degenerate 3d orbitals split into 2 sets of different energy levels, separated by a small energy gap (ΔE).

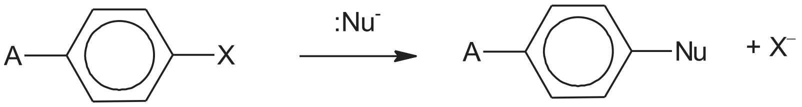
ΔE corresponds to the energy of visible light. An electron from the lower energy d orbital absorbs a specific wavelength of visible light and is promoted to a half-filled, higher energy 3d orbital. d-to-d transition can take place and colour observed is complementary to the colour absorbed.

deoxygenated haemocyanin contains Cu^{+}: [Ar] $3d^{10}$
Cu(I) has fully filled 3 d-orbitals ($3d^{10}$). Hence, d-to-d electron transition cannot occur, and no visible light is absorbed, which accounts for it being colourless.

(c) Most aromatic compounds undergo electrophilic substitution.

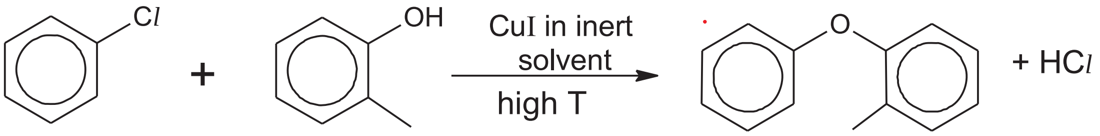
However it is possible for aryl halides to undergo a limited number of nucleophilic substitution reactions with strong nucleophiles.

An example of a reaction is as follows:



An example of an aryl nucleophilic substitution is the *Ullmann coupling* reaction where hydrocarbons fragments are coupled, using copper compounds as a catalyst.

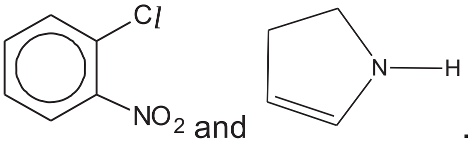
An example is indicated in reaction **1** below.



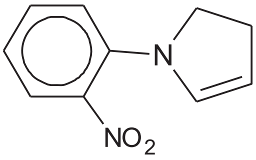
reaction **1**

(i) The conditions for the *Ullmann coupling* reactions are usually harsh conditions, and yet give low yield.

In a similar reaction under the same temperature and pressure, the two compounds below were reacted together:



Deduce and draw the structure of the product for the above reaction. [1]



(ii) Predict, with reasoning, if the above reaction in **(c)(i)** will result in a higher or lower yield compared to reaction **1**. [2]

The presence of the electron-withdrawing NO_2 group on the benzene increase the $\delta+$ on the carbon which attracts nucleophile more strongly

As such, the above reaction will result in a higher yield.

(iii) Like copper(I) iodide, aqueous Fe^{2+} is a good homogeneous catalyst used in the decomposition of aqueous hydrogen peroxide as indicated below.

$$2H_2O_2(aq) \rightarrow 2H_2O(l) + O_2(g)$$

With reference to relevant data in the *Data Booklet*, suggest a mechanism for the catalysis of the above reaction by aqueous Fe^{2+}. [3]

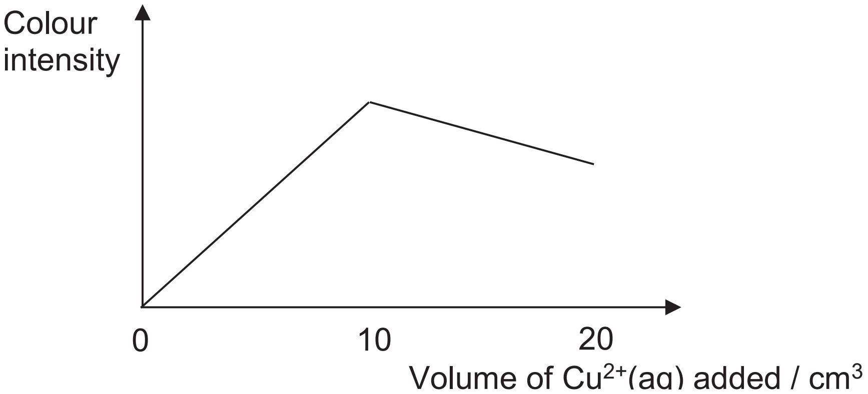
$H_2O_2 + 2H^+ + 2e \rightarrow 2H_2O$ $E^\theta = +1.77V$
$Fe^{2+} \rightarrow Fe^{3+} + e$ $E^\theta = -0.77V$
Step 1 Overall: $H_2O_2 + 2H^+ + 2 Fe^2 \rightarrow 2H_2O + 2Fe^{3+}$ $E^\theta_{cell} = +1.00V$
mark for calculating E^θ_{cell}]

$H_2O_2 \rightarrow O_2 + 2H^+ + 2e$ $E^\theta = +0.68V$
$Fe^{3+} + e \rightarrow Fe^{2+}$ $E^\theta = +0.77V$
Step 2 Overall: $H_2O_2 + 2 Fe^{3+} \rightarrow O_2 + 2Fe^{3+} 2H^+$ $E^\theta_{cell} = +0.09V$

(d) Copper(II) species can have various coordination numbers, though tetracoordinated copper(II) species are not as common as hexacoordinated ones.

The formula of a methylamine-copper complex ion, $[Cu(CH_3NH_2)_x(H_2O)_2]^{2+}$, can be determined using a colorimeter.

In an experiment, a solution of 0.050 mol dm^{-3} of $Cu^{2+}(aq)$ was added 1 cm^3 at a time to 20 cm^3 of 0.100 mol dm^{-3} of aqueous CH_3NH_2. The colour intensity of the resultant solution after each addition was measured using a colorimeter. The following graph was obtained.

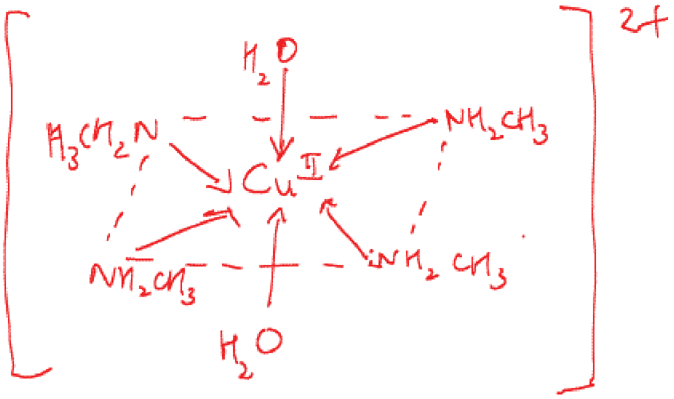


(i) Using the graph, determine the value of ***x.*** [2]

No. of mol of $Cu^{2+} = (0.10/1000) \times 0.05 = 5 \times 10^{-4}$
No. of mol of $CH_3NH_2 = (20/1000) \times 0.1 = 2 \times 10^{-3}$

$1/x = (5 \times 10^{-4})/(2 \times 10^{-3})$
$x = 4$

(ii) Draw the structure of the methylamine-copper complex ion. [1]



(e) Mercury is poisonous as it can cause many health problems ranging from neurological, respiratory to cardiovascular problems. One possible treatment for mercury poisoning involves administering a solution of $EDTA^{4-}$, a common hexadentate ligand which forms complexes with many metal ions.

Copper and calcium ions are essential minerals required by the body. Using relevant data from below, comment on the use of $EDTA^{4-}$ as a treatment for mercury poisoning and comment on its effect on the concentrations of copper and calcium ions in the body.

Equilibrium	K_c /mol^{-1} dm^3
$Ca^{2+} + EDTA^{4-} \rightleftharpoons [Ca(EDTA)]^{2-}$	6×10^{10}
$Cu^{2+} + EDTA^{4-} \rightleftharpoons [Cu(EDTA)]^{2-}$	5×10^{18}
$Hg^{2+} + EDTA^{4-} \rightleftharpoons [Hg(EDTA)]^{2-}$	6.3×10^{21}

[2]

As K_c of $[Hg(edta)]^{2-}$ is higher than that of $[Ca(edta)]^{2-}$ and $[Cu(edta)]^{2-}$, Hg^{2+} will be **removed first** in preference of Cu^{2+} when edta is used. As such, it is useful in the removal of heavy metals (such as Hg) from the body.

However, when a high dosage of EDTA is added, Cu^{2+}, which are essential for health, will also be removed due to the shifting of the position of equilibrium to the right, favoring the formation of the complexes. (as K_c of $[Hg(edta)]^{2-}$ $[Cu(edta)]^{2-}$ are closer in magnitude)

Hence, limited amount of edta should be administered to prevent the loss of Ca^{2+} and Cu^{2+}.

[Total:20]

End of Paper

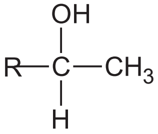
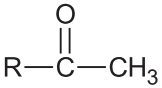
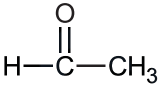
MYE Practical Exam Mark Scheme

Qn	Skills assessed	Marking scheme	Mark	Mark ref
1(a)(i)	PDO Layout **P1**	Tabulates temperature and volume of FA 2 added in the table. Table has correct headers and units.	1	**1**
	PDO Record **P2**	All the volumes are recorded to the nearest 0.05 cm^3 and temperature to 0.1 °C	1	**2**
(a)(ii)	PDO Layout **P3**	Axes correct way round + correct labels + units + scale. Sensible linear scale must be chosen so that the plotted points occupy at least half the graph grid in both x and y directions.	1	**3**
	PDO Layout **P4**	All points correctly plotted to within ±1/2 small square. Checks all points and put ticks if correct.	1	**4**
	PDO Mani **P5**	Graph line must be best fit-lines. Lines should be extrapolated until they cross. Do not allow mark if clearly anomalous points are included or it the lines do not cross each other	1	**5**
(a)(iii)	PDO Mani **P6**	Correct reading to within ±1/2 small square of $T_{maximum}$. Correct calculation of $\Delta T_{maximum}$. Correct reading of $V_{equivalence}$.	1	**6**
	MMO Quality **M1** **M2**	Award MR 7 based on the difference, $\Delta T_{maximum}$, between student's and supervisor's $\Delta T_{maximum}$ value. Give 1 mark if this difference is ≤ 0.3 °C Award MR 8 based on the difference, $V_{equivalence}$, between student's and supervisor's $V_{equivalence}$ value. Give 1 mark if this difference is ≤ 0.75 cm^3 Shift 1: Jessie 10.75 cm^3 and 5.1 °C, Kelly 10.40 cm^3 and 4.88 °C Shift 2: Joseph 10.33 cm^3 and 5.3 °C, Russell 10.00 cm^3 and 5.7 °C (Physics) Shift 3: Jessie 12.40 cm^3 and 4.85 °C (Biology), Russell 12.00 cm^3 and 6.7 °C (Physics)	1 1	**7** **8**

(b)(i)	ACE Interpret **A1**	Calculates percentage error for 40 cm^3 of FA 1 using measuring cylinder and burette % error (measuring cylinder) = (0.5 / 40) x 100 % % error (burette) = [(2 x 0.05) / 40] x 100 %	1	**9**
(b)(ii)	ACE Interpret **A2**	States that the apparatus is burette and explains that $NaHCO_3$ is the limiting reagent thus accuracy is essential.	1	**10**
(b)(iii)	PDO Layout **P7**	Records T_{FA1}, T_{FA3} and $T_{mixture}$ to 0.1 °C.	1	**11**
(c)(i)	ACE Interpret **A3**	$[NaOH] = (25.0 \times 10^{-3} / V_{equivalence} \times 10^{3}) \times 1.00$	1	**12**
(c)(ii)	ACE Interpret **A4** **A5**	$Q = (V_{equivalence} + 25.0)(1.00)\ c\ \Delta T_{maximum}$ $n(NaHCO_3) = 1.00 \times 25.0/1000 = 0.025$ mol $\Delta H_{reaction1} = - q / n(NaHCO_3)$	1 1	**13** **14**
(d)	ACE Interpret **A6** **A7**	$\Delta T_{maximum2} = \lvert T_{mixture} - T_{average} \rvert$ $q = (V_{FA\ 1} + V_{FA3}) \times 4.18 \times \Delta T_{maximum2}$ $\Delta H_{reaction2} = +q / 40.0 \times 10^{-3}$	 1 1	 **15** **16**
	PDO Display **P8**	Shows working in all calculations in 1(a), 1(b), 1(c) and 1(d) All calculations must be relevant although they may not be complete or correct	1	**17**
	PDO Display **P9**	Shows appropriate significant figures (3 or 4) in all final answers in 1(a), 1(b), 1(c) and 1(d)	1	**18**
	PDO Display **P10**	Shows appropriate units in all final answers in 1(a), 1(b), 1(c) and 1(d)	1	**19**

(e)	ACE Interpret **A8** **A9** **A10**	$$\begin{tikzcd} CO_2 + 2H_2O + CO_3^{2-} \arrow[r, "\Delta H_{r3}"] & 2HCO_3^- + H_2O \\ HCO_3^- + H^+ + CO_3^{2-} + H_2O \arrow[u, "\Delta H_{r2}"] & 2HCO_3^- + H^+ + OH^- \arrow[l, "\Delta H_{r1}"'] \arrow[u, "\Delta H_n"'] \end{tikzcd}$$ Each part of cycle not balanced deduct 1 mark $\Delta H_{reaction3}$ = (-57.1) + (-**(c)(ii)**) + (-**(d)**)	2 1	**20** **21** **22**
2(a)	PDO Layout **P11**	Tabulates volume of **FA 6**, water and time taken for blue colour to appear in the table. All the volumes are recorded to 1 d.p. and time to nearest 0.1 s.	1	**21**
	ACE Interpret **A11**	Adds volume of water to maintain a constant total volume of 71 cm^3.	1	**22**
	ACE Interpret **A12**	Correctly calculates V_{FA6} x t and V_{FA6}^2 x t.	1	**23**
(b)(i)	ACE Interpret **A13**	Explains that the same volume of $S_2O_3^{2-}$ is used in each experiment, thus same amount, thus amount of I_2 reacted is the same which gives a constant concentration of I_2.	1	**24**
(b)(ii)	ACE Conclusion **A15**	Explains that V_{FA6} x t is constant for experiment 1 to 3, n = 1. Thus, order of reaction w.r.t bromate(V) is 1.	1	**25**
(c)	ACE Interpret **A16**	Correctly calculates V_{FA5} x t and V_{FA5}^2 x t and correctly deduces the order of reaction with respect to H^+.	1	**26**
	ACE Conclusion **A17**	Explains that V_{FA5}^2 x t is constant for experiment 1 to 3, n = 2. Thus, order of reaction w.r.t H^+ is 2.	1	**28**
(d)	ACE Conclusion	States that is the statement is not valid and explains that to calculate half-life, concentration of sulfuric acid concentration of	1	**29**

	A19	bromate(V) is not in large excess (x10).		
(e)	ACE Interpret **A20**	States that excess I_2 left in the flask will react with the $S_2O_3^{2-}$ in the new experiment. As there is lesser $S_2O_3^{2-}$ for the new experiment, less I_2 is reacted, the time taken to produce the I_2 will be shorter in the second experiment and hence observe the blue colour faster. or State that the excess chemicals (H^+, BrO_3^-, I^-) left in the flask will increase the concentrations of (H^+, BrO_3^-, I^-) in the next reaction. This will cause the rate of reaction to increase and the time taken to produce the I_2 will be shorter and hence observe the blue colour faster.	1	**30**
(f)(i)	Plan **Pl 1** **Pl 2**	Suggest appropriate volumes of H^+, $KBrO_3$ and KI to make a mixture of total volume 250 cm^3. Ensures that [KI] is at least 10x lesser than [H^+] and [$KBrO_3$].	1 1	**31** **32**
(ii)	ACE Interpret **A21** **A22**	States that colour is blue and/or purple Explains that since the observed colour of iodine is yellow-orange, the complimentary colour is absorbed.	1 1	**33** **34**
(iii)	PDO Layout **P8** ACE Interpret **A23**	Axes correct way round + correct labels + units + scale + labeling of 50, 75 and 100% [I_2]. 1st order product time graph with 2 constant consecutive half-lives.	1 1	**35** **36**
	ACE Conclusion **A24**	States that the order of reaction with respect to [I^-] will have constant half-lives.	1	**37**
3(a)(i)	MMO/ PDO Collecting	7 observation points – 2 with negative results Observations correctly recorded		

	M4 **M5**	6-7 = 3 4-5 = 2 2-3 = 1 0-1 = 0	3	**38** **39** **40**
(ii)	ACE Conclusion **A25** **A26**	Argues for **FA 8** is ethanal as it is the only one to form a silver mirror as it is oxidised by Tollens' reagent or the only one to form brick red precipitate as it is oxidised by Fehling's solution. Argues for **FA 9** is propan-2-ol as it is oxidised to decolourise potassium manganate(VII) or oxidised to form a yellow precipitate by aqueous iodoine but not oxidised by Tollens' or Fehling's.	1 1	**41** **42**
(b)(i)	ACE Interpret **A27**	Correctly identifies the structural feature as  $R-C(OH)(H)-CH_3$ and/or  $R-C(=O)-CH_3$ where R = H or alkyl group. Labelling of R is optional.	1	**43**
(b)(ii)	ACE Interpret **A28**	Give the correct structural formula  $H-C(=O)-CH_3$	1	**44**
(c)(i)	ACE Conclusion **A29**	Suggests Al^{3+}, Ba^{2+}, Mg^{2+}, Zn^{2+} (Ca^{2+} and Mn^{2+}) as cations that may be present.	1	**45**
(c)(ii)	Plan **Pl 3**	Selects NaOH(aq) and NH_3(aq) for identification of cation.	1	**46**
	MMO/ PDO Collecting **M6** **M7**	Gives observation of NaOH(aq) with cation. White precipitate with NaOH(aq) dropwise for Al^{3+}, Mg^{2+} and Zn^{2+}. White precipitate dissolves in excess NaOH(aq) for Al^{3+} and Zn^{2+}. [1] Gives observation of NH_3(aq) with cation. White precipitate with NH_3(aq) dropwise for Al^{3+} and Zn^{2+}. White precipitate dissolves in excess NH_3(aq) for Zn^{2+} but not Al^{3+} [1]	1 1	**47** **48**
	ACE	Concludes that **FA 10** contains Zn^{2+}	1	**49**

	Conclusion **A30**			
3(d)	Plan	Tests include (a) adding Br_2(aq), Br_2(l) or cold dilute alkaline $KMnO_4$ (b) $AgNO_3$(aq) (c) hot acidified $K_2Cr_2O_7$ (d) heat with NaOH(aq), cool, HNO_3(aq), followed by $AgNO_3$(aq)		
	PI 4	Selects reagents that would unambiguously identify 2 compounds with positive tests for each. [1] **or**	3	**50**
	PI 5	Selects reagents that would unambiguously identify 3 compounds with positive tests for each. [2] **or**		**51**
	PI 6	Selects reagents that would unambiguously identify 4 compounds with positive tests for each. [3]		**52**
	PI 7	Outlines a logical sequence/order of testing; doesn’t test compounds already identified [1]	1	**53**
	PI 8	Some ambiguity in links etc, but worthy of credit [1] or	2	**54**
	PI 9	Clearly and unambiguously links the testing sequence with the compounds to be identified [2]		**55**

RIVER VALLEY HIGH SCHOOL
YEAR 6 PRELIMINARY EXAMINATION II

CANDIDATE NAME

CLASS 6

CENTRE NUMBER S 3 0 4 4

INDEX NUMBER 0 0

H2 CHEMISTRY 9729/01

Paper 1 Multiple Choice

21 Sep 2017
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 and **0** blank pages.

[Turn over

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.*

At room temperature and pressure, a sample of 2 dm^3 of polluted air was passed through limewater so that all the carbon dioxide present was precipitated as calcium carbonate. The mass of calcium carbonate formed was 0.05 g.

What is the percentage, by volume, of carbon dioxide in the air sample?

A 0.30% **B** 0.57%

C 0.60% D 1.20%

2 When Tl^+(aq) reacts with VO_3^-(aq), Tl^{3+}(aq) and V^{2+}(aq) are formed.

Assuming the reaction goes to completion, how many moles of Tl^+(aq) and VO_3^-(aq) would result in a mixture containing equal number of moles of VO_3^-(aq) and V^{2+}(aq) once the reaction had taken place?

	Moles of Tl^+(aq)	Moles of VO_3^-(aq)
A	1	2
B	1	3
C	2	3
D	3	4

3 Which of the following statements about the carbonate ion, CO_3^{2-}, are correct?

1 The carbon atom is sp^2-hybridised.

2 The carbon in CO_3^{2-} has an octet electronic configuration.

3 It has the same bond angle as the nitrate ion, NO_3^-.

A 1 only

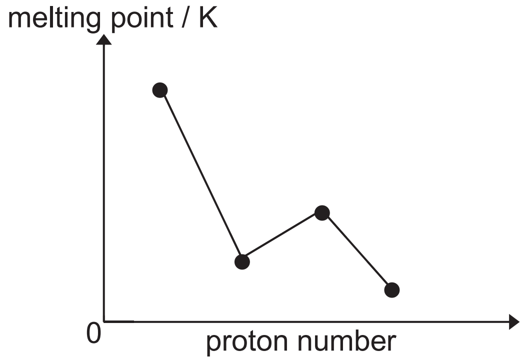
B 1 and 2 only

C 2 and 3 only

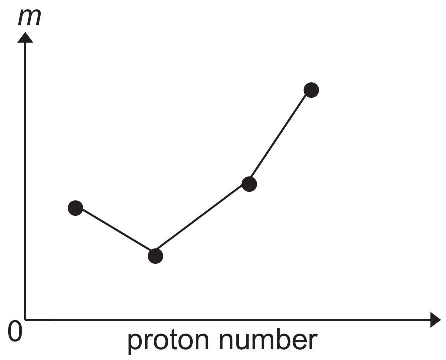
D 1, 2 and 3 only

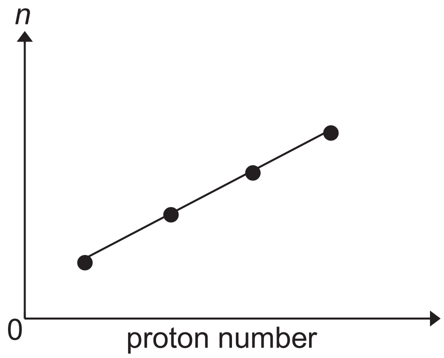
4 The diagram represents the melting points of four consecutive elements in the third period of the Periodic Table.

.



The sketches below represent another two properties, *m* and *n*, of the elements.





What are the properties *m* and *n*?

	Property *m*	Property *n*
A	third ionisation energy	electronegativity
B	number of valence electrons	boiling point
C	ionic radius	effective nuclear charge
D	electrical conductivity	atomic radius

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

Species containing one or more unpaired electrons are said to be paramagnetic as they can be attracted by an external magnetic field.

Which of the following species are paramagnetic?

1 Cr^{3+}

2 Fe^{2+}

3 Cu^{+}

A 1 only

B 1 and 2 only

C 1 and 3 only

D 2 and 3 only

6 Which pair of compounds meets the criteria below?

- The first compound has a larger bond angle than the second compound.
- The second compound is more polar than the first compound.

A CO_2, BCl_3 **B** $IClF_2$, ClO_2 **C** HCN, SO_3 **D** CO_2, NCl_3

7 Flask **X** contains 1 dm^3 of helium at a pressure of 2 kPa and flask **Y** contains 2 dm^3 of neon at a pressure of 1 kPa.

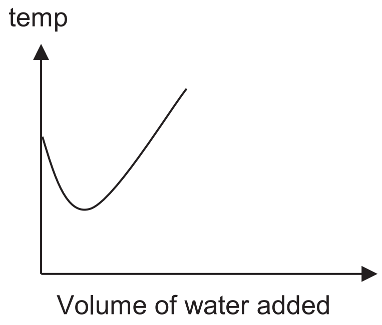
If the flasks are connected at constant temperature, what is the final pressure?

A 1.00 kPa **B** 1.33 kPa **C** 1.67 kPa **D** 2.00 kPa

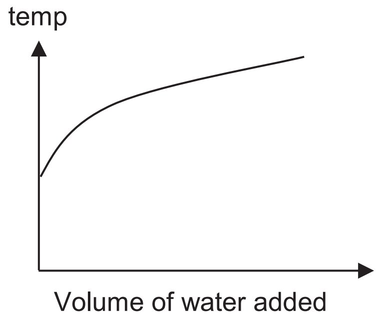
8 When water is stirred with glucose, strong hydrogen bonds are initially formed between glucose molecules and water molecules, but as more water is added, these hydrogen bonds are broken.

Which graph best represents the observed temperature changes?

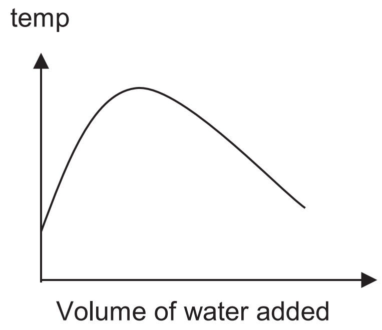
A



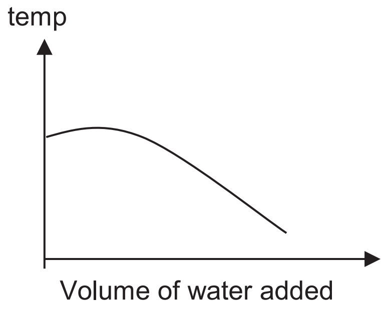
B



C



D



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

A student dissolved 8.4 g of sodium fluoride in 250 g of water.

Given the following thermodynamic data,

Lattice energy of NaF = -918 kJ mol^{-1}

Enthalpy change of hydration of F^- = -457 kJ mol^{-1}

Enthalpy change of hydration of Na^+ = -390 kJ mol^{-1}

What would be the initial temperature of the water if the final temperature of the solution is 20.00 °C?

Assume that the specific heat capacity of water is 4.2 J g^{-1} K^{-1}.

A 6.48 °C **B** 33.08 °C **C** 33.52 °C **D** 47.62 °C

10 Ammonia gas and hydrogen chloride gas react to form ammonium chloride as shown in the equation below:

$$NH_3(g) \;+\; HCl(g) \;\rightarrow\; NH_4Cl(s) \qquad \Delta H^\ominus = -176 \text{ kJ mol}^{-1}$$

The standard entropy change of this reaction is −284 J K^{-1} mol^{-1}.

Which of the following statements is **not** correct?

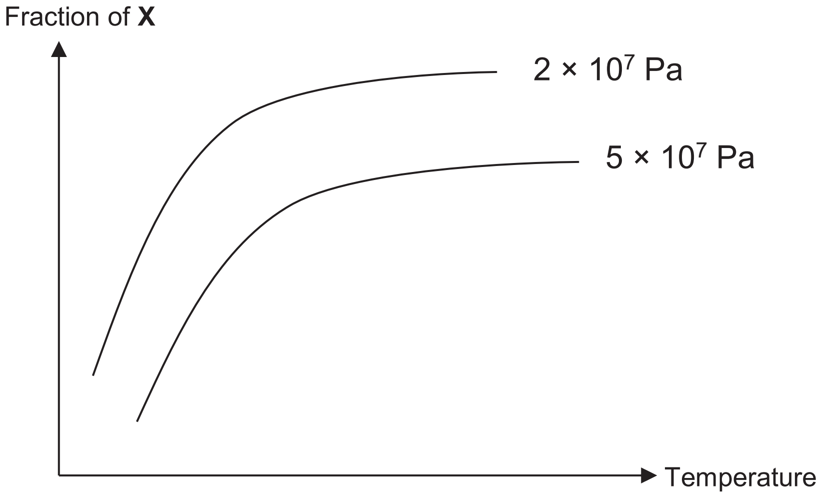
A The reaction is spontaneous at 500 K.

B There is an increase in order due to the formation of a solid from gases.

C The reaction becomes non-spontaneous at temperatures higher than 620 K.

D Under standard conditions, $\Delta G^\ominus = +8.4 \times 10^7$ J mol^{-1}.

11 The graph below shows how the fraction of a substance, **X**, in an equilibrium mixture varies with temperature at pressures of 2×10^7 Pa and 5×10^7 Pa.



Which underlined compound represents **X**?

A $2N_2(g) + 6\underline{H_2O}(g) \rightleftharpoons 4NH_3(g) + 3O_2(g) \quad \Delta H = +1267 \text{ kJ mol}^{-1}$

B $C(s) + H_2O(g) \rightleftharpoons H_2(g) + \underline{CO}(g) \quad \Delta H = +131 \text{ kJ mol}^{-1}$

C $2SO_2(g) + O_2(g) \rightleftharpoons 2\underline{SO_3}(g) \quad \Delta H = -197 \text{ kJ mol}^{-1}$

D $N_2(g) + 3H_2(g) \rightleftharpoons 2\underline{NH_3}(g) \quad \Delta H = -92 \text{ kJ mol}^{-1}$

12 The solubility products of some sparingly soluble silver compounds are shown below.

Which compound, in saturated solution, contains the lowest concentration of silver ions?

	Compound	Solubility Product
A	silver arsenate(V), Ag_3AsO_4	1.0×10^{-22} mol^4 dm^{-12}
B	silver bromide, AgBr	5.0×10^{-13} mol^2 dm^{-6}
C	silver carbonate, Ag_2CO_3	8.1×10^{-12} mol^3 dm^{-9}
D	silver chromate(VI), Ag_2CrO_4	1.1×10^{-12} mol^3 dm^{-9}

13 The kinetics of the reaction between iodide and peroxodisulfate can be investigated by varying the volume of the reactants used. The two reactants are mixed in the presence of a known amount of $Na_2S_2O_3$ and a little starch. The time taken for an intense blue colour to be observed is then determined.

Experiment	Volume used/cm^3			t/s
	1.0 mol dm^{-3} KI	0.040 mol dm^{-3} $Na_2S_2O_8$	H_2O	
1	10.0	5.0	25.0	170
2	15.0	5.0	20.0	113
3	15.0	10.0	15.0	57
4	20.0	20.0	0.0	x

What is the value of x?

A 21 **B** 28 **C** 85 **D** 63

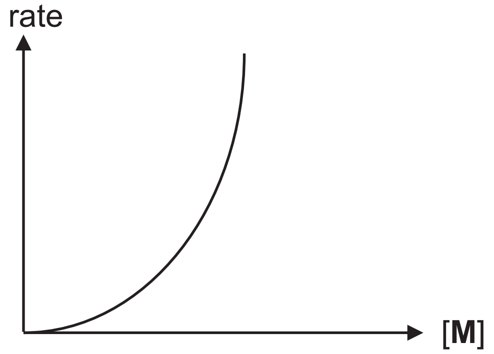
14 **L**, **M** and **N** react to form **P** and **Q** as shown.

$$\mathbf{L} + \mathbf{M} + \mathbf{N} \rightarrow \mathbf{P} + \mathbf{Q}$$

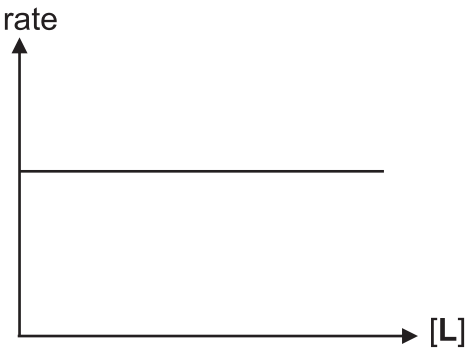
The rate equation for this reaction is rate = k[**M**][**N**].

Which of the following graphs is correct of the above reaction, when **N** is in excess?

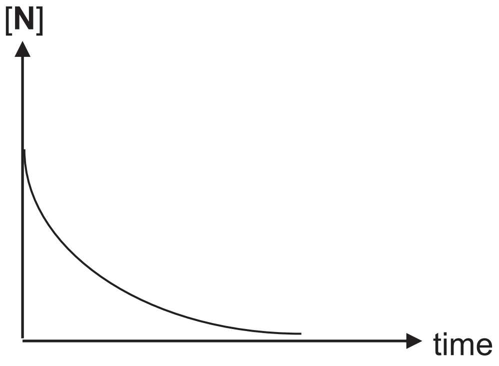
A



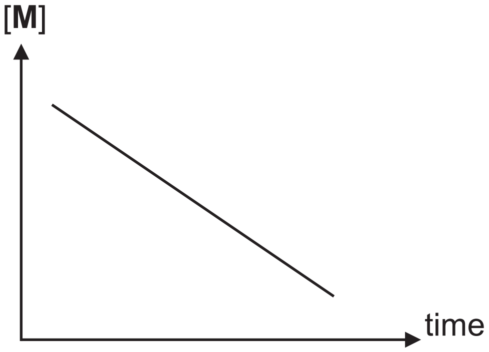
B



C



D



15 The silver halides, AgC*l* and AgBr, are both sparingly soluble in water. AgC*l* dissolves in dilute NH_3(aq) but AgBr can only dissolve in concentrated NH_3.

Which statement helps to explain this observation?

A The complex ion in [Ag(NH_3)$_2$]Br is more stable than the complex ion in [Ag(NH_3)$_2$]C*l*.

B A higher concentration of NH_3 ligand is required to form [Ag(NH_3)$_2$]Br.

C The lattice energy of AgBr(s) is numerically larger than that of AgC*l*(s).

D The solubility product of AgBr(s) is smaller than that of AgC*l*(s).

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

Hydroxyapatite, a basic calcium phosphate, $Ca(OH)_2.3Ca_3(PO_4)_2$, is the mineral found in bone.

Older people may lose calcium ions from the hydroxyapatite, weakening the bone structure. For such cases, strontium salts are administered to strengthen the bone. The strontium ions replace the lost calcium ions in the hydroxyapatite.

Which statements are correct?

1 Strontium ions have similar ionic radii as calcium ions and so may easily replace them in hydroxyapatite.

2 Strontium hydroxide is more soluble than calcium hydroxide and so will precipitate better in the bone structure.

3 There is ionic and covalent bonding in hydroxyapatite which gives it strength.

A 1 only

B 2 only

C 1 and 3 only

D 1, 2 and 3 only

17 Given weighed samples of the same mixture of magnesium carbonate and barium carbonate, which method will **not** allow the mole fraction of magnesium carbonate in the mixture to be estimated?

A Add a known volume of 0.1 mol dm^{-3} HNO_3(aq) in excess and back titrate the excess acid.

B Add an excess of HC*l*(aq) followed by an excess of H_2SO_4(aq); filter, dry and weigh the precipitate.

C Add an excess of HNO_3(aq) and measure, at room temperature and pressure, the volume of CO_2 liberated.

D Heat the mixture at 170°C for 10 minutes. Cool and weigh the mass of residue.

18 When aqueous ammonia is added to a solution containing hexaaquairon(III) ions, $[Fe(H_2O)_6]^{3+}$, a red-brown precipitate is formed which does not dissolve when excess ammonia is added.

What is the role of ammonia molecules in this reaction?

A Brønsted-Lowry base

B Lewis acid

C Ligand

D Reducing agent

19 Adding concentrated HC*l*(aq) to $CuSO_4$(aq) causes the colour of the solution to change from blue to yellow.

Which row best explains this observation? You are given that in the visible spectrum, red light has the lowest energy and violet light has the highest energy.

	Number of d-electrons around copper	Energy gap between the d-orbitals
A	Remains the same	Increase
B	Remains the same	Decrease
C	Changes	Increase
D	Changes	Decrease

20 Scandium, Sc, is the first of the d-block elements in the Periodic Table.

Which properties of scandium are consistent with this fact?

1 Scandium has an ionic chloride.

2 Scandium readily forms oxidation states of +3 and +4.

3 Compounds containing Sc^{3+} are coloured.

A 1 only

B 2 only

C 1 and 2 only

D 2 and 3 only

21 Alkynes are a series of non-cyclic hydrocarbons with the general formula, C_nH_{2n-2} containing one carbon-carbon triple bond per molecule.

How many alkynes with 6 carbon atoms satisfies the above formula?

A 5

B 6

C 7

D 8

22 During the preparation of many organic compounds, by-products are formed. This usually occurs because the reagents can react in more than one way, depending on the conditions used, or because the products formed may react with the reactants.

2-bromobutane may be prepared by slowly adding concentrated sulfuric acid to sodium bromide to form hydrogen bromide which reacts with butan-2-ol. The reaction mixture is kept cool to optimise the reaction yield.

$$CH_3CH(OH)CH_2CH_3 + HBr \rightarrow CH_3CH(Br)CH_2CH_3 + H_2O$$

What could be a by-product of this reaction if the temperature is allowed to rise?

1 $CH_2{=}CHCH_2CH_3$

2 $CH_2BrCH_2CH_2CH_3$

3 $CH_3CBr_2CH_2CH_3$

A 1 only

B 1 and 2 only

C 2 and 3 only

D 1, 2 and 3 only

23 Which method is able to separate benzene from a mixture of benzene and an amine?

A Extracting the amine with ethanol

B Nitrating the benzene with a nitrating agent to precipitate the solid

C Shaking the mixture with dilute aqueous acid

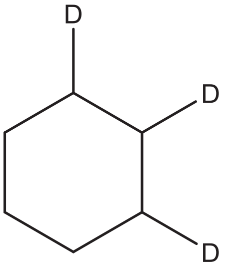
D Extracting the benzene with hexane

24 Deuterium is an isotope of hydrogen, ${}^{2}_{1}H$.

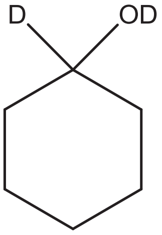
Which compound can be formed by the addition of D_2 to another molecule, in the presence of platinum catalyst?

1 $CH_3CD_2ND_2$

2



3



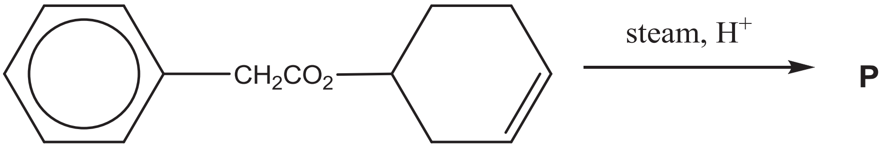
A 1 only

B 1 and 2 only

C 1 and 3 only

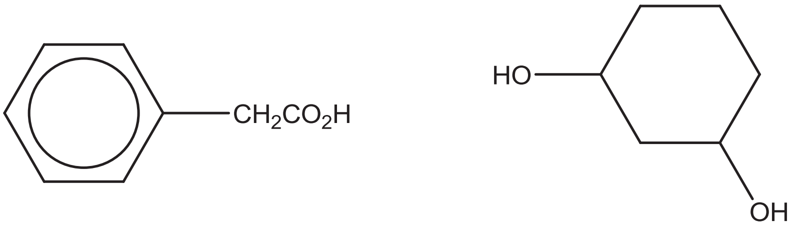
D 2 and 3 only

25 The diagram shows a reaction.

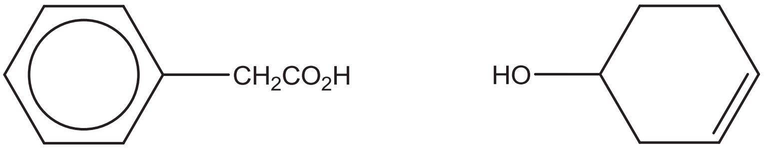


What could be the final products, **P**?

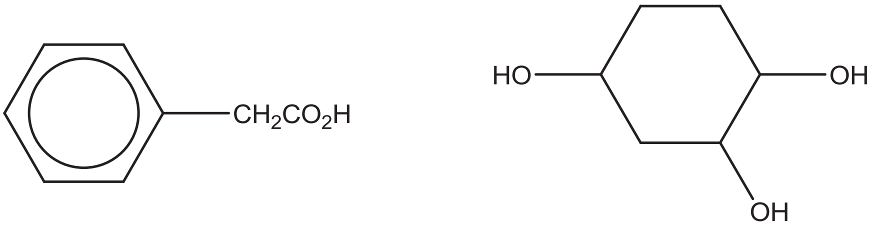
A



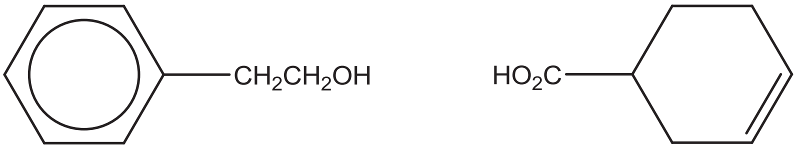
B



C



D



26 Which salt will give a solution with the lowest pH in aqueous solution?

A $C_2H_5NH_3^+Cl^-$

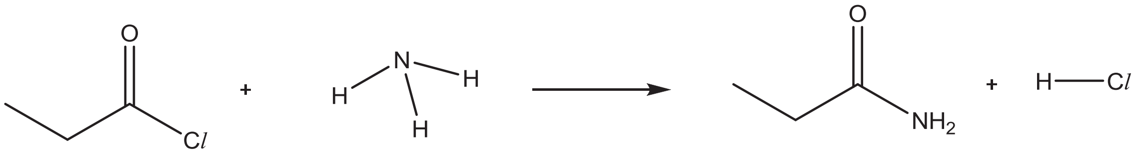
B $NH_4^+Cl^-$

C $C_6H_5NH_3^+Cl^-$

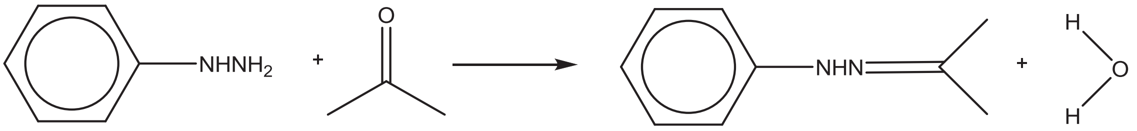
D K^+Cl^-

27 Which transformations involve a nucleophile?

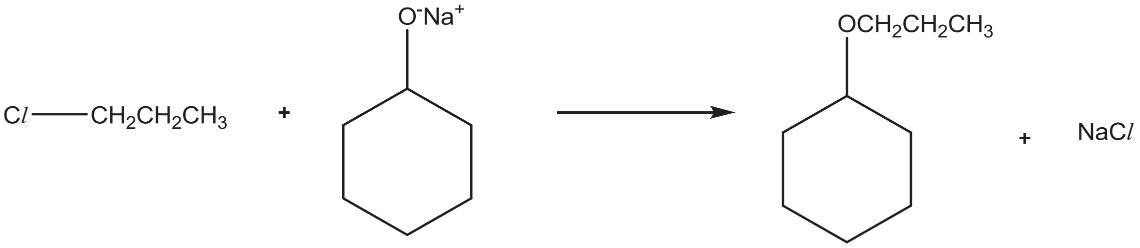
1



2



3



A 1 only

B 3 only

C 1 and 3 only

D 1, 2 and 3 only

Use of the Data Booklet is relevant to Questions 28 - 30.

28 When a dilute sulfate solution of a metal **J** is electrolysed, the metal **J** and a diatomic gas **K** are produced at the cathode and the anode respectively in the molar ratio 2:1.

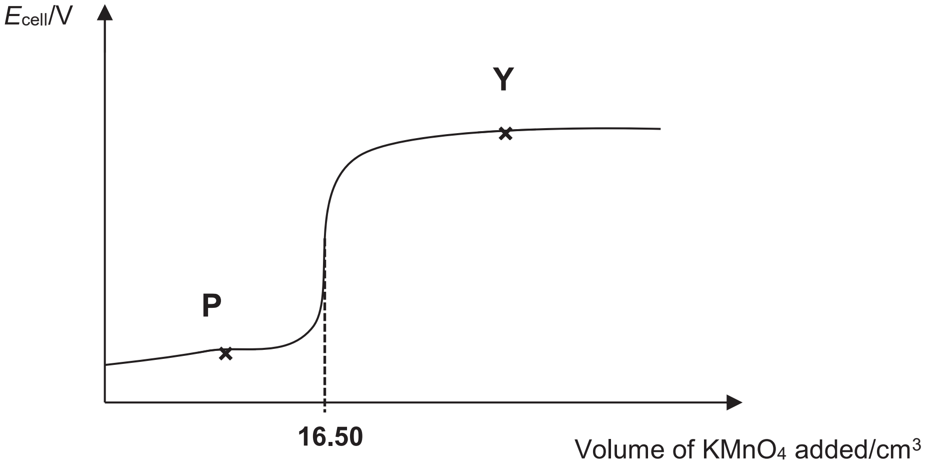
In another experiment, the same quantity of electricity is used to electrolyse a saturated sodium chloride solution and a gas **L** is evolved at the anode.

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

29 Iron(II) salts are often used as a dietary supplement to help cure some forms of anaemia. The amount of iron in such a pill may be estimated by titration with $KMnO_4$ (aq).

A dietary supplement pill was dissolved in 10 cm^3 of dilute sulfuric acid and titrated using 0.0200 mol dm^{-3} $KMnO_4$. The E_{cell} was measured against a standard hydrogen electrode and the following graph was obtained.



Which of the following lists appropriate approximate *E* values, in volts, for the points **P** and **Y**?

	Point **P**	Point **Y**
A	1.52	1.96
B	0.77	1.52
C	0.75	0.77
D	0.75	1.52

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

An electrolytic cell containing Mn^{2+} and another metal ion, $\mathbf{Y}^{3+}$, is connected to Mn and Pt electrodes. The reactions that took place are

$$Mn \rightarrow Mn^{2+} + 2e^{-}$$

$$\mathbf{Y}^{3+} + 3e^{-} \rightarrow \mathbf{Y}$$

Which of the following statements are correct?

1 The Mn electrode is the anode.

2 A possible identity of **Y** is aluminium.

3 The number of moles of **Y** deposited is 1.5 times the number of moles of Mn^{2+} formed.

A 1 only

B 2 only

C 1 and 2 only

D 1 and 3 only

RIVER VALLEY HIGH SCHOOL
YEAR 6 PRELIMINARY EXAMINATION II

CANDIDATE NAME											
CLASS											
CENTRE NUMBER	S	3	0	4	4		INDEX NUMBER	0	0		

H2 CHEMISTRY 9729/02

Paper 2 Structured Questions

13 Sep 2017
2 hours

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST.

DO NOT OPEN THIS BOOKLET UNTIL YOU ARE TOLD TO DO SO.

Write your name, class and index number in the spaces at the top of this page.
Write in dark blue or black pen.
You may use an HB pencil for any diagrams or graphs.
Do not use staples, paper clips, highlighters, glue or correction fluid.

Answer **all** questions in the spaces provided on the Question Paper.
The use of an approved scientific calculator is expected, where appropriate.
A Data Booklet is provided.

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

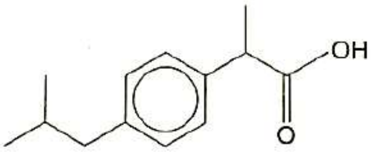
Paper 2

P2	**1**	**2**	**3**	**4**	**5**	**SF**	**UNITS**	**Total (P2)**	
	17	**14**	**14**	**15**	**15**			**75**	
P1	**30**	**P3**	**80**	**Total**	**185**	**P4**	**55**	**Grade**	

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

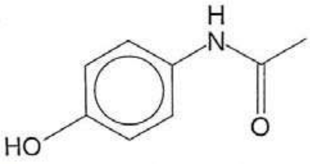
Answer **all** questions in the spaces provided.

1 Among the many pharmaceutical drugs manufactured worldwide, one of the most important types is the painkillers. The structures of three such painkillers are shown.



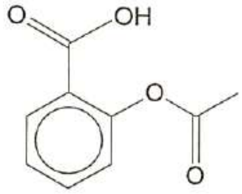
ibuprofen

(M_r = 206)



paracetamol

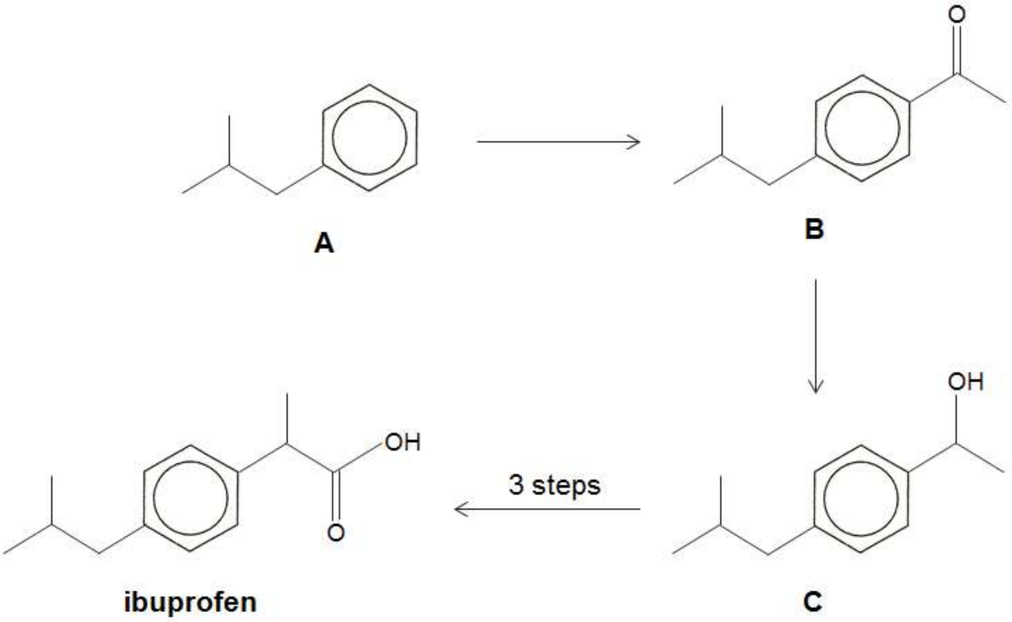
(M_r = 151)



aspirin

(M_r = 180)

Ibuprofen is used to treat arthritis and relieve pain, fever and swelling. It is available over-the-counter in 200 and 400 mg tablets. The recommended dosage varies with body mass and indication, but 1.20 g is considered the maximum daily adult dosage. Long term use of ibuprofen can lead to stomach ulcers. Ibuprofen can be synthesised via the following process:



(a) A man bought some ibuprofen tablets of dosage 200 mg over the counter and consumed one pill 4 times a day. Explain if this level of consumption safe for the man.

....

.... **[1]**

(b) State the *type of reaction* that converts Compound **A** to **B**.

.... **[1]**

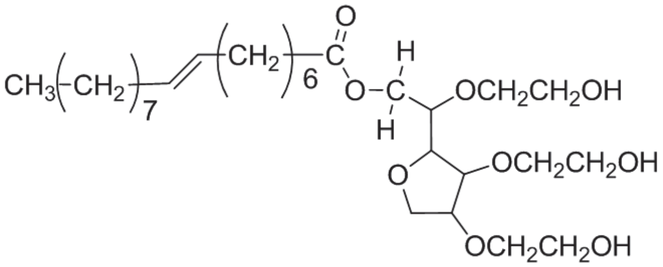
(c) In the laboratory, Compound **C** can be converted to ibuprofen using a 3-step synthesis route.

Suggest reagents and conditions for each step, and draw the structures of all intermediates.

[5]

(d) Young children often find it difficult to swallow tablets. Thus, ibuprofen is supplied as an "infant formula" emulsion.

Given that ibuprofen and water are immiscible, an emulsifier such as polysorbate 80 is used to create a homogeneous mixture.



polysorbate 80

Explain why this molecule is able to act as an emulsifier.

………………………………………………………………………………………………

………………………………………………………………………………………………

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

(e) A certain pharmaceutical brand claims that the ibuprofen tablets it manufactures are 95.0% pure by mass.

To investigate this claim, 5.00 g of a sample was crushed and dissolved in 250 cm^3 of 0.450 mol dm^{-3} aqueous KOH. 25.0 cm^3 of this solution was withdrawn and titrated against sulfuric acid. The unreacted KOH in this solution required 25.50 cm^3 of 0.180 mol dm^{-3} of sulfuric acid for complete neutralisation.

Showing relevant calculations, deduce if the claim is valid.

[3]

(f) Compare the acidity of ibuprofen and aspirin. Explain your answer.

………………………………………………………………………………………

………………………………………………………………………………………

………………………………………………………………………………………

………………………………………………………………………………………

………………………………………………………………………………………

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

(g) Describe two simple chemical tests to distinguish between ibuprofen, paracetamol and aspirin.

………………………………………………………………………………………

………………………………………………………………………………………

………………………………………………………………………………………

………………………………………………………………………………………

………………………………………………………………………………………

……………………………………………………………………………………… **[4]**

[Total: 17]

2 **(a)** Gaseous ethane can be used as a fuel for campers. A company manufactures compressed gaseous ethane in 400 cm^3 metal canisters. A typical metal canister at room temperature contains compressed gaseous ethane at a pressure of 4.00 atm.

(i) Suggest a reason why gaseous ethane in the metal canister does not behave like an ideal gas.

……………………………………………………………………………………

……………………………………………………………………………………

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

(ii) One metal canister is used for heating water and the pressure decreases from 4.00 atm to 1.50 atm. Assuming that the compressed ethane behaves ideally, calculate the mass of water at room temperature that could be brought to boiling if the process is 80% efficient. The enthalpy change of combustion of ethane is –1420 kJ mol^{-1}.

[3]

(iii) Suggest a reason why butane is a better fuel for campers compared to ethane.

……………………………………………………………………………………

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

(b) Calcium fluoride is used for dental protection. It dissolves readily in water with an enthalpy change of solution of –125 kJ mol^{-1}. It is given that the lattice energy of calcium fluoride is –2350 kJ mol^{-1} while the enthalpy change of hydration of calcium ion is –1560 kJ mol^{-1}.

With the aid of a labelled energy level diagram, calculate the enthalpy change of hydration of fluoride ion.

[4]

(c) Liquid hydrazine reacts with oxygen to form nitrogen and steam which could involve the following energy cycle shown below.

$$\begin{tikzcd}
N_2H_4(l) + O_2(g) \arrow[r] \arrow[d] & N_2(g) + 2H_2O(g) \arrow[d] \\
N_2H_4(g) + O_2(g) \arrow[r] & 2N(g) + 4H(g) + 2O(g)
\end{tikzcd}$$

(i) Given that the enthalpy change of vapourisation of hydrazine is +58.0 kJ mol^{-1}, use appropriate bond energies from the *Data Booklet* to calculate the enthalpy change of reaction between liquid hydrazine and oxygen.

[2]

(ii) The reaction shown above has a positive ΔS value. Account for its significance.

………………………………………………………………………………….

………………………………………………………………………………….

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

(iii) Hence, under what conditions of temperature will the reaction be spontaneous?

………………………………………………………………………………….

………………………………………………………………………………….

………………………………………………………………………………….

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

[Total: 14]

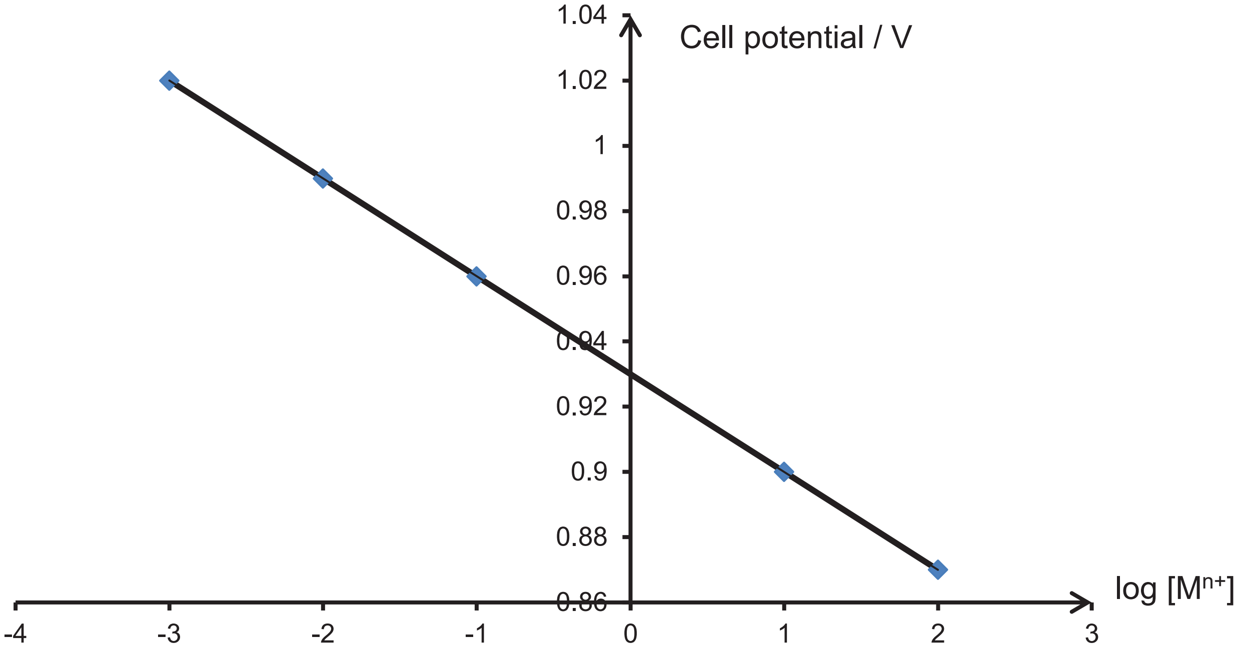
3 An experiment was set up to investigate how the cell potential of a cell containing a metal, M, in contact with an aqueous solution of its ions, $M^{n+}(aq)$, changed as $M^{n+}(aq)$ was diluted.

Since a standard hydrogen half-cell was not available, a half-cell consisting of Cl^-, ClO^- in alkaline medium under standard conditions was used to connect to the half-cell with M in contact with $M^{n+}(aq)$.

(a) Draw the setup of the galvanic cell as described above.

[3]

The cell potential was measured for various concentrations of M^{n+}(aq) and the results of cell potential against log $[M^{n+}]$ obtained are plotted in the graph as shown below.



(b) It is known that the cell potential of a cell, E_{cell}, is related to the standard electrode potential, $E^{\ominus}_{\text{cell}}$, by the equation:

$$E_{cell} = E^{\ominus}_{\text{cell}} - \frac{0.06\,\lg[M^{n+}]}{n}$$

(i) Use your graph to determine the gradient and the charge, n, of the M^{n+} ions.

[2]

(ii) Use your graph to determine the $E^{\ominus}_{\text{cell}}$, showing your working clearly.

[2]

(iii) In the determination of standard electrode potential of a half-cell, the polarity of standard hydrogen electrode can either be positive or negative.

The standard electrode potential for Cl^-, ClO^- in alkaline conditions is +0.80 V.

Hence, calculate the standard electrode potential of the metal, M, and suggest its identity.

[2]

(iv) Suggest one purpose of a salt bridge in a galvanic cell.

………………………………………………………………………………

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

(v) A student suggested the use of aqueous potassium sulfate in the salt bridge. Do you think his choice is wise? Explain your reasoning.

………………………………………………………………………………

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

(c) Using Le Chatelier's Principle and relevant equations, explain why $AgCl$ is soluble in excess aqueous ammonia.

………………………………………………………………………………

………………………………………………………………………………

………………………………………………………………………………

………………………………………………………………………………

………………………………………………………………………………

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

[Total: 14]

4 Viridian is a blue-green pigment used commonly in paints, inks, and stained glasses. The major constituent of viridian is the compound chromium(III) oxide, Cr_2O_3, that gives its characteristic colour.

Alumina, which is the common name for the chemical aluminium oxide (Al_2O_3), is a white solid which is commonly used as abrasive owing to its high hardness rating.

(a) Define the term *transition element.*

…………………………………………………………………………………………

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

(b) In terms of structure and bonding, explain why alumina has a high hardness rating.

…………………………………………………………………………………………

…………………………………………………………………………………………

…………………………………………………………………………………………

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

(c) Both Cr_2O_3 and Al_2O_3 are amphoteric oxides. Describe the observations and write balanced equations when Cr_2O_3 is dissolved in HC*l*(aq) and NaOH(aq). You can assume that the coordination number of chromium in NaOH(aq) is 6.

In HC*l*(aq)

Equation:

…………………………………………………………………………………………

Observation:

…………………………………………………………………………………………

In NaOH(aq)

Equation:

…………………………………………………………………………………………

Observation:

………………………………………………………………………………………… **[4]**

(d) Explain why the resultant solution is coloured when Cr_2O_3 is dissolved in acid.

…………………………………………………………………………………………

…………………………………………………………………………………………

…………………………………………………………………………………………

…………………………………………………………………………………………

…………………………………………………………………………………………

…………………………………………………………………………………………

…………………………………………………………………………………………

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

(e) Another chromium-containing compound, $CrCl_3$, also exhibits similar properties to $AlCl_3$.

Predict the pH of the solution when a solid sample of $CrCl_3$ is dissolved in water. Use equations to justify your answer where possible.

…………………………………………………………………………………………

…………………………………………………………………………………………

…………………………………………………………………………………………

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

(f) *Use of the Data Booklet is relevant to this question.*

The element chromium shows a relatively similar increase in the 1st, 2nd, 3rd and 4th ionisation energy. Aluminium, however, shows a significant difference between its 3rd and 4th ionisation energy.

(i) By means of an equation, express the 2nd ionisation energy of chromium.

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

(ii) Explain fully why the 4th ionisation energy of aluminium has a significantly larger magnitude compared to its 3rd ionisation energy.

……………………………………………………………………………………

……………………………………………………………………………………

……………………………………………………………………………………

……………………………………………………………………………………

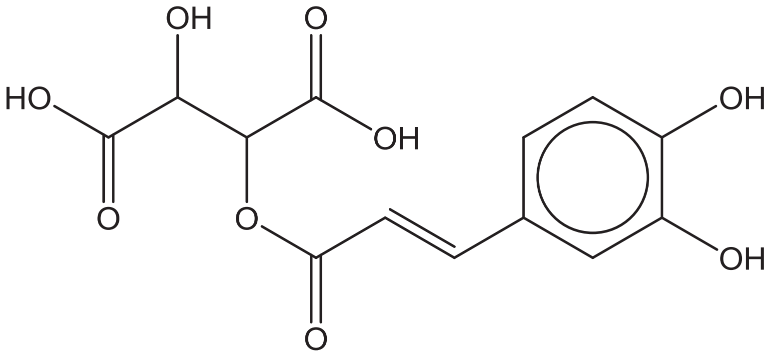
……………………………………………………………………………………

……………………………………………………………………………………

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

[Total: 15]

5 Caftaric acid is a compound found in grapes and is responsible for the yellowish-gold colour seen in some white wines.



caftaric acid

(a) Deduce the molecular formula of caftaric acid.

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

(b) **(i)** State the type(s) of stereoisomerism exhibited by caftaric acid.

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

(ii) Hence, state the total number of stereoisomers of caftaric acid.

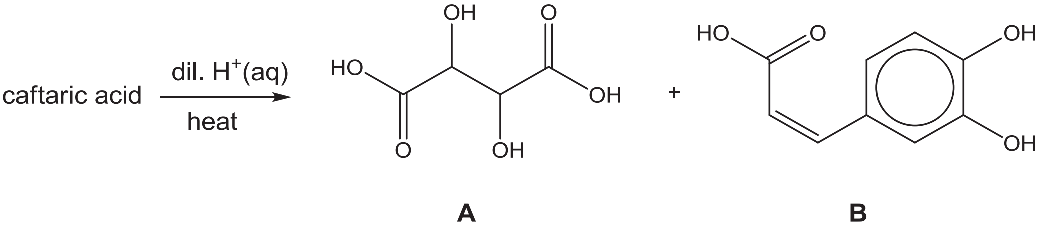
……………………………………………………………………………… **[1]**

(c) The level of caftaric acid can be used to estimate the oxidation levels that a wine has undergone. Wines that undergo a high degree of oxidation, such as pressed wine, will have little to no caftaric acid in them.

Suggest the carbon-containing products formed when caftaric acid is heated with excess acidified $KMnO_4$(aq).

[3]

(d) On heating with dilute aqueous acid, caftaric acid produces two compounds **A** and **B**.



(i) State the *type of reaction* caftaric acid is undergoing when **A** and **B** are formed.

.... **[1]**

(ii) There are three types of molecules of **A**, one of which has no effect on plane polarised light.

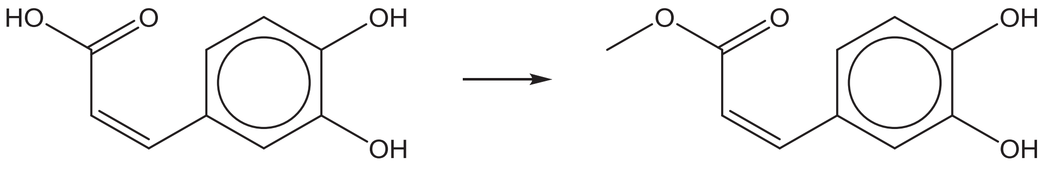
Suggest the structure of the molecule and explain why it has no effect on plane polarised light.

....

....

.... **[2]**

(e) Under suitable conditions, the carboxylic acid functional group in compound **B** can be converted to its methyl ester.



B

(i) State the *type of reaction* undergone by **B** above.

.... **[1]**

(ii) Suggest the reagents and conditions for the above reaction.

.... **[1]**

(f) Another method for conversion of carboxylic acids to their methyl esters involves the reaction with diazomethane, $:\overset{-}{C}H_2-\overset{+}{N}\equiv N$, in an inert solvent.

$$RCO_2H + CH_2N_2 \rightarrow RCO_2CH_3 + N_2$$

This reaction occurs via a two-step mechanism.

- The carboxylic acid reacts with diazomethane to form a carboxylate ion intermediate in the first step.
- N_2 is formed in the second step.

Suggest the mechanism for this reaction. Show any relevant lone pairs, dipoles and charges, and indicate the movement of electron pairs with curly arrows.

[4]

[Total: 15]

END OF PAPER

RIVER VALLEY HIGH SCHOOL
YEAR 6 PRELIMINARY EXAMINATION II

CANDIDATE NAME	
CLASS	6
CENTRE NUMBER	S
INDEX NUMBER	

H2 CHEMISTRY 9729/03

Paper 3 Free Response

19 September 2017

2 hours

Candidates answer on separate paper.

Additional Materials: Answer Paper
Cover Page
Data Booklet

READ THESE INSTRUCTIONS FIRST

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

Section A
Answer **all** questions.

Section B
Answer **one** question.

Begin each question on a fresh sheet of paper.
The use of an approved scientific calculator is expected, where appropriate.
A Data Booklet is provided. Do not write anything on it.
You are reminded of the need for good English and clear presentation in your answers.

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

This document consists of **14** printed pages and **2** blank pages.

Section A

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

1 **(a)** Under suitable conditions, SCl_2 reacts with water to produce a yellow solid and an acidic solution **A**. Solution **A** contains a mixture of SO_2(aq) and another compound.

(i) State the oxidation number of S in SCl_2 . **[1]**

(ii) Construct an equation for the reaction between SCl_2 and water. **[1]**

(iii) In the Contact Process, one important step is the conversion of SO_2 to SO_3 as shown below.

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

A 2.00 L flask was filled with 0.0400 mol SO_2 and 0.0200 mol O_2. At equilibrium, the flask contained 0.0296 mol of SO_3. Determine the value of K_c, stating its unit. **[3]**

(b) During the electrolysis of dilute sulfuric acid using a current of 0.75 A for 90 min and platinum electrodes, the volume of oxygen gas collected was recorded and is shown in Table 1.1 below.

Table 1.1

Time / min	Volume of O_2 gas / cm^3
20	55
40	110
60	165
80	220

(i) Plot a graph of volume of O_2 gas over time.
Use x axis: 2 cm for 10 min ; y axis: 2 cm for 50 cm^3 **[2]**

(ii) Give equations for the reactions that occur at each electrode in the electrolysis of sulfuric acid. **[2]**

(iii) On the same graph, draw and label a line (H_2) to predict the volume of hydrogen that would be given off during the same experiment. **[1]**

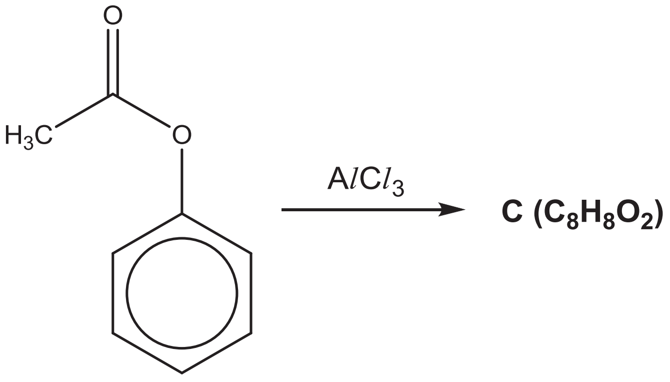
(iv) On the same graph, draw and label a line (O_2) to predict the volume of oxygen that would be given off if a current of 0.3 A was used instead in the original experiment. **[1]**

(v) In a second experiment, the platinum electrodes were replaced with graphite electrodes. The volume of gas collected at the anode was 150 cm^3 while the volume of hydrogen gas collected was 220 cm^3.

The difference in volume of gas collected at the anode between the two experiments was due to the production of CO gas at the anode.

Calculate the volume of CO gas produced at the anode. **[2]**

(c) About 100 years ago, in a reaction discovered by German chemist Karl Fries, compound **B** was converted into compound **C** when heated with $AlCl_3$.



B

Compound **C** is a structural isomer of **B**.

It is insoluble in water but dissolves in aqueous sodium hydroxide.

It gives a yellow ppt with alkaline aqueous iodine and a white ppt with aqueous bromine.

(i) Suggest the structure for compound **C**. **[1]**

The various reactions of compound **C** can be represented as follows:

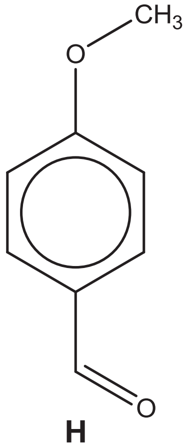
$$\begin{tikzcd}
 & D + E \\
C \arrow[ur, "I_2\text{, NaOH}"] \arrow[r, "Br_2\text{ (aq)}"] \arrow[dr, "\text{NaOH (aq)}"'] & F \\
 & G
\end{tikzcd}$$

(ii) Suggest the structures for **D** to **G**. **[4]**

Compound **H**, as shown below, is another structural isomer of **B.**

It has a ether functional group whose general formula is R–O−R’.

Compound **H** can be formed via a reaction between a substituted phenoxide ion and an alkyl halide molecule.



H

(iii) Describe the mechanism when compound **H** is formed as described above. **[3]**

[Total: 21]

BLANK PAGE

2 In the late 1940s, Willard Libby developed the radiocarbon dating method for determining the age of an object containing organic material by using the properties of radiocarbon (^{14}C), a radioactive isotope of carbon. The principle of carbon dating is as such:

During its life, a plant or animal is exchanging carbon with its surroundings, so the carbon it contains will have the same proportion of ^{14}C as the atmosphere. Once it dies, it ceases to acquire ^{14}C, but the ^{14}C within its biological material at that time will continue to decay, and so the ratio of ^{14}C to ^{12}C in its remains will gradually decrease.

Because ^{14}C decays with first order kinetics, the proportion of radiocarbon can be used to determine how long it has been since a given sample stopped exchanging carbon – the older the sample, the less ^{14}C will be left.

(a) A sample of carbon dioxide gas (that contained both $^{12}CO_2$ and $^{14}CO_2$) was analysed to determine the proportion of $^{14}CO_2$ found within. Analysis results showed that there is one $^{14}CO_2$ molecule for every 10^{12} CO_2 molecules.

(i) Calculate the number of $^{14}CO_2$ molecules in a 10.0 dm^3 carbon dioxide gas sample, measured under s.t.p. **[2]**

(ii) Calculate the mass of $^{14}CO_2$ in the 10.0 dm^3 sample. **[1]**

(iii) Hence, explain why it would be difficult to determine the proportion of $^{14}CO_2$ by means of mass measurement. **[1]**

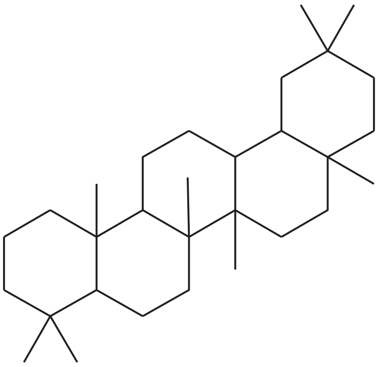
(b) To more accurately determine the proportion of ^{14}C in a sample of graphite, the graphite is vaporised and ionised to $C^+(g)$ ions. These ions were then passed through 2 electric plates.

Given that H^+ is deflected with an angle of 8.4°, what is the angle of deflection for $^{14}C^+$ ions under the same experimental set-up? **[1]**

(c) The half-life of ^{14}C is 5730 years. Determine the time that has elapsed for a piece of wood from a dead tree to contain 30.0% of its original ^{14}C. **[2]**

(d) The age of crude oil is far older than what could be determined from radiocarbon dating.

To measure the age of a crude oil sample, a method involving the measurement of the relative amount of oleanane is used instead.



Oleanane

(i) What is the number of chiral carbons in an oleanane molecule? **[1]**

(ii) Free radical substitution of oleanane with Cl_2 produces a mixture of various products.

Given that tertiary hydrogen atoms are the most reactive towards free radical substitution, suggest the structures of two possible mono-chlorinated oleanane which are formed in high proportions. **[2]**

(e) Benzene is obtained from the fractional distillation of crude oil. It can be converted to a series of different useful chemicals such as phenylamine. The formation of phenylamine involves the direct reaction of nitrobenzene and hydrogen gas in the presence of a heterogeneous catalyst.

A series of experiments were carried out at a specific temperature to investigate the kinetics of this reaction:

Experiment	[nitrobenzene] / mol dm^{-3}	[H_2] / mol dm^{-3}	Initial rate / mol dm^{-3} s^{-1}
1	0.010	0.010	4.50×10^{-5}
2	0.015	0.010	6.74×10^{-5}
3	0.020	0.020	1.80×10^{-4}
4	0.030	x	4.05×10^{-4}

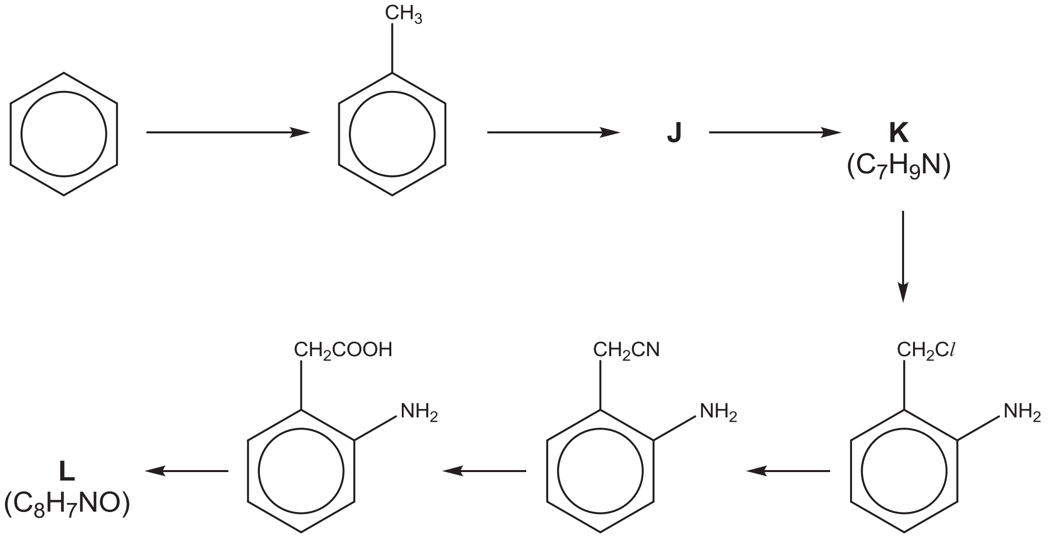
(i) Define the term *heterogeneous catalyst*. **[2]**

(ii) Determine the order of reaction with respect to nitrobenzene and H_2. **[2]**

(iii) Calculate the rate constant, stating its units. **[1]**

(iv) Hence, determine the value of x. **[1]**

(f) Benzene is made to undergo a series of reactions as shown:



(i) Suggest the structures of **J** and **K**. **[2]**

(ii) Given that compound **L** is neutral, suggest the reagent used in the final step and the structure of **L**. **[2]**

[Total: 20]

BLANK PAGE

3 Chromium is a transition metal commonly found in the earth's crust. It is usually mined as chromite.

Period 4 Element	Ti	V	Cr	Mn	Fe	Co	Ni	Cu
Atomic radius / nm	0.132	0.122	0.117	0.117	0.116	0.116	0.115	0.117

(a) Explain why the atomic radius for transition elements remains relatively constant. **[2]**

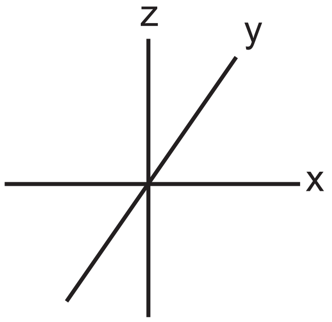
(b) **(i)** Write the electronic configuration for Cr^{3+} ion. **[1]**

(ii) Chromium forms octahedral complexes with the general formula $CrCl_3.6H_2O$. One of them dissolves in water to form a violet solution which turned green upon warming. An excess of aqueous silver nitrate was added separately to solutions containing 0.0100 mol of each complex. The violet complex gave 1.50 g of precipitate, while the green complex gave 4.40 g of precipitate.

Deduce the formulae of the two complex ions.

Write the equation for the conversion of the violet complex to the green complex. **[3]**

(iii) Using the Cartesian axes, like those shown below,



draw **fully-labelled** diagrams of the following :

- One of the d orbital at the lower energy level in an octahedral complex. Label this diagram “Lower energy level”.
- One of the d orbital at the upper energy level in an octahedral complex. Label this diagram “Upper energy level”. **[2]**

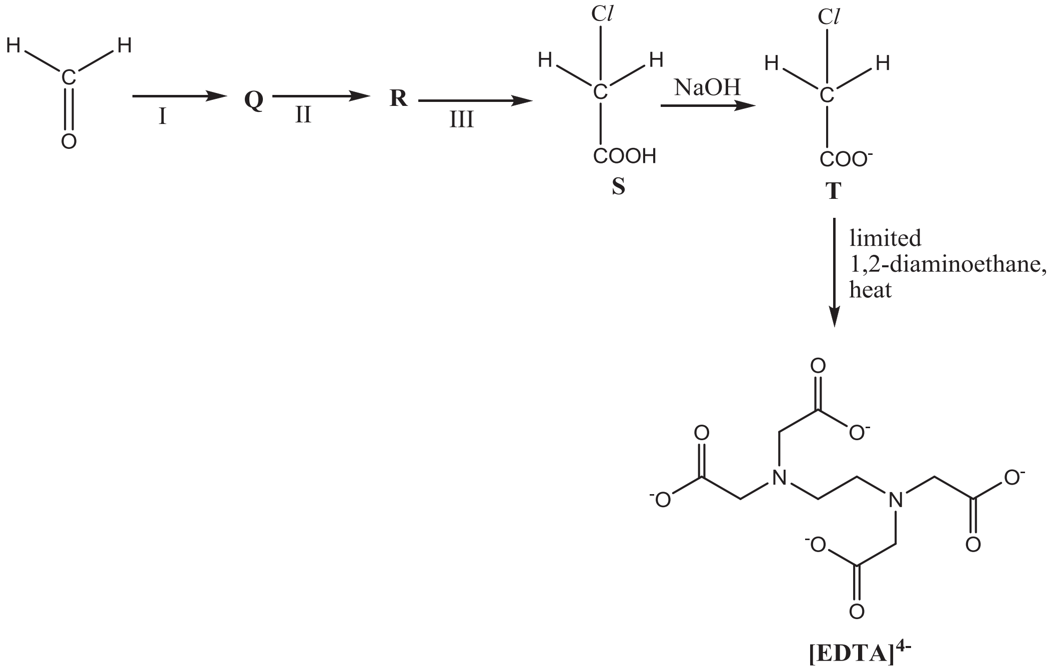
(c) When sodium carbonate is added to a dichromate(VI) solution, the solution turned yellow.

$$\underset{\text{orange}}{Cr_2O_7^{2-}(aq)} + 2OH^-(aq) \rightleftharpoons \underset{\text{yellow}}{2CrO_4^{2-}(aq)} + H_2O(l)$$

Using a relevant equation, explain the above observation. **[2]**

(d) Ethylenediamine tetraacetate, $[EDTA]^{4-}$, is a ligand that acts as a chelating agent. It is widely used to remove transition metal ions such as those of chromium from aqueous solutions.

A possible reaction scheme used to synthesise $[EDTA]^{4-}$ from methanal is given below.



(i) Suggest the reagents and conditions in steps I, II and III. **[3]**

(ii) Draw the displayed formulae of intermediates **Q** and **R**. **[2]**

(iii) State the type of reaction when **T** is converted to $[EDTA]^{4-}$.

Give a reason why a limited amount of 1,2-diaminoethane is used. **[2]**

(iv) Define the term *ligand*. State the number of coordinate bonds that a $[EDTA]^{4-}$ ligand can form with a central metal ion. **[2]**

[Total: 19]

Section B

Answer **one** question from this section.

4 This question concerns the chemistry of the oxides of some elements.

(a) The oxides of Period 3 show different reactions with water.

Describe the reactions, if any, of the oxides SiO_2 and SO_3 with water.

Include the approximate pH value of any resulting solutions, and write equations for any reactions that occur. **[3]**

(b) Carbon combusts in oxygen to form two common oxides, CO and CO_2. These oxides are also formed when solid magnesium oxalate, MgC_2O_4, is heated strongly.

(i) Write an equation, with state symbols, to represent the thermal decomposition of solid magnesium oxalate. **[1]**

(ii) Explain why magnesium oxalate decomposes at a lower temperature than barium oxalate, BaC_2O_4. **[2]**

Carbon also forms compounds with other Group 16 elements like sulfur and selenium. The properties of some of these compounds, along with CO_2, are given in Table 4.1.

Table 4.1

Compound	Structure	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

(iii) Explain, in terms of structure and bonding, the difference in the boiling point of CS_2 and COS. **[2]**

(iv) Explain why

- CO_2 has no overall dipole moment.
- COSe has a greater dipole moment than COS. **[2]**

(c) Aside from the common oxides, carbon forms a series of reactive oxocarbons. One such compound is tricarbon monoxide, C_3O, a reactive molecule found in space.

(i) Suggest a structure of tricarbon monoxide. Indicate clearly any lone pairs present. **[1]**

Tricarbon monoxide is isoelectronic to cyanogen, $(CN)_2$. The molecule of cyanogen contains a C–C single bond.

(ii) 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]**

(iii) Suggest the shapes of tricarbon monoxide and cyanogen. **[1]**

(d) Another oxycarbon is pentacarbon dioxide, C_5O_2. It can be obtained by heating compound **X**, $C_6H_6O_3$, at a high temperature. **X** exists in equilibrium with its isomer, **Y**.

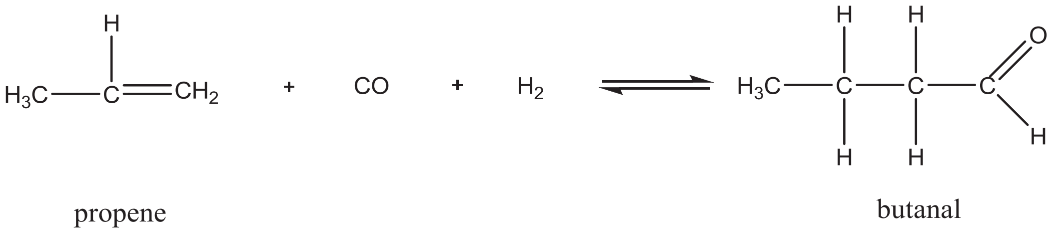
X does not react with aqueous bromine. **X** also gives an orange precipitate with 2,4-DNPH but does not give a silver mirror with Tollens' reagent. When reacted with limited bromine under ultraviolet light, **X** produced **only one** mono-brominated compound.

Y reacts with dilute nitric acid to form **only one** mono-nitrated compound, **Z**.

Suggest the structures of compounds **X**, **Y** and **Z**. Explain your reasoning. **[7]**

[Total: 20]

5 **(a)** Hydroformylation is an industrial process for the formation of aldehydes from alkenes.



(i) Determine the oxidation numbers of carbon-1, carbon-2 and carbon-4 in butanal. **[1]**

(ii) The hydroformylation of propene can result in the formation of two isomeric products. Given that the mechanism of hydroformylation resembles the electrophilic addition of alkenes, suggest the structure of the other isomer apart from butanal. **[1]**

(iii) Write the K_p expression for the reaction above, stating its units. **[1]**

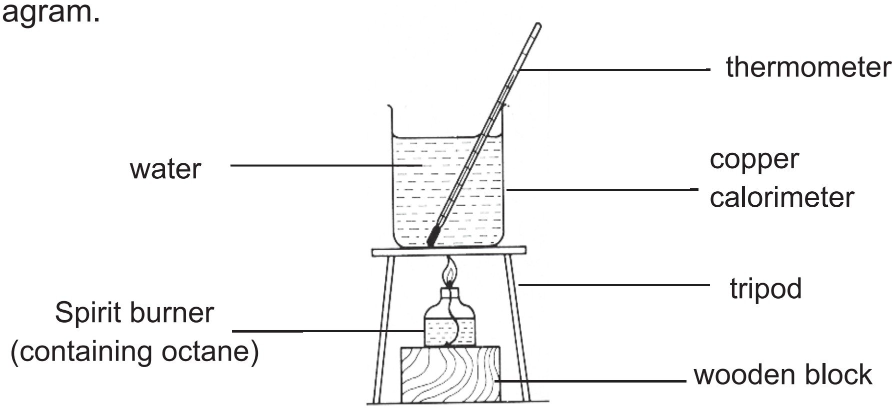
(iv) When an equimolar mixture of propene, CO and H_2 at an initial pressure of 120 Pa was allowed to reach equilibrium at 550 K, the partial pressure of butanal was found to be 38.5 Pa.

Calculate a value of K_p at 550 K. **[2]**

(v) Hence, predict the sign of ΔG for the reaction. Explain your reasoning taking into account the thermodynamic considerations of the reaction. **[2]**

(b) Other important use of hydrocarbons include fuels, plastics, paints and solvents. In some countries, where crude oil is either scarce or expensive, biofuels such as ethanol are also increasingly being used for fuels instead of hydrocarbons.

(i) James carried out an experiment to determine the enthalpy change of combustion of octane, C_8H_{18}, using the apparatus shown in the diagram.



These are the results that James obtained:

Volume of water = 1000 cm^3

Initial temperature of water = 29.6 °C

Highest temperature of water = 50.0 °C

Initial mass of burner and octane = 59.35 g

Final mass of burner and octane = 53.77 g

Heat capacity of calorimeter = 770 $J\ K^{-1}$

Use these results and data from the *Data Booklet* to determine the experimental enthalpy change of combustion of octane. **[3]**

(ii) The accurate experimental enthalpy change of combustion of three hydrocarbons are given in Table 5.1.

Table 5.1

Alkane	Formula	ΔH_c/ kJ mol^{-1}
Heptane	C_7H_{16}	–4817
Octane	C_8H_{18}	–5470
Nonane	C_9H_{20}	–6125

Suggest what the regular increase in the values of ΔH_c given in the table represents. **[1]**

(iii) Draw a pair of enantiomers of heptane. **[1]**

(iv) Alkanes are also used in dry cleaning of clothing and textiles. Dry cleaning involves soaking the clothes in a solvent other than water. Recently, the use of supercritical carbon dioxide as a dry cleaning solvent has also been gaining popularity. Supercritical carbon dioxide is a fluid state of carbon dioxide which is maintained at or above its critical temperature.

Suggest two possible reasons why supercritical carbon dioxide is a better solvent than organic solvents like hexane. **[2]**

(c) Many modern methods of chemical analysis rely on the use of sophisticated instruments. For many years, scientists relied on traditional laboratory apparatus for chemical analysis.

Many qualitative tests and some volumetric analysis used depended on an application of the principles of solubility product.

Data for use in this question are given in Table 5.2.

Table 5.2

	Colour	Solubility / mol dm^{-3}	K_{sp} (25 °C)
AgCl	White	1.42×10^{-5}	2.02×10^{-10}
AgI	Yellow	8.95×10^{-9}	8.01×10^{-17}
Ag_2CrO_4	Red	9.10×10^{-5}	3.01×10^{-12}

(i) Aqueous $AgNO_3$ is added to solutions containing 0.100 mol dm^{-3} Cl^-(aq) or 0.0100 mol dm^{-3} CrO_4^{2-}(aq). What concentration of Ag^+ must be present to cause the precipitation of

I: $AgCl$

II: Ag_2CrO_4? **[2]**

(ii) Standard solutions of silver nitrate can be used in volumetric analysis to determine the concentration of chloride ions in a sample of water. When the titration is carried out, $AgNO_3$(aq) of known concentration is added slowly to the solution that contains Cl^- ions. A small quantity of aqueous potassium chromate(VI), K_2CrO_4 (0.01 mol dm^{-3}) is also added as an indicator.

Using the data given in Table 5.2 and your answers in **(c)(i)**, predict using calculations what you would see at the beginning of the titration and at the end-point and explain why K_2CrO_4(aq) can be used as an indicator in this titration. **[4]**

[Total: 20]

- End of Paper –

RIVER VALLEY HIGH SCHOOL

YEAR 6 PRACTICAL EXAMINATION

H2 CHEMISTRY 9729

23RD AUG 2017

2 hour 30 minutes

NAME ______________________________

CLASS 6 (   )

INDEX NO. ______________________________

INSTRUCTIONS TO CANDIDATES

DO NOT OPEN THIS BOOKLET UNTIL YOU ARE TOLD TO DO SO.

Read these notes carefully.

Write your name, class and index number in the spaces at the top of this page.
Give details of the practical shift and laboratory where appropriate, in the boxes provided.
Write in dark blue or black pen.
You may use an HB pencil for any diagrams or graph.
Do not use staples, paper clips, highlighters, glue or correction fluid.

Shift
Laboratory

*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 15 and 16.

For Examiner's Use	
1	/ 21
2	/ 15
3	/ 9
4	/ 10
Total	/ 55

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

1 **Determine the the percentage by mass of sodium ethanedioate in a mixture of sodium ethanedioate and ethanedioic acid.**

This experiment involves **two steps**.
In step one, you will carry out a titration to find the amount of acid, $H_2C_2O_4$, present in **FB 3**.
In step two, you will carry out a second titration to find the total amount of ethanedioate ion, $C_2O_4^{2-}$, present in **FB 3**.
Finally, you will use the values found in the two steps to calculate the percentage by mass of sodium ethanedioate in **FB 3**.

FB 1 is 0.100 mol dm^{-3} sodium hydroxide, NaOH
FB 2 is 0.0200 mol dm^{-3} potassium manganate(VII), $KMnO_4$
FB 3 is a mixture of aqueous sodium ethanedioate, $Na_2C_2O_4$, and ethanedioic acid, $H_2C_2O_4$
FB 4 is approximately 2 mol dm^{-3} sulfuric acid
thymolphthalein indicator

Read through the whole method before starting any practical work.

(a) Method

<u>Step 1</u>

1. Fill the burette labelled **FB 1** with **FB 1**.
2. Pipette 25.0 cm^3 of **FB 3** into a conical flask.
3. Add 1 dropper full of thymolphthalein.
4. Titrate **FB 3** in the conical flask with **FB 1** until a pale blue colour is seen.
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 **FB 1** added in each accurate titration.

Step 2

1. Pipette 25.0 cm^3 of **FB 3** into a conical flask.
2. Using a measuring cylinder, add about 25 cm^3 of 2 mol dm^{-3} sulfuric acid, **FB 4**, to the flask.
3. Place the conical flask on a hotplate and heat to about 65°C.
4. Fill the burette labelled **FB 2** with **FB 2**.
5. Use an appropriate method to carefully transfer the hot conical flask onto a white tile under the burette.
6. Titrate the mixture in the conical flask with **FB 2** until a permanent pale pink colour is seen. If a permanent brown colour is seen, stop the titration and begin **Step 2** again.
7. Carry out as many accurate titrations as you think necessary to obtain consistent results.
8. Record in a suitable form below all of your burette readings and the volume of **FB 2** added in each accurate titration.

M1	
M2	
M3	

[3]

(b) (i) From your titration results in **Step 1**, obtain a suitable value to be used in your calculations. Show clearly how you have obtained this value.

M4	
M5	

25.0 cm^3 of **FB 3** required …………. cm^3 of **FB 1**

[2]

(b) (ii) Write an equation for the reaction between sodium hydroxide and ethanedioic acid to give sodium ethanedioate and water. [1]

M6	

………………………………………………………………………………………..

(b) (iii) Use your answer from **(b)(i)** to calculate the amount of sodium hydroxide, **FB 1**, required to react with 25.0 cm^3 of **FB 3** in **Step 1**.

M7	

Amount of NaOH = ……………………….

[1]

(b) (iv) Use your answer to **(b)(iii)** to determine the amount of ethanedioic acid in 25.0 cm^3 of **FB 3**.

M8	

Amount of $H_2C_2O_4$ in 25.0 cm^3 of **FB 3** = ...

[1]

(c) (i) From your titration results in **Step 2**, obtain a suitable value to be used in your calculations. Show clearly how you have obtained this value.

M9	
M10	
M11	

25.0 cm^3 of **FB 3** required ………….. cm^3 of **FB 2**.

[3]

(c) (ii) Use your answer from **(c)(i)** to calculate the amount of potassium manganate(VII), **FB 2**, required to react with 25.0 cm^3 of **FB 3** in **Step 2**.

M12

Amount of $KMnO_4$ = ...
[1]

(c) (iii) The equation for the reaction between acidified manganate(VII) ions and ethanedioate ions is shown below.

$$2MnO_4^- (aq) + 5C_2O_4^{2-} (aq) + 16H^+ (aq) \rightarrow 2Mn^{2+} (aq) + 10CO_2(g) + 8H_2O(l)$$

Calculate the total amount of ethanedioate ions in 25.0 cm^3 of **FB 3**.

M13

Total amount of $C_2O_4^{2-}$ in 25.0 cm^3 of **FB 3** = ………………
[1]

(c) (iv) Use your answers to **(b)(iv)** and **(c)(iii)** to calculate the amount of ethanedioate ions which came from the sodium ethanedioate dissolved in 25.0 cm^3 of **FB 3**.

M14

Amount of $C_2O_4^{2-}$ from $Na_2C_2O_4$ in 25.0 cm^3 of **FB 3** = ……………….
[1]

(d) (i) Use your answer to **(b)(iv)** to calculate the mass of ethanedioic acid, $H_2C_2O_4$, in 25.0 cm^3 of **FB 3**. [A_r: H, 1.0; C, 12.0; O, 16.0]
(If you were unable to answer **(b)(iv)**, you may assume that the amount of ethanedioic acid is 6.51×10^{-4} mol.)

M15

Mass of ethanedioic acid = ...
[1]

(d) (ii) Use your answer to **(c)(iv)** to calculate the mass of sodium ethanedioate, $Na_2C_2O_4$ in 25.0 cm^3 of **FB 3**. [A_r: C, 12.0; O, 16.0; Na, 23.0]
(If you were unable to answer **(c)(iv)**, you may assume that the amount of sodium ethanedioate is 4.13×10^{-4} mol.)

M16	

Mass of sodium ethanedioate = ...
[1]

(d) (iii) Calculate the percentage by mass of sodium ethanedioate in **FB 3**.

M17	

Percentage by mass of sodium ethanedioate is ....
[1]

(e) (i) A student suggested that using a burette to measure the 25.0 cm^3 of acid would give a more accurate result than using a pipette.

The percentage error of a 25.0 cm^3 pipette is 0.24 %. Is the student correct? Explain your answer. [2]

………………………………………………………………………………………..

M18	
M19	

………………………………………………………………………………………..

………………………………………………………………………………………..

……………………………………………………………………………………….

(e) (ii) A student decided to use a 25.0 cm^3 pipette instead of a measuring cylinder to measure the volume of **FB 4** in **Step 2**.

State and explain whether this alteration will improve the accuracy of the calculation of the percentage by mass of sodium ethanedioate in the mixture. [2]

M20	
M21	

………………………………………………………………………………………..

………………………………………………………………………………………..

………………………………………………………………………………………..

[Total: 21]

BLANK PAGE

2 Investigate how the rate of the following reaction varies with the concentration of sodium thiosulfate, $Na_2S_2O_3$.

$$Na_2S_2O_3\,(aq) + H_2SO_4\,(aq) \rightarrow S\,(s) + Na_2SO_4\,(aq) + SO_2\,(g) + H_2O\,(l)$$

The rate of the reaction above can be found by measuring how long it takes for the solid sulfur formed to obscure the printing on the insert provided.

Care should be taken to avoid inhalation of SO_2(g) that is given off during this reaction.

FC 5 is 1.0 mol dm^{-3} sulfuric acid, H_2SO_4
FC 6 is 0.10 mol dm^{-3} sodium thiosulfate, $Na_2S_2O_3$

(a) Method

1. Using the 50 cm^3 measuring cylinder, transfer 45 cm^3 of **FC 6** into a 100 cm^3 beaker.
2. Using the 25 cm^3 measuring cylinder, measure 10 cm^3 of **FC 5**.
3. Tip the **FC 5** into the **FC 6** in the beaker and **immediately** start the stopwatch.
4. Stir the mixture once with a glass rod and place the beaker on top of the printed insert. Cover the beaker with a petri dish.
5. View the printed insert from above so that it is seen through the mixture.
6. Record the time, to the nearest second, when the printing on the insert **just** disappears.
7. Empty and rinse the beaker. Shake out as much of the water as possible and dry the inside of the beaker.

You will repeat the experiment to find out how the time for the printing on the insert to disappear changes when a different volume of **FC 6** is used.

8. Using the 50 cm^3 measuring cylinder, transfer 20 cm^3 of **FC 6** and 25 cm^3 of distilled water into the 100 cm^3 beaker.
9. Using the 25 cm^3 measuring cylinder, add 10 cm^3 of **FC 5** to the mixture and **immediately** start timing.
10. Stir the mixture once with a glass rod and place it on top of the printed insert.
11. View the printed insert from above so that it is seen through the mixture.
12. Record the time, to the nearest second, when the printing on the insert **just** disappears.
13. Select suitable volumes of **FC 6 and** distilled water for **two** further experiments to investigate the effect of volume of sodium thiosulfate on the time taken for the printing on the insert to **just** disappear. The volume of **FC 6** used should range from 0 cm^3 to 45 cm^3.

In the space below, record, in an appropriate form, all measurements of volume, time, and 1/time.

M1	
M2	
M3	
M4	
M5	

[5]

(b) Plot 1/time against the volume of **FC 6**. Draw the most appropriate line, taking into account all the points. [3]

M6	M7	M8

(c) Why was the total volume of solution kept constant in the experiments? [1]

……………………………………………………………………………………………

M9	

……………………………………………………………………………………………

(d) Using the graph of 1/time against the volume of **FC 6,** draw a conclusion about the relationship between the concentration of sodium thiosulfate used and the rate of reaction. Hence, state the order of reaction with respect to sodium thiosulfate. [2]

……………………………………………………………………………………………

M10	
M11	

……………………………………………………………………………………………

……………………………………………………………………………………………

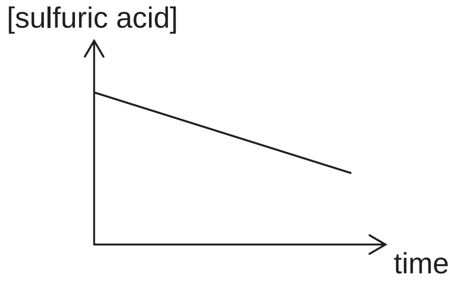
(e) In the four experiments, which value of the time measured had the greatest error? Explain your answer. [2]

……………………………………………………………………………………………

M12	
M13	

……………………………………………………………………………………………

(f) Another student conducts another experiment for the same reaction where the sodium thiosulfate is in large excess. The concentration of acid is monitored as the reaction progresses. His results are as shown below.



M14	
M15	

Deduce the order of reaction with respect to sulfuric acid. [2]

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

[Total: 15]

3 Organic Analysis

Before starting parts (a) and (b), half-fill a 250 cm^3 beaker with water and heat with a hotplate to approximately 60 ^{0}C. You will use this as a hot water bath.

(a) **FD 7**, **FD 8** and **FD 9** are solutions each containing a single compound which could be ethanol, ethanal or propanone. To identify each compound you will react the samples with Tollens' reagent and with acidified potassium manganate(VII).

<u>Preparation of Tollens' reagent</u>

1. To approximately 2 cm depth of aqueous silver nitrate in a boiling tube, add approximately 0.5 cm depth of aqueous sodium hydroxide.
2. Add aqueous ammonia a little at a time with continuous shaking until the brown precipitate just dissolves. Do not add an excess of ammonia.

Complete the table below.

test	*observations*		
	FD 7	**FD 8**	**FD 9**
To a 1 cm depth of each solution in a clean test-tube, add a few drops of the Tollens' reagent that you have prepared. **Do not shake the tube**. If no reaction is seen, warm the tube in the hot water bath.			
To a 1 cm depth of each solution in a test-tube, add 1 cm depth of dilute sulfuric acid. Then add a few drops of aqueous potassium manganate(VII). If no reaction is seen, warm the tube in the hot water bath.			
Identity			

[4]

M1	M2	M3	M4

(b) **FD 10** is an aqueous solution of an organic compound. Carry out the following tests.

test	*observations*
To a 1 cm depth of **FD 10** in a test-tube, add 1 cm depth of dilute sulfuric acid. Then add a few drops of aqueous potassium manganate(VII). If no reaction is seen, place the test-tube in the hot water bath and leave to stand.	
To a 1 cm depth of **FD 10** in a test-tube, carefully add a small spatula measure of sodium hydrogen carbonate.	

[2]

M5	M6

(c) State the type(s) of reactions that **FD 10** have undergone in **(b)**. [2]

…………………………………………………………………………………………..

…………………………………………………………………………………………..

M7	
M8	

(d) You are given that the M_r of **FD 10** is 46.0. State the identity of **FD 10.** [1]
[A_r: C, 12.0; O, 16.0; H, 1.0; Cl, 35.5; N, 14.0]

…………………………………………………………………………………………..

M9	

[Total: 9]

4 Planning

When heated, aqueous hydrogen peroxide, H_2O_2, decomposes to form oxygen and water.

$$2H_2O_2\,(aq) \rightarrow 2H_2O\,(l) + O_2\,(g)$$

The decomposition can also occur at room temperature if a suitable catalyst is added. Both of the solids, manganese(IV) oxide and lead(IV) oxide, will catalyse the decomposition.

You are provided with:

- 0.150 mol dm^{-3} solution of hydrogen peroxide
- a syringe with a capacity of 100 cm^3
- apparatus normally found in a school laboratory

(a) (i) Using the information given above, you are required to write a plan to determine the more efficient catalyst for the decomposition of aqueous hydrogen peroxide. Your plan should include:

- a fully labelled diagram of the apparatus to be used
- a calculation of the volume in cm^3 of the aqueous hydrogen peroxide that could be used such that an appropriate volume of oxygen could be collected.
- the measurements you would take that and how you would use them to deduce which catalyst is more efficient.

The molar volume of a gas at 20 °C is 24.0 dm^3.

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

[9]

M1	M2	M3	M4	M5	M6	M7	M8	M9

(ii) What other feature of the catalyst should be controlled during the experiment? [1]

…………………………………………………………………………………… **M10** ☐

[Total : 10]

~END OF PAPER~

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 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)

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

For each candidate

- 1 × 25 cm^3 pipette
- 2 × 50 cm^3 burette
- 1 × burette stand and clamp
- 1 × funnel (for filling burette)
- 2 × 250 cm^3 conical flask
- 2 × 250 cm^3 beaker
- 1 × 100 cm^3 beaker
- 1 × 50 cm^3 measuring cylinder
- 1 × 25 cm^3 measuring cylinder
- 1 × white tile
- 1 × white insert with cross
- 1 × petri dish
- 1 × hotplate
- 1 × spatula
- 6 clean test-tubes
- 1 × boiling tube
- 1 × test-tube rack

- 1 × test-tube holder
- 1 × glass rod
- 4 × teat/dropping pipette
- 1 × wash bottle containing distilled water
- 1 × thermometer (–10 °C to +110 °C at 1 °C)
- 1 × stopwatch
- paper towels
- access to a balance reading to at least 0.1 g

For each candidate

hazard	label	per candidate	identity	notes (hazards given in this column are for the raw materials)
[H]	**FB 1**	100 cm^3	0.1 mol dm^{-3} sodium hydroxide	Dissolve 4.0 g NaOH **[C]** in each dm$_3$ of solution.
[N]	**FB 2**	120 cm^3	0.02 mol dm^{-3} potassium manganate(VII)	Dissolve 3.16 g $KMnO_4$ **[N] [O] [H]** in each dm$_3$ of solution.
	FB 3	230 cm^3	solution containing a mixture of ethanedioic acid and sodium ethanedioate	Dissolve 3.80 g $HOOCCOOH.2H_2O$ **[H]** and 2.00 g $Na_2C_2O_4$ **[H]** in each dm^3 of solution.
[C]	**FB 4**	150 cm^3	2.0 mol dm^{-3} sulfuric acid	Cautiously pour 110 cm^3 of concentrated (98 %) sulfuric acid **[C]** into 800 cm^3 of distilled water with continuous stirring. Make the solution up to 1 dm^3 with distilled water. **Care** – *concentrated* H_2SO_4 *is very corrosive*.
[F]	**thymolphthalein indicator**	5 cm^3	thymolphthalein	.
[H]	**FC 5**	100 cm^3	1.0 mol dm^{-3} sulfuric acid	Cautiously pour 55 cm^3 of concentrated (98%) sulfuric acid [C] into 500 cm^3 of distilled water with continuous stirring. Make the solution up to 1 dm^3 with distilled water Care: concentrated H_2SO_4 is very corrosive.
	FC 6	180 cm^3	0.1 mol dm^{-3} sodium thiosulfate	Dissolve 24.8 g of $Na_2S_2O_3.5H_2O$ in each dm^3 of solution. The solid should be dissolved in boiled distilled water that has been cooled in a closed vessel. This prevents oxidation of the thiosulfate by dissolved oxygen.
	FD 7	10 cm^3	0.10 mol dm^{-3} magnesium sulfate	Dissolve 24.6 g of $MgSO_4.7H_2O$ in each dm^3 of solution.
***[F] [H]**	**FE 8**	5 cm^3	1.0 mol dm^{-3} glucose	Dissolve 180 g of glucose in each dm^3 of solution. This should be provided in a stoppered container.
***[F] [H]**	**FE 9**	5 cm^3	distilled water	Provided in a stoppered container.
[F] [H]	**FE 10**	5 cm^3	ethanol	Ethanol [F], or IMS, Industrial Methylated Spirits [F] [H]. Provided in a stoppered container.
[C]	**FE 11**	5 cm^3	3.0 mol dm^{-3} methanoic acid	Dilute 126 cm^3 of HCOOH, methanoic acid (90%) [C] to 1 dm^3 with distilled water.

Bench reagents

hazard	Label	notes
[H]	**dilute hydrochloric acid**	All concentrations to be around 2.0 mol dm^{-3} Except sulfuric acid (1.0 mol dm^{-3})
[C]	**dilute nitric acid**	
[H]	**dilute sulfuric acid**	
[H]	**aqueous ammonia**	
[C]	**aqueous sodium hydroxide**	
[H]	**0.1 mol dm^{-3} barium nitrate**	
[H] [N]	**0.05 mol dm^{-3} silver nitrate**	
[H]	**limewater**	
[N]	**0.02 mol dm^{-3} potassium manganate(VII)**	
	0.1 mol dm^{-3} potassium iodide	
	Red & Blue litmus paper	

Answers to Paper 1

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

RIVER VALLEY HIGH SCHOOL
YEAR 6 PRELIMINARY EXAMINATION II

CANDIDATE NAME					
CLASS					
CENTRE NUMBER	S	3	0	4	4
INDEX NUMBER	0	0			

H2 CHEMISTRY
9729/02

Paper 2 Structured Questions

13 Sep 2017

2 hours

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST.

DO NOT OPEN THIS BOOKLET UNTIL YOU ARE TOLD TO DO SO.

Write your name, class and index number in the spaces at the top of this page.
Write in dark blue or black pen.
You may use an HB pencil for any diagrams or graphs.
Do not use staples, paper clips, highlighters, glue or correction fluid.

Answer **all** questions in the spaces provided on the Question Paper.
The use of an approved scientific calculator is expected, where appropriate.
A Data Booklet is provided.

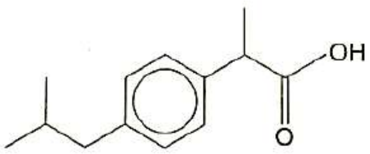
At the end of the examination, fasten all your work securely together.
The number of marks is given in brackets [ ] at the end of each question or part question.

For Examiner's Use									
Paper 2									
P2	1	2	3	4	5	SF	UNITS	Total (P2)	
	17	14	14	15	15			75	
P1	30	P3	80	Total	185	P4	55	Grade	

This paper consists of **XX** printed pages.

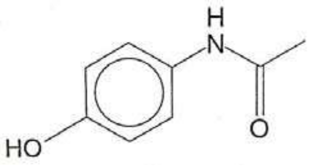
Answer **all** questions in the spaces provided.

1 Among the many pharmaceutical drugs manufactured worldwide, one of the most important types is the painkillers. The structures of three such painkillers are shown.



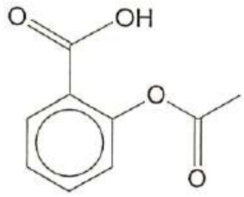
ibuprofen

(M_r = 206)



paracetamol

(M_r = 151)

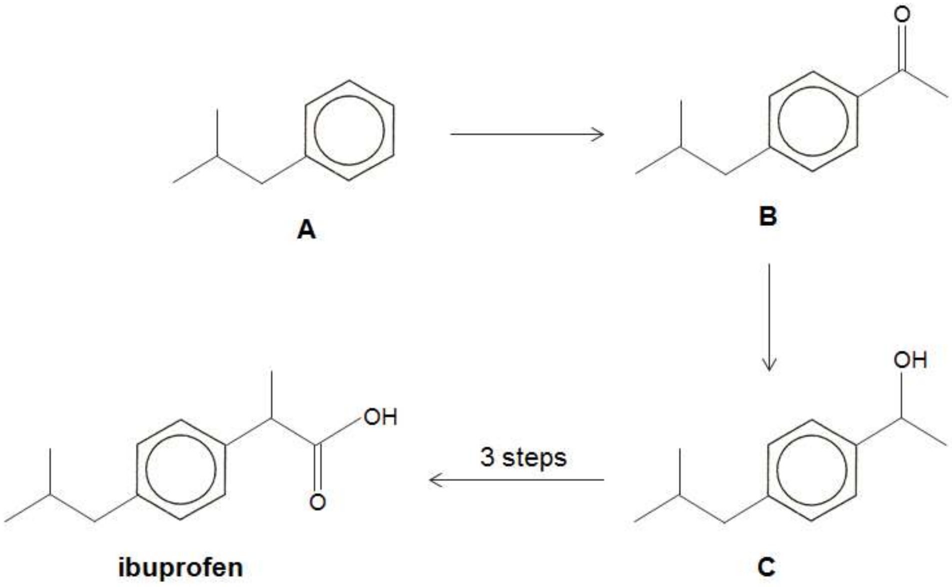


aspirin

(M_r = 180)

Ibuprofen is used to treat arthritis and relieve pain, fever and swelling. It is available over-the-counter in 200 and 400 mg tablets. The recommended dosage varies with body mass and indication, but 1.20 g is considered the maximum daily adult dosage. Long term use of ibuprofen can lead to stomach ulcers.

Ibuprofen can be synthesised via the following process:



(a) A man bought some ibuprofen tablets of dosage 200 mg over the counter and consumed one pill 4 times a day. Explain if this level of consumption safe for the man.

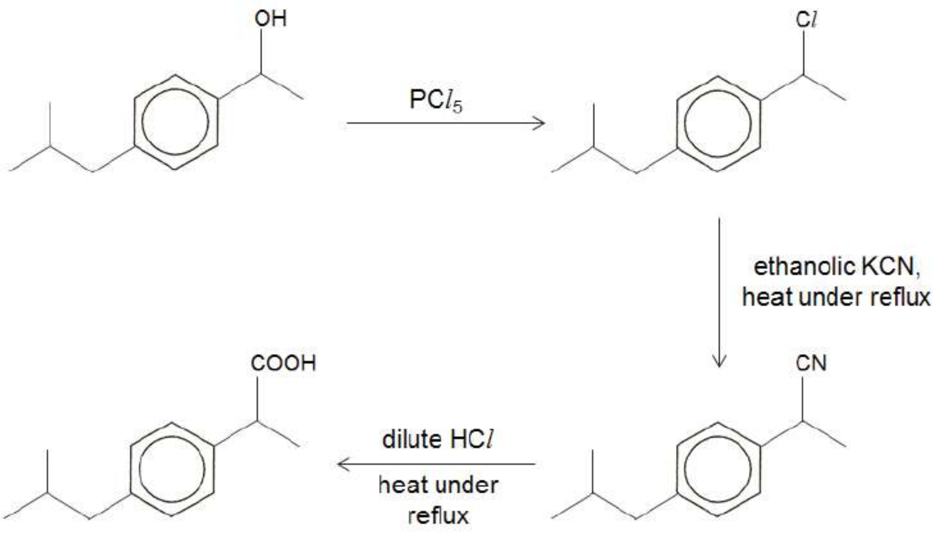
Since 4 x 200 = 800 mg is lower than the maximum dosage of 1200 mg, the level of consumption is safe for the man. **[1]**

(b) State the *type of reaction* that converts Compound **A** to **B**.

Electrophilic substitution **[1]**

(c) In the laboratory, Compound **C** can be converted to ibuprofen using a 3-step synthesis route.

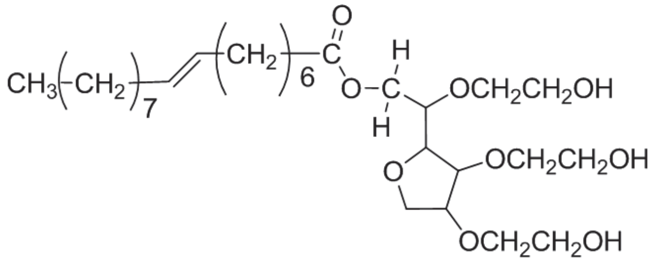
Suggest reagents and conditions for each step, and draw the structures of all intermediates.



[5]

(d) Young children often find it difficult to swallow tablets. Thus, ibuprofen is supplied as an "infant formula" emulsion.

Given that ibuprofen and water are immiscible, an emulsifier such as polysorbate 80 is used to create a homogeneous mixture.



polysorbate 80

Explain why this molecule is able to act as an emulsifier.

The -OH polar groups allow the molecule to be soluble in water, while the non-polar hydrocarbon groups allow the molecule to be soluble in oil / non-polar liquids.

[1]

(e) A certain pharmaceutical brand claims that the ibuprofen tablets it manufactures are 95.0% pure by mass.

To investigate this claim, 5.00 g of a sample was crushed and dissolved in 250 cm^3 of 0.450 mol dm^{-3} aqueous KOH. 25.0 cm^3 of this solution was withdrawn and titrated against sulfuric acid. The unreacted KOH in this solution required 25.50 cm^3 of 0.180 mol dm^{-3} of sulfuric acid for complete neutralisation.

Showing relevant calculations, deduce if the claim is valid.

Amount of H_2SO_4 = $\frac{25.50}{1000} \times 0.180$

= 0.00459 mol

Amount of unreacted KOH = 0.00459 x 2

= 0.00918 mol

Amount of unreacted KOH (in 250 cm^3) = 0.0918 mol

Amount of KOH reacted with ibuprofen sample = $\frac{250}{1000} \times 0.450 - 0.0918$

= 0.0207 mol

Since ibuprofen ≡ KOH,

Amount of ibuprofen = 0.0207 mol

Mass of ibuprofen = 0.0207 x [13(12.0) + 18(1.0) + 2(16.0)]

= 4.26 g

Percentage purity = $\frac{4.26}{5.00} \times 100\%$

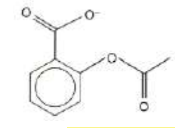
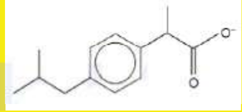
= 85.2%

Hence, the claim is invalid.

[3]

(f) Compare the acidity of ibuprofen and aspirin. Explain your answer.

Aspirin is a stronger acid than ibuprofen.

The anion of aspirin, , is more stable than the anion of ibuprofen, , as the negative charge is delocalised over the COO^- group and into the benzene ring.

[2]

(g) Describe two simple chemical tests to distinguish between ibuprofen, paracetamol and aspirin.

Test: Add neutral $FeCl_3$(aq)

[4]

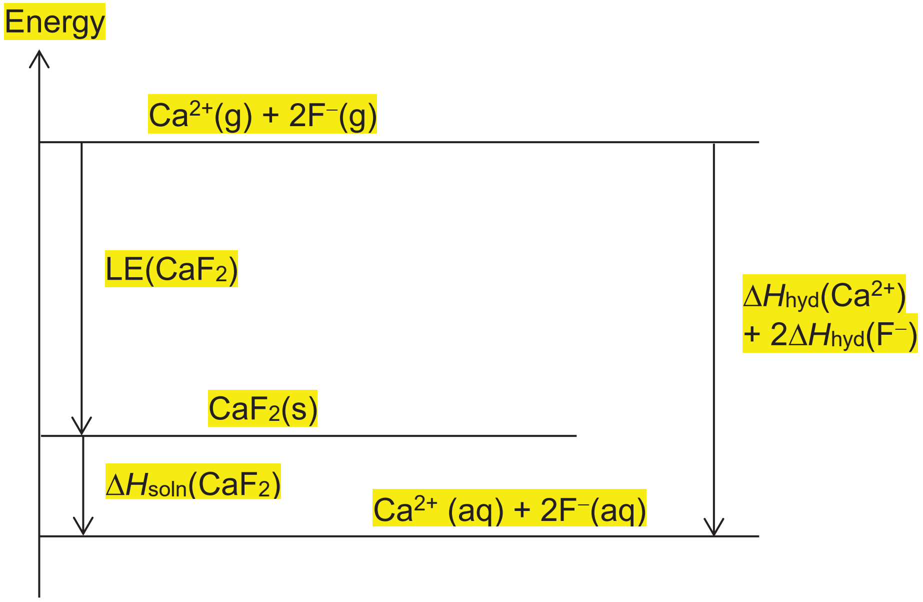
		Observations: Violet colouration forms for paracetamol. No violet colouration forms for ibuprofen and aspirin. Test: Heat with acidified $KMnO_4(aq)$ Observations: Purple $KMnO_4$ turns colourless for ibuprofen. $KMnO_4$ remains purple for paracetamol and aspirin.		
				[Total: 17]

2	**(a)**	Gaseous ethane can be used as a fuel for campers. A company manufactures compressed gaseous ethane in 400 cm^3 metal canisters. A typical metal canister at room temperature contains compressed gaseous ethane at a pressure of 4.00 atm.		
		(i)	Suggest a reason why gaseous ethane in the metal canister does not behave like an ideal gas.	
			Due to high pressure in the canister, volume of the ethane molecules is not negligible compared to volume of the metal canister / intermolecular forces of attraction between ethane molecules are not negligible.	**[1]**
		(ii)	One metal canister is used for heating water and the pressure decreases from 4.00 atm to 1.50 atm. Assuming that the compressed ethane behaves ideally, calculate the mass of water at room temperature that could be brought to boiling if the process is 80% efficient. The enthalpy change of combustion of ethane is –1420 kJ mol^{-1}.	
			Using $pV = nRT$, $(2.50 \times 101325)(400 \times 10^{-6}) = n\,(8.31)(293)$ n = amount of ethane used = 0.0416 mol Heat evolved from combustion of ethane = 0.0416×1420 = 59.1 kJ $0.80 \times 59.1 \times 10^3$ = Mass of water $\times 4.18 \times (100 – 20)$ Mass of water = 141 g	**[3]**
		(iii)	Suggest a reason why butane is a better fuel for campers compared to ethane.	

Butane has a higher magnitude of enthalpy change of combustion / More heat is produced per mole of butane combusted / Butane is more compressible, and therefore more portable. **[1]**

(b) Calcium fluoride is used for dental protection. It dissolves readily in water with an enthalpy change of solution of –125 kJ mol^{-1}. It is given that the lattice energy of calcium fluoride is –2350 kJ mol^{-1} while the enthalpy change of hydration of calcium ion is –1560 kJ mol^{-1}.

With the aid of a labelled energy level diagram, calculate the enthalpy change of hydration of fluoride ion.



By Hess' Law,

$\Delta H_{soln}(CaF_2) = –LE(CaF_2) + \Delta H_{hyd}(Ca^{2+}) + 2\Delta H_{hyd}(F^{-})$

$–125 = –(–2350) + (–1560) + 2\Delta H_{hyd}(F^{-})$

$\Delta H_{hyd}(F^{-}) = –458$ kJ mol^{-1} **[4]**

(c) Liquid hydrazine reacts with oxygen to form nitrogen and steam which could involve the following energy cycle shown below.

$$\begin{tikzcd}
N_2H_4(l) + O_2(g) \arrow[r] \arrow[d] & N_2(g) + 2H_2O(g) \arrow[d] \\
N_2H_4(g) + O_2(g) \arrow[r] & 2N(g) + 4H(g) + 2O(g)
\end{tikzcd}$$

(i) Given that the enthalpy change of vapourisation of hydrazine is +58.0 kJ mol^{-1}, use appropriate bond energies from the *Data Booklet* to calculate the enthalpy change of reaction between liquid hydrazine and oxygen.

$\Delta H_r = \Delta H_{vap}(N_2H_4) + [BE(N–N) + 4BE(N–H) + BE(O=O)]$

$– [BE(N≡N) + 4BE(O–H)]$

$= +58 + [(+160) + 4(+390) + (+496)] – [(+944) + 4(+460)]$

$= –510$ kJ mol^{-1}

[2]

(ii) The reaction shown above has a positive ΔS value*.* Account for its significance.

There is an increase in disorder of the system. The amount of gaseous molecules increases from 1 mol to 3 mol as the reaction proceeds.

[1]

(iii) Hence, under what conditions of temperature will the reaction be spontaneous?

$\Delta G = \Delta H – T\Delta S$

Since ΔS is positive, $–T\Delta S$ is negative. Given that the calculated ΔH is negative, ΔG is negative and the reaction is spontaneous at all temperatures.

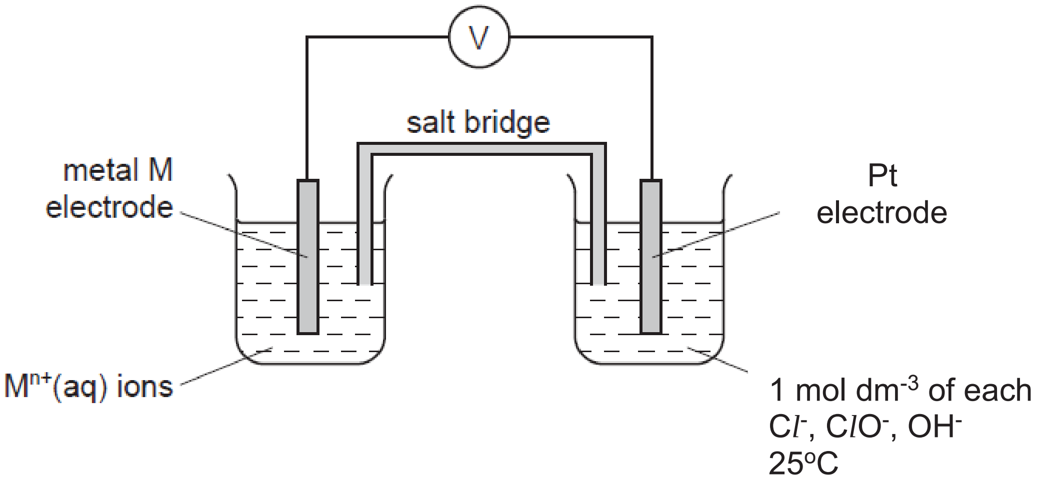
[2]

[Total: 14]

3 An experiment was set up to investigate how the cell potential of a cell containing a metal, M, in contact with an aqueous solution of its ions, $M^{n+}(aq)$, changed as $M^{n+}(aq)$ was diluted.

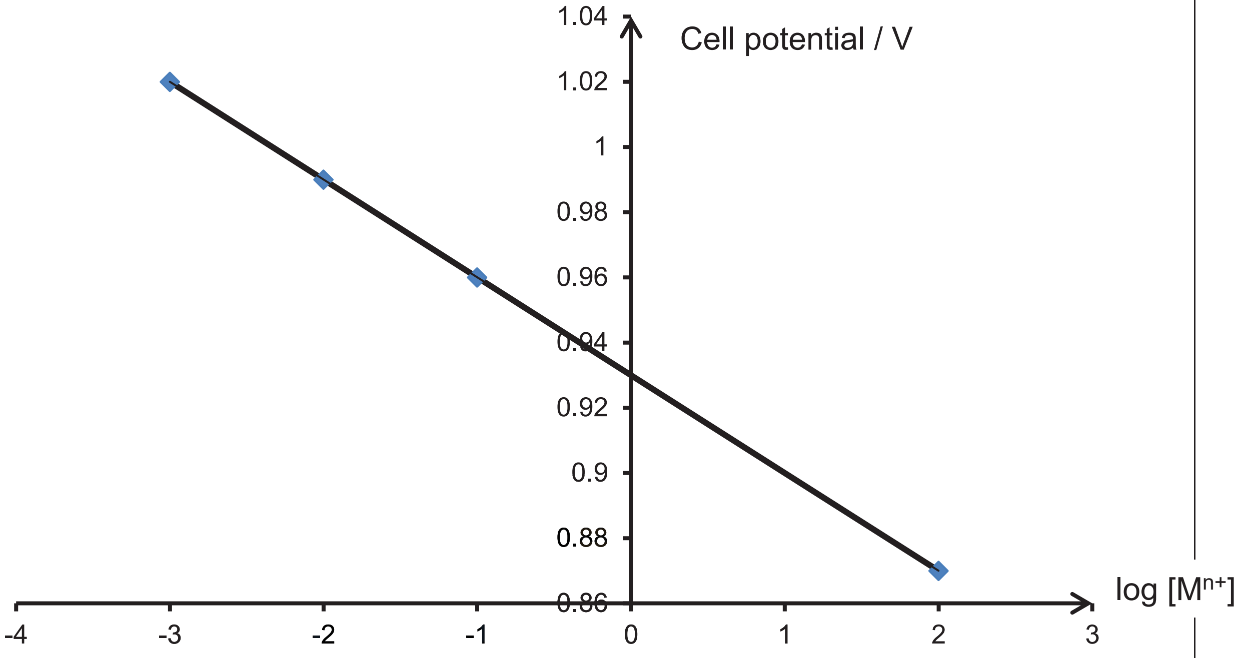
Since a standard hydrogen half-cell was not available, a half-cell consisting of Cl^-, ClO^- in alkaline medium under standard conditions was used to connect to the half-cell with M in contact with M^{n+}(aq).

(a) Draw the setup of the galvanic cell as described above.



[3]

The cell potential was measured for various concentrations of M^{n+}(aq) and the results of cell potential against log [M^{n+}] obtained are plotted in the graph as shown below.



(b) It is known that the cell potential of a cell, E_{cell}, is related to the standard electrode potential, $E^{\ominus}_{cell}$, by the equation:

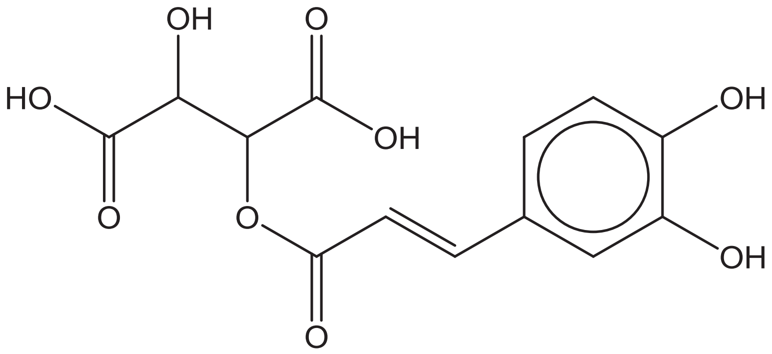
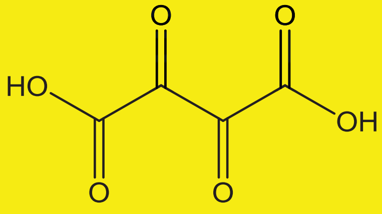
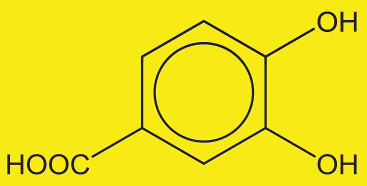
$$E_{cell} = E^{\ominus}_{cell} - \frac{0.06\lg[M^{n+}]}{n}$$

		(i)	Use your graph to determine the gradient and the charge, n, of the M^{n+} ions.	
			Gradient = −0.0300 **– 0.06 / n = -0.0300** **n = 2**	**[2]**
		(ii)	Use your graph to determine the $E^{\ominus}_{cell}$, showing your working clearly.	
			$\log_{10}1 = 0$ **y-intercept = 0.93 V or uses equation to calculate**	**[2]**
		(iii)	In the determination of standard electrode potential of a half-cell, the polarity of standard hydrogen electrode can either be positive or negative. The standard electrode potential for Cl^-, ClO^- in alkaline conditions is +0.80 V. Hence, calculate the standard electrode potential of the metal, M, and suggest its identity.	
			$E^{\ominus}$ for M = 0.80 – 0.93 = –0.13 V M is Pb.	**[2]**
		(iv)	Suggest one purpose of a salt bridge in a galvanic cell.	
			To allow movement of ions / complete the circuit OR To maintain electrical neutrality / charge or ion balance	**[1]**
		(v)	A student suggested the use of aqueous potassium sulfate in the salt bridge. Do you think his choice is wise? Explain your reasoning.	
			Not wise $PbSO_4$ is insoluble/ is a ppt. Will affect *E* values.	**[2]**
	(c)	Using Le Chatelier's Principle and relevant equations, explain why $AgCl$ is soluble in excess aqueous ammonia.		
		$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$ ---------- (1) $Ag^+(aq) + 2NH_3(aq) \rightleftharpoons [Ag(NH_3)_2]^+(aq)$ When excess NH_3 is added, diammine silver complex is formed.		**[2]**

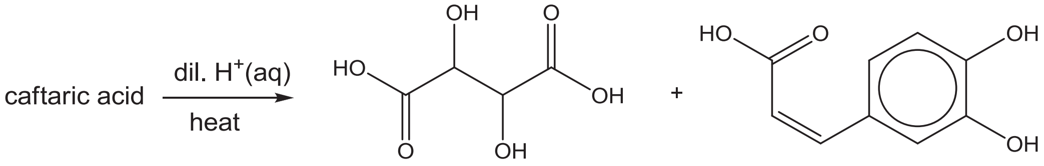
		POE in (1) is shifted to the right as [Ag^+] decreases. $AgCl$ dissolves.	
		[Total: 14]	

4	Viridian is a blue-green pigment used commonly in paints, inks, and stained glasses. The major constituent of viridian is the compound chromium(III) oxide, Cr_2O_3, that gives its characteristic colour. Alumina, which is the common name for the chemical aluminium oxide (Al_2O_3), is a white solid which is commonly used as abrasive owing to its high hardness rating.		
	(a)	Define the term *transition element.*	
		A transition element is a d-block element which forms at least one stable ion (compound) with a partially filled d subshell.	**[1]**
	(b)	In terms of structure and bonding, explain why alumina has a high hardness rating.	
		Alumina has a giant ionic structure. Strong electrostatic forces of attractions between Al^{3+} and O^{2-} ions which is difficult to overcome.	**[2]**
	(c)	Both Cr_2O_3 and Al_2O_3 are amphoteric oxides. Describe the observations and write balanced equations when Cr_2O_3 is dissolved in HCl(aq) and NaOH(aq). You can assume that the coordination number of chromium in NaOH(aq) is 6.	
		In HCl(aq) Equation: $Cr_2O_3 + 6HCl \rightarrow 2CrCl_3 + 3H_2O$ Observation: (Blue)-green solid dissolves in HCl(aq) to give a green solution In NaOH(aq) Equation: $Cr_2O_3 + 6NaOH + 3H_2O \rightarrow 2Na_3[Cr(OH)_6]$ Observation: (Blue)-green solid dissolves in NaOH(aq) to give a dark green solution	**[4]**
	(d)	Explain why the resultant solution is coloured when Cr_2O_3 is dissolved in acid.	
		The solution contains Cr^{3+} which has a partially filled 3d subshell. In the presence of H_2O ligands, the 3d orbitals are split into 2 sets of orbitals with	**[3]**

			different energy level. The difference in energies (ΔE) between these 2 sets of non-degenerate 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 is the complement of the colour absorbed.	
	(e)		Another chromium-containing compound, $CrCl_3$, also exhibits similar properties to $AlCl_3$. Predict the pH of the solution when a solid sample of $CrCl_3$ is dissolved in water. Use equations to justify your answer where possible.	
			pH of solution = 3.0 $CrCl_3 + 6H_2O \rightarrow [Cr(H_2O)_6]^{3+} + 3Cl^-$ $[Cr(H_2O)_6]^{3+} \rightleftharpoons [Cr(H_2O)_5(OH)]^{2+} + H^+$ OR $[Cr(H_2O)_6]^{3+} + H_2O \rightleftharpoons [Cr(H_2O)_5(OH)]^{2+} + H_3O^+$	**[2]**
	(f)		*Use of the Data Booklet is relevant to this question.* The element chromium shows a relatively similar increase in the 1st, 2nd, 3rd and 4th ionisation energy. Aluminium however, shows a significant difference between its 3rd and 4th ionisation energy.	
		(i)	By means of an equation, express the 2nd ionisation energy of chromium.	
			$Cr^+(g) \rightarrow Cr^{2+}(g) + e^-$ $\qquad \Delta H = 2^{nd}$ IE	**[1]**
		(ii)	Explain fully why the 4th ionisation energy of aluminium has a significantly larger magnitude compared to its 3rd ionisation energy.	
			Al^{2+}: $1s^2\ 2s^2\ 2p^6\ 3s^1$ Al^{3+}: $1s^2\ 2s^2\ 2p^6$ Fourth electron is removed from an inner principal quantum shell which is closer to the nucleus while the 3rd electron is removed from the outermost shell. The fourth electron in the inner shell (2p subshell) also experiences a greater effective nuclear charge/ less shielding effect compared to the electron in the outermost shell (3p subshells).	**[2]**
				[Total: 15]

5	Caftaric acid is a compound found in grapes and is responsible for the yellowish-gold colour seen in some white wines.  **caftaric acid**			
	(a)		Deduce the molecular formula of caftaric acid.	
			$C_{13}H_{12}O_9$	**[1]**
	(b)	**(i)**	State the type(s) of stereoisomerism exhibited by caftaric acid.	
			Enantiomerism and cis-trans isomerism	**[1]**
		(ii)	Hence, state the total number of stereoisomers of caftaric acid.	
			8 (2^2 enantiomers × 2 cis-trans)	**[1]**
	(c)		The level of caftaric acid can be used to estimate the oxidation levels that a wine has undergone. Wines that undergo a high degree of oxidation, such as pressed wine, will have little to no caftaric acid in them. Suggest the carbon-containing products formed when caftaric acid is heated with excess acidified $KMnO_4$(aq).	
			 ,  and CO_2	**[3]**

(d) On heating with dilute aqueous acid, caftaric acid produces two compounds **A** and **B**.



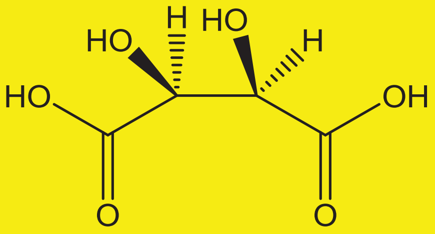
A **B**

(i) State the *type of reaction* caftaric acid is undergoing when **A** and **B** are formed.

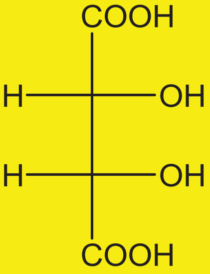
(Acidic) Hydrolysis **[1]**

(ii) There are three types of molecules of **A**, one of which has no effect on plane polarised light.

Suggest the structure of the molecule and explain why it has no effect on plane polarised light.



OR

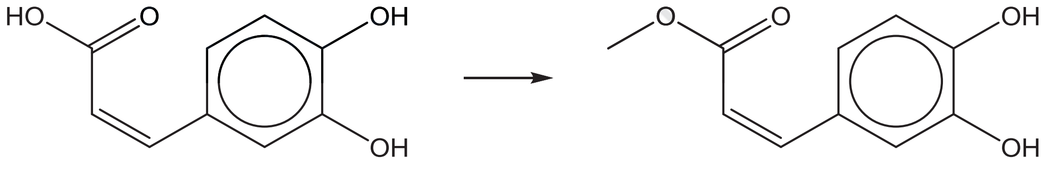


[1]

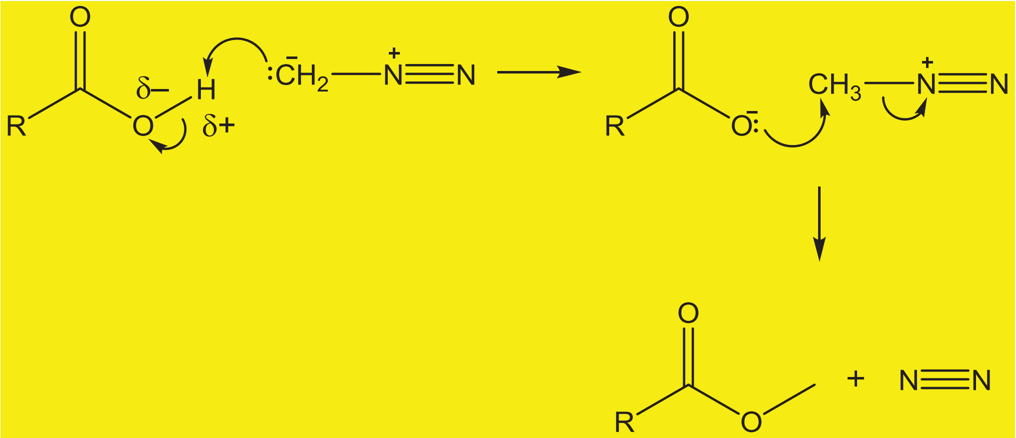
(Accept if OH and H are swapped on both carbon)

There is a plane of symmetry in the molecule so the rotation of plane polarised light by the two chiral centres will cancel each other out. **[2]**

(e) Under suitable conditions, the carboxylic acid functional group in compound **B** can be converted to its methyl ester.



B

		(i)	State the *type of reaction* undergone by B above.	
			Condensation	**[1]**
		(ii)	Suggest the reagents and conditions for the above reaction.	
			Methanol, (a few drops of) concentrated H_2SO_4, heat (under reflux)	**[1]**
	(f)		Another method for conversion of carboxylic acids to their methyl esters involves the reaction with diazomethane, $:\overset{-}{C}H_2-\overset{+}{N}\equiv N$, in an inert solvent. $RCO_2H + CH_2N_2 \rightarrow RCO_2CH_3 + N_2$ This reaction occurs via a two-step mechanism. • The carboxylic acid reacts with diazomethane to form a carboxylate ion intermediate in the first step. • N_2 is formed in the second step. Suggest the mechanism for this reaction. Show any relevant lone pairs, dipoles and charges, and indicate the movement of electron pairs with curly arrows.	
				**[4]**
				[Total: 15]

END OF PAPER

RIVER VALLEY HIGH SCHOOL
YEAR 6 PRELIMINARY EXAMINATION II

CANDIDATE NAME												
CLASS	6											
CENTRE NUMBER	S						INDEX NUMBER					

H2 CHEMISTRY
9729/03

Paper 3 Free Response

19 September 2017

2 hours

Candidates answer on separate paper.

Additional Materials: Answer Paper
Cover Page
Data Booklet

READ THESE INSTRUCTIONS FIRST

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

Section A
Answer **all** questions.

Section B
Answer **one** question.

Begin each question on a fresh sheet of paper.
The use of an approved scientific calculator is expected, where appropriate.
A Data Booklet is provided. Do not write anything on it.
You are reminded of the need for good English and clear presentation in your answers.

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

This document consists of XX printed pages.

Section A

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

1 **(a)** Under suitable conditions, SCl_2 reacts with water to produce a yellow solid and an acidic solution **A**. Solution **A** contains a mixture of $SO_2(aq)$ and another compound.

(i) State the oxidation number of S in SCl_2 . **[1]**

+2

(ii) Construct an equation for the reaction between SCl_2 and water. **[1]**

$2SCl_2 + 2H_2O \rightarrow S + SO_2 + 4HCl$

(iii) In the Contact Process, one important step is the conversion of SO_2 to SO_3 as shown below.

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

A 2.00 L flask was filled with 0.0400 mol SO_2 and 0.0200 mol O_2. At equilibrium, the flask contained 0.0296 mol of SO_3. Determine the value of K_c, stating its unit. **[3]**

	$2SO_2$	+	O_2	$\rightleftharpoons$	$2SO_3$
I / mol	0.04		0.02		0
C / mol	−0.0296		–0.0148		+0.0296
E / mol	0.0104		0.0052		0.0296

K_c

$$= \frac{[0.0296/2]^2}{[0.0104/2]^2[0.0052/2]}$$

= 3116

= 3120 $mol^{-1}\ dm^3$

(b) During the electrolysis of dilute sulfuric acid using a current of 0.75 A for 90 min and platinum electrodes, the volume of oxygen gas collected was recorded and is shown in the Table 1.1 below.

Table 1.1

Time / min	Volume of O_2 gas / cm^3
20	55
40	110
60	165
80	220

(i) Plot a graph of volume of O_2 gas over time.
Use x axis: 2 cm for 10 min ; y axis: 2 cm for 50 cm^3 **[2]**

See graph paper

(ii) Give equations for the reactions that occur at each electrode in the electrolysis of sulfuric acid. **[2]**

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

Anode: $2H_2O(l) \rightarrow 4H^+(aq) + O_2(g) + 4e^-$

(iii) On the same graph, draw and label a line (H_2) to predict the volume of hydrogen that would be given off during the same experiment. **[1]**

See graph paper. Each point is twice the value of graph in (ii).

(iv) On the same graph, draw and label a line (O_2) to predict the volume of oxygen that would be given off if a current of 0.3 A was used instead in the original experiment. **[1]**

See graph paper. Each point is (3/7.5) the value of graph in (ii).

(v) In a 2nd experiment, the platinum electrodes were replaced with graphite electrodes. The volume of gas collected at the anode was 150 cm^3 while the volume of hydrogen gas collected was 220 cm^3.

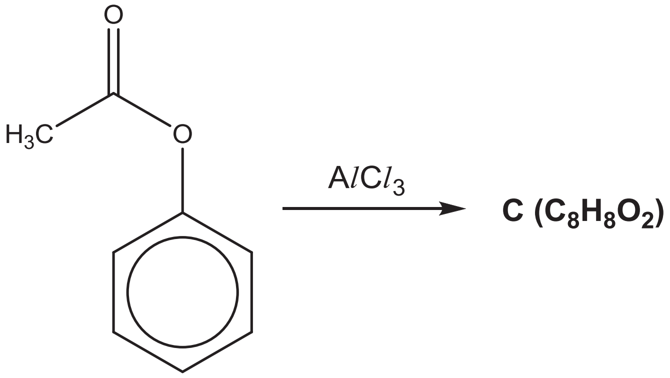
The difference in volume of gas collected at the anode between the two experiments was due to production of CO gas at the anode.

Calculate the volume of CO gas produced at the anode. **[2]**

$C + \frac{1}{2} O_2 (g) \longrightarrow CO (g)$
If no reaction with anode, volume of gas is 110 cm^3
Let volume of O_2 reacted to form CO be x
$110 - x + 2x = 150$
$x = 40$ cm^3

V_{CO} = 2(40) = **80 cm^3**

(c) About 100 years ago, in a reaction discovered by German chemist Karl Fries, compound **B** was converted into compound **C** when heated with $AlCl_3$.



B

Compound **C** is a structural isomer of **B**.

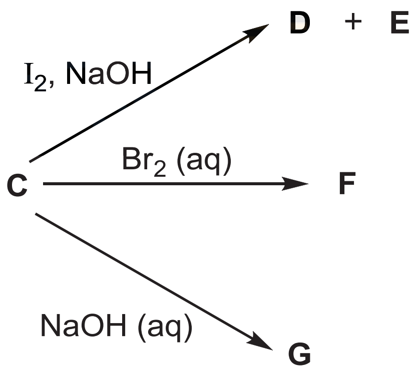
It is insoluble in water but dissolves in aqueous sodium hydroxide.

It gives a yellow ppt with alkaline aqueous iodine and a white ppt with aqueous bromine.

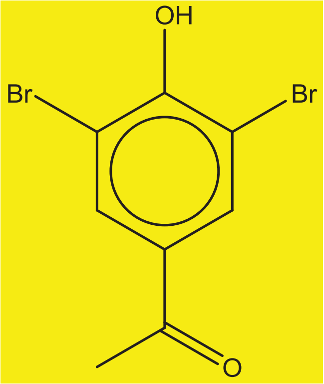
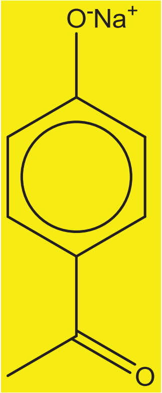
(i) Suggest the structure for compound **C**. **[1]**

Accept 1,2 and 1,3 isomers.

The various reactions of compound **C** can be represented as follows:



		(ii)	Suggest the structures for **D** to **G**.	**[4]**

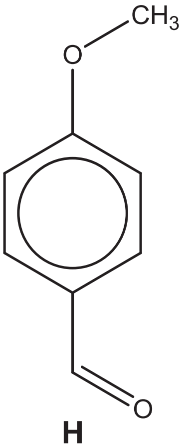
	CHI_3	**D** and **E** are interchangeable.
D	**E**	
		
F	**G**	

Accept 1,2- and 1,3 isomers for all.

Compound **H**, as shown below, is another structural isomer of **B.**

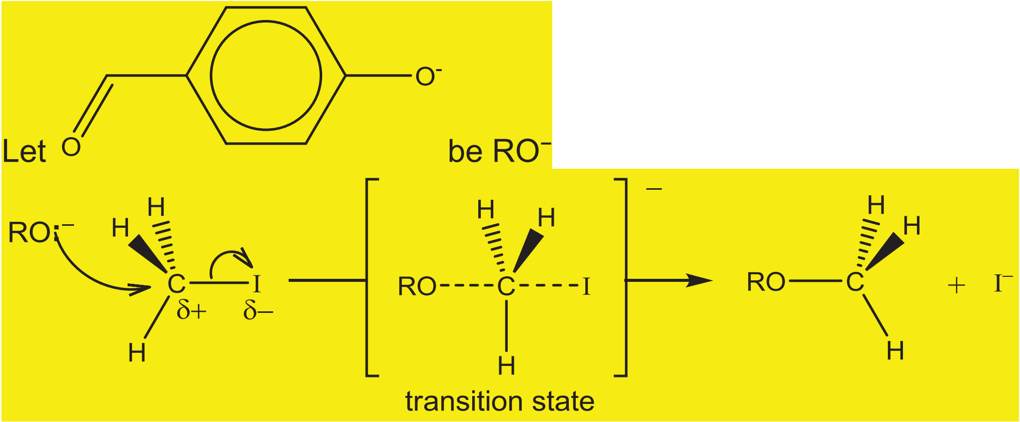
It has a ether functional group whose general formula is R–O–R'.

Compound **H** can be formed via a reaction between a substituted phenoxide ion and an alkyl halide molecule.



H

(iii) Describe the mechanism when compound **H** is formed as described above. **[3]**



[Total: 21]

2 In the late 1940s, Willard Libby developed the radiocarbon dating method for determining the age of an object containing organic material by using the properties of radiocarbon (^{14}C), a radioactive isotope of carbon. The principle of carbon dating is as such:

During its life, a plant or animal is exchanging carbon with its surroundings, so the carbon it contains will have the same proportion of ^{14}C as the atmosphere. Once it dies, it ceases to acquire ^{14}C, but the ^{14}C within its biological material at that time will continue to decay, and so the ratio of ^{14}C to ^{12}C in its remains will gradually decrease.

Because ^{14}C decays with first order kinetics, the proportion of radiocarbon can be used to determine how long it has been since a given sample stopped exchanging carbon – the older the sample, the less ^{14}C will be left.

(a) A sample of carbon dioxide gas (that contained both $^{12}CO_2$ and $^{14}CO_2$) was analysed to determine the proportion of $^{14}CO_2$ found within. Analysis results showed that there is one $^{14}CO_2$ molecule for every 10^{12} CO_2 molecules.

(i) Calculate the number of $^{14}CO_2$ molecules in a 10.0 dm^3 carbon dioxide gas sample, measured under s.t.p. **[2]**

Number of moles of CO_2 $= \frac{10}{22.7}$

$= 0.441$ mol

Number of $^{14}CO_2$ molecules $= 0.441 \times \frac{6.02\times10^{23}}{10^{12}}$

$= 2.65 \times 10^{11}$ molecules

(ii) Calculate the mass of $^{14}CO_2$ in the 10.0 dm^3 sample. **[1]**

Mass of $^{14}CO_2$ = $\frac{2.65\times10^{11}}{6.02\times10^{23}} \times (14.0 + 16.0 \times 2)$

= 2.03×10^{-11} g

(iii) Hence, explain why it would be difficult to determine the proportion of $^{14}CO_2$ by means of mass measurement. **[1]**

The amount/mass of $^{14}CO_2$ is too small to be accurately measured.

(b) To more accurately determine the proportion of ^{14}C in a sample of graphite, the graphite is vaporised and ionised to C^+(g) ions. These ions were then passed through 2 electric plates.

Given that H^+ is deflected with an angle of 8.4°, what is the angle of deflection for $^{14}C^+$ ions under the same experimental set-up? **[1]**

$^{14}C^+$ deflected by $\left(\frac{1}{14}\right)(8.4)$ = 0.60°

(c) The half-life of ^{14}C is 5730 years. Determine the time that has elapsed for a piece of wood from a dead tree to contain 30.0% of its original ^{14}C. **[2]**

Let the number of half-life be n

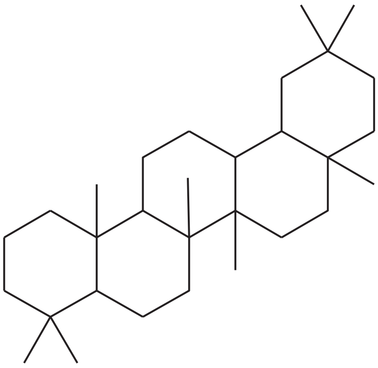
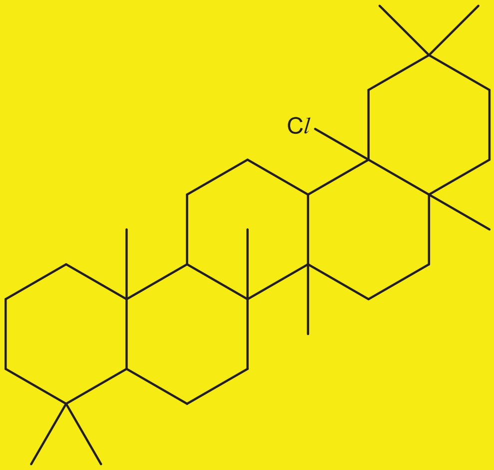
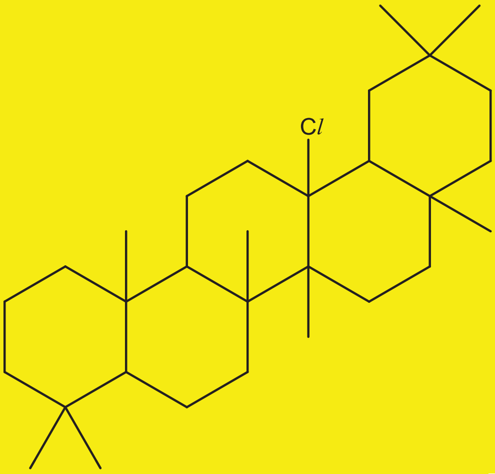
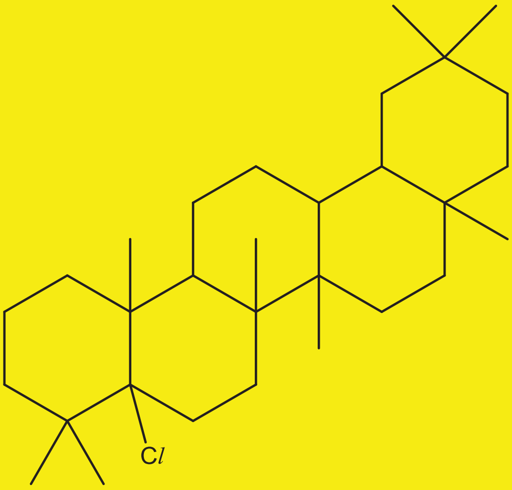
$$\frac{30.0}{100} = \left(\frac{1}{2}\right)^n$$

$$n = \frac{lg\left(\frac{30.0}{100}\right)}{lg\left(\frac{1}{2}\right)}$$

n = 1.74 **[1]**

Time taken = 5730 × 1.74 = **<u>9970 years</u>**

(d) The age of crude oil is far older than what could be determined from radiocarbon dating.

			To measure the age of a crude oil sample, a method involving the measurement of the relative amount of oleanane is used instead.  Oleanane	
		(i)	What is the number of chiral carbons in an oleanane molecule?	**[1]**
			8	
		(ii)	Free radical substitution of oleanane with Cl_2 produces a mixture of various products. Given that tertiary hydrogen atoms are the most reactive towards free radical substitution, suggest the structures of two possible mono-chlorinated oleanane which are formed in high proportions.	**[2]**
			   	

(e) Benzene is obtained from the fractional distillation of crude oil. It can be converted to a series of different useful chemicals such as phenylamine. The formation of phenylamine involves the direct reaction of nitrobenzene and hydrogen gas in the presence of a heterogeneous catalyst.

A series of experiments were carried out at a specific temperature to investigate the kinetics of this reaction:

Experiment	[nitrobenzene] / mol dm^{-3}	[H_2] / mol dm^{-3}	Initial rate / mol dm^{-3} s^{-1}
1	0.010	0.010	4.50×10^{-5}
2	0.015	0.010	6.74×10^{-5}
3	0.020	0.020	1.80×10^{-4}
4	0.030	x	4.05×10^{-4}

(i) Define the term *heterogeneous catalyst*. **[2]**

A catalyst is a substance that increases the rate of reaction by providing an alternative reaction pathway of lowered activation energy, and is regenerated at the end of the reaction. A heterogeneous catalyst is one that is not in the same phase as the reactants.

(ii) Determine the order of reaction with respect to nitrobenzene and hydrogen. **[2]**

Comparing experiment 1 and 2, when [nitrobenzene] is increased to 1.5 times, the reaction rate is increased to 1.5 times. Hence, it is first order with respect to nitrobenzene.

Let the rate equation be: Rate = k[nitrobenzene][H_2]^a

Comparing experiment 2 and 3:

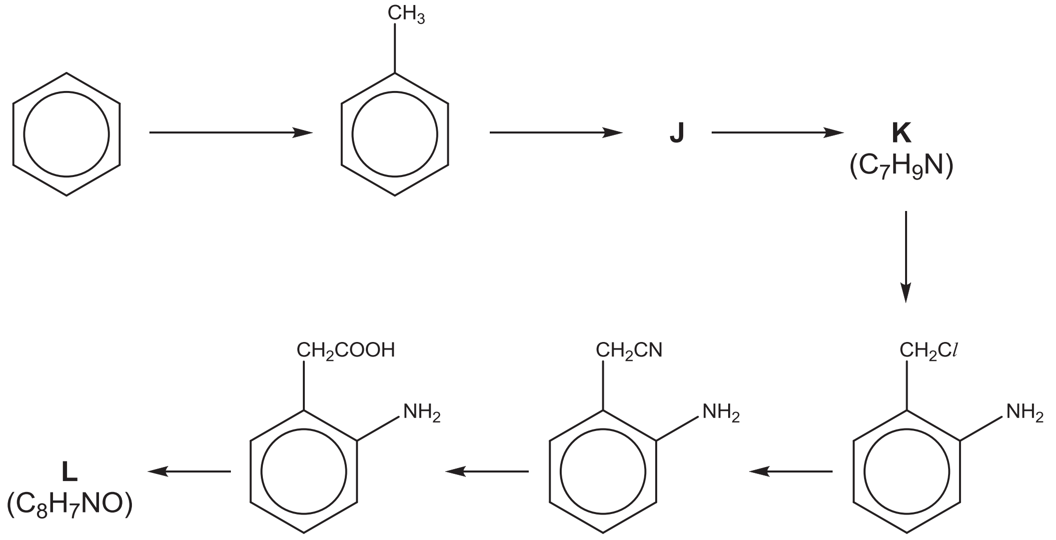
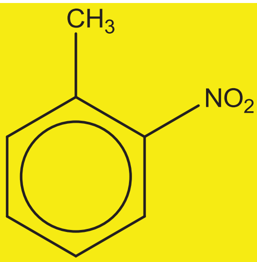
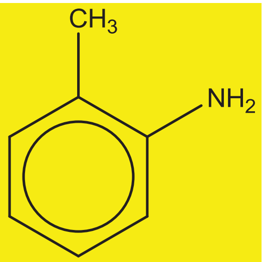
$$\frac{6.74\times10^{-5}}{1.80\times10^{-4}} = \frac{k(0.015)(0.01)^a}{k(0.02)(0.02)^a}$$

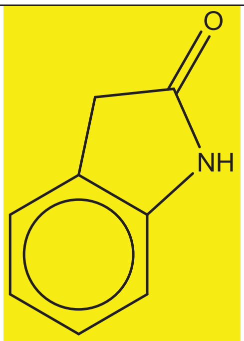
$$\left(\frac{6.74\times10^{-5}}{1.80\times10^{-4}}\right)\left(\frac{0.02}{0.015}\right) = \left(\frac{0.01}{0.02}\right)^a$$

$$a = 1$$

(iii) Calculate the rate constant, stating its units. **[1]**

Using experiment 1:

			$4.50 \times 10^{-5} = k(0.01)(0.01)$ k = 0.450 mol^{-1} dm^{3} s^{-1}	
		(iv)	Hence, determine the value of x.	**[1]**
			$4.05 \times 10^{-4} = (0.45)(0.03)x$ $x = 0.0300$ (mol dm^{-3})	
	(f)	Benzene is made to undergo a series of reactions as shown:  		
		(i)	Suggest the structures of **J** and **K**.	**[2]**
			J: **K**:   	
		(ii)	Given that compound **L** is neutral, suggest the reagent used in the final step and the structure of **L**.	**[2]**
			PCl_5 or $SOCl_2$ Structure of **L:**	



[Total: 20]

3 Chromium is a transition metal commonly found in the earth's crust. It is usually mined as chromite.

Period 4 Element	Ti	V	Cr	Mn	Fe	Co	Ni	Cu
Atomic radius / nm	0.132	0.122	0.117	0.117	0.116	0.116	0.115	0.117

(a) Explain why the atomic radius for transition elements remains relatively constant. **[2]**

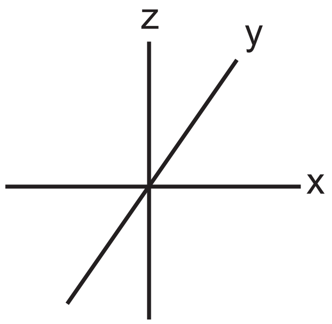
Across the transition elements, nuclear charge increases but screening effect also increases due to electrons added to the inner 3d subshell. Therefore, the effective nuclear charge is approximately the same. The attraction between the nucleus and the valence electrons remain about the same. Thus, atomic radius remains almost constant.

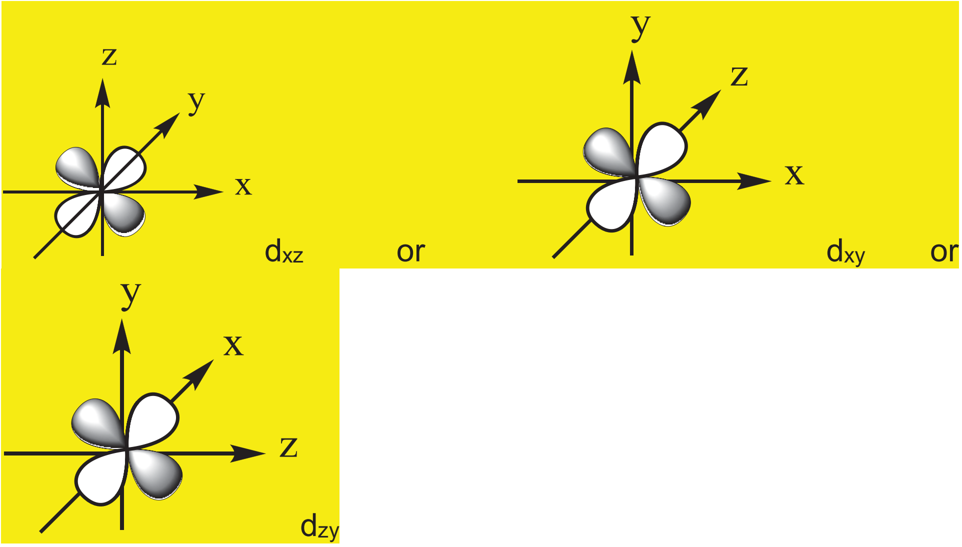
(b) **(i)** Write the electronic configuration for Cr^{3+} ion. **[1]**

Cr^{3+} : $1s^2 2s^2 2p^6 3s^2 3p^6 3d^3$

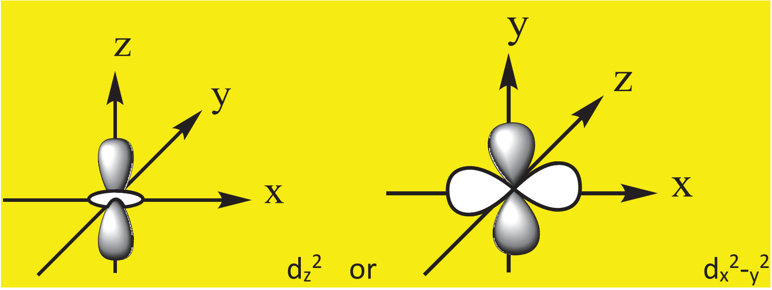
(ii) Chromium forms octahedral complexes with the general formula $CrCl_3.6H_2O$. One of them dissolves in water to form a violet solution which turned green upon warming. An excess of aqueous silver nitrate was added separately to solutions containing 0.0100 mol of each complex. The violet complex gave 1.50 g of precipitate, while the green complex gave 4.40 g of precipitate.

Deduce the formulae of the two complex ions. **[3]**

			Write the equation for the conversion of the violet complex to the green complex.	
			Amt of chloride from the green complex = 4.40 / 143.5 = 0.0306 mol Ratio of chloride: complex = 3:1 Formula of green complex: $[Cr(H_2O)_6]^{3+}$ Amt of chloride from violet complex = 1.50 / 143.5 = 0.0105 mol Ratio of chloride : complex = 1:1 Formula of violet complex: $[Cr(H_2O)_4(Cl)_2]^+$ $[Cr(H_2O)_4(Cl)_2]^+(aq) + 2H_2O(l) \rightarrow [Cr(H_2O)_6]^{3+}(aq) + 2\,Cl^-(l)$	
		(iii)	Using the Cartesian axes, like those shown below,  draw **fully-labelled** diagrams of the following : • One of the d orbital at the lower energy level in an octahedral complex. Label this diagram “Lower energy level”. • One of the d orbital at the upper energy level in an octahedral complex. Label this diagram “Upper energy level”.	**[2]**



Lower energy level



Upper energy level

(c) When sodium carbonate is added to a dichromate(VI) solution, the solution turned yellow.

$$\underset{\text{orange}}{Cr_2O_7^{2-}(aq)} + 2OH^-(aq) \rightleftharpoons \underset{\text{yellow}}{2CrO_4^{2-}(aq)} + H_2O(l)$$

Using a relevant equation, explain the above observation. **[2]**

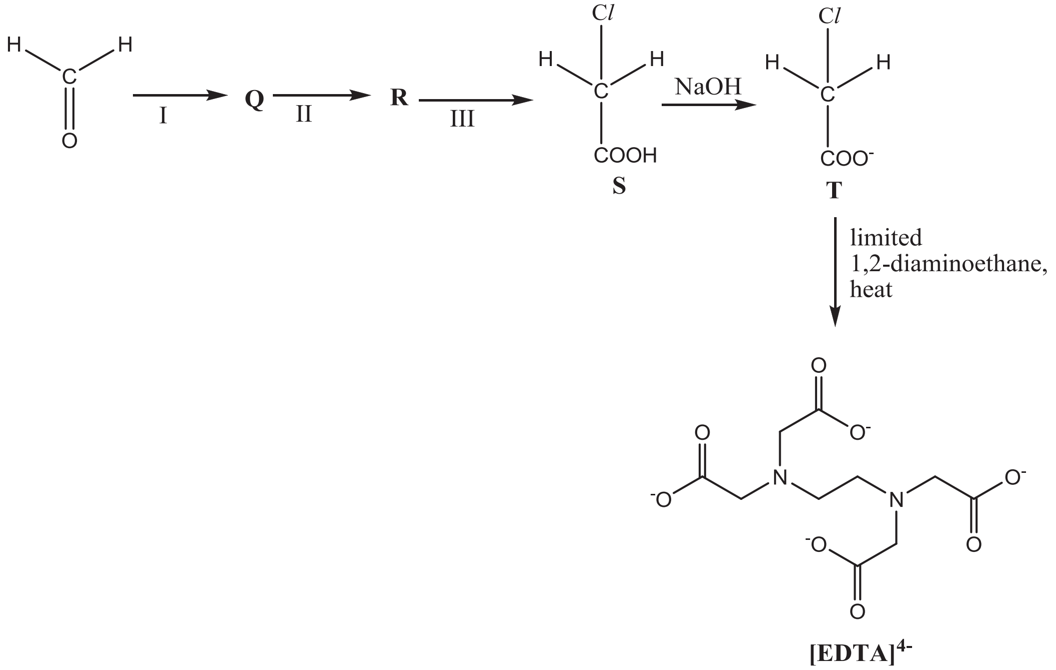
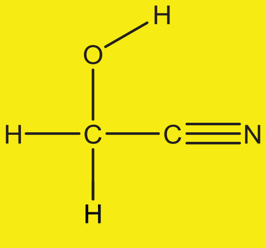
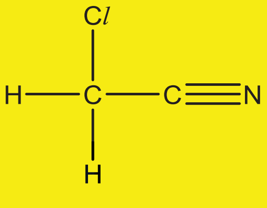
When Na_2CO_3 is added, the concentration of OH^- increased.

$$CO_3^{2-}(aq) + H_2O(l) \rightleftharpoons HCO_3^-(aq) + OH^-(aq)$$

The equilibrium position will shift to the right to remove some of the added OH^-, changing the solution to yellow.

(d) Ethylenediamine tetraacetate, $[EDTA]^{4-}$, is a ligand that acts as a chelating agent. It is widely used to remove transition metal ions such as those of chromium from aqueous solutions.

A possible reaction scheme used to synthesise $[EDTA]^{4-}$ from methanal is given below.

				
		(i)	Suggest the reagents and conditions in steps I, II and III.	[3]
			Step I : HCN with small amount of NaCN Step II : $PCl_5/PCl_3/SOCl_2$ Step III : H_2SO_4(aq) heat under reflux	
		(ii)	Draw the displayed formulae of intermediates **Q** and **R**.	[2]
			 **Q**  **R**	
		(iii)	State the type of reaction when **T** is converted to $[EDTA]^{4-}$. Give a reason why a limited amount of 1,2-diaminoethane is used.	[2]
			Nucleophilic substitution To enable multiple substitution on the amine group.	
		(iv)	Define the term *ligand*. State the number of coordinate bonds that a $[EDTA]^{4-}$ ligand can form with a central metal ion.	[2]

			A ligand is an ion or molecule which contains at least one atom bearing a lone pair of electrons which can be donated into the low-lying vacant orbital of the central metal atom or ion forming a co-ordinate (dative) bond. 6 coordinate bonds.	
			[Total: 19]	

Section B

Answer **one** question from this section.

4	This question concerns the chemistry of the oxides of some elements.		
	(a)	The oxides of Period 3 show different reactions with water. Describe the reactions, if any, of the oxides SiO_2 and SO_3 with water. Include the approximate pH value of any resulting solutions, and write equations for any reactions that occur.	**[3]**
		SiO_2 does not react with water/is insoluble in water. Hence, pH remains at 7. SO_3 reacts/hydrolyse with water to give acidic solutions (pH = 2). $SO_3(l) + H_2O(l) \rightarrow H_2SO_4(aq)$	
	(b)	Carbon combusts in oxygen to form two common oxides, CO and CO_2. These oxides are also formed when solid magnesium oxalate, MgC_2O_4, is heated strongly.	

(i) Write an equation, with state symbols, to represent the thermal decomposition of solid magnesium oxalate. **[1]**

$MgC_2O_4(s) \rightarrow MgO(s) + CO_2(g) + CO(g)$

(ii) Explain why magnesium oxalate decomposes at a lower temperature than barium oxalate, BaC_2O_4. **[2]**

Mg^{2+} is smaller/has a smaller ionic radius and has a higher charge density, and hence a greater polarising power, than Ba^{2+}. It weakens the bonds in the $C_2O_4^{2-}$ anion to a greater extent and hence MgC_2O_4 is less thermally stable.

Carbon also forms compounds with other Group 16 elements like sulfur and selenium. The properties of some of these compounds, along with CO_2, are given in Table 4.1.

Table 4.1

Compound	Structure	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

(iii) 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 interactions between CS_2 molecules than the permanent dipole-induced dipole interactions between COS molecules. Hence, CS_2 has a higher boiling point.

(iv) Explain why

- CO_2 has no overall dipole moment.
- COSe has a greater dipole moment than COS. **[2]**

- CO_2 is linear and hence the dipoles cancel out.
- C=S bond is more polar than C=Se (since S is more electronegative than Se). There is smaller difference between

the dipole moment of C=O and C=S than that between C=O and C=Se.

(c) Aside from the common oxides, carbon forms a series of reactive oxocarbons. One such compound is tricarbon monoxide, C_3O, a reactive molecule found in space.

(i) Suggest a structure of tricarbon monoxide. Indicate clearly any lone pairs present. **[1]**

Tricarbon monoxide is isoelectronic to cyanogen, $(CN)_2$. The molecule of cyanogen contains a C–C single bond.

(ii) 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]**

(iii) Suggest the shapes of tricarbon monoxide and cyanogen. **[1]**

They are both **linear**.

(d) Another oxycarbon is pentacarbon dioxide, C_5O_2. It can be obtained by heating compound **X**, $C_6H_6O_3$, at a high temperature. **X** exists in equilibrium with its isomer, **Y**.

X does not react with aqueous bromine. **X** also gives an orange precipitate with 2,4-DNPH but does not give a silver mirror with Tollens' reagent. When reacted with limited bromine under ultraviolet light, **X** produced **only one** mono-brominated compound.

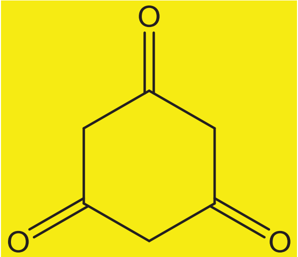
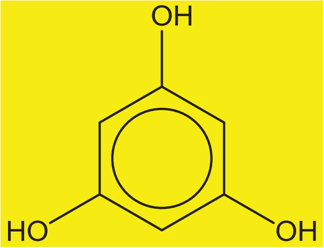
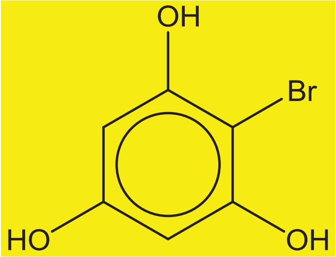
Y reacts with dilute nitric acid to form **only one** mono-nitrated compound, **Z**.

Suggest the structures of compounds **X**, **Y** and **Z**. Explain your reasoning. **[7]**

Information/Reaction	**Deduction**
X/Y has C:H ratio of 1:1	**X/Y** might contain a benzene ring.
X does not undergo electrophilic substitution nor electrophilic addition with $Br_2(aq)$	**X** does not contain a phenol nor a C=C.
X undergoes condensation with 2,4-DNPH but does not undergo oxidation with Tollens' reagent.	**X** is a ketone.

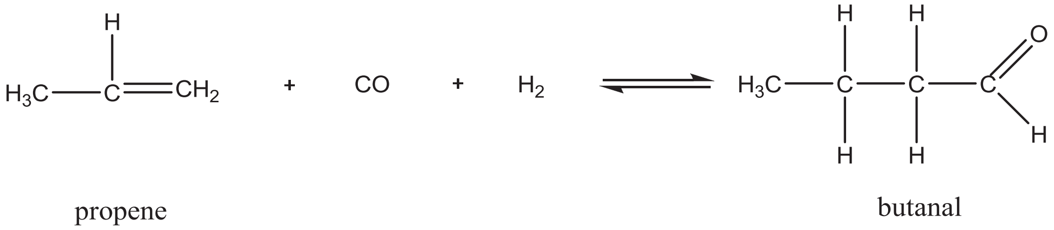
X undergoes <u>free-radical substitution</u> with Br_2 to give only one monobromo compound.	**X** is <u>highly symmetrical</u>.
Y undergoes <u>electrophilic substitution</u> with $HNO_3(aq)$ to give only one mono-nitrated compound.	**Y** is a <u>phenol</u>. **Y** is also <u>highly symmetrical</u>.

Structures:

		
X	**Y**	**Z**

[Total: 20]

5 **(a)** Hydroformylation is an industrial process for the formation of aldehydes from alkenes.



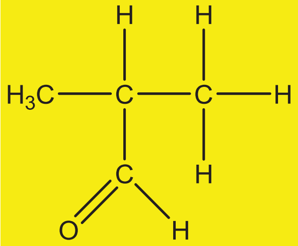
(i) Determine the oxidation numbers of carbon-1, carbon-2 and carbon-4 in butanal. **[1]**

C1: +1

C2: -2

C4: -3

(ii) The hydroformylation of propene can result in the formation of two isomeric products. Given that the mechanism of hydroformylation resembles the electrophilic addition of alkenes, suggest the structure of the other isomer apart from butanal. **[1]**



(iii) Write the K_p expression for the reaction above, stating its units. **[1]**

$K_p = \frac{P_{CH_3CH_2CH_2CHO}}{P_{CH_3CH=CH_2}P_{CO}P_{H_2}}$ Units: atm^{-2} / Pa^{-2}

(iv) When an equimolar mixture of propene, CO and H_2 at an initial pressure of 120 atm was allowed to reach equilibrium at 550 K, the partial pressure of butanal was found to be 38.5 atm.

Calculate a value of K_p at 550 K. **[2]**

	C_3H_6 +	CO +	H_2 ⇌	$CH_3CH_2CH_2CHO$
Initial partial pressure / Pa	40	40	40	0
Eqm partial pressure / Pa	40–38.5 = 1.5	40–38.5 = 1.5	40–38.5 = 1.5	38.5

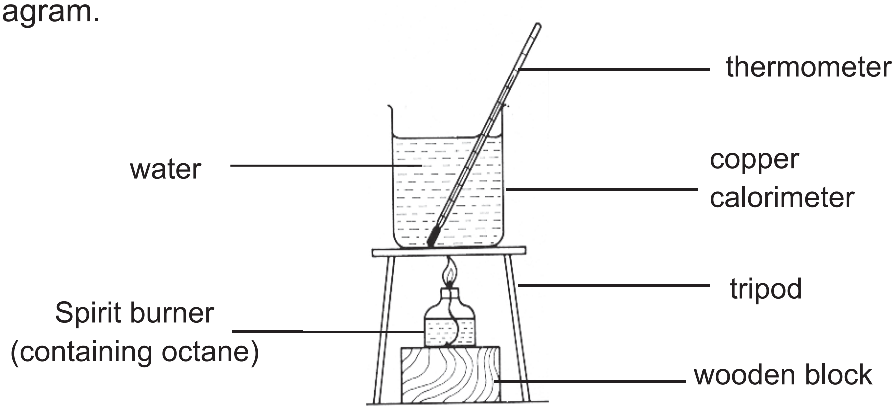
$K_p = \frac{38.5}{1.5 \times 1.5 \times 1.5} = 11.4$ Pa^{-2}

(v) Hence, predict the sign of ΔG for the reaction. Explain your reasoning taking into account the thermodynamic considerations of the reaction. **[2]**

ΔG is negative due to K_p is large (greater than 1) and position of equilibrium lies very much to the right.

(b) Other important use of hydrocarbons include fuels, plastics, paints and solvents. In some countries, where crude oil is either scarce or expensive, biofuels such as ethanol are also increasingly being used for fuels instead of hydrocarbons.

(i) James carried out an experiment to determine the enthalpy change of combustion of octane, C_8H_{18}, using the apparatus shown in the diagram.



These are the results that James obtained:

Volume of water = 1000 cm^3

Initial temperature of water = 29.6 °C

Highest temperature of water = 50.0 °C

Initial mass of burner and octane = 59.35 g

Final mass of burner and octane = 53.77 g

Heat capacity of calorimeter = 770 $J\ K^{-1}$

Use these results and data from the *Data Booklet* to determine the experimental enthalpy change of combustion of octane. **[3]**

Heat evolved = $1000 \times 4.18 \times 20.4 + 770 \times 20.4 = 101000$ J

Amount of octane reacted = $\frac{59.35-53.77}{8\times12.0 + 18\times1.0}$ = 4.89×10^{-2} mol

Enthalpy change of combustion of octane = $-\frac{101000}{4.89\times10^{-2}}$

= -2060 kJ mol^{-1}

(ii) The accurate experimental enthalpy change of combustion of three hydrocarbons are given in Table 5.1.

Table 5.1

Alkane	Formula	ΔH_c/ kJ mol^{-1}
Heptane	C_7H_{16}	–4817
Octane	C_8H_{18}	–5470

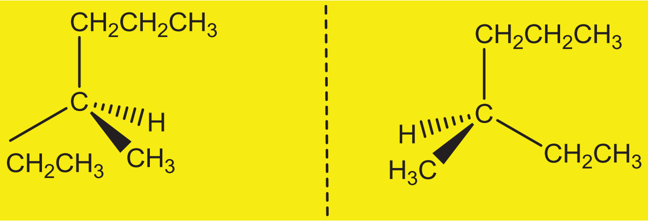
[1]

Nonane	C_9H_{20}	–6125

Suggest what the regular increase in the values of ΔH_c given in the table represents.

The regular increase in the ΔH_c (~650kJ mol^{-1}) is due to the combustion of the $–CH_2–$ group.

(iii) Draw a pair of enantiomers of heptane. **[1]**



(iv) Alkanes are also used in dry cleaning of clothing and textiles. Dry cleaning involves soaking the clothes in a solvent other than water. Recently, the use of supercritical carbon dioxide as a dry cleaning solvent has also been gaining popularity. Supercritical carbon dioxide is a fluid state of carbon dioxide which is maintained at or above its critical temperature.

Suggest two possible reasons why supercritical carbon dioxide is a better solvent than organic solvents like hexane. **[2]**

CO_2 is:

- cheap
- non-flammable
- readily available
- easily vaporised under low pressure/high temperature
- safe/non-toxic.
- odourless

(c) Many modern methods of chemical analysis rely on the use of sophisticated instruments. For many years, scientists relied on traditional laboratory apparatus for chemical analysis.

Many qualitative tests and some volumetric analysis used depended on an application of the principles of solubility product.

Data for use in this question are given in Table 5.2.

Table 5.2

	Colour	Solubility/ mol dm^{-3}	K_{sp} (25 °C)
AgC*l*	White	1.42×10^{-5}	2.02×10^{-10}
AgI	Yellow	8.95×10^{-9}	8.01×10^{-17}
Ag_2CrO_4	Red	9.10×10^{-5}	3.01×10^{-12}

(i) Aqueous $AgNO_3$ is added to solutions containing 0.100 mol dm^{-3} Cl^-(aq) or 0.0100 mol dm^{-3} CrO_4^{2-}(aq). What concentration of Ag^+ must be present to cause the precipitation of

I: AgC*l*

II: Ag_2CrO_4? **[2]**

I: $[Ag^+] = \frac{2.02\times10^{-10}}{0.1} = 2.02 \times 10^{-9}$ mol dm^{-3}

II: $[Ag^+] = \sqrt{\frac{3.01\times10^{-12}}{0.01}} = 1.73 \times 10^{-5}$ mol dm^{-3}

(ii) Standard solutions of silver nitrate can be used in volumetric analysis to determine the concentration of chloride ions in a sample of water. When the titration is carried out, $AgNO_3$(aq) of known concentration is added slowly to the solution that contains Cl^- ions. A small quantity of aqueous potassium chromate(VI), K_2CrO_4 (0.01 mol dm^{-3}) is also added as an indicator.

Using the data given in Table 5.2 and your answers in **(c)(i)**, predict using calculations what you would see at the beginning of the titration and at the end-point and explain why K_2CrO_4(aq) can be used as an indicator in this titration. **[4]**

At the beginning, a white ppt AgC*l* is observed

At the end point, a red ppt of Ag_2CrO_4 is observed

When all AgC*l* is precipitated, $[Ag^+] = 1.42 \times 10^{-5}$ when IP of Ag_2CrO_4 $= [Ag^+]^2[CrO_4^{2-}] = (1.42 \times 10^{-5})^2(0.01) = 2.02 \times 10^{-12}$ which is lower than K_{sp} of Ag_2CrO_4.

So, at the end point, Ag_2CrO_4 only precipitates when all AgC*l* has precipitated.

[Total: 20]

- End of Paper -

RIVER VALLEY HIGH SCHOOL

YEAR 6 PRACTICAL EXAMINATION

H2 CHEMISTRY 9729

23RD AUG 2017

2.5 HOURS

NAME ____________________

CLASS 6 (   )

INDEX NO. ____________________

INSTRUCTIONS TO CANDIDATES

DO NOT OPEN THIS BOOKLET UNTIL YOU ARE TOLD TO DO SO.

Read these notes carefully.

Write your name, class and index number in the spaces at the top of this page.
Give details of the practical shift and laboratory where appropriate, in the boxes provided.
Write in dark blue or black pen.
You may use an HB 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.*

Shift
Laboratory

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.

For Examiner's Use	
1	/ 21
2	/ 15
3	/ 9
4	/ 10
Total	/ 55

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

1 Determine the the percentage by mass of sodium ethanedioate in a mixture of sodium ethanedioate and ethanedioic acid.

This experiment involves **two steps**.
In step one, you will carry out a titration to find the amount of acid, $H_2C_2O_4$, present in **FB 3**.
In step two, you will carry out a second titration to find the total amount of ethanedioate ion, $C_2O_4^{2-}$, present in **FB 3**.
Finally, you will use the values found in the two steps to calculate the percentage by mass of sodium ethanedioate in **FB 3**.

FB 1 is 0.100 mol dm^{-3} sodium hydroxide, NaOH.
FB 2 is 0.0200 mol dm^{-3} potassium manganate(VII), $KMnO_4$.
FB 3 is a mixture of aqueous sodium ethanedioate, $Na_2C_2O_4$, and ethanedioic acid, $H_2C_2O_4$.
FB 4 is approximately 2 mol dm^{-3} sulfuric acid.
thymolthalein indicator

Read through the whole method before starting any practical work.

(a) Method

Step 1

1. Fill the burette labelled **FB 1** with **FB 1**.
2. Pipette 25.0 cm^3 of **FB 3** into a conical flask.
3. Add 1 dropper full of thymolphthalein.
4. Titrate **FB 3** in the conical flask with **FB 1** until a pale blue colour is seen.
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 **FB 1** added in each accurate titration.

Step 2

1. Pipette 25.0 cm^3 of **FB 3** into a conical flask.
2. Using a measuring cylinder, add about 25 cm^3 of 2 mol dm^{-3} sulfuric acid, **FB 4**, to the flask.
3. Place the conical flask on a hotplate and heat to about 65°C.
4. Fill the burette labelled **FB 2** with **FB 2**.
5. Use an appropriate method to carefully transfer the hot conical flask onto a white tile under the burette.
6. Titrate the mixture in the conical flask with **FB 2** until a permanent pale pink colour is seen. If a permanent brown colour is seen, stop the titration and begin **Step 2** again.
7. Carry out as many accurate titrations as you think necessary to obtain consistent results.
8. Record in a suitable form below all of your burette readings and the volume of **FB 2** added in each accurate titration.

[3]

(b) (i) From your titration results in **Step 1**, obtain a suitable value to be used in your calculations. Show clearly how you have obtained this value.

Shift 1	Shift 2	Shift 3
15.20 cm^3	15.20 cm^3	15.20 cm^3

25.0 cm^3 of **FB 3** required ………….. cm^3 of **FB 1**
[2]

(b) (ii) Write an equation for the reaction between sodium hydroxide and ethanedioic acid to give sodium ethanedioate and water.

$H_2C_2O_4 + 2NaOH \rightarrow Na_2C_2O_4 + 2H_2O$

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

(b) (iii) Use your answer from **(b)(i)** to calculate amount of sodium hydroxide, **FB 1**, required to react with 25.0 cm^3 of **FB 3** in **Step 1**.

(b)(i) × 0.10}/1000

Amount of NaOH = ………………………
[1]

(b) (iv) Use your answer to **(b)(iii)** to determine the amount of ethanedioic acid in 25.0 cm^3 of **FB 3**.

(iii)/2

Amount of $C_2O_4H_2$ in 25.0 cm^3 of **FB 3** = ...
[1]

(c) (i) From your titration results in **Step 2**, obtain a suitable value to be used in your calculations. Show clearly how you have obtained this value.

Shift 1	Shift 2	Shift 3
22.60 cm^3	22.75 cm^3	22.60 cm^3

25.0 cm^3 of **FB 3** required ………….. cm^3 of **FB 2**.
[3]

(c) (ii) Use your answer from **(c)(i)** to calculate amount of potassium manganate(VII), **FB 2**, required to react with 25.0 cm^3 of **FB 3** in **Step 2**.

(c)(i) × 0.02/1000

Amount of $KMnO_4$ = ...
[1]

(c) (iii) The equation for the reaction between acidified manganate(VII) ions and ethanedioate ions is shown below.

$2MnO_4^-(aq) + 5C_2O_4^{2-}(aq) + 16H^+(aq) \rightarrow 2Mn^{2+}(aq) + 10CO_2(g) + 8H_2O(l)$

Calculate the total amount of ethanedioate ions in 25.0 cm^3 of **FB 3**.

(c)(ii) × 5/2

Total amount of $C_2O_4^{2-}$ in 25.0 cm^3 of **FB 3** = ………………
[1]

(c) (iv) Use your answers to **(b)(iv)** and **(c)(iii)** to calculate the amount of ethanedioate ions which came from the sodium ethanedioate dissolved in 25.0 cm^3 of **FB 3**.

(c)(iii) – (b)(iv)

		Amount of $C_2O_4^{2-}$ from $C_2O_4Na_2$ in 25.0 cm^3 of **FB 3** = ………………. [1]
	(d) (i)	Use your answer to **(b)(iv)** to calculate the mass of ethanedioic acid, $H_2C_2O_4$, in 25.0 cm^3 of **FB 3**. [*Ar*: H, 1.0; C, 12.0; O, 16.0] (If you were unable to answer **(b)(iv)**, you may assume that the amount of ethanedioic acid is 6.51×10^{-4} mol.) (b)(iv) × 90.0 Mass of ethanedioic acid = ... [1]
	(d) (ii)	Use your answer to **(c)(iv)** to calculate the mass of sodium ethanedioate, $Na_2C_2O_4$ in 25.0 cm^3 of **FB 3**. [*Ar*: C, 12.0; O, 16.0; Na, 23.0] (If you were unable to answer **(c)(iv)**, you may assume that the amount of sodium ethanedioate is 4.13×10^{-4} mol.) (c)(iv) × 134.0 Mass of sodium ethanedioate = ... [1]
	(d) (iii)	Calculate the percentage by mass of sodium ethanedioate present in **FB 3**. {mass $Na_2C_2O_4$ in (ii)/total mass} × 100 [total mass = (d)(i) + (d)(ii)] Percentage by mass of sodium ethanedioate present is .... [1]
	(e) (i)	A student suggested that using a burette to measure the 25.0 cm^3 of acid would give a more accurate result than using a pipette. The percentage error of a 25.0 cm^3 pipette is 0.24 %. Is the student correct? Explain your answer. [2] Student is incorrect use of burette: {0.10/25} × 100 = 0.40% compared to 0.24% or apparatus error of pipette is ±0.06 compared with apparatus error of burette is ±0.10
	(e) (ii)	A student decided to use a 25.0 cm^3 pipette instead of a measuring cylinder to measure the volume of **FB 4** in **Step 2**. State and explain whether this alteration will improve the accuracy of the calculation of the percentage by mass of sodium ethanedioate in the mixture. [2] No improvement as acid in excess

2 **Investigate how the rate of the following reaction varies with the concentration of sodium thiosulfate, $Na_2S_2O_3$.**

$$Na_2S_2O_3\,(aq) + H_2SO_4\,(aq) \rightarrow S\,(s) + Na_2SO_4\,(aq) + SO_2\,(g) + H_2O\,(l)$$

The rate can be found by measuring how long it takes for the solid sulfur formed to obscure the printing on the insert provided.

Care should be taken to avoid inhalation of SO_2(g) that is given off during this reaction.

FC 5 is 1.0 mol dm^{-3} sulfuric acid, H_2SO_4
FC 6 is 0.10 mol dm^{-3} sodium thiosulfate $Na_2S_2O_3$

(a) **Method**

1. Using the 50 cm^3 measuring cylinder transfer 45 cm^3 of **FC 6** into a 100 cm^3 beaker.
2. Using the 25 cm^3 measuring cylinder measure 10 cm^3 of **FC 5**.
3. Tip the **FC 5** into the **FC 6** in the beaker and **immediately** start timing.
4. Stir the mixture once with a glass rod and place the beaker on top of the printed insert. Cover the beaker with a petri dish.
5. View the printed insert from above so that it is seen through the mixture.
6. Record the time, to the nearest second, when the printing on the insert **just** disappears.
7. Empty and rinse the beaker. Shake out as much of the water as possible and dry the outside of the beaker.

You will repeat the experiment to find out how the time for the printing on the insert to disappear changes when a different volume of **FC 6** is used.

8. Using the 50 cm^3 measuring cylinder transfer 20 cm^3 of **FC 6** and 25 cm^3 of distilled water into the 100 cm^3 beaker.
9. Using the 25 cm^3 measuring cylinder, add 10 cm^3 of **FC 5** to the mixture and **immediately** start timing.
10. Stir the mixture once with a glass rod and place it on top of the printed insert.
11. View the printed insert from above so that it is seen through the mixture.
12. Record the time, to the nearest second, when the printing on the insert **just** disappears.
13. Select suitable volumes of **FC 6 and** distilled water for **two** further experiments to investigate the effect of volume of sodium thiosulfate on the time taken for the printing on the insert to **just** disappear. The volume of **FC 6** used should range from 0 cm^3 to 45 cm^3.

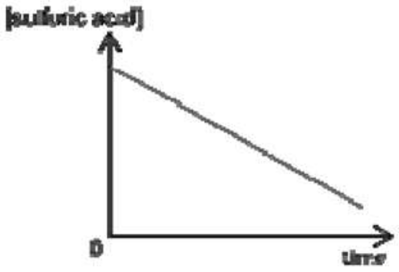
In the space below, record, in an appropriate form, all measurements of volume, time, and 1/time.

[5]

(b) Plot 1/time against the volume of **FC 6**. Draw the most appropriate line, taking into account all the points.

[3]

(c) Why was the total volume of solution kept constant in the experiments? [

		Volume of FC 6 is directly proportional to its concentration (if total volume is constant)
	(d)	Using the graph of 1/time against the volume of **FC 6,** draw a conclusion about the relationship between the concentration of sodium thiosulfate used and the rate of reaction. Hence, state the order of reaction with respect to sodium thiosulfate. [2] Rate of reaction is proportional to concentration of FC 6 (allow directly proportional). Order of reaction is 1.
	(e)	In the four experiments, which value of the time measured had the greatest error? Explain your answer. [2] Either shortest time as greatest percentage/ fractional error or longest time as greatest uncertainty in judging when printing is obscured
	(f)	Another student conducts another experiment for the same reaction where the sodium thiosulfate is in large excess. The concentration of acid is monitored as the reaction progresses. His results are as shown below.  Deduce the order of reaction with respect to sulfuric acid. [2] The constant gradient indicates a constant rate of reaction. Zero order with respect to sulfuric acid
		[Total: 13]

3 Organic Analysis

Before starting parts (a) and (b), half-fill a 250 cm^3 beaker with water and heat with a hotplate to approximately 60 $^\circ$C. You will use this as a hot water bath.

(a) **FD 7**, **FD 8** and **FD 9** are solutions each containing a single compound which could be ethanol, ethanal or propanone. To identify each compound you will react the samples with Tollens' reagent and with acidified potassium manganate(VII).

Preparation of Tollens' reagent

1. To approximately 2 cm depth of aqueous silver nitrate in a boiling tube, add approximately 0.5 cm depth of aqueous sodium hydroxide.

2. Add aqueous ammonia a little at a time with continuous shaking until the brown precipitate just dissolves. Do not add an excess of ammonia.

Complete the table below

test	*observations*		
	FD 7	**FD 8**	**FD 9**
To a 1 cm depth of each solution in a clean, dry test-tube add a few drops of the Tollens' reagent that you have prepared. **Do not shake the tube**. If no reaction is seen, warm the tube in the hot water bath.	silver mirror/black or brown or grey ppt	No ppt	No ppt
To a 1 cm depth of each solution in a test-tube, add a 1 cm depth of dilute sulfuric acid. Then add a few drops of aqueous potassium manganate(VII). If no reaction is seen, warm the tube in the hot water bath.	Purple $KMnO_4$ turns colourless/ decolourised	Purple $KMnO_4$ remains purple	Purple $KMnO_4$ turns colourless/ decolourised
Identity	ethanal	propanone	ethanol

[4]

(b) **FD 10** is an aqueous solution of an organic compound. Carry out the following tests. You do not need to identify **FD 10**.

test	*observations*
To a 1 cm depth of **FD 10** in a test-tube add a 1 cm depth of dilute sulfuric acid. Then add a few drops of aqueous potassium manganate(VII). If no reaction is seen, place the test-tube in the hot water bath and leave to stand.	Purple $KMnO_4$ turns colourless/ decolourises
To a 1 cm depth of **FD 10** in a test-tube, carefully add a small spatula measure of sodium hydrogen carbonate.	Effervescence/fizzing/bubbles Colourless, odourless gas evolved that gives a white ppt with limewater

[2]

(c) State the type(s) of reactions that **FD 10** have undergone in **(b)**. [2]

	Oxidation Acid-carbonate
(d)	Given that the Mr of **FD 10** is 46.0. State its identity. [1] [Ar: C, 12.0; O, 16.0; H, 1.0; C*l*, 35.5; N, 14.0]
	HCOOH

[Total: 9]

4 Planning

When heated, aqueous hydrogen peroxide, H_2O_2, decomposes to form oxygen and water.

$$2H_2O_2\,(aq) \rightarrow 2H_2O\,(l) + O_2\,(g)$$

The decomposition can also occur at room temperature if a suitable catalyst is added. Both of the solids, manganese(IV) oxide and lead(IV) oxide, will catalyse the decomposition.

You are provided with:

- 0.150 mol dm^{-3} solution of hydrogen peroxide
- a syringe with a capacity of 100 cm^3
- apparatus normally found in a school laboratory

(a) (i) Using the information given above, you are required to write a plan to determine the more efficient catalyst for the decomposition of aqueous hydrogen peroxide. Your plan should include:

- a fully labelled diagram of the apparatus to be used
- a calculation of the volume in cm^3 of the aqueous hydrogen peroxide that could be used such that an appropriate volume of oxygen could be collected.
- the measurements you would take and how you would use them to deduce which catalyst is more efficient.

The molar volume of a gas at 20 °C is 24.0 dm^3.

- Diagram shows a container with both chemicals named and attached to a syringe connected without leaks.
- Container shows the catalyst and hydrogen peroxide separated and ready to mix.
- Rubber bung
- Well-greased 100 cm^3 syringe (labelled)
- 250 cm^3 conical flask (labelled)
- Delivery tube

At least half the capacity of syringe for M4
Amt of oxygen in 100 cm^3 of oxygen = 100/24000 = 0.00417 mol
Amt of H_2O_2 = 2 × 0.00417 = 0.00834 mol
Volume of hydrogen peroxide = (0.00834 × 1000)/0.15 = 55.6 cm^3

1. Measure 55.0 cm^3 of aqueous hydrogen peroxide into a 250 cm^3 conical flask using a 100 cm^3 measuring cylinder.

2. Weigh accurately 0.10 g (acceptable range: 0.1 to 1 g) of solid manganese(IV)

oxide into a plastic vial using the weighing balance.

3. Setup the experiment as shown in the diagram above.

4. Shake the conical flask to topple the solid into the aqueous hydrogen peroxide and start the stopwatch.

5. Record the time taken when 90 cm^3 (at least half the capacity of the collecting vessel) of gas is collected (when solid manganese(IV) oxide is used.)

6. Repeat the above steps using lead(IV) oxide instead.

7. The more efficient catalyst is the solid that requires the shorter time to collect 90.0 cm^3 of gas.

Alternative method:

- Record volume of gas in time intervals of less than 1 min and plot graphs

[9]

(ii) What other feature of the catalyst should be controlled?

Surface area

[1]

[Total : 10]

~END OF PAPER~

SERANGOON JUNIOR COLLEGE
General Certificate of Education Advanced Level
Higher 2

CANDIDATE NAME	
CLASS	

CHEMISTRY
JC2 Preliminary Examination
Paper 1 Multiple Choice

9729/01
22 Sep 2017
1 hour

Additional Materials: Data Booklet
Optical Mark Sheet (OMS)

READ THESE INSTRUCTIONS FIRST

On the separate multiple choice OMS given, write your name, subject title and class in the spaces provided. Shade correctly your FIN/NRIC number.

There are **30** questions in this paper. Answer **all** questions.
For each question there are four possible answers **A**, **B**, **C** and **D**.
Choose the one you consider correct and record your choice using a **soft pencil** on the separate OMS.
Each correct answer will score one mark.
A mark will not be deducted for a wrong answer.

You are advised to fill in the OMS as you go along; no additional time will be given for the transfer of answers once the examination has ended.

Any rough working should be done in this question paper.

This document consists of **16** printed pages and **0** blank page.

Answer all questions

1 An acidified solution of the salt $KClO_x$ will oxidise Fe^{2+}(aq) to Fe^{3+}(aq) quantitatively, the chlorine being reduced to Cl^-(aq).

When 0.302 g of the salt $KClO_x$ was reacted with 0.540 mol dm^{-3} Fe^{2+}(aq) in the presence of H^+(aq), 21.0 cm^3 of Fe^{2+}(aq) was needed for complete reaction.

Which of the following is the value of x?

A 1

B 2

C 3

D 4

2 A student made up a 0.10 mol dm^{-3} solution of $Ba(OH)_2.8H_2O$ which she found in the laboratory cupboard and left the solution in an open beaker. A week later, she returned to the laboratory, used the solution for titration with 0.10 mol dm^{-3} HCl and was surprised to discover that her titres were lower than expected.

Which of the following explains why the values were so low?

A Some of the barium hydroxide has reacted with carbon dioxide in the air to form solid barium carbonate.

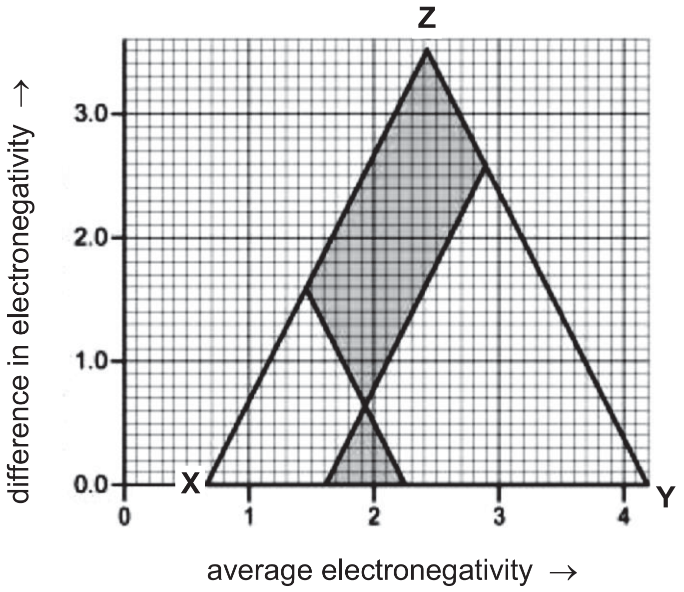
B Some water had evaporated from the barium hydroxide solution.

C The concentration of HCl was less than the stated 0.10 mol dm^{-3}.

D The crystals had less water of crystallisation than stated.

3 The type of bonding between two elements can be rationalised and even predicted using a van Arkel triangle. The triangle is based on electronegativity values. Difference in electronegativity is plotted along the y–axis and average electronegativity is plotted along the x–axis.

What is the type of bonding present at each of these bonding extremes, labelled **X**, **Y** and **Z** on the triangle?



	X	Y	Z
A	metallic	covalent	ionic
B	covalent	metallic	ionic
C	covalent	ionic	metallic
D	ionic	covalent	metallic

4 Equimolar amounts of aqueous ClO_2 and hydroxide ions react according to the equation below.

$$2ClO_2\,(aq) + 2OH^-\,(aq) \rightarrow ClO_3^-\,(aq) + ClO_2^-\,(aq) + H_2O\,(l)$$

Which statement is correct?

A The shape changes from linear in ClO_2 to bent in ClO_2^-.

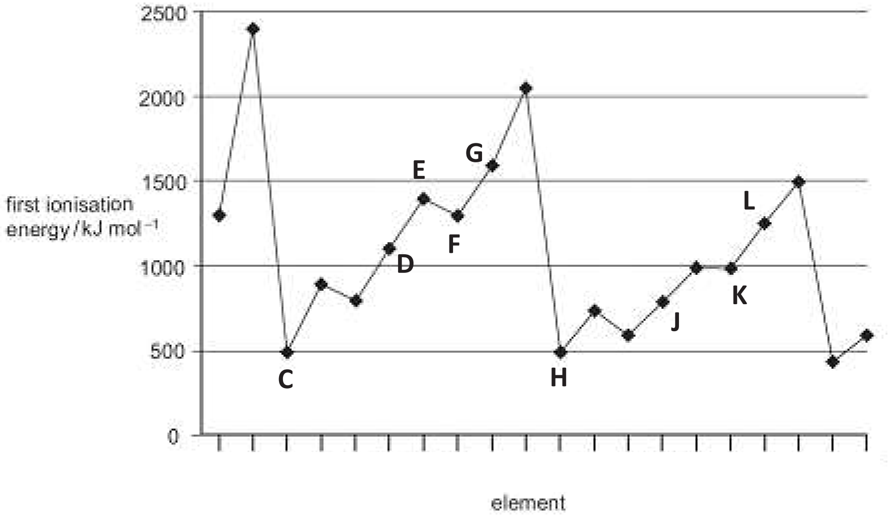
B The shape changes from bent in ClO_2 to trigonal planar in ClO_3^-.

C The bond angle changes from about 120° in ClO_2 to 107° in ClO_3^-.

D The bond angle changes from about 105° in ClO_2 to 107° in ClO_3^-.

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

The first ionisation energies of successive elements in the Periodic Table are represented in the graph.



Which of the following statements about elements **C** to **L** are correct?

1 **E** and $\mathbf{J}^-$ have half–filled p–orbitals.

2 Chlorides of **D** and **J** undergo hydrolysis.

3 **F** and **K** reacts to form acidic compounds.

4 **D** and **F** forms compounds with formula **DF** and $\mathbf{DF_2}$.

5 **G** and **L** forms compounds with variable oxidation states from –1 to +7.

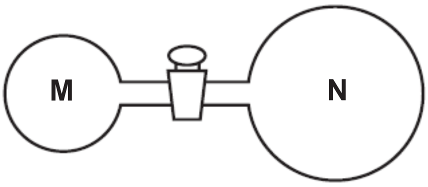
A 1 and 4 only

B 2 and 5 only

C 1, 3 and 4 only

D 2, 3 and 5 only

6 Two glass vessels **M** and **N** are connected by a closed valve.



M contains helium at 25 °C at a pressure of 1×10^5 Pa. **N** has been evacuated, and has three times the volume of **M**. In an experiment, the valve is opened and the whole set-up placed in boiling water.

What is the final pressure in the system?

A 3.13×10^4 Pa

B 3.76×10^4 Pa

C 1.00×10^5 Pa

D 1.33×10^5 Pa

7 Consider the following equilibrium system:

$$Fe_3O_4(s) + CO(g) \rightleftharpoons CO_2(g) + 3FeO(s) \qquad \Delta H = +ve$$

Given that $K_p = K_c\,(RT)^{\Delta n}$, where Δn is the sum of gaseous products – sum of gaseous reactants.

Which of the following statements are correct?

1 $K_c = K_p$ for this system.

2 The equilibrium constant, K_c, for this reaction has no units.

3 Adding FeO causes the position of equilibrium to shift to the left.

4 Increasing the temperature causes the position of equilibrium to shift to the right.

A 1 and 2 only

B 1 and 3 only

C 2, 3 and 4 only

D 1, 2 and 4 only

8 In an experiment to measure the enthalpy change of neutralisation, 20 cm^3 of aqueous sulfuric acid containing 0.02 mol of H_2SO_4 is placed in a plastic cup of negligible heat capacity.

A 20 cm^3 sample of aqueous sodium hydroxide containing 0.04 mol of NaOH, at the same initial temperature, is added and the temperature rises by 15 K.

If the heat capacity per unit volume of the final solution is 4.2 J K^{-1} cm^{-3}, what is the enthalpy change of neutralisation?

A $-\left(\dfrac{20\times4.2\times15}{0.04\times1000}\right)$ kJ mol^{-1}

B $-\left(\dfrac{40\times4.2\times15}{0.04\times1000}\right)$ kJ mol^{-1}

C $-\left(\dfrac{20\times4.2\times15}{0.02\times1000}\right)$ kJ mol^{-1}

D $-\left(\dfrac{40\times4.2\times15}{0.02\times1000}\right)$ kJ mol^{-1}

9 The conversion of graphite into diamond is a non–spontaneous reaction at 298 K. The entropy change of this reaction is negative at 298 K.

$$\text{C(graphite)} \rightarrow \text{C(diamond)} \qquad \Delta G = +3.08\ \text{kJ mol}^{-1}\ ,\ \ \Delta S = -3.3\ \text{J mol}^{-1}\ \text{K}^{-1}$$

With reference to the enthalpy change, ΔH, of the reaction above, which statements are correct?

1 Enthalpy change of atomisation of diamond is more endothermic than that of graphite.

2 Enthalpy change of combustion of diamond is more exothermic than that of graphite.

3 Bond energy of carbon–carbon bonds in graphite is greater than that in diamond.

4 The activation energy to convert graphite to diamond is lower than the activation energy for the reverse reaction.

A 1 and 4 only

B 2 and 3 only

C 1, 2 and 3 only

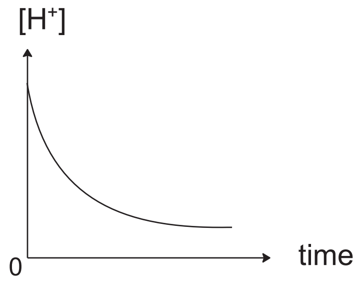
D 2, 3 and 4 only

10 The reaction between acidified KI and aqueous H_2O_2 involves the following steps:

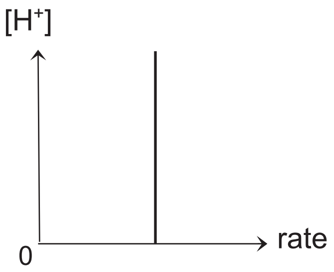
$H_2O_2 + I^-$	→	$H_2O + OI^-$	slow
$OI^- + H^+$	→	HOI	fast
$HOI + H^+ + I^-$	→	$I_2 + H_2O$	fast

Which graph would be obtained?

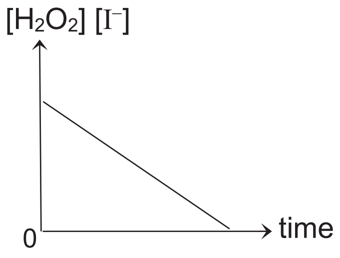
A



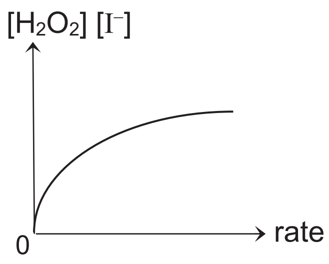
B



C



D



11 Compounds of beryllium are amphoteric, like compounds of aluminium.

In which equations is the beryllium-containing reactant acting as a Brønsted-Lowry acid?

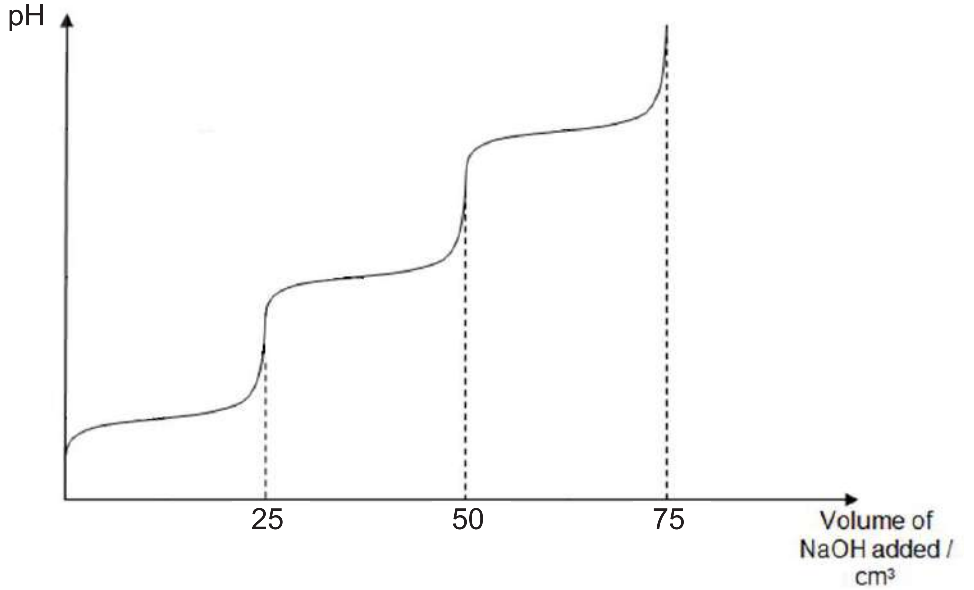
A $BeO(s) + 2OH^-(aq) + H_2O(l) \rightarrow [Be(OH)_4]^{2-}(aq)$

B $BeCl_2 + 4H_2O \rightarrow Be(H_2O)_4^{2+} + 2Cl^-$

C $2Be + O_2 \rightarrow 2BeO$

D $Be(H_2O)_2(OH)_2 + 2OH^- \rightarrow Be(OH)_4^{2-} + 2H_2O$

12 25 cm^3 of 1 mol dm^{-3} of the fully protonated form of compound **L** was titrated against a standard sodium hydroxide solution of a similar concentration and the following titration curve was obtained.



Which of the following compounds is a possible identity of compound **L**?

A $NH_2CH(CH_2CH_2CONH_2)COOH$

B $NH_2CH(CH_2CH_2CH_2OH)COOH$

C $NH_2CH(CH_2CH_2CH_2NH_2)COOH$

D $NH_2CH(CH_2CH_2CHO)COOH$

13 A sparingly soluble calcium salt dissociates in solution according to the equation:

$$Ca_3\mathbf{Q}_2\ (s) \rightleftharpoons 3Ca^{2+}\ (aq) + 2\mathbf{Q}^{3-}\ (aq)$$

If the solubility product of $Ca_3\mathbf{Q}_2$ is ***p***, what is the concentration of $\mathbf{Q}^{3-}$ at equilibrium in a saturated solution of $Ca_3\mathbf{Q}_2$ (aq)?

A $2p^{\frac{1}{5}}$

B $2(\frac{p}{36})^{\frac{1}{5}}$

C $2(\frac{p}{72})^{\frac{1}{5}}$

D $2(\frac{p}{108})^{\frac{1}{5}}$

14 A transition metal cation can exist in a 'high spin' or 'low spin' state while exposed to different ligands in an octahedral complex.

A 'high-spin' state has the electrons occupying all the d-orbitals singly first, before pairing in the lower energy d-orbitals.

A 'low-spin' state has the lower energy d-orbitals filled first, pairing up if necessary, before the higher energy d-orbitals are filled.

Which cation would have the largest number of unpaired electrons?

A 'High-spin' Mn^{3+}

B 'High-spin' Fe^{3+}

C 'Low-spin' Co^{2+}

D 'Low-spin' Ni^{4+}

15 Which of the following is **not** a result of the small energy gap between 3d and 4s orbitals?

A Transition metals have higher electrical conductivity than aluminium.

B Transition metals can exhibit variable oxidation states.

C Transition metals have higher melting point than calcium.

D Transition metals ions are usually coloured.

16 Use of the Data Booklet is relevant to this question.

Two catalysed reactions and their respective catalysts are shown below.

Reaction	**Equation**	**Catalyst**
I	$S_2O_8^{2-} + 2I^- \rightarrow 2SO_4^{2-} + I_2$	Fe^{3+}
II	$2MnO_4^- + 5C_2O_4^{2-} + 16H^+ \rightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$	Mn^{2+}

Which statements about the reactions and the catalysts are correct?

1 Mn^{2+} is an auto-catalyst in reaction **II**.

2 Fe^{2+} could replace Fe^{3+} as a heterogeneous catalyst in reaction **I**.

3 Mn^{2+} could replace Fe^{3+} as a homogeneous catalyst in reaction **I**.

4 Both catalysts increase the energetic feasibility of their respective reactions.

A 1 and 3 only

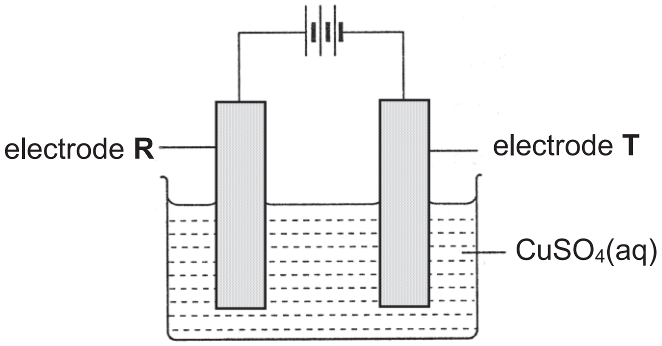
B 2 and 3 only

C 1, 2 and 4 only

D 2, 3 and 4 only

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

Impure copper obtained from copper ores can be purified by electrolysis as shown below. The cell potential is adjusted such that copper of the impure copper electrode dissolves and impurities such as silver, iron and zinc can be removed through this process.



Which statement is **not** correct regarding the above electrolytic process?

A Reduction occurs at electrode **T**.

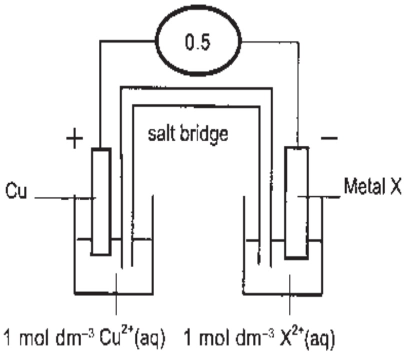
B Electrode **R** contains impure copper.

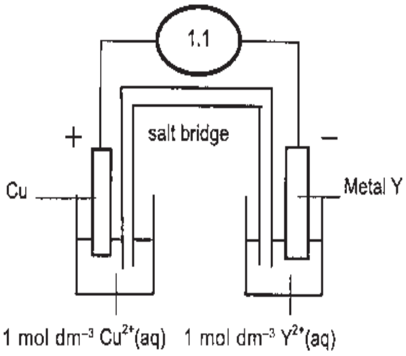
C Zinc impurity goes into the solution as Zn^{2+} ions.

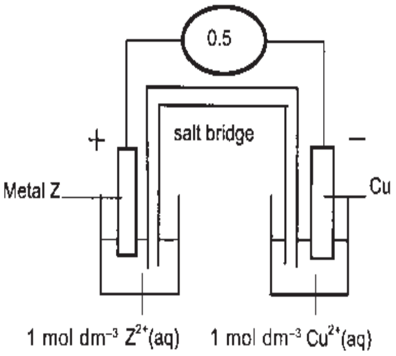
D Iron and silver impurities fall to the bottom as sludge.

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

Three electrochemical cells are set up as shown below. The *e.m.f* in volts is shown on each voltmeter.







These *e.m.f* indicate the order of reactivity of the metals. The order of the weakest to the strongest reducing agent is

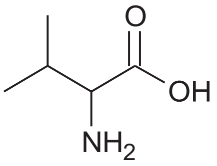
A **X**, **Y**, Cu, **Z**

B Cu, **Z**, **X**, **Y**

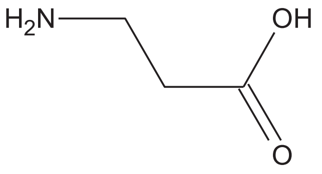
C **Z**, Cu, **X**, **Y**

D **Y**, **X**, **Z**, Cu

19 Valine is a naturally occurring amino acid.



Valine



3-aminopropanoic acid

Which statement about valine and 3-aminopropanoic acid is correct?

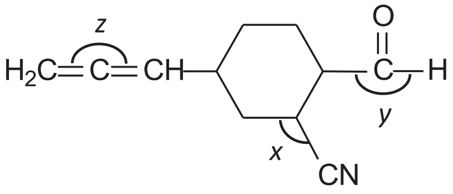
A Both compounds are able to form zwitterions.

B Both compounds are able to react with ethanoic acid to give amide.

C Both compounds are able to react with $NaBH_4$ in methanol to give alcohol.

D Both compounds are soluble in water due to the formation of intermolecular hydrogen bonding.

20 Which of the following statements are correct about compound **U**?



compound **U**

1 The bond angles in compound **U** increase in the order ***x*** < ***y*** < ***z***.

2 There is only one sp hybridised carbon atom in compound **U**.

3 There are 26 σ and 5 π bonds.

4 Compound **U** is planar.

A 1 and 2 only

B 1 and 3 only

C 1, 2 and 4 only

D 2, 3 and 4 only

21 Deuterium (D or ^2H) is a heavy isotope of hydrogen. A deutero-hydrocarbon has the part structural formula shown below.

$CDH=CH–CH=C(C_3H_7)_2$

What is the total number of isomers with the above part-structural formula?

A 2

B 4

C 8

D 10

22 The molecule of benzene, C_6H_6 is a regular hexagon in which the π electrons are described as delocalised.

Which of the following statements support this structure?

1 Benzene is a good conductor of electricity.

2 Addition reactions of benzene take place more easily than substitution.

3 All C–C bonds lengths in benzene are intermediate between C–C bond in an alkane and C=C bond in an alkene.

4 The enthalpy change of hydrogenation of benzene is less exothermic than that predicted for cyclohexatriene.

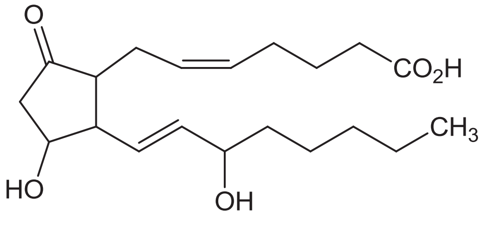
A 1 and 3 only

B 3 and 4 only

C 1, 2 and 3 only

D 1, 2 and 4 only

23 PGE_2 is a prostaglandin that has pharmacological activity.

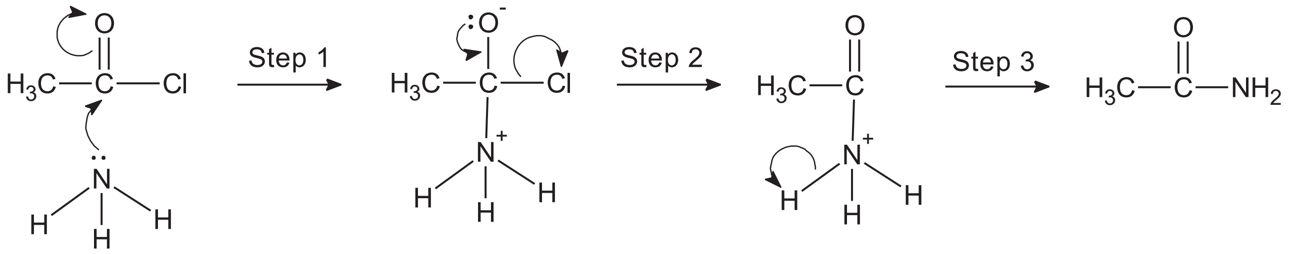


PGE_2

Which of the following is incorrect?

	Reducing agent	Number of hydrogen atoms incorporated per molecule of PGE_2
A	H_2 / Ni	6
B	Na in ethanol	8
C	$NaBH_4$ in methanol	6
D	$LiAlH_4$ in dry ether	4

24 A mechanism for the reaction between ammonia and ethanoyl chloride is given below.



Which of the following statements are correct?

1 The ammonia behaves as a nucleophile.

2 The loss of proton in **step 3** is shown incorrectly.

3 The ammonia attacks an electron-deficient carbon atom.

4 The rate of reaction will increase if ethanoyl bromide is used.

A 1, 2, 3 and 4

B 1, 3 and 4 only

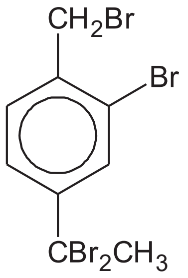
C 1 and 3 only

D 2 and 4 only

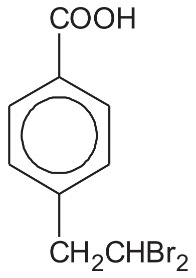
25 Diols formed on the same carbon atom are generally unstable and will undergo the following reaction.

$$RCR'(OH)_2 \rightarrow RCOR' + H_2O$$

Compounds **V** and **W** are both reacted with hot aqueous NaOH followed by dilute HC*l* at room temperature.



Compound **V**



Compound **W**

Which reagents could be used to distinguish the final products of **V** and **W**?

1 2,4−DNPH
2 Fehling's solution
3 Sodium carbonate
4 Hot acidified $K_2Cr_2O_7$
5 Iodine in aqueous NaOH

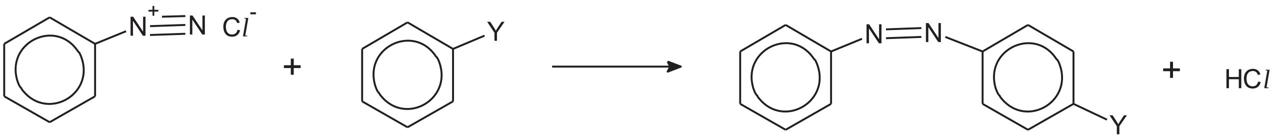
A 1 and 2 only
B 3 and 4 only
C 1, 4 and 5 only
D 2, 3 and 5 only

26 The ozone depletion potential (ODP) of a chemical compound is the relative amount of degradation to the ozone layer it can cause, with trichlorofluoromethane being fixed at an ODP of 1.0.

Which of the following compounds has an ODP of greater than 1.0?

A methane
B dichlorodifluoromethane
C chlorotrifluoromethane
D bromotrifluoromethane

27 Azo coupling is an organic reaction between a diazonium compound and another aromatic compound that produces an azo compound.



diazonium

Which of the following correctly represents the type of reaction and the role of diazonium compound?

	Type of reaction	**Role of diazonium**
A	nucleophilic substitution	nucleophile
B	electrophilic substitution	electrophile
C	nucleophilic substitution	electrophile
D	electrophilic substitution	nucleophile

28 What is the order of increasing pH of 1 mol dm^{-3} of each organic compound?

A CH_3CO_2Na, CH_3CO_2H, CF_3CO_2H, $HOCH_2CHO$

B CH_3CO_2Na, $HOCH_2CHO$, CH_3CO_2H, CF_3CO_2H

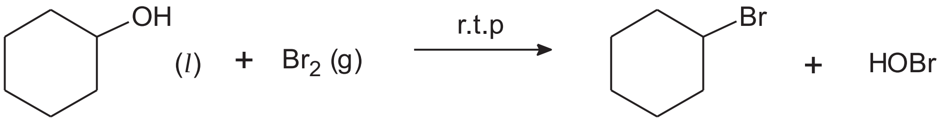
C CF_3CO_2H, CH_3CO_2H, $HOCH_2CHO$, CH_3CO_2Na

D CF_3CO_2H, CH_3CO_2H, CH_3CO_2Na, $HOCH_2CHO$

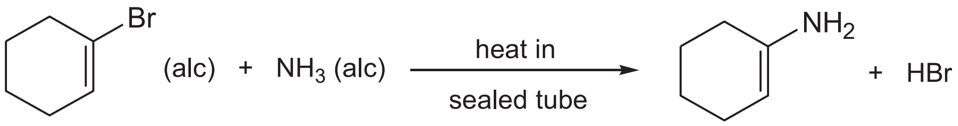
29 Which reaction gives the best yield of products?

[(*alc*) indicates an alcoholic solution.]

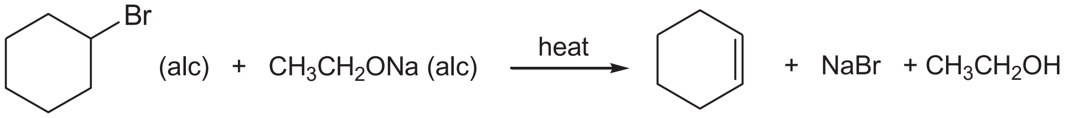
A



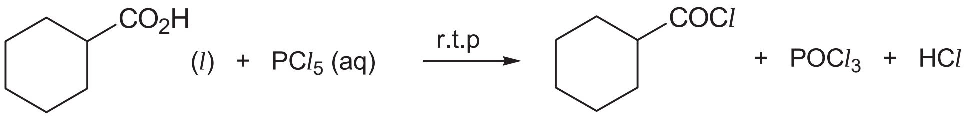
B



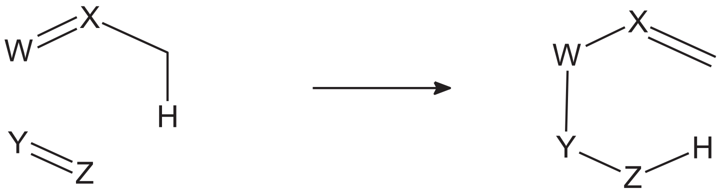
C



D



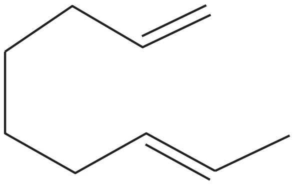
30 The Alder-ene reaction is a reaction between two alkenes and is capable of forming new carbon-carbon bonds. An example of the Alder-ene reaction is given below:



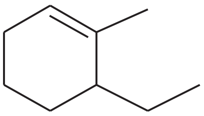
Note: W, X, Y & Z are carbon atoms and other hydrogens are not sho

The Alder-ene reaction typically produces many products as the roles of the two alkenes can be exchanged.

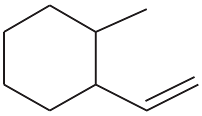
Which compound will **not** be formed when the following compound undergoes Alder-ene reaction?



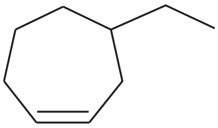
A



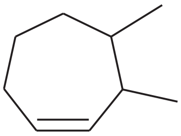
B



C



D



SERANGOON JUNIOR COLLEGE
General Certificate of Education Advanced Level
Higher 2

CANDIDATE NAME	
CLASS	

CHEMISTRY 9729/02

JC2 Preliminary Examination **13 Sept 2017**
Paper 2 Structured Questions **2 hours**

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write in dark blue or black pen.
You may use an HB pencil for any diagrams or graphs.
Do not use staples, paper clips, glue or correction fluid.

Answer **all** questions in the spaces provided on the Question Paper.
The use of an approved scientific calculator is expected, where appropriate.
A Data Booklet is provided.

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

For Examiner's Use	
1	/ 8
2	/ 18
3	/ 25
4	/ 24
TOTAL	**/ 75**

This document consists of 24 printed pages

1 The size of an atom can be measured using the distance between the nuclei of two atoms.

For example, the 'metallic radius' of the Na atom is half the distance between two Na atoms in the crystal lattice of the metal. The 'covalent radius' of the C*l* atom is taken to be half the distance between the nuclei in a Cl_2 molecule. Finally, the 'van der Waals' radius' of the A_r atom is assumed to be half the distance between two atoms in the solid state.

These three types of radius are commonly known as 'atomic radii' and the corresponding values for Period 3 elements can be found in the Data Booklet.

(a) **(i)** Explain the general trend in atomic radius across Period 3.

……………………………………………………………………………………………..

……………………………………………………………………………………………..

……………………………………………………………………………………………..

……………………………………………………………………………………………..

[2]

(ii) Suggest a reason for the anomaly in the measurement of atomic radius for argon.

……………………………………………………………………………………………..

……………………………………………………………………………………………..

……………………………………………………………………………………………..

[1]

(b) **(i)** State the general relationship between atomic radius and first ionisation energy across Period 3.

……………………………………………………………………………………………..

……………………………………………………………………………………………..

……………………………………………………………………………………………..

[1]

(ii) Explain why the relationship does not hold from P to S**.**

………………………………………………………………………………………………

………………………………………………………………………………………………

………………………………………………………………………………………………

………………………………………………………………………………………………

[1]

(c) Across period 3, the elements changes from metallic to non-metallic nature. Correspondingly, the difference in electronegativity between the elements and the oxide decreases, giving rise to different types of oxides.

A, **B** and **C** are Period 3 elements, from Na to S, inclusive.

- **A** has the highest melting point among Period 3 elements.
- **B** has the highest electrical conductivity in Period 3.
- **C** burns in air with a coloured flame.
- **B** and **C** can show the same oxidation state in their compounds.

Identify **A**, **B** and **C** and hence, write equations, including state symbols, to show the acid-base properties of their oxides.

[Give the chemical formulae for only the highest oxide formed.]

………………………………………………………………………………………………

………………………………………………………………………………………………

………………………………………………………………………………………………

………………………………………………………………………………………………

………………………………………………………………………………………………

………………………………………………………………………………………………

………………………………………………………………………………………………

[Total : 8]

2 Benzoic acid occurs naturally in many plants and it has many uses. It is an important precursor for the industrial synthesis of many organic substances.

(a) The benzoic acid and sodium benzoate buffer is commonly used as food preservatives in many acidic foods such as salad dressings and carbonated drinks.

(i) With the aid of relevant chemical equations, explain how the system can control pH when a small amount of base is added.

………………………………………………………………………………………………

………………………………………………………………………………………………

………………………………………………………………………………………………

………………………………………………………………………………………………

[1]

(ii) Given that the acid dissociation constant for benzoic acid is 6.3 x 10^{-5} mol dm^{-3}, calculate the mass of solid sodium benzoate required to be added to 250 cm^3 of 0.50 mol dm^{-3} of benzoic acid to form a buffer solution with an initial pH 4.

[2]

(iii) To achieve the optimal buffering capacity of a 25 cm^3 sample of the buffer prepared in **(a)(ii),** a standard solution of 1.5 mol dm^{-3} sodium hydroxide was added. Calculate the volume of sodium hydroxide needed.

[3]

(b) The presence of benzoic acid in plant extracts can be confirmed using neutral iron(III) chloride according to the following equation.

$$Fe^{3+}(aq) + 3C_6H_5COOH(aq) \longrightarrow Fe(C_6H_5CO_2)_3(s) + 3H^+(aq)$$

When 50 cm^3 iron(III) chloride is added to an equal volume of the plant extract, 0.0532 g of iron(III) benzoate, $Fe(C_6H_5CO_2)_3$ precipitate is formed.

The resultant mixture has a pH value of 2.33.

(i) Calculate the amount of benzoic acid that has reacted with neutral iron(III) chloride solution and H^+ in the mixture.

[1]

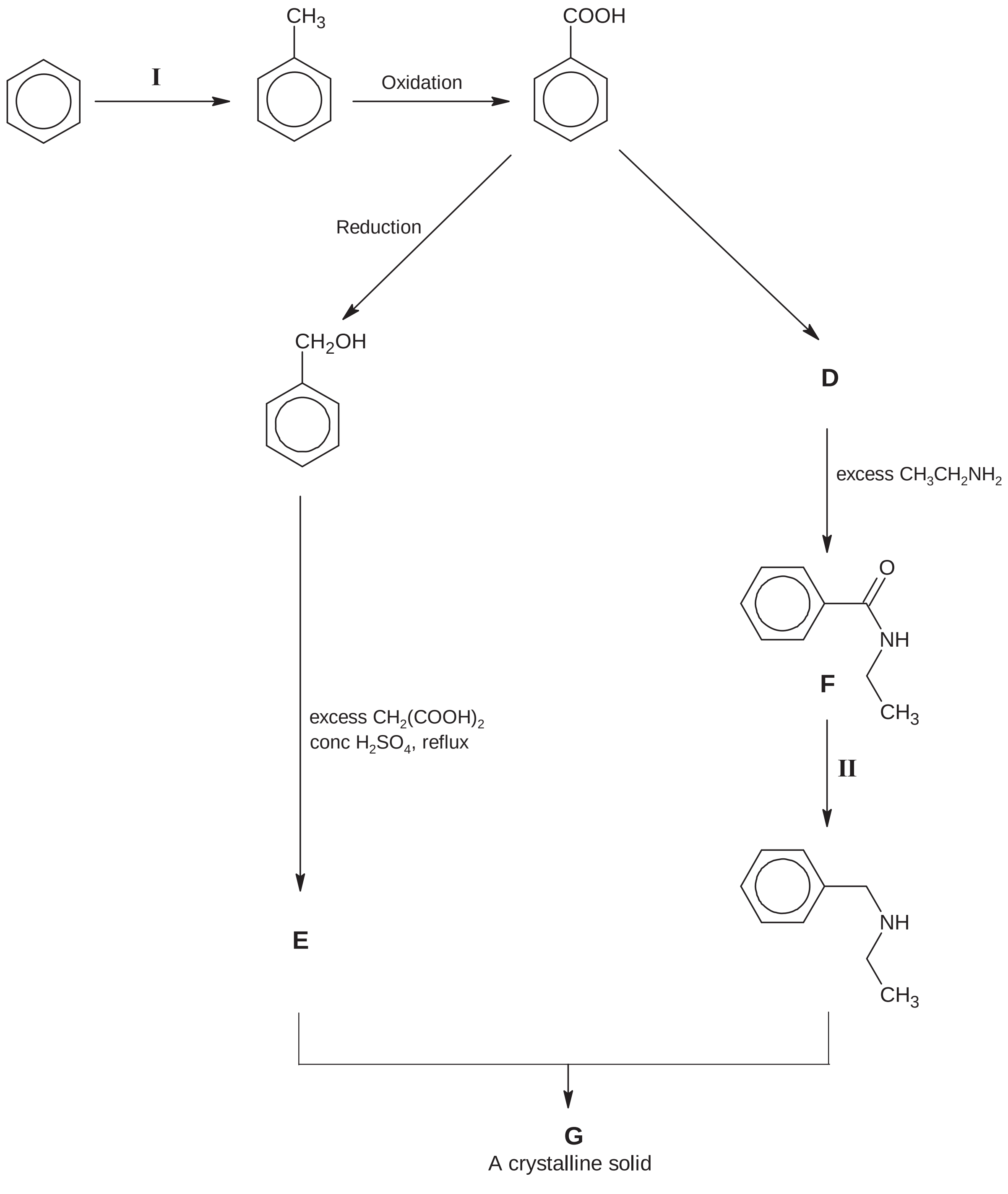
(ii) Assuming that the H^+ ions in solution are formed from the dissociation of benzoic acid and the reaction of benzoic acid with iron(III) chloride, calculate the concentration of benzoate ions in the equilibrium mixture.

[2]

(iii) Calculate the K_{sp} of iron(III) benzoate, given that the concentration of iron(III) ions in the mixture is 1.83×10^{-3} mol dm^{-3} at equilibrium.

[1]

(c) Benzoic acid is involved in the reaction scheme below:



(i) Draw the structures for **D**, **E** and **G** in the boxes below.

D	**E**
G	

[3]

(ii) Suggest the reagents and conditions for reactions **I** and **II**.

Reaction **I**: ……………………………………………………………

Reaction **II**: ……………………………………………………………

[2]

(iii) Compound **F** was heated with aqueous sodium hydroxide and excess carbon dioxide was bubbled through the solution.

Given the acid dissociation constants below, suggest the products that would be formed after the introduction of carbon dioxide.

acid	**formula**	**K_a / mol dm^{-3}**
carbonic acid	H_2CO_3	4.5×10^{-7}
benzoic acid	C_6H_5COOH	6.3×10^{-5}
ethylamine salt	$CH_3CH_2NH_3^+$	1.6×10^{-11}

…………………………………………………………………………………………

…………………………………………………………………………………………

…………………………………………………………………………………………

…………………………………………………………………………………………

[3]

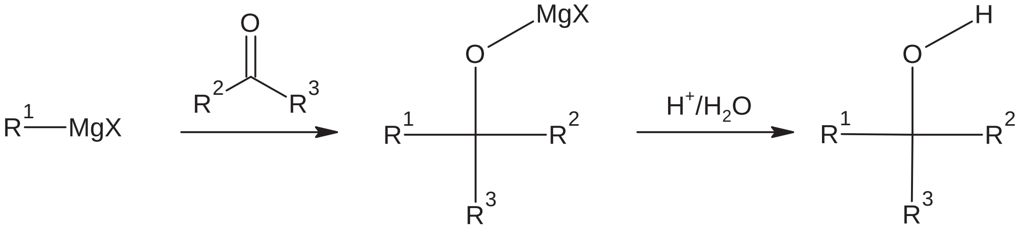
[Total : 18]

3 Grignard reagents are organomagnesium halides, RMgX commonly used in organic synthesis. The R in RMgX behaves like an anion, R^- and is a strong Lewis base. It can be made by the reaction between halogenoalkane and magnesium under anhydrous conditions, using ether as a solvent.

$$R^1\text{—}X \quad + \quad Mg \longrightarrow R^1\text{—}MgX$$

where R= alkyl group, X= C*l*, Br, I

In a Grignard reaction, the Grignard reagent behaves as a nucleophile and may be added to a carbonyl compound for the formation of an alcohol. This reaction is useful for the formation of carbon–carbon bonds.



(a) **(i)** Suggest, with an equation, why the synthesis of Grignard reagent has to be done under anhydrous conditions.

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

[2]

(ii) Besides organomagnesium compounds, organolithium compounds can be formed between lithium and relevant organic substances. Account for the similarity in the reactions involving lithium and magnesium.

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

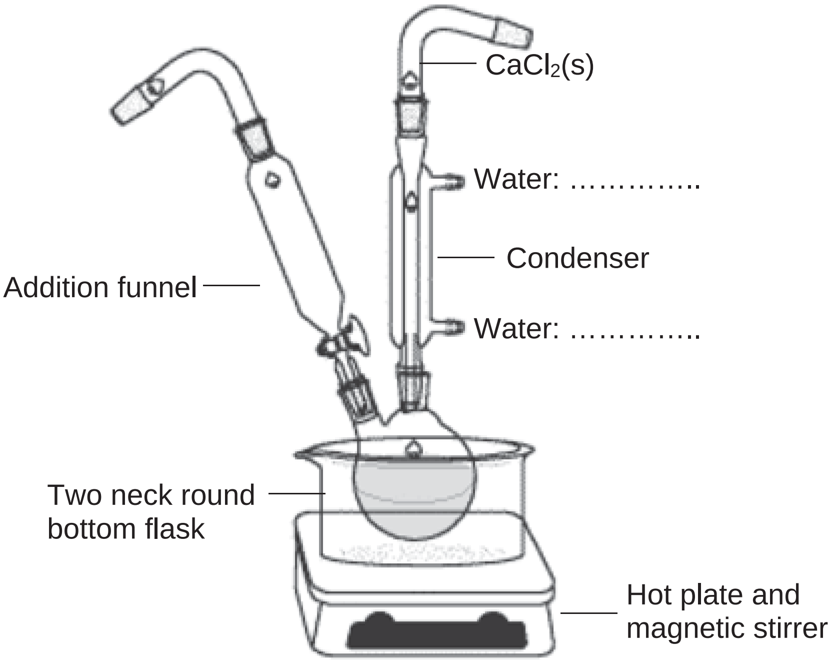
……………………………………………………………………………………………

[2]

The preparation and set up of Grignard synthesis of 2-methylhexan-2-ol is described below:

Table 3.1

Compound	**Melting pt / °C**	**Boiling pt / °C**	**Molar mass / g mol^{-1}**	**Density / g cm^{-3}**	**Solubility in water**
1-bromobutane	−11.2	101.4	136.9	1.27	Insoluble
Magnesium	651	1100	24.3	1.74	Insoluble
Diethyl ether	−116.3	34.6	74.0	0.713	Insoluble
Propanone	−94.7	56.1	58.0	0.785	Soluble
Sulfuric acid	10.3	337	98.1	1.84	Soluble
2-methylhexan-2-ol	−	143	116.0	0.82	Soluble



Preparation of Grignard reagent, RMgX

1. Add 15 g of 1-bromobutane and 3 g of magnesium into the 250 cm^3 two-neck round bottom flask.

2. Add 50 cm^3 of anhydrous diethyl ether using the addition funnel. Gently stir the mixture under reflux for 30 minutes. The reaction is exothermic and will boil without external heat.

3. When the reaction is complete, cool the reaction mixture using an ice bath.

(b) **(i)** With reference to Table 3.1, suggest why a reflux set up is necessary in this organic synthesis.

…………………………………………………………………………………………

…………………………………………………………………………………………

…………………………………………………………………………………………

[1]

(ii) On the diagram on page 10, label and account for the direction of water flow.

…………………………………………………………………………………………

…………………………………………………………………………………………

[1]

(iii) Some heating may be required at the beginning as the initial rate of formation of RMgX is slow. Magnesium metal has to be scrapped or sliced into smaller pieces to increase the reaction rate.

Write an equation to suggest why magnesium may not be as reactive as expected.

…………………………………………………………………………………………

[1]

(iv) Excess diethyl ether is added to keep the Grignard reagent at a low concentration. This will prevent the Grignard reagent from reacting with unreacted 1-bromobutane. Draw the structure of the organic by-product.

[1]

Synthesis of alcohol

4. Using the addition funnel, add 6.5 g (dissolved in 15 cm^3 of diethyl ether) of propanone to the Grignard reagent.

5. To a separate 250 cm^3 beaker, add 100 cm^3 of ice water and 4 cm^3 of concentrated sulfuric acid and mix well.

6. When the reaction with propanone is completed, add the reaction mixture into a 250 cm^3 beaker, sitting in an ice bath. Carefully transfer sulfuric acid solution from step 5 into reaction mixture. Stir gently to mix well.

(c) **(i)** Using Table 3.1, calculate the theoretical mass of 2-methylhexan-2-ol.

[2]

(ii) The actual yield for 2-methylhexan-2-ol is 4 g. Calculate the percentage yield for this reaction.

[1]

(iii) Suggest why the addition of sulfuric acid has to be carried out in an ice bath in step 6.

…………………………………………………………………………………………………

[1]

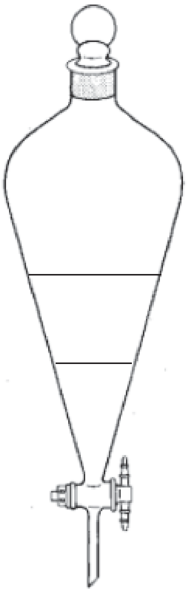
Solvent extraction

7. Add the mixture from step 6 into a 500 cm^3 separation funnel and add 10 cm^3 of diethyl ether. Shake the separation funnel, releasing any gas formed. Allow the layers to separate and collect both layers separately.

8. Repeat step 7 with the aqueous layer and a fresh sample of 10 cm^3 diethyl ether. Collect and combine each ether layer.

9. The combined ether layer is poured back to the separation funnel and mixed with several 20 cm^3 portions of 5 % sodium bicarbonate solution until no more carbon dioxide is generated.

(d) **(i)** After step 7, there are two layers in the separation funnel. Identify the ether and aqueous layer in the diagram below.



Upper layer: ……………………….

Bottom layer: ………………………..

Explain your answer.

…………………………………………………………………………………………

…………………………………………………………………………………………

[1]

(ii) Give a reason for the addition of sodium bicarbonate in Step 9.

…………………………………………………………………………………………

[1]

(iii) During solvent extraction, both propanone and 2-methylhexan-2-ol are found in the ether layer. Comment on the solubility of 2-methylhexan-2-ol in diethyl ether.

…………………………………………………………………………………………

…………………………………………………………………………………………

…………………………………………………………………………………………

…………………………………………………………………………………………

…………………………………………………………………………………………

[1]

(iv) Suggest different chemical tests to positively identify propanone and 2-methylhexan-2-ol in the ether layer.

…………………………………………………………………………………………

…………………………………………………………………………………………

…………………………………………………………………………………………

…………………………………………………………………………………………

[2]

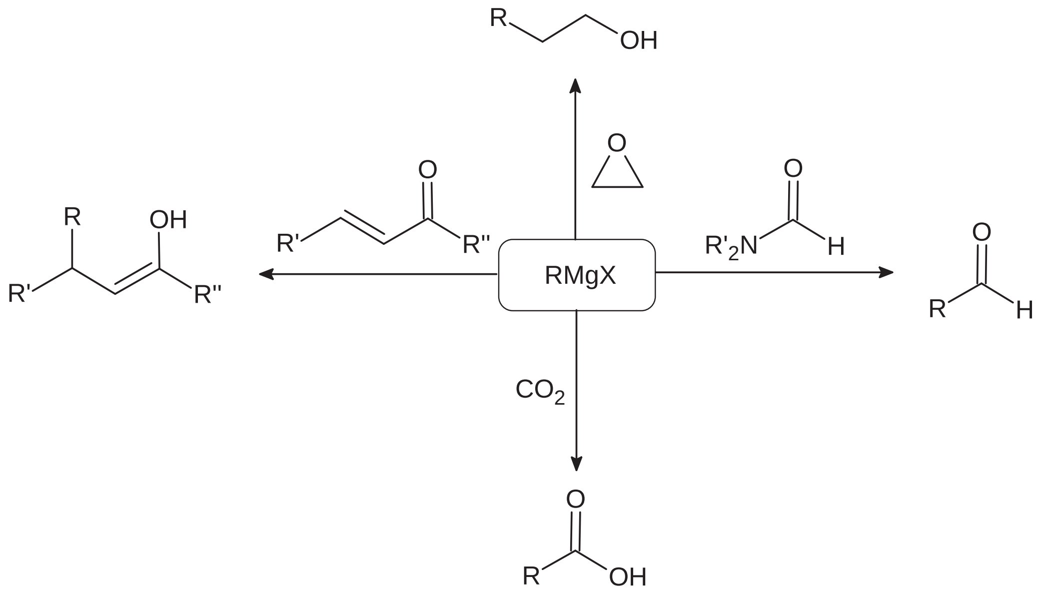
(v) Suggest how crude 2-methylhexan-2-ol can be purified from the ether layer.

…………………………………………………………………………………………

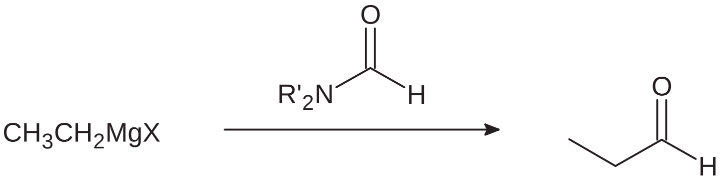
…………………………………………………………………………………………

[1]

(e) Grignard reagent is used widely in organic synthesis due to its ability to increase carbon chain length. Four unique reactions involving the use of Grignard reagent are shown in the reaction map below.



(i) The following Grignard reaction to form propanal achieved a very low yield as the aldehyde formed can react with the Grignard reagent again.



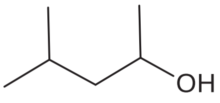
Describe the mechanism between propanal and the Grignard reagent, CH_3CH_2MgX to form the corresponding alcohol.

[2]

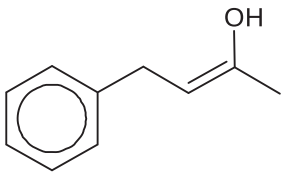
(ii) Starting with a suitable Grignard reagent, propose an alternative 3-step synthesis pathway to synthesise propanal.

[3]

(iii) Using different reaction types from the reaction map on page 15, suggest appropriate pairs of reagents in the synthesis of compounds **H** and **I**.



H



I

Reagent pair for H:	**Reagent pair for I**:

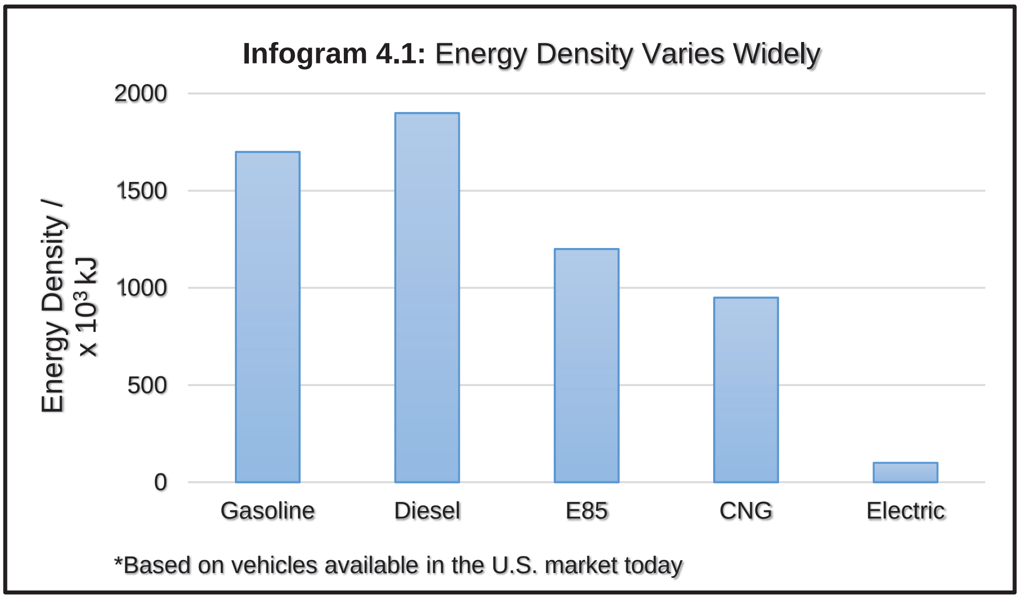
[2]

[Total: 25]

4 The use of electric vehicles has been increasing popular in the U.S. For example, hydrogen fuel cell vehicles produces zero carbon emission.

Despite the advantages of electric cars, petrol-engined cars are still widely used today. One problem with electric vehicles is their poor performance, inconvenience of finding a charging station and it takes a long time to recharge the batteries. Petrol-engined cars are better as their energy supply can be replaced over 6 million times faster than electric cars.

The infogram below shows how energy density varies widely with different fuels. Energy density is the energy produced per unit dimension of a fuel and this determines the practicality of a fuel.



Infogram 4.1: Energy Density Varies Widely

*Based on vehicles available in the U.S. market today

However, using petrol (which contains a mixture of alkanes) has its own problems. One such problem is that it's a finite resource, and another is pollution. Hence, there is a need to improve the performance of petrol in car engines so that it burns as cleanly and efficiently as possible and to find alternative sources of fuel to replace petrol.

Some data for five fuels are given in **Table 4.2**.

Fuel	**Formula**	**Standard enthalpy change of combustion, $\Delta H_c^{\ominus}$ / kJ mol^{-1}**	**Relative molecular mass**	**Energy density (energy transferred on burning 1 kg of fuel) / kJ kg^{-1}**
octane	C_8H_{18} (*l*)	– 5470	114.0	
1,2-xylene	C_8H_{10} (*l*)	− 4540	106.0	
carbon	C(s)	– 393	12.0	
methanol	CH_3OH(*l*)	– 726	32.0	
hydrogen	H_2(g)	– 286	2.0	

(a) Give an example of a pollutant that can arise from the use of petrol and state a detrimental effect of the pollutant.

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

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

[1]

(b) Complete Table 4.2 by calculating the energy density for all fuels. [1]

(c) **(i)** On the basis of energy density, which is the best fuel in Table 4.2.

……………………………………………………………………………………

[1]

(ii) Suggest a practical difficulty in using hydrogen rather than methanol as a fuel.

……………………………………………………………………………………

……………………………………………………………………………………

[1]

(d) Using the given data above, comment on the feasibility of using electric cars in the near future.

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

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

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

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

[1]

Octane is commonly used as a fuel or a precursor in the production of other chemicals. The term “octane rating” is often used in the petroleum industry for rating the ability of octane’s various branched isomers in reducing engine knock in vehicles.

One important factor in making petrol is getting the right octane rating to reduce the problem of ‘knocking’. Knocking occurs when the combustion of fuel is not smooth. Knocking reduces engine power, leading to wear and tear in the engine and results in wastage of petrol. Hence, highly branched alkanes are desirable in petrols as they have higher octane ratings and reduce knocking.

Another factor for getting the right properties of petrol is the blending of petrol. In cold weather, it is difficult to vaporise petrol, which makes ignition difficult. On the other hand, in hot weather, petrol vaporises easily. Hence, petrol companies make different blends of petrol for different seasons and climates.

You are to use the information provided above to answer parts **(e)** and **(f)**.

(e) Apart from using alkanes with high octane ratings, another way to deal with the problem of knocking is through the addition of an antiknock agent, tetra-ethyl lead (**TEL**). **TEL** is a highly volatile colourless liquid which aids in the formation of free radicals. However, this method is not commonly used nowadays.

Explain, with the aid of a suitable equation, how **TEL** helps to overcome the problem of knocking and give a reason why its usage is limited nowadays.

…………………………………………………………………………………………………

…………………………………………………………………………………………………

…………………………………………………………………………………………………

…………………………………………………………………………………………………

…………………………………………………………………………………………………

…………………………………………………………………………………………………

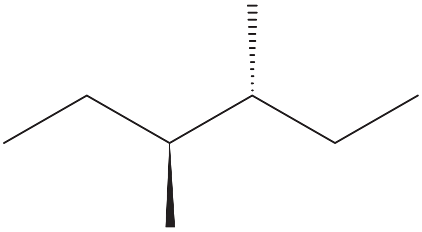
…………………………………………………………………………………………………

…………………………………………………………………………………………………

[3]

(f) Compounds **J**, **K** and **L** are isomers of the hydrocarbon octane, C_8H_{18}.

The table below shows the boiling points and data relating to the optical activity of the compounds.

Structure	**Boiling Point / °C**	**Number of chiral centres**	**Optical Activity**
Isomer **J**	120	1	Yes
 Isomer **K**	118	2	No
Isomer **L**	107	0	No

(i) Suggest why isomer **K** does not exhibit enantiomerism.

………………………………………………………………………………………………

………………………………………………………………………………………………

………………………………………………………………………………………………

[1]

(ii) Propose the structures of compounds **J** and **L**.

Isomer J :	**Isomer L :**

[2]

(iii) In terms of structure and bonding, identify which of your proposed compounds (**J** or **L**) would be a more suitable fuel for use in summer and winter respectively.

Your answer should show clear and detailed comparison in your choice of fuel.

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

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

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

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

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

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

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

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

[2]

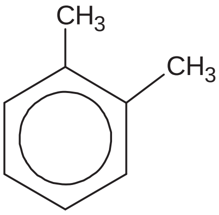
(iv) Controlled chlorination of isomer **K** in the presence of UV light produces different mono-chlorinated products with a molecular formula of $C_8H_{17}Cl$.

Draw the structural formula of any **two** possible isomers and state the ratio in which they are formed.

[2]

(g) The performance of hydrocarbons as fuels is largely improved by catalytic reforming. Reforming takes straight chain hydrocarbons in the C_6 to C_8 range from the gasoline or naphtha fractions and rearranges them into compounds containing benzene rings. They are used to make fuels with high octane number. Hydrogen is produced as a by-product of the reactions. A catalytic mixture of Pt and Al_2O_3 at a temperature of 500 ^oC and pressure of 20 atm is used.

An example of a product is 1,2-xylene.



(i) Write a balanced equation when octane undergoes the 'reforming' process to form 1,2-xylene.

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

[1]

(ii) What *type of reaction* has the octane undergone?

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

[1]

(iii) 1,4–xylene can be produced by a similar process. Suggest the structural formula of a C_8 alkane which might produce 1,4-xylene.

[1]

(iv) By means of an energy cycle, show and calculate the standard enthalpy change of reaction that produces 1,2-xylene from octane.

[2]

(v) Using data from the Data Booklet, calculate the enthalpy change of the reaction which reforms octane into 1,2-xylene.

[2]

(vi) By considering your answers in **(g)(iv)** and **(v)**, suggest if they are accurate descriptions of the reformation process.

…………………………………………………………………………………………

…………………………………………………………………………………………

…………………………………………………………………………………………

…………………………………………………………………………………………

[1]

(vii) Briefly explain whether you would expect the above reaction to have its ΔG value to be more negative than its corresponding ΔH_r.

…………………………………………………………………………………………

…………………………………………………………………………………………

…………………………………………………………………………………………

…………………………………………………………………………………………

[1]
[Total : 24]

SERANGOON JUNIOR COLLEGE
General Certificate of Education Advanced Level
Higher 2

CANDIDATE NAME	
CLASS	

CHEMISTRY 9729/03
JC2 Preliminary Examination 20 Sept 2017
Paper 3 Free Response 2 hours

Candidates answer on separate paper.

Additional materials : Answer Paper
Data Booklet
2 Cover Pages

READ THESE INSTRUCTIONS FIRST

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

Section A
Answer **all** questions.

Section B
Answer **one** question.

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

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

This document consists of **11** printed pages and **1** blank page.

Section A

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

1 **(a)** Oxides of nitrogen, NO_x are a mixture of gases that are composed of nitrogen and oxygen. They are formed during combustion processes in power plants.

Thermal NO_x refers to NO_x formed through high temperature oxidation of the diatomic nitrogen found in combustion air.

The formation rate is a function of temperature and the residence time of nitrogen at that temperature. At high flame temperatures, molecular nitrogen and oxygen dissociate into their atomic states and participate in a series of reactions.

The two principal reactions producing thermal nitric oxide, NO are as follows.

Step 1 O atoms react reversibly with N_2 to form NO.

Step 2 N atoms liberated react with O_2 to produce more NO.

Nitrogen dioxide typically arises via the oxidation of nitric oxide by oxygen in the atmosphere.

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

(i) Write the two principal reactions involved in the formation of thermal nitric oxide in combustion. [1]

(ii) Hence, determine the rate determining step. [1]

(iii) Suggest a method to reduce the formation of thermal NO_x. [1]

(b) Catalytic converters are used to reduce the output of NO_x into the environment. One example is the removal of nitric oxide by reaction with hydrogen gas using platinum catalyst.

		ΔH
$NO + NO \rightleftharpoons N_2O_2$	fast	positive
$N_2O_2 + H_2 \rightarrow H_2O + N_2O$	slow	negative
$N_2O + H_2 \rightarrow N_2 + H_2O$	fast	negative

(i) Write the rate equation for the above reaction, showing clearly how you derive it. [2]

(ii) Draw the probable energy profile diagram for this overall exothermic reaction. [2]

(iii) Using an appropriate sketch of the Maxwell–Boltzmann distribution curve, explain how the addition of platinum affects the rate of chemical reaction. [3]

(c) The NO_2 reacts with O_2 in the atmosphere to form colourless nitrogen pentoxide, N_2O_5 in equilibrium.

$$4\ NO_2\,(g) + O_2\,(g) \rightleftharpoons 2\ N_2O_5(g)$$

Dinitrogen pentoxide is a rare example of a compound that adopts two structures depending on the conditions. As a gas in the atmosphere, dinitrogen pentoxide exists as a molecule. However, it exists as an ionic salt in the solid state.

(i) Gaseous N_2O_5 is a symmetrical molecule with the two nitrogen atoms bonded to one central oxygen atom.

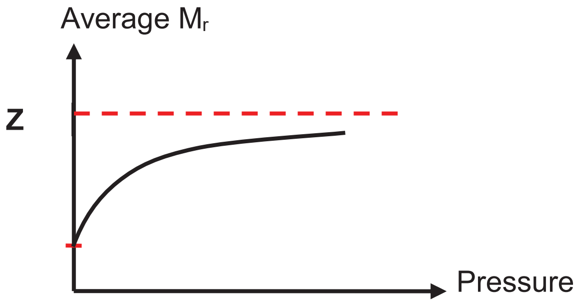
Draw a dot-and-cross diagram to show the bonding in N_2O_5 molecule. Use your diagram to:

- State the shape and the bond angle with respect to nitrogen
- Suggest with reasoning, the polarity of the molecule. [3]

(ii) A ratio of 4 to 1 mole of gaseous NO_2 and O_2 with a total initial pressure of 2.25 atm was placed in a 1000 cm^3 vessel. The total pressure at equilibrium was 1.5 atm. Calculate K_p for this equilibrium. [3]

(iii) Calculate the average M_r of the gases at equilibrium. [1]

(iv) The variation of M_r is as shown in the sketch.



Predict a value for **Z** and account for the shape of the graph. [2]

(d) Solid N_2O_5 dissolved in chloroform may be used to replace concentrated nitric acid and sulfuric acid in the nitration of benzene.

(i) Suggest why solid N_2O_5 can be used in for nitration of benzene. [1]

(ii) 0.60 mol of solid N_2O_5 was dissolved in chloroform. Some N_2O_5 decompose back into oxygen and nitrogen dioxide with a rate constant of $1.0 \times 10^{-5}\ s^{-1}$ at 45 °C.

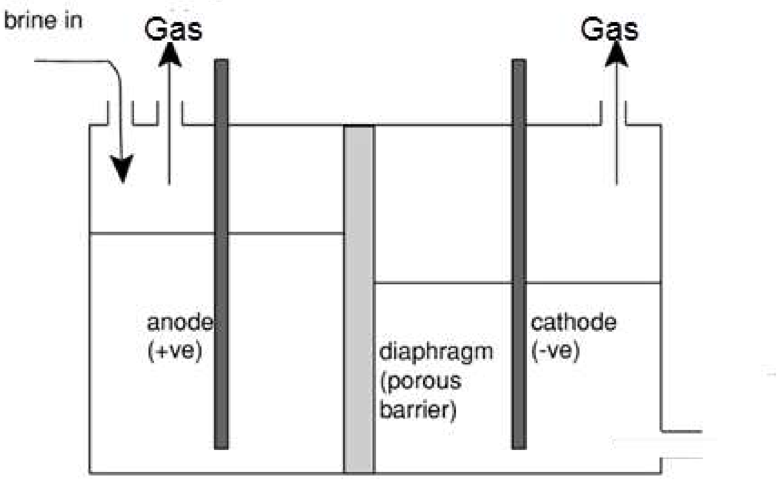
The gases produced are collected in a 10 dm^3 container over a period of 40 hours. Calculate the resultant pressure.
[Assume that the products do not dissolve in chloroform.] [3]

[Total : 23]

2 Chlorine is a yellow-green gas that was first synthesised around 1630. Chlorine forms a variety of oxides such as chlorate(VII), ClO_4^- and chlorate(V), ClO_3^-.

(a) Chlorine gas can be produced from the electrolysis of brine (concentrated sodium chloride solution) using a diaphragm cell with inert electrodes.

A diaphragm is used to keep the products of electrolysis from mixing and hence, prevent the formation of undesirable by-products.



(i) Write the ion-electron half-equations, with state symbols, for the reactions taking place at the electrodes. [2]

(ii) Calculate the mass of chlorine gas produced if a current of 5 A was passed for 7 hours through the electrolytic cell. [2]

(b) In some industrial electrolytic cells, the products of electrolysis of brine are allowed to react further when the diaphragm is removed. Two chlorine-containing products are formed, depending on the operating conditions used. At low temperatures, one of the products is a chloro-oxoanion with an oxidation state of +1.

(i) State the type of reaction taking place. [1]

(ii) Give an overall balanced equation for the reaction described above. [1]

(c) With reference from the Data Booklet, explain why dilute aqueous sodium chloride cannot be used as the electrolyte for the manufacture of chlorine in this electrolysis. [1]

(d) The standard electrode potentials, $E^\ominus$, and standard Gibbs free energy changes, $\Delta G^\ominus$, of different chlorine-containing species are tabulated below.

	Half-equation	**$E^\ominus$ / V**	**$\Delta G^\ominus$ / kJ mol^{-1}**
1	$ClO_4^- + 2H^+ + 2e^- \rightleftharpoons ClO_3^- + H_2O$	+1.19	–230
2	$2ClO_3^- + 12H^+ + 10e^- \rightleftharpoons Cl_2 + 6H_2O$	+1.47	**?**
3	$Cl_2 + 2e^- \rightleftharpoons 2Cl^-$	+1.36	–262

These electrode potentials can be summarised using the Latimer diagram shown below. In a Latimer diagram, the most highly oxidised form of the element is on the left, with successively lower oxidation states to the right. The electrode potentials are shown on the arrows.

$$\begin{tikzcd}
ClO_4^- \arrow[r, "+1.19\ \mathrm{V}"] & ClO_3^- \arrow[r, "+1.47\ \mathrm{V}"] \arrow[rr, bend right, "+1.45\ \mathrm{V}"'] & Cl_2 \arrow[r, "+1.36\ \mathrm{V}"] & Cl^-
\end{tikzcd}$$

(i) Calculate $\Delta G^\ominus$ for half-equation 2. [1]

(ii) The standard electrode potential of converting ClO_3^- to Cl^- is found to be +1.45 V, instead of +2.83 V. The number of electrons transferred in each step must be taken into account.

I: Write a half-equation for the conversion of ClO_3^- to Cl^-

II: Using your knowledge of Hess' Law for $\Delta G^\ominus$ and your answer to **(d)(i)**, show with the aid of an energy cycle that the $E^\ominus$ for the conversion of ClO_3^- to Cl^- is +1.45 V.

[4]

(iii) With the help of the Latimer diagram provided, calculate $E^\ominus_{cell}$ of the reaction below. Hence, determine its $\Delta G^\ominus_{cell}$.

$$4ClO_3^-(aq) \longrightarrow 3ClO_4^-(aq) + Cl^-(aq)$$

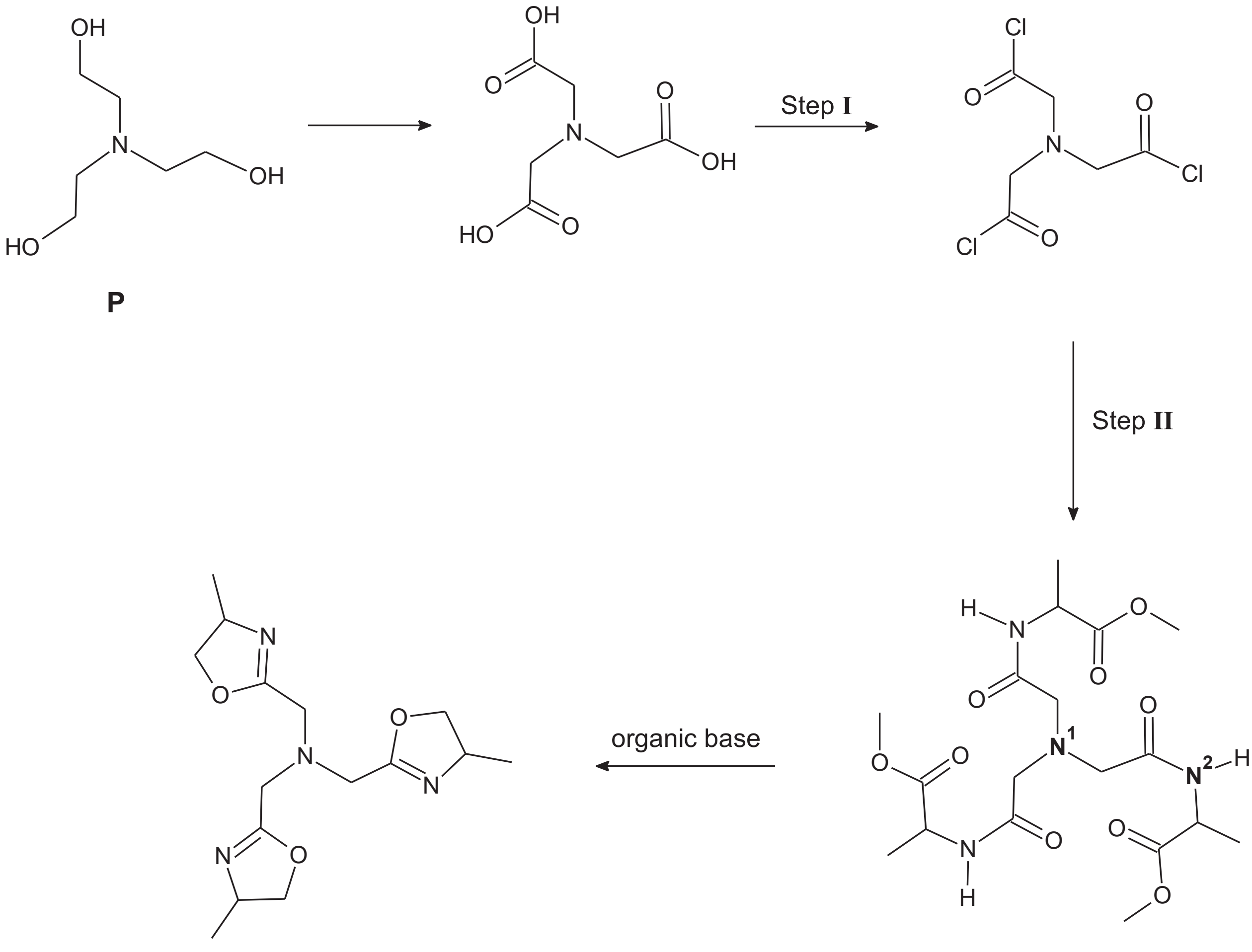
[2]

(iv) With reference to the *Data Booklet*, predict what will happen when an excess of acidified hydrogen peroxide solution is added to a solution of Cl^-(aq). [3]

[Total: 17]

3 Trisoxazoline are organic molecules that can function as ligands. Despite their huge molecular structure, they are able to form stable complexes with metals. Metal complexes with trisoxazoline are commonly used as catalyst in organic synthesis.

(a) The reaction scheme below illustrates the synthesis of trisoxazoline.



Trisoxazoline
($C_{15}H_{24}N_4O_3$)

(i) Suggest the reagents and conditions required for step **I** and step **II**. [2]

(ii) Explain the difference in basicity for N^1 and N^2 present in **R**. [2]

(iii) Propose a 2-step reaction scheme to synthesise compound **P** from ethene. [2]

Trisoxazolines are usually applied to transition metals, such as copper, to form complexes. These complexes are useful in advanced organic synthesis to make specific isomers.

Table 1 shows some properties of the copper complexes, where K_{stab} refers to the stability constant of the complex, e.g.

$$Cu^{2+} + L \rightleftharpoons [CuL]^{2+} \qquad K_{stab} = \frac{[CuL]^{2+}}{[Cu^{2+}][L]}$$

Table 1

Complex	log(K_{stab})	Colour	Shape of complex
copper(II)-trisoxazoline	12.9	green	distorted tetrahedral
copper(II)-EDTA	18.8	blue	octahedral
copper(II)-en	18.7	violet	octahedral

(b) Describe the feature of the trisoxazoline molecule that enable it to act as polydentate ligand. Hence, state the type of bond formed between the ligand and the central Cu(II) ion and give the coordination number of the complex. [2]

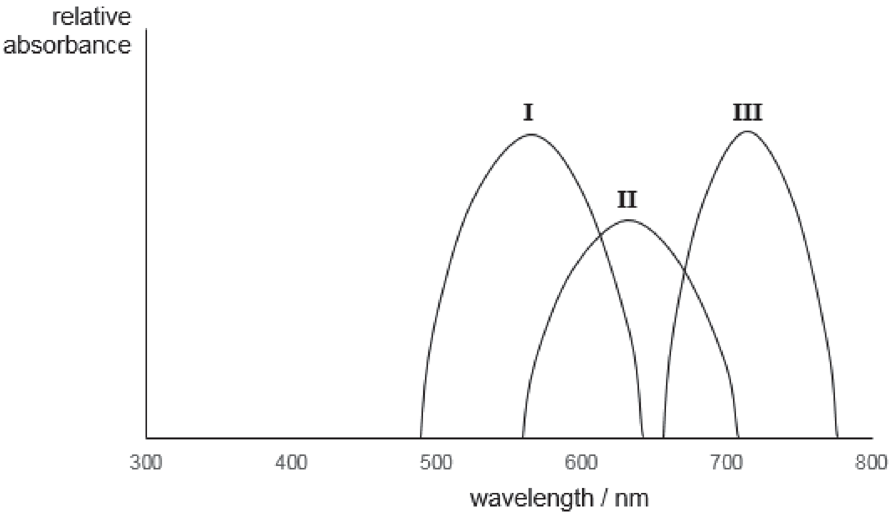
(c) **(i)** Using copper(II)-EDTA as an example, explain why the five d-orbitals are split into two different energy levels. [2]

(ii) Draw the shapes of the d-orbitals at the higher energy level. [1]

(iii) Explain why the copper(II) complexes are coloured. [3]

(iv) The visible absorption spectrum of the three complexes is shown below where each peak represents one complex.

[A visible absorption spectrum is a graph depicting the absorption of radiation by a material over a range of visible light wavelengths.]



Identify the copper(II) complex responsible for each absorption peak. Hence, arrange the three complexes in order of increasing magnitude of their energy gap.

[2]

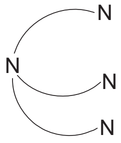
(d) Using Table 1, comment on the spontaneity of forming the respective copper(II) complexes. [2]

(e) Other than copper(II) ions, it was found that copper(I) ions are also able to form complexes with trisoxazoline.

(i) Predict and explain the colour of solid copper(I)-trisoxazoline complex. [1]

(ii) Analysis was done on copper(I)-trisoxazoline complex. The relative molecular mass of the complex was apparently 743.0. Further analysis showed that each copper(I) ion is bonded to three nitrogen atoms.

Propose the structure of copper(I)-trisoxazoline complex.

[You may use  to represent trisoxazoline.]

[1]

[Total: 20]

BLANK PAGE

Section B is on the next page

Section B

Answer **one** question in this section.

4 **(a)** At r.t.p, 1.2 dm^3 of chlorine gas is reacted with 6.7 g of compound **A**, $C_9H_{10}O$, to give compound **B**. On addition of PCl_5, **A** gives white fumes. Treatment of **A** with NaBr and concentrated H_2SO_4 under reflux gives a mixture of compounds **C** and **D**. **C** and **D** have the same molecular formula $C_9H_{10}Br_2$ and each contains only *one* chiral centre.

(i) When NaBr is mixed with concentrated H_2SO_4, the following observations are made.

- White fumes produced
- Reddish brown liquid formed
- Pungent gas decolourised purple $KMnO_4$

It is suggested that a displacement reaction occurred first, producing white fumes. Some of the white fumes further react with H_2SO_4 via a redox reaction. Using the above information, write the two corresponding chemical equations for this reaction. [2]

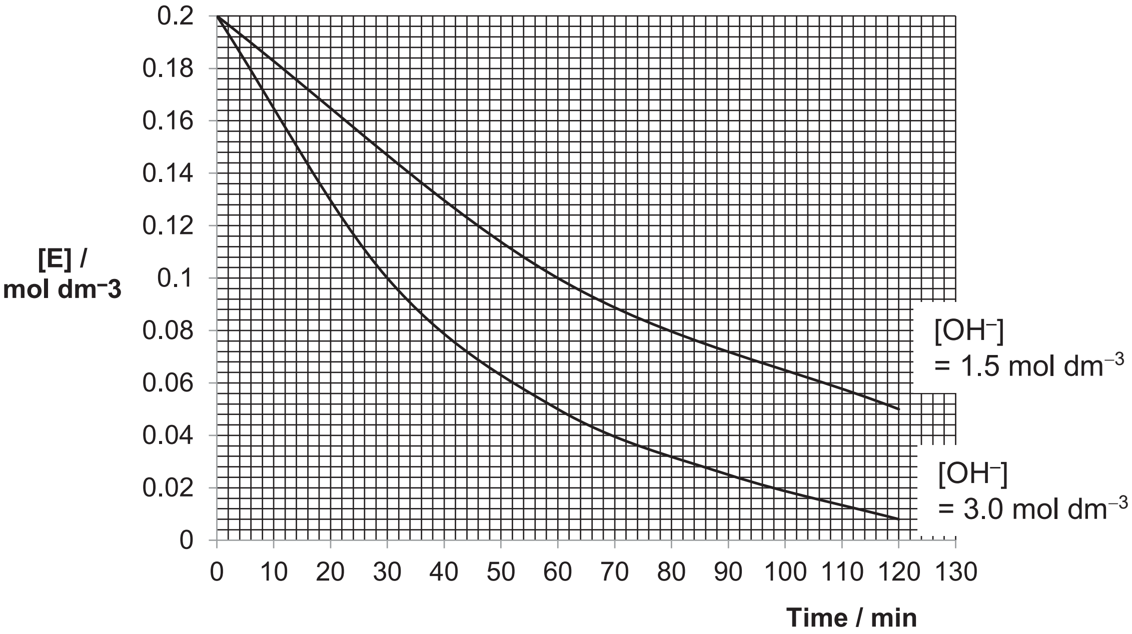
(ii) Using your answer in **(a)(i),** deduce the identities of **A** to **D**. [5]

(iii) Account for the relative quantity of compound **C** and **D** formed. [1]

(b) **E** is another constitutional isomer of **C** and **D**. A series of chemical experiments were conducted on **E**.

Experiment 1:

The reaction kinetics of **E** with aqueous sodium hydroxide was determined by monitoring the change in concentration of **E** with time.



Experiment 2:

0.2 mol of **D** and **E** were treated separately with boiling aqueous sodium hydroxide. The products from each compound were then acidified with nitric acid and then treated with silver nitrate solution.

The results obtained are shown below:

	Observation upon adding $AgNO_3$	**Mass of ppt / g**
D	formation of cream-coloured precipitate	75.12
E	formation of cream-coloured precipitate	37.56

(i) Using experiment 1, deduce the rate equation. [3]

(ii) Using Experiment 2 and **(b)(i)**, propose a possible structure of **E** and draw the mechanism for the reaction of **E** with NaOH(aq). [3]

(c) Depending on the mechanism, the solvent affects the stability of nucleophile and/or reaction intermediates in the nucleophilic substitution of halogenoalkanes. The table below shows the rate of reaction when different halogenoalkanes and solvents are used.

Solvent	**Type**	**Dielectric constant, ε**	**Relative rates for reaction with OH^-**	
			1° RX in S_N2	**3° RX in S_N1**
CH_3OH	Protic	33	1	4
H_2O	Protic	78	7	150 000
CH_3COOH	Protic	6	1	1
CH_3COCH_3	Aprotic	21	5000	-

Dielectric constant, ε, is a measure of the solvent polarity and ability to insulate charge.

(i) Suggest, using **only** structure and bonding, the difference between *protic* and *aprotic* solvents. [1]

(ii) Explain the effect of solvent on the relative rate of S_N2 reactions. [2]

(iii) Explain, with an aid of a diagram, how water increases the rate of S_N1 reaction. [2]

(iv) Name a solvent, other than those given in the table, that will result in a slower rate for S_N1 than ethanoic acid. [1]

[Total: 20]

5 **(a)** Using only the elements C, H and O, draw the structural formulae of **three** organic compounds, each containing a single carbon atom with an oxidation state of zero, +2 and +4 respectively. [3]

(b) Hot, concentrated potassium manganate (VII) oxidises several classes of organic compounds to ketones, carboxylic acids or carbon dioxide. By this means, the structures of compounds can be determined. Some compounds are easily oxidised, while others require longer heating.

The following describes some reactions of compounds **F** and **K**, and of their oxidation products.

F, $C_8H_{12}O$ reacts with excess potassium manganate (VII) to produce single organic products, **G,** $C_4H_6O_5$ while **K,** $C_{12}H_{12}$**,** reacts with the same reagent to produce **H,** $C_{10}H_{10}O_3$. Carbon dioxide is produced in both reactions in a mole ratio of 2 : 1 respectively. During oxidation of **F**, four moles of carbon dioxide were liberated.

Although **F** reacts with potassium manganate (VII), it gives no reaction with potassium dichromate (VI). When 0.10 mol of **F** is reacted with an excess of sodium metal, 1.2 dm^3 of hydrogen is formed, measured at room temperature and pressure.

G reacts with excess concentrated sulfuric acid to give **I**, $C_4H_4O_4$. Upon further oxidation, **I** is found to give **J,** $C_3H_2O_5$, and an inorganic by-product.

H gives a positive iodoform test and dissolves in aqueous sodium hydroxide. Upon further oxidation of **H**, **L,** $C_9H_6O_6$, and a similar inorganic by-product formed from **I** is also produced.

(i) Deduce the structure of compounds **F** to **L**, explaining the chemistry of the reactions described. [11]

(ii) State the type(s) of stereoisomerism shown by compound **F** and give one further piece of relevant information about it. [2]

(iii) Hence, predict the total number of isomers shown by **F**. [1]

(iv) When compound **K** undergoes prolonged heating with $KMnO_4$ to give **L**, **K** exhibits **two** types of constitutional isomerism.

Name the specific types of isomerism shown by compound **K** and hence, draw the **displayed formulae** of the isomers. [3]

[Total : 20]

SERANGOON JUNIOR COLLEGE
General Certificate of Education Advanced Level
Higher 2

CANDIDATE NAME	
CLASS	

CHEMISTRY 9729/04

JC2 Preliminary Examination **25 Aug 2017**
Paper 4 Practical **2 hr 30 min**

Candidates answer on the Question Paper

READ THESE INSTRUCTIONS FIRST

Write your name and class on all the work you hand in.
Give details of the practical shift and laboratory in the boxes provided.
Write in dark blue or black pen on both sides of the paper.
You may use a soft pencil for any diagrams, graphs or rough work.
Do not use staples, paper clips, highlighters, glue or correction fluid.

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

The use of an approved scientific calculator is expected, where appropriate.
You may lose marks if you do not show your working or if you do not use appropriate units.
Qualitative Analysis Notes are printed on pages 22 and 23.

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

Shift
Laboratory

For Examiner's Use	
1	/14
2	/19
3	/12
4	/10
TOTAL	**/ 55**

This document consists of 22 printed pages and 2 blank pages.

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

1 You are to determine the concentration of aqueous copper(II) sulfate by titration. The concentration of Cu^{2+} ions in a solution can be found by reaction with an excess of aqueous iodide ions to produce iodine. The amount of iodine formed can be found by titration with thiosulfate ions, $S_2O_3^{2-}$.

FB 1 is aqueous copper(II) sulfate, $CuSO_4$.
FB 2 is 0.100 mol dm^{-3} sodium thiosulfate, $Na_2S_2O_3$.
FB 3 is aqueous potassium iodide, KI.
starch indicator

(a) Method

(i)
1. Fill the burette with **FB 2**.
2. Using a pipette, transfer 25.0 cm^3 of **FB 1** into a conical flask.
3. Use an appropriate measuring cylinder, transfer 10 cm^3 of **FB 3** to the same conical flask.
4. Titrate this mixture with **FB 2** until the colour of the mixture changes from brown to yellow-brown. An off-white precipitate will also be present in the flask throughout the titration.
5. Add 5 drops of starch indicator.
6. Continue the titration until the blue-black colour of the starch-iodine complex just disappears leaving the off-white precipitate.
7. Record your titration results in the space provided below. Make certain that your recorded results show the precision of your working.
8. Repeat points **1** to **7** as necessary until consistent results are obtained.

Results

I	
II	
III	
IV	
V	

[5]

(ii) From your titrations, obtain a suitable volume of **FB 2** to be used in your calculations. Show clearly how you obtained this volume.

volume of **FB 2** = ……………………………………[1]

(b) **(i)** The equations for the formation of iodine and its reaction with thiosulfate ions are given below.

$$2Cu^{2+} + 4I^- \rightarrow 2CuI + I_2$$
$$I_2 + 2S_2O_3^{2-} \rightarrow S_4O_6^{2-} + 2I^-$$

Calculate the amount of thiosulfate ions, $S_2O_3^{2-}$, present in the volume of **FB 2** in **(a)(ii)**.

amount of $S_2O_3^{2-}$ = ……………………………………[1]

(ii) Using the equations above, calculate the amount of Cu^{2+} ions present in 25.0 cm^3 of **FB 1**.

amount of Cu^{2+} = ……………………………………[1]

(iii) Calculate the concentration, in mol dm^{-3}, of copper(II) sulfate in **FB 1**.

concentration of $CuSO_4$ = ……………………………………[1]

(c) Two students repeated the experiment but each obtained different values for the concentration of $CuSO_4$.

The students each suggested possible improvements.

Student 1 suggested that a larger volume of potassium iodide, **FB 3**, should be added.
Student 2 suggested that the contents of the conical flask should be filtered before titration.

Comment on the effectiveness of **each** of these possible improvements.
Explain your answers.

Student 1

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

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

Student 2

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

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

(d) The maximum error in each burette reading is ±0.05 cm^3.
The maximum error in each titration is therefore ±0.10 cm^3.
The 25.0 cm^3 pipette, used in this titration, is labelled with an error of ±0.06 cm^3.

Explain why the maximum error when 25.0 cm^3 of solution is run from a pipette is only ±0.06 cm^3 and not ±0.12 cm^3.

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

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

(e) Considering the maximum errors from the pipette and burette used, calculate the total percentage error in one titration.

[2]
[Total: 14]

BLANK PAGE

2 You are to determine the enthalpy change of reaction, ΔH, for the reaction shown below.

$$Cu(s) + H_2SO_4(aq) \rightarrow CuSO_4(aq) + H_2(g)$$

Since copper is an unreactive metal it does not react directly with dilute acids. You will therefore need to find the enthalpy change of reaction for two reactions that do occur. The equations for these two reactions are below.

$Mg(s) + H_2SO_4(aq) \rightarrow MgSO_4(aq) + H_2(g)$ **Reaction 1**

$Mg(s) + CuSO_4(aq) \rightarrow MgSO_4(aq) + Cu(s)$ **Reaction 2**

You will carry out experiments to find the enthalpy changes for each of **Reaction 1** and **Reaction 2** and use these values to calculate the enthalpy change for the reaction of copper with sulfuric acid.

TURN OVER FOR EXPERIMENTAL METHOD

Determining the enthalpy change for Reaction 1

For Examiner's use

$Mg(s) + H_2SO_4(aq) \rightarrow MgSO_4(aq) + H_2(g)$ **Reaction 1**

(a) Method

FB 4 is 1.00 mol dm^{-3} sulfuric acid, H_2SO_4.
FB 5 is magnesium powder, Mg.

Read through the method before you start any practical work and prepare suitable tables for your results.

1. Weigh the stoppered weighing bottle containing **FB 5**. Record the mass.
2. Support the styrofoam cup in the 250cm^3 beaker.
3. Use the measuring cylinder to transfer 25cm^3 of **FB 4** into the styrofoam cup.
4. Measure the temperature of **FB 4** in the styrofoam cup and start the stop watch. Record this temperature as being the temperature at time = 0.
5. Measure, and record, the temperature of this **FB 4** every half minute for 2 minutes.
6. At time = 2.5 minutes, add **FB 5** to the acid and stir carefully to reduce acid spray.
   ***Caution: Inhalation of the fumes may cause choking.**
7. Measure the temperature of the mixture in the cup at time = 3 minutes and then every half minute up to time = 7 minutes.
8. Continue stirring occasionally throughout this time.
9. Weigh the weighing bottle that had contained **FB 5**. Record the mass.
10. Calculate and record the mass of **FB 5** added to the sulfuric acid.
11. Discard the used styrofoam cup.

Results

I	
II	
III	
IV	
V	

[5]

(b) **(i)** On the grid below plot a graph of temperature (y-axis) against time (x-axis).

For Examiner's use

[2]

(ii) Complete the graph by inserting **two**, **straight** lines of best fit:

- one to show the temperature up to time = 2.5 minutes,
- one to show the temperature after time = 2.5 minutes.

[1]

(iii) From your graph, use the two straight lines of best fit to calculate the change in temperature at time = 2.5 minutes.

temperature change = ……………………………………[1]

(c) Calculations

(i) In the reaction in **(a)**, the sulfuric acid was in excess. Without carrying out any additional tests, what observation could you have made during your experiment to confirm this?

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

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

(ii) Calculate the energy change that occurred during the reaction in **(a)**.

[Assume that 4.2 J is needed to raise the temperature of 1.0 cm^3 of solution by 1.0°C.]

energy change = ……………………………………[1]

(iii) Use your answer to **(ii)** to calculate the enthalpy change, in kJ mol^{-1}, for the reaction between sulfuric acid and magnesium.

[A_r : Mg, 24.3]

$$Mg(s) + H_2SO_4(aq) \rightarrow MgSO_4(aq) + H_2(g) \qquad \textbf{Reaction 1}$$

enthalpy change for **Reaction 1** = ……………………………………[1]

Determining the enthalpy change for Reaction 2

For Examiner's use

$Mg(s) + CuSO_4(aq) \rightarrow MgSO_4(aq) + Cu(s)$ **Reaction 2**

(d) Method

FB 6 is 1.00 mol dm^{-3} copper(II) sulfate, $CuSO_4$.
FB 7 is magnesium powder, Mg.

Read through the method before you start any practical work and prepare suitable tables for your results.

1. Weigh the weighing bottle containing **FB 7**. Record the mass.
2. Support the styrofoam cup in the 250cm^3 beaker.
3. Use the measuring cylinder to transfer 25cm^3 of **FB 6** into the styrofoam cup.
4. Measure the temperature of **FB 6** in the styrofoam cup and record the temperature.
5. Add the **FB 7** to the **FB 6** in the cup and stir the mixture constantly.
6. Measure and record the maximum temperature reached during the reaction.
7. Calculate and record the maximum temperature change that occurred during the reaction.
8. Weigh the weighing bottle that had contained **FB 7**. Record the mass.
9. Calculate and record the mass of **FB 7** added to the copper(II) sulfate.
10. Empty the contents of the styrofoam cup into the bottle labelled **waste**.
11. Discard the used styrofoam cup.

Results

I	
II	

[2]

(e) **Calculations**

(i) Show, using suitable calculations, that the copper(II) sulfate was in excess in the reaction.
[*A*r : Mg, 24.3]

Formatted: Font: 11 pt, Complex Script Font: 11 pt

[1]

(ii) Hence, calculate the enthalpy change, in kJ mol^{-1}, for the reaction between magnesium and copper(II) sulfate.

[Assume that 4.2 J is needed to raise the temperature of 1.0cm^3 of solution by 1.0°C.]

$Mg(s) + CuSO_4(aq) \rightarrow MgSO_4(aq) + Cu(s)$ **Reaction 2**

enthalpy change for **Reaction 2** = ……………………………………[1]

Enthalpy change for Reaction 3

Reaction 3 is shown below.

$Cu(s) + H_2SO_4(aq) \rightarrow CuSO_4(aq) + H_2(g)$ **Reaction 3**

(f) Use your values for the enthalpy changes for **Reactions 1** and **2** to calculate the enthalpy change for **Reaction 3**.

$Mg(s) + H_2SO_4(aq) \rightarrow MgSO_4(aq) + H_2(g)$ **Reaction 1**

$Mg(s) + CuSO_4(aq) \rightarrow MgSO_4(aq) + Cu(s)$ **Reaction 2**

Show clearly how you obtained your answer.

(If you were unable to calculate the enthalpy changes for **Reactions 1** and **2**, you should assume that the value for **Reaction 1** is – 444 kJ mol^{-1} and that the value for **Reaction 2** is – 504 kJ mol^{-1}. Note: these are not the correct values.)

enthalpy change for **Reaction 3** = ……………………………………[1]

(g) **(i)** The method you used to determine the enthalpy change for **Reaction 1** was more accurate than the method you used to determine the enthalpy change for **Reaction 2**. Suggest why the method used for **Reaction 2** was less accurate. Explain your answer.

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

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

[1]

(ii) A student suggested that the accuracy of the method used for **Reaction 2** could be improved by using a larger volume of copper(II) sulfate. Is this a correct suggestion? Give a reason for your answer.

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

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

[1]

[Total : 19]

3 Qualitative Analysis

At each stage of any test, you are to record details of the following.

- Colour changes seen
- The formation of any precipitate
- The solubility of such precipitates in an excess of the reagent added

Where 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.

FB 8 is a solution containing 2 cations and 1 anion.

(a)

Test	Procedure	Observation
1	To 1 cm depth of **FB 8** in a test tube, add aqueous ammonia until it is in excess.	
2	To 1 cm depth of **FB 8** in a **boiling tube**, add aqueous sodium hydroxide until it is in excess. Then heat the boiling tube gently with care. Keep the mixture for **Test 3**.	
3	To the mixture from **Test 2**, add 1 cm depth of aqueous hydrogen peroxide. Shake the boiling tube gently.	
4	To 1 cm depth of **FB 8** in a test tube, add aqueous barium chloride, followed by dilute hydrochloric acid.	

[4]

(b) Using your observations above, identify the ions in **FB 8**. Give evidence to support your conclusion.

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

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

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

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

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

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

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

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

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

[3]

(c) What type of reaction has taken place in **Test 3**? Explain your answer.

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

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

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

[1]

(d) **FB 9** is an aqueous solution, containing one cation and one anion.
Carry out the following tests in test-tubes.
Complete the table by recording your observations.

Test	**Procedure**	**Observations**
5	To 1 cm depth of **FB 9**, add aqueous sodium hydroxide until it is in excess.	
6	To 1 cm depth of **FB 9**, add a piece of magnesium ribbon.	
7	To 1 cm depth of **FB 9**, add 2 drops of aqueous silver nitrate, followed by aqueous ammonia until in excess.	

[2]

(e) Using your observations above, identify the ions in **FB 9**. Give evidence to support your conclusion.

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

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

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

[2]

[Total: 12]

4 Many transition metal complex ions are coloured. It is possible to use this property to determine the concentration of a solution of a coloured ion. A few cm^3 of the solution is placed inside a *spectrometer*.

A *spectrometer* measures the amount of light that is absorbed when a specific wavelength of visible light is shone through a coloured solution. It does this by comparing the amount of light passing through the sample with the amount of light passing through the pure solvent. The amount of light absorbed is expressed as an absorbance value. The more concentrated the solution, the higher the absorbance value.

Beer-Lambert's Law states that the absorbance values, A, is directly proportional to the concentration of absorbing species, c, as shown below. The general Beer-Lambert's Law is usually written as,

$$A = \varepsilon c l$$

Where ε is the molar extinction coefficient and l is the path length, which is usually 1.0cm.

This equation can be used to calculate the absorbance value when the concentration of copper(II) ions is known.

You may assume that you are provided with the following in the subsequent parts of the question.

- **FB 1** from Question 1
- solid hydrated copper(II) sulfate, $CuSO_4.5H_2O$ (M_r = 249.6);
- access to a spectrometer and instructions for its use;
- graph paper;
- the apparatus and chemicals normally found in a school or college laboratory.

(a) The spectrometer is set to use the wavelength of light that is absorbed most strongly by the copper(II) ions.

Suggest a colour in the visible spectrum from which a suitable wavelength of light might be chosen. Explain your answer.

……

……

[1]

(b) Spectrometry can be used to determine the concentration of a solution of aqueous copper(II) sulfate, **FB 1**. A series of known, but different, concentrations of copper(II) sulfate is prepared. A spectrometer is used to measure the absorbance of each solution.

According to Beer-Lambert's Law, a graph of absorbance against concentration is then plotted. This graph is known as *calibration* line.

The experiment is then repeated using a solution of unknown concentration. By comparing the absorbance of this solution with the calibration line, the concentration of copper(II) ions in the unknown solution can be determined.

Propose a simple plan on how you would prepare

- a 100.0 cm^3 of 1.00 mol dm^{-3} standard aqueous copper(II) sulfate;
- a suitable range of diluted solutions of accurate concentrations

You are to show detailed calculations and suitable tables (where appropriate) in your answer.

(i) a 100.0 cm^3 of 1.00 mol dm^{-3} standard aqueous copper(II) sulfate;

…………………………………………………………………………………………………

…………………………………………………………………………………………………

…………………………………………………………………………………………………

…………………………………………………………………………………………………

…………………………………………………………………………………………………

…………………………………………………………………………………………………

…………………………………………………………………………………………………

…………………………………………………………………………………………………

…………………………………………………………………………………………………

…………………………………………………………………………………………………

…………………………………………………………………………………………………

…………………………………………………………………………………………………

…………………………………………………………………………………………………

…………………………………………………………………………………………………

…………………………………………………………………………………………………

…………………………………………………………………………………………………

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

(ii) a suitable range of diluted solutions of accurate concentrations, keeping the total volume of each solution constant at 20.00 cm^3.

…………………………………………………………………………………………………

…………………………………………………………………………………………………

…………………………………………………………………………………………………

…………………………………………………………………………………………………

…………………………………………………………………………………………………

…………………………………………………………………………………………………

…………………………………………………………………………………………………

…………………………………………………………………………………………………

…………………………………………………………………………………………………

…………………………………………………………………………………………………

…………………………………………………………………………………………………

…………………………………………………………………………………………………

…………………………………………………………………………………………………

…………………………………………………………………………………………………

…………………………………………………………………………………………………

…………………………………………………………………………………………………

…………………………………………………………………………………………………

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

(c) Using the solutions prepared in **(b)**, the absorbance value of each copper(II) sulfate solution can be determined and hence a calibration line can be obtained via the spectrometer.

Describe a plan to determine the concentration of **FB 1**.

Your plan should include details of:

- calculation of the absorbance value for each copper(II) sulfate solution prepared in **(b)**, given ε of $CuSO_4$ is **2.81** $mol^{-1} dm^{3} cm^{-1}$.
- a sketch of the calibration line you would expect to obtain;
- a brief outline of how the results would be obtained.
- how the calibration line would be used to determine the concentration of copper(II) ions in **FB 1**.

…………………………………………………………………………………………………

…………………………………………………………………………………………………

…………………………………………………………………………………………………

…………………………………………………………………………………………………

…………………………………………………………………………………………………

…………………………………………………………………………………………………

…………………………………………………………………………………………………

…………………………………………………………………………………………………

…………………………………………………………………………………………………

…………………………………………………………………………………………………

…………………………………………………………………………………………………

…………………………………………………………………………………………………

…………………………………………………………………………………………………

…………………………………………………………………………………………………

…………………………………………………………………………………………………

…………………………………………………………………………………………………

…………………………………………………………………………………………………

…………………………………………………………………………………………………

…………………………………………………………………………………………………

…………………………………………………………………………………………………

[3]

(d) Given that the absorbance for **FB 1** is 0.286, calculate the concentration of **FB 1**.

For Examiner's use

concentration of **FB 1** = ……………………………………[1]

[Total : 10]

Qualitative Analysis Notes
[ppt. = precipitate]
(a) Reactions of aqueous cations

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

(b) Reactions of anions

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)	SO2 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

BLANK PAGE

2017 SRJC H2 Chemistry 9729

Preliminary Examination Paper 1 Solution

1 An acidified solution of the salt $KClO_x$ will oxidise $Fe^{2+}(aq)$ to $Fe^{3+}(aq)$ quantitatively, the chlorine being reduced to $Cl^-(aq)$.

When 0.302 g of the salt $KClO_x$ was reacted with 0.540 mol dm^{-3} $Fe^{2+}(aq)$ in the presence of $H^+(aq)$, 21.0 cm^3 of $Fe^{2+}(aq)$ was needed for complete reaction.

Which of the following is the value of x?

A 1
B 2
C 3
D 4

Answer: **B**

$ClO_x^- + 2xe^- \rightarrow Cl^-$
$Fe^{2+} \rightarrow Fe^{3+} + e^-$
$\therefore\ 2xFe^{2+} \equiv ClO_x^-$
OR mole ratio of ClO_x^- : Fe^{2+} is
1 : $2x$

Amount of Fe^{2+} used = $\frac{21.0}{1000} \times 0.540$ = 0.01134 mol

Amount of ClO_x^- = $\frac{0.01134}{2\boldsymbol{x}}$ mol

Amount of $KClO_x$ = $\frac{0.302}{39.1+35.5+\boldsymbol{x}(16)}$

Amount of ClO_x^- = $\frac{0.302}{39.1+35.5+\boldsymbol{x}(16)} = \frac{0.01134}{2\boldsymbol{x}}$

$$\frac{2(0.302)\boldsymbol{x}}{0.01134} = 74.6 + \boldsymbol{x}(16)$$

$$53.263\boldsymbol{x} - 16\boldsymbol{x} = 74.6$$

$$\boldsymbol{x} = 1.99 \approx \mathbf{2}$$

2 A student made up a 0.10 mol dm^{-3} solution of $Ba(OH)_2.8H_2O$ which she found in the laboratory cupboard and left the solution in an open beaker. A week later, she returned to the laboratory, used the solution for titration with 0.10 mol dm^{-3} HCl and was surprised to discover her titres were lower than expected.

Which of the following explains why the values were so low?

A Some of the barium hydroxide has reacted with carbon dioxide in the air to form solid barium carbonate.
B Some water had evaporated from the barium hydroxide solution.
C The concentration of HCl was less than the stated 0.10 mol dm^{-3}.
D The crystals had less water of crystallisation than stated.
Answer : A

A: will lower the concentration of $Ba(OH)_2$ and thus a lower than expected titre value.

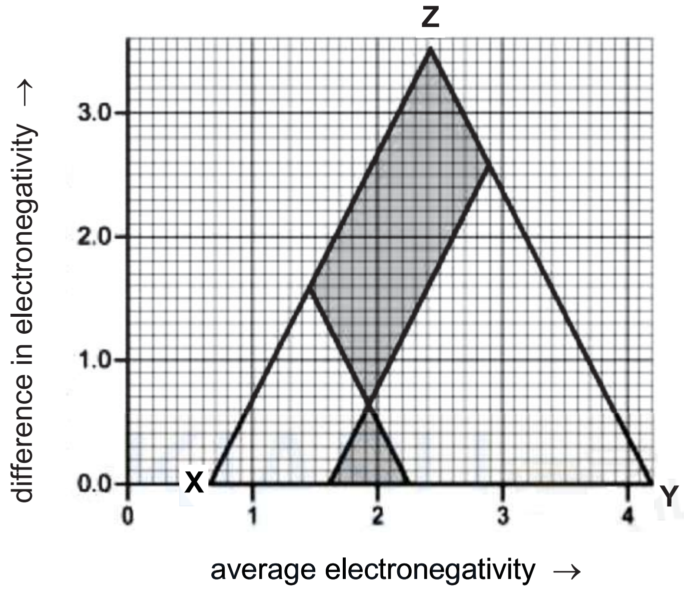
B: will increase the concentration of $Ba(OH)_2$ and cause the titre value to be higher than expected.

C: will cause the titre value to be higher than expected.

D: will increase the concentration of $Ba(OH)_2$ and thus a higher than expected titre value.

3 The type of bonding between two elements can be rationalised and even predicted using a van Arkel triangle. The triangle is based on electronegativity values. Difference in electronegativity is plotted along the y–axis and average electronegativity is plotted along the x–axis.

What is the type of bonding present at each of these bonding extremes, labelled **X**, **Y** and **Z** on the triangle?



	X	Y	Z
A	metallic	covalent	ionic
B	covalent	metallic	ionic
C	covalent	ionic	metallic
D	ionic	covalent	metallic

Answer: **A**

Difference in electronegativity is zero for **X** & **Y**
⇒ metallic bonding or covalent bonding.
Since metals have low electronegativity
⇒ **X** is metallic bonding.

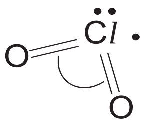
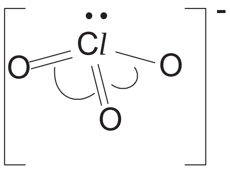
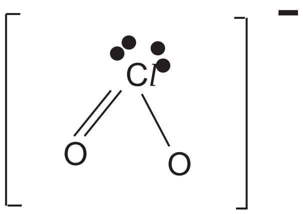
4 Equimolar amou ct according to the equation below.

$$2ClO_2\,(aq) + 2OH^-\,(aq) \rightarrow ClO_3^-\,(aq) + ClO_2^-\,(aq) + H_2O\,(l)$$

Which statement is correct?

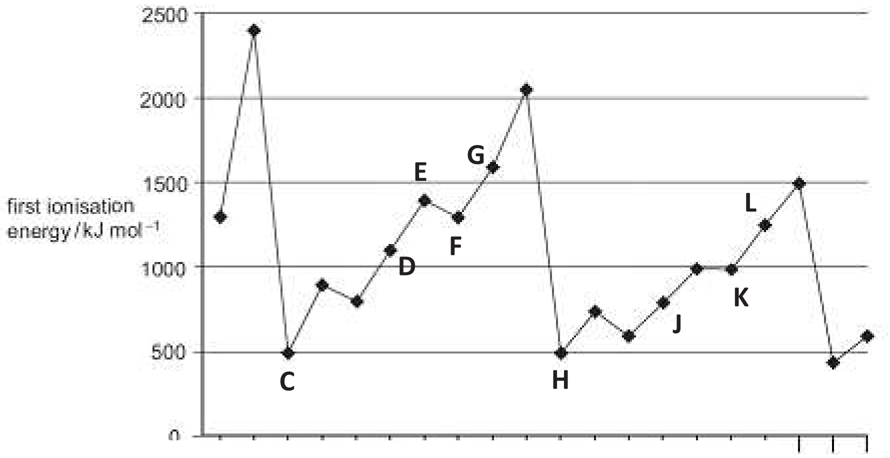
A The shape changes from linear in ClO_2 to bent in ClO_2^-.
B The shape changes from bent in ClO_2 to trigonal planar in ClO_3^-.
C The bond angle changes from about 120° in ClO_2 to 107° in ClO_3^-.
D The bond angle changes from about 105° in ClO_2 to 107° in ClO_3^-.

Answer: D

ClO_2	ClO_3^-	ClO_2^-
 Bond angle ≈ 105° Shape: bent	 Bond angle ≈107° Shape: trigonal pyramidal	 Bond angle ≈105° Shape: bent

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

The first ionisation energies of successive elements in the Periodic Table are represented in the graph.



Which of the following statements about elements **C** to **L** are correct?

1 **E** and **J**⁻ have half–filled p–orbitals.
2 Chlorides of **D** and **J** undergo hydrolysis.
3 **F** and **K** reacts to form acidic compounds.
4 **D** and **F** forms compounds with formula **DF** and **DF**$_2$.
5 **G** and **L** forms compounds with variable oxidation states from –1 to +7.

A 1 and 4 only
B 2 and 5 only
C 1, 3 and 4 only
D 2, 3 and 5 only

Answer : C (Statements 1, 3, 4 only)

Elements **C** and **H** are from group 1 as they have the lowest first I.E.
They are lithium and sodium respectively.

1 is correct.
E is from Group 15 and J is from Group 14.
Element **E** is nitrogen and has half-filled 2p orbitals.
Element **J** is silicon, and Si^- has half-filled 3p orbitals.

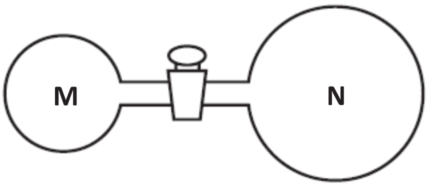
2 is wrong.
D and J are from Group 14.
D is a Period 2 element and is carbon. It cannot undergo hydrolysis as they do not have low lying d-orbitals to accommodate the lone pair of electrons from water, hence no hydrolysis can occur.

3 is correct.
Element **F** is oxygen and element **K** is sulfur. SO_2 and SO_3 are acidic in nature.

4 is correct.
Element **D** is carbon and **F** is oxygen. Hence **DF** and **DF**$_2$ is possible (ie, CO and CO_2).

5 is wrong.
Elements **G** is fluorine and **L** is chlorine. Chlorine can have variable oxidation states from –1 to +7, but fluorine only exists in states of –1 and 0.

6 Two glass vessels **M** and **N** are connected by a closed valve.



M contains helium at 25 °C at a pressure of 1 x 10^5 Pa. **N** has been evacuated, and has three times the volume of **M**. In an experiment, the valve is opened and the whole set-up placed in boiling water.

What is the final pressure in the system?

A 3.13×10^4 Pa
B 3.76×10^4 Pa
C 1.00×10^5 Pa
D 1.33×10^5 Pa
Answer: A

Let the volume of M be v, hence volume of N is 3v. Total volume = 4v

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

$$\frac{10^5 \times v}{298} = \frac{P_2 \times 4v}{373}$$

$P_2 = 3.13 \times 10^4$ Pa

7 Consider the following equilibrium system:

$$Fe_3O_4(s) + CO(g) \rightleftharpoons CO_2(g) + 3FeO(s) \qquad \Delta H = +ve$$

Given that $K_p = K_c\,(RT)^{\Delta n}$, where Δn is the sum of gaseous products – sum of gaseous reactants.

Which of the following statements are correct?

1 $K_c = K_p$ for this system.
2 The equilibrium constant, K_c, for this reaction has no units.
3 Adding FeO causes the position of equilibrium to shift to the left.
4 Increasing the temperature causes the position of equilibrium to shift to the right.

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

Answer : **D**

1 is correct: $\Delta n = 0$, $K_c = K_p$ for this system
2 is correct: $K_c = \frac{[CO_2]}{[CO]}$ no units
3 is incorrect: FeO is a solid. Position of equilibrium is not affected by it.
4 is correct: Increasing temperature would favour the forward endothermic reaction. Position of equilibrium would shift to the right.

8 In an experiment to measure the enthalpy change of neutralisation, 20 cm^3 of aqueous sulfuric acid containing 0.02 mol of H_2SO_4 is placed in a plastic cup of negligible heat capacity.

A 20 cm^3 sample of aqueous sodium hydroxide containing 0.04 mol of NaOH, at the same initial temperature, is added and the temperature rises by 15 K.

If the heat capacity per unit volume of the final solution is 4.2 J K^{-1} cm^{-3}, what is the enthalpy change of neutralisation?

A $-\left(\frac{20 \times 4.2 \times 15}{0.04 \times 1000}\right)$ kJ mol^{-1}

B $-\left(\frac{40 \times 4.2 \times 15}{0.04 \times 1000}\right)$ kJ mol^{-1}

C $-\left(\frac{20 \times 4.2 \times 15}{0.02 \times 1000}\right)$ kJ mol^{-1}

D $-\left(\frac{40 \times 4.2 \times 15}{0.02 \times 1000}\right)$ kJ mol^{-1}

Answer : **B**

$$\underset{0.02}{H_2SO_4} + \underset{0.04}{2\,NaOH} \rightarrow Na_2SO_4 + 2H_2O$$

$$Q = -\frac{mc\Delta T}{nH_2O\text{x}1000} = -\frac{40\times4.2\times15}{0.04\times1000} = -63\text{kJmol}^{-1}$$

9 The conversion of graphite into diamond is a non–spontaneous reaction at 298 K. The entropy change of this reaction is negative at 298 K.

C(graphite) → C(diamond) $\Delta G = +3.08 \text{ kJ mol}^{-1}$, $\Delta S = -3.3 \text{ J mol}^{-1} \text{ K}^{-1}$

With reference to the enthalpy change, ΔH, of the reaction above, which statements are correct?

1 Enthalpy change of atomisation of diamond is more endothermic than that of graphite.

2 Enthalpy change of combustion of diamond is more exothermic than that of graphite.

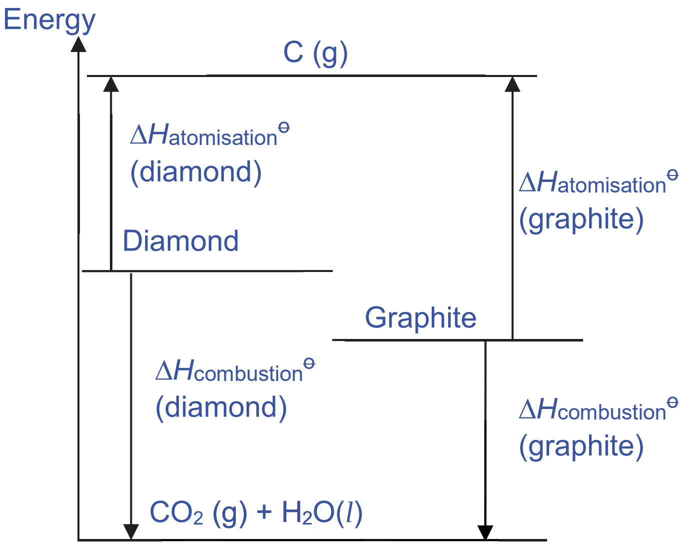
3 Bond energy of carbon–carbon bonds in graphite is greater than that in diamond.

4 The activation energy to convert graphite to diamond is lower than the activation energy for the reverse reaction.

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

Answer : **B (2 & 3 are correct)**

$$\Delta G = \Delta H - T\Delta S$$
$$3.08 = \Delta H - (298)(-3.3/1000)$$
$$\Delta H = +2.10 \text{ kJ mol}^{-1}$$



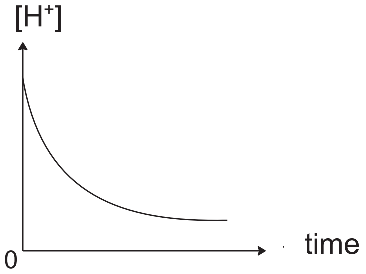
The carbon in graphite is sp^2 hybridised and carbon in diamond is sp^3 hybridised. Since the s character is higher in C-C bond in graphite, it will be a stronger bond than C-C bond in diamond.

10 The reaction between acidified KI and aqueous H_2O_2 involves the following steps:

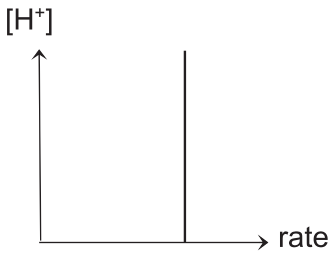
$H_2O_2 + I^-$	→	$H_2O + OI^-$	slow
$OI^- + H^+$	→	HOI	fast
$HOI + H^+ + I^-$	→	$I_2 + H_2O$	fast

Which graph would be obtained?

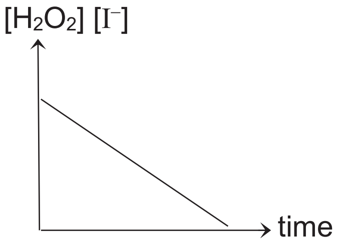
A



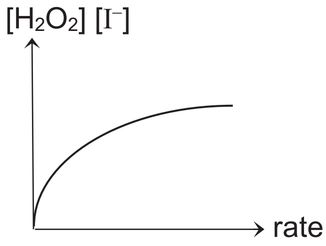
B



C

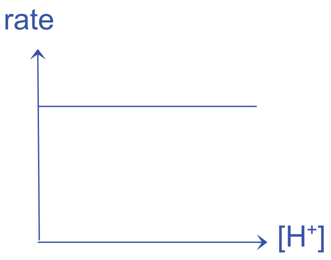


D



Answer: **B**

Base on the slow step, rate = k $[H_2O_2]$ $[I^-]$
The rate is independent of $[H^+]$.



11 Compounds of beryllium are amphoteric, like compounds of aluminium.

In which equations is the beryllium-containing reactant acting as a Brønsted-Lowry acid?

A $BeO(s) + 2OH^-(aq) + H_2O(l) \rightarrow [Be(OH)_4]^{2-}(aq)$
B $BeCl_2 + 4H_2O \rightarrow Be(H_2O)_4^{2+} + 2Cl^-$
C $2Be + O_2 \rightarrow 2BeO$
D $Be(H_2O)_2(OH)_2 + 2OH^- \rightarrow Be(OH)_4^{2-} + 2H_2O$

Answer: **D**

A Brønsted-Lowry acid is a proton donor.

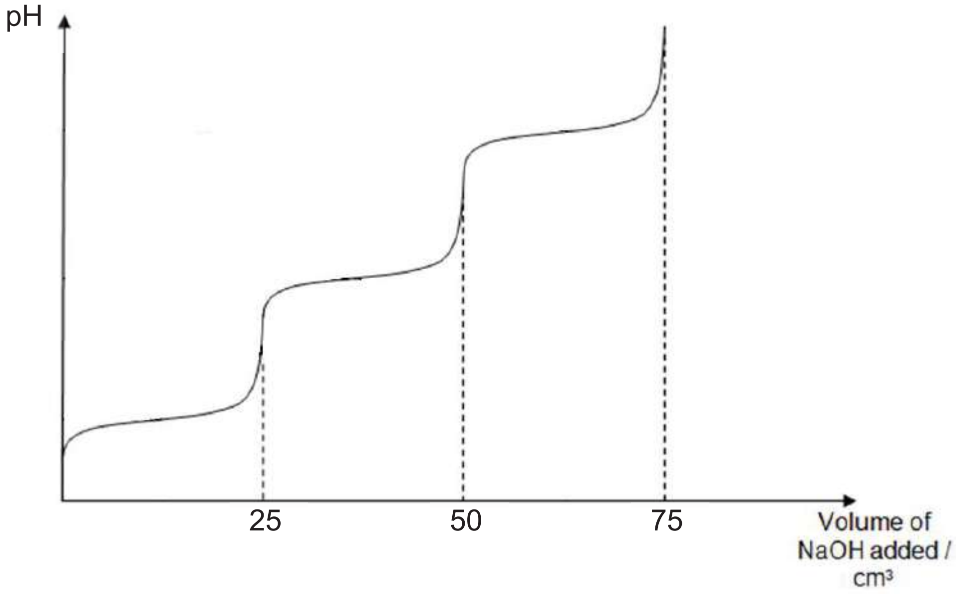
A: This is neutralisation reaction but BeO is not a Brønsted-Lowry acid as it does not donate a H^+ ion.

B: This is simply a dissociation reaction and $BeCl_2$ is not a Brønsted-Lowry acid as it does not donate a H^+ ion.

C: This is a combustion reaction.

D: $Be(H_2O)_2(OH)_2$ is acting as a Brønsted-Lowry acid as 2 H_2O molecules are deprotonated to form 2 additional OH^- ions and result in a negatively charged $Be(OH)_4^{2-}$ ion.

12 25 cm^3 of 1 mol dm^{-3} of the fully protonated form of compound **O** was titrated against a standard sodium hydroxide solution of a similar concentration and the following titration curve was obtained.



Which of the following compounds is a possible identity of compound **O**?

A $NH_2CH(CH_2CH_2CONH_2)COOH$
B $NH_2CH(CH_2CH_2CH_2OH)COOH$
C $NH_2CH(CH_2CH_2CH_2NH_2)COOH$
D $NH_2CH(CH_2CH_2CHO)COOH$

Answer: C
All amine groups are protonated and can act as a bronsted-lowry acid.

A : only two acidic groups as the amide on the R group is neutral

B : only two acidic groups as the OH on the R group is not able to be neutralised by NaOH

C : three acidic groups

D : only two acidic groups as the aldehyde on the R group is also neutral

13 A sparingly soluble calcium salt dissociates in solution according to the equation:

$$Ca_3\mathbf{Q}_2\,(s) \rightleftharpoons 3Ca^{2+}\,(aq) + 2\mathbf{Q}^{3-}\,(aq)$$

If the solubility product of $Ca_3\mathbf{Q}_2$ is p, what is the concentration of $\mathbf{Q}^{3-}$ at equilibrium in a saturated solution of $Ca_3\mathbf{Q}_2$ (aq)?

A $2p^{\frac{1}{5}}$

B $2(\frac{p}{36})^{\frac{1}{5}}$

C $2(\frac{p}{72})^{\frac{1}{5}}$

D $2(\frac{p}{108})^{\frac{1}{5}}$

Answer: D

$Ca_3\mathbf{Q}_2\,(s) \rightleftharpoons 3Ca^{2+}\,(aq) + 2\mathbf{Q}^{3-}\,(aq)$

Let solubility be x mol dm^{-3}

$K_{sp} = [Ca^{2+}]^3\,[Q^{3-}]^2$

$p = (3x)^3(2x)^2$

$p = (27x^3)(4x^2)$

$p = 108x^5$

$x = (\frac{p}{108})^{\frac{1}{5}}$

$2x = 2(\frac{p}{108})^{\frac{1}{5}}$

14 A transition metal cation can exist in a 'high spin' or 'low spin' state while exposed to different ligands in an octahedral complex.

A 'high-spin' state has the electrons occupying all the d-orbitals singly first, before pairing in the lower energy d-orbitals.

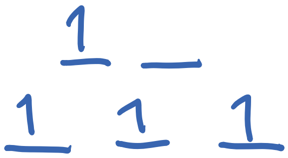
A 'low-spin' state has the lower energy d-orbitals filled first, pairing up if necessary, before the higher energy d-orbitals are filled.

Which cation would have the largest number of unpaired electrons?

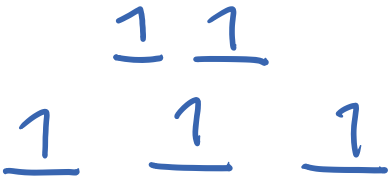
A 'High-spin' Mn^{3+}
B 'High-spin' Fe^{3+}
C 'Low-spin' Co^{2+}
D 'Low-spin' Ni^{4+}

Answer: B

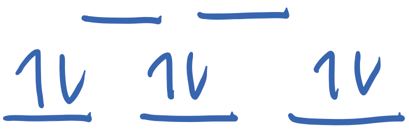
A: ‘High-spin’ Mn^{3+} → 4 unpaired electrons



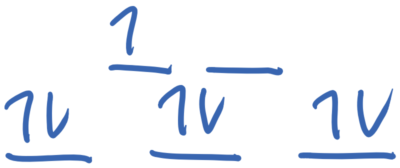
B: ‘High-spin’ Fe^{3+} → 5 unpaired electrons



D: ‘Low-spin’ Ni^{4+} → no unpaired electrons



C: ‘Low-spin’ Co^{2+} → 1 unpaired electron



15 Which of the following is **not** a result of the small energy gap between 3d and 4s orbitals?

A Transition metals have higher electrical conductivity than aluminium.
B Transition metals can exhibit variable oxidation states.
C Transition metals have higher melting point than calcium.
D Transition metals ions are usually coloured.
Answer : **D**

The smaller energy gap allow for valence electrons to be removed from both 3d and 4s orbitals. This leads to transition metals having higher conductivity, having variable oxidations states and higher melting point.

The energy gap is due to absorption in the visible light region due to d-d orbital splitting and transition.

16 Use of the Data Booklet is relevant to this question.

Two catalysed reactions and their respective catalysts are shown below.

Reaction	**Equation**	**Catalyst**
I	$S_2O_8^{2-} + 2I^- \rightarrow 2SO_4^{2-} + I_2$	Fe^{3+}
II	$2MnO_4^- + 5C_2O_4^{2-} + 16H^+ \rightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$	Mn^{2+}

Which statements about the reactions and the catalysts are correct?

1 Mn^{2+} is an auto-catalyst in reaction **II**.
2 Fe^{2+} could replace Fe^{3+} as a heterogeneous catalyst in reaction **I**.
3 Mn^{2+} could replace Fe^{3+} as a homogeneous catalyst in reaction **I**.
4 Both catalysts increase the energetic feasibility of their respective reactions.

A 1 and 3
B 2 and 3
C 1, 2 and 4 only
D 2, 3 and 4 only
Answer: A (1 and 3 only)

1 is correct: Mn^{2+} is a catalyst as well as a product of reaction **II**. Thus, Mn^{2+} is an auto-catalyst.

2 is incorrect: Fe^{2+} can replace Fe^{3+} as homogeneous catalyst, not heterogeneous catalyst.

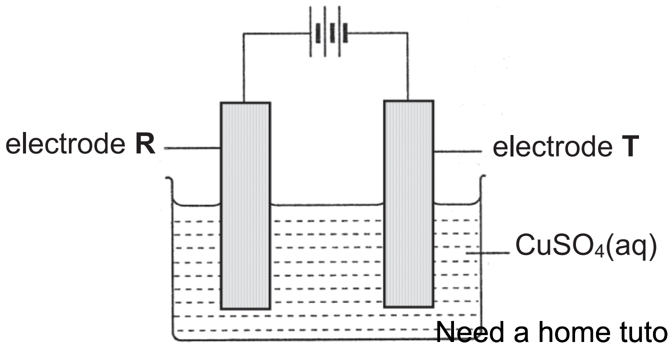
3 is correct:
From Data Booklet: $E^\ominus(S_2O_8^{2-}/SO_4^{2-}) = +2.01$ V
$E^\ominus(I_2/I^-) = +0.54$ V
$E^\ominus(Mn^{3+}/Mn^{2+}) = +1.54$ V

$2Mn^{2+} + S_2O_8^{2-} \rightarrow 2Mn^{3+} + 2SO_4^{2-}$
$E^\ominus_{cell} = 2.01 - 1.54 = +0.47 \text{ V} > 0$
$2Mn^{3+} + 2I^- \rightarrow 2Mn^{2+} + I_2$
$E^\ominus_{cell} = 1.54 - 0.54 = +1.00 \text{ V} > 0$
Thus, Mn^{2+} could replace Fe^{3+} as a homogeneous catalyst in reaction I.

4 is incorrect: ΔH remains the same for a catalysed or uncatalysed reaction. Reaction will remain just as energetically feasible.

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

Impure copper obtained from copper ores can be purified by electrolysis as shown below. The cell potential is adjusted such that copper of the impure copper electrode dissolves and impurities such as silver, iron and zinc can be removed through this process.



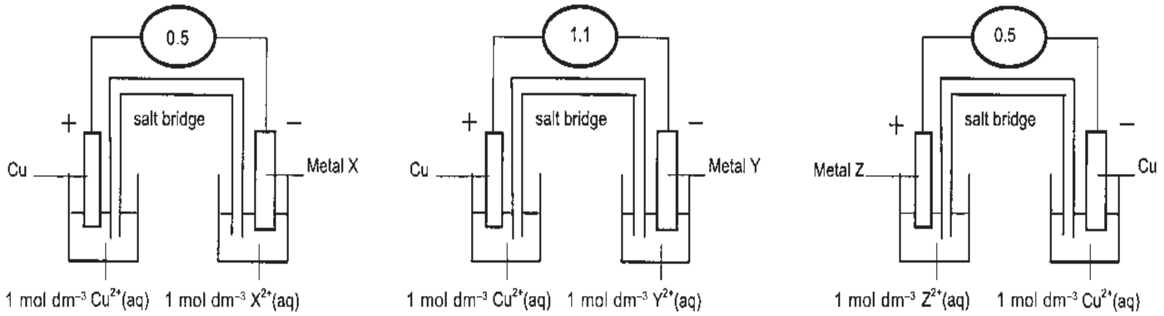
Which statement is **not** correct regarding the above electrolytic process?

A Reduction occurs at electrode **T**.
B Electrode **R** contains impure copper.
C Zinc impurity goes into the solution as Zn^{2+} ions.
D Iron and silver impurities fall to the bottom as sludge.
Answer: D

Option A is correct: Electrode T is the cathode where reduction occurs.
Option B is correct. Electrode R is the anode which contains impure copper.
Option C is correct. $E^{\ominus}(Zn^{2+}/Zn)$ is more negative than $E^{\ominus}(Cu^{2+}/Cu)$, hence Zn will be oxidised to form Zn^{2+} ions.
Option D is incorrect. $E^{\ominus}(Fe^{2+}/Fe)$ is more negative than $E^{\ominus}(Cu^{2+}/Cu)$, hence Fe will be oxidised to form Fe^{2+} ions, instead of falling to the bottom as sludge.

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

Three electrochemical cells are set up as shown below. The *e.m.f* in volts is shown on each voltmeter.



These *e.m.f* indicate the order of reactivity of the metals. The order of the weakest to the strongest reducing agent is

A **X**, **Y**, Cu, **Z**
B Cu, **Z**, **X**, **Y**
C **Z**, Cu, **X**, **Y**
D **Y**, **X**, **Z**, Cu
Answer: C

$E^{\ominus}(Cu^{2+}/Cu) = +0.34$ V

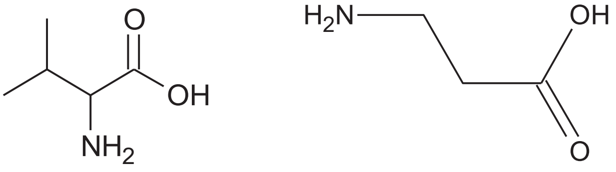
For electrochemical cell on the left, Cu^{2+}/Cu half-cell is the cathode. Hence, $E^{\ominus}(X^{2+}/X) = 0.34 - 0.5 = -0.16$ V

For electrochemical cell in the centre, Cu^{2+}/Cu half-cell is the cathode. Hence, $E^{\ominus}(Y^{2+}/Y) = 0.34 - 1.1 = -0.76$ V

For electrochemical cell on the right, Cu^{2+}/Cu half-cell is the anode. Hence, $E^{\circ}(Z^{2+}/Z) = 0.5 + 0.34 = +0.84$ V

Order of weakest reducing regent (least easily oxidised, least negative $E^{\ominus}$ value) to strongest reducing agent (most easily oxidised, most negative $E^{\ominus}$ value): Z, Cu, X, Y

19 Valine is a naturally occurring amino acid.



Valine 3-aminopropanoic acid

Which statements about valine and 3-aminopropanoic acid are correct?

A Both compounds are able to form zwitterions.
B Both compounds are able to react with ethanoic acid to give amide.
C Both compounds are able to react with $NaBH_4$ in methanol to give alcohol.
D Both compounds are soluble in water due to the formation of intermolecular hydrogen bonding.

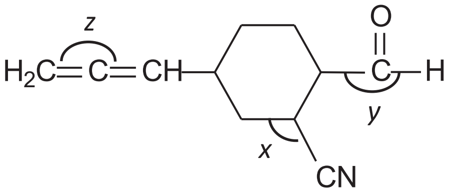
Answer: A

Option B is incorrect: Both compounds are not able to react with ethanoic acid to give amide. Acid-base neutralization would occur, producing a salt.

Option C is incorrect: Both compounds are not able to react with $NaBH_4$ in methanol to give alcohol. They must react with $LiAlH_4$ in dry ether.

Option D is incorrect: Both valine and 3-aminopropanoic acid are soluble in water due to formation of ion-dipole interactions, not hydrogen bonding.

20 Which of the following statements are correct about compound **U**?



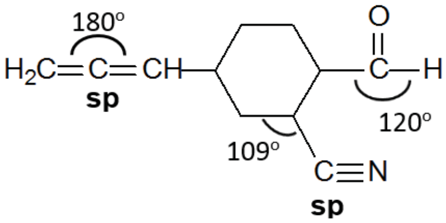
compound **U**

1 The bond angles in compound **U** increase in the order ***x*** < ***y*** < ***z***.
2 There is only one sp hybridised carbon atom in compound **U**.
3 There are 26 σ and 5 π bonds.
4 Compound **U** is planar.

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

Answer : **B** (1 and 3 are correct)

26 σ and 5 π bonds.



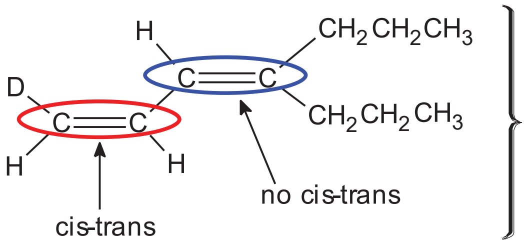
21 Deuterium (D or ^2H) is a heavy isotope of hydrogen. A deutero-hydrocarbon has the part structural formula shown below.

$$CDH{=}CH{-}CH{=}C(C_3H_7)_2$$

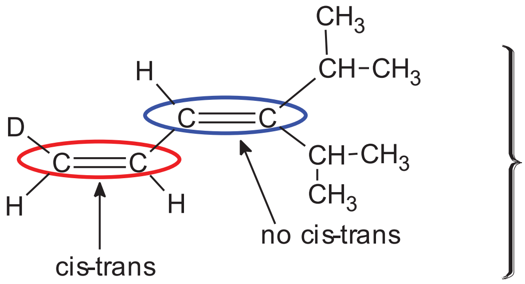
What is the total number of isomers with the above part-structural formula?

A 2
B 4
C 8
D 10

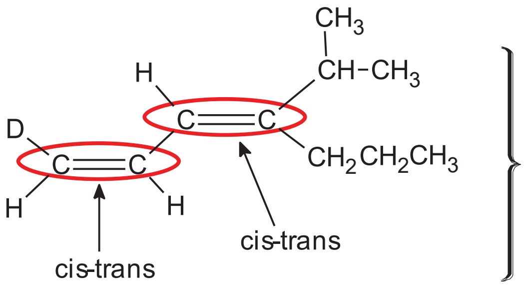
Answer: C



no. of isomer = 2



no. of isomer = 2



no. of isomer = 2^2 = 4

Total no. of isomers = 8

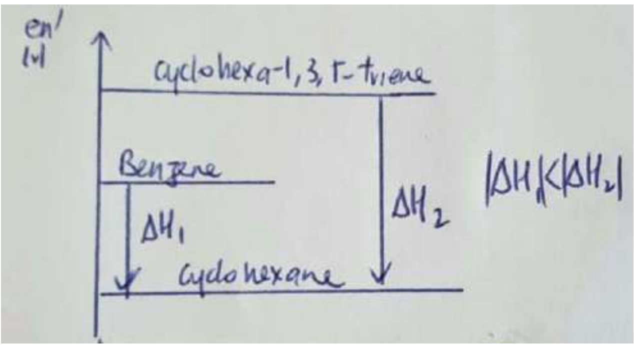
22 The molecule of benzene, C_6H_6 is a regular hexagon in which the π electrons are described as delocalised.

Which of the following statements support this structure?

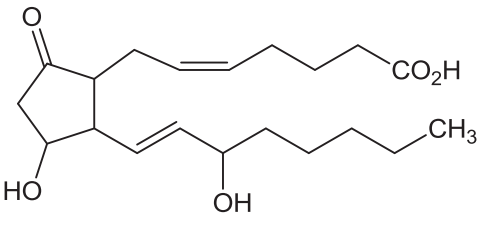
1 Benzene is a good conductor of electricity.
2 Addition reactions of benzene take place more easily than substitution.
3 All C–C bonds lengths in benzene are intermediate between C–C bond in an alkane and C=C bond in an alkene.
4 The enthalpy change of hydrogenation of benzene is less exothermic than that predicted for cyclohexatriene.

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

Answer : B (3 and 4 are correct)

1	Benzene is a simple molecular structure and does not conduct electricity.
2	Benzene will undergo substitution reactions easily as a result of its resonance stability.
3	The bond order of all C−C bonds in benzene are 1.5 due to resonance which arises from the continuous overlap of unhybridised p-orbitals.
4	Benzene is more stable than cyclohexa-1,3,5-triene due to resonance. Thus, it exists at a lower energy level (see below). Hydrogenation of benzene gives cyclohexane. 

23 PGE_2 is a prostaglandin that has pharmacological activity.



PGE_2

Which of the following is incorrect?

	Reducing agent	Number of hydrogen atoms incorporated per molecule of PGE_2
A	H_2 / Ni	6
B	Na in ethanol	8
C	$NaBH_4$ in methanol	6
D	$LiAlH_4$ in dry ether	4

Answer : **C**

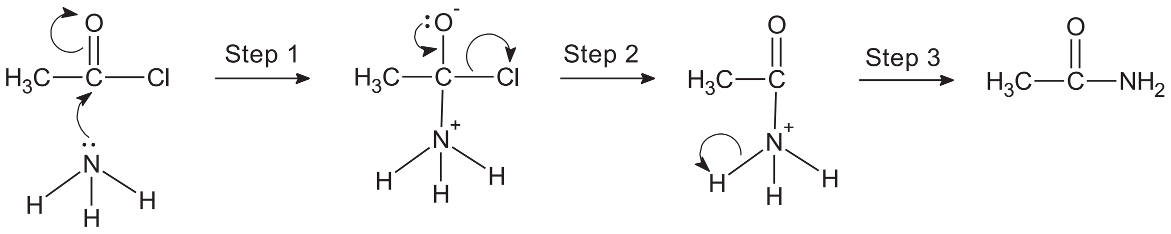
A H_2 / Ni will reduce the ketone and the two C=C. H_2 / Ni cannot reduce the carboxylic acid. Hence **6 hydrogen atoms** will be incorporated in the product.

B Na in ethanol will reduce all the functional groups – ketone, the two C=C. H_2 / Ni and the carboxylic acid. Hence **8 hydrogen atoms** will be incorporated in the product.

C $NaBH_4$ in methanol will only reduce the ketone. Carboxylic acid and C=C cannot be reduced. Hence **only 2 hydrogen atoms** will be incorporated in the product.

D $LiAlH_4$ in dry ether will reduce the ketone and carboxylic acid. C=C cannot be reduced. Hence **4 hydrogen atoms** will be incorporated in the product.

24 A mechanism for the reaction between ammonia and ethanoyl chloride is given below.



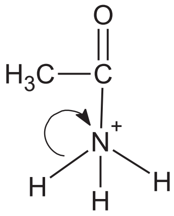
Which of the following statements are correct?

1 The ammonia behaves as a nucleophile.
2 The loss of proton in **step 3** is shown incorrectly.
3 The ammonia attacks an electron-deficient carbon atom.
4 The rate of reaction will increase if ethanoyl bromide is used.

A 1, 2, 3 and 4.
B 1, 3 and 4 only
C 1 and 3 only.
D 2 and 4 only.
Answer : A (1,2,3 and 4)

1: Correct. NH_3 has a lone pair of electrons and uses it to attack the electron deficient carbon.

2: Correct. The arrow in step 3 is shown incorrectly. The correct arrow movement should be



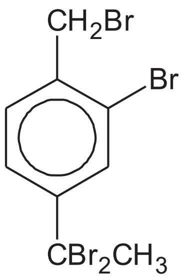
3: Correct. The carbon has two electron withdrawing groups (oxygen and chlorine) bonded to it, resulting in an very electron-deficient carbon.

4: Step 2 involves the breakage of C-Cl bond. Comparing the bond energy of C-Cl (340 kJ) and C-Br (280 kJ), less energy required to break the C-Br bond, activation energy for the reaction involving ethanoyl bromide will be lower, hence the rate of reaction will be faster.

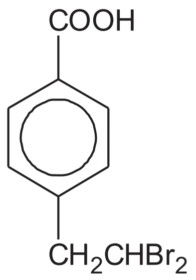
25 Diols formed on the same carbon atom are generally unstable and will undergo the following reaction.

$$RCR'(OH)_2 \rightarrow RCOR' + H_2O$$

Compounds **V** and **W** are both reacted with hot aqueous NaOH followed by dilute HC*l* at room temperature.



Compound **V**



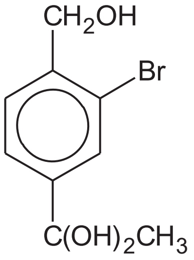
Compound **W**

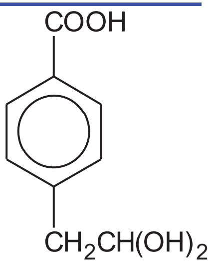
Which reagents could be used to distinguish the final products of **V** and **W**?

1 2,4 DNPH
2 Fehling's solution
3 Sodium carbonate
4 Hot acidified $K_2Cr_2O_7$
5 Iodine in aqueous NaOH

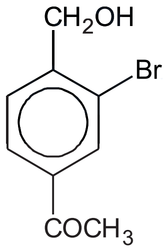
A 1 and 2 only
B 3 and 4 only
C 1, 4 and 5 only
D 2, 3 and 5 only
Answer : D (2, 3 and 5 only)

The halogenoalkanes will undergo **nucleophilic substitution** to give alcohols.

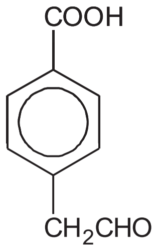




Diols on the same C atom are unstable, hence they **decompose (with the loss of water)** to give the respective **carbonyl compounds**.



V1



W1

1	+ve for V1	+ve for W1
2	-ve for V1	+ve for W1
3	-ve for V1	+ve for W1
4	+ve for V1	+ve for W1
5	+ve for V1	-ve for W1

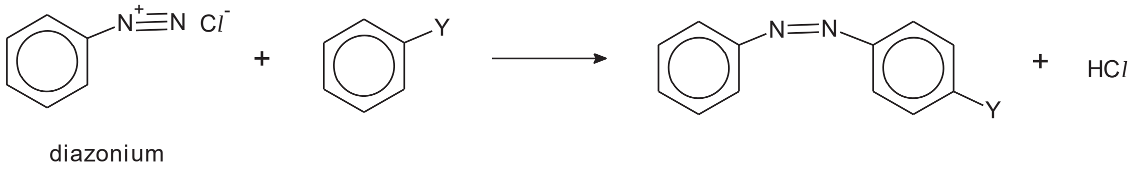
26 The ozone depletion potential (ODP) of a chemical compound is the relative amount of degradation to the ozone layer it can cause, with trichlorofluoromethane being fixed at an ODP of 1.0.

Which of the following compounds has an ODP of greater than 1.0?

A methane
B dichlorodifluoromethane
C chlorotrifluoromethane
D bromotrifluoromethane
Answer: D

C-Br is weaker than C-Cl bond. Less energy is required to homolytically break C-Br bond, hence the bromide radical will be easier to generate. Bromide radical would then break down ozone.

27 Azo coupling is an organic reaction between a diazonium compound and another aromatic compound that produces an azo compound.



Which of the following correctly represents the type of reaction and the role of diazonium compound?

	Type of reaction	**Role of diazonium**
A	nucleophilic substitution	nucleophile
B	electrophilic substitution	electrophile
C	nucleophilic substitution	electrophile
D	electrophilic substitution	nucleophile

Answer: B

Diazonium has a positive charge, hence it is an electrophile. Electrophilic substitution occurs on the benzene ring.

28 What is the order of increasing pH of 1 mol dm^{-3} of each organic compound?

A CH_3CO_2Na, CH_3CO_2H, CF_3CO_2H, $HOCH_2CHO$
B CH_3CO_2Na, $HOCH_2CHO$, CH_3CO_2H, CF_3CO_2H
C CF_3CO_2H, CH_3CO_2H, $HOCH_2CHO$, CH_3CO_2Na
D CF_3CO_2H, CH_3CO_2H, CH_3CO_2Na, $HOCH_2CHO$
Answer: C

CF_3CO_2H and CH_3CO_2H are both acids, both pH < 7, CF_3CO_2H has 3 electron-withdrawing fluorine which stabilises the conjugate to greater extent, CF_3CO_2H is the strongest acid, hence lowest pH.

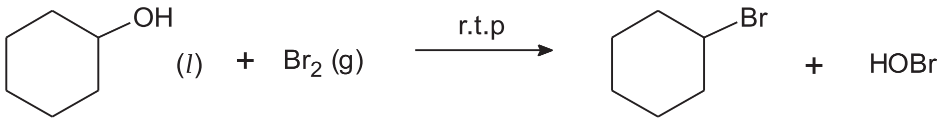
$HOCH_2CHO$ has alcohol and aldehyde hence it is neutral, pH = 7.

CH_3CO_2Na is the conjugate base of CH_3CO_2H, hence it has a pH > 7.

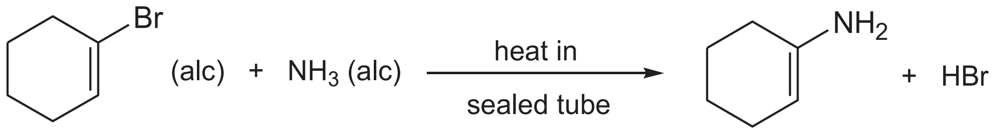
29 Which reaction gives the best yield of products?

[(*alc*) indicates an alcoholic solution.]

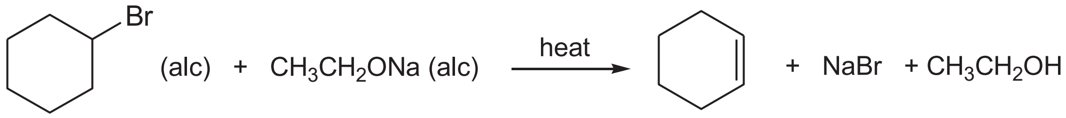
A



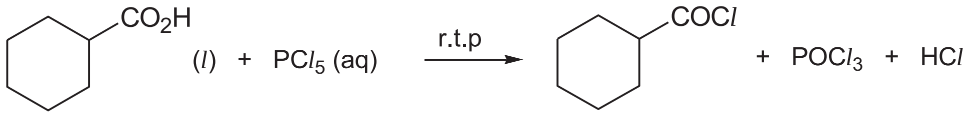
B



C



D



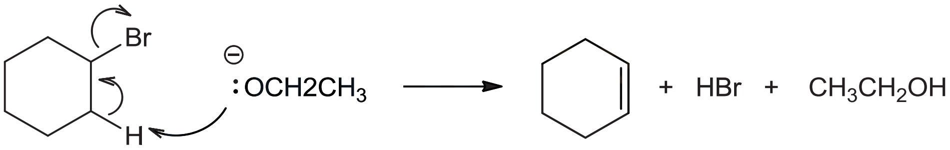
Answer: C

A Substitution of OH with Br requires HBr or PBr_3, as the C-O is strong and difficult to break.

B Br attached to C=C is unreactive towards nucleophilic substitution as the p orbital on Br overlaps with the π orbital of C=C, resulting in partial double bond character for the carbon-bromine bond which requires more energy to break.

C Elimination of HBr can take place in presence of a strong base in alcoholic medium.

$CH_3CH_2O^-$ is a stronger base than OH^- since the ethyl group is electron donating which intensify the negative charge on oxygen. Thus it is able to abstract the H atom on the carbon next to carbon attached to Br.

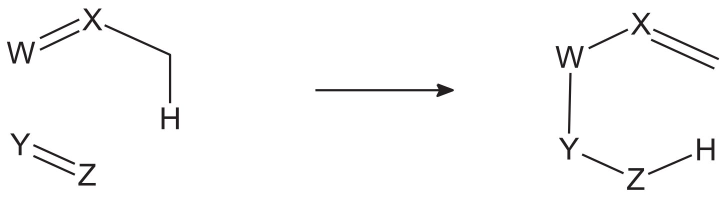


Na^+ is a spectator ion.

D PCl_5 will hydrolyse in aqueous medium and hence anhydrous PCl_5 should be used instead.

$PCl_5 + H_2O \rightarrow 5HCl + H_3PO_4$

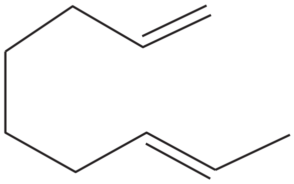
30 The Alder-ene reaction is a reaction between two alkenes and is capable of forming new carbon-carbon bonds. An example of the Alder-ene reaction is given below:



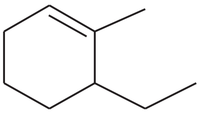
Note: W, X, Y & Z are carbon atoms and other hydrogens are not sho

The Alder-ene reaction typically produces many products as the roles of the two alkenes can be exchanged.

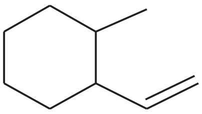
Which compound will **not** be formed when the following compound undergoes Alder-ene reaction?



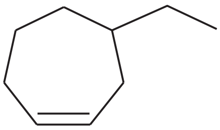
A



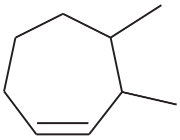
B



C

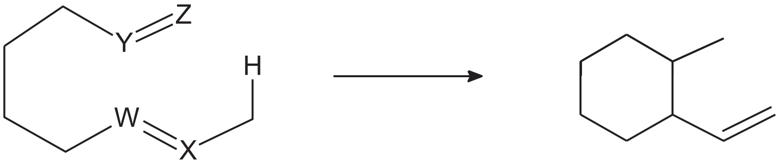


D

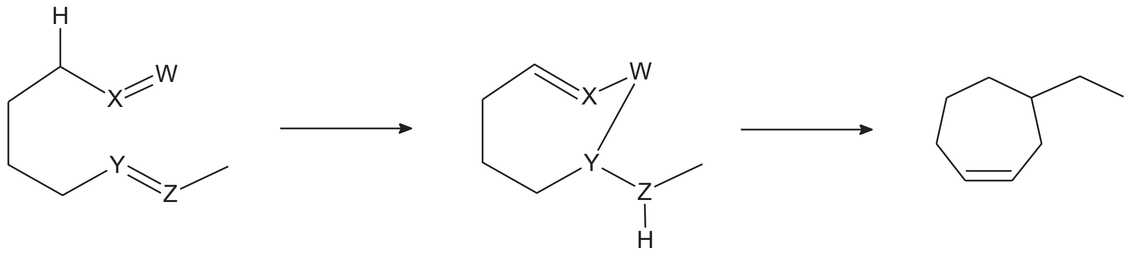


Answer: **A**

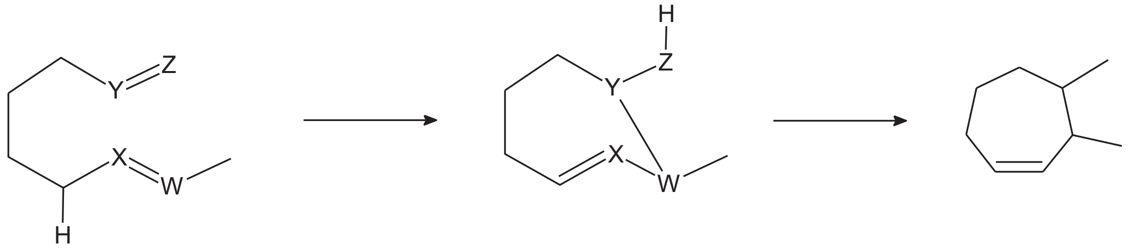
B:



C:



D:



2017 SRJC H2 Chemistry 9729
Preliminary Examination Paper 2 Solution

1 The size of an atom can be measured using the distance between the nuclei of two atoms.

For example, the 'metallic radius' of the Na atom is half the distance between two Na atoms in the crystal lattice of the metal. The 'covalent radius' of the C*l* atom is taken to be half the distance between the nuclei in a Cl_2 molecule. Finally, the 'van der Waals' radius' of the A_r atom is assumed to be half the distance between two atoms in the solid state.

These three types of radius are commonly known as 'atomic radii' and the corresponding values for Period 3 elements can be found in the Data Booklet.

(a) **(i)** Explain the general trend in atomic radius across Period 3.

Across Period 3, **nuclear charge increases as no. of protons increases. Shielding effect remains relatively constant** due to the **same no. of electron shells. Effective nuclear charge increases. Stronger electrostatic forces of attraction between nucleus and valence electrons lead to decrease in atomic radius.**

[2]

(ii) Suggest a reason for the anomaly in the measurement of atomic radius for argon.

The instantaneous dipole-induced dipole interactions between the two Ar atoms are **much weaker** than the strong metallic bonds for metals and strong covalent bonds for molecules. Thus, the two atoms for Ar will be **further apart** leading to a much higher measurement.

[1]

(b) **(i)** State the general relationship between atomic radius and first ionisation energy across Period 3.

The first ionisation energy is **inversely proportional** to atomic radius.

[1]

(ii) Explain why the relationship does not hold from P to S**.**

It is easier to remove an electron from S due to the **inter-electronic repulsion between the paired electrons** in the **same 3p orbital of S.** Thus 1st IE decreases from P to S.

[1]

(c) Across period 3, the elements changes from metallic to non-metallic nature. Correspondingly, the difference in electronegativity between the elements and the oxide decreases, giving rise to different types of oxides.

A, **B** and **C** are Period 3 elements, from Na to S, inclusive.

- **A** has the highest melting point among Period 3 elements.
- **B** has the highest electrical conductivity in Period 3.
- **C** burns in air with a coloured flame.
- **B** and **C** can show the same oxidation state in their compounds.

Identify **A**, **B** and **C** and hence, write equations, including state symbols, to show the acid-base properties of their oxides.

[Give the chemical formulae for only the highest oxide formed.]
A – Si
$SiO_2(s) + 2NaOH(conc.) \rightarrow Na_2SiO_3(aq) + H_2O(\mathit{l})$

B – A*l*
$Al_2O_3(s) + 6HCl(aq) \rightarrow 2AlCl_3(aq) + 3H_2O(\mathit{l})$
$Al_2O_3(s) + 2NaOH(aq) + 3H_2O(\mathit{l}) \rightarrow 2NaAl(OH)_4(aq)$

C – P_4 or P
$P_4O_{10}(s) + 12NaOH(aq) \rightarrow 4Na_3PO_4(aq) + 6H_2O(\mathit{l})$

[3]
[Total : 8]

2 Benzoic acid occurs naturally in many plants and it has many uses. It is an important precursor for the industrial synthesis of many organic substances.

(a) The benzoic acid and sodium benzoate buffer is commonly used as food preservatives in many acidic foods such as salad dressings and carbonated drinks.

(i) With the aid of relevant chemical equations, explain how the system can control pH when a small amount of base is added.

When small amount of OH^- is added,

$\mathbf{C_6H_5COOH + OH^- \longrightarrow C_6H_5COO^- + H_2O}$

The **added OH^- is removed as $C_6H_5COO^-$, pH remains fairly constant**.

[1]

(ii) Given that the acid dissociation constant for benzoic acid is 6.3×10^{-5} mol dm^{-3}, calculate the mass of solid sodium benzoate required to be added to 250 cm^3 of 0.50 mol dm^{-3} of benzoic acid to form a buffer solution with an initial pH 4.

$pK_a = -\lg(6.3 \times 10^{-5}) = 4.20$

$$pH = pK_a + \lg\frac{[\text{benzoate}]}{[\text{benzoic acid}]}$$

$$4 = 4.20 + \lg\frac{[\text{benzoate}]}{[0.50]}$$

[benzoate] = **0.3155 mol dm^{-3}**

Amt of benzoate = $0.3155 \times \frac{250}{1000} = 0.07887$ mol

Mass of sodium benzoate required = 0.07887 x (144.0) = **11.4 g**

[2]

(iii) To achieve the optimal buffering capacity of a 25 cm^3 sample of the buffer prepared in **(ii)**, a standard solution of 1.5 mol dm^{-3} sodium hydroxide was added. Calculate the volume of sodium hydroxide needed.

Amt of benzoic acid in sample = $\frac{25}{1000} \times 0.5 = 0.0125$ mol

Amt of benzoate in sample = $\frac{25}{1000} \times 0.3155 = 0.007888$ mol

At maximum buffering capacity: [benzoic acid] = [benzoate]

Amt of benzoic acid = amt of benzoate = $\frac{0.0125 + 0.007888}{2} = 0.01019$ mol

Amt of NaOH to add = 0.0125 – 0.01019 = 0.00231 mol

Vol of NaOH required = $\frac{0.00231}{1.5}$ = **1.54 cm^3**

[3]

(b) The presence of benzoic acid in plant extracts can be confirmed using neutral iron(III) chloride according to the following equation.

$$Fe^{3+}(aq) + 3C_6H_5COOH(aq) \longrightarrow Fe(C_6H_5CO_2)_3(s) + 3H^+(aq)$$

When 50 cm^3 iron(III) chloride is added to an equal volume of the plant extract, 0.0532 g of iron(III) benzoate, $Fe(C_6H_5CO_2)_3$ precipitate is formed.

The resultant mixture has a pH value of 2.33.

(i) Calculate the amount of benzoic acid that has reacted with neutral iron(III) chloride solution and H$^+$ in the mixture.

Amt of $Fe(C_6H_5CO_2)_3 = \dfrac{0.0532}{418.8} = 0.000127$ mol

Amt of benzoic acid reacted = 3 x 0.000127 = **<u>0.000381 mol</u>**

$[H^+] = 10^{-2.33} = 0.004677 \text{ mol dm}^{-3}$

Amt of H$^+$ in mixture = $0.004677 \times \dfrac{100}{1000} =$ **<u>0.000468 mol</u>**

[1]

(ii) Assuming that the H$^+$ ions in solution are formed from the dissociation of benzoic acid and the reaction of benzoic acid with iron(III) chloride, calculate the concentration of benzoate ions in the equilibrium mixture.

Total amt of H$^+$ in solution = 0.0004677 mol

Amount of H$^+$ produced from acid and Fe^{3+} reaction = 0.0003811 mol

Amount of H$^+$ produced from benzoic acid dissociation
= 0.0004677 – 0.0003811 = 0.000086611 mol

$C_6H_5CO_2^- \equiv H^+$

$[C_6H_5CO_2^-] = 0.0000866 \div \dfrac{100}{1000} =$ **<u>0.000866 mol dm^{-3}</u>**

[2]

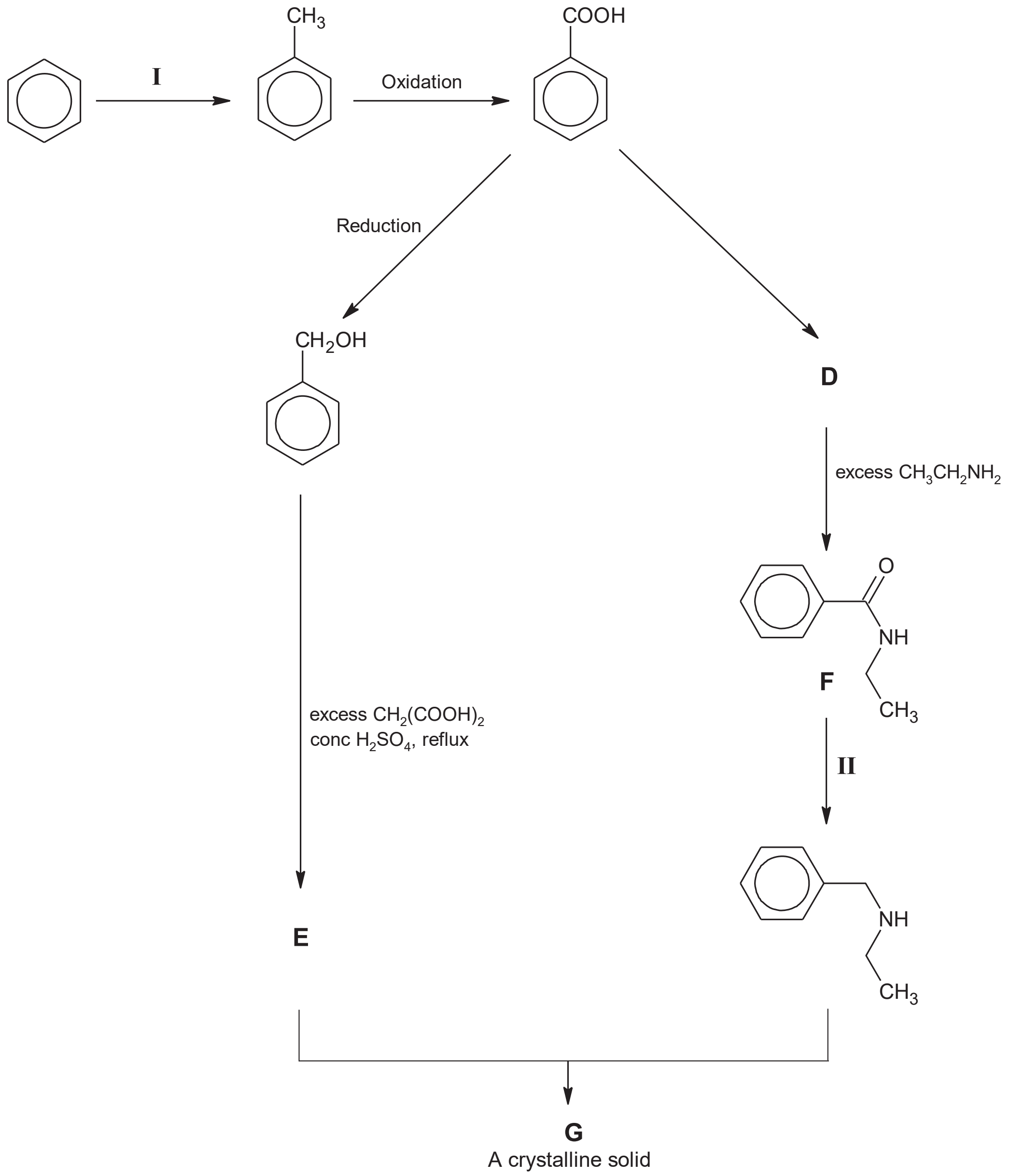
(iii) Calculate the K_{sp} of iron(III) benzoate, given that the concentration of iron(III) ions in the mixture is 1.83×10^{-3} mol dm^{-3} at equilibrium.

$K_{sp} = [Fe^{3+}][C_6H_5CO_2^-]^3$

$K_{sp} = (1.83\times10^{-3})(0.0008611)^3 =$ **1.19×10^{-12} mol^4 dm^{-12}**

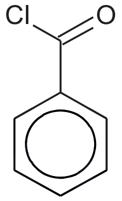
[1]

(c) Benzoic acid is involved in the reaction scheme below:

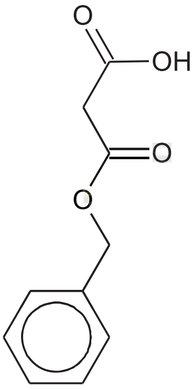


(i) Draw the structures for **D**, **E** and **G** in the boxes below.

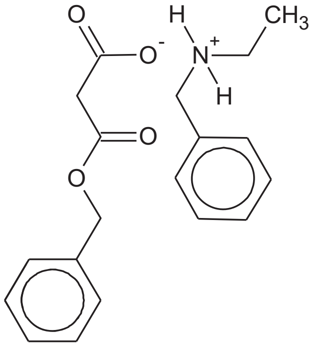
D



E



G



[3]

(ii) Suggest the reagents and conditions for reactions **I** and **II**.

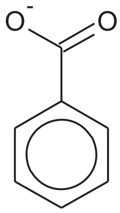
Reactions **I**: **CH_3Br, anhydrous $FeBr_3$ (s)**
Reactions **II**: **$LiAlH_4$ in dry ether, rtp**

[2]

(iii) Compound **F** was heated with aqueous sodium hydroxide and excess carbon dioxide was bubbled through the solution.

Given the acid dissociation constants below, suggest the products that would be formed after the introduction of carbon dioxide.

acid	**formula**	**K_a / mol dm^{-3}**
carbonic acid	H_2CO_3	4.5×10^{-7}
benzoic acid	C_6H_5COOH	6.3×10^{-5}
ethylamine salt	$CH_3CH_2NH_3^+$	1.6×10^{-11}

Products formed:  and **$CH_3CH_2NH_3^+$**

Benzoate salt will not be neutralised by carbon dioxide.
Benzoic acid is a stronger acid than carbonic acid as shown by the K_a values, thus suggesting that the benzoate ion is more stable than carbonate.

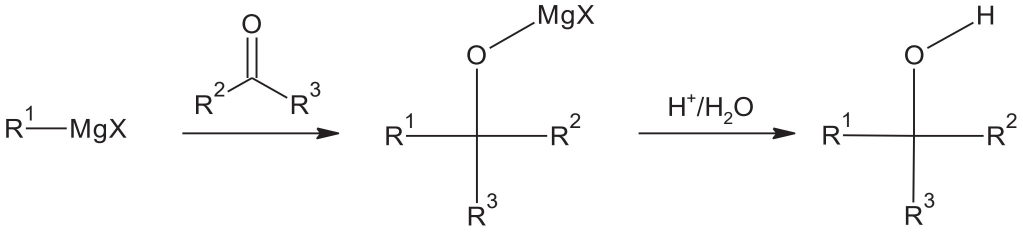
[3]
[Total : 18]

3 Grignard reagents are organomagnesium halides, RMgX commonly used in organic synthesis. The R in RMgX behaves like an anion, R^- and is a strong Lewis base. It can be made by the reaction between halogenoalkane and magnesium under anhydrous conditions, using ether as a solvent.

$$R^1{-}X \quad + \quad Mg \longrightarrow R^1{-}MgX$$

where R= alkyl group, X= C*l*, Br, I

In a Grignard reaction, the Grignard reagent behaves as a nucleophile and may be added to a carbonyl compound for the formation of an alcohol. This reaction is useful for the formation of carbon–carbon bonds.



(a) **(i)** Suggest, with an equation, why the synthesis of Grignard reagent has to be done under anhydrous conditions.

The **R in RMgX reacts with water** to form an alkane, destroying the nucleophile for the Grignard reaction.

$RMgX + H_2O \rightarrow RH + (OH)MgX$
or
$R^- + H_2O \rightarrow RH + OH^-$

[2]

(ii) Besides organomagnesium compounds, organolithium compounds can be formed between lithium and relevant organic substances. Account for the similarity in the reactions involving lithium and magnesium.

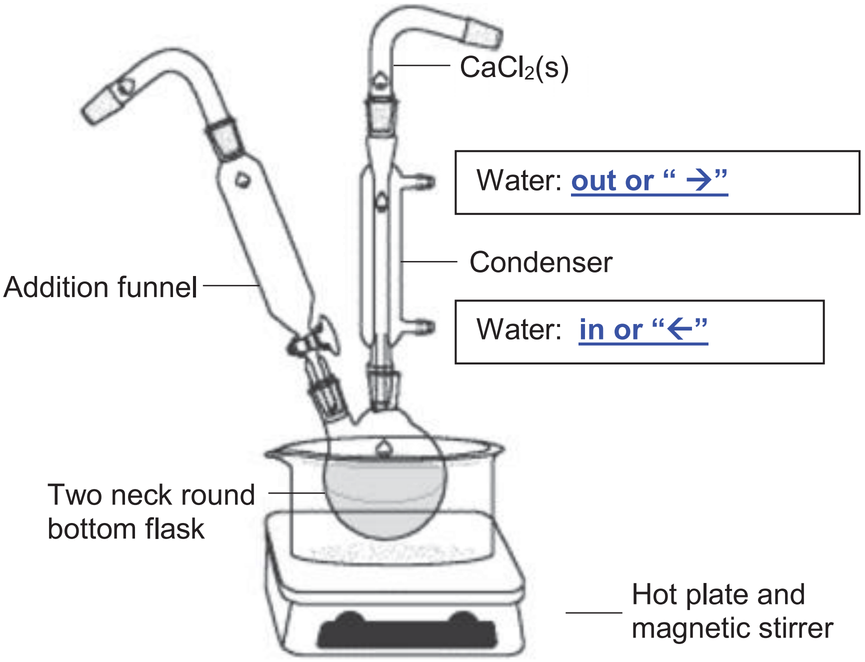
q+: $Mg^{2+} > Li^+$
r+: $Mg^{2+} > Li^+$
Li^+ and Mg^{2+} have **similar charge density**

[2]

The preparation and set up of Grignard synthesis of 2-methylhexan-2-ol is described below:

Table 3.1

Compound	Melting pt / °C	Boiling pt / °C	Molar mass / g mol^{-1}	Density / g cm^{-3}	Solubility in water
1-bromobutane	−11.2	101.4	136.9	1.27	Insoluble
Magnesium	651	1100	24.3	1.74	Insoluble
Diethyl ether	−116.3	34.6	74.0	0.713	Insoluble
Propanone	−94.7	56.1	58.0	0.785	Soluble
Sulfuric acid	10.3	337	98.1	1.84	Soluble
2-methylhexan-2-ol	−	143	116.0	0.82	Soluble



<u>Preparation of Grignard reagent, RMgX</u>

1. Add 15 g of 1-bromobutane and 3 g of magnesium into the 250 cm^3 two-neck round bottom flask.

2. Add 50 cm^3 of anhydrous diethyl ether using the addition funnel. Gently stir the mixture under reflux for 30 minutes. The reaction is exothermic and will boil without external heat.

3. When the reaction is complete, cool the reaction mixture using an ice bath.

(b) **(i)** With reference to Table 3.1, suggest why a reflux set up is necessary in this organic synthesis.

The reflux set up is to **minimise the loss of volatile organic compounds** such **as diethyl ether**.

[1]

(ii) On the diagram above, label and account for the direction of water flow.

Water 'IN' should be connected at the bottom of the reflux condenser to ensure all hot volatile organic vapour is condensed **immediately** into the flask or ensure **efficient cooling**.

[1]

(iii) Some heating may be required at the beginning as the initial rate of formation of RMgX is slow. Magnesium metal has to be scrapped or sliced into smaller pieces to increase the reaction rate.

Write an equation to suggest why magnesium may not be as reactive as expected.

Mg is not as reactive as the surface of Mg is covered by inert/unreactive MgO.

$\mathbf{Mg + \frac{1}{2} O_2 \rightarrow MgO}$

[1]

(iv) Excess diethyl ether is added to keep the Grignard reagent at a low concentration. This will prevent the Grignard reagent from reacting with unreacted 1-bromobutane. Draw the structure of the organic by-product.

octane

[1]

Synthesis of alcohol

4. Using the addition funnel, add 6.5 g (dissolved in 15 cm^3 of diethyl ether) of propanone to the Grignard reagent.

5. To a separate 250 cm^3 beaker, add 100 cm^3 of ice water and 4 cm^3 of concentrated sulfuric acid and mix well.

6. When the reaction with propanone is completed, add the reaction mixture into a 250 cm^3 beaker, sitting in an ice bath. Carefully transfer sulfuric acid solution from step 5 into reaction mixture. Stir gently to mix well.

(c) **(i)** Using Table 3.1, calculate the theoretical mass of 2-methylhexan-2-ol.

Amt of 1-bromobutane = $\frac{15}{136.9}$ = 0.1096 mol
Amt of Mg = $\frac{3}{24.3}$ = 0.1235 mol (in excess)
Amt of propanone = $\frac{6.5}{58.0}$ = 0.112 mol (in excess)

Mole ratio: 1 bromobutane: 2-methylhexan-2-ol
Mass of 2-methylhexan-2-ol = 0.1096 x 116.0 = **12.7 g**

[2]

(ii) The actual yield for 2-methylhexan-2-ol is 4 g. Calculate the percentage yield for this reaction.

Actual % yield = $\frac{4}{12.7}$ x 100 = **31.5 %**

[1]

(iii) Suggest why the addition of sulfuric acid has to be carried out in an ice bath in step 6.

[1]

The reaction of sulfuric acid with unreacted Mg is **highly exothermic**.

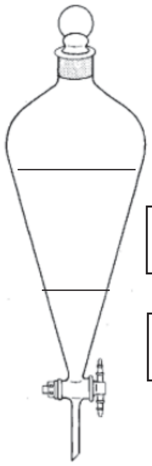
Solvent extraction

7. Add the mixture from step 6 into a 500 cm^3 separation funnel and add 10 cm^3 of diethyl ether. Shake the separation funnel, releasing any gas formed. Allow the layers to separate and collect both layers separately.

8. Repeat step 7 with the aqueous layer and a fresh sample of 10 cm^3 diethyl ether. Collect and combine each ether layer.

9. The combined ether layer is poured back to the separation funnel and mixed with several 20 cm^3 portions of 5 % sodium bicarbonate solution until no more carbon dioxide is generated.

(d) **(i)** After step 7, there are two layers in the separation funnel. Identify the ether and aqueous layer in the diagram below.



Upper layer: Ether/organic layer

Bottom layer: Aqueous layer **[1] for both**

Explain your answer.
Diethyl ether is **less dense than water**. [1]

(ii) Give a reason for the addition of sodium bicarbonate in Step 9.

To remove unreacted traces of **sulfuric acid** in the **ether layer**

[1]

(iii) During solvent extraction, both propanone and 2-methylhexan-2-ol are found in the ether layer. Comment on the solubility of 2-methylhexan-2-ol in diethyl ether.

The presence of **hydrophobic / non polar alkyl group** in 2-methylhexan-2-ol allow more **favourable instantaneous dipole – induced dipole interactions** with diethyl ether.

[1]

(iv) Suggest different chemical tests to positively identify propanone and 2-methylhexan-2-ol in the ether layer.

Add **2-4 DNPH, r.t.p**: formation of **orange ppt** suggest presence of propanone
Or **I_2(aq), NaOH(aq) and heat**: **yellow ppt** and **decolourisation of brown iodine** solution.

Add **PCl_5(s), r.t.p**: **White fumes** in the presence of 2-methylhexan-2-ol
Or
use **Na(s) r.t.p**: hydrogen gas which **extinguish lighted splint with "pop" sound**

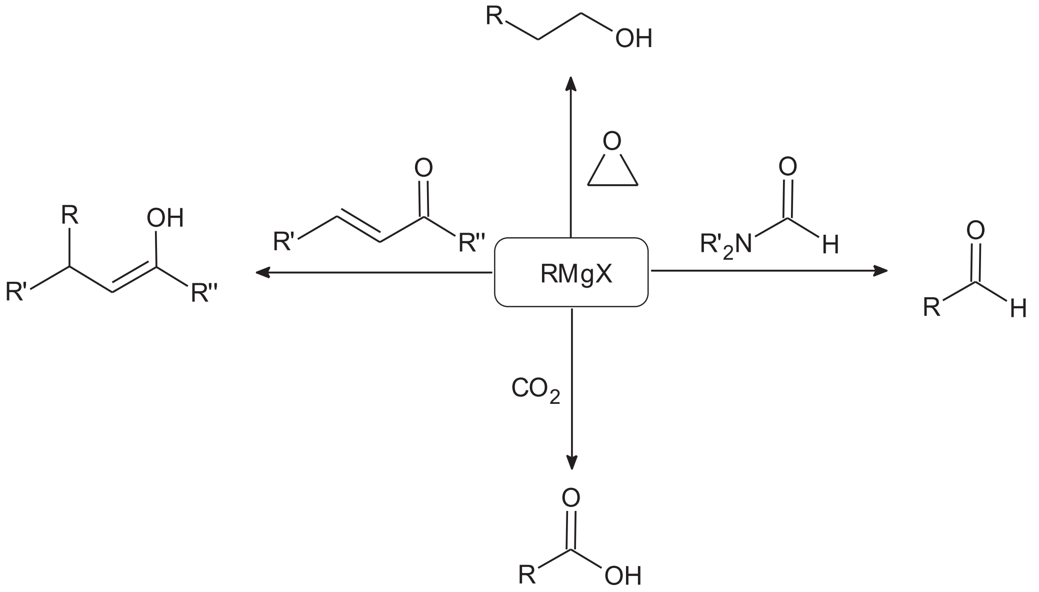
[2]

(v) Suggest how crude 2-methylhexan-2-ol can be purified from the ether layer.

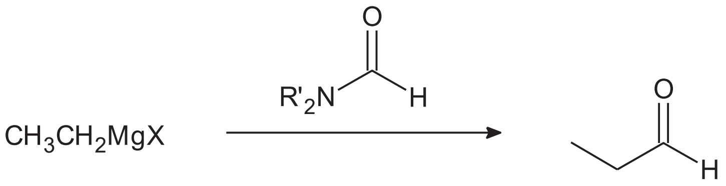
Via **distillation.** Since propanone and diethyl ether has lower boiling point, propanone and diethylether will be collected as the first distillate.

[1]

(e) Grignard reagent is used widely in organic synthesis due to its ability to increase carbon chain length. Four unique reactions involving the use of Grignard reagent are shown in the reaction map below.

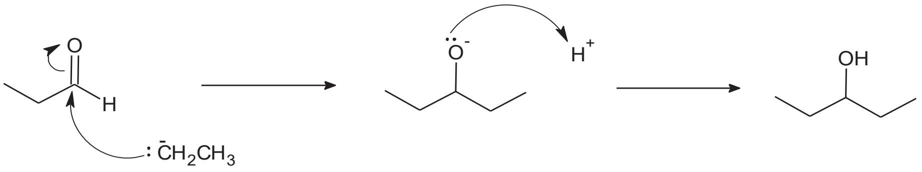


(i) The following Grignard reaction to form propanal achieved a very low yield as the aldehyde formed can react with the Grignard reagent again.

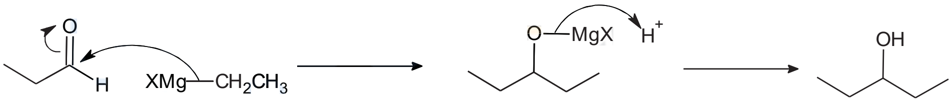


Describe the mechanism between propanal and the Grignard reagent, CH_3CH_2MgX to form the corresponding alcohol.

Nucleophilic addition.



Or



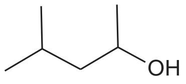
[2]

(ii) Starting with a suitable Grignard reagent, propose an alternative 3-step synthesis pathway to synthesise propanal.

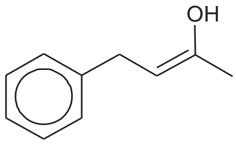
$$\begin{tikzcd} CH_3CH_2MgX \arrow[r, "CO_2\ (g)"] & CH_3CH_2COOH \arrow[r, "LiAlH_4\text{ in dry ether}", "r.t.p"'] & CH_3CH_2CH_2OH \arrow[d, "K_2Cr_2O_7,\ H_2SO_4\ (aq)"', "\text{heat with distillation}"'] \\ & & CH_3CH_2CHO \end{tikzcd}$$

[3]

(iii) Using different reaction types from the reaction map above, suggest appropriate pairs of reagents in the synthesis of compounds **H** and **I**.

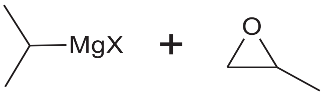


H

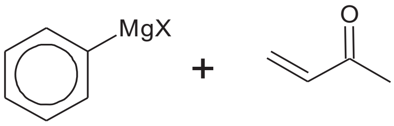


I

H:



I:

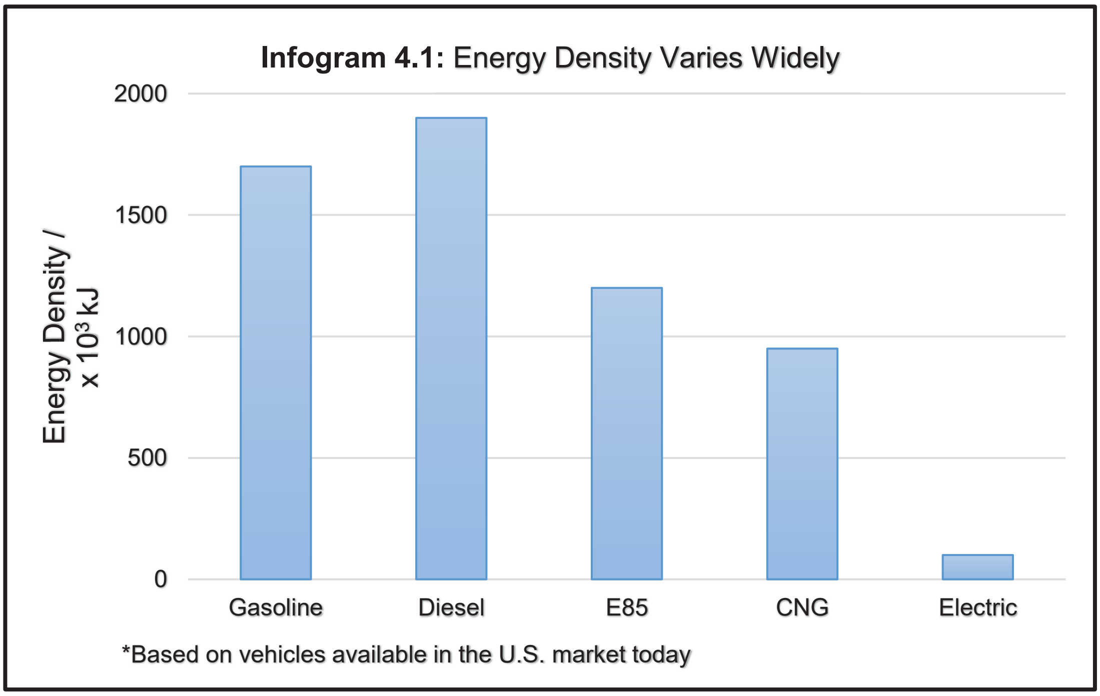


[2]
[Total: 25]

4 The use of electric vehicles has been increasing popular in the U.S. For example, hydrogen fuel cell vehicles produces zero carbon emission.

Despite the advantages of electric cars, petrol-engined cars are still widely used today. One problem with electric vehicles is their poor performance, inconvenience of finding a charging station and it takes a long time to recharge the batteries. Petrol-engined cars are better as their energy supply can be replaced over 6 million times faster than electric cars.

The infogram below shows how energy density varies widely with different fuels. Energy density is the energy produced per unit dimension of a fuel and this determines the practicality of a fuel.



Infogram 4.1: Energy Density Varies Widely

*Based on vehicles available in the U.S. market today

However, using petrol (which contains a mixture of alkanes) has its own problems. One such problem is that it's a finite resource, and another is pollution. Hence, there is a need to improve the performance of petrol in car engines so that it burns as cleanly and efficiently as possible and to find alternative sources of fuel to replace petrol.

Some data for five fuels are given in **Table 4.2**.

Fuel	**Formula**	**Standard enthalpy change of combustion, ΔH_c^o / kJ mol^{-1}**	**Relative molecular mass**	**Energy density (energy transferred on burning 1 kg of fuel) / kJ kg^{-1}**
octane	C_8H_{18} (*l*)	– 5470	114.0	
1,2-xylene	C_8H_{10} (*l*)	– 4540	106.0	
carbon	C(s)	– 393	12.0	
methanol	CH_3OH(*l*)	– 726	32.0	
hydrogen	H_2(g)	– 286	2.0	

(a) Give an example of a pollutant that can arise from the use of petrol and state a detrimental effect of the pollutant.

- Carbon monoxide / CO – causes **carbon monoxide poisoning**
- Unburnt hydrocarbons – becomes **photochemical smog** in strong sunlight
- Lead bromide vapour – causes **brain damage**
- Sulphur dioxide / SO_2 – causes **acid rain**

[1]

(b) Complete Table 4.2 by calculating the energy density for all fuels. [1]

Fuel	Formula	Standard enthalpy change of combustion, $\Delta H_c^{\ominus}$ / kJ mol^{-1}	Relative molecular mass	Energy density (energy transferred on burning 1 kg of fuel) / kJ kg^{-1}
octane	C_8H_{18} (*l*)	– 5470	114.0	48000
1,2-xylene	C_8H_{10} (*l*)	– 4540	106.0	42800
carbon	C(s)	– 393	12.0	32800
methanol	CH_3OH(*l*)	– 726	32.0	22700
hydrogen	H_2(g)	– 286	2.0	143000

(c) **(i)** On the basis of energy density, which is the best fuel in table 4.2.

Hydrogen as it has the highest energy density.

[1]

(ii) Suggest a practical difficulty in using hydrogen rather than methanol as a fuel.

1. It is a light gas and **occupies too much volume**
   ⇒ storage difficult
2. It is also **flammable/ explosive** ⇒ cause **safely concerns**.

[1]

(d) Using the given data above, comment on the feasibility of using electric cars in the near future.

[1]

Despite the high energy density of hydrogen, gasoline/petrol is still the preferred choice as it is efficient in producing energy for consumer's use.

Octane is commonly used as a fuel or a precursor in the production of other chemicals. The term "octane rating" is often used in the petroleum industry for rating the ability of octane's various branched isomers in reducing engine knock in vehicles.

One important factor in making petrol is getting the right octane rating to reduce the problem of 'knocking'. Knocking occurs when the combustion of fuel is not smooth. Knocking reduces engine power, leading to wear and tear in the engine and results in wastage of petrol. Hence, highly branched alkanes are desirable in petrols as they have higher octane ratings and reduce knocking.

Another factor for getting the right properties of petrol is the blending of petrol. In cold weather, it is difficult to vaporise petrol, which makes ignition difficult. On the other hand, in hot weather, petrol vaporises easily. Hence, petrol companies make different blends of petrol for different seasons and climates.

You are to use the information provided above to answer parts **(e)** and **(f)**.

(e) Apart from using alkanes with high octane ratings, another way to deal with the problem of knocking is through the addition of an antiknock agent, tetra-ethyl lead (**TEL**). **TEL** is a highly volatile colourless liquid which aids in the formation of free radicals. However, this method is not commonly used nowadays.

Explain, with the aid of a suitable equation, how **TEL** helps to overcome the problem of knocking and give a reason why its usage is limited nowadays.

The **weak lead-carbon bonds** in tetra-ethyl lead are easily broken, giving **$CH_3CH_2\bullet$ which initiates smooth burning**.

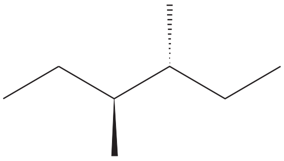
$$Pb(CH_2CH_3)_4 \rightarrow Pb + 4\ CH_3CH_2\bullet$$

PbO will be formed, which coats car cylinders and reduces their effectiveness over time
Or **Release of toxic lead compounds into the atmosphere**

[3]

(f) Compounds **J**, **K** and **L** are isomers of the hydrocarbon octane, C_8H_{18}.

The table below shows the boiling points and data relating to the optical activity of the compounds.

Structure	**Boiling Point / °C**	**Number of chiral centres**	**Optical Activity**
Isomer J	120	1	Yes
 **Isomer K**	118	2	No
Isomer L	107	0	No

(i) Suggest why isomer **K** does not exhibit enantiomerism.

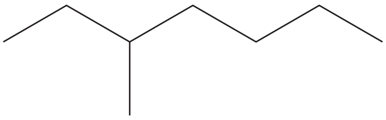
There is a **plane of symmetry in the molecule** or both chiral centres contain the same groups attached to it, forming a meso compound.

Or
The two chiral centres **rotate the plane of polarised light** to the same extent but in the opposite direction hence cancelling out the optical activity.

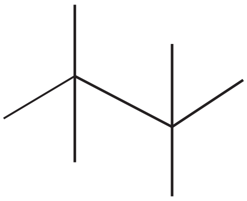
[1]

(ii) Propose the structures of compounds **J** and **L**.

Isomer J :



Isomer L :



[2]

(iii) In terms of structure and bonding, identify which of your proposed compounds (**J** or **L**) would be a more suitable fuel for use in summer and winter respectively.

Your answer should show clear and detailed comparison in your choice of fuel.

[2]

M$_r$: J = L

Molecular shape : J (elongated) vs L (spherical)

Surface area of contact : J > L

Extent of weak instantaneous dipole-induced dipole: J > L

Energy requirement: J > L

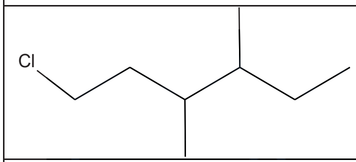
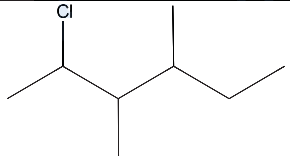
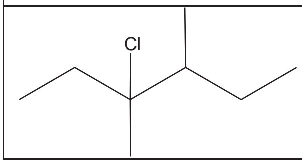
Boiling point: J > L

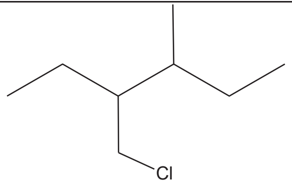
Volatility : J < L

Hence, with more volatile alkanes (with a lower boiling point) like **L in winter petrol**, it will be **easier for the petrol to vaporise** and with less volatile alkanes like **J** (with a higher boiling point) in **summer petrol**, it will be **harder for the petrol to vaporise**.

(iv) Controlled chlorination of isomer **K** in the presence of UV light produces different mono-chlorinated products with a molecular formula of $C_8H_{17}Cl$.

Draw the structural formula of any **two** possible isomers and state the ratio in which they are formed.

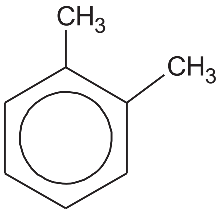
Structural formula	**mole ratio**	
	**6**	**3**
	**4**	**2**
	**2**	**1**

	6	3

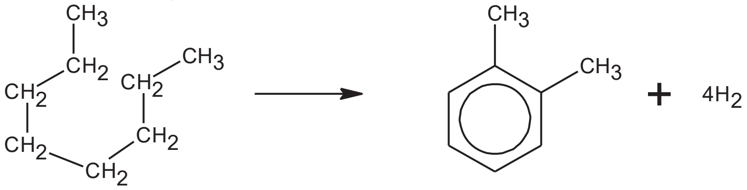
[2]

(g) The performance of hydrocarbons as fuels is largely improved by catalytic reforming. Reforming takes straight chain hydrocarbons in the C_6 to C_8 range from the gasoline or naphtha fractions and rearranges them into compounds containing benzene rings. They are used to make fuels with high octane number. Hydrogen is produced as a by-product of the reactions. A catalytic mixture of Pt and Al_2O_3 at a temperature of 500 °C and pressure of 20 atm is used.

An example of a product is 1,2-xylene.



(i) Write a balanced equation when octane undergoes the 'reforming' process to form 1,2-xylene.



1,2-xylene

Or

$C_8H_{18} \rightarrow C_8H_{10} + 4H_2$

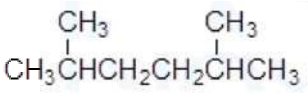
[1]

(ii) What *type of reaction* has the octane undergone?

Oxidation / aromatisation / cyclisation

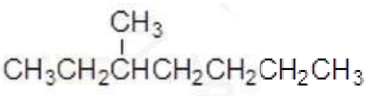
[1]

(iii) 1,4–xylene can be produced by a similar process. Suggest the structural formula of a C_8 alkane which might produce 1,4-xylene.



$CH_3\overset{\overset{CH_3}{|}}{C}HCH_2CH_2\overset{\overset{CH_3}{|}}{C}HCH_3$

or

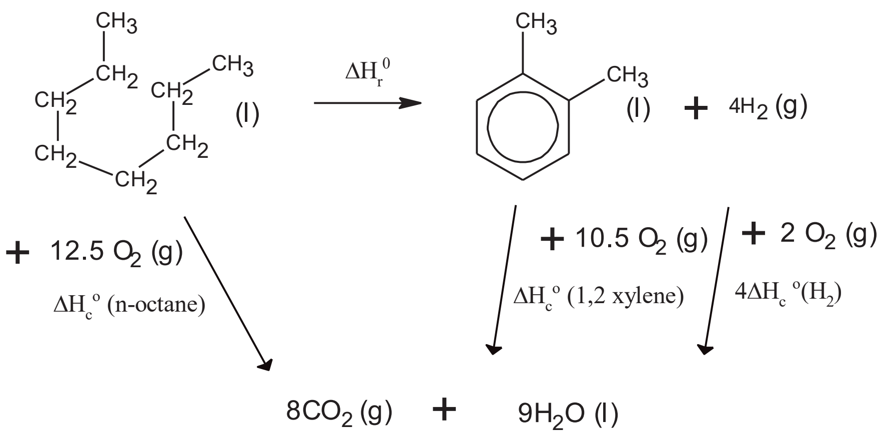


$CH_3CH_2\overset{\overset{CH_3}{|}}{C}HCH_2CH_2CH_2CH_3$

[1]

(iv) By means of an energy cycle, show and calculate the standard enthalpy change of reaction that produces 1,2-xylene from octane.

[2]



ΔH_r^o = -5470 – [(-4540) + 4(-286)] = **+214** kJ mol^{-1}

(v) Using data from the Data Booklet, calculate the enthalpy change of the reaction which reforms octane into 1,2-xylene.

Bond broken	Bonds formed
7 C - C	2 C – C
18 C – H	6 C$\overset{\cdots}{-}$C
	10 C – H
	4 H – H

ΔH_r = 7(+350) + 18(+410) – [2(+350) + 6(+520) + 10(+410) + 4(+436)]
= (+9830) – (+9664) = **+166 kJ mol^{-1}**

[2]

(vi) By considering your answers in **(g)(iv)** and **(v)**, suggest if they are accurate descriptions of the reformation process.

(g)(iv) involve the use of **enthalpy values at standard conditions**.

(g)(v) **did not include the enthalpy change of vaporisation** as octane and xylene are liquids in standard states.

Hence, both are inaccurate descriptions as **reforming take place at 500 °C and pressure of 20 atm which are non-standard conditions.** *(Underline portion is necessary to get this mark. Must make reference to the passage.)*

[1]

(vii) Briefly explain whether you would expect the above reaction to have its ΔG value to be more negative than its corresponding ΔH_r.

Since, ΔG = ΔH - TΔS,
ΔS > 0 because there is a production of **4 moles of H_2**, which results in **n(gas) to increase after the reaction**. Hence, ΔG value will be **more negative**.

[1]

[Total : 24]

2017 SRJC H2 Chemistry 9729
Preliminary Examination Paper 3 Solution
Section A

1 **(a)** Oxides of nitrogen, NO_x are a mixture of gases that are composed of nitrogen and oxygen. They are formed during combustion processes in power plants.

Thermal NO_x refers to NO_x formed through high temperature oxidation of the diatomic nitrogen found in combustion air.

The formation rate is a function of temperature and the residence time of nitrogen at that temperature. At high flame temperatures, molecular nitrogen and oxygen dissociate into their atomic states and participate in a series of reactions.

The two principal reactions producing thermal nitric oxide, NO are as follows.

Step 1 O atoms react reversibly with N_2 to form NO.

Step 2 N atoms liberated react with O_2 to produce more NO.

Nitrogen dioxide typically arises via the oxidation of nitric oxide by oxygen in the atmosphere.

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

(i) Write the two principal reactions involved in the formation of thermal nitric oxide in combustion. [1]

Step 1 : $\mathbf{N_2 + O \rightleftharpoons NO + N}$
Step 2 : $\mathbf{N + O_2 \rightarrow NO + O}$

(ii) Hence, determine the rate determining step. [1]

Step 1. Step **1** involves the breaking of very strong **N≡N (triple) bond** which requires a large amount of energy to overcome.

(iii) Suggest a method to reduce the formation of thermal NO_x. [1]

Reduce peak flame **temperature**/**Reduce time** of gas spent in flame.

(b) Catalytic converters are used to reduce the output of NO_x into the environment. One example is the removal of nitric oxide by reaction with hydrogen gas using platinum catalyst.

		ΔH
$NO + NO \rightleftharpoons N_2O_2$	fast	positive
$N_2O_2 + H_2 \rightarrow H_2O + N_2O$	slow	negative
$N_2O + H_2 \rightarrow N_2 + H_2O$	fast	negative

(i) Write the rate equation for the above reaction, showing clearly how you derive it. [2]

rate = k $[N_2O_2][H_2]$

N_2O_2 is an intermediate and should not be included in the rate equation.

Let the equilibrium constant of step 1 be **K**.

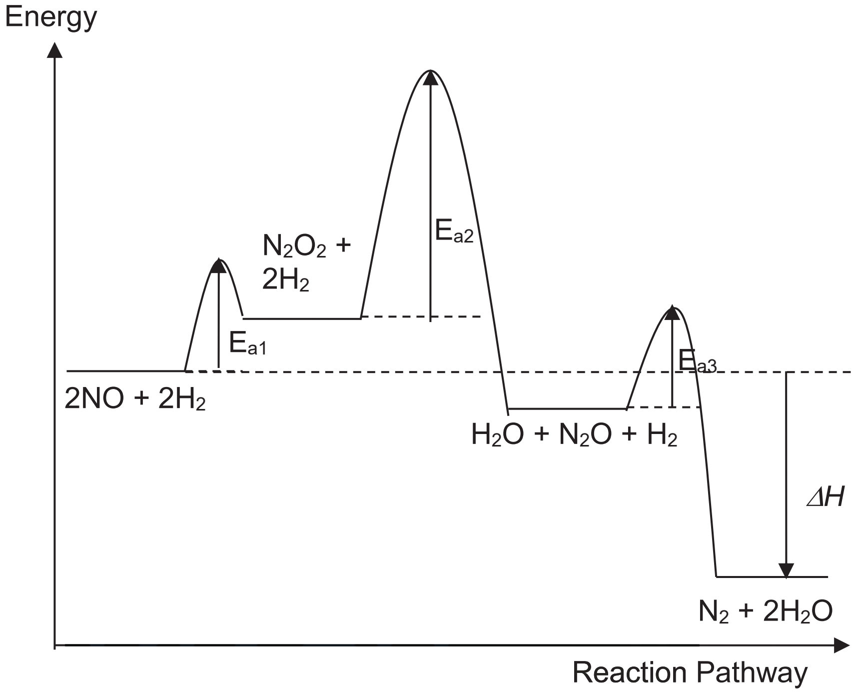
$$K = \frac{[N_2O_2]}{[NO]^2}$$

$[N_2O_2] = \mathbf{K}[NO]^2$

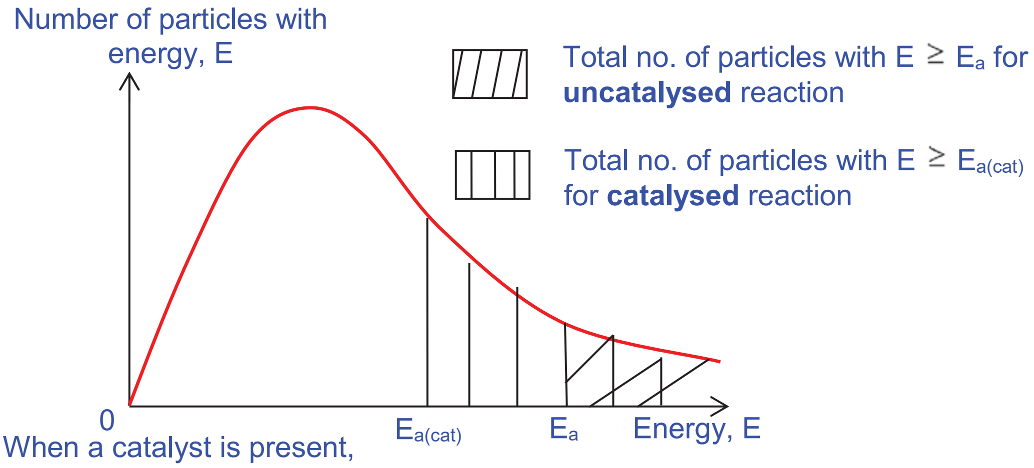
rate = $k\mathbf{K}[NO]^2[H_2] = k'[NO]^2[H_2]$

where $k' = k\mathbf{K}$

(ii) Draw the probable energy profile diagram for this overall exothermic reaction. [2]



(iii) Using an appropriate sketch of the Maxwell–Boltzmann distribution curve, explain how the addition of platinum affects the rate of chemical reaction. [3]



When a catalyst is present,

-**activation energy is lowered**

-**more reactant particles with energy ≥ $E_{a(cat)}$**

-**more effective collisions**

-**rate of reaction is proportional to the frequency of effective collisions**

rate of reaction increases

(c) The NO_2 reacts with O_2 in the atmosphere to form colourless nitrogen pentoxide, N_2O_5 in equilibrium.

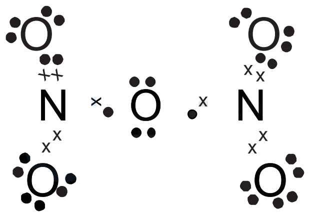
$$4\ NO_2\ (g) + O_2\ (g) \rightleftharpoons 2\ N_2O_5(g)$$

Dinitrogen pentoxide is a rare example of a compound that adopts two structures depending on the conditions. As a gas in the atmosphere, dinitrogen pentoxide exists as a molecule. However, it exists as an ionic salt in the solid state.

(i) Gaseous N_2O_5 is a symmetrical molecule with the two nitrogen atoms bonded to one central oxygen atom.

Draw a dot-and-cross diagram to show the bonding in N_2O_5 molecule. Use your diagram to:

- State the shape and the bond angle with respect to nitrogen
- Suggest with reasoning, the polarity of the molecule. [3]



O–N–O bond angle is **120°**, **trigonal planar**

N_2O_5 is **polar**. The centre O atom is bent. Hence the **dipole moment does not cancel out/ there is net dipole moment.**

(ii) A ratio of 4 to 1 mole of gaseous NO_2 and O_2 with a total initial pressure of 2.25 atm was placed in a 1000 cm^3 vessel. The total pressure at equilibrium was 1.5 atm. Calculate K_p for this equilibrium. [3]

Initial pressures
$P_{NO2} = 4/5 \times 2.25 =$ **<u>1.8 atm</u>**
$P_{O2} = 1/5 \times 2.25 =$ **<u>0.45 atm</u>**

	$4\ NO_2(g)$	+	$O_2(g)$	$\rightleftharpoons$	$2\ N_2O_5(g)$
Initial P/ atm	1.8		0.45		0
Change P / atm	$-2x$		$-0.5x$		$+x$
Eqm P / atm	$1.8 - 2x$		$0.45 - 0.5x$		$+x$

$P_{total} = 1.8 - 2x + 0.45 - 0.5x + x = 1.5$ atm
$x = 0.500$ atm

$$K_p = \frac{P(N_2O_5)^2}{P(O_2)\ P(NO_2)^4}$$

$$K_p = \frac{0.50^2}{0.2 \times 0.8^4}$$

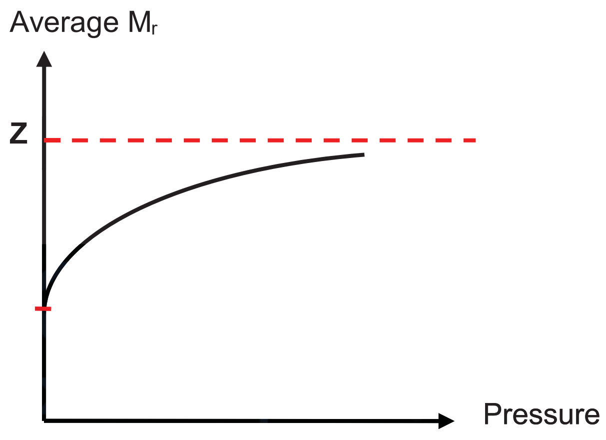
$K_p =$ **<u>3.05 atm^{-3}</u>**

(iii) Calculate the average M_r of the gases at equilibrium. [1]

Average M_r = Sum of mole fraction x M_r

$$= \frac{0.5}{1.5} \times 108.0 + \frac{0.2}{1.5} \times 32.0 + \frac{0.8}{1.5} \times 46.0 = \underline{\mathbf{64.8}}$$

(iv) The variation of M_r is as shown in the sketch.



Predict a value for **Z** and account for the shape of the graph. [2]

Z = 108.0

By LCP, as pressure increases, the **<u>position of equilibrium would shift right</u>** to **<u>decrease the amount of gas</u>**. Hence, more N_2O_5 will be produced as **<u>average M_r increases</u>**.

A curve with decreasing rate and not straight line is obtained as the rate of N_2O_5 formation decreases with decreasing NO_2 and O_2. Also, the repulsion increases as NO_2 and O_2 molecules are forced closer together with increasing pressure, resulting in a gentler gradient.

The **maximum M_r approaches 108.0** but does not reach 108 as the **equilibrium mixture must always contain all three gases**.

(d) Solid N_2O_5 dissolved in chloroform may be used to replace concentrated nitric acid and sulfuric acid in the nitration of benzene.

(i) Suggest why solid N_2O_5 can be used in for nitration of benzene. [1]

$[NO_2^+][NO_3^-]$

N_2O_5 contains nitronium ion, **NO_2^+** which is an **electrophile** in the electrophilic substitution of benzene.

(ii) 0.60 mol of solid N_2O_5 was dissolved in chloroform. Some N_2O_5 decompose back into oxygen and nitrogen dioxide with a rate constant of $1.0 \times 10^{-5}\ s^{-1}$ at 45 °C.

The gases produced are collected in a 10 dm^3 container over a period of 40 hours. Calculate the resultant pressure.

[Assume that the products do not dissolve in chloroform.] [3]

Since decomposition follows a first order w.r.t. N_2O_5 (based on units of k)

$$t_{1/2} = \frac{\ln 2}{k} = \frac{\ln 2}{1.0 \times 10^{-5}} = 6.931 \times 10^4\ s$$

$$\text{Number of } t_{1/2} = \frac{40 \times 60 \times 60}{6.931 \times 10^4} = \underline{\mathbf{2.08}}$$

$N_2O_5 \rightarrow 2\ NO_2 + \frac{1}{2}\ O_2$

After 40 hours, 0.60 x 0.75 = **0.45 mol** of N_2O_5 has decomposed.

$n_{(\text{gaseous products})} = 2(0.45) + \frac{1}{2}(0.45) = 1.125$ mol

$pV = nRT$

$$p = \frac{1.125 \times 8.31 \times 318}{10 \times 10^{-3}} = \mathbf{2.97 \times 10^5\ Pa} = 2.97\ \text{bar}$$

Alternative answer

$$n_{N2O5} = 0.60\left(\frac{1}{2}\right)^{2.08} = 0.1419$$

After 40 hours, 0.60 – 0.1419 = 0.4581 mol of N_2O_5 has decomposed.

$n_{(\text{gaseous products})} = 2(0.4581) + \frac{1}{2}(0.4581) = 1.145$ mol

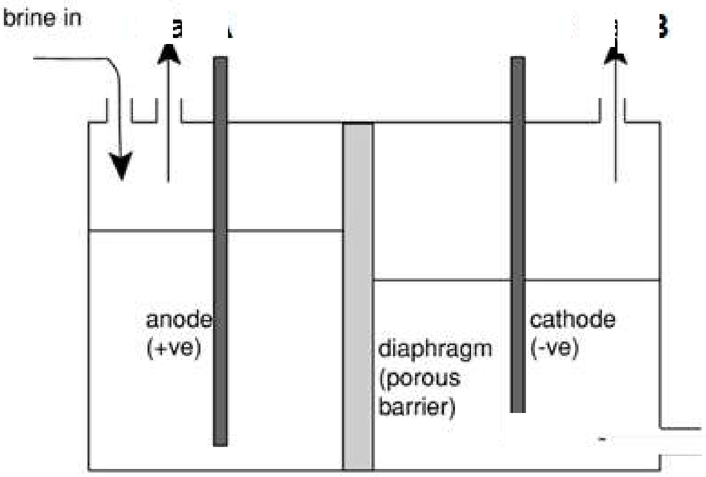
$$p = \frac{1.145 \times 8.31 \times 318}{10 \times 10^{-3}} = \mathbf{3.03 \times 10^5\ Pa} = 3.03\ \text{bar}$$

[Total : 23]

2 Chlorine is a yellow-green gas that was first synthesised around 1630. Chlorine forms a variety of oxides such as chlorate(VII), ClO_4^- and chlorate(V), ClO_3^-.

(a) Chlorine gas can be produced from the electrolysis of brine (concentrated sodium chloride solution) using a diaphragm cell with inert electrodes.

A diaphragm is used to keep the products of electrolysis from mixing and hence, prevent the formation of undesirable by-products.



(i) Write the ion-electron half-equations, with state symbols, for the reactions taking place at the electrodes. [2]

Cl^- (anion) would migrate to the anode and be oxidised to Cl_2 gas.

Anode reaction: $2Cl^- (aq) \rightarrow Cl_2 (g) + 2e$

Cathode reaction: $2\underline{H_2O} (l) + 2e \rightarrow H_2 (g) + 2OH^- (aq)$

(ii) Calculate the mass of chlorine gas produced if a current of 5 A was passed for 7 hours through the electrolytic cell. [2]

$Q = I \times t = 5 \times 7 \times 60 \times 60 = 1.26 \times 10^5$ C

$Q = n_e \times F$

Amount of electrons passed = $\dfrac{1.26 \times 10^5}{96500}$ = 1.306 mol

Amount of chlorine = $\dfrac{1.306}{2}$ = 0.653 mol

Mass of chlorine produced = 0.653 x 2 x 35.5 = **<u>46.4 g</u>**

(b) In some industrial electrolytic cells, the products of electrolysis of brine are allowed to react further when the diaphragm is removed. Two chlorine-containing products are formed, depending on the operating conditions used. At low temperatures, one of the products is a chloro-oxoanion with an oxidation state of +1.

(i) State the type of reaction taking place. [1]

Disproportionation

(ii) Give an overall balanced equation for the reaction described above. [1]

$Cl_2 + 2e \rightarrow 2Cl^-$ ---(1)

$Cl_2 + 4OH^- \rightarrow 2ClO^- + 2H_2O + 2e$ ----(2)

Overall: $\mathbf{Cl_2\,(g) + 2OH^-\,(aq) \rightarrow Cl^-\,(aq) + ClO^-\,(aq) + H_2O\,(\mathit{l})}$

(c) With reference from the Data Booklet, explain why dilute aqueous sodium chloride cannot be used as the electrolyte for the manufacture of chlorine in this electrolysis. [1]

$Cl_2 + 2e^- \rightleftharpoons 2Cl^-$ $E^\ominus = +1.36$ V -----(1)

$O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O$ $E^\ominus = +1.23$V ---(2)

When dilute sodium chloride is used, the $E^\ominus$ (O_2/H_2O) is less positive than $E^\ominus$ (Cl_2/Cl^-) and H_2O is preferentially oxidised at the anode to give O_2 gas, instead of chlorine gas.

(d) The standard electrode potentials, $E^\ominus$, and standard Gibbs free energy changes, $\Delta G^\ominus$, of different chlorine-containing species are tabulated below.

	Half-equation	**$E^\ominus$ / V**	**$\Delta G^\ominus$ / kJ mol^{-1}**
1	$ClO_4^- + 2H^+ + 2e^- \rightleftharpoons ClO_3^- + H_2O$	+1.19	–230
2	$2ClO_3^- + 12H^+ + 10e^- \rightleftharpoons Cl_2 + 6H_2O$	+1.47	**?**
3	$Cl_2 + 2e^- \rightleftharpoons 2Cl^-$	+1.36	–262

These electrode potentials can be summarised using the Latimer diagram shown below. In a Latimer diagram, the most highly oxidised form of the element is on the left, with successively lower oxidation states to the right. The electrode potentials are shown on the arrows.

$$\begin{tikzcd}
ClO_4^- \arrow[r, "+1.19\text{ V}"] & ClO_3^- \arrow[r, "+1.47\text{ V}"] \arrow[rr, bend right, "+1.45\text{ V}"'] & Cl_2 \arrow[r, "+1.36\text{ V}"] & Cl^-
\end{tikzcd}$$

(i) Calculate ΔG° for half-equation 2. [1]

$2ClO_3^- + 12H^+ + 10e^- \rightleftharpoons Cl_2 + 6H_2O$

$\mathbf{\Delta G^\ominus = -nFE^\ominus}$

$= -(10)(1.47)(96500) = -1418.6 = \mathbf{-1420\ kJ\ mol^{-1}}$

(ii) The standard electrode potential of converting ClO_3^- to Cl^- is found to be +1.45 V, instead of +2.83 V. The number of electrons transferred in each step must be taken into account.

I: Write a half-equation for the conversion of ClO_3^- to Cl^-

II: Using your knowledge of Hess' Law for $\Delta G^\ominus$ and your answer to **(d)(i)**, show with the aid of an energy cycle that the $E^\ominus$ for the conversion of ClO_3^- to Cl^- is +1.45 V.

[4]

I : $2ClO_3^- + 12H^+ + 12e^- \rightarrow 2Cl^- + 6H_2O$

Or

$ClO_3^- + 6H^+ + 6e^- \rightarrow Cl^- + 3H_2O$

$$\begin{tikzcd}
2ClO_3^-\,(aq) + 12H^+\,(aq) + 12e^- \arrow[rr, "\Delta G^\ominus = ?"] \arrow[dr, "\textbf{Ans from (b)(i)}\ \ \Delta G^\ominus = -1418.6\ kJ\ mol^{-1}"'] & & 2Cl^-\,(aq) + 6H_2O\,(l) \\
& Cl_2\,(g/aq) + 2e^- + 6H_2O\,(l) \arrow[ur, "\Delta G^\ominus = -262\ kJ\ mol^{-1}"'] &
\end{tikzcd}$$

Applying Hess Law,

$\Delta G^\ominus = -1418.6 + (-262) = \underline{\mathbf{-1680.6\ kJ\ mol^{-1}}}$

$E^\ominus = -[-1680.6 \times 10^3 / (12 \times 96500)] = \underline{\mathbf{+1.45\ V}}$ (shown)

(iii) With the help of the Latimer diagram provided, calculate $E^\ominus_{cell}$ of the reaction below. Hence, determine its $\Delta G^\ominus_{cell}$.

$$4ClO_3^-(aq) \longrightarrow 3ClO_4^-(aq) + Cl^-(aq)$$

[2]

Using Latimer diagram: $E^\ominus_{cell} = +1.45 - (+1.19) = \underline{\mathbf{+0.26\ V}}$

1 ClO_3^- ion is reduced to Cl^-, gaining 6 electrons.
3 ClO_3^- ions are oxidised to 3 ClO_4^- ions, losing 3 x 2 = 6 electrons
Amount of electrons transferred = 6 mol
$\Delta G^\ominus_{cell} = -(6)(96500)(+0.26) = \underline{\mathbf{-151\ kJ\ mol^{-1}}}$

(iv) With reference to the *Data Booklet*, predict what will happen when an excess of acidified hydrogen peroxide solution is added to a solution of Cl^-(aq). [3]

$H_2O_2 + 2H^+ + 2e^- \rightleftharpoons 2H_2O$	(+1.77)
$Cl_2 + 2e^- \rightleftharpoons 2Cl^-$	(+1.36)
$2ClO_3^- + 12H^+ + 10e^- \rightleftharpoons Cl_2 + 6H_2O$	(+1.47)
$ClO_4^- + 2H^+ + 2e^- \rightleftharpoons ClO_3^- + H_2O$	(+1.19)

$H_2O_2\,(aq) + 2H^+\,(aq) + 2Cl^-\,(aq) \rightarrow Cl_2\,(aq) + 2H_2O\,(l)$
$E^\circ_{cell} = (+1.77) - (1.36) = \mathbf{+0.41\ V} > 0$ ∴ reaction is feasible.

$Cl_2\,(aq) + 5H_2O_2\,(aq) \rightarrow 2ClO_3^-\,(aq) + 4H_2O\,(l) + 2H^+\,(aq)$
$E^\circ_{cell} = (+1.77) - (+1.47) = \underline{\mathbf{+0.30\ V}} > 0$ ∴ reaction is feasible.

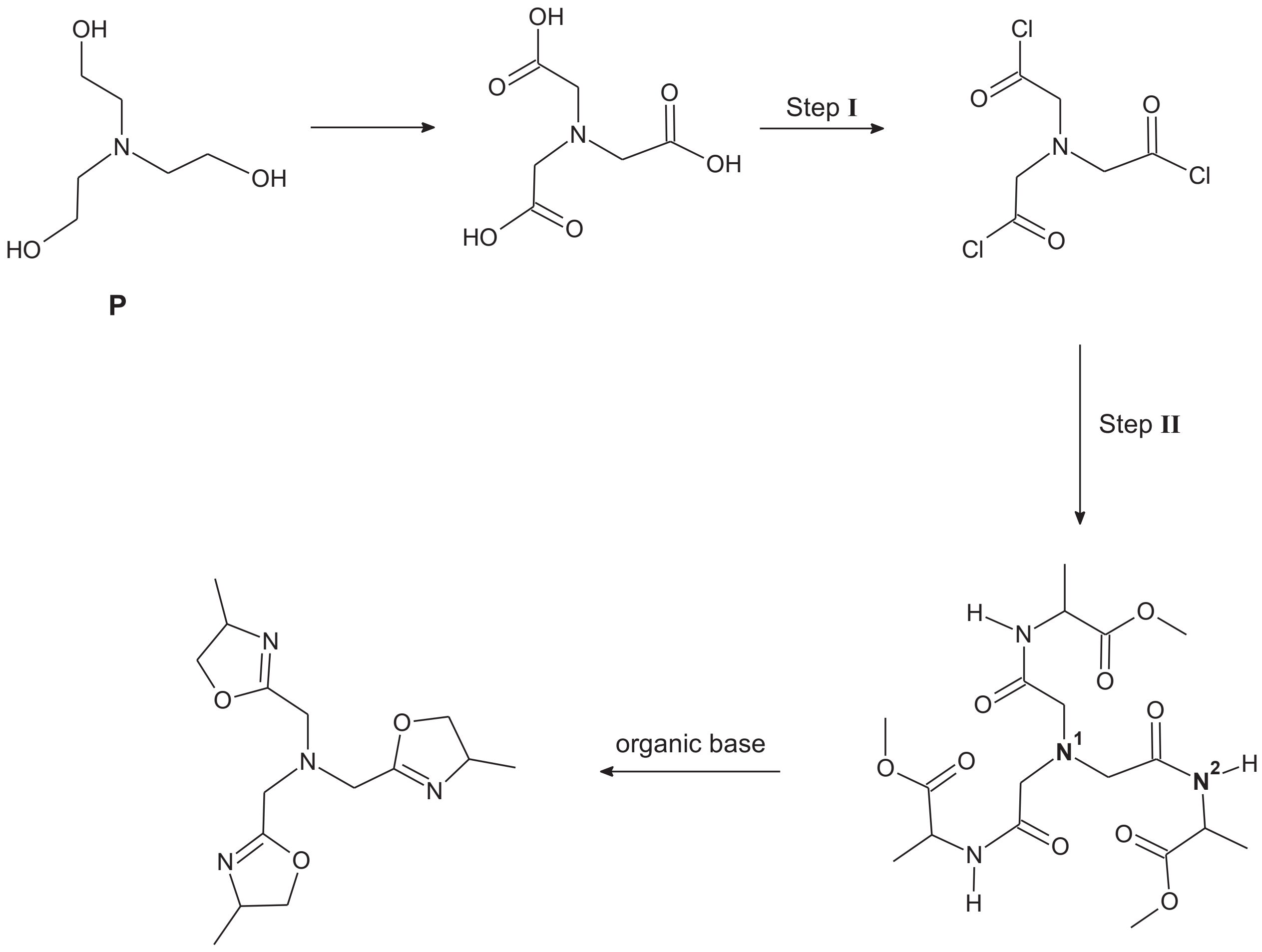
$H_2O_2\,(aq) + ClO_3^-\,(aq) \rightarrow H_2O\,(l) + ClO_4^-\,(aq)$
$E^\circ_{cell} = (+1.77) - (+1.19) = \underline{\mathbf{+0.58\ V}} > 0$ ∴ reaction is feasible.

Cl^- will be oxidised to Cl_2, then to ClO_3^- and finally to ClO_4^- while H_2O_2 will be reduced to H_2O.

[Total: 17]

3 Trisoxazoline are organic molecules that can function as ligands. Despite their huge molecular structure, they are able to form stable complexes with metals. Metal complexes with trisoxazoline are commonly used as catalyst in organic synthesis.

(a) The reaction scheme below illustrates the synthesis of trisoxazoline.



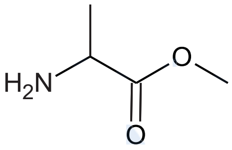
P

R

Trisoxazoline
($C_{15}H_{24}N_4O_3$)

(i) Suggest the reagents and conditions required for step **I** and step **II**. [2]

Step I: **PCl_5(s), rtp or PCl_3(s), rtp or $SOCl_2$(*l*), rtp**

Step II: 

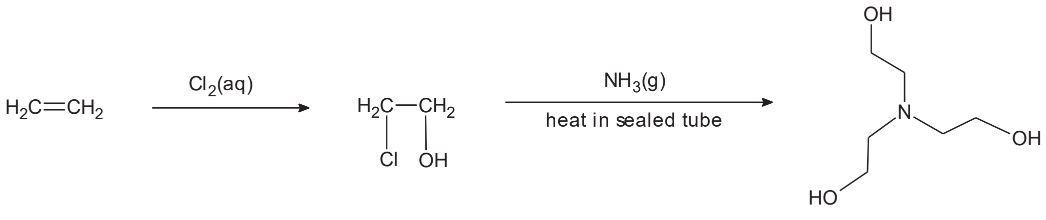
, rtp

(ii) Explain the difference in basicity for N^1 and N^2 present in **R**. [2]

N^2 on amide is <u>neutral</u> as the **<u>lone pair of electrons is delocalised with the π-electrons of C=O</u>**. Hence lone pair of electrons not available to form dative bond with proton.

N^1 atom is <u>basic</u> as **<u>the lone pair of electrons is available to form dative bond with proton</u>**.

(iii) Propose a 2-step reaction scheme to synthesise compound **P** from ethene. [2]



P

Trisoxazolines are usually applied to transition metals, such as copper, to form complexes. These complexes are useful in advanced organic synthesis to make specific isomers.

Table 1 shows some properties of the copper complexes, where K_{stab} refers to the stability constant of the complex, e.g.

$$Cu^{2+} + L \rightleftharpoons [CuL]^{2+}$$

$$K_{stab} = \frac{[CuL]^{2+}}{[Cu^{2+}][L]}$$

Table 1

Complex	log(K_{stab})	Colour	Shape of complex
copper(II)-trisoxazoline	12.9	green	distorted tetrahedral
copper(II)-EDTA	18.8	blue	octahedral
copper(II)-en	18.7	violet	octahedral

(b) Describe the feature of the trisoxazoline molecule that enable it to act as polydentate ligand. Hence, state the type of bond formed between the ligand and the central Cu(II) ion and give the coordination number of the complex. [2]

The presence of 4 **<u>N atoms with lone pairs available</u>** to form **<u>dative bonds</u>** with metal centre. Coordination number is **<u>4</u>**

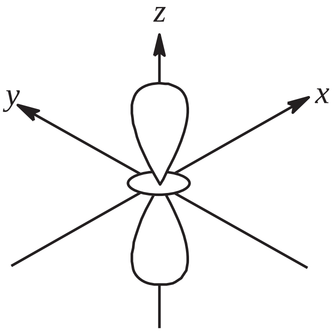
(c) **(i)** Using copper(II)-EDTA as an example, explain why the five d-orbitals are split into two different energy levels. [2]

The lone pair of electrons on EDTA approaches the Cu^{2+} along the axis of octahedral complex.

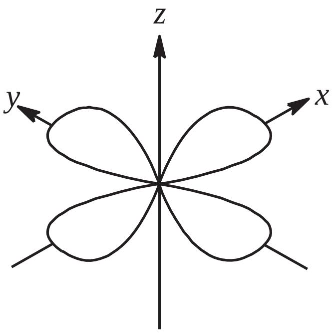
The d_{x2-y2} and d_{z2} orbitals lie along the **<u>x, y, z axis</u>** will experience **<u>greater inter-electronic repulsion</u>** as the **<u>electrons</u>** in these **<u>d orbitals are pointing towards the lone pairs of electrons from EDTA</u>**.

Hence, the five d orbitals will be split into 2 energy levels - the d_{xy}, d_{yz} and d_{xz} orbitals at a **<u>lower energy level</u>** and the d_{z2} and d_{x2-y2} orbitals at a higher energy level.

(ii) Draw the shapes of the d-orbitals at the higher energy level. [1]



d_{z^2}



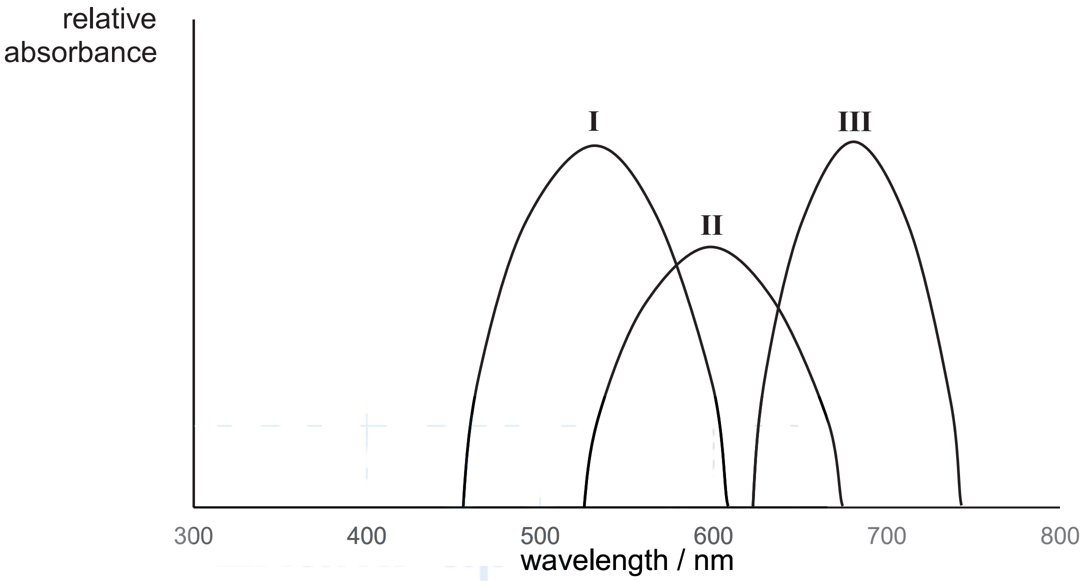
$d_{x^2-y^2}$

(iii) Explain why the copper(II) complexes are coloured. [3]

Presence of ligands **splits the d-orbitals into 2 energy levels**.
1 of the d-electrons **absorbs certain wavelength from the visible light spectrum** and undergoes **d-d transition**.

The d-electron is promoted to a higher energy level. The **remaining wavelengths are transmitted and the complementary colour of the wavelength absorbed is observed**.

(iv) The visible absorption spectrum of the three complexes is shown below where each peak represents one complex.
[A visible absorption spectrum is a graph depicting the absorption of radiation by a material over a range of visible light wavelengths.]



Identify the copper(II) complex responsible for each absorption peak. Hence, arrange the three complexes in order of increasing magnitude of their energy gap. [2]

I: copper(II)-en
II : copper(II)-EDTA
III : copper(II)-trisoxazoline
Since $\Delta E \propto \frac{1}{\lambda}$, energy gap in increasing order:
copper(II)-trisoxazoline < copper(II)-EDTA < copper(II)-en

(d) Using Table 1, comment on the spontaneity of forming the respective copper(II) complexes. [2]

$\Delta G^\ominus = -RT \ln K$

K_{stab}: copper(II)-EDTA > copper(II)-ethylenediamine > copper(II)-trisoxazoline

Magnitude of $\Delta G^\ominus$:

copper(II)-EDTA > copper(II)-ethylenediamine > copper(II)-trisoxazoline

spontaneity: **Cu(II)-EDTA > Cu(II)-en > Cu(II)-trisoxazoline**

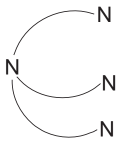
(e) Other than copper(II) ions, it was found that copper(I) ions are also able to form complexes with trisoxazoline.

(i) Predict and explain the colour of solid copper(I)-trisoxazoline complex. [1]

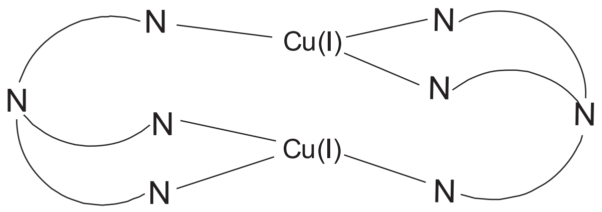
White. The **d-orbitals are fully filled** in copper(I), **no d-d transition**.

(ii) Analysis was done on copper(I)-trisoxazoline complex. The relative molecular mass of the complex was apparently 743.0. Further analysis showed that each copper(I) ion is bonded to three nitrogen atoms.

Propose the structure of copper(I)-trisoxazoline complex.

[You may use  to represent trisoxazoline.]

[1]



[Total: 20]

Section B

4 **(a)** At r.t.p, 1.2 dm^3 of chlorine gas is reacted with 6.7 g of compound **A**, $C_9H_{10}O$, to give compound **B**. On addition of PCl_5, **A** gives white fumes. Treatment of **A** with NaBr and concentrated H_2SO_4 under reflux gives a mixture of compounds **C** and **D**. **C** and **D** have the same molecular formula $C_9H_{10}Br_2$ and each contains only *one* chiral centre.

(i) When NaBr is mixed with concentrated H_2SO_4, the following observations are made.

- White fumes produced
- Reddish brown liquid formed
- Pungent gas decolourised purple $KMnO_4$

It is suggested that a displacement reaction occurred first, producing white fumes. Some of the white fumes further react with H_2SO_4 via a redox reaction. Using the above information, write the two corresponding chemical equations for this reaction. [2]

$NaBr + H_2SO_4 \rightarrow HBr + NaHSO_4$
$2HBr + H_2SO_4 \rightarrow Br_2 + SO_2 + H_2O$

(ii) Using your answer in **(a)(i),** deduce the identities of **A** to **D**. [5]
Amt of A = 6.7/134 = 0.05 mol
Amt of Cl_2 = 1.2/24 = 0.05 mol

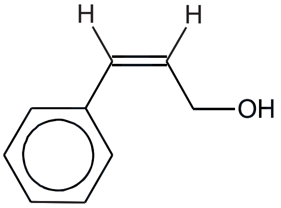
A has similar ratio of C and H atoms, and no. of C > 6
➔ **A** contains a benzene ring

A undergoes **electrophilic addition** with chlorine gas
➔ **A** contains **1 alkene** functional group (or C=C) and **B** is a **halogenoalkane/chloroalkane**

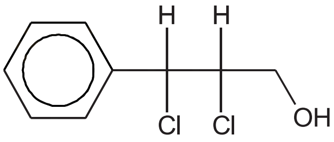
A undergoes **nucleophilic substitution** with PCl_5 to give white fumes of HCl
➔ **A** is an **alcohol**

A undergoes both **electrophilic addition and nucleophilic substitution** to give **C** and **D**.
Since **C** and **D** each only contains 1 chiral centre,

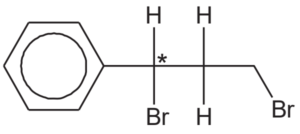
A can only be



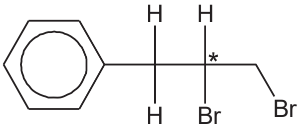
B:



C and **D**:



(major)



(minor)

(iii) Account for the relative quantity of compound **C** and **D** formed. [1]

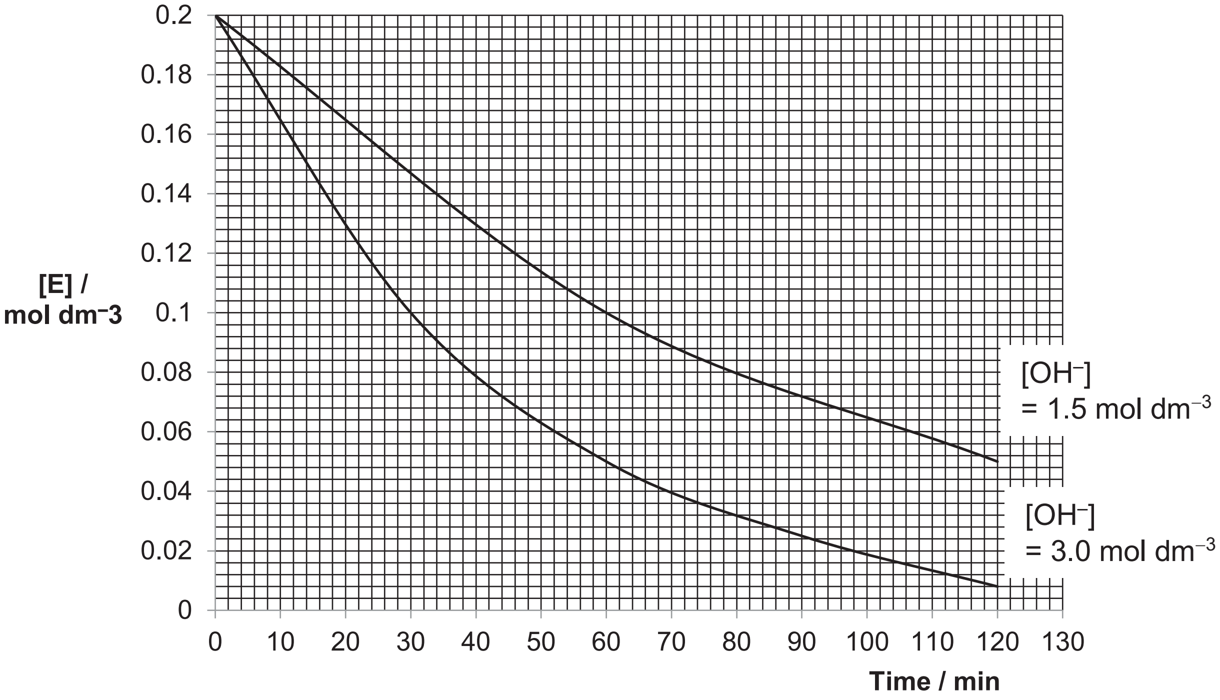
Compound **C** is the major product while **D** is the minor product.

For compound **D**, the benzylic **carbocation intermediate is more stable** due to **resonance / positive charge dispersed into the benzene ring.**

(b) **E** is another constitutional isomer of **C** and **D**.
A series of chemical experiments were conducted on **E**.

Experiment 1:

The reaction kinetics of **E** with aqueous sodium hydroxide was determined by monitoring the change in concentration of **E** with time.



Experiment 2:

0.2 mol of **D** and **E** were treated separately with boiling aqueous sodium hydroxide. The products from each compound were then acidified with nitric acid and then treated with silver nitrate solution.

The results obtained are shown below:

	Observation upon adding $AgNO_3$	**Mass of ppt / g**
D	formation of cream-coloured precipitate	75.12
E	formation of cream-coloured precipitate	37.56

(i) Using experiment 1, deduce the rate equation. [3]

using $[OH^-]$ = 3.0 mol dm^{-3} graph,

$t_{1/2}$ is constant at 30 min, reaction is 1st order with respect to E.

OR

using $[OH^-]$ = 1.5 mol dm^{-3} graph,

$t_{1/2}$ is constant at 60 min reaction is 1st order with respect to E.

Using initial rate method,

Initial rate for graph where $[OH^-]$ = 1.5 mol dm^{-3}

= 0.2/110 = 0.001818 mol dm^{-3} min^{-1}

Initial rate for graph where $[OH^-]$ = 3.0 mol dm^{-3}
= 0.2/52 = <u>0.003846 mol dm^{-3} min^{-1}</u>
As $[OH^-]$ increases 2 times, initial rate also increases 2 times
$(\frac{0.004}{0.00211} = 1.90 \approx 2)$

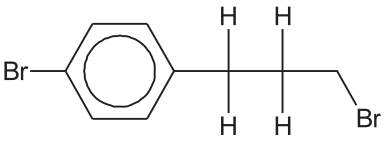
Hence, **order of reaction with respect to OH^- is 1.**
<u>Rate = k [E] $[OH^-]$</u>

(ii) Using Experiment 2 and **(b)(i)**, propose a possible structure of **E** and draw the mechanism for the reaction of **E** with NaOH(aq). [3]

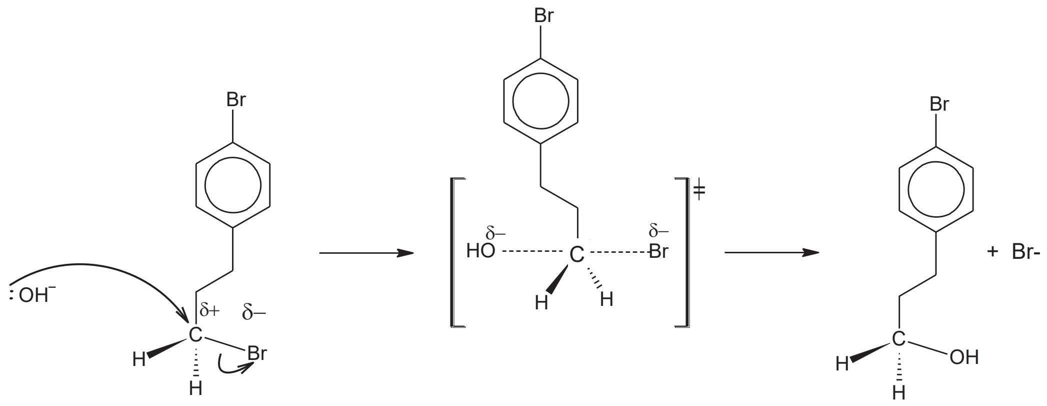
From (b)(ii), E undergoes S_N2 mechanism
→ it is a **1° halogenoalkane**

From expt 2, 0.2 mol of **E** forms 0.2 mol of AgBr
→ There is **only one** Br in the alkyl side chain

E is



(accept any mono substituted position of Br on benzene with 1° or 2° bromoalkane)



(c) Depending on the mechanism, the solvent affects the stability of nucleophile and/or reaction intermediates in the nucleophilic substitution of halogenoalkanes. The table below shows the rate of reaction when different halogenoalkanes and solvents are used.

Solvent	Type	Dielectric constant, ε	Relative rates for reaction with OH^-	
			1° RX in S_N2	3° RX in S_N1
CH_3OH	Protic	33	1	4
H_2O	Protic	78	7	150 000
CH_3COOH	Protic	6	1	1
CH_3COCH_3	Aprotic	21	5000	-

Dielectric constant, ε, is a measure of the solvent polarity and ability to insulate charge.

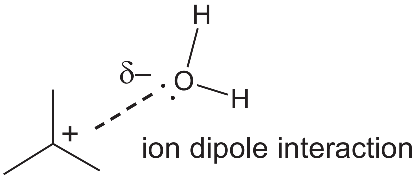
(i) Suggest, using **only** structure and bonding, the difference between *protic* and *aprotic* solvents. [1]

Protic refers to molecules with **<u>H atoms that can be used to form hydrogen bond</u>**. Aprotic solvents can only form **<u>permanent dipole- permanent dipole interactions between molecules/ have no H atoms that can form hydrogen bond</u>**

(ii) Explain the effect of solvent on the relative rate of S_N2 reactions. [2]

For S_N2, protic solvent like water can form **hydrogen bond with OH^-**. Hence **decreasing the nucleophilic ability of OH^-** and lower the rate of reaction.
While aprotic solvent like CH_3COCH_3, do not form hydrogen bond and hence the **lone pair of electron** on **OH^- is more available to attack the electron deficient C on 1° RX.**

(iii) Explain, with an aid of a diagram, how water increases the rate of S_N1 reaction. [2]

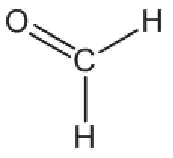


The ion dipole interaction **stabilised the carbocation/reaction intermediate**

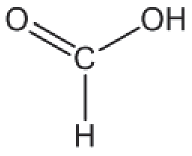
(iv) Name a solvent, other than those given in the table, that will result in a slower rate for S_N1 than ethanoic acid. [1]
Name of any suitable hydrocarbon e.g Benzene, hexane ..etc

[Total: 20]

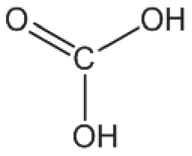
5 **(a)** Using only the elements C, H and O, draw the structural formulae of **three** organic compounds, each containing a single carbon atom with an oxidation state of zero, +2 and +4 respectively. [3]



O.S. = 0



O.S. = +2



O.S. = +4

(b) Hot, concentrated potassium manganate (VII) oxidises several classes of organic compounds to ketones, carboxylic acids or carbon dioxide. By this means, the structures of compounds can be determined. Some compounds are easily oxidised, while others require longer heating.

The following describes some reactions of compounds **F** and **K**, and of their oxidation products.

F, $C_8H_{12}O$ reacts with excess potassium manganate (VII) to produce single organic products, **G,** $C_4H_6O_5$ while **K,** $C_{12}H_{12}$**,** reacts with the same reagent to produce **H,** $C_{10}H_{10}O_3$. Carbon dioxide is produced in both reactions in a mole ratio of 2 : 1 respectively. During oxidation of **F**, four moles of carbon dioxide were liberated.

Although **F** reacts with potassium manganate (VII), it gives no reaction with potassium dichromate (VI). When 0.10 mol of **F** is reacted with an excess of sodium metal, 1.2 dm^3 of hydrogen is formed, measured at room temperature and pressure.

G reacts with excess concentrated sulfuric acid to give **I**, $C_4H_4O_4$. Upon further oxidation, **I** is found to give **J,** $C_3H_2O_5$, and an inorganic by-product.

H gives a positive iodoform test and dissolves in aqueous sodium hydroxide. Upon further oxidation of **H**, **L,** $C_9H_6O_6$, and a similar inorganic by-product formed from **I** is also produced.

(i) Deduce the structure of compounds **F** to **L**, explaining the chemistry of the reactions described. [11]

F and **K** undergoes **strong oxidation** with $KMnO_4$ to give **G** and **H**
→ Since there is a decrease in no of C atoms after oxidation, both F and K must contain **alkenes**.

F liberates four mole of carbon dioxide
→ **F** contains (terminal) **alkenes**.

F undergoes **redox** with Na metal
→ 0.10mol ≡ 1.2dm^3 ≡ 1H_2 ≡ 1ROH
→ **F** contains only 1 **alcohol.**

F **does not undergo strong oxidation** with $K_2Cr_2O_7$
→ **F** contains a **tertiary alcohol.**

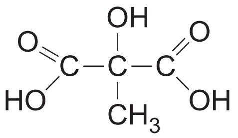
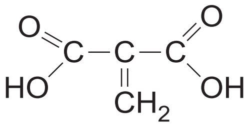
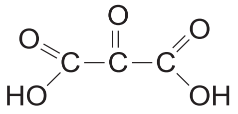
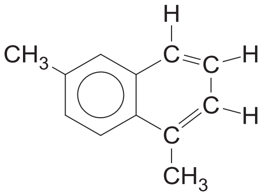
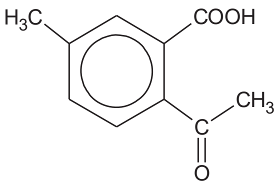
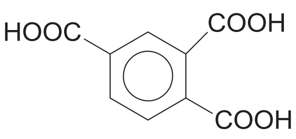
F undergoes **elimination** with excess concentrated sulfuric acid to give **I**, $C_4H_4O_4$
→ **F** contains an **alcohol.**

I further oxidises to give **J,** $C_3H_2O_5$, and an inorganic by-product
→ **I** contains 4 **carboxylic acid** and **CO_2** is the by-product

H undergoes **mild oxidation** with iodoform
→ **H** contains a **terminal methyl ketone**
(since it is an [O] product, it cannot be a methyl carbinol)

H dissolves in aqueous sodium hydroxide.
→ **H** contains an **acidic group** (i.e. – COOH)

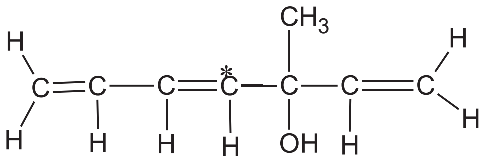
L is an oxidised product
→ **L** contains a **tricarboxylic acid** and the inorganic product is **CO_2**.

		
G	**I**	**J**
		
K	**H**	**L**

Note : methyl group can be on any position

(ii) State the type(s) of stereoisomerism shown by compound **F** and give one further piece of relevant information about it. [2]

F:



Enantiomerism:
F has **no plane of symmetry. OR**
F **rotates plane polarised light. OR**
F has a pair of **non-superimposable images.**

Cis-trans:
Restricted rotation about C=C OR
two different substituents about each C on C=C

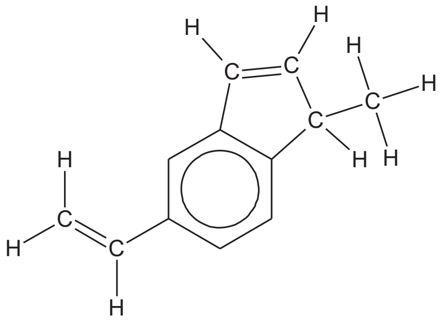
(iii) Hence, predict the total number of isomers shown by **F**. [1]

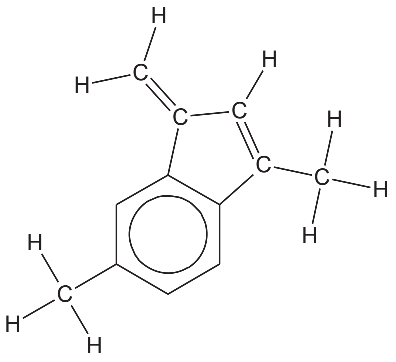
no of enantiomers present = **4**

(iv) When compound **K** undergoes prolonged heating with $KMnO_4$ to give **L**, **K** exhibits **two** types of constitutional isomerism.

Name the specific types of isomerism shown by compound **K** and hence, draw the **displayed formulae** of the isomers. [3]

Positional and Chain isomerism





[Total : 20]

SERANGOON JUNIOR COLLEGE
General Certificate of Education Advanced Level
Higher 2

CANDIDATE NAME	
CLASS	

CHEMISTRY

9729/04

JC2 Preliminary Examination **25 Aug 2017**

Paper 4 Practical **2 hr 30 min**

Candidates answer on the Question Paper

Additional Materials:

READ THESE INSTRUCTIONS FIRST

Write your name and class on all the work you hand in.
Give details of the practical shift and laboratory in the boxes provided.
Write in dark blue or black pen on both sides of the paper.
You may use a soft pencil for any diagrams, graphs or rough work.
Do not use staples, paper clips, highlighters, glue or correction fluid.

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

The use of an approved scientific calculator is expected, where appropriate.
You may lose marks if you do not show your working or if you do not use appropriate units.
Qualitative Analysis Notes are printed on pages ______

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

Shift
Laboratory

For Examiner's Use	
1	
2	
3	
4	
TOTAL	**/ 55**

This document consists of ___ printed pages and ___ blank page.

1 You are to determine the concentration of aqueous copper(II) sulfate by titration. The concentration of Cu^{2+} ions in a solution can be found by reaction with an excess of aqueous iodide ions to produce iodine. The amount of iodine formed can be found by titration with thiosulfate ions, $S_2O_3^{2-}$.

FB 1 is aqueous copper(II) sulfate, $CuSO_4$.
FB 2 is 0.100 mol dm^{-3} sodium thiosulfate, $Na_2S_2O_3$.
FB 3 is aqueous potassium iodide, KI.
starch indicator

(a) Method

(i)
1. Fill the burette with **FB 2**.
2. Using a pipette, transfer 25.0 cm^3 of **FB 1** into a conical flask.
3. Use an appropriate measuring cylinder, transfer 10 cm^3 of **FB 3** to the same conical flask.
4. Titrate this mixture with **FB 2** until the colour of the mixture changes from brown to yellow-brown. An off-white precipitate will also be present in the flask throughout the titration.
5. Add 5 drops of starch indicator.
6. Continue the titration until the blue-black colour of the starch-iodine complex just disappears leaving the off-white precipitate.
7. Record your titration results in the space provided below. Make certain that your recorded results show the precision of your working.
8. Repeat points **1** to **7** as necessary until consistent results are obtained.

Results

Initial burette reading / cm^3	0.00	0.00
Final burette reading / cm^3	25.10	25.10
Volume of **FB 2** used / cm^3	25.10	25.10

[5]

(ii) From your titrations, obtain a suitable volume of **FB 2** to be used in your calculations. Show clearly how you obtained this volume.

$$\text{Volume of FB 2} = \frac{25.10 + 25.10}{2} = 25.10\ \text{cm}^3$$

volume of **FB 2** = ...[1]

(b) (i) The equations for the formation of iodine and its reaction with thiosulfate ions are given below.

$$2Cu^{2+} + 4I^- \rightarrow 2CuI + I_2$$
$$I_2 + 2S_2O_3^{2-} \rightarrow S_4O_6^{2-} + 2I^-$$

Calculate the amount of thiosulfate ions, $S_2O_3^{2-}$, present in the volume of **FB 2** in **(a)(ii)**.

amount of $S_2O_3^{2-}$ = $\frac{0.1 \times (a)(ii)}{1000} = \frac{0.1 \times 25.10}{1000}$ = 2.51×10^{-3} mol

amount of $S_2O_3^{2-}$ = ...[1]

(ii) Using the equations above, calculate the amount of Cu^{2+} ions present in 25.0 cm^3 of **FB 1**.

$2S_2O_3^{2-} \equiv I_2 \equiv 2Cu^{2+}$

amount of Cu^{2+} = (b)(i) = 2.51×10^{-3} mol

amount of Cu^{2+} = ...[1]

(iii) Calculate the concentration, in mol dm^{-3}, of copper(II) sulfate in **FB 1**.

concentration of $CuSO_4$ = $\frac{(b)(ii) \times 1000}{25.0} = \frac{2.51 \times 10^{-3} \times 1000}{25.0}$

= 0.100 mol dm^{-3}

concentration of $CuSO_4$ = ...[1]

(c) Two students repeated the experiment but each obtained different values for the concentration of $CuSO_4$.

The students each suggested possible improvements.

Student 1 suggested that a larger volume of potassium iodide, **FB 3**, should be added. Student 2 suggested that the contents of the conical flask should be filtered before titration.

Comment on the effectiveness of **each** of these possible improvements.
Explain your answers.

Student 1 No effect because KI (FB 3) already in excess.

Student 2 Not effective because some iodine stays on the filter paper.

[2]

(d) The maximum error in each burette reading is ± 0.05 cm^3.
The maximum error in each titration is therefore ± 0.10 cm^3.
The 25.0 cm^3 pipette used in this titration, is labelled with an error of ± 0.06 cm^3.

Explain why the maximum error when 25.0 cm^3 of solution is run from a pipette is only ± 0.06 cm^3 and not $\pm 0.12 cm^3$.

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

The mark on the pipette was only read once.
…………………………………………………………………………………………………....

[1]

(e) Considering the maximum errors from pipette and burette, calculate the total percentage error in one titration.

error from pipette = $\frac{0.06}{25.0} \times 100\%$ = 0.24%
% error from burette = $\frac{2 \times 0.05}{25.70(volume\ from\ 1\ titration)} \times 100\%$ = 0.39%
Total % error = 0.24 + 0.39 = 0.63%

[2]
[Total: 14]

2 You are to determine the enthalpy change of reaction, ΔH, for the reaction shown below.

$$Cu(s) + H_2SO_4(aq) \rightarrow CuSO_4(aq) + H_2(g)$$

Since copper is an unreactive metal it does not react directly with dilute acids. You will therefore need to find the enthalpy change of reaction for two reactions that do occur. The equations for these two reactions are below.

$Mg(s) + H_2SO_4(aq) \rightarrow MgSO_4(aq) + H_2(g)$ **Reaction 1**

$Mg(s) + CuSO_4(aq) \rightarrow MgSO_4(aq) + Cu(s)$ **Reaction 2**

You will carry out experiments to find the enthalpy changes for each of **Reaction 1** and **Reaction 2** and use these values to calculate the enthalpy change for the reaction of copper with sulfuric acid.

TURN OVER FOR EXPERIMENTAL METHOD

Determining the enthalpy change for Reaction 1

$Mg(s) + H_2SO_4(aq) \rightarrow MgSO_4(aq) + H_2(g)$ **Reaction 1**

I (a) Method

FB 4 is 1.00 mol dm^{-3} sulfuric acid, H_2SO_4.
FB 5 is magnesium powder, Mg.

Read through the method before you start any practical work and prepare a suitable table for your results.

1. Weigh the stoppered weighing bottle containing **FB 5**. Record the mass.
2. Support the styrofoam cup in the 250cm^3 beaker.
3. Use the measuring cylinder to transfer 25cm^3 of **FB 4** into the styrofoam cup.
4. Measure the temperature of **FB 4** in the styrofoam cup and start the stop watch. Record this temperature as being the temperature at time = 0.
5. Measure, and record, the temperature of this **FB 4** every half minute for 2 minutes.
6. At time = 2.5 minutes, add **FB 5** to the acid and stir carefully to reduce acid spray.
   ****Caution : Inhalation of the fumes may cause choking.***
7. Measure the temperature of the mixture in the cup at time = 3 minutes and then every half minute up to time = 7 minutes.
8. Continue stirring occasionally throughout this time.
9. Weigh the weighing bottle that had contained **FB 5**. Record the mass.
10. Calculate and record the mass of **FB 5** added to the sulfuric acid.
11. Discard the used styrofoam cup.

Mass of weighing bottle and FB 5 before transfer /g	
Mass of weighing bottle and residual FB 5 /g	
Mass of FB 5 used /g	0.195

Time / min	Temperature / °C
0	
0.5	
1.0	
1.5	
2.0	
2.5	
3.0	
3.5	
4.0	
4.5	
5.0	
5.5	
6.0	
6.5	
7.0	

[5]

(b) **(i)** On the grid below plot a graph of temperature (*y*-axis) against time (*x*-axis).

[2]

(ii) Complete the graph by inserting **two**, **straight** lines of best fit:

- one to show the temperature up to time = 2.5 minutes,
- one to show the temperature after time = 2.5 minutes.

[1]

(iii) From your graph, use the two straight lines of best fit to calculate the change in temperature at time = 2.5 minutes.

temperature change = ... [1]

(c) Calculations

(i) In the reaction in **(a)**, the sulfuric acid was in excess. Without carrying out any additional tests, what observation could you have made during your experiment to confirm this?

All the magnesium / solid dissolved / disappeared or all solid / Mg has gone / been used up or no solid / Mg left

[1]

(ii) Calculate the energy change that occurred during the reaction in **(a)**.

[Assume that 4.2 J is needed to raise the temperature of 1.0cm^3 of solution by 1.0°C.]

Energy change = 25 × 4.2 × b(iii) = XXX J

energy change = ……………………………………[1]

(iii) Use your answer to **(ii)** to calculate the enthalpy change, in kJ mol^{-1}, for the reaction between sulfuric acid and magnesium.

[A_r : Mg, 24.3]

$$Mg(s) + H_2SO_4(aq) \rightarrow MgSO_4(aq) + H_2(g) \quad \textbf{Reaction 1}$$

$$\Delta H = -\frac{(ii) \times 24.3}{1000 \times \text{mass of Mg}} = -\text{xxx kJ mol}^{-1}$$

enthalpy change for **Reaction 1** = ……………………………………[1]

Determining the enthalpy change for Reaction 2

$$Mg(s) + CuSO_4(aq) \rightarrow MgSO_4(aq) + Cu(s) \quad \textbf{Reaction 2}$$

(d) Method

FB 6 is 1.00 mol dm^{-3} copper(II) sulfate, $CuSO_4$.
FB 7 is magnesium powder, Mg.

Read through the method before you start any practical work and prepare a suitable table for your results.

1. Weigh the weighing bottle containing **FB 7**. Record the mass.
2. Support the styrofoam cup in the 250cm^3 beaker.
3. Use the measuring cylinder to transfer 25cm^3 of **FB 6** into the styrofoam cup.
4. Measure the temperature of **FB 6** in the styrofoam cup and record the temperature.
5. Add the **FB 7** to the **FB 6** in the cup and stir the mixture constantly.
6. Measure and record the maximum temperature reached during the reaction.

7. Calculate and record the maximum temperature change that occurred during the reaction.
8. Weigh the weighing bottle that had contained **FB 7**. Record the mass.
9. Calculate and record the mass of **FB 7** added to the copper(II) sulfate.
10. Empty the contents of the styrofoam cup into the bottle labelled **waste**.

Mass of weighing bottle and FB 7 before transfer /g	
Mass of weighing bottle and residual FB 7 /g	
Mass of FB 7 used /g	

Initial temperature / °C	
Maximum temperature / °C	
Maximum temperature change /°C	

[2]

(e) Calculations

(i) Show, using a suitable calculation, that the copper(II) sulfate was in excess in the reaction.

[A_r : Mg, 24.3]

Amount of $CuSO_4$ = $\frac{25 \times 1}{1000}$ = 0.025 mol

Amount of Mg = $\frac{\text{mass of FB 7}}{24.3}$ = xxx mol

Hence $CuSO_4$ is in excess.

[1]

(ii) Hence, calculate the enthalpy change, in kJ mol^{-1}, for the reaction between magnesium and copper(II) sulfate.

[Assume that 4.2 J is needed to raise the temperature of 1.0cm^3 of solution by 1.0°C.]

$$Mg(s) + CuSO_4(aq) \rightarrow MgSO_4(aq) + Cu(s)$$ **Reaction 2**

ΔH = $\frac{25 \times 4.2 \times \Delta T}{\text{amt of Mg from (i)}}$ = xxx kJ mol^{-1}

enthalpy change for **Reaction 2** = ……………………………………[1]

Enthalpy change for Reaction 3

Reaction 3 is shown below.

$Cu(s) + H_2SO_4(aq) \rightarrow CuSO_4(aq) + H_2(g)$ **Reaction 3**

(f) Use your values for the enthalpy changes for **Reactions 1** and **2** to calculate the enthalpy change for **Reaction 3**.

$Mg(s) + H_2SO_4(aq) \rightarrow MgSO_4(aq) + H_2(g)$ **Reaction 1**

$Mg(s) + CuSO_4(aq) \rightarrow MgSO_4(aq) + Cu(s)$ **Reaction 2**

Show clearly how you obtained your answer.

(If you were unable to calculate the enthalpy changes for **Reactions 1** and **2**, you should assume that the value for **Reaction 1** is – 444 kJ mol^{-1} and that the value for **Reaction 2** is – 504 kJ mol^{-1}. Note: these are not the correct values.)

$$\begin{tikzcd}
MgSO_4(aq) + Cu(s) + H_2SO_4(aq) \arrow[rr, "\Delta H \text{ reaction 3}"] & & CuSO_4(aq) + H_2(g) + MgSO_4(aq) \\
& Mg(s) + CuSO_4(aq) + H_2SO_4(aq) \arrow[ul, "\Delta H \text{ reaction 2}"] \arrow[ur, "\Delta H \text{ reaction 1}"'] &
\end{tikzcd}$$

ΔH reaction 3 = ΔH reaction 1 − ΔH reaction 2 = xxx

enthalpy change for **Reaction 3** = ...[1]

(g) **(i)** The method you used to determine the enthalpy change for **Reaction 1** was more accurate than the method you used to determine the enthalpy change for **Reaction 2**. Suggest why the method used for **Reaction 2** was less accurate. Explain your answer.

- Lower ΔH and so higher % error
- No correction made for loss of heat on cooling
- Some bubbles / gas / H2 in reaction 2 so wrong reaction taking place
- Not all Mg reacts / reaction does not go to completion in 2 (so not all energy released)
- Reaction 2 slower so more heat loss

[1]

(ii) A student suggested that the accuracy of the method used for **Reaction 2** could be improved by using a larger volume of copper(II) sulfate. Is this a correct suggestion? Give a reason for your answer.

No, since (larger volume of solution means) smaller ΔT OR
Yes, since there would be a smaller T rise so less heat would be lost.

[1]

[Total: 18]

3 Qualitative Analysis

At each stage of any test, you are to record details of the following.

- Colour changes seen
- The formation of any precipitate
- The solubility of such precipitates in an excess of the reagent added

Where gases are released, they should be identified by a test, described in the appropriate place in your observations.

You should indicate clearly at what stage in a test a change occurs.
No additional tests for ions present should be attempted.

FB 8 is a solution containing 2 cations and 1 anion.

(a)

Test	Procedure	Observation
1	To 1 cm depth of **FB 8** in a test tube, add aqueous ammonia until it is in excess.	• (grey) Green ppt formed, insoluble in excess NH_3. • Green ppt turned brown on contact with air
2	To 1 cm depth of **FB 8** in a **boiling tube**, add aqueous sodium hydroxide until it is in excess. Then heat the boiling tube gently with care. Keep the mixture for **Test 3**.	• Green ppt formed, insoluble in excess NaOH. • Gas evolved that turned moist red litmus paper blue. • Green ppt turned brown (grey) upon heating.
3	To the mixture from **Test 2**, add 1 cm depth of aqueous hydrogen peroxide. Shake the boiling tube gently.	• Ppt / solid turned brown / red-brown. • Effervescence observed. Gas evolved relights a glowing splint / glows brighter.
4	To 1 cm depth of **FB 8** in a test tube, add aqueous barium chloride, followed by dilute hydrochloric acid.	• White ppt formed, insoluble in HC*l*.

[4]

(b) Using your observations above, identify the ions in **FB 8**. Give evidence to support your conclusion.

Fe^{2+}: From Tests 1 and 2, green ppt formed, turned brown on contact with air, insoluble in excess NaOH and NH_3

NH_4^+: From Test 2, gas evolved that turned moist red litmus paper blue when warmed with NaOH.

SO_4^{2-}: From Test 4, white ppt formed when $BaCl_2$ is added, insoluble in HC*l*.

[3]

(c) What type of reaction has taken place in **Test 3**? Explain your answer.

Redox reaction.

Explanation:

- Iron(II) ions converted / oxidised to iron(III) ions
- Hydrogen peroxide converted / reduced to oxygen gas.
- Hydrogen peroxide decomposed to give oxygen gas

[1]

(d) **FB 9** is an aqueous solution, containing one cation and one anion.
Carry out the following tests in test-tubes.
Complete the table by recording your observations.

Test	Procedure	Observations
5	To 1 cm depth of **FB 9**, add aqueous sodium hydroxide until it is in excess.	• No ppt formed.
6	To 1 cm depth of **FB 9**, add a piece of magnesium ribbon.	• Effervescence observed. • Gas evolved extinguished lighted splint with a 'pop' sound.
7	To 1 cm depth of **FB 9** in a test tube, add 2 drops of aqueous silver nitrate, followed by aqueous ammonia until in excess.	• White ppt formed, soluble in NH_3 (aq) to form a colourless solution.

[2]

(e) Using your observations above, identify the ions in **FB 9**. Give evidence to support your conclusion.

H^+: hydrogen gas evolved, extinguished lighted splint with 'pop' sound.
Cl^-: White ppt formed, soluble in NH_3 (aq) to form a colourless solution.

[2]
[Total: 12]

4 Many transition metal complex ions are coloured. It is possible to use this property to determine the concentration of a solution of a coloured ion. A few cm^3 of the solution is placed inside a *spectrometer*.

A *spectrometer* measures the amount of light that is absorbed when a specific wavelength of visible light is shone through a coloured solution. It does this by comparing the amount of light passing through the sample with the amount of light passing through the pure solvent. The amount of light absorbed is expressed as an absorbance value, The more concentrated the solution, the higher the absorbance value.

Beer-Lambert's Law states that the absorbance values, A, is directly proportional to the concentration of absorbing species, c, as shown below. The general Beer-Lambert's Law is usually written as,

$$A = \varepsilon c l$$

Where ε is the molar extinction coefficient and l is the path length, which is usually 1.0cm.

This equation can be used to calculate the absorbance value when the concentration of copper(II) ions is known.

You may assume that you are provided with the following in the subsequent parts of the question.

- **FB1** from Question 1
- solid hydrated copper(II) sulfate, $CuSO_4.5H_2O$;
- access to a spectrometer and instructions for its use;
- graph paper;
- the apparatus and chemicals normally found in a school or college laboratory.

(a) The spectrometer is set to use the wavelength of light that is absorbed most strongly by the copper(II) ions.

Suggest a colour in the visible spectrum from which a suitable wavelength of light might be chosen. Explain your answer.

Orange. Cu^{2+} is blue in colour. Hence, it will absorb colours that are complementary to **blue.**

[1]

(b) Spectrometry can be used to determine the concentration of a solution of aqueous copper(II) sulfate. A series of known, but different, concentrations of copper(II) sulfate is prepared. A spectrometer is used to measure the absorbance of each solution.

According to Beer-Lambert's Law, a graph of absorbance against concentration is then plotted. This graph is known as *calibration* line.

The experiment is then repeated using a solution of unknown concentration. By comparing the absorbance of this solution with the calibration line, the concentration of copper(II) ions in the unknown solution can be determined.
Propose a simple plan on how you would prepare

- a 100.0cm^3 of 1.00 moldm^{-3} standard aqueous copper(II) sulfate;
- a suitable range of diluted solutions of accurate concentrations

You are to show detailed calculations and suitable tables (where appropriate) in your answer.

(i) a 100.0cm^3 of 1.00 moldm^{-3} standard aqueous copper(II) sulfate;

Preparation of the 100 cm^3 of 1.00 mol dm^{-3} aqueous copper (II) sulfate standard solution

Amount of $CuSO_4.5H_2O$ needed = (100/1000) x 1 = 0.100
Mass of $CuSO_4.5H_2O$ needed = 0.100 x (63.4+32.1+16x4+5x18) = 24.95 g

1. Weigh accurately about **24.95 g** of $CuSO_4.5H_2O$ using a clean, dry weighing bottle using a mass balance by recording the mass of the $CuSO_4.5H_2O$ and weighing bottle as shown in the table below.

Mass reading table

Mass of weighing bottle with $CuSO_4.5H_2O$ / g	***x***
Mass of **empty** weighing bottle / g	***y***
Mass of $CuSO_4.5H_2O$ / g	***x - y***

2. Transfer the weighed solid into a 100 cm^3 beaker and dissolve it using distilled water and stir.

3. Transfer the solution and washings into a **100 cm^3 volumetric flask**.

4. Reweigh the empty weighing bottle and record its mass.

5. Make up to the mark with distilled water and shake well to obtain a homogeneous solution.

(ii) a suitable range of diluted solutions of accurate concentrations, keeping the total volume of each solution to be constant at 20.00cm^3

Preparation of a suitable range of diluted standard solutions

6 different solutions with different concentrations of $CuSO_4$ (aq) were prepared, as shown in the following table:

Table 2

Solution	**Volume of 1.0 moldm^{-3} of $CuSO_4$ (aq) / cm^3**	**Volume of deionized water / cm^3**	**Total volume / cm^3**	**[$CuSO_4$] / mol dm^{-3}**	Absorbance value
1	20.00	0.00	20.00	1.000	
2	10.00	10.00	20.00	0.500	
3	5.00	15.00	20.00	0.250	
4	2.50	17.50	20.00	0.125	
5	1.50	18.50	20.00	0.075	
6	0.50	19.50	20.00	0.025	

1. To prepare 0.500 mol dm^{-3} of $CuSO_4$ (aq), add 10.00 cm^3 of 1.00 mol dm^{-3} $CuSO_4$ standard solution into a 50 cm^3 beaker using a burette.
2. Using a separate burette, add 10.00 cm^3 of deionised water into the beaker and stir using a glass rod to obtain a homogenous solution.
3. Repeat the above steps to obtain diluted solutions of different concentrations using the volumes in Table 2.

[5]

(c) Using the solutions prepared in **(b)**, the absorbance value of each copper(II) sulfate solution can be determined and hence a calibration line can be obtained via the spectrometer.

Describe a plan to determine the concentration of **FB 1**.

Your plan should include details of:

- calculation of the absorbance value for each copper(II) sulfate solution prepared in **(b)**, given ε of $CuSO_4$ is **2.81** mol^{-1} dm^3 cm^{-1}.
- a sketch of the calibration line you would expect to obtain;
- a brief outline of how the results would be obtained.
- how the calibration line would be used to determine the concentration of copper(II) ions in **FB 1**.

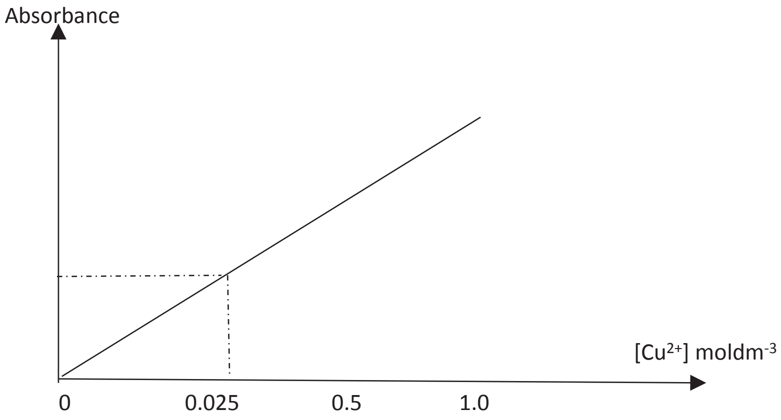
Table of results

Solution	**[$CuSO_4$] / mol dm^{-3}**	**Absorbance value**
1	1.000	2.81
2	0.500	1.41
3	0.250	0.70
4	0.125	0.35
5	0.075	0.21
6	0.025	0.07

Using the spectrometer

1. Spectrometer is set up to absorb the wavelength of orange (600nm).

2. A few cm^3 of each of the 6 $CuSO_4$ solutions are run by the spectrometer and the absorbance values are recorded in Table 2.
3. Plot a graph of absorbance value versus [$CuSO_4$].
4. Draw the best-fit straight line passing through the origin. This is the calibration line.



Analysing solution FB1

1. Run a few cm^3 of **FB1** in the spectrometer and record the absorbance value, A_x.
2. Using the graph drawn earlier, a horizontal line is drawn from this value to intersect the calibration line. By drawing a vertical line from the intersection point, [Cu^{2+}] in **FB1** can be determined.

[3]

(d) Given that the absorbance for **FB 1** is 0.286, calculate the concentration of **FB 1**.

Applying Beer-Lambert's Law, A = εcl

0.286 = (2.81)(c)(1)

c = **0.105 moldm^{-3}**

concentration of **FB 1** = ……………………………………[1]

[Total : 10]

Qualitative Analysis Notes
[ppt. = precipitate]
(a) Reactions of aqueous cations

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

(b) Reactions of anions

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)	SO2 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 EXAMINATIONS

Chemistry

Higher 2 **9729/01**

Paper 1 Multiple Choice **18 September 2017**

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 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.

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 and **1** blank page.

1 During a laboratory practical exercise, a student tried to determine the concentration of $Fe^{2+}(aq)$ and $Fe^{3+}(aq)$ in a given mixture through two different experiments.

1. 25.0 cm^3 aliquot of the $Fe^{2+}(aq)$ and $Fe^{3+}(aq)$ mixture solution required 15.00 cm^3 of 0.1 mol dm^{-3} of acidified $KMnO_4$ solution for complete oxidation.
2. Using another 25.0 cm^3 aliquot, all the $Fe^{3+}(aq)$ was first reduced to $Fe^{2+}(aq)$ using zinc metal before requiring 34.20 cm^3 of the same $KMnO_4$ solution for complete oxidation.

What is the concentration of $Fe^{2+}(aq)$ and $Fe^{3+}(aq)$ in the given mixture?

A 0.012 mol dm^{-3} $Fe^{2+}(aq)$ and 0.0154 mol dm^{-3} $Fe^{3+}(aq)$

B 0.180 mol dm^{-3} $Fe^{2+}(aq)$ and 0.230 mol dm^{-3} $Fe^{3+}(aq)$

C 0.300 mol dm^{-3} $Fe^{2+}(aq)$ and 0.384 mol dm^{-3} $Fe^{3+}(aq)$

D 0.300 mol dm^{-3} $Fe^{2+}(aq)$ and 0.684 mol dm^{-3} $Fe^{3+}(aq)$

2 A number of elements in the actinoid series are radioactive and undergo decay to other elements. The following equation is an example of such decay.

$$^{241}_{94}Pu \rightarrow \text{element } \mathbf{A} + 9\,^{4}_{2}He + 5\,^{0}_{-1}e$$

Which of the following gives the identity of element **A**?

	Mass number	Atomic number
A	205	81
B	205	86
C	223	81
D	237	90

3 Which of the following shows an increase in the bond angle of the compound from left to right?

A	NH_3	H_2S	SiH_4
B	PH_3	NH_3	$AlCl_3$
C	PH_3	PF_3	PCl_3
D	XeF_4	SCl_6	CCl_4

4 In which of the following does Statement **II** give a correct explanation for Statement **I**?

	Statement **I**	Statement **II**
1	Magnesium has a higher melting point than sodium.	Magnesium has more delocalised valence electrons which results in stronger metallic bonds.
2	Glycine, H_2NCH_2COOH, has a higher melting point than 2–hydroxyethanoic acid, $HOCH_2COOH$.	Glycine can form stronger hydrogen bonds than 2–hydroxyethanoic acid.
3	Chloromethane undergoes nucleophilic substitution more easily than fluoromethane.	The C–C*l* bond in chloromethane is weaker than the C–F bond in fluoromethane.

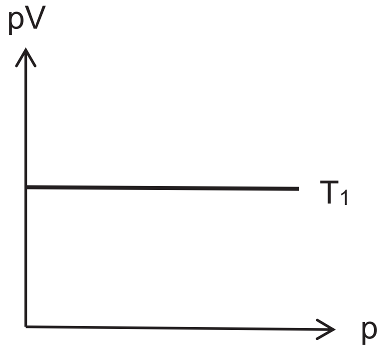
A 2 and 3

B 1 and 2

C 1 and 3

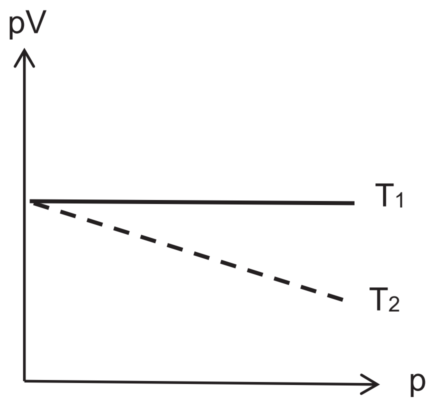
D 1, 2, and 3

5 The graph of pV against p is plotted for an ideal gas at constant temperature for a fixed mass of gas at T_1.

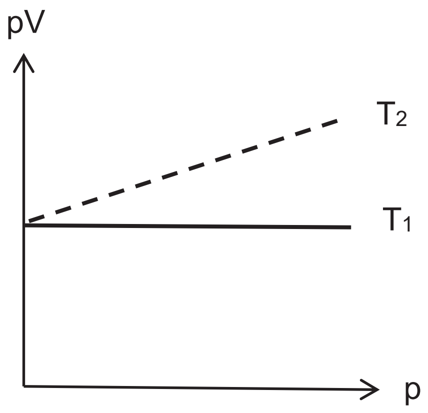


Which diagram shows the new graph at a lower temperature at T_2?

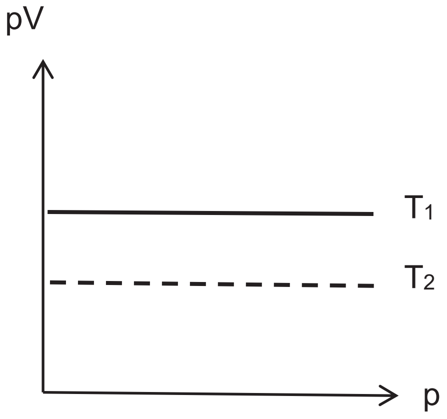
A



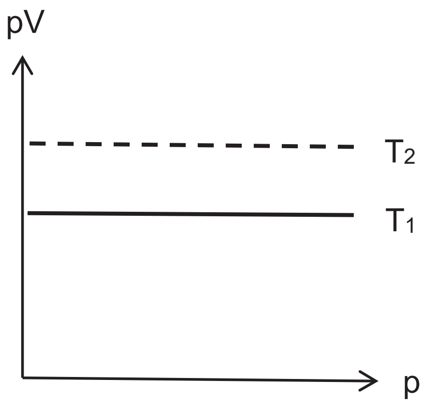
B



C



D



6 The enthalpy change of formation of carbon monoxide and carbon dioxide are given below.

ΔH_f (CO)= –110 kJ mol^{-1}

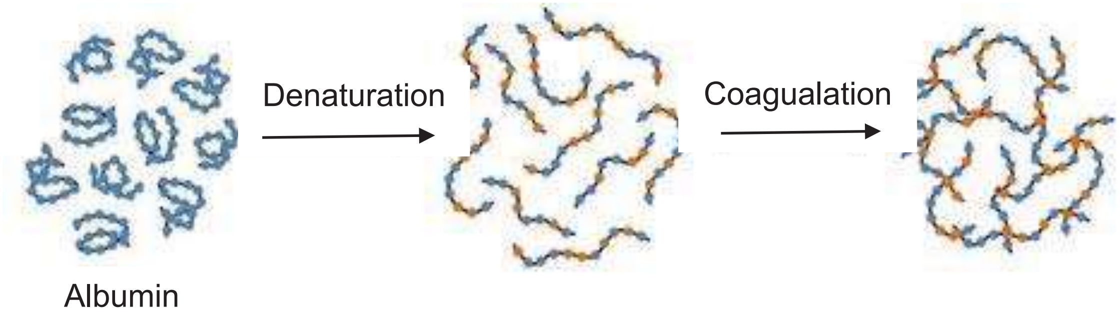
ΔH_f (CO_2)= –393 kJ mol^{-1}

Which of these statements are correct?

1 Carbon dioxide is energetically more stable than carbon monoxide.
2 The enthalpy change of combustion of carbon is –283 kJ mol^{-1}.
3 ΔH_f (CO_2) – ΔH_c (CO) has the same value as enthalpy change of formation of CO.

A 1 and 3 **B** 1 and 2 **C** 2 and 3 **D** 1 only

7 A raw egg white contains the protein, albumin, which is made of chains of amino acids that fold into specific and stable three-dimensional structure.
Heating the protein in an egg white causes the intermolecular forces to break and "unfold" the protein. In this state, albumin is denatured and will readily coagulate to form an extensive protein network.

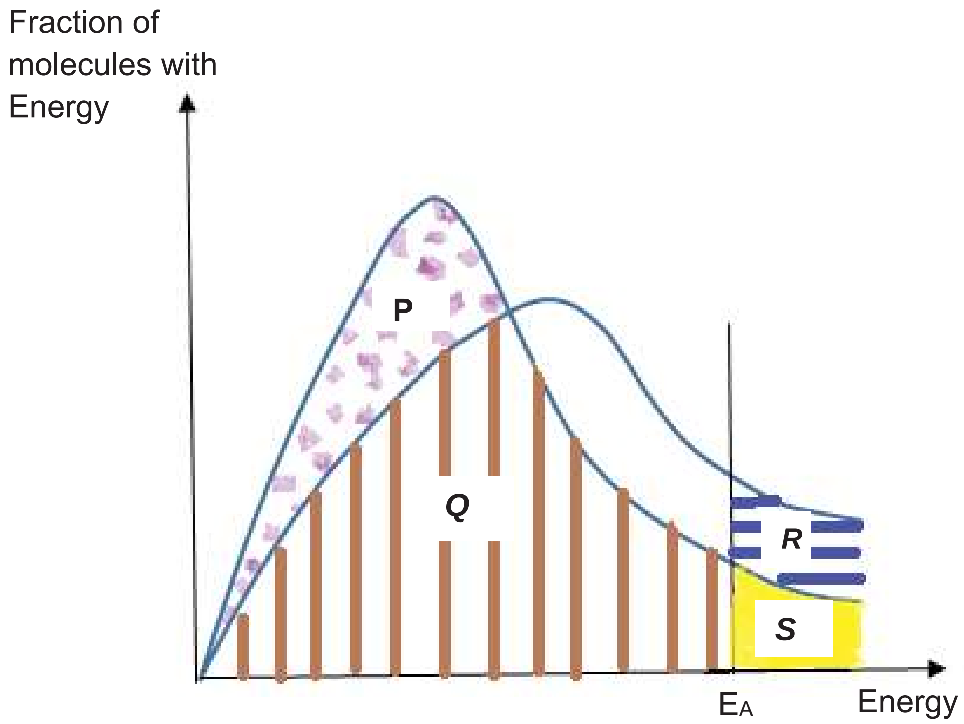


What are the correct signs of ΔS, ΔH, and ΔG for denaturation of albumin during cooking?

	ΔS	ΔH	ΔG
A	+	+	–
B	+	+	+
C	–	–	+
D	–	+	–

8 The diagram shows the Maxwell–Boltzmann energy distribution curves for air molecules at room temperature and inside the car engines where it is being combusted. The letters ***P***, ***Q***, ***R** and **S*** refer to the separate areas.

Which expression gives the fraction of the air molecules present inside the car engine?



A $\frac{S}{P}$ **B** $\frac{R+S}{P+Q+S}$ **C** $\frac{S}{P+Q+S}$ **D** $\frac{S}{P+Q}$

9 An experiment was carried out to investigate the kinetics of the reaction between ammonium peroxodisulfate, $(NH_4)_2S_2O_8$, an oxidising agent, and potassium iodide, KI, in the presence of a little starch.

$$S_2O_8^{2-}(aq) + 2I^-(aq) \rightarrow 2SO_4^{2-}(aq) + I_2(aq)$$

The volume of the $(NH_4)_2S_2O_8$ and KI solutions in the mixture, together with the time taken for the mixture to darken for the various experimental runs are given below:

Experiment	Volume used / cm^3			Time / s
	1.0 mol dm^{-3} KI	0.040 mol dm^{-3} $(NH_4)_2S_2O_8$	H_2O	
1	10.0	5.0	25.0	170
2	15.0	5.0	20.0	113
3	15.0	10.0	15.0	56.5
4	20.0	20.0	0.0	?

Which of the following statements about the reaction is false?

A The reaction can be catalysed by $Fe(NO_3)_2(aq)$.

B The reaction involves the formation of an intermediate.

C The time taken for the mixture to darken in Experiment 4 is 40.5 s.

D The slow step involves the reaction between 1 mole of $(NH_4)_2S_2O_8$ and 1 mole of KI.

10 Silver chloride establishes an equilibrium with the relatively stable complex ion, $[Ag(NH_3)_2]^+$

$$AgCl(s) + 2NH_3(aq) \rightleftharpoons [Ag(NH_3)_2]^+(aq) + Cl^-(aq)$$

Which of the following statements is correct?

A When acid is slowly added to the mixture, a white precipitate is observed.

B The K_c expression is $K_c = \frac{[[Ag(NH_3)_2]^+]\,[Cl^-]}{[AgCl]\,[NH_3]^2}$

C Added more NH_3 to the solution when equilibrium is established will decrease its K_c value.

D Removal of some AgCl(s) causes the position of equilibrium to shift left.

11 At a total pressure of 1.2 atm, sulfur trioxide is 50% dissociated according to the following equation at 150 K.

$$2SO_3\,(g) \rightleftharpoons 2SO_2\,(g) + O_2(g)$$

What is the mole fraction of oxygen in this equilibrium mixture?

A 0.60 **B** 0.20 **C** 0.30 **D** 0.24

12 Which of the following mixtures when dissolved in large amount of water could act as buffer solutions?

1 2 mol of HI and 1 mol of $CH_3CH_2NH_2$
2 2 mol of CH_3COCl and 3 mol of NaOH
3 2 mol of $CH_3CH_2NH_2$ and 1 mol of H_2SO_4

A 2 only
B 2 and 3
C 1 and 3
D None of the above

13 The solubility of 2 sparingly soluble solids MX_2 and LY is being determined experimentally.

Which of the following statements is always true?

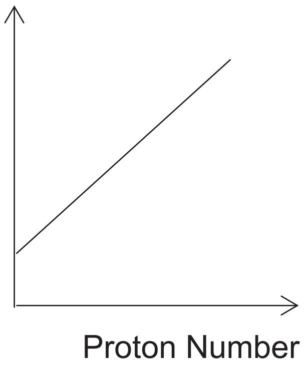
A The solubility product of MX_2 increases with increasing temperature.

B MX_2 will always be more soluble than LY if MX_2 has a higher K_{sp} value.

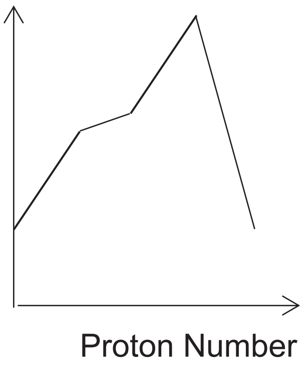
C The K_{sp} value of LY can be calculated from any concentration of L^+ and Y^-.

D Given that the solubility of LY is exothermic, the K_{sp} of LY will only change when temperature changes.

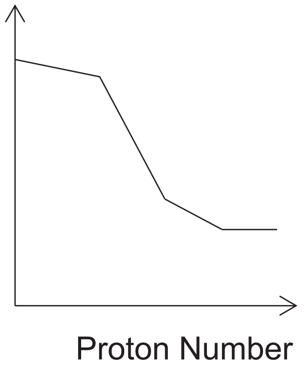
14 The following graphs show the variation of a property of the elements Na to P.



Graph 1



Graph 2



Graph 3

Which of the following correctly describes the property of the graphs?

	Graph 1	**Graph 2**	**Graph 3**
A	Electronegativity	Melting point of oxide	pH of oxide
B	Ionic radius	Melting point of element	pH of oxide
C	Covalent character	Melting point of chlorides	pH of chloride
D	Electronegativity	Melting point of element	pH of chloride

15 1.0 mol dm^{-3} aqueous solutions of three elements in Group 17 of the Periodic Table have standard electrode potentials as follows.

$X_2(aq) + 2e^- \rightleftharpoons 2X^-(aq)$ $E^\ominus = +1.36$ V

$Y_2(aq) + 2e^- \rightleftharpoons 2Y^-(aq)$ $E^\ominus = +1.07$ V

$Z_2(aq) + 2e^- \rightleftharpoons 2Z^-(aq)$ $E^\ominus = +0.54$ V

Which statements are correct?

1 There is an increase in oxidising power in the sequence X_2, Y_2, Z_2.

2 The reaction $X_2(aq) + 2Z^-(aq) \longrightarrow 2X^-(aq) + Z_2(aq)$ is spontaneous under standard conditions.

3 Z has the lowest electron affinity.

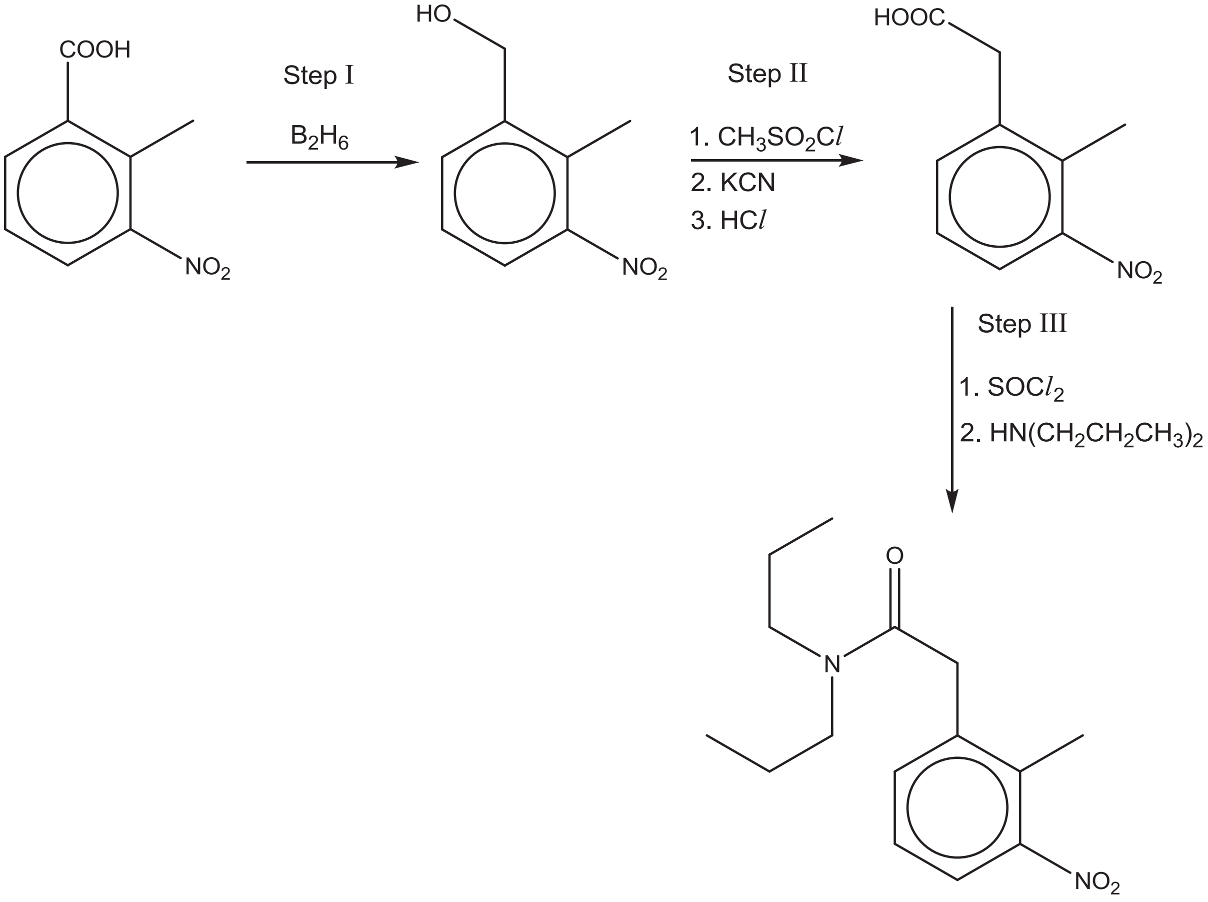
A 1 and 2

B 1 and 3

C 2 and 3

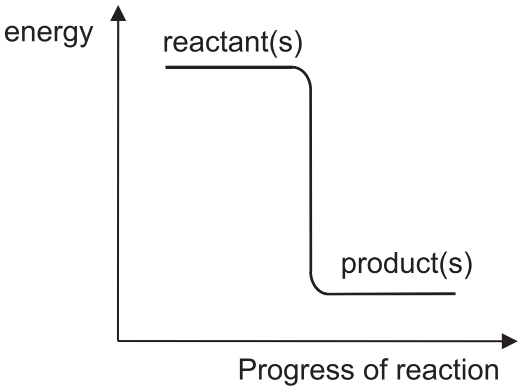
D 1, 2 and 3

16 Which of the following shows the correct type of reaction(s) occurring for each step of the synthesis?



	Step I	Step II	Step III
A	Oxidation	Substitution followed by condensation	Condensation
B	Oxidation	Acid base reaction followed by oxidation	Substitution followed by condensation
C	Reduction	Substitution followed by hydrolysis	Substitution followed by condensation
D	Reduction	Hydrolysis followed by oxidation	Condensation

17 An energy level diagram for a single reaction step is shown below.



To which of the following steps in the reaction of ethane with bromine in the presence of light does this diagram apply?

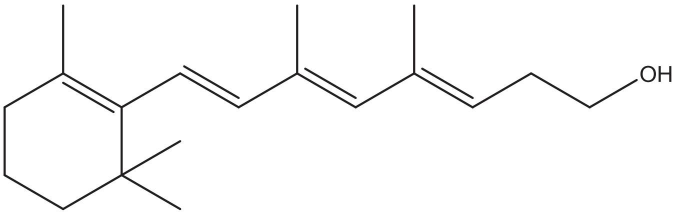
A $Br_2 \longrightarrow Br\bullet + Br\bullet$

B $CH_3CH_3 + Br\bullet \longrightarrow CH_3CH_2\bullet + HBr$

C $CH_3CH_2\bullet + Br_2 \longrightarrow CH_3CH_2Br + Br\bullet$

D $CH_3CH_2\bullet + CH_3CH_2\bullet \longrightarrow CH_3CH_2CH_2CH_3$

18 The structure of Vitamin A is shown below.



Vitamin A

Which of the following statements about Vitamin A is true?

A White fumes is observed when it is treated with excess ethanoyl chloride.

B When it reacts completely with $LiAlH_4$ in dry ether, a saturated compound that contains 4 chiral carbon centres is produced.

C Effervescence is observed when it reacts with hot alkaline potassium manganate(VII) solution.

D 1 mol of Vitamin A reacts with excess sodium metal to produce 22.7 dm^3 of hydrogen gas at 273 K and 1 bar.

19 An optically active sample of 2–chlorobutane, $CH_3CH_2CHClCH_3$, was heated under reflux with aqueous sodium hydroxide to produce compound **Q**, which rotates plane of polarised light.

Which of the following statements about the reaction are correct?

1 The reaction occurred via a S_N1 mechanism.

2 $CH_3CH_2CH_2OCH_3$ is a functional group isomer of **Q**.

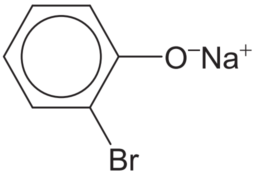
3 The rate of reaction increases when the sample is replaced with 2–bromobutane.

4 **Q** reacts with concentrated sulfuric acid at 170 °C to give a mixture of three isomeric alkenes.

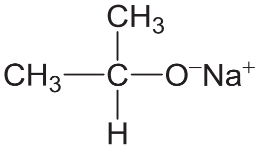
A 1 and 3 only
B 2 and 3 only
C 2 and 4 only
D 2, 3 and 4 only

20 Which of the following salts has the smallest pK_b?

A

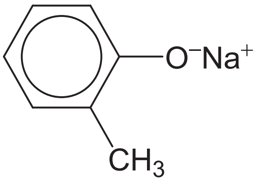


B

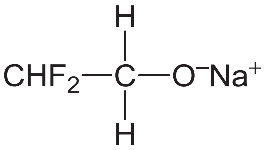


$CH_3CH(CH_3)O^-Na^+$

C



D



$CHF_2CH_2O^-Na^+$

21 The uncatalysed reaction between propanal and HCN proceeds via two steps and the rate equation for the formation of cyanohydrin is as follows.

$$\text{Rate} = k[CH_3CH_2CHO][CN^-]$$

Which of the following statements is correct?

A The intermediate formed in this reaction is planar.

B Only one product is obtained since this is an addition reaction.

C The uncatalysed reaction between propanone and HCN occurs at a faster rate than that of propanal.

D The same product can be obtained by heating 1–chloropropan–1–ol with ethanolic NaCN.

22 ^{18}O is an isotope of oxygen.

When butylethanoate is hydrolysed with dilute sulfuric acid in the presence of $H_2{}^{18}O$, a mixture of 2 products is formed. Which of the following pairs gives the correct structures of the two products?

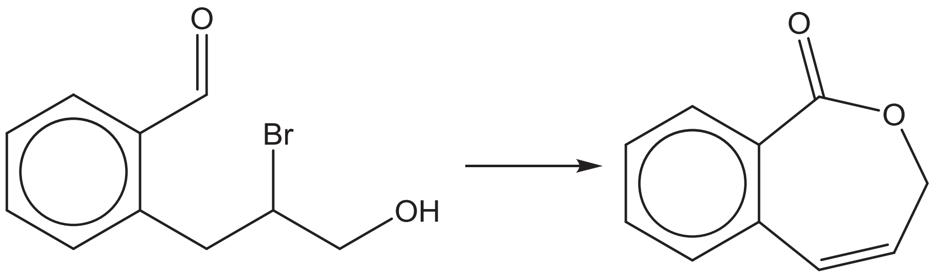
A $CH_3CH_2CH_2CH_2OH$ and $CH_3CO^{18}OH$

B $CH_3CH_2CH_2CH_2{}^{18}OH$ and CH_3CO_2H

C CH_3CH_2OH and $CH_3CH_2CH_2CO^{18}OH$

D $CH_3CH_2{}^{18}OH$ and $CH_3CH_2CH_2COOH$

23



Compound **L**

Compound **M**

Which of the following sequence of reagents and conditions can be used to carry out the conversion above?

	Stage 1	**Stage 2**	**Stage 3**
A	warm with ammonical silver nitrate solution	hot NaOH(aq)	heat in the presence of concentrated H_2SO_4
B	warm with Fehling's solution	heat in the presence of concentrated H_2SO_4	hot NaOH(aq)
C	warm with ammonical silver nitrate solution	hot NaOH(alc)	heat in the presence of concentrated H_2SO_4
D	warm with Fehling's solution	heat in the presence of concentrated H_2SO_4	hot NaOH(alc)

24 Compound **W** has the following properties :

- Empirical formula : C_3H_7N
- Decolourises aqueous bromine
- Reacts with hot acidified $KMnO_4$ to form an α–amino acid

Which of the following could be compound **W**?

1 $CH_2{=}CHCH_2NH_2$

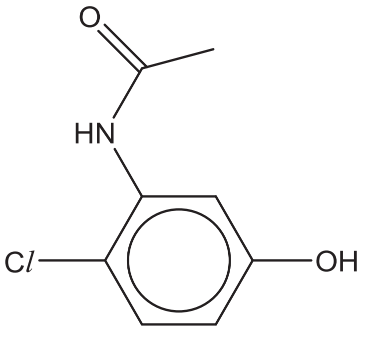
2 $CH_3CH{=}CHNH_2$

3 $CH_2(NH_2)CH_2CH{=}CHCH_2CH_2NH_2$

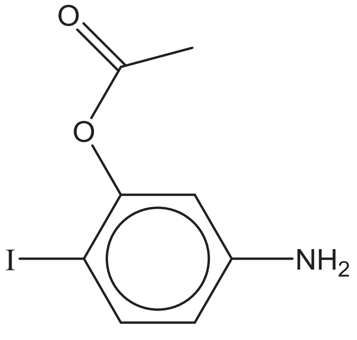
4 $CH_2(NH_2)CH_2CH_2CH{=}CHCH_2NH_2$

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

25 Which of the following reagents would give different observations when added to both compounds in separate test–tubes?



Compound **Y**



Compound **Z**

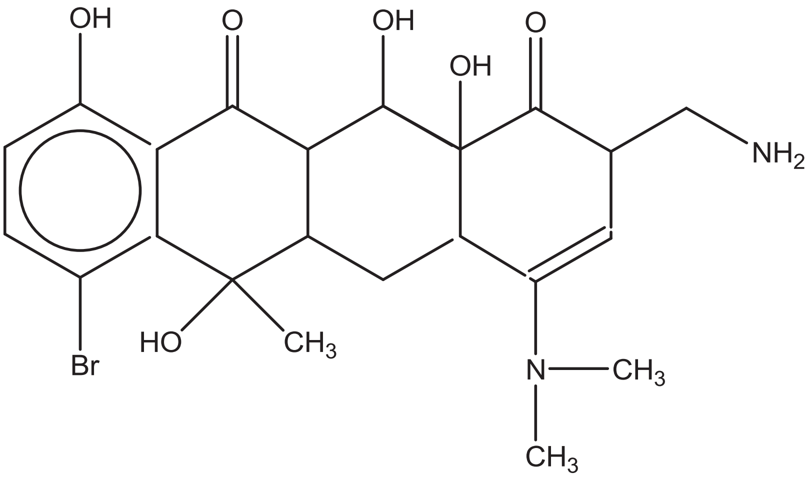
A aqueous bromine

B 2,4–dinitrophenylhydrazine

C $LiAlH_4$ in dry ether, followed by hot acidified $KMnO_4$

D ethanolic silver nitrate

26 Compound **X** is an isomer of the antibiotic *Aureomycin*.



Compound **X**

Which of the following statements are true for compound **X**?

1 1 mole of **X** reacts with 5 moles of propanoyl chloride.

2 1 mole of compound **X** reacts with 3 moles of hydrogen gas in the presence of Ni catalyst at 150 ^{0}C.

3 1 mole of compound **X** reacts with 6 moles of HBr(g) at room temperature.

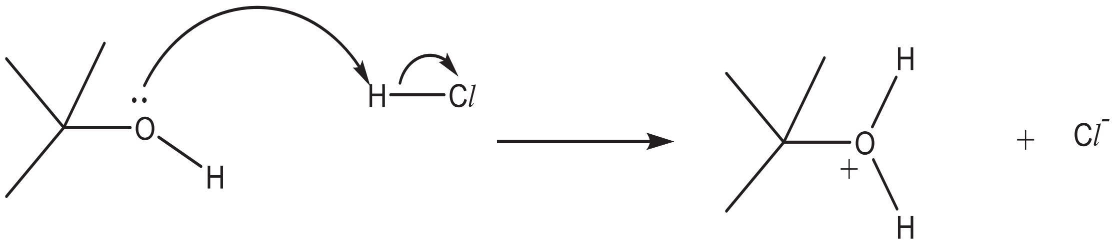
A 1 only

B 1 and 2

C 2 and 3

D 1, 2 and 3

27 Alkyl halides can be prepared from alcohol. The first step in the mechanism involves the following:



What is the role of the alcohol in the above step?

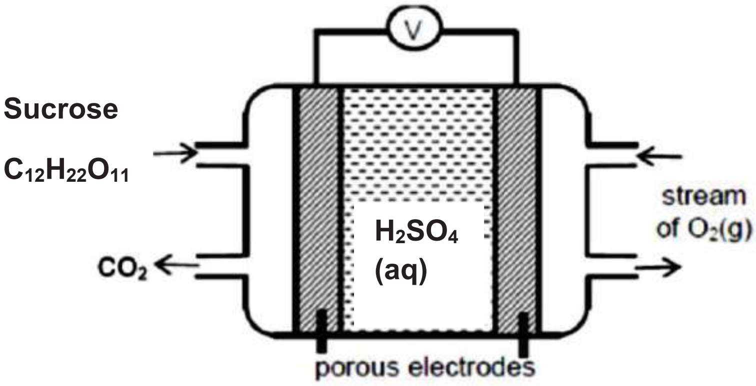
A Brønsted–Lowry acid

B Lewis base

C Ligand

D Electrophile

28 A microbial fuel cell (MFC) is a bio–electrochemical system that drives an electric current by using bacteria and mimicking bacterial interactions found in nature. An example of an MFC is as shown below with $E^\theta_{cell} = +1.25$ V.



Which of the following statements about the above MFC is **not** correct?

A Electrons flow from the right electrode to the left electrode.

B H^+ is produced at the anode.

C Sucrose is oxidised in this reaction.

D $E^\theta_{(anode)}$ is –0.02 V.

29 0.0170 mol of chromium(III) iodide reacts with excess ammonia to form compound **Y** which has a coordination number of 6. When a solution of **Y** is treated with an excess of aqueous silver nitrate, 0.0340 mol of solid is precipitated.

What is the formula of compound **Y**?

A $Cr(NH_3)_3I_3$

B $Cr(NH_3)_4I_3$

C $Cr(NH_3)_5I_3$

D $Cr(NH_3)_6I_3$

30 The table shows the electronic configuration of three elements in the Periodic Table. (The elements are represented by letters which are not their symbols.)

Element	Electronic configuration
P	$[Ar]4s^1$
Q	$[Ar]3d^74s^2$
R	$[Ar]3d^{10}4s^1$

Which of the following statements are correct?

1 $\mathbf{Q}_2O_3$ is likely to exist.

2 First ionisation energy of **P** is lower than that of **R**.

3 The compound **R**I is a white solid.

A 1 only

B 1 and 2

C 2 and 3

D 1, 2 and 3

NAME		**Class**	

ST ANDREW’S JUNIOR COLLEGE

JC2 PRELIMINARY EXAMINATION

Chemistry (9729) **11 September 2017**

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**	**6**	**Total**
Marks	/17	/5	/10	/16	/6	/21	/75

This document consists of **19** printed pages (including this page).

Answer **all** the questions

1 Sulfur is a common element on Earth that forms many important chemical compounds.

One of these compounds is sodium thiosulfate, $Na_2S_2O_3$, an ionic compound used to treat several medical conditions, such as cyanide poisoning and fungal growths.

(a) (i) Draw a dot-and-cross diagram for sodium thiosulfate, $Na_2S_2O_3$. State the shape and bond angle in the thiosulfate ion.

[2]

(ii) Below are the melting points of sodium thiosulfate and sulfur.

Compound	**Melting point / °C**
Sodium thiosulfate	49
Sulfur, S_8	115

Explain why sulfur has a higher melting point than sodium thiosulfate.

……………………………………………………………………………………

……………………………………………………………………………………

……………………………………………………………………………………

……………………………………………………………………………………

……………………………………………………………………………………

……………………………………………………………………………………[3]

(b) Another important sulfur compound is sulfuric acid, H_2SO_4. Before the Contact Process was discovered, concentrated sulfuric acid for industrial purposes was produced by the following method.

The mineral pyrite, FeS_2, was first heated in air and oxidised to solid $Fe_2(SO_4)_3$ and sulfur dioxide gas.

$Fe_2(SO_4)_3$ decomposes at 480 °C to form iron(III) oxide and sulfur trioxide gas. The sulfur trioxide gas could be mixed with any volume of water to produce sulfuric acid of the desired concentration. However, this process was expensive and not efficient.

(i) Write a balanced equation, with state symbols for the reaction between pyrite, FeS_2, and oxygen to form $Fe_2(SO_4)_3$.

…………………………………………………………………………………….[1]

(ii) With the aid of an equation, define the term standard enthalpy change of formation of gaseous sulfur trioxide, SO_3.

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

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

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

…………………………………………………………………………………….[2]

(iii) Given the following information, determine the enthalpy change of formation of gaseous sulfur trioxide SO_3.

$Fe_2(SO_4)_3(s) \rightarrow Fe_2O_3(s) + 3SO_3(g)$ $\Delta H_{rxn} = +95\ kJ\ mol^{-1}$

Substance	**ΔH_f / kJ mol^{-1}**
$Fe_2(SO_4)_3(s)$	–2107
$Fe_2O_3(s)$	–824

[3]

(iv) Use the appropriate bond energies given in the *Data Booklet* and the data below to calculate another value for the standard enthalpy change of formation of gaseous sulfur trioxide SO_3.

$\frac{1}{8}S_8(s) + O_2(g) \rightarrow SO_2(g)$ $\Delta H_f = -297\ kJ\ mol^{-1}$

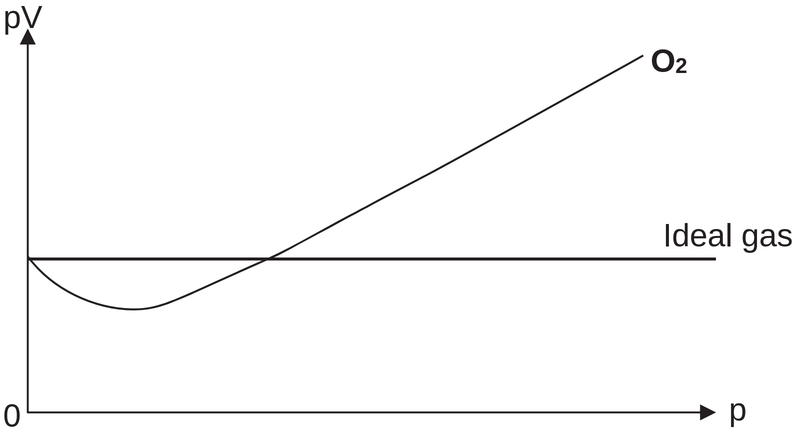
[3]

(v) Suggest a reason for the discrepancy between the values in **(b)(iii)** and **(b)(iv)**.

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

……………………………………………………………………………………….[1]

(c) The value of pV is plotted against p for 1 mol of oxygen O_2, where p is the pressure and V is the volume of the gas at 300 K.



(i) On the diagram above, draw and label the graph of pV against p for SO_3 at 300 K. [1]

(ii) Explain the difference between the graph of SO_3 and the graph of O_2.

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

……………………………………………………………………………………….[1]

[Total: 17]

2 Transition elements show typical properties that distinguish them from s-block elements, such as calcium. These include variable oxidation states in their compounds, and the formation of coloured complex ions.

(a) An ion of manganese has 3 electrons in its 3d subshell. Suggest the oxidation state of this manganese ion.

…………………………………………………………………………………….[1]

(b) The following table gives data about some physical properties of the elements calcium, chromium, and manganese.

Property	**Ca**	**Cr**	**Mn**
Atomic radius (metallic) / nm	0.197	0.129	0.132
Ionic radius (2+) / nm	0.099	0.073	0.083
Melting point / K	1112	1907	1246
Density / g cm^{-3}	1.54	7.19	7.43
Electrical conductivity / x 10^{6} S cm^{-1}	0.298	0.0774	0.00695

(i) Explain why the atomic radii of chromium and manganese are similar to each other.

……………………………………………………………………………………

……………………………………………………………………………………

……………………………………………………………………………………

…………………………………………………………………………………….[2]

(ii) Explain why the density of manganese is significantly greater than that of calcium, using relevant data from the table and the *Data Booklet*. (No calculations are required.)

……………………………………………………………………………………

……………………………………………………………………………………

……………………………………………………………………………………

……………………………………………………………………………………[2]

[Total: 5]

3 A student investigated the thermal decomposition of two carbonates, calcium carbonate and barium carbonate in the following way to determine its exact composition. He used the same amount, in moles, of each carbonate.

$\boldsymbol{M}CO_3\,(s) \rightarrow \boldsymbol{M}O(s) + CO_2\,(g)$ ***M*** is Ca or Ba

He heated the carbonates separately for 5 minutes. The solid obtained after heating was then shaken with distilled water to form an alkaline solution. A portion of the solid remained insoluble and was filtered. A sample of the alkaline filtrate was titrated with hydrochloric acid. No effervescence was observed during the titration.

(a) **(i)** Suggest which carbonate is less likely to decompose completely. Explain your answer.

……………………………………………………………………………………

……………………………………………………………………………………

……………………………………………………………………………………

……………………………………………………………………………………[2]

(ii) It was observed that the volume of acid used in the titration was smaller for the carbonate which did not decompose completely.

Explain how the incomplete decomposition can result in a lower volume of acid used in the titration.

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

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

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

……………………………………………………………………………………….[2]

(b) Explain the difference between the magnitude of the lattice energies of calcium carbonate and calcium oxide.

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

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

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

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

(c) Given that the decomposition of calcium carbonate is an endothermic reaction.

$$\Delta H = +178 \text{ kJ mol}^{-1} \text{ and } \Delta S = +159 \text{ J K}^{-1} \text{ mol}^{-1}$$

Calculate the minimum temperature at which this reaction becomes spontaneous.

[2]

(d) Beryllium oxide can react with sodium hydroxide.

$$BeO + 2NaOH \rightarrow Na_2BeO_2 + H_2O$$

Explain this behaviour despite Be being a Group 2 element.

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

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

[Total: 10]

4 Gaseous phosphorus(V) chloride dissociates according to the following equation.

$$PCl_5\,(g) \rightleftharpoons PCl_3\,(g) + Cl_2\,(g)$$

Different amounts of the three gases were placed in a closed container and allowed to come to equilibrium at 200 °C. The experiment was repeated at 425 °C.
The equilibrium partial pressure of the three gases at each temperature are given in the table below.

	Partial pressure / x 10^{-3} N m^{-2}		
temperature/°C	PCl_5	PCl_3	Cl_2
200	1.46	11.8	2.77
425	7.61	0.211	0.368

(a) **(i)** Write the expression for the equilibrium constant, K_p, for this reaction. Give the units.

Expression…………………………………………………………………………

Units…………………………………………………………………………[2]

(ii) Calculate the value of K_p at each of the temperatures given.

[2]

(iii) Is the forward reaction exothermic or endothermic? Explain your answer.

…………………………………………………………………………………

…………………………………………………………………………………[2]

(b) What will be the effect on the equilibrium partial pressure of PCl_5 when the following changes are carried out on this new equilibrium? Explain your answers clearly.

(i) The pressure of the system is halved at constant temperature.

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

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

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

……………………………………………………………………………………….[2]

(ii) Helium gas is added at constant volume and temperature.

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

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

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

……………………………………………………………………………………….[2]

Chloroethane can be made by reacting PCl_3 with ethanol, via nucleophilic substitution mechanism.

$$PCl_3 + CH_3CH_2OH \rightarrow CH_3CH_2Cl + HOPCl_2$$

(c) Outline a simple chemical test that can be carried out to see if chloroethane is produced in the mixture after reacting with PCl_3.

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

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

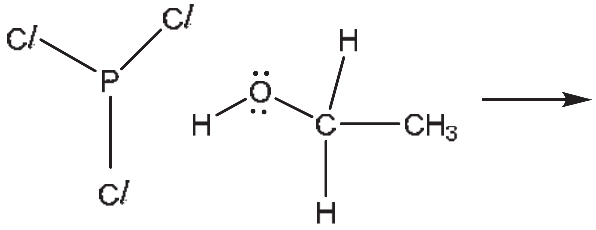
………………………………………………………………………………….............

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

(d) The mechanism is thought to involve these steps.

- The first step is where P-C*l* bond breaks. P is electron deficient and reacts with alcoholic O to form a protonated oxygen intermediate.
- The C-O bond is broken. C*l*⁻ act as a nucleophile.

Complete the diagram to suggest a mechanism to show how chloroethane is formed. Show all charges and relevant lone pairs and show the movement of electron pairs by using curly arrows.



[3]

(e) Explain why chlorobenzene cannot be made in the same way using phenol and PCl_3.

………………………………………………………………………………………………

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

[Total: 16]

5 Bromine reacts with organic compounds in different ways.

(a) When butane reacts with gaseous bromine in the presence of ultraviolet light, the major product was 2-bromobutane instead of 1-bromobutane. Using the stability of the intermediates, explain the observation.

………………………………………………………………………………………………

………………………………………………………………………………………………

………………………………………………………………………………………………

………………………………………………………………………………………………

………………………………………………………………………………………………

………………………………………………………………………………………………

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

(b) A solution of 2-bromobut-2-ene, upon heating with ethanolic silver nitrate solution, does not form a cream precipitate.

Upon addition of concentrated sulfuric acid in the cold and followed by heating with ethanolic silver nitrate, 2-bromobut-2-ene formed a cream precipitate.

Explain the above observations.

………………………………………………………………………………………………

………………………………………………………………………………………………

………………………………………………………………………………………………

………………………………………………………………………………………………

………………………………………………………………………………………………

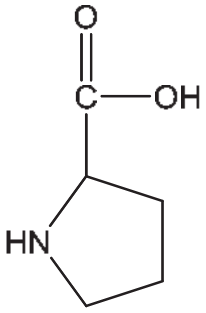
………………………………………………………………………………………………[3]

[Total: 6]

Turn Over

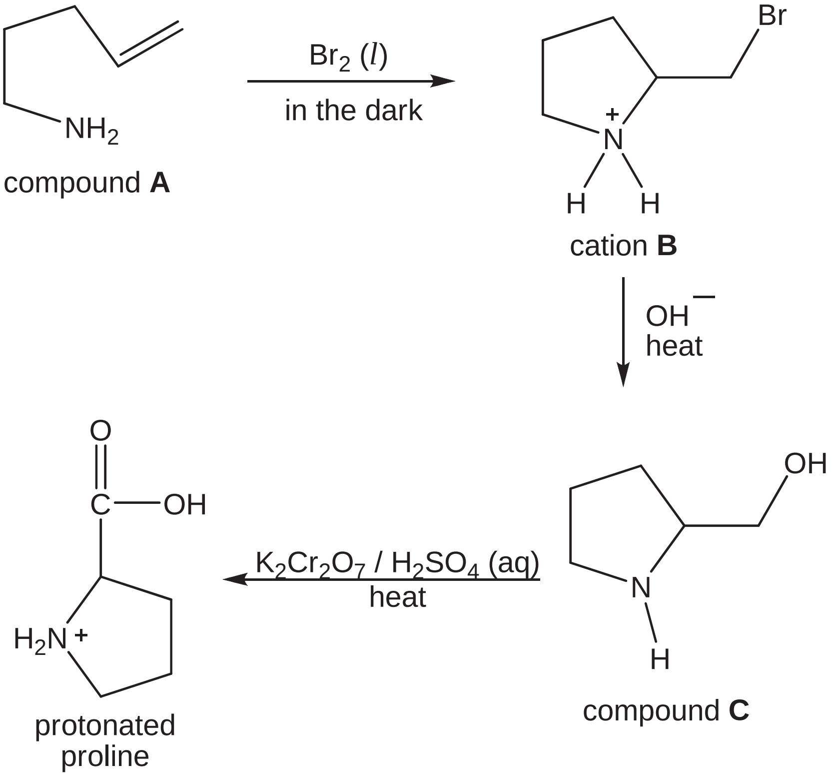
6 Proteins, found within the human body, are formed by amino acids. These amino acids are classified as either essential (cannot be synthesised by the human body) or non-essential (can be synthesised by the human body) amino acids.

(a)



Proline

Proline, one of the non-essential amino acids, is associated with the production of collagen which promotes healthy skin and heart muscle. Protonated proline can potentially be synthesised in the following manner.



The reaction of compound **A** with liquid bromine occurs via a two-step mechanism.

- compound **A** reacts with bromine to form a carbocation intermediate in the first step.
- the ammonium ion is formed in the second step.

(i) Name and suggest the mechanism for this reaction. Show any relevant lone pairs, dipoles and charges, and indicate the movement of electron pairs with curly arrows.

[3]

(ii) This synthesis also produces another organic compound (molecular formula $C_5H_{10}NO_3Br$). Suggest the skeletal formula of the cation.

[1]

(iii) Compound **C** was extracted and reacted with 1 mole of ethanoyl chloride to form a neutral compound **D** with molecular formula $C_7H_{13}NO_2$. Draw the structure of compound **D**. Explain why this product is formed.

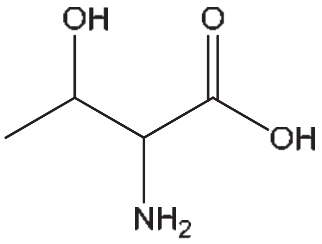
Structure

Explanation……………………………………………………………………………

…………………………………………………………………………………………

…………………………………………………………………………………………[2]

(b)



Threonine

Threonine, one of the essential amino acids, maintains protein balance within the human body and supports the cardiovascular, liver, central nervous and immune system functions.
In the laboratory, threonine could be synthesised from but-2-enoic acid.

(i) State the type of isomerism exhibited by but-2-enoic acid.

…………………………………………………………………………………………[1]

(ii) Suggest a 2-step synthesis for the formation of threonine from but-2-enoic acid, showing the intermediate clearly in your answer.

[3]

(iii) By considering the stereoisomers of threonine, suggest why only 25% of the synthesised threonine could be used in the human body.

………………………………………………………………………………………

………………………………………………………………………………………

………………………………………………………………………………………

……………………………………………………………………………………[2]

(c) **(i)** Suggest whether threonine or proline has the more basic amine group. Explain your answer.

………………………………………………………………………………………

………………………………………………………………………………………

………………………………………………………………………………………

……………………………………………………………………………………[2]

(ii) Explain, in terms of their structures, the higher solubility of threonine in water as compared to benzoic acid in water.

………………………………………………………………………………………

………………………………………………………………………………………

………………………………………………………………………………………

………………………………………………………………………………………[2]

(d) According to dieticians, a teenager requires approximately 1.00 g of calcium each day. This particular mineral is found predominantly in milk, cheeses and yogurts, which most individuals consume in the morning.

(i) Procedure to extract calcium ions is stated as follows :

1. A cup of milk (300 ml) was first filtered to remove impurities before excess amounts of sodium carbonate was added to form $CaCO_3$.
2. The mixture was then refiltered and the white residue (assumed to be solely calcium carbonate) was washed once again with deionised water and filtered again.
3. The white residue was then dissolved in 0.500 dm^3 of 0.160 mol dm^{-3} hydrochloric acid. 25.0 cm^3 of this resulting solution was then titrated against 0.125 mol dm^{-3} sodium hydroxide. The titre volume was found to be 26.45 cm^3.

What is the recommended number of cups of milk each day a teenager should consume to meet the daily requirements?

[3]

(ii)

Compound	Amount per serving
Vitamin A	5000 IU
Vitamin C	300 mg
Vitamin D	600 IU
Vitamin E	30 IU
Vitamin K	80 mcg
Thiamin (Vitamin B-1)	50 mcg
Riboflavin (Vitamin B-2)	50 mg
Vitamin B-12 (as Cyanocobalamin)	50 mcg
Calcium (as in calcium carbonate)	200 mg
Magnesium (as magnesium oxide)	50 mg
Zinc (as zinc oxide)	25 mg
Selenium (as L-Selenomethionate)	200 mcg
Molybdenum (as sodium molybdate)	75 mcg

A typical multivitamin dietary supplement tablet would have the above composition. Given that the teenager does not consume any form of dairy products, how many tablets would a teenager need to take to achieve the daily requirement of calcium?

[1]

(iii) A student wants to test the validity of the composition of calcium in this tablet and decided to follow the steps mentioned in **(d)(i)**.

State 1 possible problem that the student would face.

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

…………………………………………………………………………………….[1]

[Total: 21]

~END OF PAPER~

NAME		Class	

ST ANDREW'S JUNIOR COLLEGE

JC2 PRELIMINARY EXAMINATION

Chemistry (9729) **15 September 2017**

Paper 3 Free Response **2 hours**

Additional Materials: Data Booklet, Writing Paper

READ THESE INSTRUCTIONS:

Write in dark blue or black pen.

You may use an HB pencil for any diagrams or graphs.

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

Section A

Answer **all** questions. Marks [60]

Section B

Answer **one** question. Marks [20]

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

A Data Booklet is provided.

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

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

This document consists of **14** printed pages (including this page).

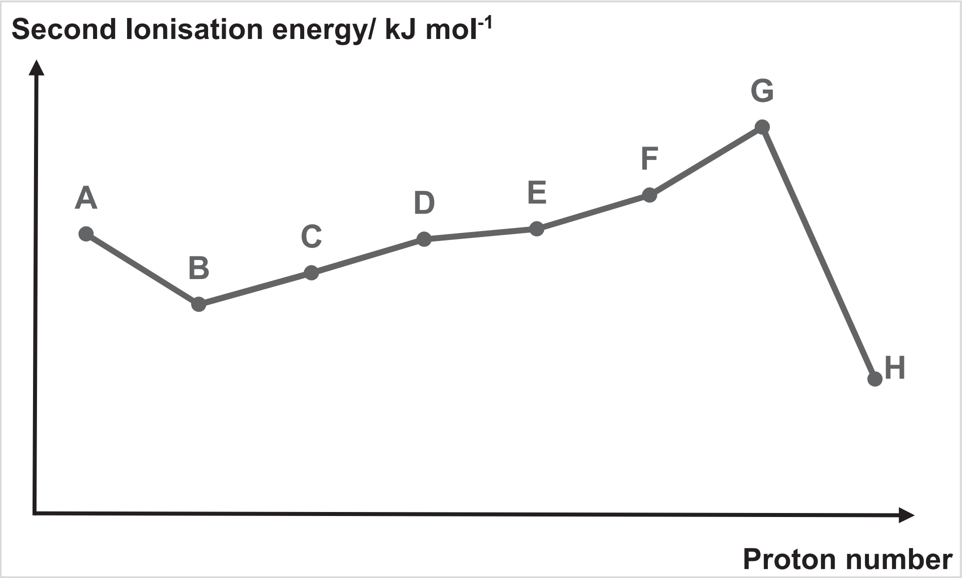
Section A

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

1 **(a)** Iodine is a lustrous purple-black solid at standard conditions that sublimes readily to form a violet gas.

(i) Give the equation that represents the *second ionisation energy* of *iodine*. [1]

(ii) The graph below shows the second ionisation energies of eight elements with consecutive atomic number. [2]



Which of the above elements, **A** to **H**, is iodine? Explain your answer.

(iii) Explain the trend in second ionisation energies from elements **A** to **G**, including the irregularity for element **B**. [4]

(iv) Suggest, with reason, which of the above elements, **A** to **H**, can form an amphoteric oxide. [2]

Hence, write an equation to show the reaction of this amphoteric oxide with hydrochloric acid. (You are not required to provide the identity of the element in the equation.)

1 **(b)** Hydrogen peroxide reacts with acidified iodide ions to liberate iodine, according to the following equation:

$$H_2O_2(aq) + 2H^+(aq) + 2I^-(aq) \rightarrow 2H_2O(l) + I_2(aq)$$

The rate of reaction can be measured by the increase in the concentration of iodine formed over time. The reaction was determined to be zero order with respect to $[H^+]$.

The following results were obtained by varying the concentrations of hydrogen peroxide and iodide ions.

Expt	Initial $[H_2O_2(aq)]$ / mol dm^{-3}	Initial $[I^-(aq)]$ / mol dm^{-3}	Initial rate / mol dm^{-3} min^{-1}
1	0.020	0.040	1.2×10^{-4}
2	0.020	0.050	1.5×10^{-4}
3	0.050	0.040	3.0×10^{-4}
4	0.020	0.500	1.5×10^{-3}
5	0.050	1.000	7.5×10^{-3}

(i) What is understood by the terms *order of reaction* and *half-life*. [2]

(ii) Determine the order of the reaction with respect to $[H_2O_2]$ and $[I^-]$ and hence suggest the units of the rate constant of this reaction. [3]

(iii) The half-life of hydrogen peroxide in experiment 4 was 9.24 min. Predict the half-life of hydrogen peroxide in experiment 5. [1]

To investigate the rate of the above reaction, a teacher suggested titrating the iodine formed with sodium thiosulfate solution at specified time intervals.

(iv) Write an equation for the reaction between iodine and thiosulfate. [1]

1 **(b)** **(v)** Suggest how the reaction can be quenched at specified time intervals. [1]

(vi) With reference to the *Data Booklet*, explain why hydrochloric acid is not a suitable acid used for the reaction between hydrogen peroxide and iodide. [2]

[Total:19]

2 Metals have been used widely since ancient times.

(a) An electrochemical cell is constructed using solutions of $NaHSO_4$, H_2SO_3, and $MnSO_4$ with suitable electrodes.

The relevant half reactions are:

$$HSO_4^-(aq) + 3H^+(aq) + 2e^- \rightleftharpoons H_2SO_3(aq) + H_2O \qquad E^\ominus = +0.17\ V$$

$$Mn^{2+}(aq) + 2e^- \rightleftharpoons Mn(s) \qquad E^\ominus = -1.18\ V$$

(i) Draw a fully labelled diagram of the above electrochemical cell to measure the cell potential under standard conditions, indicating clearly the direction of the electron flow in the external circuit. [3]

(ii) Write a balanced equation for the reaction that would take place if the electrodes of the cell were connected together by an external circuit. [1]

(iii) Calculate the standard cell potential for this cell [1]

(iv) Calculate the standard Gibbs free energy change, $\Delta G^\ominus$, for the cell above. [1]

(v) Suggest, with reasons, what happens to the $E^\ominus_{cell}$ when the following are done to the electrochemical cell above. [4]

1) The pH of the HSO_4^-/H_2SO_3 half−cell is increased.

2) A solution of sodium hydroxide to the Mn^{2+}/Mn half−cell.

2 **(b)** In an electrolytic cell, a current of 0.250 A is passed through a concentrated solution of a chloride of iron, producing iron metal and gas, **Y**.

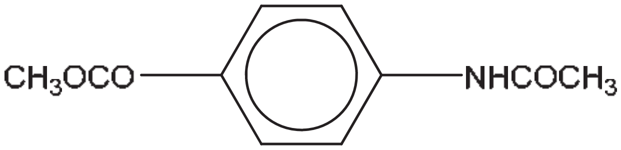
(i) Write the equation for the half-reaction take occurs at the anode. [1]

(ii) When the cell operates for 2 hours, 0.521 g of iron is deposited at one of the electrodes. Determine the formula of the chloride of iron in the original solution. [2]

(iii) Write a balanced equation for the overall reaction that occurs in the cell. [1]

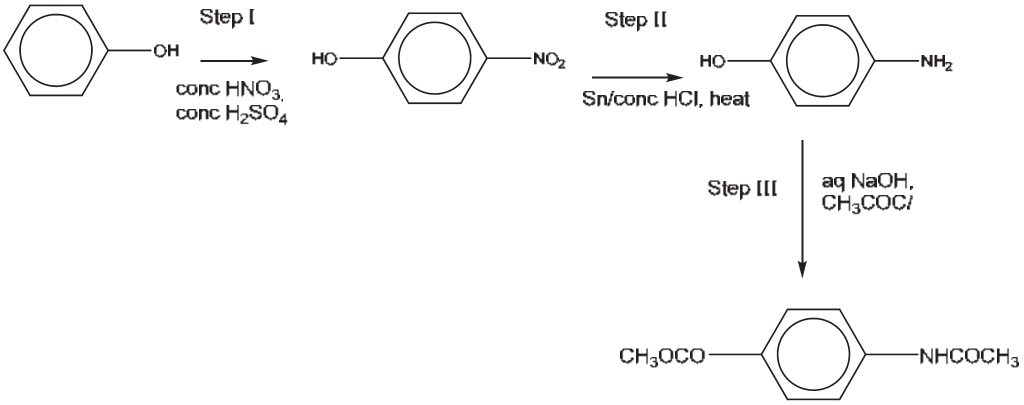
(iv) Calculate the current that would produce the gas **Y** from the solution at a rate of 2.50 g per hour. [2]

(c) Metals are also used as catalysts in organic synthesis. The derivative of acetaminophene is investigated for the treatment of headaches.

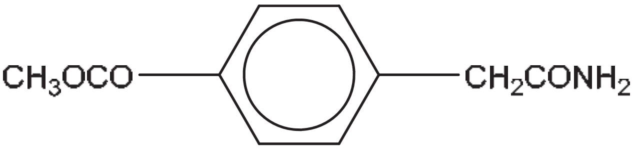


Derivative of acetaminophene

(i) A student suggested a flawed synthesis of the derivative of acetaminophene starting from phenol. Identify and explain the error in each step. [3]



2 **(c)** **(ii)** Compound **Z** is an isomer of the derivative of acetaminophene. Suggest a simple chemical test to distinguish between the derivative of acetaminophene and compound **Z**. [2]



compound **Z**

[Total:21]

3 **(a)** Blood obtains its colour from its respiratory proteins which occur as octahedral metal complexes. It is different in different organisms.

Protein	Source	Metal per subunit	De-oxygenated colour	Oxygenated colour
Haemoglobin	Mammals, birds, fish, reptiles, insects	1 Fe	red-purple	red
Haemocyanin	mollusks, crustaceans, spiders	2 Cu	colourless	blue

(i) Explain why oxygenated haemoglobin and haemocyanin are coloured. [3]

(ii) Using the Cartesian axes, like those shown in Figure 3.1, draw **fully labelled** diagrams of the following. [2]

- One of the d-orbitals at the lower energy level in an octahedral complex. Label the diagram “lower”.
- One of the d-orbtials at the upper energy level in an octahdral complex. Label this diagram “upper”.

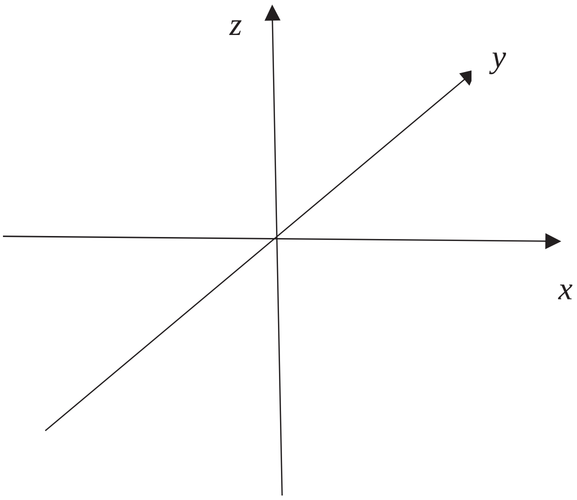
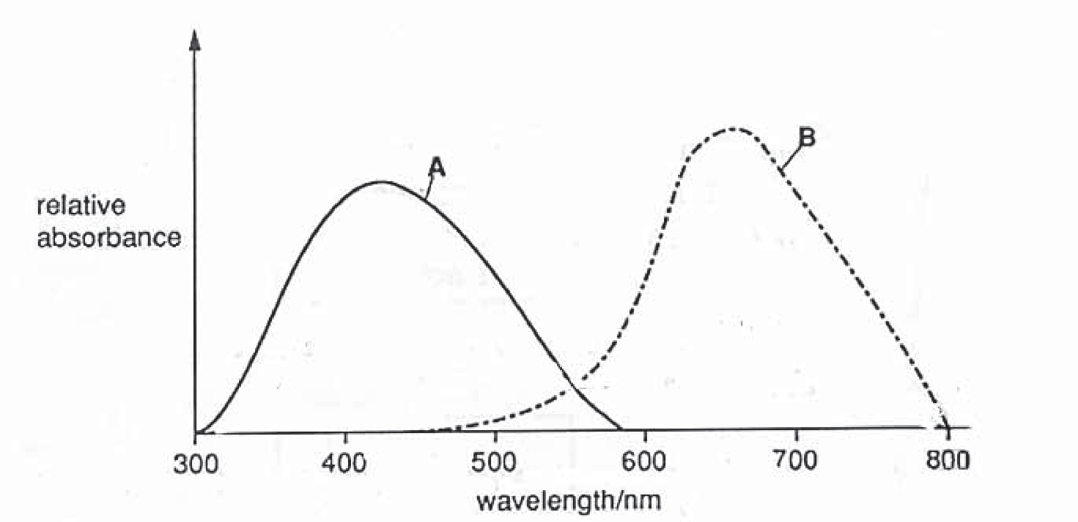


Figure 3.1

(iii) Explain why the splitting of the d subshell occurs in an octahedral complex using your answer in **(a)(ii)**. [2]

3 **(b)** Oxygenated haemoglobin and haemocyanin were analysed and the absorption spectrum was observed.



Colour	Wavelength (nm)	Colour	Wavelength (nm)
Violet	380 – 400	**Yellow**	560 – 580
Blue	400 – 490	**Orange**	580 – 620
Green	490 – 560	**Red**	620 – 800

(i) Which graph represents the absorption spectrum of oxygenated haemocyanin? Explain your answer. [2]

(ii) Which oxygenated blood (haemoglobin or haemocyanin) has a larger energy gap between the d subshells after splitting? Explain your answer. [2]

(iii) The deoxygenated haemocyanin has a Cu^+ central ion. State the electronic configuration of Cu^+. Hence, suggest why the deoxygenated haemocyanin is colourless? [2]

3 **(c)** Carbon monoxide, chlorine and phosgene are the best known toxic gases. Many of these gases are assigned an NFPA 704 health rating of 4 (may be lethal) or 3 (may cause serious or permanent injury).

Toxic Gas	Chemical formula	Colour	Odour	NFPA 704 Health Rating
carbon monoxide	CO	colourless	No	3
chlorine	Cl_2	green	Yes	4
phosgene	CCl_2O	colourless	No	4

(i) Describe, in terms of bonding, what happens when carbon monoxide is absorbed in the human blood and hence, explain why it is given a NFPA 704 health rating of 3. [2]

(ii) Chlorine was widely used as a chemical warfare in World War I. However, it was replaced by phosgene as a more effective chemical warfare. Suggest one possible reason why chlorine was replaced by phosgene. [1]

(d) Phosgene reacts with water to release hydrogen chloride and carbon dioxide gas.

$$CCl_2O + H_2O \rightarrow CO_2 + 2HCl \quad \text{------------Reaction } \mathbf{1}$$

(i) Draw the dot-and-cross diagram of phosgene and suggest its bond angle. [2]

(ii) Suggest the type of reaction involved in Reaction **1**. [1]

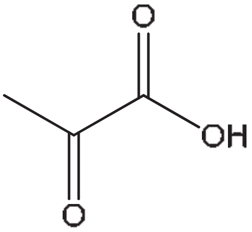
(iii) Gaseous spills of phosgene can be removed using ammonia. The reaction is similar to Reaction **1**. Suggest how phosgene reacts with ammonia, using a chemical equation . [1]

[Total:20]

Section B

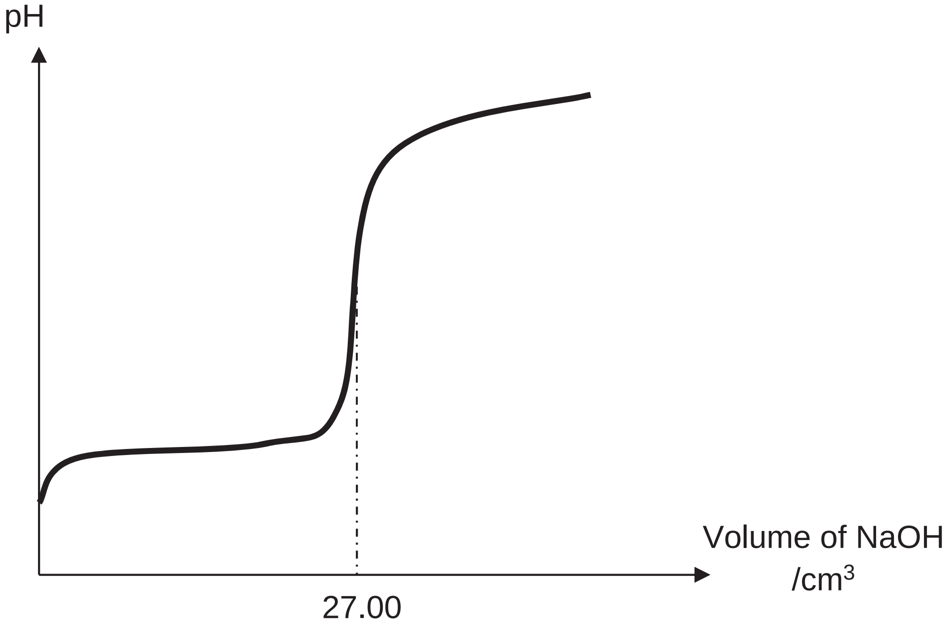
Answer **one** question from this section.

4. Pyruvic acid is an important component in the human body. It is involved in various processes such as the Krebs Cycle.



Pyruvic acid

(a) 30.0 cm^3 of pyruvic acid was titrated against 0.15 mol dm^{-3} of NaOH. The following titration curve was obtained.



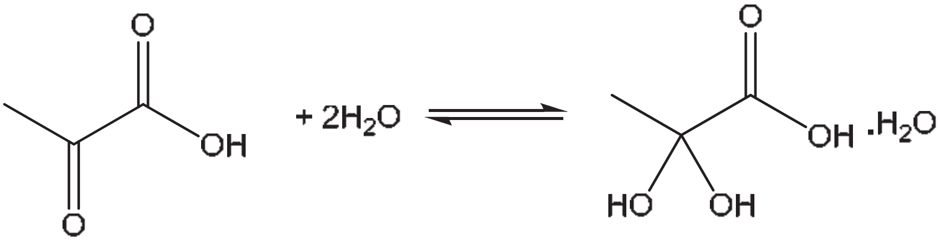
(i) Given that the solution of pyruvic acid is only 15.3 % dissociated, calculate the value of K_a for pyruvic acid, stating clearly its units. [2]

(ii) Calculate the volume of NaOH added to obtain a solution of pH 12. [2]

(iii) Suggest a suitable indicator for this titration. [1]

4 **(a)** **(iv)** Blood has a working pH of 7.35 to 7.45. Suggest why pyruvic acid is found in trace amounts in blood. Hence, draw the major species of pyruvic acid in blood. [2]

(b) An experiment to study the equilibrium between pyruvic acid and its hydrated form was done by Y. Pocker in 1969. The following data was obtained.



pyruvate hydrate

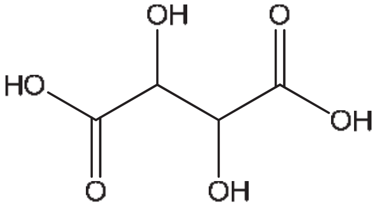
Temperature/ K	[pyruvate hydrate] / [pyruvic acid]
278	3.47
294	1.75
304	1.06
324	0.47

(i) Deduce whether the hydration of pyruvic acid is an endothermic or exothermic reaction. [2]

(ii) The pyruvate hydrate has a higher pK_a value than pyruvic acid. Explain. [2]

(c) Suggest a 2-step synthesis for the formation of carbon dioxide from pyruvic acid. [3]

4 **(d)** Pyruvic acid was first synthesised in the laboratory through the distillation of tartaric acid with potassium hydrogen sulfate. The structure of tartaric acid is shown below.



Tartaric acid

(i) Suggest why tartaric acid has a much higher melting point than pyruvic acid. [2]

(ii) There are three stereoisomers present in tartaric acid. Two of them rotate plane of polarised light in opposite direction, whereas one has no effect on plane of polarised light. [4]

Draw **all** the stereoisomers of tartaric acid and explain why one of the stereoisomers does not rotate the plane of polarised light.

[Total: 20]

5 **(a)** Thallium(I) chromate, Tl_2CrO_4, has a solubility product of 8.67 x 10^{-13} mol^3 dm^{-9} at 25 ^oC.

(i) Calculate the solubility of Tl_2CrO_4 in 0.05 mol dm^{-3} K_2CrO_4. [2]

(ii) Given that the numerical K_{sp} value of $BaCrO_4$ is 1.17 x 10^{-10}, deduce which precipitate will be formed first if K_2CrO_4 was added slowly into a solution containing 0.015 mol dm^{-3} of Ba^{2+} and 0.015 mol dm^{-3} Tl^+. [2]

(b) Transition elements are known to form coloured complexes. Chromium is one of the common transition element used today.

(i) An equilibrium exists between chromate(VI) ion and dichromate(VI) ions. [2]

$$2CrO_4^{2-} + 2H^+ \rightleftharpoons Cr_2O_7^{2-} + H_2O$$

Explain why changes in pH will cause changes in the colour of the solution.

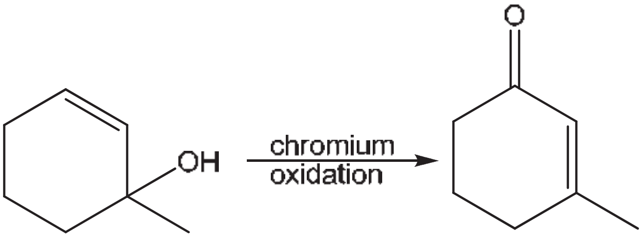
(ii) When gallium, Ga, is added to an acidified $Na_2Cr_2O_7$ solution, a series of colour changes takes place until a blue solution is obtained. [3]

Using relevant data from the *Data Booklet* and the data given below, explain the observation of the colour changes.

$$Ga^{3+} + 3e^- \rightleftharpoons Ga \qquad E^\ominus = -0.53\text{V}$$

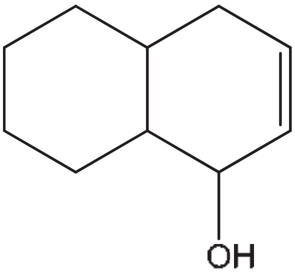
(iii) Suggest why the blue solution slowly changes to a green solution when it is left standing in air. [1]

(c) Chromium oxidation is a special type of reaction in which oxidation and a rearrangement takes place. An example of a chromium oxidation is as shown.



1-methylcyclohex-2-enol 3-methylcyclohex-2-enone

(i) Draw the structure of the product when the following compound undergoes chromium oxidation. [1]



(ii) Suggest a simple chemical test to distinguish between 1-methylcyclohex-2-enol and 3-methylcyclohex-2-enone. [2]

5 **(d)** Compound **F**, $C_4H_9O_3N$, is a neutral and chiral compound which is soluble in water. When compound **F** is heated with dilute sulfuric acid and potassium dichromate(VI), compound **G**, $C_4H_6O_5$, is formed. 1 mol of compound **G** reacts with aqueous sodium carbonate to produce 1 mol of CO_2. If compound **F** is heated with concentrated sulfuric acid and potassium dichromate(VI), compound **H**, $C_4H_4O_4$, is formed instead. When compound **F** reacts with $LiAlH_4$ in dry ether, a compound **J** which is no longer neutral is formed. [7]

Deduce the structures of compounds **F**, **G** **H** and **J**, and explain the reactions involved.

[Total: 20]

~END OF PAPER~

Name:		**Shift:**	
Class:		**Laboratory:**	

ST ANDREW'S JUNIOR COLLEGE

PRELIMINARY PRACTICAL EXAMINATION

Chemistry **29 August 2017**

Higher 2 **2 hours 30 minutes**

Additional Materials: Qualitative Analysis notes

READ THESE INSTRUCTIONS FIRST.

Write your name and class on all the work you hand in.
Give details of the practical shift and laboratory in the boxes provided above.

Write in dark blue or black pen.

You may use a soft pencil for any diagrams or graphs.

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

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

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

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

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

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

Planning	Practical
14	41

This paper consists of **18** printed pages including this page and quantitative analysis notes.

1 Determination of the M_r of a hydrated ethandioate salt

Calcium ethanedioate is the major component of the most common type of human kidney stones. It is one of a series of salts formed from ethanedioic acid, $H_2C_2O_4$. Another of these salts can be represented by the formula $\mathbf{X}_2C_2O_4.H_2O$, where **X** is a Group 1 metal.

Solution **Q** contains 64.5 g dm^{-3} of $\mathbf{X}_2C_2O_4.H_2O$ in deionised water. You are not provided with **Q.**

FA 1 is a diluted solution of **Q**, in which 35.70 cm^3 of **Q** was made up to 250 cm^3 with deionised water in a graduated flask.

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.

In this question, you will perform a titration. The data from this titration will be used to determine:

- the concentration of $C_2O_4^{2-}$ in **Q**,
- the M_r of $\mathbf{X}_2C_2O_4.H_2O$, and hence the identity of **X**.

(a) **Titration of FA 1 against FA 2**

In this titration, **FA 2** is run from the burette into the conical flask containing **FA 1** and **FA 3**. Initially, the colour of the **FA 2** will take some time to disappear.

After some **FA 2** has been added, sufficient Mn^{2+}(aq) ions will be present to allow the reaction to occur faster.

The end-point is reached when a permanent pale pink colour is obtained.

(i)
1. Fill the burette with **FA 2**.
2. Using a pipette, transfer 25.0 cm^3 of **FA 1** into the conical flask.
3. Using an appropriate measuring cylinder, transfer 50.0 cm^3 of **FA 3** to the same conical flask.
4. Heat this solution to about 65 °C.
5. Run **FA 2** from the burette into this flask until a **permanent** pale pink colour is obtained.
6. Record your titration results in the space provided on page 3. Make certain that your recorded results show the precision of your working.
7. Repeat points **1** to **6** as necessary until consistent results are obtained.
8. **Turn off your Bunsen burner**.

Results

[5]

(ii) 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]

(b) **(i)** The equation for the reaction between ethanedioate ions and manganate(VII) ions is shown below.

$5C_2O_4^{2-}(aq) + 2MnO_4^{-}(aq) + 16H^{+}(aq) \rightarrow 10CO_2(g) + 2Mn^{2+}(aq) + 8H_2O(l)$

Calculate the amount, in moles of ethanedioate ions, $C_2O_4^{2-}$ in 25.0 cm^3 of **FA 1**.

Amount of $C_2O_4^{2-}$ in 25 cm^3 of **FA 1** =…………………………… [1]

1 **(b)** **(ii)** Determine the concentration, in mol dm^{-3}, of $C_2O_4^{2-}$ in **Q**.

Concentration of $C_2O_4^{2-}$ in **Q** =……………………… **[2]**

(iii) Use your answer to **(b)(ii)** to calculate the M_r of the ethanedioate salt.

M_r of the ethanedioate salt = ……………………..

Hence, deduce the identity of **X**.
Show your working.

[A_r: C, 12.0; O, 16.0; H, 1.0; Li, 6.9; Na, 23.0; K, 39.1; Rb, 85.5; Cs, 132.9; Fr. 223.0]

[3]

X is …………………..

1 **(c)** A student performed the experiment in **(a)(i)** using a sample of another ethanedioate salt. The student obtained a mean titre value of 22.20 cm^3. The teacher calculated that the volume of **FA 2** required should have been 22.40 cm^3. The teacher told the student that the total percentage error from the apparatus in the experiment was 0.4 %.

Calculate the error in the student's result, based on these data. State **and** explain whether or not the student's result is accurate.

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

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

[Total: 14]

2 Evaluation of the reliability of a gas collection method in determining a value for the M_r of the ethanedioate salt.

In this experiment, you will react the ethanedioate salt with potassium manganate(VII), in the presence of a small amount of manganese(II) ions. You will measure the volume of CO_2 gas produced at timed intervals and determine the maximum volume of CO_2 gas produced.

FA 4 is a solution containing manganese(II) ions, Mn^{2+}.

You will need access to the **FA 1**, **FA 2** and **FA 3** solutions you used earlier.

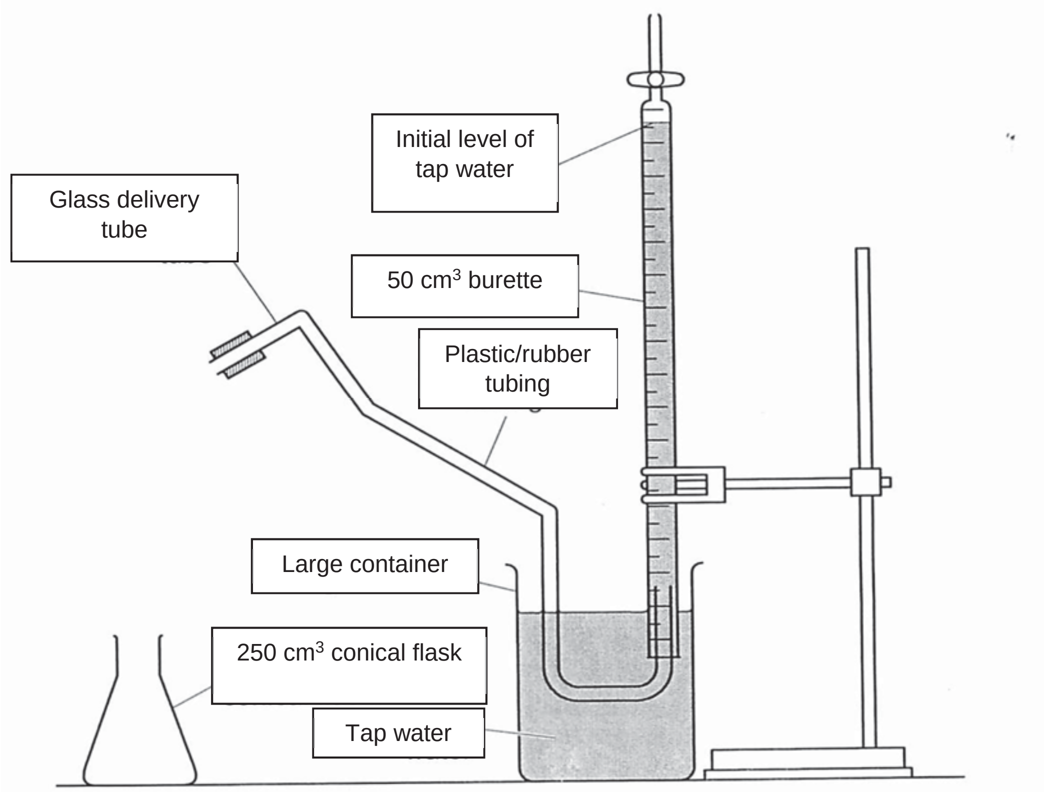


Fig. 2.1

You will measure the level of water in the burette at timed intervals.

In an appropriate format in the space provided on page 7, prepare a table in which you may record each burette reading and the time it was taken.

In addition, your table will need to show the total volume of CO_2 collected up to that time, recorded to one decimal place.

1. Set up the apparatus as shown in Fig. 2.1. You should insert the plastic/rubber tubing to a sufficient depth so that it will not subsequently shake loose.
2. Adjust the water level in the burette until it is between 48.0 cm^3 and 50.0 cm^3. You may find it helpful to use an empty dropping pipette to introduce small amounts of air from the bottom of the burette tube.
3. Use appropriate measuring cylinders to add to the 250 cm^3 conical flask.
   - 20.0 cm^3 of **FA 1**
   - 50.0 cm^3 of **FA 3**
4. Using a dropping pipette, add about 1 cm^3 of **FA 4** to the conical flask.
5. Using an appropriate measuring cylinder, measure out 30.0 cm^3 of **FA 2.**
6. Transfer the **FA 2** into the conical flask and insert the bung into the conical flask.
7. Allow any bubbles created in the burette when the bung was inserted in the conical flask to rise to the top. Start the stopwatch, read and record the initial water level in the burette.
8. Note: Once you have started the stopwatch, allow it to continue running for the duration of the experiment. You must not stop the stopwatch until the reaction is complete.
9. Check that the plastic/rubber tubing is securely positioned in the burette.
10. Hold the flask by its neck and gently swirl it continuously.
11. At t = 0.5 min, read and record the water level in the burette, to 1 decimal place, together with the time it was measured, in your table.
12. Continue to gently swirl the flask. Read and record the water level in the burette every half minute, until the reaction is complete.

(a) (i) Experimental Results

[3]

2 **(a)** **(ii)** Plot on the grid below, a graph of the volume of CO_2 on the y-axis, against time, *t,* on the x-axis.

Draw the most appropriate line, taking into account all of your points.

[4]

2 **(a)** **(iii)** The equation for the reaction between ethanedioate ions and manganate(VII) ions is shown below.

$5C_2O_4^{2-}(aq) + 2MnO_4^{-}(aq) + 16H^{+}(aq) \rightarrow 10CO_2(g) + 2Mn^{2+}(aq) + 8H_2O(l)$

Use this equation, and appropriate data from your graph, to calculate a value for the amount, in moles of ethanedioate ions, $C_2O_4^{2-}$, present in 20.0 cm^3 of **FA 1**.

[molar volume of gas = 24.0 dm^3 mol^{-1} at r.t.p.]

[1]

Amount of ethanedioate ions, $C_2O_4^{2-}$, in 20.0 cm^3 of **FA 1** = …………………..

(b) **(i)** Using your answer to question **1(b)(i)**, calculate the amount of ethanedioate ions in 20.0 cm^3 of **FA 1**. Hence, determine the maximum volume of CO_2 at r.t.p. that could have been produced from 20.0 cm^3 of **FA 1**.

maximum volume of CO_2 produced from 20.0 cm^3 of **FA 1** =……………

[4]

(ii) Suggest a reason for the difference between the total volume of CO_2 you collected and the maximum volume of CO_2 calculated in **2(b)(i).**

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

(iii) Suggest an improvement to this experiment that would overcome this problem.

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

2 **(b)** **(iv)** In Question **1** you calculated a value for the M_r of the ethanedioate salt. The total volume of CO_2 collected in **2(a)(i)** could also be used to calculate a value for the M_r of the ethanedioate salt.

Suggest which of these two *Mr* values would be higher. Explain your answer.

……………………………………………………………………………………

……………………………………………………………………………………

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

(c) The presence of Mn^{2+} ions, which are produced in the reaction between MnO_4^- ions and $C_2O_4^{2-}$ ions, is thought to catalyse this reaction.

(i) A student performed the experiment you performed in **2(a)(i)** but forgot to add **FA 4** to the mixture of **FA 1** and **FA 3** before adding the **FA 2**.

The student performed the experiment at the same temperature as your experiment and obtained the graph shown in **Fig. 2.2**.

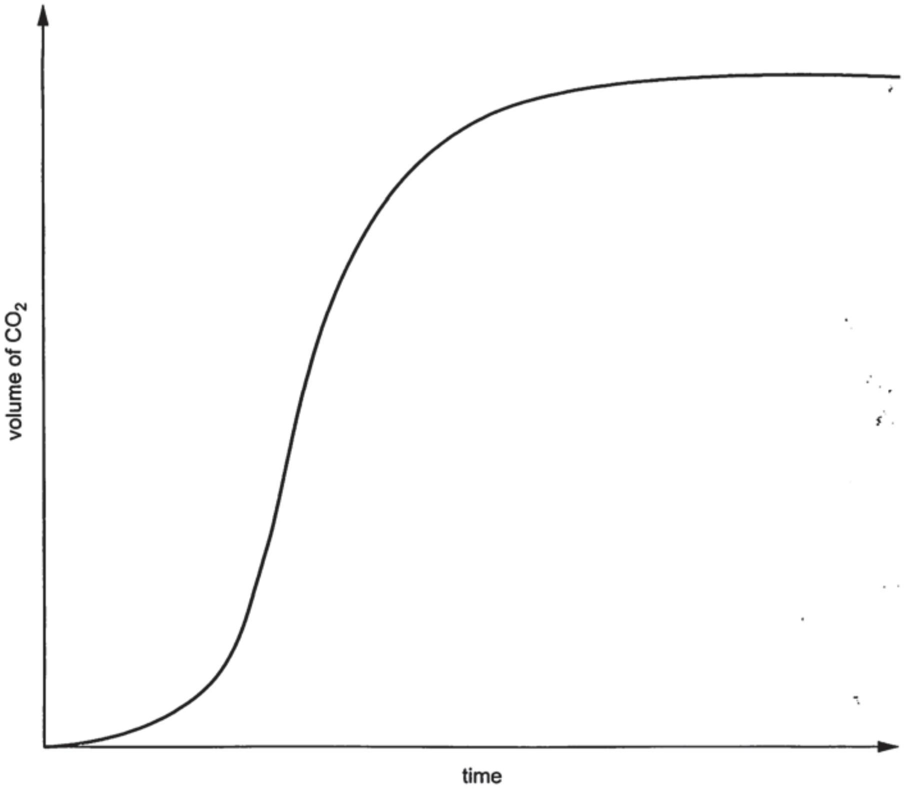


Fig. 2.2

2 **(c)** **(i)** Consider the **shape** of the graph in **Fig 2.2** and your graph in **2(a)(ii)**.

Describe one major difference between the shapes. Suggest an explanation for your answer.

Difference ……………………………………………………………………………

……………………………………………………………………………………..

Explanation …………………………………………………………………………

………………………………………………………………………………………

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

(ii) For the titration in **1(a)(i)** between ethanedioate ions, $C_2O_4^{2-}$, and manganate(VII) ions, MnO_4^-, the solution needs to be at about 65 °C at the start. As cold **FA 2** is added, the temperature of the mixture decreases. However, this decrease in temperature does not cause the rate of reaction between $C_2O_4^{2-}$ ions and MnO_4^- ions added from the burette to decrease.

Suggest an explanation for this.

………………………………………………………………………………………

………………………………………………………………………………………

………………………………………………………………………………………

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

2 **(d)** **Planning**

The oxidation of iodide ions, I^-, by peroxodisulfate ions, $S_2O_8^{2-}$, is known to be catalysed by Fe^{2+} or Fe^{3+} ions.

A similar reaction, shown below, in which ethanedioate ions, $C_2O_4^{2-}$, are oxidised by peroxodisulfate ions, $S_2O_8^{2-}$, may be catalysed by Cu^{2+} ions and by Ag^+ ions.

$$S_2O_8^{2-} + C_2O_4^{2-} \rightarrow 2\ SO_4^{2-} + 2\ CO_2$$

(i) Suggest an explanation why both of these reactions are slow when performed in the absence of a catalyst.

……………………………………………………………………………………………

……………………………………………………………………………………………

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

(ii) Plan an investigation to test how well, **if at all**, Cu^{2+} ions and by Ag^+ ions catalyse the reaction between $C_2O_4^{2-}$ ions and $S_2O_8^{2-}$ ions.

In your plan, you should include details of:

- the reactants and conditions that you would use,
- the apparatus you would use and the procedure you would follow,
- the measurements you would take,
- an outline of how you would use your results to compare the effectiveness of each ion as a potential catalyst.

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

………………………………………………………………………………………

………………………………………………………………………………………

……………………………………………………………………………………..

………………………………………………………………………………………

………………………………………………………………………………………

………………………………………………………………………………………

……………………………………………………………………………………..

………………………………………………………………………………………

………………………………………………………………………………………

………………………………………………………………………………………

……………………………………………………………………………………..

………………………………………………………………………………………

………………………………………………………………………………………

………………………………………………………………………………………

……………………………………………………………………………………..

………………………………………………………………………………………

………………………………………………………………………………………

………………………………………………………………………………………

……………………………………………………………………………………..

………………………………………………………………………………………

………………………………………………………………………………………

………………………………………………………………………………………

……………………………………………………………………………………..

………………………………………………………………………………………

……………………………………………………………………………………… **[7]**

[Total: 26]

3 You are provided with the solid **K12** which contains one cation given in the Qualitative Analysis Notes.

You are to perform the tests below to identify the cation present in **K12** and suggest the nature of **K12.** Record your observations in the spaces provided. Your answers should include

- Details of colour changes and precipitates formed,
- The names of any gases evolved and details of the test used to identify each one.

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.

Tests	**Observations and Deductions**
1 Heat **K12** alone.	
2 Warm **K12** with dilute hydrochloric acid. Keep the solution.	
3 To the solution from test **2**, add dilute nitric acid and barium nitrate(V) solution	
4 Warm **K12** with a freshly made solution of iron(II) sulfate solution.	
5 Dissolve **K12** in dilute nitric acid. Add manganese(II) sulfate solution and two drops of silver nitrate(V) solution to act as a catalyst. Boil the mixture.	
6 Warm **K12** with sodium hydroxide solution.	

Nature of **K12:** ______________________________

Cation it contains: ______________________________ **[9]**

[Total: 9]

4 **Planning**

You are provided with 3 unlabelled bottles and each bottle contains one of the following organic compounds,

- Butanamide
- Lactic acid, $CH_3CH(OH)CO_2H$
- Pyruvic acid, CH_3COCO_2H

(a) Outline a sequence of simple chemical tests to identify each of the above organic substances. You may use any other common laboratory chemical reagents and apparatus, if necessary. You are **not** allowed to identify the substances by elimination. You are reminded that most of the compounds listed are *flammable* liquids. **[3]**

Test	**Expected Observations & Deductions**

(b) Suggest a safety measure that you would consider in carrying out your plan.

____

____ **[1]**

(c) State the required reagents and conditions. Draw a set-up of the apparatus for the synthesis of pyruvic acid from lactic acid.

[2]

[Total: 6]

The End

<u>2017 SAJC H2 Chemistry Preliminary Practical Examination</u>
<u>PREPARATION LIST</u>

Apparatus List:

2 × burettes
1 × 25.0 cm^3 pipette
1 × pipette filler
1 × retort stand and clamp
2 × funnels
2 × 250 cm^3 conical flasks
2 x 50 cm^3 measuring cylinders
1 × 25 cm^3 measuring cylinder
2 × dropping pipettes
1 × white tile
1 x thermometer
1 x stopwatch, reading to at least 0.1 s
1 × 250 cm^3 conical flask complete with rubber bung and glass delivery tube with at least 35 cm of plastic/ rubber tubing attached

1 x large container (water trough)
1 x wash bottle (deionised water)
1 x test-tube rack
7 x test tubes
1 x test tube brush;
1 x spatula
1 x test-tube holder;
1 x Bunsen burner
1 x tripod stand
1 x wire gauze
1 x delivery tube
1 x glass rod
1 x wooden splinter
1 x marker
1 x goggles

Communal:

filter paper
filter paper/ litmus box

toilet roll
lighter

Chemical List:

Chemical basket:
FA1
FA2
FA3
FA4

Communal:
K12

<u>Reagent Rack</u>
aqueous sodium hydroxide
aqueous ammonia
aqueous silver nitrate(V) solution
aqueous nitric acid
aqueous sulfuric acid
aqueous hydrochloric acid
aqueous barium nitrate (V) solution
aqueous potassium manganate (VII)
aqueous calcium hydroxide
iron (II) sulfate solid
aqueous manganese(II) sulfate

Q1 and Q2

hazard	label	per candidate	identity	Notes (hazards given in this column are for the raw materials)
	FA 1	150 cm^3	0.0500 mol dm^{-3} potassium ethanedioate	Dissolve 9.21 g of $K_2C_2O_4.H_2O$ **[HH]** in deionised water and make up the solution to 1 dm^3.
	FA2	150 cm^3	0.0200 mol dm^{-3} potassium manganate(VII)	Dissolve 3.16 g of $KMn0_4$ **[O][MH][N]** in about 250 cm^3 of deionised water, then add deionised water to 1 dm^3.
[MH]	**FA3**	250 cm^3	1.0 moldm^{-3} sulfuric acid	Cautiously pour 55 cm^3 of concentrated (98%) sulfuric acid [C] into 500 cm^3 of deionised water with continuous stirring. Make the solution up to 1 dm^3 with deionised water. Care: *concentrated sulfuric acid is very corrosive.*
	FA4	5 cm^3	0.100 moldm^{-3} manganese(II) sulfate	Dissolve 16.9g of $MnS0_4.H_2O$ **[HH][N]** in each 1 dm^3 of solution.

Q3

Title	**Practical Inorganic Analysis** **Deduce the identities of the organic compounds K 12**		
Label Code	**Chemicals**	**Preparation**	**Per Student**
	$(NH_4)_2S_2O_8$	-	2-3 g/student
[MH]	1.0 mol dm^3 HCl (bench reagent)	Standard lab preparation	5cm^3 / student (bench reagent)
	Nitric acid		2cm^3/student
	Barium nitrate (V) solution		2cm^3/student
	Iron(II) sulfate crystal		2cm^3/student
	Manganese (II) sulfate solution		2cm^3/student
	Silver nitrate(V) solution		1cm^3/student (bench reagent)
aqueous sodium hydroxide [C]	2.0 mol dm^3 NaOH	Dissolve 80.0 g of NaOH **[C]** in each dm^3 of solution. **Care**: the process of solution is exothermic and any concentrated solution is very corrosive.	4 cm^3/student (bench reagent)

2017 H2 Chemistry Paper 1 Worked Solution

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

1 Amt of $KMnO_4$ used for first experiment = 0.1 x 15/1000 = 1.5 x 10^{-3} mol

$5Fe^{2+} + MnO_4^- + 8H^+ \rightarrow 5Fe^{3+} + Mn^{2+} + 4H_2O$

Amt of Fe^{2+} present = 1.5 x 10^{-3} x 5 = 7.5 x 10^{-3} mol

$[Fe^{2+}]$ = 7.5 x 10^{-3} /(25/1000) = 0.3 mol dm^{-3}

Amt of $KMnO_4$ used for second experiment =0.1 x 34.2/1000 = 3.42 x 10^{-3} mol

Amt of Fe^{2+} present = 0.0171 mol

Amt of Fe^{3+} originally in 25 cm^3 = 0.0171 – (7.5 x 10^{-3}) = 9.6 x 10^{-3} mol

$[Fe^{3+}]$ = 9.6 x 10^{-3} / (25/1000) = 0.384 mol dm^{-3}

Ans: C

2 9 x 4 = 36 nuclides were lost, hence the mass number of element A is now 241 – 36 = 205.

9 x 2 = 18 protons were lost, hence the atomic number of element A before accounting for the electrons is 94 – 76. However, the implication of $_{-1}^{0}e$ is that each electron lost increases the atomic number by 1, so 5 electrons means that the atomic number increases by 5. Hence 76 + 5 = 81.

Ans: A

3 A is not correct. From NH_3 to H_2S, the shape changes from trigonal pyramidal to bent, hence the bond angle actually decreases.

B is correct. PH_3 has a smaller bond angle than NH_3 as P is less electronegative than N, hence the bond pairs are further away from the central atom and experience less bond–pair–bond pair repulsion, hence leading to a smaller bond angle in PH_3. $AlCl_3$ has a larger bond angle than NH_3 as it is trigonal planar with a bond angle of 120 °.

C is not correct. From PH_3 to PF_3, H is less electronegative than F, hence the bonding electron pairs are closer to the central atom in PH_3, hence experience greater bond–pair–bond pair repulsion, hence leading to a greater bond angle in PH_3. From PH_3 to PF_3, there is a decrease in bond angle.

D is not correct. XeF_4 is square planar with bond angle of 90°. SCl_6 is also square planar with bond angle of 90°. Hence there is no increase in bond angle.

Ans: B

4 Glycine forms zwitterions and has an ionic lattice structure with strong electrostatic forces of attraction between the zwitterions, hence has a higher melting point than 2–hydroxyethanoic acid.

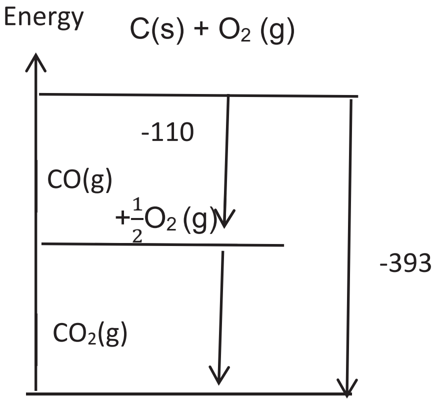
Ans: C

5 pV = nRT. For fixed mass of gas at constant T, pV α k. Hence graph should be horizontal line with gradient k.

At lower T, pV should be be lower than original.

Ans: C

6



Ans: A

7 $\Delta G = \Delta H - T\Delta S$

ΔH will be positive, because interactions in the protein are broken going to the unfolded state. ΔS will also be positive, because the unfolded state is more disordered with coil being more random. ΔG is negative as denaturation is spontaneous when egg is cooked.

Ans: A

8 At a higher temperature, the graph is skewed towards the right. Area under the graph represents the number of molecules with energy greater than or equal to E_{A}.

Ans: B

9 Since total vol is constant, [reactants] is α to its vol

Rate α 1/time

Comparing expt 1 & 2, when $[I^-]$ increases 1.5 times, rate increases 170/113 = 1.5 times. Hence 1st order wrt $[I^-]$

Comparing expt 2 and 3, $[S_2O_8^{2-}]$ increases 2 times, rate increases 113/56.5 = 2 times. Hence 1st order wrt $[S_2O_8^{2-}]$

⇨ Rate = k $[S_2O_8^{2-}][I^-]$

Comparing Expt 1 & 4, when $[I^-]$ increases 2 times and $[S_2O_8^{2-}]$ increases 4 times, rate should increase 8 times. Hence time in Expt 4 = 170/8 = 21.3 s.

Since Rate = k $[S_2O_8^{2-}][I^-]$, slow step should involve 1 mole of $(NH_4)_2S_2O_8$ and 1 mole of KI. Since overall eqn involves 2 moles of I^-, the reaction must have more than 1 step. Hence reaction should involve intermediates.

Fe^{2+} can act as homogenous catalyst in the reaction which is slow due to the reaction between two anions:

Step 1: **$\underline{2Fe^{2+} + S_2O_8^{2-} \rightarrow 2Fe^{3+} + 2SO_4^{2-}}$**

$E^{\ominus}_{cell}$ = +2.01 – (+0.77) = + 1.24 V (> 0, reaction is feasible)

Step 2: **$\underline{2Fe^{3+} + 2I^- \rightarrow 2Fe^{2+} + I_2}$**

$E^{\ominus}_{cell}$ = +0.77 – (+0.54) = + 0.23 V (> 0, reaction is feasible)

Ans: C

10 A: When acid is added, NH_3 is removed. Hence POE will shift left and white precipitate of Ag*Cl* is formed.

B: K_c expression does not include solids.

C: K_c expression is not affected by concentration

D: Removing solid does not shift POE.

Ans: A

11 $2SO_3\text{ (g)} \rightleftharpoons 2SO_2\text{ (g)} + O_2\text{(g)}$

	$2SO_3$ (g)	$2SO_2$ (g)	O_2(g)
Initial/atm	x	0	0
Eqm/atm	0.5x	0.5x	0.25x

0.5x+0.5x+0.25x = 1.2

x = 0.96

Mole fraction of O_2 = 0.25(0.96) / 1.2 = 0.2

Alternatively,

$2SO_3\text{ (g)} \rightleftharpoons 2SO_2\text{ (g)} + O_2\text{(g)}$

	$2SO_3$ (g)	$2SO_2$ (g)	O_2(g)
Initial/mol	x	0	0
Eqm/mol	0.5x	0.5x	0.25x

Mole Fraction of O_2 = (0.25x)/ (0.5x+0.5x+0.25x) = 0.2

Ans: B

12 1) HI is a strong acid. $CH_3CH_2NH_2$ will be protonated. No more weak base present. Not a buffer.

2) 2 mol of HCl and 2 mol of CH_3COOH will be formed from the hydrolysis of CH_3COCl . 2 mole of HCl reacts with 2 moles of NaOH, leaving 1 mole of NaOH. 1 mol of CH_3COONa will be formed from the acid base reaction of 2 moles of CH_3COOH with 1 mole of NaOH, leaving 1 mol of CH_3COOH. Since there is 1 mol of

CH_3COONa and 1 mol of CH_3COOH, a buffer is formed (Think about the species and the possibility of reacting)

3) H_2SO_4 is a stong dibasic acid which will cause $CH_3CH_2NH_2$ to be protonated. Not a buffer

Ans: A

13 $MX_2 (s) \rightleftharpoons M^{2+} (aq) + 2X^- (aq)$

$LY (s) \rightleftharpoons L^+ (aq) + Y^- (aq)$

A: Ksp increase only when the fwd reaction is endothermic while Ksp decrease when the reaction is exothermic.

B: For solute containing different number of ions, solubility should be calculated to determine which is more soluble. Ksp can only be used for comparison of the no. of ions that made up the two solutes are similar.

C: To calculate for any concentration of ion, it should be IONIC PRODUCT

D: If the solublity of LH is exothermic, a higher temperature will lower the Ksp since the k_b increase a greater extent than k_f.

Ans: D

14 Graph 1: Electronegativity increases across the period.

Graph 2: Si has the highest melting point as it requires the most energy to overcome the strong network of covalent bonding in its giant covalent lattice. P_4 are held by weak id-id interaction, hence low mpt.

Graph 3:

	NaCl	$MgCl_2$	$AlCl_3$	$SiCl_4$	PCl_5
pH	7	6.5	3	1-2	1-2

Ans: D

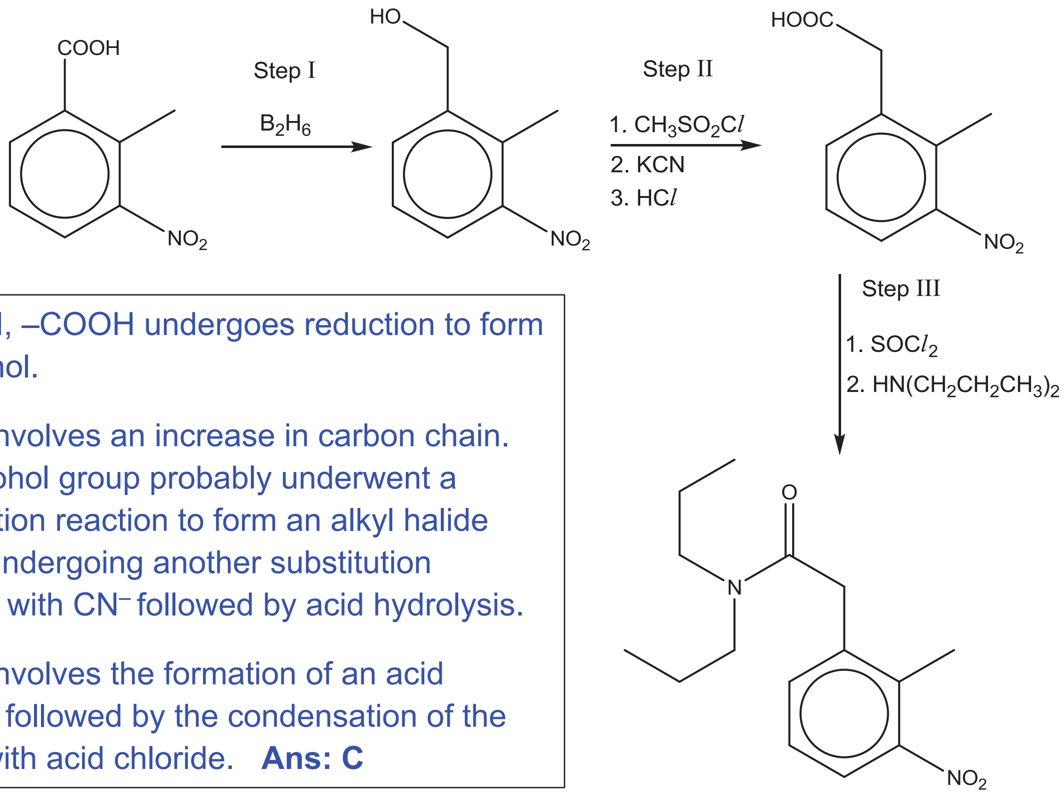
15 1. From the more positive $E^\ominus$, it can be seen the X_2 has the greatest tendency to be reduced. Hence, it has the greatest oxidising power.

2. The $E^{\ominus}$cell will be +1.36 – (+0.54) = +1.90 > 0. Hence, the reaction will occur.

3. From the data booklet, Z_2 is I_2 which is the largest atomic radius, so it has the least tendency to attract electrons to form negatively charge species. Hence, lowest E.A.

Ans: C

16 Which of the following shows the correct type of reaction(s) occurring for each step of the synthesis?



In Step I, –COOH undergoes reduction to form an alcohol.

Step 2 involves an increase in carbon chain. The alcohol group probably underwent a substitution reaction to form an alkyl halide before undergoing another substitution reaction with CN^- followed by acid hydrolysis.

Step 3 involves the formation of an acid chloride followed by the condensation of the amine with acid chloride. **Ans: C**

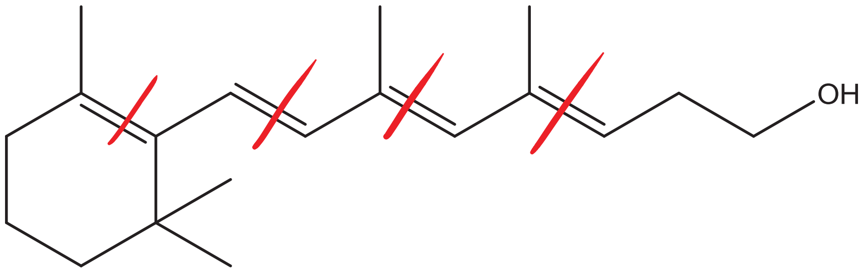
17 The reaction does not have an activation barrier (zero E_A) which means it must be a very energetically favourable reaction which does not involve any bond breaking.

Ans: D

18 **A:** HCl (white fumes) is formed when the alcohol reacts with ethanoyl chloride.

B: is wrong as alkene does not undergo reduction with $LiAlH_4$.

C: is wrong since CO_2 would not be produced when the compound undergoes strong oxidation. No presence of ethanedioic acid that can break down into CO_2.



D: 1 mol of Vitamin A produces 0.5 mol of H_2 and that is 22.7/2 = 11.35 dm^3 at stp.

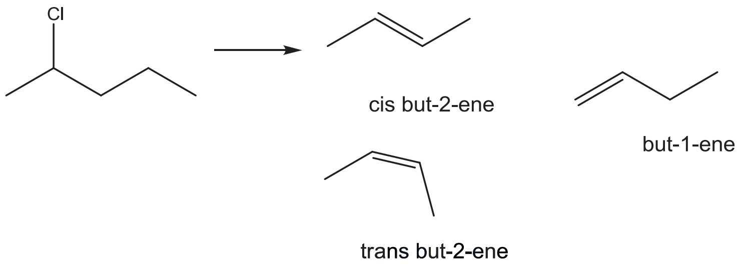
Ans: A

19 Option 1 is wrong since $CH_3CH_2CHClCH_3$ undergoes S_N2 nucleophilic to give a optically active product, $CH_3CH_2CH(OH)CH_3$. The product would be a racemic mixture if it underwent S_N1 mechanism.

Option 2 is correct as $CH_3CH_2CH(OH)CH_3$ and $CH_3CH_2CH_2OCH_3$ are functional group isomers.

Option 3 is correct as C–Br bond is weaker than C–Cl bond and so rate of substitution will increase when the sample is 2–bromobutane.

Option 4 is correct as $CH_3CH_2CH(OH)CH_3$ undergoes elimination with conc, H_2SO_4 to give but–1–ene, cis–but–2–ene and trans–but–2–ene.

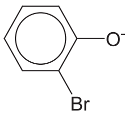


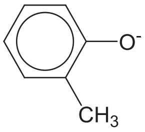
Ans: **D**

20 Conjugate base with smallest pK_b (largest K_b) is the strongest conjugate base; it must come from the weakest acid (smaller K_a).

Strength of acidity is dependent on stability of conjugate anion. The greater the **extent of charge dispersal, the more stable the conjugate anion**.

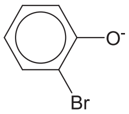
Order of **decreasing stability of conjugate anion**:

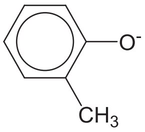


, 

, $CHF_2CH_2O^-$,$(CH_3)_2CHO^-$

Correct order in increasing K_b:



, 

, $CHF_2CH_2O^-$,$(CH_3)_2CHO^-$

Ans: **B**

21 Option A is wrong since the intermediate $CH_3CH_2CH(CN)O^-$ has a tetrahedral shape.

Option B is wrong since a racemic mixture of $CH_3CH_2CH(OH)CN$ would be obtained.

Option C is wrong since there are more –R groups surrounding the carbonyl C in propanone, making the C less electron deficient and also hindering the attack of the nucleophile. Hence the rate should be slower.

Option D is correct due to nucleophilic substitution where the Cl is substituted by CN to give the same product. $CH_3CH_2CH(OH)CN$

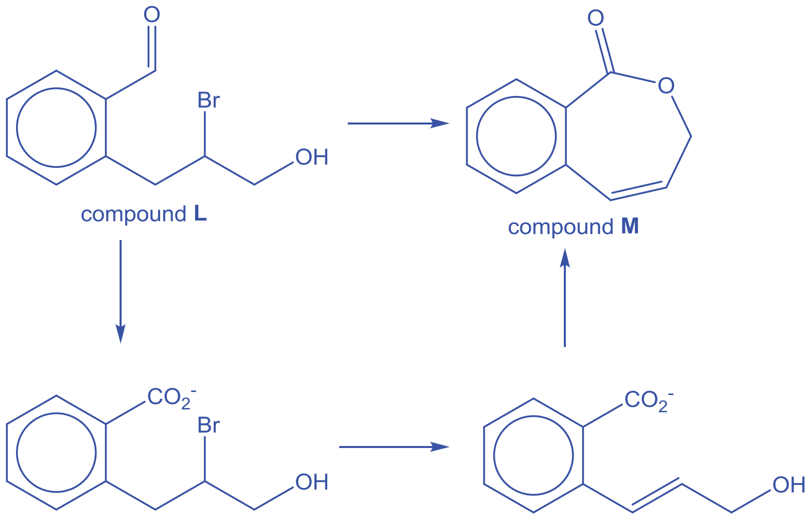
Ans: D

22 Butyl ethanoate is formed from butanol and ethanoic acid

$CH_3CH_2CH_2CH_2O\mathbf{OCCH_3}$ + $\mathbf{H^{18}O}$-H → $CH_3CH_2CH_2CH_2OH$ and $\mathbf{CH_3CO^{18}OH}$

Ans: A

23

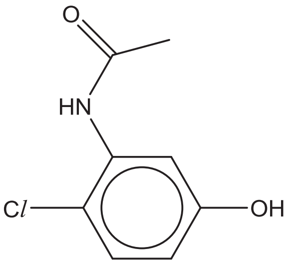


Ans: C

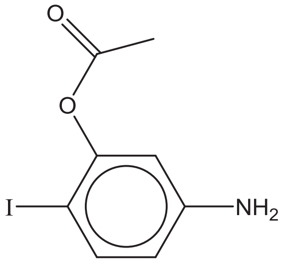
24 α–amino acid has a $H_2N\text{-}CH(R)\text{-}COOH$ structure. Hence, after oxidative cleavage Option 1 and 4 are probable with the correct empirical formulae.

Ans: B

25 Which of the following reagents would give different observations when added to both compounds in separate test–tubes?



Compound **Y**

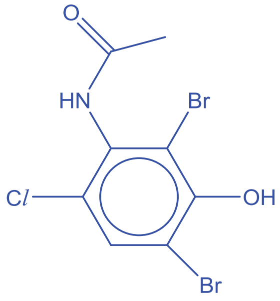


Compound **Z**

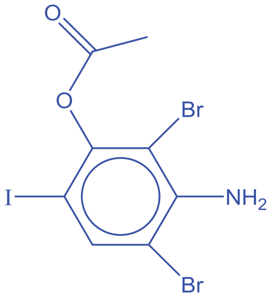
A aqueous bromine

Both compounds would decolourise orange aqueous bromine and form white precipitates.

product of compound **Y**



product of compound **Z**



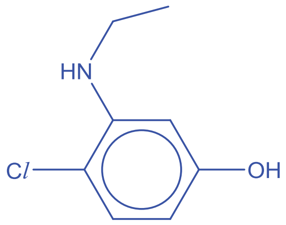
B 2,4–dinitrophenylhydrazine

Neither compounds have carbonyl functional groups and hence not form orange precipitate.

C $LiAlH_4$ in dry ether, followed by hot acidified $KMnO_4$

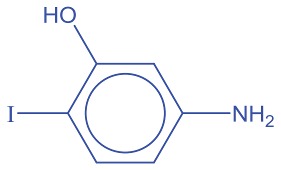
Both compounds would undergo reduction with $LiAlH_4$ and form the following :

product of compound **Y**



products of compound **Z**

CH_3CH_2OH



The ethanol would undergo oxidation and decolourise $KMnO_4$.

D ethanolic silver nitrate

Aryl halides would not form precipitate with ethanolic silver nitrate.

Ans: C

26

1. Acid chloride reacts with phenol and alcohol to form ester and amine to form amide. Note that the lone pair of e on N (next to the C=C) is delocalised into the double bond hence nucleophilic subst to form amide is not possible.
2. Alkenes and ketones can be reduced by hydrogen gas to form alkane and secondary alcohol respectively.

3. HBr(g) can react with the alkene via electrophilic addition, the aliphatic alcohol to form RBr via nucleophilic substitution, and both amine functional groups in an acid base reaction.

Ans: B

27 Lone pair of electron on O in alcohol is donated into the empty orbital of H^+.

Ans: B

28 Sucrose is oxidised to carbon dioxide gas while oxygen is reduced to water. Hence electrons will flow from left (anode) to right (cathode).

$E^\theta(O_2/H_2O) = +1.23$ V

$+1.25 = +1.23 - E^\theta_{(anode)}$

$E^\theta_{(anode)} = -0.02$ V **Ans: A**

29 Since 1 mol of complex forms 2 mol of AgI (s), only one iodide ion is present in the complex. Therefore, there should be 5 ammonia ligands in the complex (since complex has co-ordination number 6). Y is $[Cr(NH_3)_5I]\ I_2$.

Ans: C

30 1) Q can use its 3 unpaired 3d and 4s electrons to form ions or bonds hence can exhibit oxidation states from +1 to +5. Therefore $\mathbf{Q_2O_3}$ (oxidation number of Q is +3) is likely to exist.

2) R has a higher nuclear charge than P. Although R has additional electrons (i.e. the 10 3d electrons) in an inner sub–shell, they provide relatively poor shielding (when compared to the 3s and 3p electrons) to the outermost 4s electrons because they are occupying highly diffuse d orbitals. (strength of shielding effect: s > p > d). Hence, the valence 4s electrons of R experience greater effective nuclear charge and are attracted more strongly to the nucleus, resulting in R having a larger 1st IE than P.

3) R^+ has a fully filled d orbital hence d–d transition is not able to take place. Hence the compound is a white solid.

Ans: D

NAME		**Class**	

ST ANDREW'S JUNIOR COLLEGE

JC2 PRELIMINARY EXAMINATION

Chemistry (9729) **11 September 2017**

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:

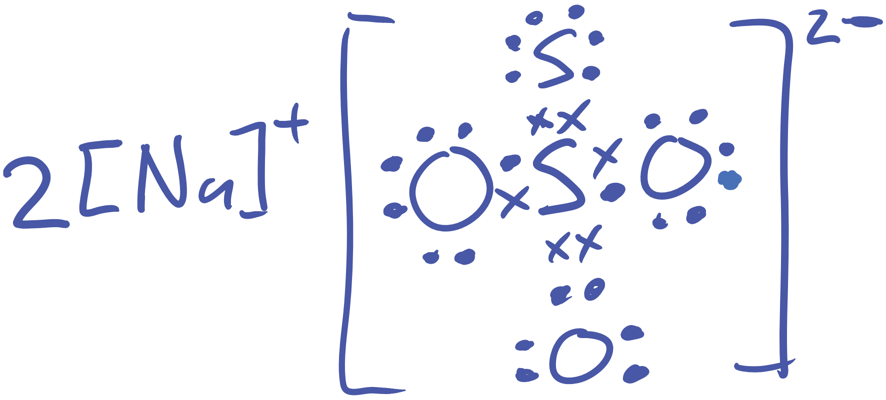
Question	**1**	**2**	**3**	**4**	**5**	**6**	**Total**
Marks	**17**	**5**	**10**	**16**	**6**	**21**	**75**

This document consists of XX printed pages (including this page).

Answer **all** the questions

1 Sulfur is a common element on Earth that forms many important chemical compounds. One of these compounds is sodium thiosulfate, $Na_2S_2O_3$, an ionic compound used to treat several medical conditions, such as cyanide poisoning and fungal growths.

(a) **(i)** Draw a dot-and-cross diagram for sodium thiosulfate, $Na_2S_2O_3$. State the shape and bond angle in the thiosulfate ion. [2]



shape around sulfur – tetrahedral

bond angle - 109°

1 mark for correct dot-cross diagram

1 mark for both shape and bond angle

Double bond between S-S atoms is accepted

Additional electrons can be shown as either dot or cross. Triangle/square/circle/any other shape cannot accept.

(ii) Below are the melting points of sodium thiosulfate and sulfur.

Compound	**Melting point / °C**
Sodium thiosulfate	49
Sulfur, S_8	115

Explain why sulfur has a higher melting point than sodium thiosulfate. [3]

Sodium thiosulfate has a giant ionic lattice structure with electrostatic forces of attraction between Na^+ and $S_2O_3^{2-}$ ions. [1]

Sulfur/S_8 is a simple non-polar covalent molecules with instantaneous-dipole-induced-dipole (id-id) interactions between its molecules.[1]

The large number of electrons in each sulfur molecule leads to strong id-id interactions, which require more energy to overcome compared to the ionic bonds in sodium thiosulfate, hence it has a higher melting point than sodium thiosulfate[1]

(b) Another important sulfur compound is sulfuric acid, H_2SO_4. Before the Contact Process was discovered, concentrated sulfuric acid for industrial purposes was produced by the following method.

The mineral pyrite, FeS_2, was first heated in air and oxidised to solid $Fe_2(SO_4)_3$ and sulfur dioxide gas.

$Fe_2(SO_4)_3$ decomposes at 480 °C to form iron(III) oxide and sulfur trioxide gas. The sulfur trioxide gas could be mixed with any volume of water to produce sulfuric acid of the desired concentration. However, this process was expensive and not efficient.

(i) Write a balanced equation, with state symbols for the reaction between pyrite, FeS_2, and oxygen to form $Fe_2(SO_4)_3$. [1]

$2FeS_2(s) + 7O_2(g) \rightarrow Fe_2(SO_4)_3(s) + SO_2(g)$ [1]

(ii) With the aid of an equation, define the term standard enthalpy change of formation of gaseous sulfur trioxide, SO_3. [2]

Standard enthalpy of formation of gaseous SO_3 is the energy released or required when 1 mole of gaseous SO_3 is formed from its constituent elements under standard conditions of 298 K and 1 bar. [1]

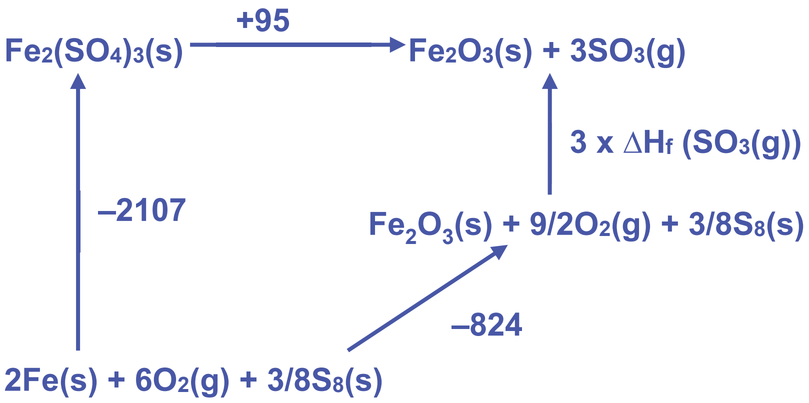
$1/8\ S_8(s) + 3/2\ O_2(g) \rightarrow SO_3(g)$ [1]

(iii) Given the following information, determine the enthalpy change of formation of gaseous sulfur trioxide SO_3.

$Fe_2(SO_4)_3(s) \rightarrow Fe_2O_3(s) + 3SO_3(g) \qquad \Delta H_{rxn} = +95\ kJ\ mol^{-1}$

Substance	**ΔH_f / kJ mol^{-1}**
$Fe_2(SO_4)_3(s)$	–2107
$Fe_2O_3(s)$	–824

[3]



2 marks for energy cycle

$3 \times \Delta H_f (SO_3(g)) + (-824) = -2107 + 95$

$3 \times \Delta H_f (SO_3(g)) = -1188$

$\Delta H_f (SO_3(g)) = -396$ kJ mol^{-1} [1]

OR

$\Delta H_{rxn} = \Delta H_f(\text{products}) - \Delta H_f(\text{reactants}) = +95$ [1]

$-824 - (-2107 + 3\Delta H_f(SO_3(g)) = +95$

[1 mark for correct substitution of values]

$3\Delta H_f(SO_3(g)) = -1188$

$\Delta H_f (SO_3(g)) = -396$ kJ mol^{-1} [1]

(iv) Use the appropriate bond energies given in the *Data Booklet* and the data below to calculate another value for the standard enthalpy change of formation of gaseous sulfur trioxide SO_3.

$\frac{1}{8}S_8(s) + O_2(g) \rightarrow SO_2(g)$ $\Delta H_f = -297\ \text{kJ mol}^{-1}$ [3]

$$\begin{tikzcd}
\mathbf{1/8S_8(s) + 3/2\ O_2(g)} \arrow[r, "\mathbf{-297}"] \arrow[d, "\mathbf{\Delta H_f\ (SO_3(g))}"] & \mathbf{SO_2(g) + \frac{1}{2}O_2(g)} \arrow[d, "\begin{array}{l}\mathbf{\frac{1}{2}\ x\ BE\ (O_2)} \\ \mathbf{=\ \frac{1}{2}\ x\ 496} \\ \mathbf{= +248}\end{array}"] \\
\mathbf{SO_3(g)} & \mathbf{SO_2(g) + O(g)} \arrow[l, "\mathbf{-BE\ (S{=}O) = -500}"']
\end{tikzcd}$$

$\mathbf{\Delta H_f\ (SO_3(g))\ = -549\ kJ\ mol^{-1}}$

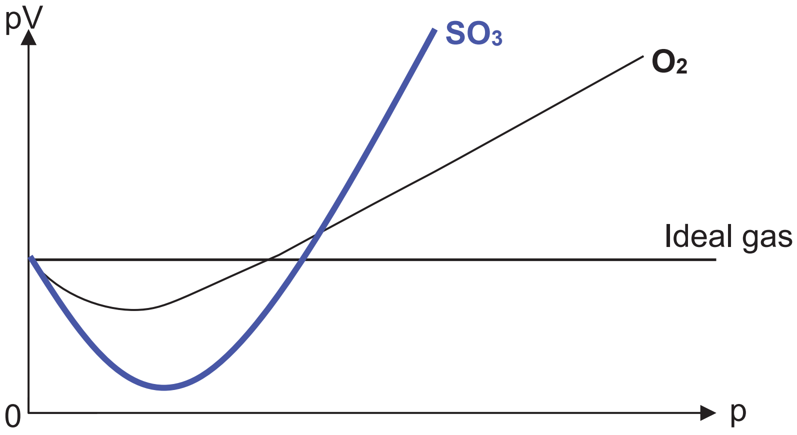
2 marks for energy cycle, ½ mark for each correct arrow with reactants and products

1 mark for calculation

(v) Suggest a reason for the discrepancy between the values in **(b)(iii)** and **(b)(iv)**. [1]

The bond energy data from the data booklet are only average values and would not apply exactly to particular compounds.[1]

(c) The value of pV is plotted against p for 1 mol of oxygen O_2, where p is the pressure and V is the volume of the gas at 300 K.



(i) On the diagram above, draw and label the graph of pV against p for SO_3 at 300 K. [1]

Can cut the ideal gas line at any point, but negative and positive deviation must be more than O_2.

(ii) Explain the difference between the graph of SO_3 and the graph of O_2. [1]

SO_3 has more electrons than O_2, hence it has stronger instantaneous-dipole-induced-dipole interactions and has greater deviation from ideality. [1]

OR

SO_3 has a larger size, hence the volume of SO_3 compared to the total volume occupied by the gas is more significant. [1]

[Total: 17]

2 Transition elements show typical properties that distinguish them from s-block elements, such as calcium. These include variable oxidation states in their compounds, and the formation of coloured complex ions.

(a) An ion of manganese has 3 electrons in its 3d subshell. Suggest the oxidation state of this manganese ion. [1]

+4 [1]

(b) The following table gives data about some physical properties of the elements calcium, chromium, and manganese.

Property	**Ca**	**Cr**	**Mn**
Atomic radius (metallic) / nm	0.197	0.129	0.132
Ionic radius (2+) / nm	0.099	0.073	0.083
Melting point / K	1112	1907	1246
Density / g cm^{-3}	1.54	7.19	7.43
Electrical conductivity / x 10^{6} S cm^{-1}	0.298	0.0774	0.00695

(i) Explain why the atomic radii of chromium and manganese are similar to each other. [2]

Mn has more proton and hence greater nuclear charge. However, the two paired electrons in the 4s subshell of Mn also experience interelectronic repulsion.[1] The effect on the radius due to nuclear charge is counteracted by the interelectronic repulsion between the two paired electrons in the 4s subshell.[1]

Accept

Proton number increases and hence nuclear charge increases from Cr to Mn. Shielding effect increases because the electrons are added to the inner 3d subshell. [1] The effect on the radius due to nuclear charge is counteracted by the effect on the radius due to the shielding effect / effective nuclear charge is approximately constant/similar. [1]

(ii) Explain why the density of manganese is significantly greater than that of calcium, using relevant data from the table and the Data Booklet. (No calculations are required.) [2]

Density = mass / volume

Manganese has atomic mass of 54.9, which is greater than the atomic mass of calcium, 40.1. [1]

Manganese has atomic radius of 0.132 nm, which is less than the atomic radius of calcium, 0.197 nm. [1] Or

Manganese has ionic radius of 0.083 nm or 0.058 nm, which is less than the ionic radius of calcium, 0.099 nm. [1]

[Total: 5]

3 A student investigated the thermal decomposition of two carbonates, calcium carbonate and barium carbonate in the following way to determine its exact composition. He used the same amount, in moles, of each carbonate.

MCO_3 (s) → ***M***O(s) + CO_2 (g) ***M*** is Ca or Ba

He heated the carbonates separately for 5 minutes. The solid obtained after heating was then shaken with distilled water to form an alkaline solution. A portion of the solid remained insoluble and was filtered. A sample of the alkaline filtrate was titrated with hydrochloric acid. No effervescence was observed during the titration.

(a) **(i)** Suggest which carbonate is less likely to decompose completely. Explain your answer. [2]

$BaCO_3$ is more thermally stable and not decomposed completely.

Ionic radius of Ba^{2+} > Ca^{2+} Hence charge density(charge/volume ≈ charge/ionic radius)of Ba^{2+} smaller than Ca^{2+}. [1] Polarising power of Ba^{2+} weaken, less able to polarise the electron cloud of carbonate, less weakening of the C-O bond in the carbonate. Hence the carbonate is less likely to decompose.[1]

(ii) It was observed that the volume of acid used in the titration was smaller for the carbonate which did not decompose completely.

Explain how the incomplete decomposition can result in a lower volume of acid used in the titration. [2]

Incomplete decomposition of $BaCO_3$ will result in smaller amount of BaO being formed [1] BaO is a basic oxide and will dissolve in water to give an alkaline solution and hence less $Ba(OH)_2$ being produced hence requiring lower volume of HC*l* for titration.[1]

$BaO + H_2O \rightarrow Ba(OH)_2$

$Ba(OH)_2 + 2HCl \rightarrow BaCl_2 + 2H_2O$

(b) Explain the difference between the magnitude of the lattice energies of calcium carbonate and calcium oxide. [2]

LE α $\left|\frac{q_+ \times q_-}{r_+ + r_-}\right|$

r^+, q^+ and q^- same for both compound. CO_3^{2-} has a larger ionic radius than O^{2-}.[1]

Thus magnitude of LE of $CaCO_3$ is smaller than that of CaO.[1]

(c) Given that the decomposition of calcium carbonate is an endothermic reaction.

$$\Delta H = +178 \text{ kJ mol}^{-1} \text{ and } \Delta S = +159 \text{ J K}^{-1} \text{ mol}^{-1}$$

Calculate the minimum temperature at which this reaction becomes spontaneous. [2]

$\Delta G = \Delta H - T\Delta S < 0$

$T > 178000/159$ [1]

$T > 1120K$

Minimum temperature is 1120 K. [1]

(d) Beryllium oxide can react with sodium hydroxide.

$$BeO + 2NaOH \rightarrow Na_2BeO_2 + H_2O$$

Explain this behaviour despite Be being a Group 2 element. [2]

Due to the high charge density of Be^{2+}[1], BeO shows a degree of covalent character / amphoteric [1] and thus able to react with a base.

[Total: 10]

4 Gaseous phosphorus(V) chloride dissociates according to the following equation.

$$PCl_5\,(g) \rightleftharpoons PCl_3\,(g) + Cl_2\,(g)$$

Different amounts of the three gases were placed in a closed container and allowed to come to equilibrium at 200 °C. The experiment was repeated at 425 °C.
The equilibrium partial pressure of the three gases at each temperature are given in the table below.

	Partial pressure / 10^{-3} N m^{-2}		
temperature/°C	PCl_5	PCl_3	Cl_2
200	1.46	11.8	2.77
425	7.61	0.211	0.368

(a) **(i)** Write the expression for the equilibrium constant, K_p, for this reaction. Give the units. [2]

$K_p = \frac{P_{PCl3}P_{Cl2}}{P_{PCl5}}$ [1]

Units: N m^{-2} [1]

(ii) Calculate the value of K_p at each of the temperatures given. [2]

At 200°C

$K_p = (11.8 \times 10^{-3})(2.77 \times 10^{-3}) / (1.46 \times 10^{-3})$

$= 0.0224$ N m^{-2} [1]

At 425°C

$K_p = (0.211 \times 10^{-3})(0.368 \times 10^{-3}) / (7.61 \times 10^{-3})$

$= 1.02 \times 10^{-5}$ N m^{-2} [1]

(iii) Is the forward reaction exothermic or endothermic? Explain your answer. [2]

According to Le Chatelier's Principle, when temperature is increased, endothermic reaction is favoured to "absorb" the additional heat. Since the positon of equilibrium shifts to the left (as evident from the higher partial pressure of PCl_5) at higher temperature, this suggests that the backward reaction is endothermic and hence the forward reaction is exothermic.[1]

Or

Since $K_p = \frac{k_f}{k_b}$, a drop in K_p as temperature increases implies that the rate of backward reaction increases to a greater extent [1]than rate of the forward reaction. This suggests that the backward reaction is endothermic and hence the forward reaction is exothermic.[1]

(b) What will be the effect on the equilibrium partial pressure of PCl_5 when the following changes are carried out on this new equilibrium? Explain your answers clearly.

(i) The pressure of the system is halved at constant temperature. [2]

When pressure is halved, position of equilibrium will shift right [1] as there are more moles of gaseous products to increase the number of moles of gases [1] to increase the pressure. Less PCl_5.

(ii) Helium gas is added at constant volume and temperature. [2]

Individual partial pressures for each gas did not change.[1]

No change in position of equilibrium. [1]

Chloroethane can be made by reacting PCl_3 with ethanol, via nucleophilic substitution mechanism.

$$PCl_3 + CH_3CH_2OH \rightarrow CH_3CH_2Cl + HOPCl_2$$

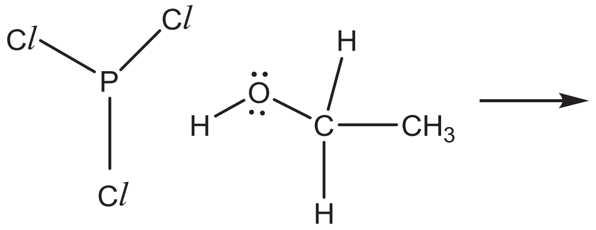
(c) Outline a simple chemical test that can be carried out to see if chloroethane is produced in the mixture after reacting with PCl_3. [2]

Heat chloroethane with aq NaOH. Cool, acidify with nitric acid, then add dilute $AgNO_3$ to sample. [1] A white precipitate should be obtained. [1]

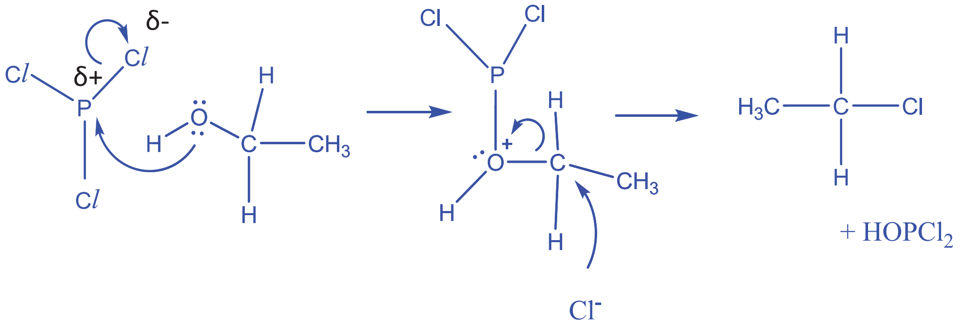
(d) The mechanism is thought to involve these steps.

- The first step is where P-C*l* bond breaks. P is electron deficient and reacts with alcoholic O to form a protonated oxygen intermediate.
- The C-O bond is broken. Cl^- act as a nucleophile.

Complete the diagram to suggest a mechanism to show how chloroethane is formed. Show all charges and relevant lone pairs and show the movement of electron pairs by using curly arrows.



[3]



Nucleophilic Substitution

2marks for both sets of arrows

1 mark for intermediate

dipoles

Lone pair on Cl during intermediate step

No penalty for slow/fast

(e) Explain why chlorobenzene cannot be made in the same way using phenol and PCl_3. [1]

The **lone pair of electrons on O can delocalise into the benzene ring** and resulting in **strengthening of the C-O bond**. [1] Hence the bond does not break easily for NS to take place.

[Total: 16]

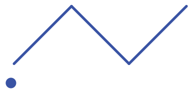
5 Bromine reacts with organic compounds in different ways.

(a) When butane reacts with gaseous bromine in the presence of ultraviolet light, the major product was 2-bromobutane instead of 1-bromobutane. Using the stability of the intermediates, explain the observation. [3]

The reaction of gaseous bromine and butane is **free radical substitution**, where the **ultraviolet light splits the bromine-bromine sigma bond in the bromine molecule homolytically** to form 2 bromine radicals / atoms. **[1 mark for either stating FRS or the formation of bromine radical]**

The bromine radical formed reacts with the butane molecule to form the following 2 different radicals.

radical **A**



radical **B** **[1]**

can describe in words – 2 alkyl groups vs 1 alkyl group / lone electron on 1st vs 2nd carbon / primary vs secondary radical

Radical **A** is formed in a larger proportion than radical **B** because the carbon with the radical in radical **A** has **1 additional electron donating alkyl group** than in radical **B**. This **stabilises the radical to a greater extent** and hence lead to the higher proportion of 2-bromobutane formed despite having a smaller number of hydrogen atoms to be substituted.**[1]**

(b) A solution of 2-bromobut-2-ene, upon heating with ethanolic silver nitrate solution, does not form a cream precipitate.

Upon addition of concentrated sulfuric acid in the cold and followed by heating with ethanolic silver nitrate, 2-bromobut-2-ene formed a cream precipitate.

Explain the above observations. [3]

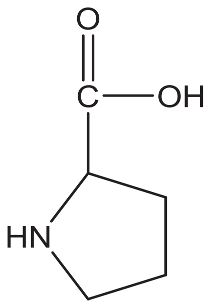
The bromine atom's lone pair of electrons would **delocalise into the alkene functional group, forming a partial double bond**. This partial double bond is **very strong** and hence would not break upon heating and thus no cream-white precipitate was formed. **[1]**

Upon addition of sulfuric acid, the pi-bond in the alkene would **undergo electrophilic addition and hence break**. **[1]** Therefore the bromine atom no longer delocalises its electrons and the carbon-bromine single bond remains. Upon heating with silver nitrate solution, **nucleophilic substitution occurs / the carbon-bromine single bond would break heterolytically, forming the bromide ion**. **[1]** Upon addition of aqueous silver nitrate, would result in the formation of silver bromide, the cream precipitate.

[Total: 6]

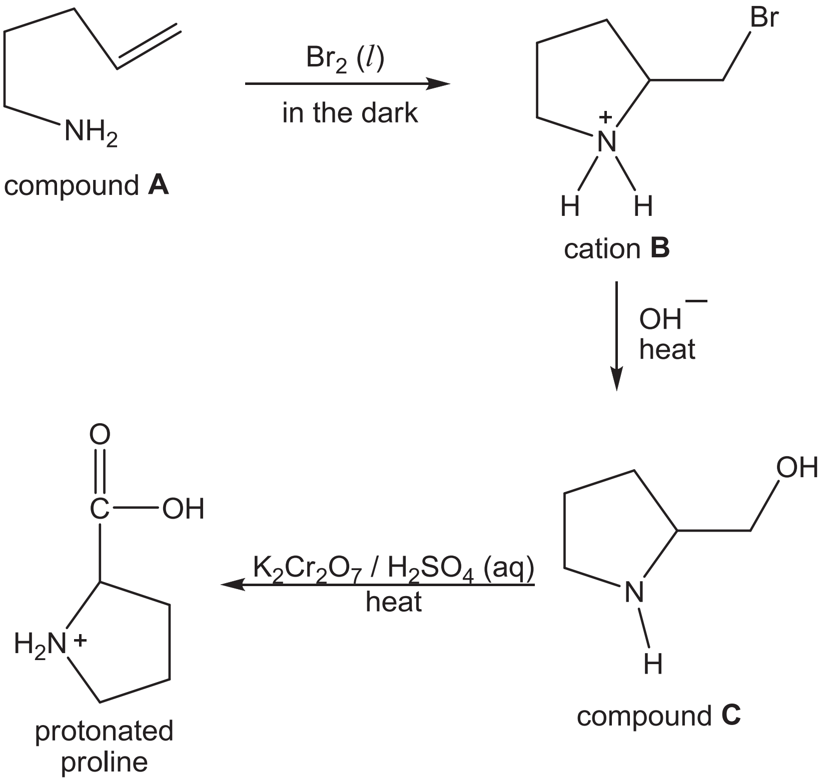
6 Proteins, found within the human body, are formed by amino acids. These amino acids are classified as either essential (cannot be synthesised by the human body) or non-essential (can be synthesised by the human body) amino acids.

(a)



Proline

Proline, one of the non-essential amino acids, is associated with the production of collagen which promotes healthy skin and heart muscle. Protonated proline can potentially be synthesised in the following manner.

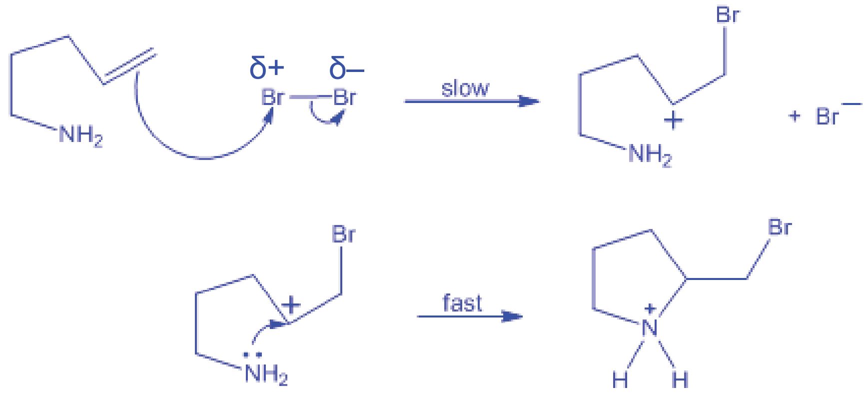


The reaction of compound **A** with liquid bromine occurs via a two-step mechanism.

- compound **A** reacts with bromine to form a carbocation intermediate in the first step.
- the ammonium ion is formed in the second step.

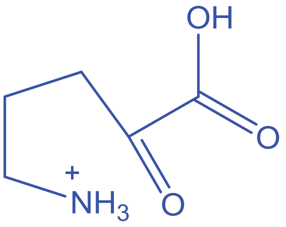
(i) Name and suggest the mechanism for this reaction. Show any relevant lone pairs, dipoles and charges, and indicate the movement of electron pairs with curly arrows. [3]

Electrophilic addition **[1]**



[1] – for each equation (inclusive of dipoles, lone pairs, slow/fast, etc.)

(ii) This synthesis also produces another organic compound (molecular formula $C_5H_{10}NO_3Br$). Suggest the skeletal formula of the cation. [1]



[1]

(iii) Compound **C** was extracted and reacted with 1 mole of ethanoyl chloride to form a neutral compound **D** with molecular formula $C_7H_{13}NO_2$. Draw the structure of compound **D**. Explain why this product is formed. [2]

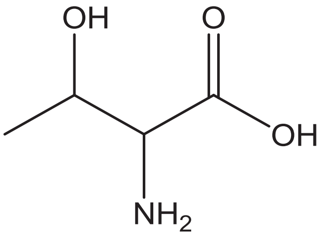
[1]

The amine functional group reacts with ethanoyl chloride as it is a stronger nucleophile as the lone pair of electrons on the nitrogen atom are **more available / likely to attack** the electron-deficient carbon on ethanoyl chloride than the oxygen atom in the alcohol functional group. [1 – availability of lone pair of electrons]

OR

N is less electronegative than O, hence l.p more available to attack. [to be confirmed as answer]

(b)



Threonine

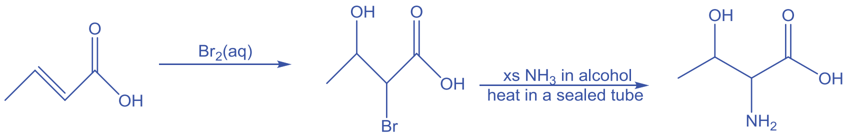
Threonine, one of the essential amino acids, maintains protein balance within the human body and supports the cardiovascular, liver, central nervous and immune system functions.

In the laboratory, threonine could be synthesised from but-2-enoic acid.

(i) State the type of isomerism exhibited by but-2-enoic acid. [1]

cis-trans isomerism

(ii) Suggest a 2-step synthesis for the formation of threonine from but-2-enoic acid, showing the intermediate clearly in your answer. [3]



reagents and conditions **[1]** for each step

intermediate **[1]**

(iii) By considering the stereoisomers of threonine, suggest why only 25% of the synthesised threonine could be used in the human body. [2]

Threonine exhibits **enantiomerism** due to the **presence of 2 chiral carbons**. **[1]** There is a total of **4 possible enantiomers** and **only one of which** matches the threonine within the human body. **[1]**

Accept optical isomers / isomerism

(c) **(i)** Suggest whether threonine or proline has the more basic amine group. Explain your answer. [2]

Proline's amine functional group is **more basic** than that of threonine's.**[1]**

Proline's amine functional group is a secondary amine whereas threonine's amine functional group is a primary amine. The **lone pars are more available for protonation due to two/more electron-donating groups** in the secondary amine, hence proline is more basic. **[1]**

OR

On top of which threonine has **an additional secondary alcohol functional group**, which **causes the availability of the lone pair of electrons on the nitrogen atom in the amine to be less available to be donated to a proton**.[1]

(ii) Explain, in terms of their structures, the higher solubility of threonine in water as compared to benzoic acid in water. [2]

Threonine exist as **a zwitterion [1]** in water whereas benzoic acid exist as a simple covalent molecule in water.

Threonine would form **ion-dipole interactions with water molecules** and **releases significantly more energy** as compared to the **hydrogen bonds** formed between benzoic acid molecules with water molecules. Thus threonine is more soluble in water as compared to benzoic acid.**[1]**

(d) According to dieticians, a teenager requires approximately 1.00 g of calcium each day. This particular mineral is found predominantly in milk, cheeses and yogurts, which most individuals consume in the morning.

(i) Procedure to extract calcium ions is stated as follows :

1. A cup of milk (300 ml) was first filtered to remove impurities before excess amounts of sodium carbonate was added to form $CaCO_3$.

2. The mixture was then refiltered and the white residue (assumed to be solely calcium carbonate) was washed once again with deionised water and filtered again.
3. The white residue was then dissolved in 0.500 dm^3 of 0.160 mol dm^{-3} hydrochloric acid. 25.0 cm^3 of this resulting solution was then titrated against 0.125 mol dm^{-3} sodium hydroxide. The titre volume was found to be 26.45 cm^3.

What is the recommended number of cups of milk each day a teenager should consume to meet the daily requirements? [3]

amount of sodium hydroxide used = 0.00330 mol

amount of excess hydrochloric acid present in 0.500 dm^3 of resulting solution = 0.0661 mol **[1]**

amount of hydrochloric acid used to dissolve the white precipitate ($CaCO_3$) = 0.0138 mol

amount of calcium carbonate = 0.00693 mol **[1]**

mass of calcium ions in 1 cup of milk = 0.278 g

no. of cups needed = 1 / 0.278 = 3.60

hence the teenager should drink about 4 cups of milk a day. **[1]**

3.6 cups also accepted as answer

(ii)

Compound	Amount per serving
Vitamin A	5000 IU
Vitamin C	300 mg
Vitamin D	600 IU
Vitamin E	30 IU
Vitamin K	80 mcg
Thiamin (Vitamin B-1)	50 mcg
Riboflavin (Vitamin B-2)	50 mg
Folic Acid	600 mcg
Vitamin B-12 (as Cyanocobalamin)	50 mcg
Calcium (as in calcium carbonate)	200 mg

Iodine (as Potassium iodide)	150 mcg
Magnesium (as magnesium oxide)	50 mg
Zinc (as zinc oxide)	25 mg
Selenium (as L-Selenomethionate)	200 mcg
Molybdenum (as sodium molybdate)	75 mcg

A typical multivitamin dietary supplement tablet would have the above composition. Given that the teenager does not consume any form of dairy products, how many tablets would a teenager need to take to achieve the daily requirement of calcium? [1]

No. of tablets = 1.0 g / 0.2 g = 5 **[1]**

(iii) A student wants to test the validity of the composition of calcium in this tablet and decided to follow the steps mentioned in **(d)(i)**.

State 1 possible problem that the student would face. [1]

1. The calcium carbonate precipitate would be formed along with copper carbonate, magnesium carbonate, etc.

   OR
2. The tablet would have to be treated initially to dissolve it completely.

[1 mark for any point]

[Total: 21]

~ END OF PAPER ~

NAME		Class	

ST ANDREW’S JUNIOR COLLEGE

JC2 PRELIMINARY EXAMINATION

Chemistry (9729) **15 September 2017**

Paper 3 Free Response **2 hours**

Additional Materials: Data Booklet, Writing Paper

READ THESE INSTRUCTIONS:

Write in dark blue or black pen.

You may use an HB pencil for any diagrams or graphs.

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

Section A

Answer **all** questions. Marks [60]

Section B

Answer **one** question. Marks [20]

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

A Data Booklet is provided.

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

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

This document consists of XX printed pages (including this page).

Section A

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

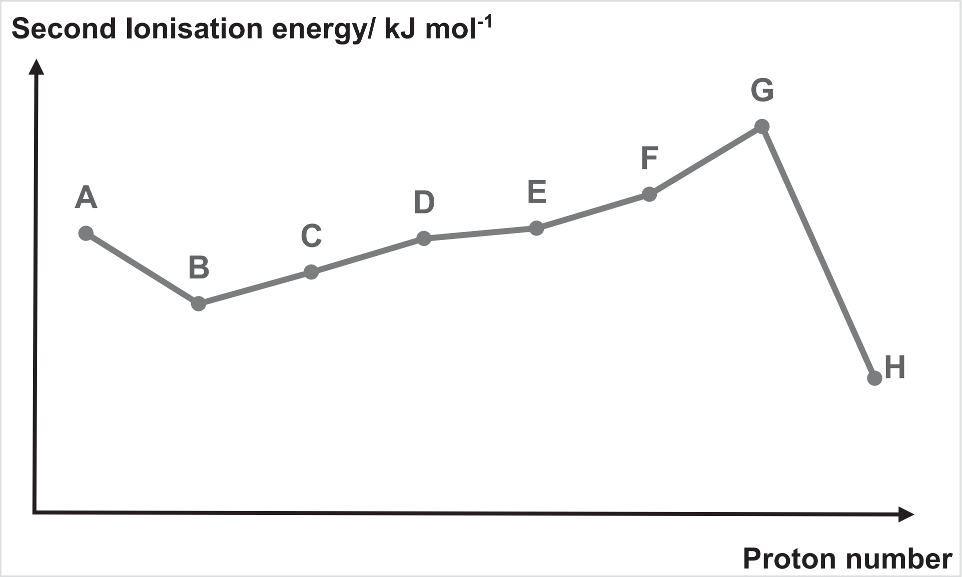
1 **(a)** Iodine is a lustrous purple-black solid at standard conditions that sublimes readily to form a violet gas.

(i) Give the equation that represents the *second ionisation energy* of *iodine*. [1]

$I^+(g) \rightarrow I^{2+}(g) + e^-$ [1]

ΔH>0 is not required since this is not a definition question.

(ii) The graph below shows the second ionisation energies of eight elements with consecutive atomic number. [2]



Which of the above elements, **A** to **H**, is iodine? Explain your answer.

Element **E**. [1] The sharp drop from **G** to **H** indicates that **G** is from Group 1 where the second ionisation energy involves the removal of an electron from the **inner** principal **quantum shell**, which is nearer to the nucleus, requiring more energy. [1] Hence Element **E** is in Group 17 and is iodine.

(iii) Explain the trend in second ionisation energies from elements **A** to **G**, including the irregularity for element **B**. [4]

The second IE generally increases from **A** to **G** because from **A** to **G**, there is an increase in proton number and hence nuclear charge while shielding effect is almost constant as electrons are added to the same quantum shell. [1] Hence effective nuclear charge increases and the attraction for the outermost electron becomes increasingly stronger. [1] More and more energy is required to remove the strongly attracted valence electron as we move across the period.

Second IE of **B** is lower than that of **A** because the electron is removed from the valence 5p subshell which is further away from the nucleus compared to the 5s subshell in **A**. [1] It also experiences additional screening effect by the two 5s. These factors outweigh the effect of increase in nuclear charge from A to B, resulting in a weaker attraction by the nucleus.[1]
Less energy is required to remove the outermost electron in **B** than that in **A**.

(iv) Suggest, with reason, which of the above elements, **A** to **H**, can form an amphoteric oxide. [2]
Hence, write an equation to show the reaction of this amphoteric oxide with hydrochloric acid. (You are not required to provide the identity of the element in the equation.)
Element **A** has amphoteric oxide since it is in Group **13** [1] and its oxide would have both ionic and covalent character.

$A_2O_3 + 6HCl \rightarrow 2ACl_3 + 3H_2O$ [1]

or

$In_2O_3 + 6HCl \rightarrow 2InCl_3 + 3H_2O$ [1]

No ecf from part (ii)

(b) Hydrogen peroxide reacts with acidified iodide ions to liberate iodine, according to the following equation:

$$H_2O_2(aq) + 2H^+(aq) + 2I^-(aq) \rightarrow 2H_2O(l) + I_2(aq)$$

The rate of reaction can be measured by the increase in the concentration of iodine formed over time. The reaction was determined to be zero order with respect to $[H^+]$.

The following results were obtained by varying the concentrations of hydrogen peroxide and iodide ions.

Expt	Initial $[H_2O_2(aq)]$ / mol dm^{-3}	Initial $[I^-(aq)]$ / mol dm^{-3}	Initial rate / mol dm^{-3} min^{-1}
1	0.020	0.040	1.2×10^{-4}
2	0.020	0.050	1.5×10^{-4}
3	0.050	0.040	3.0×10^{-4}
4	0.020	0.500	1.5×10^{-3}
5	0.050	1.000	7.5×10^{-3}

(i) What is understood by the terms *order of reaction* and *half-life*. [2]

The order of reaction with respect to a reactant is the power to which the concentration of that reactant is raised in the experimentally determined rate equation. [1]

Or Let the Rate = $k[A]^m[B]^n$, where m and n are the order of reaction wrt [A] and [B] respectively. [1]

Half-life, $t_{½}$, is the time taken for the reactant concentration to decrease to half of its original value.[1]

(ii) Determine the order of the reaction with respect to $[H_2O_2]$ and $[I^-]$ and hence suggest the units of the rate constant of this reaction. [3]

Let rate= $k[H_2O_2(aq)]^m[I^-(aq)]^n$

Compare experiments 1 & 2, keeping $[H_2O_2(aq)]$ constant

$$\frac{1.2\text{x}10^{-4}}{1.5\text{x}10^{-4}} = \frac{k(0.020)^m(0.040)^n}{k(0.020)^m(0.050)^n}$$ (or use inspection method)

n = 1

Rate of reaction is <u>1st order</u> with respect to [I^-(aq)] [1]

Compare experiments 1 & 3, keeping [I^-(aq)] constant

$$\frac{1.2\text{x}10^{-4}}{3.0\text{x}10^{-4}} = \frac{k(0.020)^m(0.040)^n}{k(0.050)^m(0.040)^n}$$ (or use comparing method)

m = 1

Rate of reaction is <u>1st order</u> with respect to [H_2O_2(aq)] [1]

Hence,

rate= k[H_2O_2(aq)][I^-(aq)]

units of k = $\text{mol}^{-1}\ \text{dm}^3\ \text{min}^{-1}$ [1]

(iii) The half-life of hydrogen peroxide in experiment 4 was 9.24 min. Predict the half-life of hydrogen peroxide in experiment 5. [1]

For Expt 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 = 9.24 min (for [I^-(aq)] = 0.500 mol dm^{-3})

$t_{1/2}$ of H_2O_2 in experiment 5 = **4.62 min** (for [I^-(aq)] = 1.00 mol dm^{-3}) [1]

To investigate the rate of the above reaction, a teacher suggested titrating the iodine formed with sodium thiosulfate solution at specified time intervals.

(iv) Write an equation for the reaction between iodine and thiosulfate. [1]

$I_2(aq) + 2S_2O_3^{2-}(aq) \rightarrow 2I^-(aq) + S_4O_6^{2-}(aq)$ [1]

State symbols not required but penalized when wrong ones are provided.

(v) Suggest how the reaction can be quenched at specified time intervals. [1]

The reaction can be quenched by:

- adding $NaOH/NaHCO_3/Na_2CO_3$ to remove the $H^+(aq)$
- sudden cooling of the reaction mixture
- sudden dilution through the addition of large volume of water

any of the above method [1]

(vi) With reference to the *Data Booklet*, explain why hydrochloric acid is not a suitable acid used for the reaction between hydrogen peroxide and iodide. [2]

$Cl_2 + 2e^- \rightleftharpoons 2Cl^-$ $E^\ominus = +1.36$ V

$H_2O_2 + 2H^+ + 2e^- \rightleftharpoons 2H_2O$ $E^\ominus = +1.77$ V

$E^\ominus_{cell} = +1.77 - 1.36 = +0.41$ V [1 for quoting and calculating]

H_2O_2 can oxidise chloride to chlorine[1] while it itself is reduced to H_2O. Hence, the oxidation of iodide may not be complete.

[Total:19]

2 Metals have been used widely since ancient times.

(a) An electrochemical cell is constructed using solutions of $NaHSO_4$, H_2SO_3, and $MnSO_4$ with suitable electrodes.

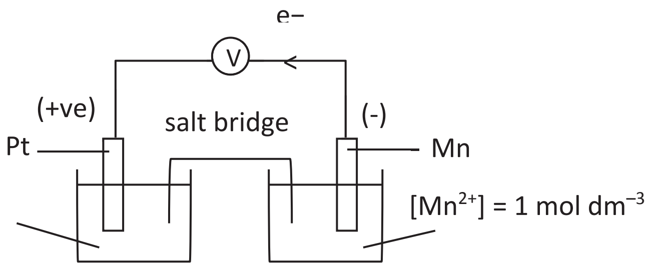
The relevant half reactions are:

$HSO_4^-(aq) + 3H^+(aq) + 2e^- \rightleftharpoons H_2SO_3(aq) + H_2O \quad E^\ominus = +0.17\ V$

$Mn^{2+}(aq) + 2e^- \rightleftharpoons Mn(s) \qquad E^\ominus = -1.18\ V$

(i) Draw a fully labelled diagram of the above electrochemical cell to measure the cell potential under standard conditions, indicating clearly the direction of the electron flow in the external circuit. [3]

T= 298 K



$[H^+] = [HSO_4^-] = [H_2SO_3]$

$= 1\ mol\ dm^{-3}$

[1] – e^- flow

[1] – voltmeter, salt bridge (can BOD from diagram) + Mn and Pt electrodes

[1] – label all the solutions (HSO_4^- , H_2SO_3, H^+) & 1 $mol\ dm^{-3}$ and temperature

(ii) Write a balanced equation for the reaction that would take place if the electrodes of the cell were connected together by an external circuit. [1]

$Mn + HSO_4^- + 3H^+ \rightarrow Mn^{2+} + H_2SO_3 + H_2O$ [1]

(iii) Calculate the standard cell potential for this cell [1]

$E^\ominus_{cell} = +0.17 - (-1.18) = +1.35\ V$ [1]

(iv) Calculate the standard Gibbs free energy change, $\Delta G^\ominus$, for the cell above. [1]

$\Delta G^\ominus = -nFE^\ominus$, where n = 2 electrons transferred

$= -2 \times 96500 \times (+1.35) = -260550 \text{ J mol}^{-1} = -261 \text{ kJ mol}^{-1}$ [1]

(v) Suggest, with reasons, what happens to the $E^\ominus_{cell}$ when the following are done to the electrochemical cell above. [4]

1) The pH of the HSO_4^- /H_2SO_3 half−cell is increased.

2) A solution of sodium hydroxide to the Mn^{2+} /Mn half−cell.

$HSO_4^-\text{ (aq)} + 3H^+\text{ (aq)} + 2e^- \rightleftharpoons H_2SO_3\text{ (aq)} + H_2O$

1. When [H⁺] is reduced /pH increases , equilibrium position shifts to the left to replenish the [H⁺], hence $E^\theta_{cathode}$ becomes less positive [1]. As E_{cell} = E (cathode) - E (anode), and E (cathode) become less positive, hence, the E_{cell} of the cell becomes less positive. [1]

$Mn^{2+}\text{(aq)} + 2e^- \rightleftharpoons Mn\text{(s)}$ E_{anode}

2. When NaOH is added, $Mn(OH)_2$ (s) will be formed and [Mn^{2+}] will decrease. Position of equilibrium will shift left to increase [Mn^{2+}], hence E_{anode} becomes more negative.[1] E_{cell} becomes more positive. [1]

(b) In an electrolytic cell, a current of 0.250 A is passed through a concentrated solution of a chloride of iron, producing iron metal and gas, **Y**.

(i) Write the equation for the half-reaction take occurs at the anode. [1]

$2\,Cl^- \rightarrow Cl_2 + 2e^-$ [1]

(ii) When the cell operates for 2 hours, 0.521 g of iron is deposited at one of the electrodes. Determine the formula of the chloride of iron in the original solution. [2]

Charge = 0.25 x 2 x 60 x 60 = 1800 C

Amt of electrons = 1800/96500 = 0.0187 mol

Amt of iron formed= 0.521/55.8 = 0.009336 mol

Mole ratio of electrons taken in: iron deposited = 0.0187: 0.009336 ≈2:1 [1]

Formula of iron chloride = $FeCl_2$ [1]

(iii) Write a balanced equation for the overall reaction that occurs in the cell. [1]

$Fe^{2+} + 2Cl^{-} \rightarrow Cl_2 + Fe$ [1]

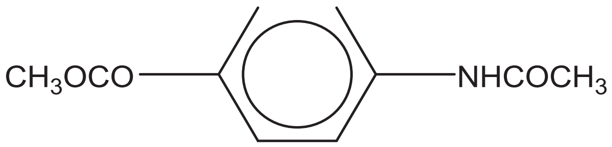
(iv) Calculate the current that would produce the gas **Y** from the solution at a rate of 2.50 g per hour. [2]

Amt of chlorine gas liberated per hour = 2.5/ 71 = 0.03521 mol

Charge required per hour= 2 x 96500 x 0.03521 = 6795 C[1]

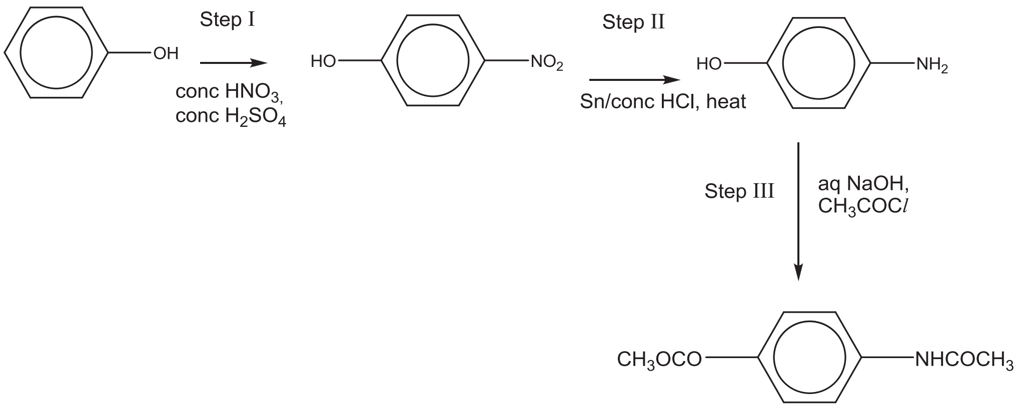
Current = Charge / time = 6795 /(60 x 60) = 1.89 A [1]

(c) Metals are also used as catalysts in organic synthesis. The derivative of acetaminophene is investigated for the treatment of headaches.



Derivative of acetaminophene

(i) A student suggested a flawed synthesis of the derivative of acetaminophene starting from phenol. Identify and explain the error in each step. [3]



Step I: Only dilute HNO_3 instead of conc H_2SO_4 and conc HNO_3 need to be used as phenol is more reactive than benzene/ or –OH group is an activating substituent.

OR conc H_2SO_4 and conc HNO_3 will produce a tri-substituted product.

OR the reagents will result in multiple substituted products.

[1]

Step II: HCl will neutralise phenylamine and form a salt instead

OR There is need to perform careful neutralisation of NaOH to remove the proton from phenylammonium ion.

[1]

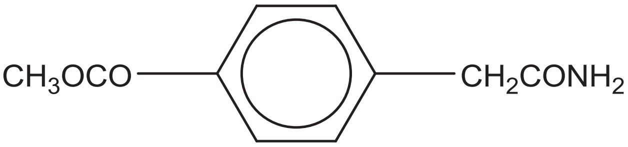
Step III: Acid chloride will hydrolyse to give CH_3CO_2H and HCl which will be neutralised by aq NaOH, hence not able to react with the phenol and phenylamine.

OR Acid chloride will react with aq NaOH, hence not able to react with the phenol and phenylamine.

OR Neutralisation takes place between acid chloride and NaOH and hence condensation will not take place.

[1]

(ii) Compound **Z** is an isomer of the derivative of acetaminophene. Suggest a simple chemical test to distinguish between the derivative of acetaminophene and compound **Z**. [2]



compound **Z**

Test: aq NaOH, heat. [1]

Observations: Compound **Z** produces pungent NH_3 gas that turns **moist** red litmus paper blue but derivative of acetaminophene does not produce pungent NH_3 that turns moist red litmus paper blue.

OR

Compound **Z** gives pungent NH_3 that forms white fumes with concentrated HCl but derivative of acetaminophene does not give pungent NH_3 that forms white fumes with concentrated HCl [1]

[Total:21]

3 **(a)** Blood obtains its colour from its respiratory proteins which occur as octahedral metal complexes. It is different in different organisms.

Protein	Source	Metal per subunit	De-oxygenated colour	Oxygenated colour
Haemoglobin	Mammals, birds, fish, reptiles, insects	1 Fe	red-purple	red

Haemocyanin	mollusks, crustaceans, spiders	2 Cu	colourless	blue

(i) Explain why oxygenated haemoglobin and haemocyanin are coloured. [3]

The oxygenated haemoglobin and haemocyanin contains transition metals ion in the centre of the complexes.

In the isolated gas phase, all partially filled 3d orbitals of the transition metal ions are degenerate. In the presence of ligand such as oxygen, the 3d orbitals split into 2 groups with a small energy gap between them. [1]

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.[1]

The light energy not absorbed is reflected and observed as colour of its the oxygenated blood. (Or the colour observed is complementary to the colour absorbed.) [1]

(ii) Using the Cartesian axes, like those shown in Figure 3.1, draw **fully labelled** diagrams of the following. [2]

- One of the d-orbitals at the lower energy level in an octahedral complex. Label the diagram “lower”.
- One of the d-orbtials at the upper energy level in an octahdral complex. Label this diagram “upper”.

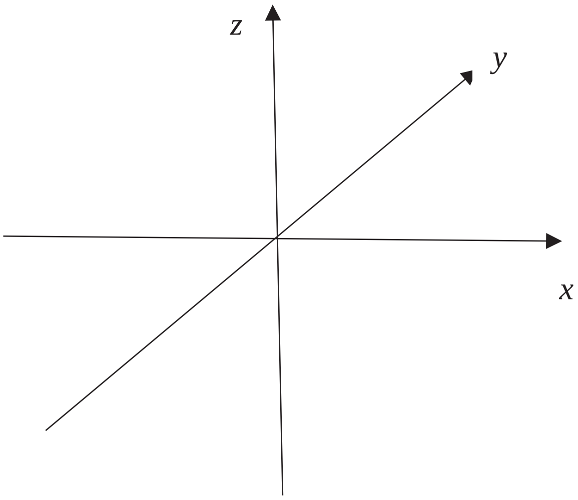
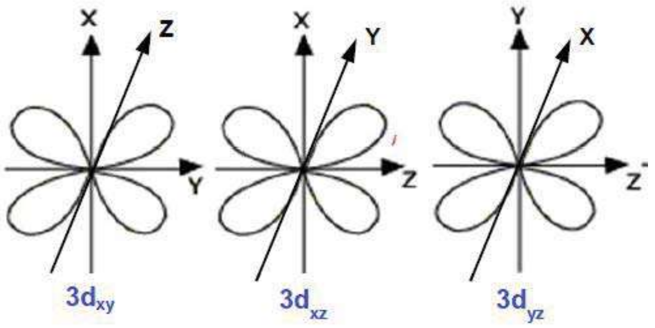
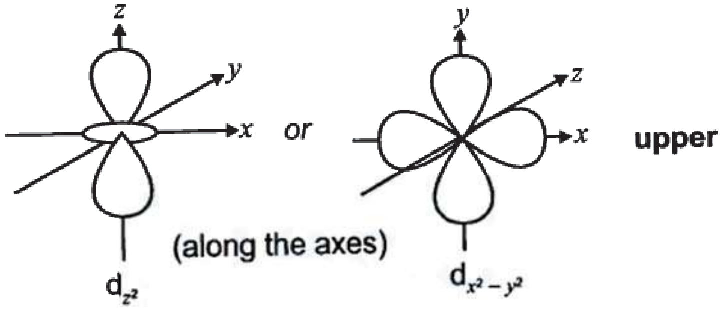


Figure 3.1

Lower: any



Upper: either



Students can change the position of x, y and z axes in their respective diagrams. Orbitals must be labelled.

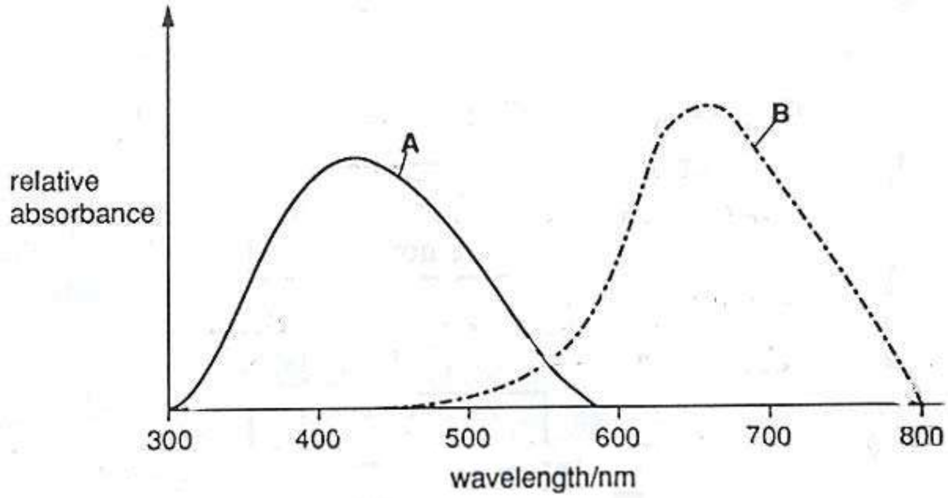
(iii) Explain why the splitting of the d subshell occurs in an octahedral complex using your answer in **(a)(ii)**. [2]

The electrons in the upper d orbitals are pointing towards the lone pairs of electrons on the ligands,[1] hence will be repelled by them and resulting in higher energy. [1]

OR

In octahedral complexes, the lone pairs of electrons on the 6 ligands approach the central ion along the axes. Thus, the energy of an electron in either the upper d orbitals ($3d_{x^2-y^2}$ or $3d_{z^2}$) experience greater electronic repulsion, resulting in higher energy. [1]

(b) Oxygenated haemoglobin and haemocyanin were analysed and the absorption spectrum was observed.



Colour	Wavelength (nm)	Colour	Wavelength (nm)
Violet	380 – 400	**Yellow**	560 – 580
Blue	400 – 490	**Orange**	580 – 620
Green	490 – 560	**Red**	620 – 800

(i) Which graph represents the absorption spectrum of oxygenated haemocyanin? Explain your answer. [2]

Graph B. [1] The wavelength not absorbed is ~380 – 470 nm. This means that the light reflected is blue/violet (accept indigo). [1]

(ii) Which oxygenated blood (haemoglobin or haemocyanin) has a larger energy gap between the d subshells after splitting? Explain your answer. [2]

Haemoglobin has a larger energy gap [1] as $\Delta E = hc/\lambda$, haemoglobin absorbs as a lower wavelength, hence it has a larger energy gap. [1]

(iii) The deoxygenated haemocyanin has a Cu^+ central ion. State the electronic configuration of Cu^+. Hence, suggest why the deoxygenated haemocyanin is colourless? [2]

Cu^+ $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10}$ [1]
Cu^+ has a fully filled 3d-subshell or fully filled 3d-orbitals. Hence, d-d transition of electrons from the lower d-orbitals to the higher orbital is not possible. [1] Hence, no energy from the visible region of the electromagnetic spectrum with wavelength corresponding to the energy gap is absorbed or reflected.

(c) Carbon monoxide, chlorine and phosgene are the best known toxic gases. Many of these gases are assigned an NFPA 704 health rating of 4 (may be lethal) or 3 (may cause serious or permanent injury).

Toxic Gas	Chemical formula	Colour	Odour	NFPA 704 Health Rating
carbon monoxide	CO	colourless	No	3

chlorine	Cl_2	green	Yes	4
phosgene	CCl_2O	colourless	No	4

(i) Describe, in terms of bonding, what happens when carbon monoxide is absorbed in the human blood and hence, explain why it is given a NFPA 704 health rating of 3. [2]

Carbon monoxide (CO) forms dative bond with Fe^{2+} in haemoglobin more readily than O_2 molecule (since Fe-CO bond is stronger than Fe-O_2 bond); or

CO displaces the oxygen in oxyhaemoglobin (HbO_2) to form carboxyhaemoglobin (HbCO).

Or

Being a stronger ligand, carbon monoxide, CO can be bonded less reversibly to the metal centre. [1]

$$HbO_2 + CO \rightarrow HbCO + O_2$$

This consequently cuts down the supply of oxygen to the body and so, accounts for the toxic nature of carbon monoxide, resulting in suffocation. This could lead to serious or permanent injury or death. [1]

Hence, it is given a NFPA 704 health rating of 3.

(ii) Chlorine was widely used as a chemical warfare in World War I. However, it was replaced by phosgene as a more effective chemical warfare. Suggest one possible reason why chlorine was replaced by phosgene. [1]

Chlorine has a distinct odour and is green in colour while phosgene is colourless and have a more subtle smell. Hence, it is more difficult for troops to detect and take counter measure. [1]

Other reasons:

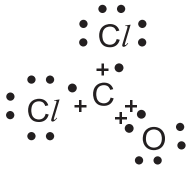
Chlorine is water-soluble and so the effect would be minimised by placing a water-soaked rag over mouth and nose.[1]

Do not accept "Phosgene is much more toxic and deadly than chlorine"; same NFPA value.

(d) Phosgene reacts with water to release hydrogen chloride and carbon dioxide gas.

$$CCl_2O + H_2O \rightarrow CO_2 + 2HCl \quad \text{------------Reaction } \mathbf{1}$$

(i) Draw the dot-and-cross diagram of phosgene and suggest its bond angle. [2]



[1]

Bond angle= 120˚ [1]

(ii) Suggest the type of reaction involved in Reaction **1**. [1]

Nucleophilic substitution or Hydrolysis [1]

(The water acts as a nucleophile; the lone pair on O of water attacks the δ+ C of phosgene)

(ii) Gaseous spills of phosgene can be removed using ammonia. The reaction is similar to Reaction **1**. Suggest how phosgene reacts with ammonia, using a chemical equation . [1]

$CCl_2O + 4NH_3 \rightarrow CO(NH_2)_2 + 2NH_4Cl$

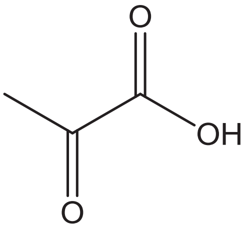
Or $CCl_2O + 2NH_3 \rightarrow CO(NH_2)_2 + 2HCl$ [1]

[Total:20]

Section B

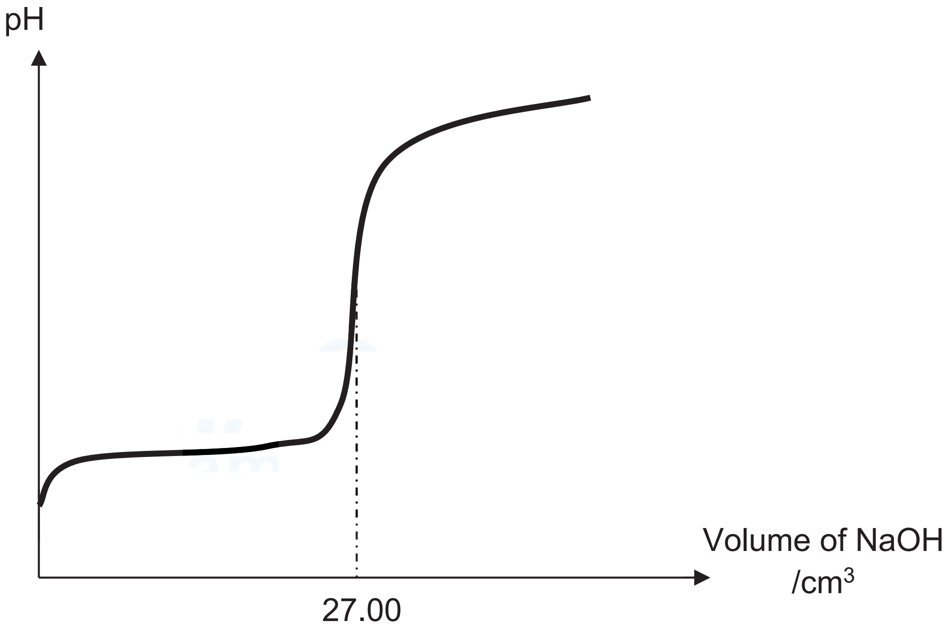
Answer **one** question from this section.

4. Pyruvic acid is an important component in the human body. It is involved in various processes such as the Krebs Cycle.



Pyruvic acid

(a) 30.0 cm^3 of pyruvic acid was titrated against 0.15 mol dm^{-3} of NaOH. The following titration curve was obtained.



(i) Given that the solution of pyruvic acid is only 15.3 % dissociated, calculate the value of K_a for pyruvic acid, stating clearly its units. [2]

[Pyruvic acid] = $\frac{0.15 \times 0.027}{0.03}$ = 0.135 mol dm^{-3}

[H^+] = 0.135 x 0.153 = 0.02065 mol dm^{-3} [1]

K_a = $\frac{0.02065^2}{0.135}$ = 3.16 x 10^{-3} mol dm^{-3} [1 with units]

Or

K_a = $(0.135)(0.153)^2$ = 3.16 x 10^{-3} mol dm^{-3} [2 with units]

(ii) Calculate the volume of NaOH added to obtain a solution of pH 12. [2]

pOH = 2

[OH^-] = 0.01 mol dm^{-3} [1]

Let the volume of NaOH added be x dm^3.

[OH^-] = $\frac{0.15(x-0.027)}{x+0.03}$ = 0.01

x = 0.0311 dm^3

31.1cm^3 of NaOH was added. [1]

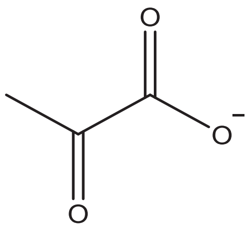
(iii) Suggest a suitable indicator for this titration. [1]

Phenolphthalein [1]

Penalise for wrong spelling

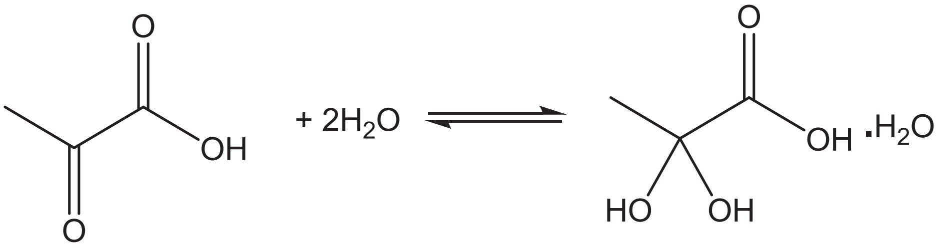
(iv) Blood has a working pH of 7.35 to 7.45. Suggest why pyruvic acid is found in trace amounts in blood. Hence, draw the major species of pyruvic acid in blood. [2]

Pyruvic acid is a weak acid. Since its pK_a value (as calculated based on (a)(i) calculation is 2.50) is less than 7 ,[1] its tendency to remain as pyruvic acid molecule in blood (which has working pH of 7.35 to 7.45) is low, hence it is only found in trace amounts in blood. [1] Hence, in blood, pyruvic acid will exist in the pyruvate(salt/conjugate base) form.



[1]

(b) An experiment to study the equilibrium between pyruvic acid and its hydrated form was done by Y. Pocker in 1969. The following data was obtained.



pyruvate hydrate

Temperature/ K	[pyruvate hydrate] [pyruvic acid]
278	3.47
294	1.75
304	1.06
324	0.47

(i) Deduce whether the hydration of pyruvic acid is an endothermic or exothermic reaction. [2]

Temperature increases, more pyruvic acid is present. Backward and forward reaction both increases. However, rate (constant) of backward reaction increases more that of forward reaction. [1] Backward reaction is the endothermic reaction. Thus hydration of pyruvic acid is exothermic. [1]

Or

Temperature increases, more pyruvic acid is present. This implies that position of equilibrium shifts left.[1] Since increase in temperature always favours the endothermic reaction, the backward reaction is endothermic.

Thus hydration of pyruvic acid is exothermic. [1]

Conclusion must be supported by correct reason. 0 if say exothermic but reason contradicts.

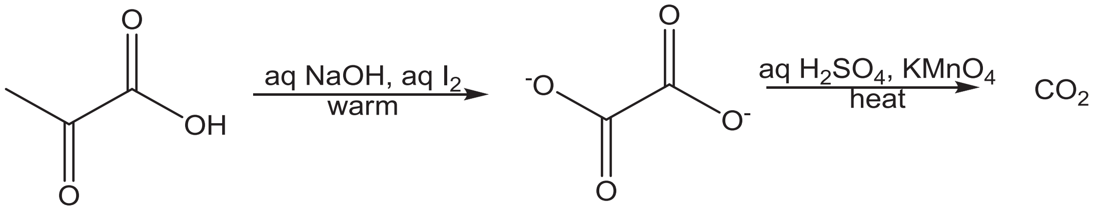
BOD and give 1 mark if only state exothermic but no reason provided.

(ii) The pyruvate hydrate has a higher pK_a value than pyruvic acid. Explain. [2]

Higher pK_a indicates that pyruvate hydrate is less acidic than pyruvic acid.[1] The -C=O group is more electron-withdrawing than the 2-OH groups, hence stabilising the conjugate base of the pyruvic acid more.[1] Hence, pyruvic acid is more acidic.

Alternate answer: Conjugate base of pyruvic acid is more resonance-stabilised due to the C=O and COO^-.

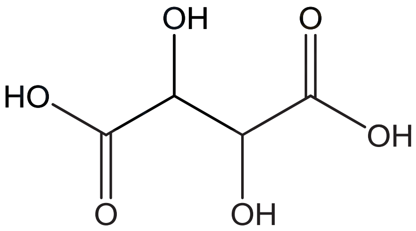
(c) Suggest a 2-step synthesis for the formation of carbon dioxide from pyruvic acid. [3]



Each reagent and condition –[1]

Intermediate – [1]

(d) Pyruvic acid was first synthesised in the laboratory through the distillation of tartaric acid with potassium hydrogen sulfate. The structure of tartaric acid is shown below.



Tartaric acid

(i) Suggest why tartaric acid has a much higher melting point than pyruvic acid. [2]

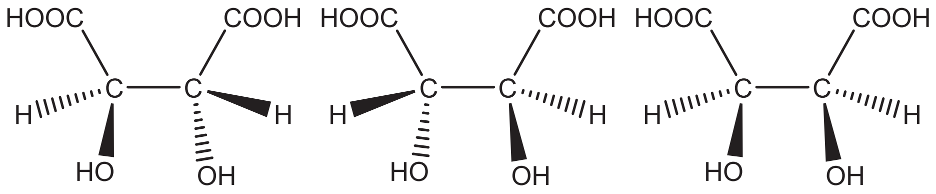
Tartaric acid and pyruvic acid are both polar simple covalent molecules with intermolecular hydrogen bonding.[1] However, tartaric acid can form more extensive intermolecular hydrogen bonding (since it has more –COOH and –OH groups). More energy required to break the more extensive intermolecular hydrogen bonding.[1]

OR

Pyruvic acid would dimerise while tartaric acid would polymerise [1] and hence id-id between the tartaric acid polymers is stronger than the id-id between pyruvic acid dimers. [1]

(ii) There are three stereoisomers present in tartaric acid. Two of them rotate plane of polarised light in opposite direction, whereas one has no effect on plane of polarised light. [4]

Draw **all** the stereoisomers of tartaric acid and explain why one of the stereoisomers does not rotate the plane of polarised light.



[1m each]

There is a plane/line of symmetry present in that stereoisomer

Or it is a meso compound. [1]

[Total: 20]

5 **(a)** Thallium(I) chromate, Tl_2CrO_4, has a solubility product of 8.67×10^{-13} $mol^3\ dm^{-9}$ at 25 °C.

(i) Calculate the solubility of Tl_2CrO_4 in 0.05 mol dm^{-3} K_2CrO_4. [2]

$K_{sp} = [Tl^+]^2[CrO_4^{2-}]$ units $mol^3\ dm^{-9}$

Let the solubility be x mol dm^{-3}

$8.67 \times 10^{-13} = [2x]^2[0.05]$ [1]

$x = 2.08 \times 10^{-6}$ mol dm^{-3} [1]

(ii) Given that the numerical K_{sp} value of $BaCrO_4$ is 1.17×10^{-10}, deduce which precipitate will be formed first if K_2CrO_4 was added slowly into a solution containing 0.015 mol dm^{-3} of Ba^{2+} and 0.015 mol dm^{-3} $\mathrm{T}l^+$. [2]

For $BaCrO_4$ ppt to form, $[CrO_4^{2-}] = \frac{1.17x10^{-10}}{0.015}$=7.8 x 10^{-9} mol dm^{-3}

For $\mathrm{T}l_2\mathrm{CrO}_4$ ppt to form, $[CrO_4^{2-}] = \frac{8.67\times10^{-13}}{0.015^2}$ = 3.85 x 10^{-9} mol dm^{-3}

[1 for both calculations]

Since less $[CrO_4^{2-}]$ is required to form $\mathrm{T}l_2\mathrm{CrO}_4$, it will precipitate first. [1]

(b) Transition elements are known to form coloured complexes. Chromium is one of the common transition element used today.

(i) An equilibrium exists between chromate(VI) ion and dichromate(VI) ions. [2]

$$2CrO_4^{2-} + 2H^+ \rightleftharpoons Cr_2O_7^{2-} + H_2O$$

Explain why changes in pH will cause changes in the colour of the solution.

When pH increases, the equilibrium position will shift left as OH^- will react with H^+. More yellow CrO_4^{2-} formed. [1] When pH decreases, the equilibrium position will shift right to remove the excess H^+. More orange $Cr_2O_7^{2-}$formed. [1]

(ii) When gallium, Ga, is added to an acidified $Na_2Cr_2O_7$ solution, a series of colour changes takes place until a blue solution is obtained. [3]

Using relevant data from the *Data Booklet* and the data given below, explain the observation of the colour changes.

$$Ga^{3+} + 3e^- \rightleftharpoons Ga \qquad E^\ominus = -0.53V$$

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

$Cr^{3+} + e \rightleftharpoons Cr^{2+}$ $\quad E^\ominus = -0.41V$ [1 for quote]

$Cr_2O_7^{2-} + 2Ga + 14H^+ \rightarrow 2Cr^{3+} + 2Ga^{3+} + 7H_2O$ E$^\ominus$ = +1.86V [1]

Orange *green [1]*

$3Cr^{3+} + Ga \rightarrow 3Cr^{2+} + Ga^{3+}$ E$^\ominus$ = +0.12V [1]

Green *blue*

$3Cr^{2+} + 2Ga \rightarrow 3Cr + 2Ga^{3+}$ E$^\ominus$ = −0.382V

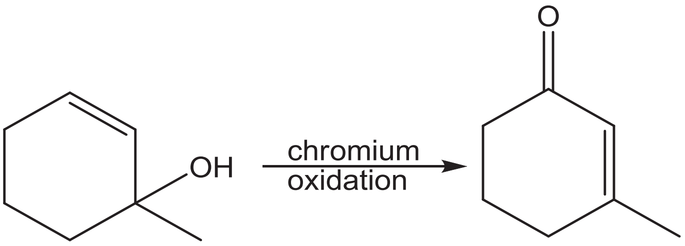
Cr^{2+} cannot be further reduced to Cr by Ga.

(iii) Suggest why the blue solution slowly changes to a green solution when it is left standing in air. [1]

Cr^{2+} is oxidised to Cr^{3+}.

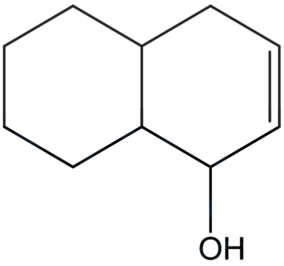
$4Cr^{2+} + O_2 + 2H_2O \rightarrow 4Cr^{3+} + 4OH^-$ $E^\ominus_{cell}$ = +0.81V [1]

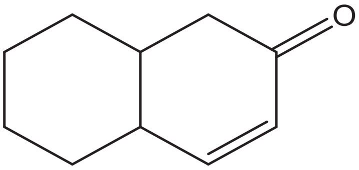
(c) Chromium oxidation is a special type of reaction in which oxidation and a rearrangement takes place. An example of a chromium oxidation is as shown.



1-methylcyclohex-2-enol 3-methylcyclohex-2-enone

(i) Draw the structure of the product when the following compound undergoes chromium oxidation. [1]





[1]

(ii) Suggest a simple chemical test to distinguish between [2]

1-methylcyclohex-2-enol and 3-methylcyclohex-2-enone.

2,4-DNPH, warm [1] No penalty for missing 'warm'

Orange ppt for 3-methylcyclohex-2-enone and no orange ppt for 1-methylcyclohex-2-enol [1]

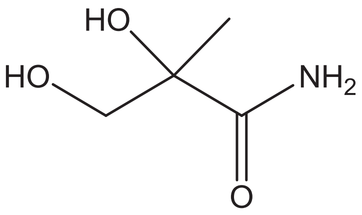
(d) Compound **F**, $C_4H_9O_3N$, is a neutral and chiral compound which is soluble in water. When compound **F** is heated with dilute sulfuric acid and potassium dichromate(VI), compound **G**, $C_4H_6O_5$, is formed. 1 mol of compound **G** reacts with aqueous sodium carbonate to produce 1 mol of CO_2. If compound **F** is heated with concentrated sulfuric acid and potassium dichromate(VI), compound **H**, $C_4H_4O_4$, is formed instead. When compound **F** reacts with $LiAlH_4$ in dry ether, a compound **J** which is no longer neutral is formed. [7]

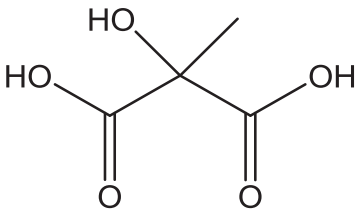
Deduce the structures of compounds **F**, **G** **H** and **J**, and explain the reactions involved.

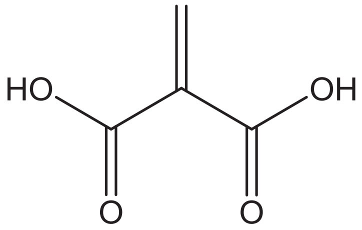
	Deduction [cap at 3 marks]
Compound **F**, $C_4H_9O_3N$, is a neutral compound which is soluble in water.	F is not a carboxylic acid or amine since it is neutral. [1] OR F can be an amide, ester or contains alcohol groups since it can form H bonding with water, making it soluble. [1]
When Compound **F** is heated with acidified potassium dichromate(VI), Compound **G**, $C_4H_6O_5$, is formed	-oxidation of primary alcohol and hydrolysis - $-CONH_2$ in **F**/ Amide is present in **F** [1]
1 mol of compound **G** reacts with aqueous sodium carbonate to produce 1 mol of CO_2.	-acid-carbonate reaction (accept acid-base reaction) **G** contains two –COOH groups [1]

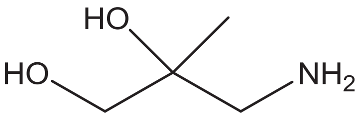
Compound **F** is heated with concentrated sulfuric acid and potassium dichromate(VI), Compound **H**, $C_4H_4O_4$, is formed instead	-elimination of water -alkene in **H** [1]
Compound **F** reacts with $LiAlH_4$ in dry ether, Compound **J** is formed	-reduction - -$CONH_2$ in F becomes –CH_2NH_2 in J[1]

Max 2 marks

F:


G:


H:


J:


1 mark each structure

[Total: 20]

d~END OF PAPER~

H2 Chemistry Preliminary Exam Practical Suggested Solution

1 Determination of the M_r of a hydrated ethandioate salt

Calcium ethanedioate is the major component of the most common type of human kidney stones. It is one of a series of salts formed from ethanedioic acid, $H_2C_2O_4$. Another of these salts can be represented by the formula $\mathbf{X}_2C_2O_4.H_2O$, where **X** is a Group 1 metal.

Solution **Q** contains 64.5 g dm^{-3} of $\mathbf{X}_2C_2O_4.H_2O$ in deionised water. You are not provided with **Q.**

FA 1 is a diluted solution of **Q**, in which 35.70 cm^3 of **Q** was made up to 250 cm^3 with deionised water in a graduated flask.

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.

In this question, you will perform a titration. The data from this titration will be used to determine:

- the concentration of $C_2O_4^{2-}$ in **Q**,
- the M_r of $\mathbf{X}_2C_2O_4.H_2O$, and hence the identity of **X**.

(a) Titration of FA 1 against FA 2

In this titration, **FA 2** is run from the burette into the conical flask containing **FA 1** and **FA 3**. Initially, the colour of the **FA 2** will take some time to disappear.

After some **FA 2** has been added, sufficient Mn^{2+}(aq) ions will be present to allow the reaction to occur faster.

The end-point is reached when a permanent pale pink colour is obtained.

(i)
1. Fill the burette with **FA 2**.
2. Using a pipette, transfer 25.0 cm^3 of **FA 1** into the conical flask.
3. Using an appropriate measuring cylinder, transfer 50.0 cm^3 of **FA 3** to the same conical flask.
4. Heat this solution to about 65 °C.
5. Run **FA 2** from the burette into this flask until a **permanent** pale pink colour is obtained.
6. Record your titration results in the space provided on page 3. Make certain that your recorded results show the precision of your working.
7. Repeat points **1** to **6** as necessary until consistent results are obtained.
8. **Turn off your Bunsen burner**.

Results

Final burette reading/ cm^3	**25.10**	**25.10**
Initial burette reading/ cm^3	**0.00**	**0.00**
Volume of FA 2/$KMnO_4$/Titrant / cm^3	**25.10**	**25.10**
Values used (Tick consistent readings ±0.10 cm^3)	✓	✓

[5]

(ii) From your titrations, obtain a suitable volume of **FA 2** to be used in your calculations.

Show clearly how you obtained this volume.

Average volume of FA 2 = (25.10 + 25.10)/2 = 25.10 cm^3

Volume of **FA 2** =…25.10 cm^3….

[1]

(b) **(i)** The equation for the reaction between ethanedioate ions and manganate(VII) ions is shown below.

$5C_2O_4^{2-}(aq) + 2MnO_4^{-}(aq) + 16H^{+}(aq) \rightarrow 10CO_2(g) + 2Mn^{2+}(aq) + 8H_2O(l)$

Calculate the amount, in moles of ethanedioate ions, $C_2O_4^{2-}$ in 25.0 cm^3 of **FA 1**.

amount of MnO_4^{-} in FA 2 = (25.10/1000) X 0.02 = 0.000502 mol

amount of $C_2O_4^{2-}$ in 25 cm^3 of FA 1 = 0.000502/2 X 5 = 0.001255 mol

[1]

Amount of $C_2O_4^{2-}$ in 25 cm^3 of **FA 1** =…0.001255 mol or 0.00126 mol…

1 **(b)** **(ii)** Determine the concentration, in mol dm^{-3}, of $C_2O_4^{2-}$ in **Q**.

amount of $C_2O_4^{2-}$ in 250 cm^3 of FA 1 = 0.001255 X 10 = 0.01255 mol

$[C_2O_4^{2-}]_{\text{in } \mathbf{Q}}$ = 0.01255 / (35.70/1000) = 0.3516 mol dm^{-3}

[2]

Concentration of $C_2O_4^{2-}$ in **Q** =…0.3516 or 0.352 mol dm^{-3}

(iii) Use your answer to **(b)(ii)** to calculate the M_r of the ethanedioate salt.

M_r of $\mathbf{X}_2C_2O_4.H_2O$ = 64.5 / 0.3516 = 183.4

M_r of the ethanedioate salt = 183.4 ……………

Hence, deduce the identity of **X**.
Show your working.

[A_r: C, 12.0; O, 16.0; H, 1.0; Li, 6.9; Na, 23.0; K, 39.1; Rb, 85.5; Cs, 132.9; Fr. 223.0]

Ar of X = [183.4 – 2(12.0) – 5(16.0) – 2(1.0)]/2 = 38.7

X = Potassium

[3]

X is K……

1 **(c)** A student performed the experiment in **(a)(i)** using a sample of another ethanedioate salt. The student obtained a mean titre value of 22.20 cm^3. The teacher calculated that the volume of **FA 2** required should have been 22.40 cm^3. The teacher told the student that the total percentage error from the apparatus in the experiment was 0.4 %.

Calculate the error in the student's result, based on these data. State **and** explain whether or not the student's result is accurate.

Student's experimental error = $\frac{22.40 - 22.20}{22.40} \times 100\% = 0.8928 = 0.893\%$

Since student's experimental error (0.893%) is more than the apparatus error(0.4%), therefore the student's result is inaccurate.

[2]

[Total: 14]

2 Evaluation of the reliability of a gas collection method in determining a value for the *M_r* of the ethanedioate salt.

In this experiment, you will react the ethanedioate salt with potassium manganate(VII), in the presence of a small amount of manganese(II) ions. You will measure the volume of CO_2 gas produced at timed intervals and determine the maximum volume of CO_2 gas produced.

FA 4 is a solution containing manganese(II) ions, Mn^{2+}.

You will need access to the **FA 1**, **FA 2** and **FA 3** solutions you used earlier.

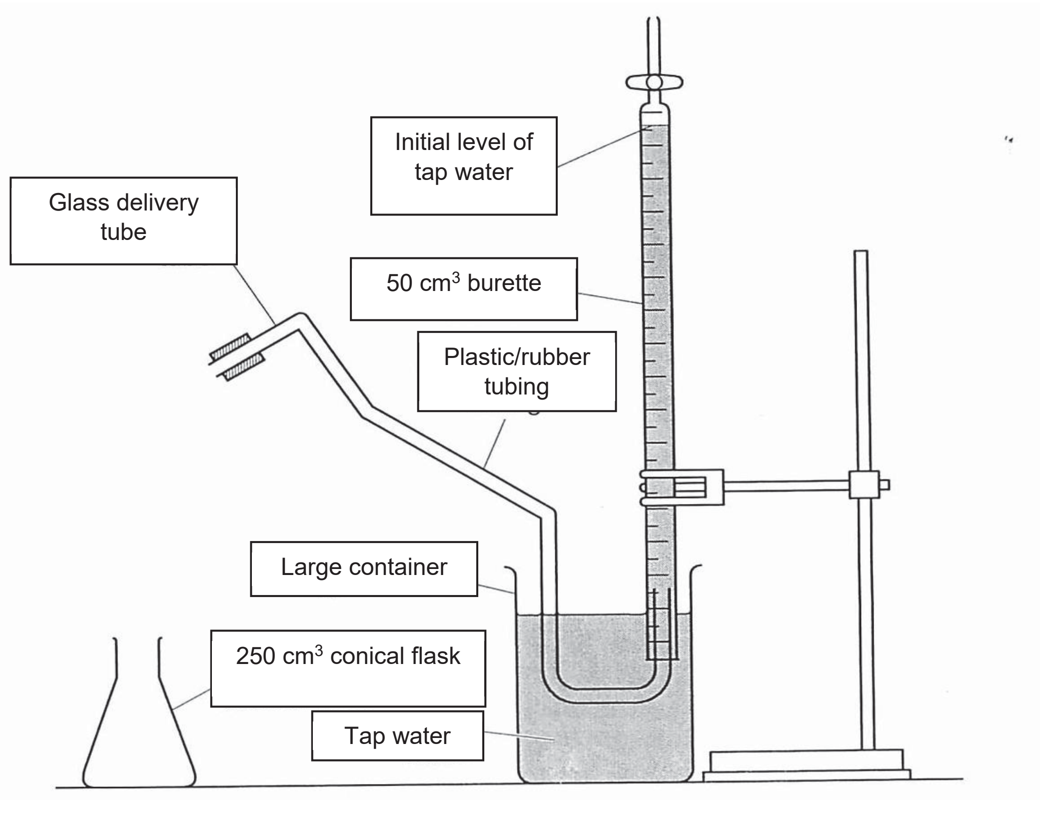


Fig. 2.1

You will measure the level of water in the burette at timed intervals.

In an appropriate format in the space provided on page 7, prepare a table in which you may record each burette reading and the time it was taken.

In addition, your table will need to show the total volume of CO_2 collected up to that time, recorded to one decimal place.

1. Set up the apparatus as shown in Fig. 2.1. You should insert the plastic/rubber tubing to a sufficient depth so that it will not subsequently shake loose.

2. Adjust the water level in the burette until it is between 48.0 cm^3 and 50.0 cm^3. You may find it helpful to use an empty dropping pipette to introduce small amounts of air from the bottom of the burette tube.
3. Use appropriate measuring cylinders to add to the 250 cm^3 conical flask.
   - 20.0 cm^3 of **FA 1**
   - 50.0 cm^3 of **FA 3**
4. Using a dropping pipette, add about 1 cm^3 of **FA 4** to the conical flask.
5. Using an appropriate measuring cylinder, measure out 30.0 cm^3 of **FA 2.**
6. Transfer the **FA 2** into the conical flask and insert the bung into the conical flask.
7. Allow any bubbles created in the burette when the bung was inserted in the conical flask to rise to the top. Start the stopwatch, read and record the initial water level in the burette.
8. Note: Once you have started the stopwatch, allow it to continue running for the duration of the experiment. You must not stop the stopwatch until the reaction is complete.
9. Check that the plastic/rubber tubing is securely positioned in the burette.
10. Hold the flask by its neck and gently swirl it continuously.
11. At *t* = 0.5 min, read and record the water level in the burette, to 1 decimal place, together with the time it was measured, in your table.
12. Continue to gently swirl the flask. Read and record the water level in the burette every half minute, until the reaction is complete.

(a) (i) Experimental Results

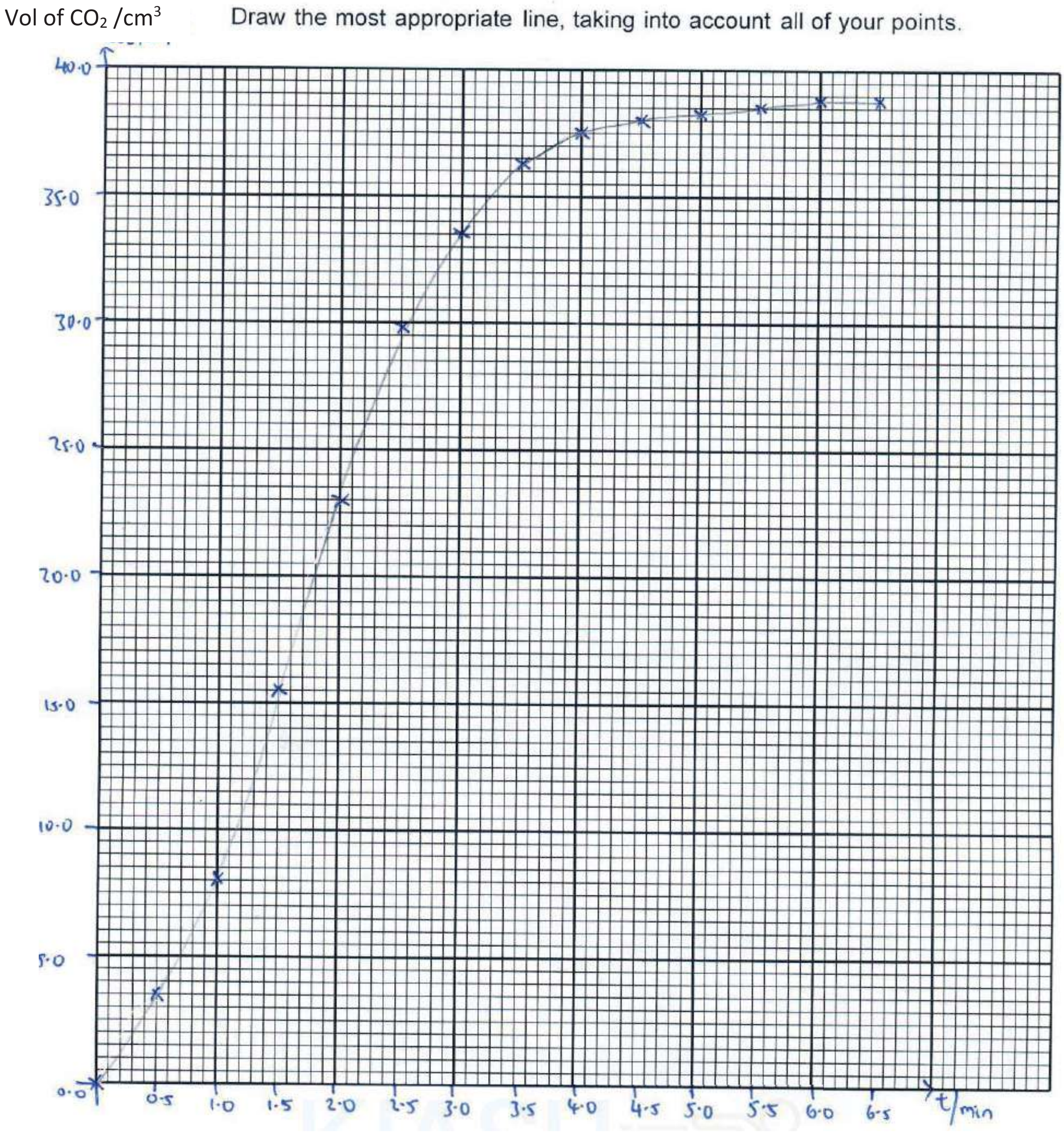
Time / t / min	Burette reading / cm^3	(Volume / vol) of CO_2 / cm^3
0.0	50.0	0.0
0.5	46.5	3.5
1.0	42.0	8.0
1.5	34.5	15.5
2.0	27.0	23.0
2.5	20.2	29.8
3.0	16.5	33.5
3.5	13.8	36.2
4.0	12.5	37.5
4.5	12.0	38.0
5.0	11.6	38.4

5.5	11.5	38.5
6.0	11.4	38.6
6.5	11.4	38.6
7.0	11.4	38.6

[3]

2 **(a)** **(ii)** Plot on the grid below, a graph of the volume of CO_2 on the y-axis, against time, *t,* on the x-axis

Draw the most appropriate line, taking into account all of your points.



[4]

2 (a) (iii) The equation for the reaction between ethanedioate ions and manganate(VII) ions is shown below.

$5C_2O_4^{2-}(aq) + 2MnO_4^-(aq) + 16H^+(aq) \rightarrow 10CO_2(g) + 2Mn^{2+}(aq) + 8H_2O(l)$

Use this equation, and appropriate data from your graph, to calculate a value for the amount, in moles of ethanedioate ions, $C_2O_4^{2-}$, present in 20.0 cm^3 of **FA 1**.

[molar volume of gas = 24.0 dm^3 mol^{-1} at r.t.p.]

From graph, max volume of CO_2 = 38.55 cm^3

amount of CO_2 produced = 38.55 / 24000 = 0.001606 mol

amount of $C_2O_4^{2-}$ in 20.0 cm^3 of FA1 = 0.001606 / 2 = 0.000803 mol

Amount of ethanedioate ions, $C_2O_4^{2-}$, in 20.0 cm^3 of **FA 1** = 0.000803 mol [1]

(b) (i) Using your answer to question **1(b)(i)**, calculate the amount of ethanedioate ions in 20.0 cm^3 of **FA 1**. Hence, determine the maximum volume of CO_2 at r.t.p. that could have been produced from 20.0 cm^3 of **FA 1**.

amount of $C_2O_4^{2-}$ in 20 cm^3 of FA 1 = 0.001255 / 25 X 20 = 0.0001004 mol

amount of CO_2 produced = 0.0001004 X 2 = 0.002008 mol

maximum volume of CO_2 = 0.002008 X 24000 = 48.19 cm^3

maximum volume of CO_2 produced from 20.0 cm^3 of **FA 1** = 48.2 cm^3 [4]

(ii) Suggest a reason for the difference between the total volume of CO_2 you collected and the maximum volume of CO_2 calculated in **2(b)(i)**.

Some of the CO_2 could have stayed dissolved in the water bath/Some CO_2 could have escaped when the conical flask was stoppered. [1]

(iii) Suggest an improvement to this experiment that would overcome this problem.

Uses a non-aqueous gas collecting system such as a frictionless gas syringe. [1]

Use a dropping funnel to add in **FA2** to start the reaction to minimise the escaping of gas.

2 **(b)** **(iv)** In Question **1** you calculated a value for the M_r of the ethanedioate salt. The total volume of CO_2 collected in **2(a)(i)** could also be used to calculate a value for the M_r of the ethanedioate salt.

Suggest which of these two M_r values would be higher. Explain your answer.

The M_r calculated from the collection of gas method will be higher as the volume measured will be lower than expected, causing the number of moles of salt to be lower and hence the M_r to be higher. **[1]**

(c) The presence of Mn^{2+} ions, which are produced in the reaction between MnO_4^- ions and $C_2O_4^{2-}$ ions, is thought to catalyse this reaction.

(i) A student performed the experiment you performed in **2(a)(i)** but forgot to add **FA 4** to the mixture of **FA 1** and **FA 3** before adding the **FA 2**.

The student performed the experiment at the same temperature as your experiment and obtained the graph shown in **Fig. 2.2**.

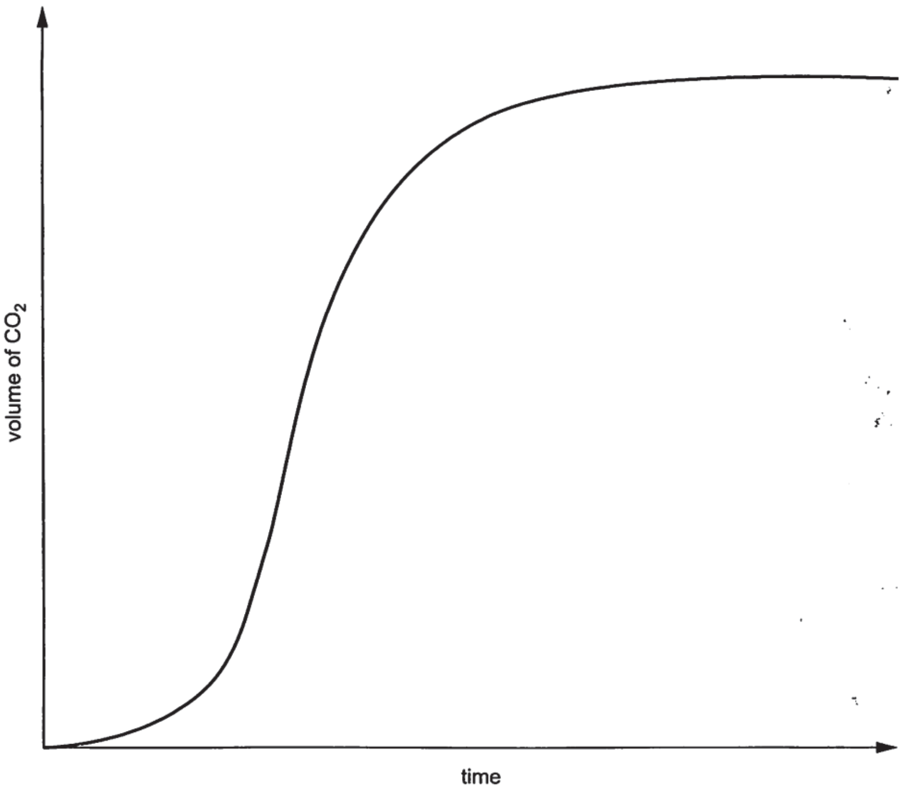


Fig. 2.2

2 **(c)** **(i)** Consider the **shape** of the graph in **Fig 2.2** and your graph in **2(a)(ii)**.

Describe one major difference between the shapes. Suggest an explanation for your answer.

Difference The graph in 2(a)(ii) is steeper at the start of the experiment.

Explanation Mn^{2+} was added right from the start and hence the reaction was catalysed right from the beginning unlike the student's experiment where there were little Mn^{2+} at the beginning to catalyse the reaction, causing the student's initial gradient to be gentler. **[2]**

(ii) For the titration in **1(a)(i)** between ethanedioate ions, $C_2O_4^{2-}$, and manganate(VII) ions, MnO_4^-, the solution needs to be at about 65 °C at the start. As cold **FA 2** is added, the temperature of the mixture decreases. However, this decrease in temperature does not cause the rate of reaction between $C_2O_4^{2-}$ ions and MnO_4^- ions added from the burette to decrease.

Suggest an explanation for this.

The stable rate is due to Mn^{2+} ions being produced. The presence of the Mn^{2+} catalyst cancels out the effect of the drop in temperature. **[1]**

2 (d) Planning

The oxidation of iodide ions, I^-, by peroxodisulfate ions, $S_2O_8^{2-}$, is known to be catalysed by Fe^{2+} or Fe^{3+} ions.

A similar reaction, shown below, in which ethanedioate ions, $C_2O_4^{2-}$, are oxidised by peroxodisulfate ions, $S_2O_8^{2-}$, may be catalysed by Cu^{2+} ions and by Ag^+ ions.

$$S_2O_8^{2-} + C_2O_4^{2-} \rightarrow 2\,SO_4^{2-} + 2\,CO_2$$

(i) Suggest an explanation why both of these reactions are slow when performed in the absence of a catalyst.

The reactants are both negatively charged and experience repulsion and thus resulted in a high activation energy barrier between them. **[1]**

(ii) Plan an investigation to test how well, **if at all**, Cu^{2+} ions and by Ag^+ ions catalyse the reaction between $C_2O_4^{2-}$ ions and $S_2O_8^{2-}$ ions.

In your plan, you should include details of:

- the reactants and conditions that you would use,
- the apparatus you would use and the procedure you would follow,
- the measurements you would take,
- an outline of how you would use your results to compare the effectiveness of each ion as a potential catalyst.

Suggested Planning Procedure

Note: It was assumed that the temperature and pressure conditions for the conduct of the 3 experiments is at rtp conditions

Experiment 1 (uncatalysed reaction)

1. Using a 50 cm^3 measuring cylinder, measure out 15 cm^3 of **$X_2C_2O_4$ of concentration 0.05 moldm^{-3}** into a 250 cm^3 conical flask. Add 5 cm^3 of deionised water using a dropping pipette (or 10 cm^3 measuring cylinder).
2. Use a separate 50 cm^3 measuring cylinder, measure out 20 cm^3 of a solution of $Na_2S_2O_8$ of concentration 0.05 moldm^{-3}.
3. Set up the apparatus as shown in Fig. 2.1
4. Check that the plastic/rubber tubing is securely positioned in the burette.
5. Transfer the 20 cm^3 of a solution of $Na_2S_2O_8$ into the conical flask and insert the bung into the conical flask. (Using dropping funnel to transfer 20 cm^3 of solution will be better to minimise gas escape.)
6. Allow any bubbles created in the burette when the bung was inserted in the conical flask to rise to the top. Start the stopwatch, read and record the initial water level in the burette.
7. Hold the flask by its neck and gently swirl it continuously.
8. At t = 0.5 min, read and record the water level in the burette, to 1 decimal place, together with the time it was measured, in your table.
9. Continue to gently swirl the flask. Read and record the water level in the burette every half minute, until the reaction is complete. i.e. at least 3 burette readings are the same.
   (Estimated volume of CO_2 is 36 cm^3)

Pre-Calculation:

No. of moles of $C_2O_4^{2-}$ (limiting agent) = 0.05x15/1000 = 0.00075 mol

Volume of CO_2 produced

= 0.00075 X 2 X 24000 = 36 cm^3 assuming r.t.p.

Catalysed Experiment 2 and 3

10. Repeat steps 1 to 9 but now with the introduction of the catalysts Ag^+ (Experiment 2) and Cu^{2+} (Experiment 3), once at each time. Do take note that 5 cm^3 of each catalyst (of equal concentration 0.100 mol dm^{-3} is to be added in **step 1**.
11. Compare the time taken for the maximum amount of CO_2 to be produced for Experiment 1 (uncatalysed reaction) with Experiment 2 (Ag^+ as catalyst) and Experiment 3 (Cu^{2+} catalyst). The better catalyst

will be the one that produces the maximum amount of CO_2 in the shortest period of time.

Or Plot the graph of the volume of CO_2 against the time taken. The more effective catalyst is determined by the catalyst that produce a steeper gradient.

Alternatively,

9. Record the time required to produce 20 cm^3 (a stated volume, based on pre-calculation) of CO_2. The more effective catalyst is determined by the catalyst that produce the volume in a shorter time.

[7]

[Total: 26]

3 You are provided with the solid **K12** which contains one cation given in the Qualitative Analysis Notes.

You are to perform the tests below to identify the cation present in **K12** and suggest the nature of **K12.** Record your observations in the spaces provided. Your answers should include

- Details of colour changes and precipitates formed,
- The names of any gases evolved and details of the test used to identify each one.

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.

Tests	Observations and Deductions
1 Heat **K12** alone.	K **12** turns to a colourless liquid. Gas evolved turns moist blue litmus red Gas evolved turns acidified $KMnO_4$ paper colourless SO_2 (g) Gas relights glowing splinter O_2(g)
2 Warm **K12** with dilute hydrochloric acid. Keep the solution.	Gas evolved turns moist blue litmus red then bleaches Cl_2 (g) Oxidising agent present

3	To the solution from test **2**, add dilute nitric acid and barium nitrate(V) solution	White ppt forms, insoluble in acid. SO_4^{2-} $BaSO_4$ ppt
4	Warm **K12** with a freshly made solution of iron(II) sulfate solution.	Pale green solution turns brown/ red brown K **12** is an oxidising agent
5	Dissolve **K12** in dilute nitric acid. Add manganese(II) sulfate solution and two drops of silver nitrate(V) solution to act as a catalyst. Boil the mixture.	Pale pink colour turns brown then to black/purple solution (ppt) Mn^{2+} oxidise to MnO_2 then to MnO_4^- K **12** is an oxidising agent
6	Warm **K12** with sodium hydroxide solution.	Colourless solution obtained. Pungent smell gas which turns moist red litmus blue NH_3 gas NH_4^+ present

Nature of **K12:** **Oxidising agent**

Cation it contains: NH_4^+

[9]

[Total: 9]

4 Planning

You are provided with 3 unlabelled bottles and each bottle contains one of the following organic compounds,

- Butanamide
- Lactic acid, $CH_3CH(OH)CO_2H$
- Pyruvic acid, CH_3COCO_2H

(a) Outline a sequence of simple chemical tests to identify each of the above organic substances. You may use any other common laboratory chemical reagents and apparatus, if necessary. You are **not** allowed to identify the substances by elimination. You are reminded that most of the compounds listed are *flammable* liquids. **[3]**

Test	Expected Observations & Deductions
Using a dropper, add 1 cm^3 of compound into 3 separate test-tubes. To 1 cm^3 of compound in a test-tube, add 2 cm^3 of aqueous NaOH. Boil/ Heat in a **water bath** for 5-10 min. Test any gas evolved with moist red litmus paper	**Moist red litmus paper turns blue (NH_3) - butanamide**
To the 2 samples that did not produce a positive observation for test 1, using a dropper to 1 cm^3 of compound in a test-tube, add 1 cm^3 of 2,4 DNPH dropwise until excess. Warm the mixture.	**Orange ppt forms. – pyruvic acid**
To 1 cm^3 of the compound in a test-tube, add 1 cm^3 of dilute sulfuric acid, follow by a few drops of $K_2Cr_2O_7$(aq). Heat the mixture in a hot water-bath for 3 -5 min.	**Orange solution turns green-lactic acid**
Alternatives: pyruvic acid can be tested with 2,4 DNPH, warm ➔ lactic acid with aqueous Na_2CO_3 ➔ butanamide with NaOH(aq), heat.	

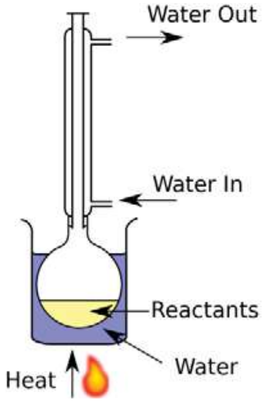
(b) Suggest a safety measure that you would consider in carrying out your plan.

Using a hot water bath for heating instead of using a direct naked flame from the Bunsen burner as most organic compounds are highly flammable.

[1]

(c) State the required reagents and conditions. Draw a set-up of the apparatus for the synthesis of pyruvic acid from lactic acid.

$KMnO_4(aq)/H_2SO_4(aq)$, heat under reflux OR $K_2Cr_2O_7(aq)/\ H_2SO_4(aq)$, heat under reflux



[2]

[Total: 6]

The End

Marking Procedure

Hierarchy to be used in calculating mean titres in question 1(a)(i):

- value of 2 identical titres
- average of titres within 0.05 cm^3
- average of titres within 0.1cm^3, etc.

Use the selected titres to determine the mean titre for the end-point.

Note: For calculations, the principle of no double penalty (error carried forward) applies. For connecting parts, marking from point of first enalty onwards will be based on correct method only.

Qn	Skills assessed	Marking Scheme	Mark	Mark Ref (MR)
1(a)(i)	PDO Layout **P1**	Tabulates initial and final burette readings and volume added in the titration table. Table has correct headers and units. Tabulation may be vertical or horizontal; lines are not essential but there should be no absences of headers. Where units have not been included in the header, there should be the appropriate unit for each entry in the table. Do NOT award this mark if any final and initial burette readings are inverted or 50 is used as the initial burette reading.	1	**1**
	PDO Record **P2**	All the final/initial burette readings, for all accurate titres in the titration table, are recorded to the nearest 0.05 cm^3. Treat all titres as "accurate" unless labelled 'rough' or first titre is recorded to a lower precision than subsequent titres.	1	**2**
	MMO Quality **M1**	Has at least two uncorrected titres for end-point within 0.10 cm^3. *Uncorrected titres refers to flawed calculated titres by the candidate.*	1	**3**
A student's 'rough'/'trial' titre value can be considered by the examiner when selecting titre values for the mean titre calculation if the student has 'validated' this value either by ticking it or by using it in an expression in (a)(ii). (By doing either of these, the student has declared it to be no longer a 'rough' / 'trial' value).				

1(a)(i)	MMO Quality Accuracy **M2** **M3**	Calculate the student's **<u>mean titre as described on page 3</u>**. Award **MR4** to **MR6** based on the difference, Δ titre, between Student's and Supervisor's mean titre. Give 2 marks Give 2 marks if this difference is ≤ ±0.20 Give 1 marks if this difference is > ±0.20 but ≤ ±0.40 Give 0 mark if this difference is > ±0.40	2	**4** **5**
(ii)	MMO Decision **M4**	Student obtains appropriate "average", to 2 d.p., from any experiments with uncorrected end-point titre values within 0.20 cm^3. Do not award this mark if the titres used are not identified either in the table (by, for example, a tick) or in a calculation. Do not award this mark if there are arithmetic errors in the table.	1	**6**
(b)(i)	ACE Interpret **A1**	(Let mean titre volume = V_m) $nMnO_4^-$ = V_m X 10^{-3} X 0.0200 = n_1 $nC_2O_4^{2-}$ in 25.0 cm^3 = n_1 X 5/2 = n_2	1	**7**
(ii)	ACE Interpret **A2** **A3**	[$C_2O_4^{2-}$] in **FA1** = n_2 ÷ (25.0/1000) [$C_2O_4^{2-}$] in **Q** = [$C_2O_4^{2-}$] in **FA1** X 250 ÷ (35.70/1000) Alternative method: $nC_2O_4^{2-}$ in 250 cm^3 = 10 n_2 [$C_2O_4^{2-}$] in **Q** = 10 n_2/ 35.7 X 1000	1 1	**8** **9**
(iii)	ACE Interpret **A4** **A5** **A6**	$M_r(X_2C_2O_4.H_2O)$ = 64.5 ÷ [$C_2O_4^{2-}$] in **Q** = M_r(Salt) A_r(**X**) = (M_r(Salt) – 88 – 18) ÷ 2 Calculates A_r (i.e ÷ 2) **and** **X** = group 1 metal closest to A_r(**X**) = (potassium/**K**)	1 1 1	**10** **11** **12**
(c)	ACE Interpret **A7**	Overall experimental error = $\frac{22.40 - 22.20}{22.40} \times 100\% = 0.890\%$ Candidate states experiment is not accurate	1	**13**

	Conclusion **A8**	**and** justifies this in terms of experimental error being> apparatus error. Allow ecf argument based on incorrectly calculated experimental error. (Note: Do not award MR14 if no calculation of error is done)	1	**14**
Question 2				
2(a)(i)	PDO Layout **P3**	Tabulates burette readings at times t = 0 until the end of the experiment, time/min and volume of CO_2/cm^3. Tables have correct headers and units Tabulations may be vertical or horizontal; lines are not essential but there should be no absences of headers. Where units have not been included in the header, there should be the appropriate unit for each entry in the table.	1	**15**
	PDO Record **P4**	All burette readings and CO_2 volumes to **0.1cm^3**, and times to **0.5 min**	1	**16**
	MMO Collecting **M5**	Full set of results with final readings which have 2 to 3 values that are the same.	1	**17**
(ii)	PDO Layout **P5**	Axes correct way round + correct labels + units + scale. Sensible linear scale must be chosen so that plotted points occupy at least half the graph grid in both x and y directions Penalise for	1	**18**
	PDO Layout **P6**	All points correctly plotted to within $\pm\frac{1}{2}$ small square. Check all points and put ticks if correct.	1	**19**
2(a)(ii)	PDO Manipulate **P7**	Graph line must be best fit line.	1	**20**

	MMO Quality **M6**	Award MR22 based on the difference, $\Delta volume_{CO2}$, between student's and Supervisor's values for the maximum volume of CO_2 collected. Give 1 mark if this difference is ≤ 5.0 cm^3 Give 0 marks for a difference > 5.0 cm^3	1	**21**
(a)(iii)	ACE Interpret **A9**	$nC_2O_4^{2-}$ = (volume of CO_2 collected ÷ 24000) /2	1	**22**
(b) (i)	ACE Interpret **A10**	$nC_2O_4^{2-}$ in 20 cm^3 of **FA1** = n_2 X (20.0/25.0) = n_3 max volume CO_2 = n_3 X 24000 X 2 (cm^3)	1	**23**
	PDO Display **P8**	Shows working in all calculations in **1(b)**, **1(c)**, **2(a)(iii)** and **2(b)(i)**. All calculations must be relevant although they may not be complete or correct. Any calculation not attempted loses this mark.	1	**24**
	PDO Display **P9**	Shows appropriate significant figures (3 or 4 sf) in **all** final answers in **1(b)**, **1(c)**, **2(a)(iii)** and **2(b)(i)**. Any calculation not attempted loses this mark.	1	**25**
	PDO Display **P10**	Shows appropriate units in all answers in **1(a)(ii),** (cm^3); **1(b)(i)**, (mol); **1(b)(ii)**, ($moldm^{-3}$); **1(c)**, (%); **2(a)(iii)**, (mol) and **2(b)(i)**, (cm^3). Any calculation not attempted loses this mark.	1	**26**
2(b)(ii)	ACE Conclusion **A11**	Collected volume of CO_2 lower than max volume as **some CO_2 dissolved in water.** OR **Some gas escaped** when/before the conical flask was stoppered. Allow other relevant answers.	1	**27**

(iii)	ACE Improve **A12**	Uses a non-aqueous gas collecting system such as a syringe. Use a dropping funnel to add in **FA2** to start the reaction to minimise the escaping of gas. Allow other relevant	1	**28**
(b)(iv)	ACE Interpret **A13**	Argues clearly that as the **volume of CO_2 measured is too low**, so n$C_2O_4^{2-}$ will be too low, so **M_r (likely to be) too high**.	1	**29**
(c)(i)	ACE Interpret **A14**	Difference: Describes that the shape of the given graph **shows a slow initial rate that increases** after some time whilst the candidate's own graph shows **a fast rate from the start** Explanation: In student's experiment without the addition of FA 4, Mn^{2+} formed by reaction catalyses the reaction and increases rate so the gradient of the graph becomes steeper.	1	**30**
	A15	Or at the beginning, there is very little Mn^{2+} to catalyse the reaction, hence the gradient of the graph is gentler.	1	**31**
(ii)	ACE Interpret **A16**	The stable rate is due to more Mn^{2+} ions being produced. As the concentration of the Mn^{2+} catalyst increases it cancels out the effect of the drop in temperature.	1	**32**
(d)(i)	Plan **PI1**	Repulsion between two negatively charged ions causes the activation energy to be high.	1	**33**
(ii)	Plan **PI2**	1. Describes a **sensible 'end-point'**; either the **time required to produce a stated volume of CO_2** or the **time needed for the reaction to be completed**.	1	**34**
	PI3	2. Proposes to use **the apparatus** specified from **2(a)** – or improved but workable apparatus and adds the catalyst before one of the reactants.	1	**35**
	PI4	3. Stipulates that the **same temperature** must be used. It is not necessary to describe how this is to be done in this case, but simply to state that it must be done. Allow the description of any sensible method of achieving this for this mark, even if 'to ensure that the same temperature is used' is not specifically stated.	1	**36**
		4. Controls concentrations and volumes for all other reactants.	1	**37**
	PI5	5. Proposes the **use of a non-catalysed control** to identify any TM Ions that do not catalyse this reaction.	1	**38**
	PI6		1	**39**

	PI7	6. Uses equal amounts (moles) of each TM ion either weighing out each TM compound or makes up equal concentrations of TM compounds solutions and uses equal volumes. **7.** Compares results on the basis of **fastest / least time** is the best catalyst. **Or compare volume within a specified time.**	1	**40**

3. Carry out the following experiments with K **12**. Enter your observations and deductions in the space provided.

Tests	Observation and Deduction
1 Heat K **12** alone	K **12** turns to a **colourless liquid**. [1] Gas evolved turns moist blue litmus paper red[1] Gas evolved **turns acidified $KMnO_4$ paper colourless** [1] SO_2 (g) [1] Gas relights glowing splinter [1] O_2(g) [1]
Warm K **12** with ilute hydrochloric acid. eep the solution.	Yellowish green gas, pungent smell, turns **moist blue litmus red then bleaches** [1] Cl_2 (g) [1] Oxidising agent present [1]
To the solution from est **2**, add dilute nitric cid and barium nitrate V) solution	White ppt forms [1] $BaSO_4$ ppt SO_4^{2-}[1]
Warm K **12** with a reshly made solution of ron(II) sulfate solution	Pale green solution turns **brown/ red brown** [1] K **12** is an oxidising agent [1]
5 Dissolve K **12** in nitric nitric acid. Add manganese(II) sulfate solution and two drops of silver nitrate(V) solution to act as a catalyst. Boil the mixture	Pale pink colour turns **brown then to black ppt (or black solution or purple solution)** [1] Mn^{2+} oxidise to MnO_2 then to MnO_4^- K **12** is an oxidising agent [1]
6 Warm K **12** with sodium hydroxide solution	**Colourless** solution obtained. [1] Pungent smell gas which turns **moist red litmus blue** [1] NH_3 gas[1] NH_4^+ present [1]

You are not required to identify K **12** but write any deductions you can about the ions it contains.

Nature of K **12**: ___**Oxidising agent**___

Cation it contains: ___NH_4^+___

[Total: 9]

9 observations	5 marks	**6-9 deductions**	**4 marks**
6-7 observations	4marks	**4-5 deductions**	**3 marks**
4-5 observations	3 marks	**2-3 deductions**	2 marks
3 observations	2 marks	**1 deductions**	1 mark
2 observations	1 marks		
1 observation	0 marks		

4.

You are provided with 3 unlabelled bottles and each bottle contains one of the following organic compounds,

- Butanamide
- Lactic acid, $CH_3CH(OH)CO_2H$
- Pyruvic acid, CH_3COCO_2H

(a) Outline a sequence of simple chemical tests to identify each of the above organic substances. You may use any other common laboratory chemical reagents and apparatus, if necessary. You are **not** allowed to identify the substances by elimination. You are reminded that most of the compounds listed are *flammable* liquids.

(a) Test	**Expected Observation**
Using a dropper, add 1 cm^3 of compound into 3 separate test-tubes. **To 1 cm^3 of compound in a test-tube, add 2 cm^3 of aqueous NaOH.** **Boil in a water bath for 5-10 min.** **Test any gas evolved with moist red litmus paper**	**Moist red litmus paper turns blue (NH_3) - butanamide**
To the 2 samples that did not produce a positive observation for test 1, using a dropper to 1 cm^3 of compound in a test-tube, add 2,4-DNPH dropwise until excess. Warm the mixture.	**Orange ppt forms. – pyruvic acid**
To 1 cm^3 of the compound in a test-tube, add a few drops (or 1-2 drops) of acidified $K_2Cr_2O_7$(aq). Heat the mixture in a hot water-bath	**Orange solution turns green-lactic acid**

If missing quantities /details, credit 1 mark for right sequence of test with correct observations.

(b) Suggest a safety measure that you would consider in carrying out your plan. [1]

Using a **hot water bath** for heating instead of using a direct naked flame from the Bunsen burner **as most organic compounds are highly flammable**.

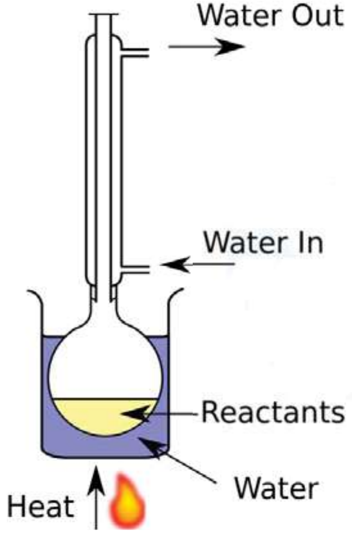
Or Wear gloves because organic acids/sulfuric acid are corrosive.

OR Wear goggles to protect the eyes from contact with chemicals.

) Draw a set-up of the apparatus for the synthesis of pyruvic acid from lactic acid. State the required reagents and conditions. [2]

Reagents and conditions:$KMnO_4$(aq)/H_2SO_4(aq), heat (under reflux) OR [1]

$K_2Cr_2O_7$(aq)/ H_2SO_4(aq), heat (under reflux)



[1]

Details of set-up must have:

- **Condenser with water in and out labelled**
- **Round-bottom flask**
- **Water bath**
- **Must label heat**

[Total: 6]

TEMASEK
JUNIOR COLLEGE

CHEMISTRY 9729/01

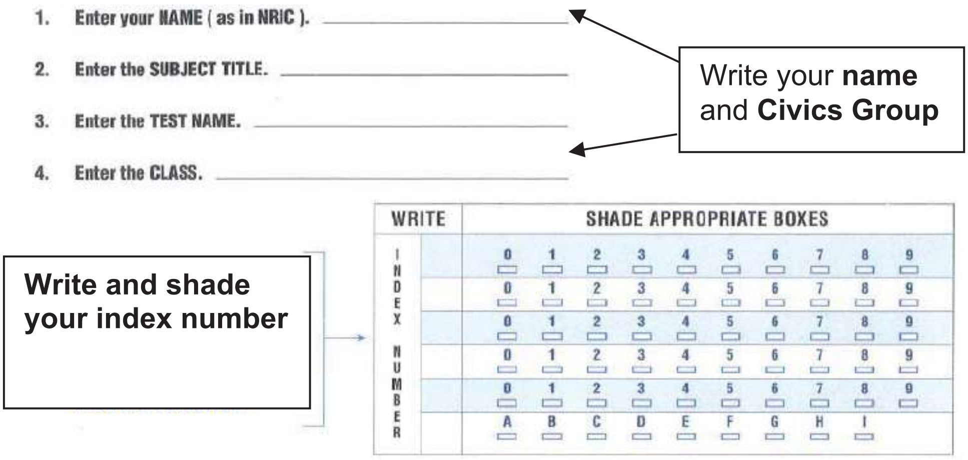
Paper 1 Multiple Choice

15th September 2017
1 hour

Additional materials: Multiple Choice Answer Sheet
Data Booklet

READ THESE INSTRUCTIONS FIRST

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



1. Enter your NAME (as in NRIC). ____________
2. Enter the SUBJECT TITLE. ____________
3. Enter the TEST NAME. ____________
4. Enter the CLASS. ____________

Write your **name** and **Civics Group**

WRITE	SHADE APPROPRIATE BOXES
INDEX NUMBER	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

Write and shade your index number

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

Read the instructions on the Answer Sheet very carefully.

Each correct answer will score one mark. A mark will not be deducted for a wrong answer.
Any rough working should be done in this booklet.
The use of an approved scientific calculator is expected, where appropriate.

This document consists of **13** printed pages.

1 The reaction between aluminium powder and anhydrous barium nitrate is used as the propellant in some fireworks. Nitrogen gas is one of the products formed.

Which volume of nitrogen, measured under room conditions, is produced when 1 g of anhydrous barium nitrate reacts with an excess of aluminium?

A 86.9 cm^3 **B** 91.8 cm^3 **C** 174 cm^3 **D** 184 cm^3

2 Which statements about relative molecular mass are correct?

1 It is the mass of one mole of the molecule.

2 It is the ratio of the average mass of a molecule to the mass of a ^{12}C atom.

3 It is the sum of the relative atomic masses of all the atoms within the molecule.

A 1, 2 and 3

B 2 and 3 only

C 2 only

D 3 only

3 The Claus process recovers sulfur from the gaseous hydrogen sulfide found in raw natural gas and from the crude oil refinery by-product gases.

reaction I $2H_2S(g) + 3O_2(g) \rightarrow 2H_2O(l) + 2SO_2(g)$

reaction II $2H_2S(g) + SO_2(g) \rightarrow 2H_2O(l) + 3S(s)$

Which statement about the Claus process is correct?

A SO_2 is a reducing agent.

B SO_2 behaves as a catalyst.

C H_2S is oxidised in the reaction.

D Reaction II is a disproportionation reaction.

4 A stream of gaseous, doubly-charged calcium ions was passed between 2 oppositely charged plates. Analysis of the deflection shows that these ions deflected at an angle of 20.0°.

Under the same electric field, an unknown gaseous ion $\mathbf{X}^+$ is deflected at an angle of 5.08°.

What is the atomic number of **X**?

A 34 **B** 45 **C** 46 **D** 79

5 Which of the following species do not have all atoms that lie on the same plane?

A CH_2CH_2 **B** I_3^- **C** XeF_4 **D** $BeCl_4^{2-}$

6 In which pair of compounds does the first compound have higher boiling point than the second compound?

A HI, HF

B MgO, NaC*l*

C CH_4, SiH_4

D *trans*-$C_2H_2Cl_2$, *cis*-$C_2H_2Cl_2$

7 A sample of m g of an organic compound is vaporised in a gas syringe and occupies *V* cm^3 at *T* K and *p* atm.

What is the relative molecular mass of the compound?

A $$\frac{m \times 24000 \times T}{p \times V \times 293}$$

B $$\frac{m \times 24000 \times (T+293)}{p \times V \times 273}$$

C $$\frac{m \times 24000 \times 293 \times p}{V \times T}$$

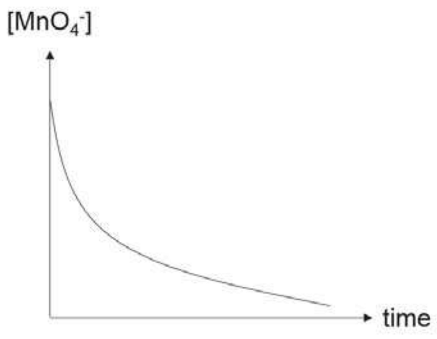
D $$\frac{m \times 24000 \times 293 \times p}{V \times (T+273)}$$

8 An autocatalytic reaction is one whereby the products catalyses the reaction. One such reaction is the reaction between ethanedioate and manganate(VII) anions.

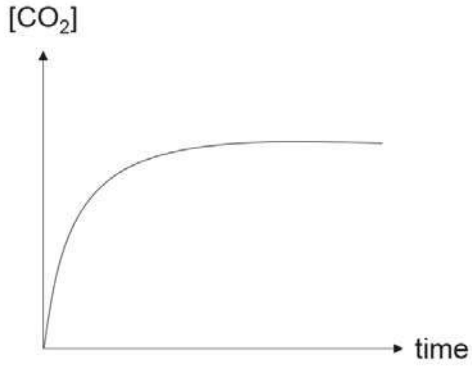
$$2MnO_4^- + 5C_2O_4^{2-} + 16H^+ \rightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$$

Which of the following graphs would be obtained for an autocatalytic reaction?

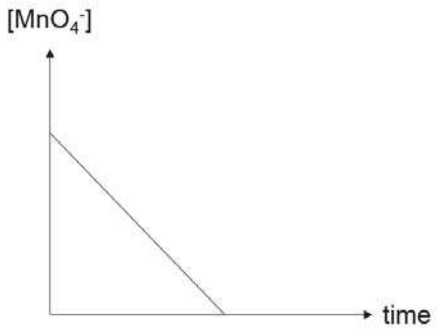
A



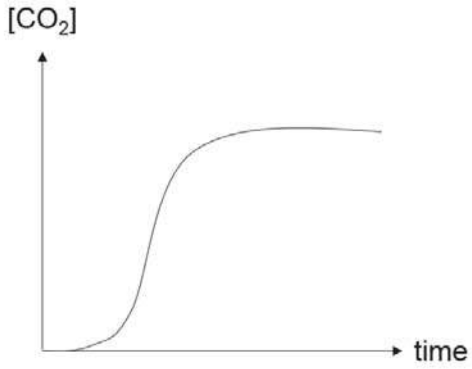
B



C



D



9 Molecular bromine, Br_2 reacts with methanoic acid, HCOOH slowly in an open beaker to produce aqueous hydrogen bromide and carbon dioxide gas.

$$Br_2(aq) + HCOOH(aq) \rightarrow 2HBr(aq) + CO_2(g)$$

Which of the following methods is **not** suitable for studying the kinetics of this reaction?

A Measuring the conductivity of the solution over time.

B Measuring the change in pressure of the reaction over time.

C Measuring the change in colour intensity of the mixture over time.

D Measuring the changes of pH of the solution over time.

10 When bromine vapourises at 58.8°C, 30.9 kJ mol^{-1} of heat was required.

What is the entropy change when 32 g of bromine is vapourised?

A -18.6 J K^{-1}

B +18.6 J K^{-1}

C -93.1 J K^{-1}

D +93.1 J K^{-1}

11 Compound **E** is a hydrocarbon. When 0.47 g of **E** was completely burnt in air, the heat produced raised the temperature of 200 g of water by 26.4 °C.

Given that the standard enthalpy change of combustion of **E** is –3290 kJ mol^{-1}, which of the following could be **E**?

1 $CH_2{=}CHCH_2CH_3$

2 $(CH_3)_2C{=}CHCH_3$

3 C_5H_{10}

A 1 only

B 3 only

C 1 and 2

D 2 and 3

12 Two equilibria are shown below.

reaction I $X_2(g) + \frac{1}{2}Y_2(g) \rightleftharpoons X_2Y(g)$
reaction II $2X_2Y(g) \rightleftharpoons 2X_2(g) + Y_2(g)$

The numerical value of K_c for reaction I is 2.
Under the same conditions, what is the numerical value of K_c for reaction II?

A $\frac{1}{2}$

B $\frac{1}{\sqrt{2}}$

C $\frac{1}{4}$

D -2

13 Consider the following equilibrium system:

$$\mathbf{P}(s) + \mathbf{Q}(g) \rightleftharpoons \mathbf{R}(g) + 3\mathbf{S}(s) \qquad \Delta H = +ve$$

0.500 mol each of **P** and **Q** were placed in a 1 dm^3 container. At equilibrium, 0.100 mol of **R** was formed.

Which of the following statement is **not** correct?

A The value of K_c is 0.25.

B K_p increases with increasing temperature.

C Increasing the pressure will not affect the equilibrium.

D Adding **P** causes the position of equilibrium to shift to the right.

14 Which of the following mixtures does not act as a buffer solution?

A 10 cm^3 of 1 mol dm^{-3} HCl and 5 cm^3 of 1 mol dm^{-3} $Mg(CH_3CH_2COO)_2$

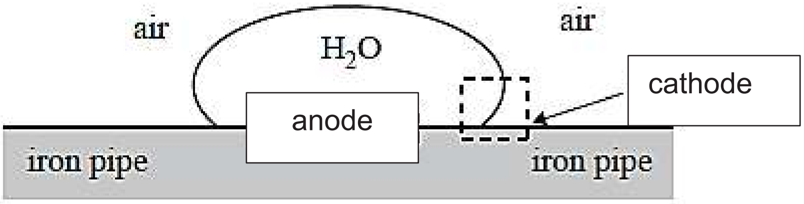
B 20 cm^3 of 1 mol dm^{-3} Na_2CO_3 and 20 cm^3 of 1 mol dm^{-3} $NaHCO_3$

C 20 cm^3 of 1 mol dm^{-3} HCl and 20 cm^3 of 2 mol dm^{-3} $CH_3CH_2NH_2$

D 10 cm^3 of 1 mol dm^{-3} $NaOH$ and 20 cm^3 of 1 mol dm^{-3} NH_4Cl

15 Iron pipes are used to transport natural gas to cities. Corrosion occurs when water droplets sit on the outer surface of the iron pipes.

Miniature galvanic cells are created, with regions such as those shown below, that act as anodes and cathodes.



Which of the following is incorrect?

A The reaction at the cathode is $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$.

B The reaction at the anode is $Fe \rightarrow Fe^{2+} + 2e^-$.

C The corrosion of iron is inhibited at low pH.

D Corrosion can be prevented by connecting it to a magnesium bar buried in the ground.

16 Copper minerals often contain magnesium and silver as impurities. An impure copper rod is purified by electrolysis using a constant current. After 1 hour, the mass of one electrode decreased by 19.0 g while the mass of the other electrode increased by 17.8 g.

Which of the following statements is correct?

1 The decreased in mass is due to the oxidation of copper, magnesium and silver.

2 The increase in mass is due to copper being formed.

3 Doubling the mass of the impure copper rod under the same set of operating conditions double the mass of the copper deposited.

A 2 only

B 1 and 2

C 1 and 3

D 2 and 3

17 Consider the oxides of period 3 elements.

Which factor generally decreases across the period?

A Covalent character

B Melting point

C pH when mixed with water

D Solubility in aqueous NaOH

18 Which property of the Group 2 elements or their compounds increases with increasing atomic number?

A Reducing power of the metal

B Magnitude of the enthalpy change of hydration of the metal ion

C Acidity of an aqueous solution of the chloride

D Tendency to form complex ions

19 The table shows the results of experiments in which the halogens X_2, Y_2, and Z_2 were added to separate aqueous solutions containing X^-, Y^- and Z^- ions.

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

Which set contains the ions X^-, Y^- and Z^- in order of their decreasing strength as a reducing agent?

	Strongest ⟶		Weakest
A	X^-	Y^-	Z^-
B	X^-	Z^-	Y^-
C	Y^-	Z^-	X^-
D	Z^-	X^-	Y^-

20 K_{stab}, is an equilibrium constant for the formation of a complex in solution.

Consider the following reaction

$$[M(H_2O)_6]^{m+}(aq) + nL^-(aq) \rightleftharpoons [M(H_2O)_{6-n}L_n]^{(m-n)+}(aq) + nH_2O(l)$$

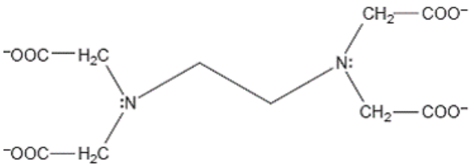
The K_{stab}, of the reaction, taking the concentration of water as being constant, is

$$K_{stab} = \frac{[[M(H_2O)_{6-n}L_n]^{(m-n)+}]}{[[M(H_2O)_6]^{m+}][L^-]^n}$$

The following table shows the colour and the value of K_{stab} of some iron complexes.

complex	**colour**	K_{stab}
$[Fe(SCN)(H_2O)_5]^{2+}(aq)$	deep red	1×10^2
$[FeF_6]^{3-}(aq)$	colourless	2×10^{15}
$[Fe(CN)_6]^{3-}(aq)$	orange-yellow	1×10^{31}
$[Fe(edta)]^{2-}(aq)$	colourless	2×10^{14}
$[Fe(edta)]^{-}(aq)$	yellow	1×10^{25}

The structure of $edta^{4-}$ is as follows:



Which of the following statements is true?

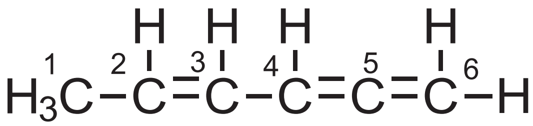
A $[Fe(SCN)(H_2O)_5]^{2+}(aq)$ absorbs red light.

B Addition of $edta^{4-}$ to a solution containing $[FeF_6]^{3-}(aq)$ does not produce any colour change.

C Addition of KCN(aq) to a solution containing $[Fe(SCN)(H_2O)_5]^{2+}(aq)$ produces an orange-yellow solution.

D Addition of Cl_2(aq) to a solution of Fe^{2+}(aq) produces a yellow solution which remains yellow when KF(aq) is added.

21



$$\overset{1}{H_3C}-\overset{H}{\overset{2}{C}}=\overset{H}{\overset{3}{C}}-\overset{H}{\overset{4}{C}}=\overset{5}{C}=\overset{H}{\overset{6}{C}}-H$$

Which bond is present in the compound above?

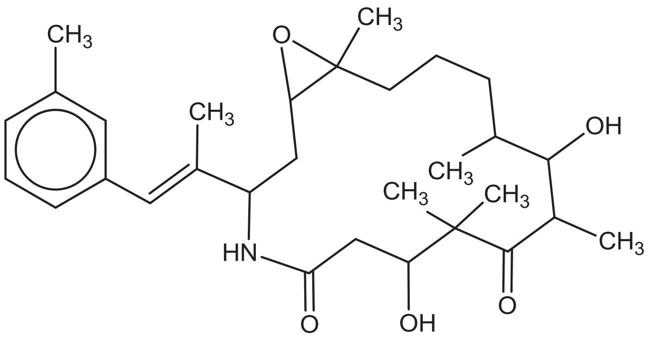
A a σ bond formed by sp^3 - sp^3 overlap between C3 and C4

B a σ bond formed by sp^2 - sp overlap between C4 and C5

C a σ bond formed by sp^2 - sp^2 overlap between C5 and C6

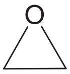
D a π bond formed by sp^2 – sp^2 overlap between C2 and C3

22 Compound **X** is an analogue of Ixabepilone which is an anticancer agent currently in clinical development.



compound **X**

Compound **X** was reacted with $NaBH_4$ in methanol.

In this reaction, the  ring remains unaltered.

What is the maximum number of stereoisomers in the product of this reaction?

A 2^7 **B** 2^8 **C** 2^9 **D** 2^{10}

23 Which of the following reactions will give an optically inactive mixture?

1 2–bromo-2-methylbutane heated with aqueous KOH

2 3-bromo-3-methylhexane heated with alcoholic NaOH

3 But–1–ene reacted with HBr dissolved in organic solvent

4 Butanone reacted with HCN, trace amount of NaOH

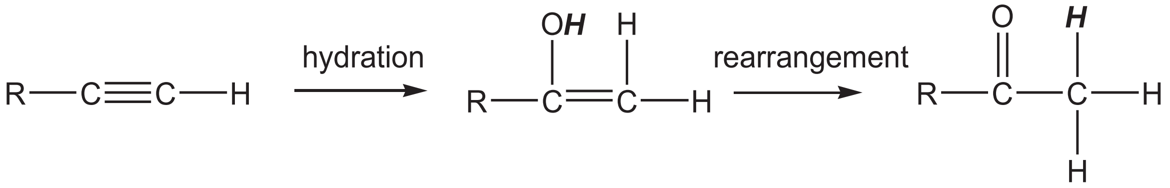
A 1 & 3

B 3 & 4

C 1, 2 & 3

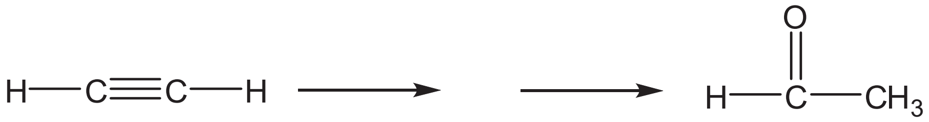
D All of the above

24 An alkyne (C≡C) undergoes hydration in a similar mechanism as an alkene. However, the formation of enol (C=C-OH) is unstable and would undergo rearrangement to form a carbonyl compound.



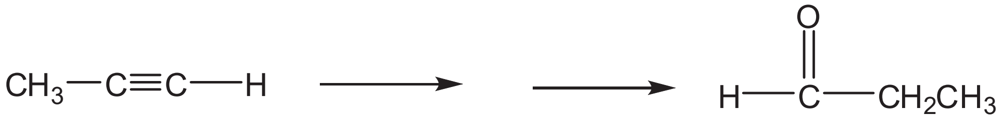
Which compound will **not** be formed when the following alkynes undergo hydration?

A



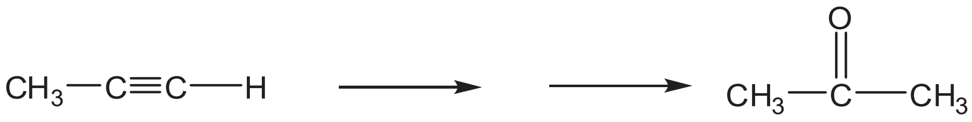
$$\mathrm{H-C\equiv C-H} \longrightarrow\quad \longrightarrow \mathrm{H-\overset{\overset{O}{\|}}{C}-CH_3}$$

B



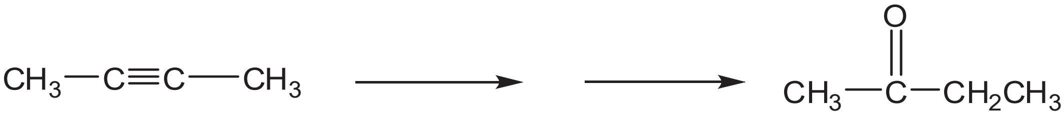
$$\mathrm{CH_3-C\equiv C-H} \longrightarrow\quad \longrightarrow \mathrm{H-\overset{\overset{O}{\|}}{C}-CH_2CH_3}$$

C



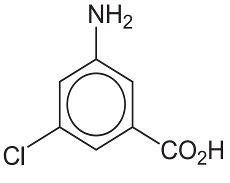
$$\mathrm{CH_3-C\equiv C-H} \longrightarrow\quad \longrightarrow \mathrm{CH_3-\overset{\overset{O}{\|}}{C}-CH_3}$$

D



$$\mathrm{CH_3-C\equiv C-CH_3} \longrightarrow\quad \longrightarrow \mathrm{CH_3-\overset{\overset{O}{\|}}{C}-CH_2CH_3}$$

25 A student wishes to synthesise compound **Q** from benzene.



Q

Which of the following routes would give the maximum yield of **Q**?

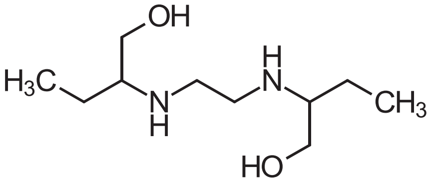
A Alkylation → nitration → chlorination → reduction → oxidation

B Nitration → alkylation → oxidation → chlorination → reduction

C Alkylation → oxidation → nitration → reduction → chlorination

D Chlorination → nitration → reduction → alkylation → oxidation

26 Ethambutol (EMB) is commonly used as first line drugs in tuberculosis treating regimes.



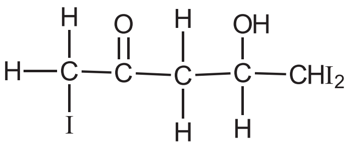
EMB

How many moles of hydrogen gas will be produced when one mole of EMB reacts with sodium?

A 1.0 **B** 2.0 **C** 3.0 **D** 4.0

27 Which of the following compound gives a yellow precipitate with alkaline aqueous iodine?

A

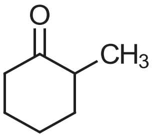


$\mathrm{ICH_2COCH_2CH(OH)CHI_2}$

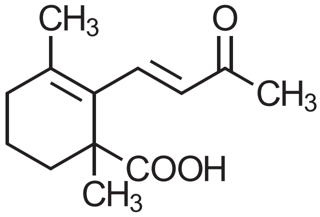
B CH_3OH

C CH_3CONH_2

D



28 Compound **Y** is a derivative of β-ionone, which is an important contributor of the aroma of roses.



Compound **Y**

What is the correct number of H atoms incorporated per molecule of Compound **Y** when Compound **Y** is reacted with each of the following reducing agents?

	Reducing agent	Number of hydrogen atoms incorporated per molecule of Compound **Y**
1	H_2 / Ni	6
2	LiA/H_4 in dry ether	8
3	$NaBH_4$ in ethanol	2

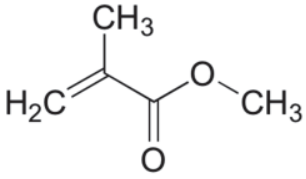
A 1 is correct only

B 1 and 3 is correct

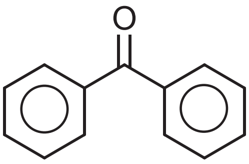
C 2 and 3 is correct

D 1,2,3 is correct

29 Methyl methacrylate and benzophenone are common ingredients found in nail polishes.



Methyl methacrylate



benzophenone

Which of the following reagents cannot be used to distinguish between these two compounds?

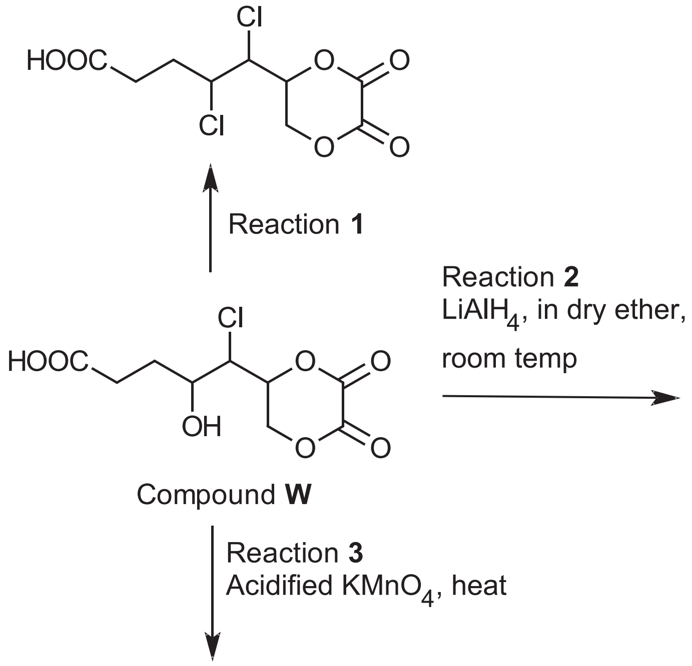
A Acidified $K_2Cr_2O_7$

B 2,4-dinitrophenylhydrazine

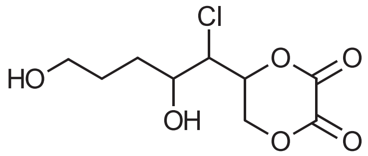
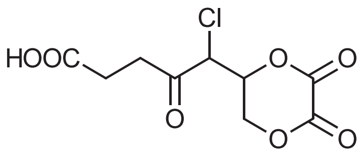
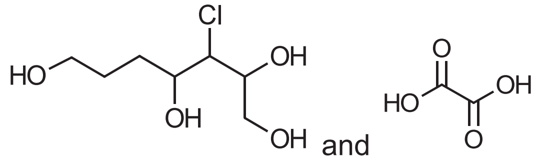
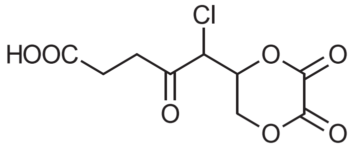
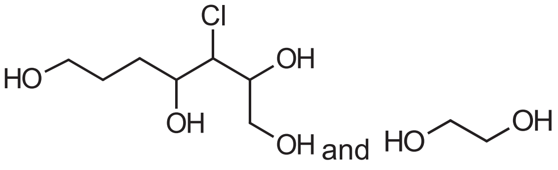
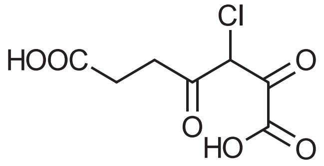
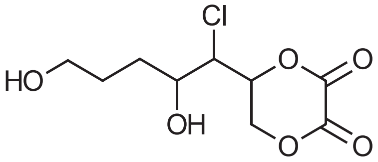
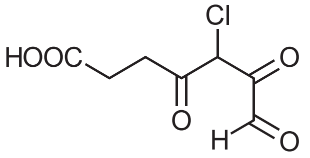
C Tollens' Reagent

D Bromine water

30 The diagram below shows a reaction scheme of compound **W**.



Which of the following shows the correct products of Reactions **2** and **3** and the type of reaction for Reaction **1**?

	Reaction 1	Product(s) of Reaction 2	Product of Reaction 3
A	Nucleophilic substitution		
B	Nucleophilic addition		
C	Nucleophilic substitution		
D	Nucleophilic addition		

PRELIMINARY EXAMINATIONS

HIGHER 2

CANDIDATE NAME									
CIVICS GROUP			/						
CENTER NUMBER	S					INDEX NUMBER			

CHEMISTRY
9729/02

Paper 2 Structured Questions **11 September 2017**

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	/ 22
2	/ 15
3	/ 21
4	/ 8
5	/ 9
Paper 1	/ 30
Paper 3	/ 80
Total	

This document consists of 18 printed pages

Answer **all** the questions

1 Silver chloride is an important photosensitive inorganic material widely used in photographic applications. It is industrially produced by mixing solutions of silver nitrate and sodium chloride.

$Ag^{+}(aq) + Cl^{-}(aq) \rightleftharpoons AgCl(s)$ $\Delta H_{ppt}^{\ominus} = -65.7 \text{ kJ mol}^{-1}$, $\Delta S_{ppt}^{\ominus} = -34.3 \text{ J mol}^{-1} \text{ K}^{-1}$

(a) **(i)** Suggest whether a lower or higher temperature should be used to increase the yield of silver chloride. Explain your answer. [2]

(ii) Calculate $\Delta G^{\ominus}$ of the precipitation of AgC*l*. [1]

(iii) In view of your answer in **(a)(ii)**, comment on the solubility of silver chloride in water. [1]

(b) **(i)** Lattice energies are not measured directly. The value calculated using Hess' Law and the Born-Haber cycle is the experimental lattice energy. [3]

Using $\Delta H_{ppt}^{\ominus}$ of AgC*l*(s), the following data and relevant data from the *Data Booklet*, calculate the experimental lattice energy of AgC*l*(s).

standard enthalpy change of formation of $Ag^{+}(aq)$	+106 kJ mol^{-1}
standard enthalpy change of formation of $Cl^{-}(aq)$	–167 kJ mol^{-1}
standard enthalpy change of atomisation of Ag(s)	+285 kJ mol^{-1}
first electron affinity of chlorine	–349 kJ mol^{-1}

The theoretical value of lattice energies are calculated using the distances between the cations and anions in the crystal structure, and the charge on each ion.

The table below shows the numerical values of experimental and theoretical lattice energies for sodium chloride and silver fluoride.

compound	experimental value/ kJ mol^{-1}	theoretical value/ kJ mol^{-1}
$NaCl$	-771	-766
AgF	-967	-953

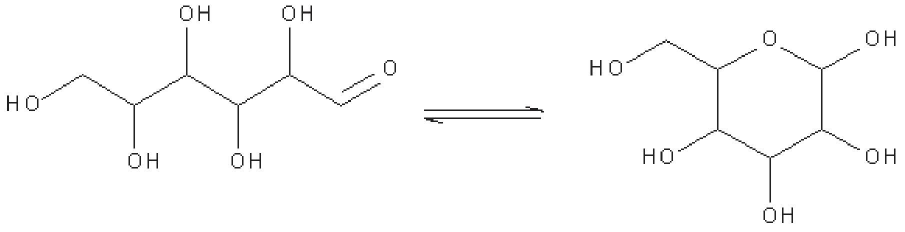
(ii) It can be seen that the experimental and theoretical values for sodium chloride and silver fluoride are quite similar. [1]

However, the theoretical value for the *silver chloride* is significantly less exothermic than the experimental value.

Suggest a reason for this.

(c) Explain, with the aid of equations, why silver chloride is soluble in aqueous ammonia while silver iodide does not dissolve in aqueous ammonia. [3]

(d) **(i)** Most of the energy our bodies need comes from carbohydrates and fat. Starch is broken down into glucose,$C_6H_{12}O_6$. Glucose exist mainly in cyclic forms with a small percentage in open chains. [1]



open-chain cyclic

State what you would observe when glucose is added to an alkaline solution of ammoniacal silver(I) nitrate.

Glucose is transported to the cells to react with oxygen via a series of steps to form carbon dioxide, water and energy.

(ii) Write a balanced equation for the reaction of glucose with oxygen. [1]

(iii) Using data from the Data Booklet, calculate the amount of energy released per mole of glucose using the **cyclic** structure. [2]

(iv) The literature value for the amount of energy released per mole of glucose is – 2800 kJ. [1]

Apart from bond energies are average values, suggest another reason for the difference between this value and that calculated in **(d)(iii)**.

____

____

____

Like carbohydrates, fats are metabolised into carbon dioxide and water and when subjected to combustion in a bomb calorimeter. The reaction of tristearin, $C_{57}H_{110}O_6$, a typical fat is as follows:

$$C_{57}H_{110}O_6 + \frac{163}{2} O_2 \rightarrow 57\ CO_2 + 55\ H_2O \quad \Delta H^\ominus = -37760\ kJ\ mol^{-1}$$

The fuel value is the energy when one gram of the material undergoes combustion. The table below shows the fuel value of carbohydrates and protein and the food label of a cup noodle:

	Fuel value / kJ g^{-1}
Carbohydrate	17
Fat (Tristearin)	To be calculated
Protein	17

Nutrition Facts
Serving Size 1 container (70g)

Amount Per Serving	
Calories 310	Calories from Fat 100
	% Daily Value*
Total Fat 12g	18%
Saturated Fat	25%
Trans Fat	
Cholesterol 0mg	0%
Sodium 1010mg	42%
Total Carbohydrate 44g	15%
Dietary Fiber 4g	16%
Sugars 4g	
Protein 8g	

(v) Determine the fuel value of tristearin and hence deduce if tristearin or carbohydrate is a better source of energy. (M_r of tristearin = 890) [2]

(vi) During reading or watching television, the average adult uses about 7 kJ/min. How many minutes of such activity can be sustained by the energy supplied by a serving of cup noodle (considering only the total fat, total carbohydrate and total protein content)? [1]

(e) In the body, glucose is also converted to energy via alcoholic fermentation. This process has been used in making beer and the side products such as esters contribute greatly to the taste and aroma of the beer. [3]

Ethyl acetate can be formed as follows

$$CH_3CO_2H + CH_3CH_2OH \rightleftharpoons CH_3CO_2CH_2CH_3 + H_2O$$

1.51 mol of CH_3CO_2H and 1.66 mol of CH_3CH_2OH was allowed to reach equilibrium in a 100 cm^3 solution. 10 cm^3 of the equilibrium mixture was extracted and large amounts of cold water was added to quench the reaction. The mixture was then titrated with 22.40 cm^3 of 2 mol dm^{-3} NaOH.

Calculate the K_c for the formation of ethyl acetate.

[Total: 22]

2 **(a)** In 1887, the Swedish scientist Svante Arrhenius postulated that acids and bases dissociate in water to form hydrogen ions, H^+, and hydroxide ions, OH^-, respectively.

(i) Suggest a limitation of the Arrhenius concept of acids and bases. [1]

A theory proposed by Danish chemist J.N. Brønsted and British chemist T.M. Lowry overcame the shortcomings of the Arrhenius theory.

(ii) Using the Brønsted–Lowry model, nitric acid can be either a Brønsted–Lowry acid or base. Write equations to show how nitric acid *reacts* as a Brønsted–Lowry acid and a Brønsted–Lowry base respectively. [2]

As an acid

As a base

(b) The following table compares the K_a values of two three-carbon carboxylic acids.

Acid	Formula	K_{a1}	K_{a2}
Propanoic	$CH_3CH_2CO_2H$	1.35×10^{-5}	—
Malonic	$HO_2CCH_2CO_2H$	1.41×10^{-3}	2.00×10^{-6}

Suggest a reason why K_{a1} of malonic acid is higher than

(i) K_a of propanoic acid [1]

(ii) K_{a2} of malonic acid [1]

(iii) 25 cm^3 of 0.10 mol dm^{-3} of NaOH is gradually added to 10 cm^3 of 0.10 mol dm^{-3} malonic acid. Calculate the pH of the mixture when the following volumes of NaOH has been added. [3]

- 0 cm^3 [considering only K_{a1} of malonic acid]

- 5 cm^3

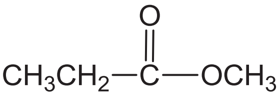
- 15 cm^3

- 25 cm^3

(iv) Using your answers in **(b)(iii)**, sketch the pH-volume added curve when 25 cm^3 of 0.10 mol dm^{-3} NaOH is gradually added to 10 cm^3 of 0.10 mol dm^{-3} malonic acid. [2]

(v) Suggest an indicator for the first equivalence point. [1]

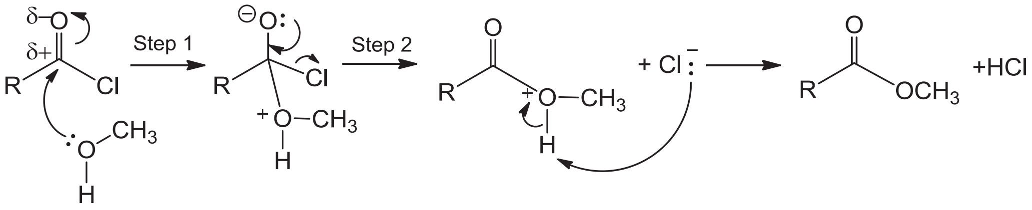
(c) Compound **A** can be directly synthesised from propanoic acid or propanoyl chloride via condensation.



$CH_3CH_2-\overset{O}{\overset{\|}{C}}-OCH_3$

Compound **A**

The formation of compound **A** from propanoyl chloride occurs via the mechanism shown below.



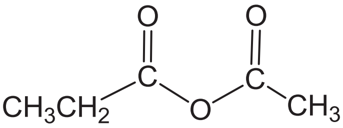
where R = CH_3CH_2—

(i) Name the reactions in step 1 and step 2. [2]

Step 1 ____

Step 2 ____

Compound **B** is a carboxylic acid anhydride that reacts similarly to an acyl chloride.



Compound **B**

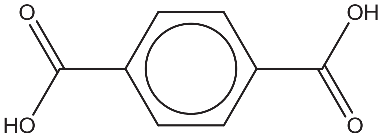
(ii) Compound **B** reacts with methanol that has been labelled with ^{18}O isotope to form compound **A**. [1]

Write an equation for the reaction showing clearly the location of the ^{18}O atom in the product. The formula of methanol can be written as $CH_3{}^{18}OH$.

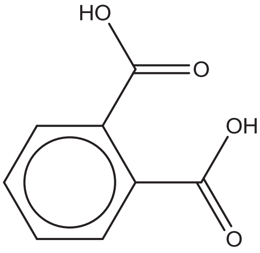
(iii) Draw the structure of another neutral product formed in the reaction. [1]

[Total: 15]

3 Terephthalic acid (TPA) and phthalic acid (PA) both have the molecular formula $C_6H_4(COOH)_2$. While TPA is used principally to make clothing and plastic bottles, PA has limited commercial application. The structures of TPA and PA are shown below.



TPA



PA

Some physical properties of TPA and PA are shown in the table below:

	TPA	PA
Appearance	White crystal	White crystal
Melting point	300 °C	207 °C
Boiling point	Decomposes	Decomposes

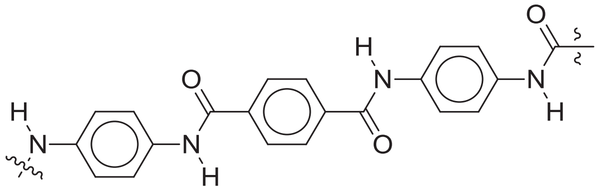
(a) Explain why TPA has a higher melting point than PA. [2]

(b) **(i)** TPA can be reduced to a diol for the synthesis of a renewable polymer.

Draw the structure of this diol and illustrate with a diagram, its interaction with water. [3]

(ii) Hence, explain why the diol in **(i)** is soluble in water. [1]

One common derivative of TPA is terephthaloyl chloride. Terephthaloyl chloride reacts with another monomer in a polymerisation reaction to form a synthetic fiber, commonly known as Kevlar®. A short chain of the Kevlar® polymer is shown below.



A strand of Kevlar® polymer

(c) **(i)** Name the type of reaction for this polymerisation reaction and suggest the structure of the other monomer to form the Kevlar® polymer. [2]

Type of reaction:

Structure of monomer:

(ii) In selecting a suitable material for the manufacture of bulletproof armour, it is necessary to ensure that the material does not shatter upon high impact force from a bullet.

With reference to the structures of gold and fluorite, CaF_2, explain why gold is more suitable for the lining of bulletproof armour. [2]

(d) **(i)** Define second ionisation energy of aluminium. [1]

(ii) Explain why the second ionisation energy of aluminium is higher than that of silicon. [1]

(e) Many chemical reactions such as the reaction between peroxodisulfate and iodide ions occur very slowly at room temperature.

$$S_2O_8^{2-} + 2I^- \rightarrow 2SO_4^{2-} + I_2$$

One way to speed up rate of reaction is to use a homogeneous catalyst.

(i) Explain why the reaction between $S_2O_8^{2-}$ and I^- has a high activation energy. [1]

(ii) A solution of iron(II) ions can be used to catalyse the reaction between $S_2O_8^{2-}$ and I^-.

Using appropriate equations, outline the catalytic role of Fe^{2+} in the $S_2O_8^{2-}$ and I^- reaction. Hence, explain with the aid of a Boltzmann distribution curve, how Fe^{2+} speeds up the rate of the reaction. [5]

A kinetics study was conducted on the reaction of $S_2O_8^{2-}$ and I^- to determine the rate equation. Varying volumes of $S_2O_8^{2-}$ and I^- were added to a mixture containing sodium thiosulfate and starch indicator, followed by topping up with suitable volume of water.

As the reaction of $S_2O_8^{2-}$ and I^- proceeds, the iodine produced will be consumed by the thiosulfate. When all thiosulfate is reacted, the remaining iodine will react with the starch indicator, forming a blue-black complex. The rate of reaction is determined by the time taken for the blue-black colouration to appear.

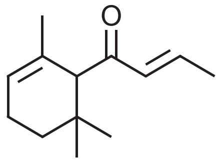
Experiment	Volume of KI / cm^3	Volume of $Na_2S_2O_8$ / cm^3	Volume of $Na_2S_2O_3$ / cm^3	Volume of water / cm^3	Time for blue-black colour / s
1	10	20	10	10	50
2	5	20	10	15	100
3	30	10	10	0	33
4	20	40	20	20	x

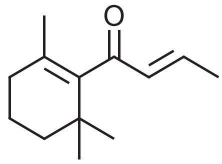
(iii) Determine the order of reaction with respect to iodide and peroxodisulfate. [2]

(iv) Hence, deduce the time taken for the blue-black colouration to appear for experiment 4. [1]

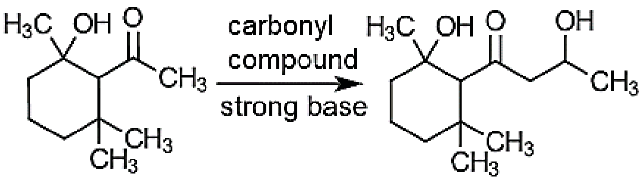
[Total: 21]

4 Rose ketones, damascenones, were discovered as active ingredients in the characteristic smell of Bulgarian rose oil. α-damascenone and β-damascenone were later discovered to give female perfumes such as *Dior's Poison* their unusual and distinctive fragrance.


α-damascenone


β-damascenone

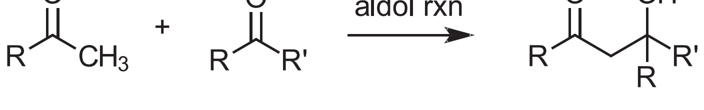
In the synthesis of damascenones in the laboratory, it was found that compound **A** is a possible precursor which could be synthesised from compound **B** via an aldol reaction.



Compound **B** Compound **A**

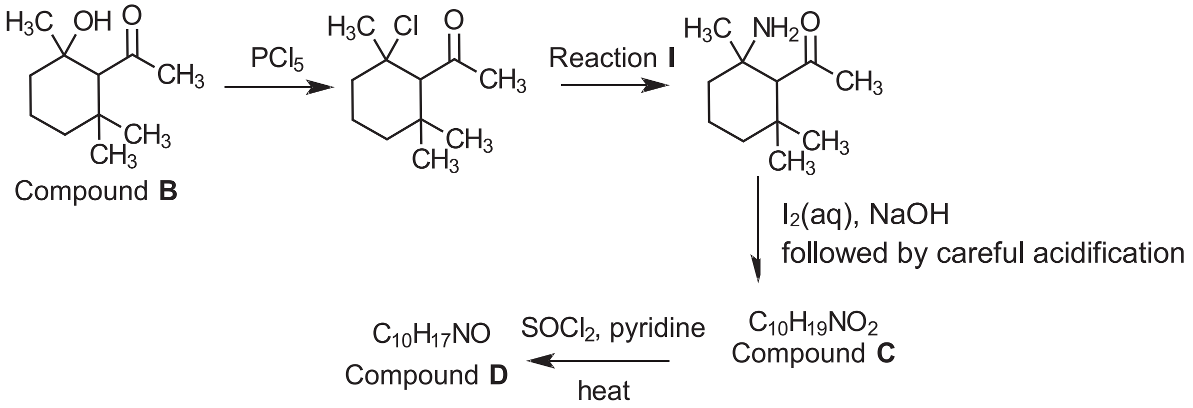
(a) State the reagent and condition required to convert compound **A** to either α-damascenone or β-damascenone. [1]

(b) With reference to an example of aldol reaction shown below, suggest an identity of the carbonyl compound reacting with compound **B** to form compound **A**.



[1]

Compound **B** can undergo a series of chemical reactions as shown in the flow chart below.

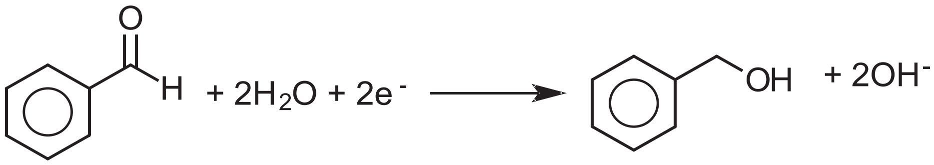


(c) State the reagents and conditions for Reaction **I**. [1]

(d) Draw the structural formulae of compounds **C** and **D**. [2]

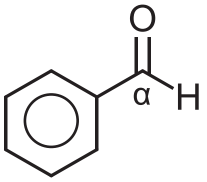
Benzaldehyde, in the presence of sodium hydroxide, undergoes the cannizzaro reaction to give benzoate ion and phenylmethanol.

(e) The ion-electron half-equation of benzaldehyde forming phenylmethanol is shown below.



Construct the ion-electron half equations for the reaction of benzaldehyde forming benzoate ion and hence, construct an overall balanced equation for the reaction. [2]

(f) Using changes in oxidation states of the carbon labelled α in benzaldehyde, state and explain the type of reaction that benzaldehyde undergoes in **(e)**. [1]



[Total: 8]

5 Organic compound **P** (M_r = 144) can be found in most leather products and is used as a mould inhibitor. **P** has the following composition by mass:

C: 50.04% H: 5.56% O: 44.40%

(a) (i) Determine the molecular formula of **P**. [2]

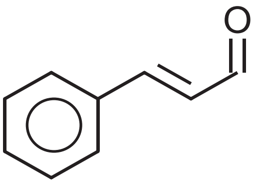
P exhibits stereoisomerism and it decolourises aqueous bromine. On heating one mole of **P** with dilute acid, two organic products **Q**, $C_4H_4O_4$ and **R** (M_r = 32) are obtained. The mole ratio of **Q** to **R** is 1:2. Vigorous effervescence was observed when **Q** reacted completely with sodium carbonate in equimolar proportions.

(ii) Draw the displayed formula of **Q**. [1]

(iii) State the functional groups present in **P**. [1]

(iv) Hence state the type of stereoisomerism exhibited by **P**. Draw and label the stereoisomers. [2]

(b) Another mould inhibitor, cinnamaldehyde has the structure shown below. [3]



Reaction of cinnamaldehyde with HBr produces a mixture that is optically inactive. Explain this observation.

[Total: 9]

TEMASEK
JUNIOR COLLEGE

CHEMISTRY **9729/03**
Paper 3 Free Response **13th September 2017**
2 hours

Candidates answer on separate paper.

Additional Materials: Answer Paper
Graph Paper
Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your Centre number, index number, name and civics group on all the work you hand in.
Write in dark blue or black pen.
You may use a HB pencil for any diagrams or graphs.
Do not use staples, paper clips, glue or correction fluid.

Section A
Answer **all** questions.

Section B
Answer **one** question.

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

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

This document consists of **14** printed pages and **2** blank pages.

Section A

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

1 Calcium carbonate is found in rocks and is the main component of pearls and the shells of eggs, snails and many marine organisms. It is the active ingredient in agricultural lime and is also medicinally used as a calcium supplement or as an antacid.

(a) **(i)** Describe and explain the trend in thermal stability of the Group 2 carbonates. [3]

(ii) Determine the minimum temperature for the spontaneous decomposition of calcium carbonate, given that $\Delta H = +178.5 \text{ kJ mol}^{-1}$ and $\Delta S = +163.2 \text{ J K}^{-1} \text{ mol}^{-1}$. [2]

(b) Limestone is predominantly calcium carbonate, a slightly soluble salt with a K_{sp} value of 3.3×10^{-9}. This rocky material began accumulating in the Earth over 400 million years ago. The Howe Caverns in the USA is a relatively young limestone cave which began forming 800 000 years ago.

(i) Determine the solubility of calcium carbonate. [1]

The principal cave-forming process is explained below.

Gaseous CO_2 is in equilibrium with aqueous CO_2 in surface water.

$CO_2(g) \rightleftharpoons CO_2(aq)$ ----- **(1)**

As surface water trickles through cracks in the ground, it meets soil-trapped air which contains higher levels of CO_2 (P_{CO_2} = 100 Pa) and hence $[CO_2(aq)]$ increases.

When this CO_2-rich water contacts limestone, more $CaCO_3$ dissolves. As a result, more rock is carved out, more water flows in and over centuries a cave is formed.

$CaCO_3(s) + CO_2(aq) + H_2O(l) \rightleftharpoons Ca^{2+}(aq) + 2HCO_3^-(aq)$ ----- **(2)**

(ii) Show that the atmospheric partial pressure of CO_2, P_{CO_2}, is 40.5 Pa. You may assume air contains 0.04% by volume CO_2. [1]

(iii) State and explain whether CO_2 in the atmosphere or soil-trapped air is behaving less ideally. [2]

Stalactites and stalagmites are rock formations that hang from ceiling of caves and rise from the floor of caves, respectively. They are formed when surface water seeps through rock and drips from the ceiling of a cave.

(iv) With reference to equilibria **(1)** and **(2)**, explain the formation of stalactites and stalagmites in limestone caves. [3]

(v) Suggest a reason why some of these rock formations can appear reddish brown or bluish green. [1]

Lakes bounded by limestone-rich soil are less likely to be impacted by acid rain. Limestone dissolves sufficiently in lake water to form a buffer system capable of mitigating the effect of acid rain.

(vi) Suggest, with the aid of an equation, how the buffer system will maintain the pH of the lake water.

[1]

Acidification due to acid rain of lakes and rivers poses a serious environmental problem. The concentration of carbonate ions in these water is small due to the high acidity, hence affecting the survivability of some marine organisms.

(vii) Suggest a reason why the survivability of some marine organisms is affected.

[1]

(c) Emission from power stations using coal, which contains sulfur, as fuel has significant environmental consequences. One of the components is sulfur dioxide, which can be oxidised by atmospheric hydroxyl radical to sulfur trioxide.

(i) Write a balanced equation to explain how sulfur trioxide contribute to acid rain.

[1]

Current power plants are fitted with flue-gas desulfurization devices. These devices heat powdered limestone in air to remove sulfur dioxide from the gases produced during coal combustion. One of the products is calcium sulfate.

(ii) Write a balanced equation for the reaction that had taken place.

[1]

(d) Sulfur and aluminium can both react with chlorine.

Aluminium chloride is a white solid that sublimes while sulfur tetrachloride, SCl_4, is an unstable pale yellow solid. Both react with water but formed different products.

(i) Predict the shape of sulfur tetrachloride, using a diagram where appropriate. Suggest the bond angle(s) in the molecule.

[2]

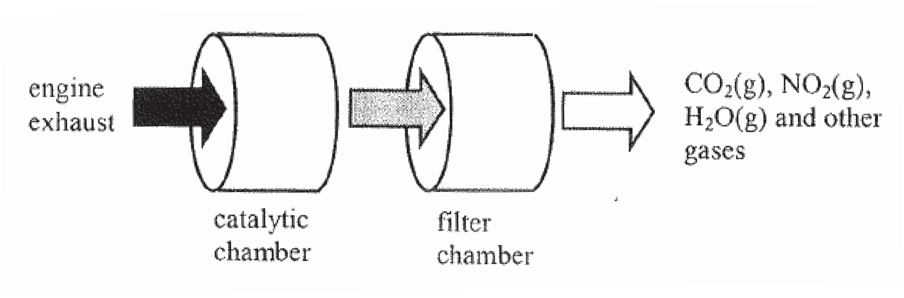
(ii) Describe and explain, with the aid of equations, the reaction of aluminium chloride with water. Suggest the pH of the resulting solution.

[3]

[Total: 22]

2 The exhaust of heavy-duty diesel engines contains a significant amount of particulate matter (PM) and harmful gases such as nitrogen oxides. A Continuous Regenerating Trap (CRT) is a device which is designed for use in exhaust systems of buses and lorries running on diesel to remove PM and some of the harmful gases. A second catalytic converter is usually installed to remove the oxides of nitrogen.

The diagram below shows how a CRT works:



(a) **(i)** Explain, with the aid of equations, why oxides of nitrogen are present in the engine exhaust.

[2]

(ii) State one harmful effect of nitrogen oxides on the environment.

[1]

(iii) State two harmful gases that are also present in the engine exhaust. Use chemical equations to show how these two gases can be removed in the catalytic chamber of a CRT.

[2]

A CRT is an automated, self-regenerating device which does not require cleaning of the filter. In a CRT, the carbon, which is the most abundant element in PM, is trapped onto the filter and is then removed by one of the harmful gases.

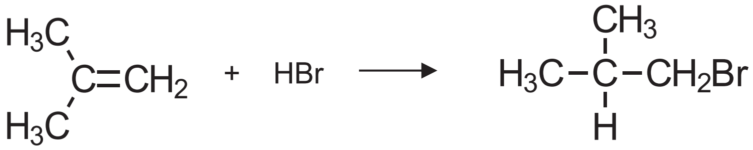
(iv) Explain, with the aid of an equation, how the carbon trapped on the filter of a CRT can be removed. Hence explain why the filter need not be cleaned.

[2]

(v) Suggest why buses and lorries equipped with CRT should not run on diesel with high sulfur content.

[1]

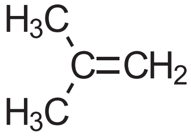
(b) In the reaction of HBr to alkenes such as methylpropene, scientists discovered that impurities such as peroxides, R-O-O-R, greatly increased the amount of anti-Markovnikov addition product as shown below.


methylpropene 1-bromo-2-methylpropane

The above reaction is explained by the 4 step free radical addition mechanism as described below.

Step 1: The reaction is initiated by the formation of RO• radicals.
Step 2: This is followed by the reaction of the RO• radical with HBr to give bromine radical.
Step 3: The bromine radical adds to the alkene via the cleaving of the pi bond.
Step 4: The radical obtained from Step 3 reacts with HBr to form the anti-Markovnikov product.

(i) Use the information given above to draw out the full mechanism for the reaction. You are advised to use structural formulae for all species, such as

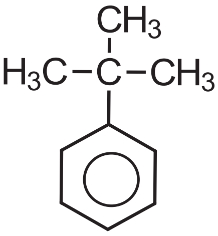

for methylpropene, so that it is clear which bonds are broken and which are formed. Indicate any unpaired electrons by a dot and use  to represent movement of an electron.

[4]

(ii) Unlike HBr, HC*l* does not undergo free radical addition to alkenes, even in the presence of peroxides. Explain this observation by quoting relevant values from the Data Booklet to substantiate your answer.

[2]

Tertiary butylbenzene is a colourless liquid widely used as a solvent for organic synthesis and also as a polymer linking agent.

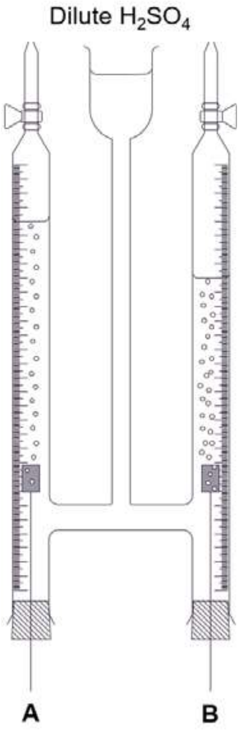

t-butylbenzene

(iii) Using 1-bromo-2-methylpropane as the starting material, suggest a 3-stage synthesis of t-butylbenzene. You should state the reagents and conditions needed for each step, and show clearly the structure of any intermediate compounds.

[3]

[Total: 17]

3 The following setup was carried out for the electrolysis of dilute sulfuric acid under room conditions, using platinum electrodes. A steady current of 2 A was applied for 1 minute through the circuit. The ratio of volume of gas produced at electrodes **A** and **B** is 1:2.



(a) **(i)** Write the half-equations for the reactions occurring at **A** and **B**. Label the polarity of each electrode clearly.

[2]

(ii) Calculate the volume of gas produced at **A** after 1 minute.

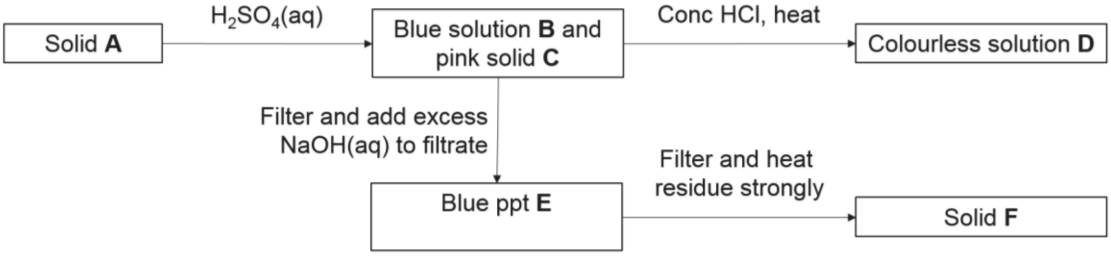
[1]

(iii) A student repeated the same experiment above, but using a copper electrode at **A** this time.

Suggest the volume of gas produced at **A** and explain your answer.

[2]

(b) Solid **A,** which is formed when a copper complex reacts with an aldehyde, is subjected to the following reactions.



Suggest the identities of **A** to **F**.

[6]

(c) Compounds **V** and **W** are gaseous hydrocarbons of empirical formulae CH_2 and CH_3 respectively. When 10 cm^3 of **V** and 10 cm^3 of **W** were completely burnt in 150 cm^3 of oxygen, the total gaseous volume decreased by 55 cm^3. After shaking the residual gases with aqueous sodium hydroxide, the total gaseous volume decreased by another 60 cm^3. When compound **V** is heated with acidified potassium manganate(VII), compound **X**, C_3H_6O, is formed.

(i) Suggest the molecular formula of **W**.

[1]

(ii) Suggest the structures of compounds **V** and **X**. Explain your answers.

[4]

(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 warmed with aqueous sodium hydroxide and iodine.

Suggest the structures of compounds **Y** and **Z**. Explain your answers.

[5]

[Total: 21]

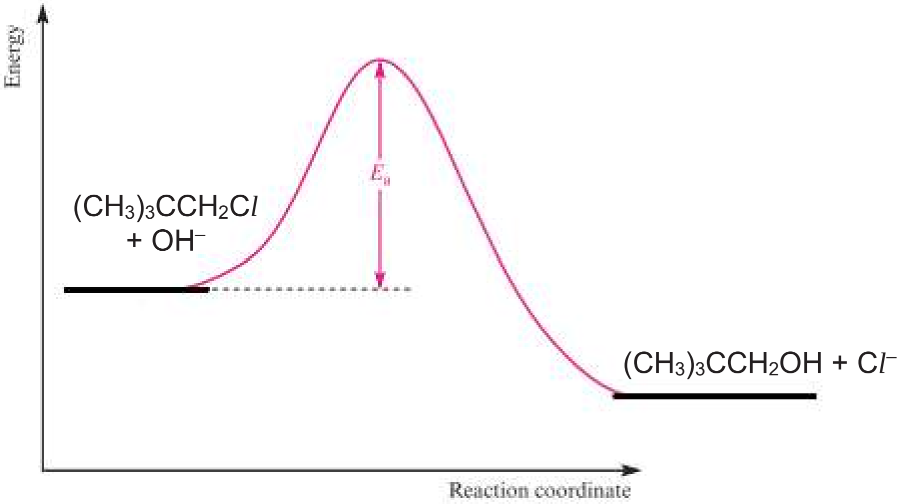
BLANK PAGE

Section B

Answer **one** question from this section.

4 **(a)** Halogenoalkanes commonly undergo nucleophilic substitution reactions. On the basis of experimental observations developed over a 70-year period, two mechanisms for nucleophilic substitutions have been proposed.

In the kinetics study of the hydrolysis of 1-chloro-2,2-dimethylpropane, $(CH_3)_3CCH_2Cl$, the energy-profile diagram of the reaction was proposed below:



(i) With reference to the energy profile diagram, describe the mechanism of the reaction between 1-chloro-2,2-dimethylpropane and hydroxide ions. The mechanism should include curly arrows to show the movement of electrons and all charges.

[2]

(ii) A student decided to verify the mechanism deduced in **(a)(i)** for the hydrolysis reaction of 1-chloro-2,2-dimethylpropane.

The following results were obtained and you may consider the overall [NaOH(aq)] to remain virtually constant at 0.10 mol dm^{-3} throughout the experiment.

Time/ min	Experiment 1 $[(CH_3)_3CCH_2Cl]$/ mol dm^{-3}
0	0.0100
40	0.0070
80	0.0049
120	0.0034
160	0.0024
200	0.0017
240	0.0012

Using appropriate axes, plot a graph of $[(CH_3)_3CCH_2Cl]$ against time and use your graphs to deduce the order with respect to the concentration of the 1-chloro-2,2-dimethylpropane, showing your working clearly.

[4]

(iii) Given the general rate equation as

$$\text{Rate} = k' \, [(CH_3)_3CCH_2Cl]^x$$

Using your answer in **(a)(ii),** calculate the rate constant k', stating its units.

[2]

(iv) When the experiment was repeated at the same temperature, the concentration of NaOH was doubled and the concentration of 1-chloro-2,2-dimethylpropane was monitored against time. The same graph was obtained as Experiment 1.

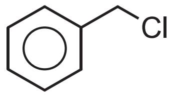
Deduce the order of reaction with respect to the concentration of hydroxide ion.

[1]

(v) Using your answers in **(a)(ii)** and **(a)(iv)**, explain if the student should agree with the proposed mechanism for the reaction in **(a)(i)**.

[1]

(b) (Chloromethyl)benzene is a primary alkyl halide.

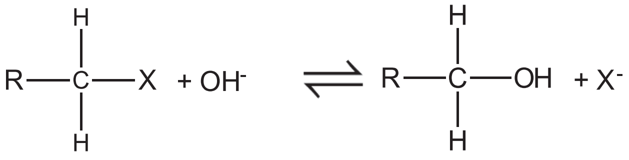


(Chloromethyl)benzene

Suggest a reason why (chloromethyl)benzene undergoes substitution via S_N1 mechanism.

[1]

(c) Different alkyl halides would have different reactivity towards nucleophilic substitution.



$$R\!-\!CH_2\!-\!X + OH^- \rightleftharpoons R\!-\!CH_2\!-\!OH + X^-$$

where X^- is a leaving group

The difference in reactivity is dependent on the stability of the leaving group. The more stable the halide ion, the better the leaving group. The pK_a values of HX is given below.

Halide (X)	**pK_a (HX)**
F	+3
Cl	–7
Br	–9
I	–10

(i) Suggest the relationship between pK_a of HX and the stability of the halide ion.

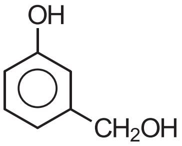
[1]

(ii) Iodomethane and chloromethane are separately reacted with hydroxide ions. Using your answer in **(c)(i)**, explain why iodomethane reacts at a faster rate.

[1]

(d) Chlorinated phenols have gained an increasing use as fungicides, herbicides, insecticides, and precursors in the synthesis of other pesticides since the early 1930s.

It can be easily synthesised from its precursor **A** using aqueous chlorine.

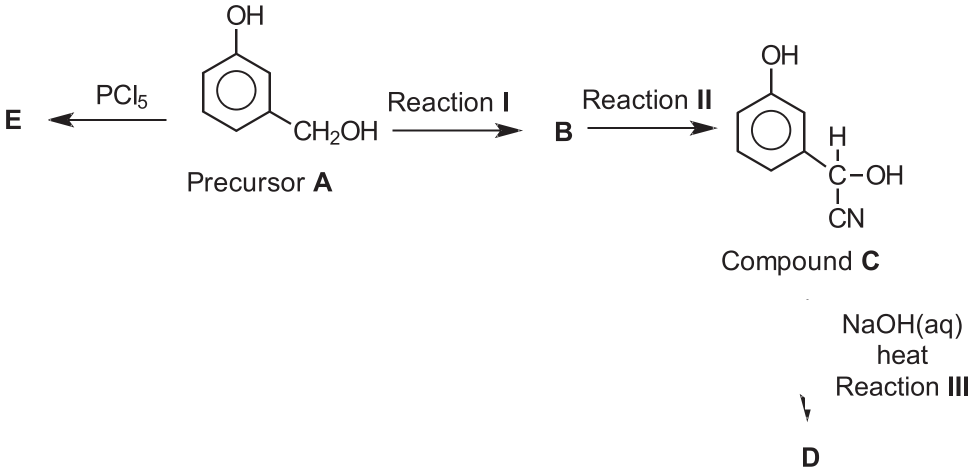


Precursor **A**

(i) Write a balanced equation for the reaction between precursor **A** and aqueous chlorine.

[1]

(ii) Precursor **A** undergoes a series of reactions shown in the reaction scheme below.



State the reagent and condition for Reaction **I** and **II**, and hence draw the structures of **B**, **D** and **E**.

[5]

(iii) Reaction **III** can be used as a distinguishing test between compound **C** and precursor **A**. State the observation for this distinguishing test.

[1]

[Total: 20]

5 **(a)** Describe and explain the relative thermal stabilities of the hydrogen halides down the group.

[2]

(b) Potassium chlorochromate (VI), $KCrClO_3$, was made using concentrated hydrochloric acid and potassium dichromate(VI).

$$K_2Cr_2O_7 + 2HCl \rightarrow 2KCrClO_3 + H_2O$$

Chlorine gas may be evolved as a side product. It was found that chlorine gas will not be produced if dilute hydrochloric acid was used instead.

Use data from the *Data Booklet* to explain why this is so.

[2]

(c) **(i)** Vanadium is a transition element that exhibits variable oxidation states.

Explain why vanadium has the ability to form compounds with different oxidation states.

[1]

(ii) A Latimer diagram shown below summarises the standard electrode potential data of vanadium complexes in acidic medium.

$$\begin{tikzcd} VO_3^- \arrow[r, "+1.00\text{ V}"] \arrow[rr, bend left, "x"] & VO^{2+} \arrow[r, "+0.34\text{ V}"] & V^{3+} \end{tikzcd}$$

x, the standard electrode potential of converting VO_3^- to V^{3+}, is **not** the summation of +1.00 V and +0.34 V. It can be calculated from ΔG°.

Write a half-equation for the conversion of VO_3^- to V^{3+}.

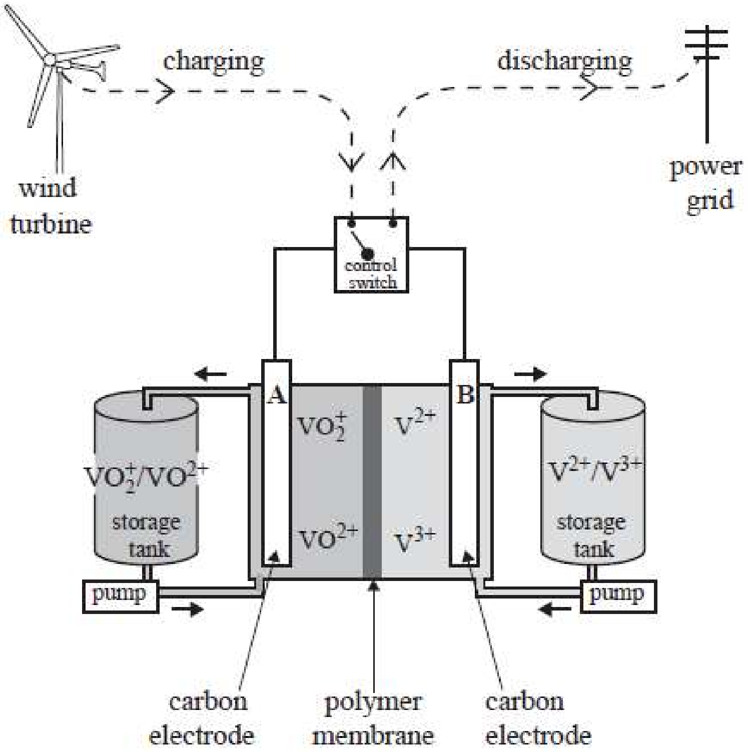
[1]

(iii) Calculate x, given that ΔG° for the conversion of VO_3^- to V^{3+} is $-129000\text{ J mol}^{-1}$.

[1]

(d) A vanadium redox battery is used to store electrical energy generated at a wind farm in Tasmania. The battery supplies electricity to the power grid as required through a control switch.

The diagram below shows the structure of a cell in a vanadium redox battery. The reactants are dissolved in an acidic solution, stored in large tanks and pumped through the cell. The cell is recharged using electricity generated by the wind turbines. A polymer membrane allows the movement of particular ions.



(i) State the polarity of electrode **A** when the cell is **discharging.** Explain your answer. [2]

(ii) Write an equation for the reaction that occurs when the cell is being **recharged**. [1]

(e) Nitrogen containing compounds such as ammonia and amines are common ligands found in transition metal complexes.

(i) Explain the relative basicities of ammonia, methylamine, dimethylamine and trimethylamine in the gaseous phase. [2]

(ii) Amides, such as ethanamide, are nitrogen containing compounds that do not exhibit basic properties like amines.

Explain why amides are neutral. [1]

(f) In 1893, Alfred Werner proposed the octahedral configuration of transition metal complexes. He was able to interpret isomeric properties using extensive studies on the octahedral cobalt complexes.

The following table gave information of two cobalt complexes **A** and **B** which are isomers of each other.

	Complex	Colour of solid	Does the complex have a dipole moment
A	$CoCl_2(NH_3)_4^+$	Violet	Yes
B	$CoCl_2(NH_3)_4^+$	Green	No

(i) Suggest structures for the cobalt complexes **A** and **B**.

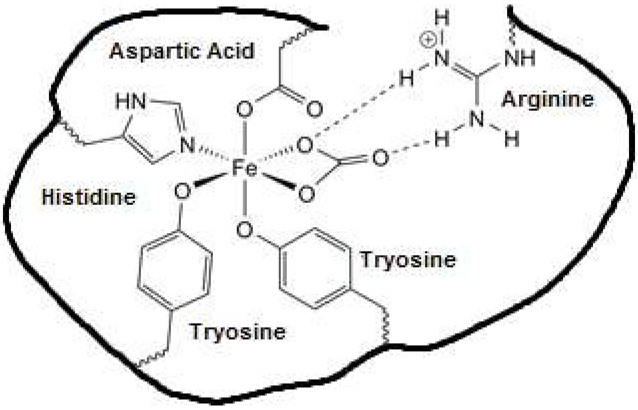
[2]

(ii) The crystal field theory can be used to explain colour of transition metal complexes.

Describe, using the shape and orientation of the d orbitals, the splitting of degenerate d orbitals into two energy levels in octahedral complexes.

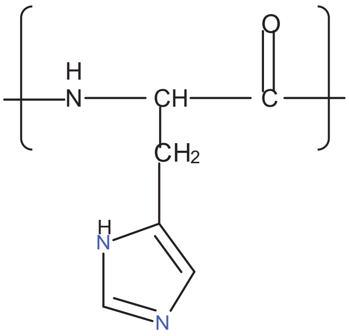
[3]

(g) R-groups on amino acids residues on protein act as ligands in biological systems. *Transferrin* is a protein in the blood that transports iron from food to the rest of the body.

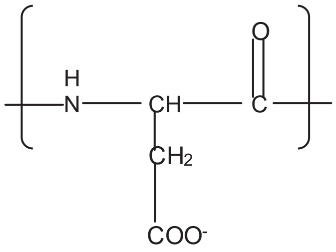


binding sites of *Transferrin*

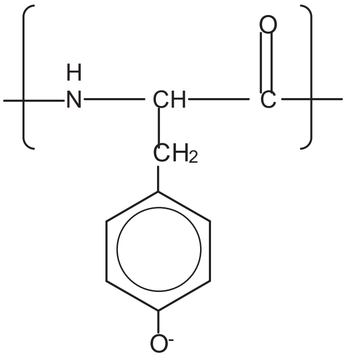
Transferrin binds to iron(III) via tryosine, histidine and aspartic acid residues as shown below.



Histidine residue
Side chain pK_a = 6.00



Aspartic acid residue
Side chain pK_a = 3.65



Tyrosine residue
Side chain pK_a = 10.07

The key to controlling uptake and release iron(III) is the change in pH. At pH 7.4, free transferrin binds to iron(III) to form the iron-transferrin complex. When the pH is lowered from 7.4 to 5.5, free iron(III) ions will be released from the protein binding site.

(i) Draw the structural formula of the tyrosine residue at its most stable state at pH 5.5.

[1]

(ii) Suggest how the decrease in pH releases iron(III) from the protein complex.

[1]

[Total: 20]

BLANK PAGE

TEMASEK
JUNIOR COLLEGE

2017 JC2 PRELIMINARY EXAMINATIONS
HIGHER 2

CANDIDATE NAME	
CIVICS GROUP	/
CENTRE NO. / INDEX NO.	/

CHEMISTRY **9729/04**

Paper 4 Practical **28 August 2017**

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 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	/ 15
2	/ 24
3	/ 16
Total	/ 55

This document consists of 15 printed pages.

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

1 **Determination of change in oxidation number of a transition metal ion, M^{2+}**

You are to determine, by titration, the change in oxidation number of a transition metal ion, $\mathbf{M}^{2+}$, when reacted with acidified potassium manganate(VII).

FA 1 is 0.0200 mol dm^{-3} potassium manganate(VII), $KMnO_4$
FA 2 is 0.0470 mol dm^{-3} transition metal salt, $\mathbf{M}SO_4$
FA 3 is 1.00 mol dm^{-3} sulfuric acid, H_2SO_4

(a) Method

(i) 1. Fill the burette with **FA 1.**

2. Using a pipette, transfer 25.0 cm^3 of **FA 2** into the conical flask.
3. Using a measuring cylinder, transfer 25.0 cm^3 of **FA 3** to the same conical flask.
4. Carry out as many accurate titrations as necessary to obtain consistent results. Add **FA 1** until the contents of the conical flask turns a permanent pale pink colour.
5. Record below, in a table form, all of your burette readings and the volume of **FA 1** added in each accurate titration.

Results

[6]

(ii) From your titrations, obtain a suitable volume of **FA 1** to be used in your calculations. Show clearly how you obtained this volume.

25.0 cm^3 of **FA 2** required ________________ cm^3 of **FA 1** [1]

(b) **Calculations**

Show your working and appropriate significant figures in the final answer to **each** step of your calculations.

(i) Calculate the amount of potassium manganate(VII) present in the volume of **FA 1** calculated in **(a)(ii)**.

amount of $KMnO_4$ = ______________________ [1]

(ii) Determine the amount of **M**SO_4 in 25.0 cm^3 of **FA 2**.

amount of **M**SO_4 in 25.0 cm^3 = ______________________ [1]

(iii) Use your answer to **(b)(i)** and **(b)(ii)** to calculate the number of moles of **M**SO_4 that react with 1 mole of $KMnO_4$

amount of **M**SO_4 = ______________________ [1]

(iv) Two possible equations for the reaction of acidified $KMnO_4$ with **M**SO_4 are shown below:

Equation 1: $2KMnO_4 + 10\mathbf{M}SO_4 + 8H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 5\mathbf{M}_2(SO_4)_3 + 8H_2O$
Equation 2: $2KMnO_4 + 5\mathbf{M}SO_4 + 8H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 5\mathbf{M}(SO_4)_2 + 8H_2O$

State and explain which of the above two equations is consistent with your answer in **(b)(iii)**.

____

____

____

____

[1]

(v) Use your answer in **(b)(iv)** to state the oxidation number of the transition metal **M** in the product of the reaction.

[1]

(c) **(i)** A student suggested that using a burette to measure 25.0 cm^3 of **FA 2** would give a more accurate result than using a pipette. The percentage error of a 25.0 cm^3 pipette is 0.24%.

Calculate the percentage error of using a burette and deduce if the above claim by the student is correct.

[2]

(ii) Another student decided to use a 25.0 cm^3 pipette instead of a measuring cylinder to measure the volume of **FA 3** in **Step 3**.

State and explain whether this alteration will improve the accuracy of the experimental results.

[1]

[Total: 15]

2 **Determination of the enthalpy change of neutralisation, ΔH_n**

You are to determine the enthalpy change for the neutralisation reaction given below.

$$HA(aq) + NaOH(aq) \rightarrow NaA(aq) + H_2O(l)$$

FA 4 is 1.80 mol dm^{-3} HA
FA 5 is aqueous sodium hydroxide, NaOH

(a) Method

Read through the instructions carefully and prepare a table below for your results before starting any practical work.

1. Support the styrofoam cup in the 250 cm^3 beaker.
2. Rinse and fill the burette with **FA 4**.
3. Use the measuring cylinder to transfer 25 cm^3 of **FA 5** into the styrofoam cup.
4. Place the thermometer in the styrofoam cup and record the temperature of the solution. Tilt the cup if necessary to ensure the thermometer bulb is fully immersed.
5. Run 5.00 cm^3 of **FA 4** into the cup. Stir, and record the new temperature of the solution and the volume of **FA 4** added.
6. Run a second 5.00 cm^3 of **FA 4** into the cup. Stir and record the new temperature and the total volume of **FA 4** added.
7. Continue adding **FA 4** in 5.00 cm^3 portions. Stir and record each new temperature and total volume of **FA 4** until a total of 45.00 cm^3 has been added.

<u>Results</u>

[2]

(b) **(i)** Plot a graph of temperature (*y*-axis) against total volume of **FA 4** added (*x*-axis) on the grid below. The temperature axis should allow you to include a point at least 2 °C greater than the maximum temperature recorded.

Draw two best-fit lines connecting all the plotted points with

- an increasing trend
- a decreasing trend.

[3]

(ii) Extrapolate the two lines until they cross.
The intersection gives the maximum temperature, T_{max}, at equivalence point.
Use your graph to determine the following and show clearly on your graph how you obtained these answers.

- Maximum temperature at the equivalence point, $T_{max,}$
- Maximum temperature change at the equivalence point, $\Delta T_{max.}$
- Total volume of **FA 4** added at the equivalence point, $V_{eq.}$

T_{max} = ________________

ΔT_{max} = ________________

$V_{eq.}$ = ________________

[3]

(c) Explain the shapes of your graph lines before the equivalence point and after the equivalence point.

(i) Before the equivalence point

[2]

(ii) After equivalence point

[1]

(d) **Calculations**

Show your working and appropriate significant figures in the final answer to **each** step of your calculations.

(i) Calculate the number of moles of HA present in the volume of **FA 4** recorded in **(b)**.

Amount of HA = ____________________

(ii) Using your answers in **(b)**, calculate the heat energy produced when **FA 4** neutralised 25 cm^3 of sodium hydroxide.
(Assume that **4.2 J** of heat energy changes the temperature of 1.0 cm^3 of solution by 1 °C.)

Heat energy produced = ____________________

(iii) Calculate the enthalpy change of neutralisation, in kJ mol^{-1}, for the reaction below.

$$HA(aq) + NaOH(aq) \rightarrow NaA(aq) + H_2O(l)$$

Enthalpy change = ____________________

[6]

(e) Apart from using a thermometer calibrated to a greater level of precision, suggest one other improvement that could be made to the **method** carried out in **(a)**.

____

____

____

[1]

Planning

The enthalpy change of solution of solid NaOH can be calculated using the enthalpy change of neutralisation of aqueous NaOH with aqueous HC*l*, ΔH_1 and the enthalpy change of reaction of solid NaOH with aqueous HC*l*, ΔH_2.

(f) Given that the enthalpy change of neutralisation of aqueous NaOH with aqueous HC*l* is –57.0 kJ mol^{-1}, construct an energy cycle and show how it can be used to determine the enthalpy change of solution of NaOH.

[1]

(g) You are to plan an experiment to determine the enthalpy change of reaction of solid NaOH with aqueous HC*l*, ΔH_2. You are provided with the following reagents and the usual laboratory apparatus.

Reagents : 50 cm^3 1 mol dm^{-3} HC*l* solution
sodium hydroxide solid

Your plan should include

- calculation to show the appropriate mass of solid sodium hydroxide to be used.
- a sequence of numbered steps, the details of the experimental procedure including the measurements to be taken and tabulation of measurements and results.
- calculation of the enthalpy change of reaction of solid NaOH with HC*l* (aq).

(Assume that **4.2 J** of heat energy changes the temperature of 1.0 cm^3 of solution by 1 °C.)
[Ar Na: 23.0, H:1.0; O:16.0]

[5]

[Total:24]

3 You are provided with the solid **FA 6** and solution **FA 7**.

You are to perform the tests below and record your observations in the spaces provided. Your answers should include

- details of colour changes and precipitates formed;
- the names of any gases evolved **and** details of the test used to identify each one.

You should indicate clearly at what stage in a test a change occurs.

If it appears that no reaction has taken place this should be clearly recorded.

Rinse and reuse test-tubes where possible.

Marks are **not** given for chemical equations.

No additional or confirmatory tests for ions present should be attempted.

Candidates are reminded that definite deductions may be made from tests where there appears to be no reaction.

(a) **FA 6** contains one cation and one anion.

	Test	*Observation*
(i)	To half a spatula-full of **FA 6** in a test-tube add excess dilute sulfuric acid. Keep the solution for test **(iii)** and **(iv)**.	
(ii)	Place a spatula-full of **FA 6** in a test-tube and heat strongly.	
(iii)	To 1 cm depth of the solution from **(i)** in a test-tube, add a few drops of aqueous sodium hydroxide Then add excess aqueous sodium hydroxide.	

(iv)	To 1 cm depth of the solution from **(i)** in a test-tube, add a few drops of aqueous ammonia. Then add excess aqueous ammonia.	

The cation present in **FA 6** is ______________________

The anion present in **FA 6** is ______________________

FA 7 contains one cation and two anions.

	Test	*Observations*
(v)	To 1 cm depth of **FA 7** in a test-tube, add a few drops of aqueous sodium hydroxide. Then add excess aqueous sodium hydroxide. Warm the mixture.	
(vi)	To 1 cm depth of **FA 7** in a test-tube, add a few drops of aqueous ammonia Then add excess aqueous ammonia.	
(vii)	To 1 cm depth of **FA 7** in a test-tube, add aqueous silver nitrate, followed by aqueous ammonia.	
(viii)	To half a spatula-full of **FA 6** in a test-tube, add 3 cm depth of **FA 7**.	
	Then add 1 cm depth of aqueous sodium thiosulfate.	

One anion present in **FA 7** is ____________________

With reference to tests **(v)**, **(vi)** and **(viii)**, suggest the identity of the cation present in **FA 7**.

____

The second anion is suspected to be the sulfate ion.

(ix) Suggest a test to verify the presence of sulfate ion in **FA 7**. Carry out the test and record your results in the space below.

[11]

(b) **FA 8** is a solution that contains the Cr^{3+}, Mg^{2+} and Cl^{-} ions.

Plan a sequence of steps by which the three ions could be separated so that each ion is present in a separate precipitate. For each of the steps, you are to specifiy the location of the ions.

You may assume that the usual bench reagents and apparatus are available for use.

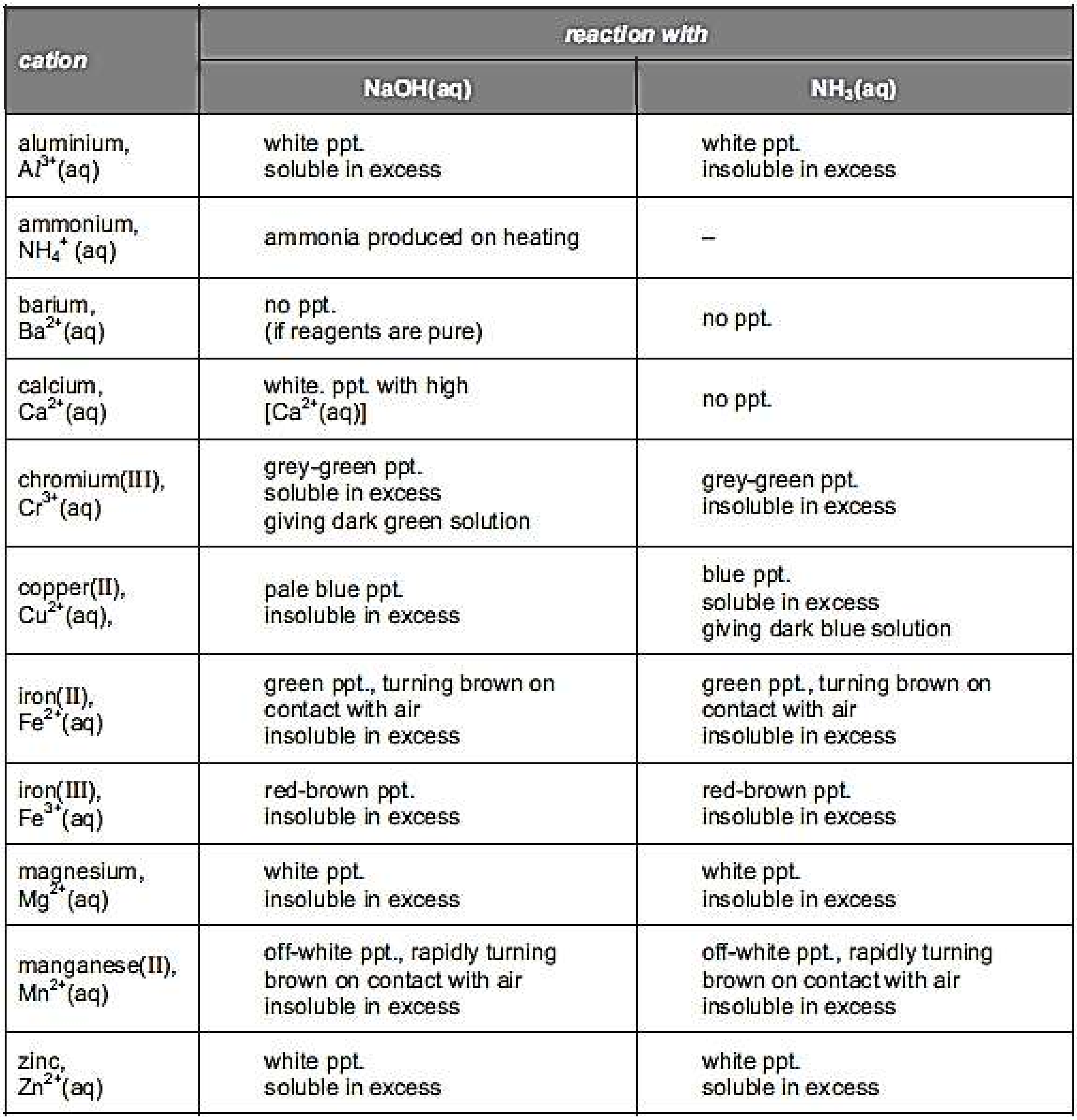
[5]

[Total: 16]

Qualitative Analysis Notes

[ppt. = precipitate]

(a) Reactions of aqueous cations



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

(b) Reactions of anions

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

(c) Tests for gases

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

(d) 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

A: 7 B: 9
C: 8 D: 6

2017 JC2 Prelim H2 CHEMISTRY MCQ Worked Solution

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

1 Answer: B

Since $Ba(NO_3)_2 \equiv N_2$, M_r of $Ba(NO_3)_2$ = 261.3
No. of moles of N_2 = No. of moles of $Ba(NO_3)_2$
$= \frac{1}{261.3} = 3.83 \times 10^{-3}$ mol
Volume of $N_2 = 3.83 \times 10^{-3} \times 24000 = 91.8$ cm^3

2 Answer: D

Definition – Relative molecular mass is the average mass of one molecule of an element or compound on a scale on which one atom of the ^{12}C isotope of carbon has a mass of 12 units.

Option **1** is incorrect. Relative molecular mass is a ratio.
Option **2** is incorrect. It should be the ratio of the average mass of a molecule to 1/12 the mass of a ^{12}C atom.
Option **3** is correct.

3 Answer: C

A is incorrect as SO_2 is an oxidizing agent and oxidises H_2S in reaction.
B is incorrect as SO_2 is the intermediate and is not regenerated in the reaction.
C is correct as H_2S (oxidation state of sulfur is -2) is oxidized to S (oxidation state 0).
D is incorrect as reaction II is a comproportionation reaction.

4 Answer: A

Angle of deflection $\theta \propto q/m$. So $\theta_{Ca} m_{Ca}/q_{Ca} = \theta_X m_X/q_X$
Mass of X = 20(40.1)/2 / 5.08 = 79 (Se)
Atomic number of **X** = 34

5 Answer: D

A: Ethene is a planar molecule which has all atoms on the plane

B: Tri-iodide has 3 lone pairs and 2 bond pairs, hence the ion is linear and all atoms lie on the same plane

C: XeF_4 has 4 bond pairs and 2 lone pairs, hence shape is square planar and all atoms lie on the same plane

D: $BeCl_4^{2-}$ has a total of 4 bond pairs (2 covalent bonds and 2 dative bonds) around Be atom. The shape is tetrahedral.

6 Answer: B

A: HF has hydrogen bonding between its molecules and hence require a larger energy to overcome compared to pd-pd between HI molecules.

B: MgO has a higher boiling point. MgO has a higher lattice energy than $NaCl$ due to larger charge and smaller ionic radii of Mg^{2+} and O^{2-} ion compared to Na^+ and Cl^-.

C: SiH_4 has a higher boiling point as its M_r is larger than CH_4 and thus the id-id interactions are stronger and more extensive than CH_4.

D: *trans*-$C_2H_2Cl_2$ has a lower boiling point as it has no net dipole moment so the molecule is non-polar and only has id-id interactions between the molecules. *cis*-$C_2H_2Cl_2$ has pd-pd interaction between the molecules and more energy is needed to overcome the stronger pd-pd interactions.

7 Answer: A

PV = nRT
At r.t.p,
R = PV/nT = (1 atm x 24000 cm^3)/(1 mol x 293K)

M_r = mRT / PV = (m x T x 24000) / (p x V x 293)

8 Answer: D

A & C: Wrong as the concentration of manganate would decrease slowly at the start of the reaction before decreasing more quickly as more Mn^{2+} catalyst is generated.

B: Wrong as the volume of CO_2 cannot be increasing rapidly at the start of the reaction due to slow rate of reaction.

9 Answer: B

A: HBr will complete dissociate to give free H^+ ions and Br^- ions. Since there is a change in the number of ions as the reaction progresses, so conductivity of the solution increases over time and can be monitored using a conductivity meter.

B: Although CO_2 gas is produced, the reaction is done at atmospheric pressure and not in a closed system, so pressure of the system will not change over time.

C: Br_2(aq) is reddish-brown and all the products are colourless, so the intensity of the solution would decolourise over time.

D: As the reaction progresses, more HBr (a strong acid) is produced, so concentration of H^+ would increase over time and can be monitoring by quenching and titration against standard NaOH.

10 Answer: B

No. of moles of bromine = 32/(79.9 x 2) = 0.200 mol

When bromine vapourises, $\Delta G = 0$ since it is an equilibrium reaction.

$\Delta H = T\Delta S$

$\Delta S = \Delta H/T = (30.9 \times 10^3 \times 0.2)/(58.8 + 273)$

$= 18.6$ J K^{-1}

11 Answer : D

Heat released when **E** is burnt = 200 x 4.18 x 26.4

= 22070 J

No. of moles of **E** = 22076 ÷ (3290 x 10^3)

= 0.00671 mol

M_r of **E** = 0.47/0.00671

= 70 (C_5H_{10})

Option 1 is incorrect as it is short of a CH_2. Options 2 & 3 are isomers of C_5H_{10}.

12 Answer : C

From reaction I,
$K_c = \frac{[X_2Y]}{[X_2][Y_2]^{\frac{1}{2}}} = 2$

For reaction II,
$K_c' = \frac{[X_2]^2[Y_2]}{[X_2Y]^2} = \frac{1}{{K_c}^2} = \frac{1}{4}$

13 Answer : D

A:	P	+	Q	$\rightleftharpoons$	R	+	3S
Initial amt/mol	-		0.5		0		-
Change in amt/mol	-		-0.1		+0.1		-
Eqm amt/mol	-		0.4		0.1		-

$K_c = \frac{[R]}{[Q]} = \frac{0.1}{0.4} = 0.25.$

B: When temperature increases, the forward reaction is favoured by Le Chatelier's Principle to absorb heat. At equilibrium, there will be greater no. of moles of R and lesser no. of moles of S. Thus, K_p increases.

C: There is equal number of moles of gas on both sides of the equation. Increasing pressure will not affect equilibrium.

D: **P** is a solid and is not included in the equilibrium constant. Changing its concentration will not affect the equilibrium.

14 Answer: A

Buffers are formed when roughly equal amount of the conjugate acid-base pair is present.

A is not a buffer as the resultant mixture only contains $CH_3CH_2CO_2H$ from the reaction between HCl and $CH_3CH_2CO_2^-$.
B is buffer as it contains HCO_3^- and CO_3^{2-}.
C is a buffer as $CH_3CH_2NH_2$ is in excess and $CH_3CH_2NH_3^+$ is formed from the reaction between $CH_3CH_2NH_2$.
D is a buffer as NH_4^+ is in excess and NH_3 is formed from the reaction between NH_4^+ and NaOH.

15 Answer: C

A & B: During rusting, oxygen is being reduced to hydroxide ions and iron being oxidised to iron(II) ions.

C: $O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O$ +1.23 V

$E^\ominus_{cell} = +1.23 - (-0.44) = +1.67$ V

Since $E^\ominus_{cell} > 0$, the reaction is spontaneous. Hence, it is not inhibited a low pH.

D: $E^\ominus_{Fe2+/Fe} = -0.44$ V $E^\ominus_{Mg2+/Mg} = -2.38$ V

Since $E^\ominus_{Mg2+/Mg}$ is more negative than $E^\ominus_{Fe2+/Fe}$, magnesium will be oxidised instead of iron. Hence, magnesium acts as a sacrificial metal and prevents corrosion.

16 Answer: A

1: $E^\ominus_{Cu2+/Cu} = +0.34$ V $E^\ominus_{Mg2+/Mg} = -2.38$ V
$E^\ominus_{Ag+/Ag} = +0.80$ V

At the anode, copper is preferentially oxidised over water to form copper(II) ions. As $E^\theta(Mg^{2+}/Mg)$ is more negative than $E^\theta(Cu^{2+}/Cu)$, magnesium will also be preferentially oxidised.

Ag will not be oxidised as $E^\theta(Ag^+/Ag)$ is more positive than $E^\theta(Cu^{2+}/Cu)$. Ag will be collected below the anode as 'anode sludge'.

The decreased in mass at the anode is due to oxidation of copper and magnesium. Silver is not being oxidised but is collected as anode sludge.

2: At the cathode, only copper(II) ions were reduced to copper. As $E^\theta(Mg^{2+}/Mg)$ is more negative than $E^\theta(Cu^{2+}/Cu)$, magnesium will not be preferentially reduced together with copper.

3: The amount of copper deposited is dependent on the magnitude of the current and time in which the current was supplied. It is not affected by the size of the electrode.

17 Answer: C

A The covalent character increase across the period.
B The melting point increase then decrease across the period.
C The pH change from basic to neutral to acidic across the period.
D Only Al_2O_3, P_4O_{10} and SO_3 are soluble in NaOH, so there is actually no trend.

18 Answer: A

The charge density decreases with increasing atomic no., hence the tendency to form complexes, acidity of the aqueous chloride solution (because ease of hydrolysis decreases) and magnitude of hydration energy decreases

The reduction potential becomes more negative with increasing atomic no., hence the metal's reducing power increases.

19 Answer: B

Since X^- can react with both Y_2 and Z_2 in the process forming X_2, it is the strongest reducing agent.

Since Y^- cannot react with both X_2 and Z_2 to form Y_2, it is the weakest reducing agent.

20 Answer: C

A is incorrect. For the complex to be red it must have absorbed blue light (complementary colour).

B is incorrect. $[FeF_6]^{3-}(aq)$ is colourless when $edta^{4-}$ is added. $[Fe(edta)]^{-}(aq)$ is formed and solution will turn yellow. *(Charge on edta is 4-).*

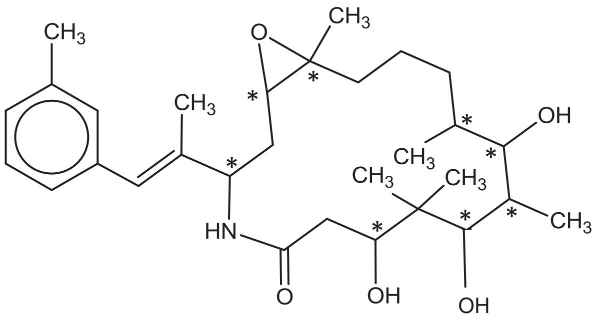
C is correct. $[Fe(CN)_6]^{3-}(aq)$ has a greater K_{stab} hence is more likely to be formed thus SCN^- and H_2O ligands will be displaced. The solution will turn orange yellow.

$E^{\theta}{}_{Cl_2/Cl^-} = +1.36V$
$E^{\theta}{}_{Fe^{3+}/Fe^{2+}} = +0.77V$
D is incorrect. Cl_2 will oxidise Fe^{2+} to Fe^{3+} turning the solution yellow. Upon addition of F^- the solution will turn colourless as $[FeF_6]^{3-}(aq)$ has a greater K_{stab}.

21 Answer: B

A: a σ bond formed by $sp^2 - sp^2$ overlap between C3 and C4
C: a σ bond formed by $sp - sp^2$ overlap between C5 and C6
D: a π bond formed by p – p overlap between C2 and C3

22 Answer: C



Since there are 8 chiral centers and 1 C=C that can exhibit cis-trans isomerism, no. of stereoisomers = 2^9.

23 Answer: D

1. Tertiary halogenoalkane undergoes S_N1 reaction with aqueous KOH. Formation of carbocation that is planar about the positively charged carbon. The nucleophile OH^- can attack the positively charged C from top and bottom with equal probability resulting in a racemic mixture that is optically not active.
2. Elimination of HBr results in alkenes that are optically not active.
3.Electrophilic addition of HBr to alkene results in formation of intermediate carbocation that will give racemic products.
4.The nucleophile CN^- attacks the planar carbonyl carbon in butanone from top and bottom with equal probability forming a racemic mixture.

24 Answer: B

$CH_3–C\equiv C–H$ will give CH_3COCH_3

25 Answer: B

A: Alkylation followed by nitration will place the alkyl and nitro gps at 1,2 or 1,4 positions. Thus the $–CO_2H$ gp and $–NH_2$ will not be at 1,3 position.
C: The last chlorination step results in –Cl at position 2 or 4 from $–NH_2$ gp.
D: Chlorination followed by nitration results in nitro gp placed at positions 2 or 4 from –Cl gp.

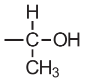
26 Answer: A

2 –OH groups in 1 mol of EMB react with Na to give 1 mol of H_2 gas.

$2\ R\text{-}OH + 2Na \rightarrow 2\ RO^-Na^+ + H_2$

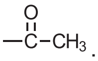
27 Answer: A

Positive test with tri-iodomethane test means



$—\overset{H}{\underset{CH_3}{C}}–OH$

or



$—\overset{O}{\overset{\|}{C}}–CH_3$.

The H-atoms in the $-CH_3$ group in the methyl alcohol and methyl ketone group when replaced by iodine atoms, are still tri-iodomethane test positive.

28 Answer: B

Compound **Y** has 2 C=C, 1 COOH and 1 ketone functional group. Every functional group in Compound **Y** that gets reduced would have 2 H atoms incorporated per molecule of Compound **Y**.

	Reducing agent	No. of hydrogen atoms incorporated per molecule of Compound **Y**	Functional group reduced
1	H_2 / Ni	6	2C=C + 1 ketone
2	LiA/H_4 in dry ether	**<u>4</u>**	1 ketone and 1 –COOH group
3	$NaBH_4$ in ethanol	2	1 ketone group

29 Answer: C

Option A: Orange dichromate turns green for methyl methacrylate as ester bond cleave and the primary alcohol part of the ester gets oxidised. Orange dichromate remains orange for benzophenone.

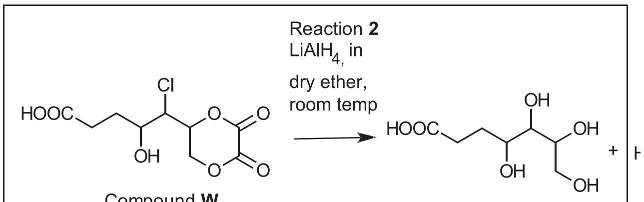
Option B: orange ppt formed for benzophenone and no orange ppt formed for methyl methacrylate.

Option C: Tollen's reagent is negative for both compounds as both compounds do not have an aldehyde functional group.

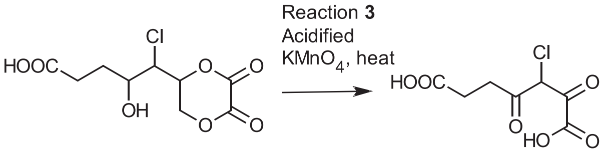
Option D: reddish-brown bromine water decolourise for methyl methacrylate due to C=C. Reddish brown bromine remain for benzophenone.

30 Answer: C

Reaction 1 – conversion of alcohol to halogenoalkane: nucleophilic substitution



Compound **W**



Compound **W**

TEMASEK
JUNIOR COLLEGE

PRELIMINARY EXAMINATIONS
HIGHER 2

CANDIDATE NAME									
CIVICS GROUP			/						
CENTER NUMBER	S					INDEX NUMBER			

CHEMISTRY
9729/02

Paper 2 Structured Questions **11 September 2017**

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	/ 22
2	/ 15
3	/ 21
4	/ 8
5	/ 9
Paper 1	/ 30
Paper 3	/ 80
Total	

This document consists of 18 printed pages

Answer **all** the questions

1 Silver chloride is an important photosensitive inorganic material widely used in photographic applications. It is industrially produced by mixing solutions of silver nitrate and sodium chloride.

$$Ag^+(aq) + Cl^-(aq) \rightleftharpoons AgCl(s) \qquad \Delta H_{ppt}^{\ominus} = -65.7\ kJ\ mol^{-1},\ \Delta S_{ppt}^{\ominus} = -34.3\ J\ mol^{-1}\ K^{-1}$$

(a) **(i)** Suggest whether a lower or higher temperature should be used to increase the yield of silver chloride. Explain your answer. [2]

• A lower temperature should be used.
• By Le Chatelier's Principle, the system will favour the forward exothermic reaction to counteract the lowered temperature. Hence, the position of equilibrium shifts to the right increasing the yield of silver chloride.

(ii) Calculate $\Delta G^{\ominus}$ of the precipitation of AgCl. [1]

• $\Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus}$
$= -65.7 - (298)(-34.3/1000)$
$= -55.5\ kJ\ mol^{-1}$

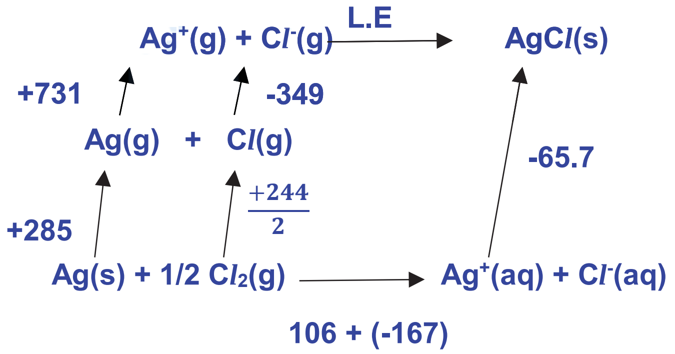
(iii) In view of your answer in **(a)(ii)**, comment on the solubility of silver chloride in water. [1]

• Since $\Delta G^{\ominus}$ is negative, precipitation is spontaneous. Hence, AgCl is insoluble/sparingly soluble in water.

(b) **(i)** Lattice energies are not measured directly. The value calculated using Hess' Law and the Born-Haber cycle is the experimental lattice energy. [3]

Using $\Delta H_{ppt}^{\ominus}$ of AgCl(s), the following data and relevant data from the *Data Booklet*, calculate the experimental lattice energy of AgCl(s).

standard enthalpy change of formation of $Ag^+(aq)$	$+106\ kJ\ mol^{-1}$
standard enthalpy change of formation of $Cl^-(aq)$	$-167\ kJ\ mol^{-1}$
standard enthalpy change of atomisation of Ag(s)	$+285\ kJ\ mol^{-1}$
first electron affinity of chlorine	$-349\ kJ\ mol^{-1}$



• cycle with state symbols

By Hess' Law,
• +285 + 731 + 122 – 349 + L.E = +106 – 167 – 65.7
L.E = • - 916 kJ mol^{-1}

The theoretical value of lattice energies are calculated using the distances between the cations and anions in the crystal structure, and the charge on each ion.

The table below shows the numerical values of experimental and theoretical lattice energies for sodium chloride and silver fluoride.

compound	experimental value/ kJ mol^{-1}	theoretical value/ kJ mol^{-1}
$NaCl$	-771	-766
AgF	-967	-953

(ii) It can be seen that the experimental and theoretical values for sodium chloride and silver fluoride are quite similar. [1]

However, the theoretical value for the *silver chloride* is significantly less exothermic than the experimental value.

Suggest a reason for this.

• The theoretical value of lattice energy is based on the assumption that $AgCl$ is ionic. However, there is some covalent character in $AgCl$ due to the large size of Cl^- ion which can be polarised by Ag^+.

(c) Explain, with the aid of equations, why silver chloride is soluble in aqueous ammonia while silver iodide does not dissolve in aqueous ammonia. [3]

•

$Ag^+(aq) + 2NH_3(aq) \rightleftharpoons [Ag(NH_3)_2]^+(aq)$ --------------------(1)

•NH_3 forms a stable soluble complex $[Ag(NH_3)_2]^+$ with the free Ag^+ ion causing $[Ag^+(aq)]$ to decrease.

•

$Ag^+(aq) + Cl^-(aq) \rightleftharpoons AgCl(s)$ ----------------(2)

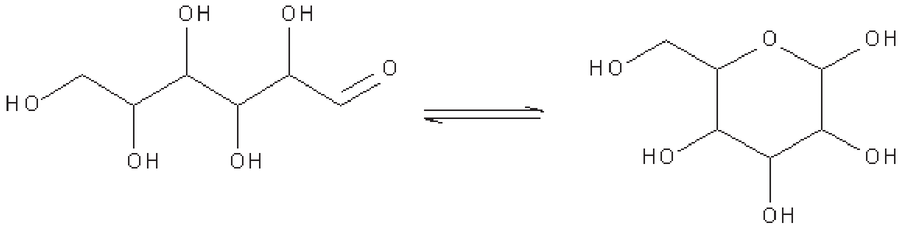
By Le Chatelier's Principle, the position of equilibrium in (2) shifts left to counteract the decrease in the $[Ag^+(aq)]$.

•

The ionic product $[Ag^+][Cl^-]$ decreases to a value lower than the K_{sp} of $AgCl$ and $AgCl$ dissolves.

The K_{sp} of AgI is much lower than K_{sp} of AgCl. The ionic product is still easily exceeded even with the decrease in $[Ag^+(aq)]$ and hence it does not dissolve.

(d) **(i)** Most of the energy our bodies need comes from carbohydrates and fat. Starch is broken down into glucose,$C_6H_{12}O_6$. Glucose exist mainly in cyclic forms with a small percentage in open chains. [1]



open-chain cyclic

State what you would observe when glucose is added to an alkaline solution of ammoniacal silver(I) nitrate.

• Silver mirror is observed.

Glucose is transported to the cells to react with oxygen via a series of steps to form carbon dioxide, water and energy.

(ii) Write a balanced equation for the reaction of glucose with oxygen. [1]

• $C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O$

(iii) Using data from the Data Booklet, calculate the amount of energy released per mole of glucose using the **cyclic** structure. [2]

Using the cyclic structure of glucose,

Bond-breaking	**Bond-Forming**
5 x C – C	**12 x C = O**
5 x O – H	**12 x O – H**
7 x C – H	
7 x C – O	
6 x O = O	

• Energy released

= +(5 x 350 + 5 x 460 + 7 x 410 + 7 x 360 + 6 x 496) – (12 x 805 + 12 x 460)

= • - 2760 kJ mol^{-1}

(iv) The literature value for the amount of energy released per mole of glucose is – 2800 kJ. [1]

Apart from bond energies are average values, suggest another reason for the difference between this value and that calculated in **(d)(iii)**.

• The ∆H calculated using bond energies applies for the reactants and products in the <u>gaseous phase</u> but the reaction involves <u>liquid H_2O</u> rather than gaseous H_2O.

Like carbohydrates, fats are metabolised into carbon dioxide and water and when subjected to combustion in a bomb calorimeter. The reaction of tristearin, $C_{57}H_{110}O_6$, a typical fat is as follows:

$$C_{57}H_{110}O_6 + \frac{163}{2} O_2 \rightarrow 57\ CO_2 + 55\ H_2O \quad \Delta H^\ominus = -37760\ \text{kJ mol}^{-1}$$

The fuel value is the energy when one gram of the material undergoes combustion. The table below shows the fuel value of carbohydrates and protein and the food label of a cup noodle:

	Fuel value / kJ g^{-1}
Carbohydrate	17
Fat (Tristearin)	To be calculated
Protein	17

Nutrition Facts
Serving Size 1 container (70g)

Amount Per Serving
Calories 310 Calories from Fat 100

	% Daily Value*
Total Fat 12g	18%
Saturated Fat	25%
Trans Fat	
Cholesterol 0mg	0%
Sodium 1010mg	42%
Total Carbohydrate 44g	15%
Dietary Fiber 4g	16%
Sugars 4g	
Protein 8g	

(v) Determine the fuel value of tristearin and hence deduce if tristearin or carbohydrate is a better source of energy. (M_r of tristearin = 890) [2]

No. of moles of tristearin in 1 g = 1/890 = 1.12 x 10^{-3} mol
• Fuel value of tristearin = 1.12 x 10^{-3} x 37760 = 42.4 kJ/g

OR

Since mass of 1 mol tristearin is 890 g
Fuel value = -37760/890 = 42.4 kJ/g

• Since more energy is produced per gram, <u>tristearin is a better source</u> of energy than carbohydrate.

(vi) During reading or watching television, the average adult uses about 7 kJ/min. How many minutes of such activity can be sustained by the energy supplied by a serving of cup noodle (considering only the total fat, total carbohydrate and total protein content)? [1]

Total energy provided by cup noodle = 12 x 42.4 + 44 x 17 + 8 x 17
= 1390 kJ

• No. of minutes that can be sustained by energy = 1390/7
= 199 min

(e) In the body, glucose is also converted to energy via alcoholic fermentation. This process has been used in making beer and the side products such as esters contribute greatly to the taste and aroma of the beer. [3]

Ethyl acetate can be formed as follows

$$CH_3CO_2H + CH_3CH_2OH \rightleftharpoons CH_3CO_2CH_2CH_3 + H_2O$$

1.51 mol of CH_3CO_2H and 1.66 mol of CH_3CH_2OH was allowed to reach equilibrium in a 100 cm^3 solution. 10 cm^3 of the equilibrium mixture was extracted and large amounts of cold water was added to quench the reaction. The mixture was then titrated with 22.40 cm^3 of 2 mol dm^{-3} NaOH.

Calculate the K_c for the formation of ethyl acetate.

$NaOH \equiv CH_3CO_2H$

No. of moles of CH_3CO_2H in 10 cm^3 = (22.40/1000) x 2
= 0.0448 mol

- **No. of moles of CH_3CO_2H in 100 cm^3 = 0.0448 x 10**
  = 0.448 mol

•

	CH_3CO_2H +	CH_3CH_2OH	$\rightleftharpoons$ $CH_3CO_2CH_2CH_3$	+ H_2O
Initial amount/mol	**1.51**	**1.66**	**0**	**0**
Change in amount/mol	**-1.06**	**-1.06**	**+1.06**	**+1.06**
Eqm amount/mol	**0.448**	**0.600**	**1.06**	**1.06**

• $K_c = \dfrac{[CH3CO2CH2CH3\ ][H2O]}{[CH3CO2H][CH3CH2OH]}$

$$= \frac{\left(\frac{1.06}{0.1}\right)\left(\frac{1.06}{0.1}\right)}{\left(\frac{0.448}{0.1}\right)\left(\frac{0.6}{0.1}\right)}$$

= 4.18

[Total: 22]

2 **(a)** In 1887, the Swedish scientist Svante Arrhenius postulated that acids and bases dissociate in water to form hydrogen ions, H^+, and hydroxide ions, OH^-, respectively.

(i) Suggest a limitation of the Arrhenius concept of acids and bases. [1]

Accept any of the answers below

- **It applies only to aqueous solutions.**
- **It does not adequately explain why such compounds as ammonia are bases.**
- **The hydrogen ion, H^+, exists as hydronium ion, H_3O^+, in water.**

A theory proposed by Danish chemist J.N. Brønsted and British chemist T.M. Lowry overcame the shortcomings of the Arrhenius theory.

(ii) Using the Brønsted–Lowry model, nitric acid can be either a Brønsted–Lowry acid or base. Write equations to show how nitric acid *reacts* as a Brønsted–Lowry acid and a Brønsted–Lowry base respectively. [2]

- **Acting as acid: $HNO_3 + NaOH \rightarrow NaNO_3 + H_2O$**
- **Acting as base: $HNO_3 + H_2SO_4 \rightarrow H_2NO_3^+ + HSO_4^-$**

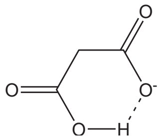
(b) The following table compares the K_a values of two three-carbon carboxylic acids.

Acid	Formula	K_{a1}	K_{a2}
Propanoic	$CH_3CH_2CO_2H$	1.35×10^{-5}	—
Malonic	$HO_2CCH_2CO_2H$	1.41×10^{-3}	2.00×10^{-6}

Suggest a reason why K_{a1} of malonic acid is higher than

(i) K_a of propanoic acid [1]

- **This is due to the <u>stabilisation of the monoanion by hydrogen bonding</u> with the unionised $-CO_2H$ group.**



(ii) K_{a2} of malonic acid [1]

- **The <u>stabilising hydrogen bonding in the monoanion of malonic acid would be destroyed</u> by the ionisation of the second $-CO_2H$ group.**

or

- **The removal of an <u>H^+ from $HO_2CCH_2CO_2^-$ that already carries a negative charge would be electrostatically unfavourable</u>.**

(iii) 25 cm^3 of 0.10 mol dm^{-3} of NaOH is gradually added to 10 cm^3 of 0.10 mol dm^{-3} malonic acid. Calculate the pH of the mixture when the following volumes of NaOH has been added. [3]

- 0 cm^3 [considering using K_{a1} of malonic acid]
- 5 cm^3
- 15 cm^3
- 25 cm^3

<u>Volume of NaOH added = 0 cm^3 (Initial pH)</u>

$K_{a1} = 1.41 \times 10^{-3}$ mol dm^{-3}

$[H^+] = \sqrt{1.41 \times 10^{-3} \times 0.10} = 0.0118$ mol dm^{-3}

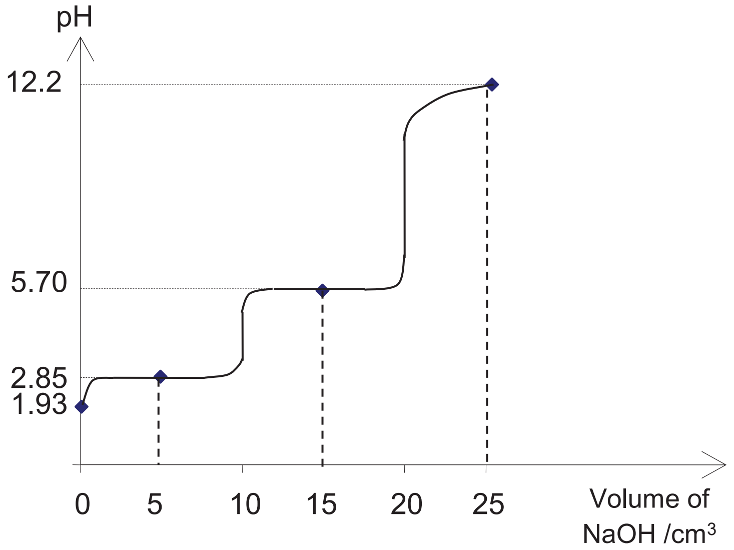
- **pH = -lg $[H^+]$ = -log 0.0118 = 1.93**

<u>Volume of NaOH added = 5 cm^3 and 15 cm^3 (Maximum buffering)</u>

- **pH at 5 cm^3 = pK_{a1} = -lg 1.41×10^{-3} = 2.85**
  pH at 15 cm^3 = pK_{a2} = -lg 2.00×10^{-6} = 5.70

Volume of NaOH added = 25 cm^3 (Excess NaOH added)
Volume of excess NaOH added = 25 -20 = 5 cm^3
No. of moles of excess NaOH = $\frac{5}{1000}$ x 0.10 = 5.00 x 10^{-4} mol
Total volume of solution = 10 + 25 = 35 cm^3
$[OH^-]$ = $\frac{5.00\times10^{-4}}{\frac{35}{1000}}$ = 0.0143 mol dm^{-3}
pOH = -log $[OH^-]$ = 1.85
- **pH = 14 – pOH = 12.2**

(iv) Using your answers in **(b)(iii)**, sketch the pH-volume added curve when 25 cm^3 of 0.10 mol dm^{-3} NaOH is gradually added to 10 cm^3 of 0.1 mol dm^{-3} malonic acid. [2]

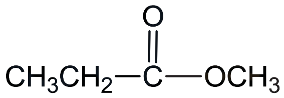


•• Correct shape of graph, correct volumes of NaOH indicated, proper labelling of axes and pH

(v) Suggest an indicator for the first equivalence point. [1]

- **Screened methyl orange or methyl orange**

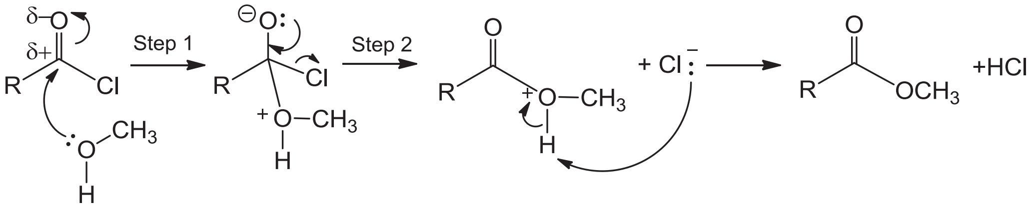
(c) Compound **A** can be directly synthesised from propanoic acid or propanoyl chloride via condensation.



$$CH_3CH_2-\overset{\overset{\large O}{||}}{C}-OCH_3$$

Compound **A**

The formation of compound **A** from propanoyl chloride occurs via the mechanism shown below.

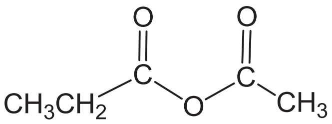


where R = CH_3CH_2—

(i) Name the reactions in step 1 and step 2. [2]

- **Step 1: Nucleophilic addition**
- **Step 2: Elimination**

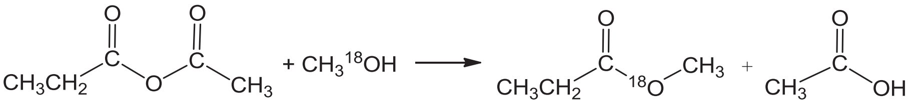
Compound **B** is a carboxylic acid anhydride that reacts similarly to an acyl chloride.



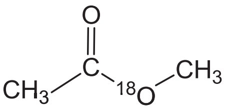
Compound **B**

(ii) Compound **B** reacts with methanol that has been labelled with ^{18}O isotope to form compound **A**. [1]

Write an equation for the reaction showing clearly the location of the $^{1(}O$ atom in the product. The formula of methanol can be written as $CH_3{}^{18}OH$.

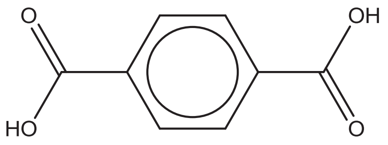
- 

(iii) Draw the structure of another neutral product formed in the reaction. [1]

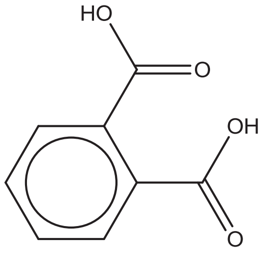
- 

[Total: 15]

3 Terephthalic acid (TPA) and phthalic acid (PA) both have the molecular formula $C_6H_4(COOH)_2$. While TPA is used principally to make clothing and plastic bottles, PA has limited commercial application. The structures of TPA and PA are shown below.



TPA



PA

Some physical properties of TPA and PA are shown in the table below:

	TPA	PA
Appearance	White crystal	White crystal
Melting point	300 °C	207 °C
Boiling point	Decomposes	Decomposes

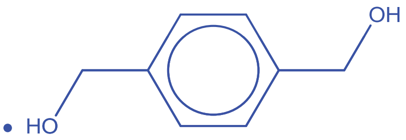
(a) Explain why TPA has a higher melting point than PA. [2]

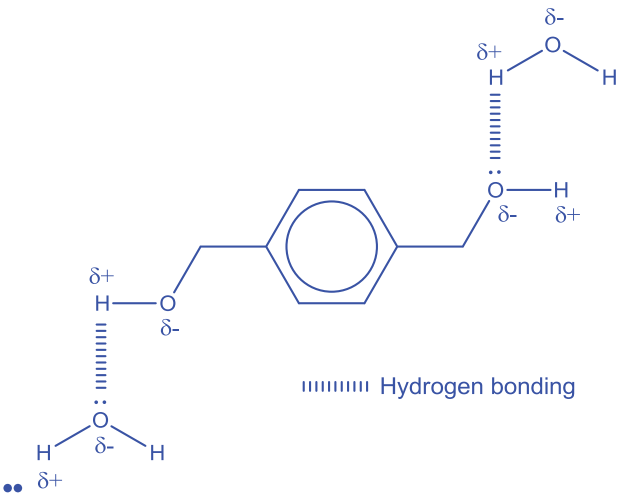
• Due to the close proximity of the 2 -COOH groups in PA, intramolecular hydrogen bonding occurs. This reduces the extent of intermolecular hydrogen bonding between PA molecules.

• In TPA, the 2 -COOH groups are further away hence only intermolecular hydrogen bonding occurs. Thus, more heat energy is needed to overcome the more extensive hydrogen bonding.

(b) **(i)** TPA can be reduced to a diol for the synthesis of a renewable polymer.

Draw the structure of this diol and illustrate with a diagram, its interaction with water. [3]

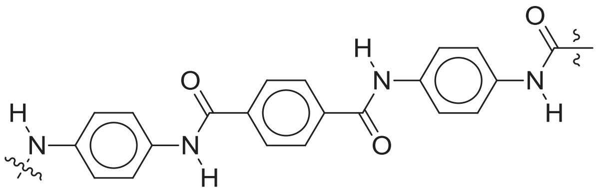




(ii) Hence, explain why the diol in **(i)** is soluble in water. [1]

• Formation of hydrogen bonds between the diol and water <u>releases sufficient energy to overcome the hydrogen bonding between diol molecules and hydrogen bonding between water molecules</u>.

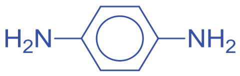
One common derivative of TPA is terephthaloyl chloride. Terephthaloyl chloride reacts with another monomer in a polymerisation reaction to form a synthetic fiber, commonly known as Kevlar®. A short chain of the Kevlar® polymer is shown below.



A strand of Kevlar® polymer

(c) **(i)** Name the type of reaction for this polymerisation reaction and suggest the structure of the other monomer to form the Kevlar® polymer. [2]

• Condensation reaction

•


(ii) In selecting a suitable material for the manufacture of bulletproof armour, it is necessary to ensure that the material does not shatter upon high impact force from a bullet.

With reference to the structures of gold and fluorite, CaF_2, explain why gold is more suitable for the lining of bulletproof armour. [2]

• When hit with a high impact force, the <u>layers of close-packed gold atoms can slide over one another without breaking the non-directional metallic bonds</u>.

However, for an ionic compound CaF_2, a • high impact force would cause layers of ions to shift and causes ions to same charge to slide next to each other, forcing the layers to come apart and shatter.

(d) **(i)** Define second ionisation energy of aluminium. [1]

• 2nd IE of aluminium is the minimum amount of energy to completely remove 1 mole of valence electrons from 1 mole of ground state gaseous Al^+ ions to form 1 mole of gaseous Al^{2+} ions.

(ii) Explain why the second ionisation energy of aluminium is higher than that of silicon. [1]

Al^+: [Ne] $3s^2$

Si^+: [Ne] $3s^2$ $3p^1$

Si has a higher nuclear charge than Al. However, • 2nd IE of Al involves the removal of 3s electron which is more strongly attracted and closer to the nucleus than the removal of 3p electron for Si. Hence, more energy is needed to remove the 3s electron.

(e) Many chemical reactions such as the reaction between peroxodisulfate and iodide ions occur very slowly at room temperature.

$$S_2O_8^{2-} + 2I^- \rightarrow 2SO_4^{2-} + I_2$$

One way to speed up rate of reaction is to use a homogeneous catalyst.

(i) Explain why the reaction between $S_2O_8^{2-}$ and I^- has a high activation energy. [1]

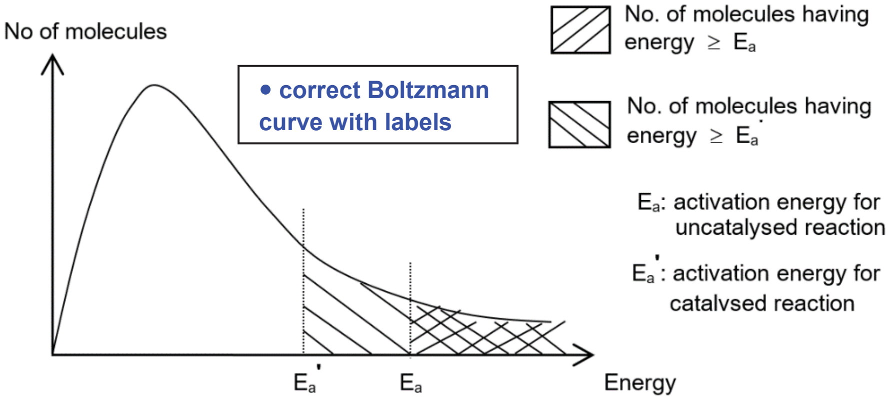
• The reaction involve the collision of 2 anions which would experience electrostatic repulsion upon contact with each other.

(ii) A solution of iron(II) ions can be used to catalyse the reaction between $S_2O_8^{2-}$ and I^-.

Using appropriate equations, outline the catalytic role of Fe^{2+} in the $S_2O_8^{2-}$ and I^- reaction. Hence, explain with the aid of a Boltzmann distribution curve, how Fe^{2+} speeds up the rate of the reaction. [5]

• $2Fe^{2+}(aq) + S_2O_8^{2-}(aq) \rightarrow 2SO_4^{2-}(aq) + 2Fe^{3+}(aq)$

• $2Fe^{3+}(aq) + 2I^-(aq) \rightarrow 2Fe^{2+}(aq) + I_2(aq)$



• correct Boltzmann curve with labels

Fe2^{+} acts as a <u>homogeneous catalyst</u> that provides an • <u>alternative pathway of lower activation energy</u> than the uncatalysed reaction, through the formation of an intermediate Fe^{3+}.

• The <u>number of reactant molecules having energy greater than or equal to the lower activation energy, E_a' increases significantly</u>.

Hence the <u>frequency of effective collisions increases</u> and the rate increases.

A kinetics study was conducted on the reaction of $S_2O_8^{2-}$ and I^- to determine the rate equation. Varying volumes of $S_2O_8^{2-}$ and I^- were added to a mixture containing sodium thiosulfate and starch indicator, followed by topping up with suitable volume of water.

As the reaction of $S_2O_8^{2-}$ and I^- proceeds, the iodine produced will be consumed by the thiosulfate. When all thiosulfate is reacted, the remaining iodine will react with the starch indicator, forming a blue-black complex. The rate of reaction is determined by the time taken for the blue-black colouration to appear.

Experiment	Volume of KI / cm^3	Volume of $Na_2S_2O_8$ / cm^3	Volume of $Na_2S_2O_3$ / cm^3	Volume of water / cm^3	Time for blue-black colour / s
1	10	20	10	10	50
2	5	20	10	15	100
3	30	10	10	0	33
4	20	40	20	20	x

(iii) Determine the order of reaction with respect to iodide and peroxodisulfate. [2]

For expt 1 to 3, total volume is kept constant, so volume of reactant ∝ concentration.

Since thiosulfate is the limiting reagent and volume is constant, relative rate ∝ 1/t, so relative rates for expt 1, 2 and 3 are 0.02, 0.01 and 0.03.

• Comparing expt 1 and 2, when conc of KI decreases by 2 times, rate decreases by 2 times → <u>1st order with respect to I^-</u>.

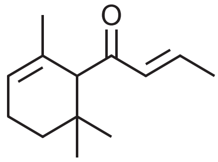
- **Comparing expt 1 and 3, when conc of KI increases by 3 times and conc of $Na_2S_2O_8$ decreases by 2 times, overall rate increases by 1.5 times (from 0.02 to 0.03) → 1st order with respect to $S_2O_8^{2-}$.**

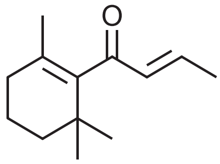
(iv) Hence, deduce the time taken for the blue-black colouration to appear for experiment 4. [1]

Since volume of all reactants double and total volume of mixture doubles, concentration of KI, $Na_2S_2O_8$ and $Na_2S_2O_3$ remain the same. Rate of reaction remains constant, so x = 50 s.

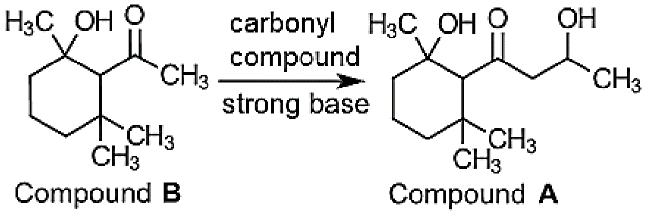
[Total: 21]

4 Rose ketones, damascenones, were discovered as active ingredients in the characteristic smell of Bulgarian rose oil. α-damascenone and β-damascenone were later discovered to give female perfumes such as *Dior's Poison* their unusual and distinctive fragrance.


α-damascenone


β-damascenone

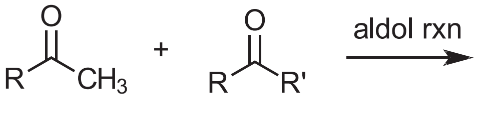
In the synthesis of damascenones in the laboratory, it was found that compound **A** is a possible precursor which could be synthesised from compound **B** via an aldol reaction.



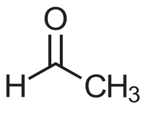
(a) State the reagent and condition required to convert compound **A** to either α-damascenone or β-damascenone. [1]

- Excess concentrated sulfuric acid, 180°C

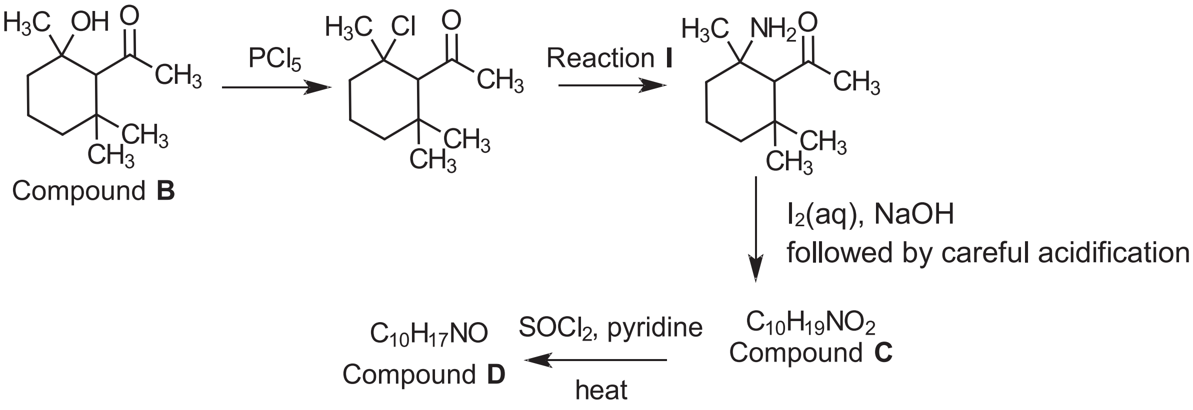
(b) With reference to an example of aldol reaction shown below, suggest an identity of the carbonyl compound reacting with compound **B** to form compound **A**.



[1]

•  ethanal

Compound **B** can undergo a series of chemical reactions as shown in the flow chart below.

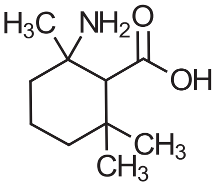


(c) State the reagents and conditions for Reaction **I**. [1]

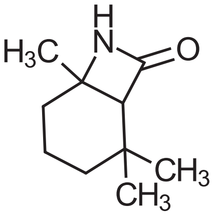
- Excess concentrated NH_3, heat in a sealed tube

(d) Draw the structural formulae of compounds **C** and **D**. [2]

- Compound **C**:

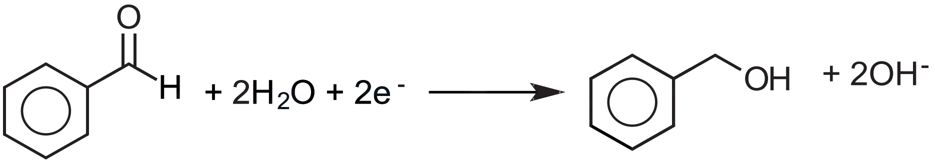


- Compound **D**:



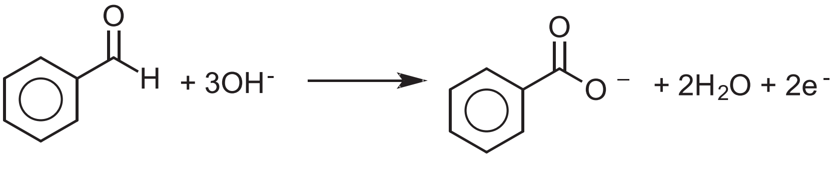
Benzaldehyde, in the presence of sodium hydroxide, undergoes the cannizzaro reaction to give benzoate ion and phenylmethanol.

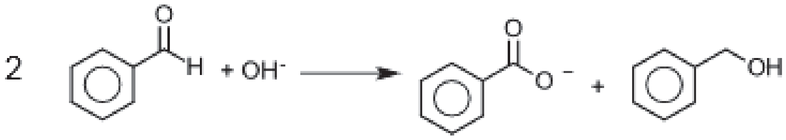
(e) The ion-electron half-equation of benzaldehyde forming phenylmethanol is shown below.



Construct the ion-electron half equations for the reaction of benzaldehyde forming benzoate ion and hence, construct an overall balanced equation for the reaction. [2]

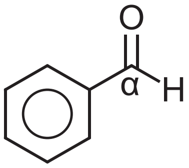
- **Oxidation:**





•Overall:

(f) Using changes in oxidation states of the carbon labelled α in benzaldehyde, state and explain the type of reaction that benzaldehyde undergoes in (e).



[1]

Disproportionation reaction.
The oxidation state of α-C in benzaldehyde changes from +1 to +3 (in benzoate ion) and –1 (in phenylmethanol) simultaneously.

[Total: 8]

5 **(a)** Organic compound **P** (M_r = 144) can be found in most leather products and is used as a mould inhibitor. P has the following composition by mass:

C: 50.04% H: 5.56% O: 44.40%

(i) Determine the molecular formula of **P**. [2]

	C	H	O
Mole ratio	**50.04/12**	**5.56/1**	**44.40/16**
	4.167	**5.56**	**2.775**
Simplest ratio	**1.50**	**2.00**	**1.00**
	3	**4**	**2**

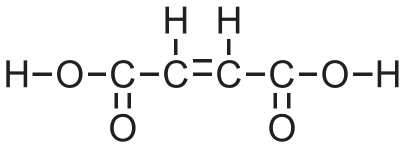
Empirical formula : $C_3H_4O_2$

$(C_3H_4O_2)_n$ = 144
36n + 4n + 32n = 144
n = 2

Molecular formula : $C_6H_8O_4$

P exhibits stereoisomerism and it decolourises aqueous bromine. On heating one mole of **P** with dilute acid, two organic products **Q**, $C_4H_4O_4$ and **R** (M_r = 32) are obtained. The mole ratio of **Q** to **R** is 1:2. Vigorous effervescence was observed when **Q** reacted completely with sodium carbonate in equimolar proportions. Vigorous effervescence was observed when **Q** reacted completely with sodium carbonate in equimolar proportions.

(ii) Draw the displayed formula of **Q**. [1]



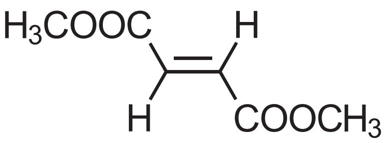
$H-O-C(=O)-C(H)=C(H)-C(=O)-O-H$

(iii) State the functional groups present in **P**. [1]

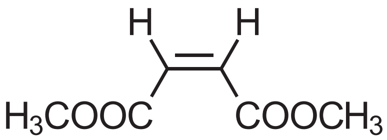
P : **alkene, ester**

(iv) Hence state the type of stereoisomerism exhibited by **P**. Draw and label the stereoisomers. [2]

Cis-trans isomerism

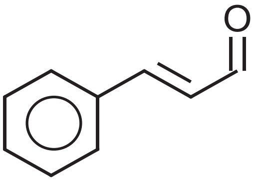


Trans



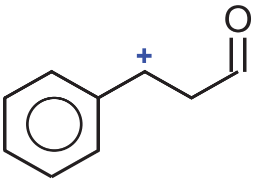
Cis

(b) Another mould inhibitor, cinnamaldehyde has the structure shown below. [3]

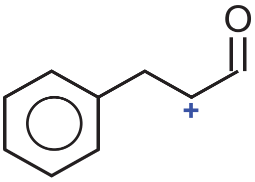


Reaction of cinnamaldehyde with HBr produces a mixture that is optically inactive. Explain this observation.

•Cinnamaldehyde undergoes electrophilic addition with HBr to form the intermediate carbocation,



or



which is planar about the C with the positive charge.
•The Br^- ion can then attack from both top and bottom of the plane with equal probability resulting in a racemic mixture.
•The resulting enantiomers rotate plane polarized light to equal extent but in opposite directions giving rise to an optically inactive mixture.

[Total: 9]

TEMASEK
JUNIOR COLLEGE

CHEMISTRY **9729/03**
Paper 3 Free Response **13th September 2017**
2 hours

Candidates answer on separate paper.

Additional Materials:	Answer Paper Graph Paper Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your Centre number, index number, name and civics group on all the work you hand in.
Write in dark blue or black pen.
You may use a HB pencil for any diagrams or graphs.
Do not use staples, paper clips, glue or correction fluid.

Section A
Answer **all** questions.

Section B
Answer **one** question.

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

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

This document consists of **14** printed pages and **2** blank pages.

Section A

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

1 Calcium carbonate is found in rocks and is the main component of pearls and the shells of eggs, snails and many marine organisms. It is the active ingredient in agricultural lime and is also medicinally used as a calcium supplement or as an antacid.

(a) **(i)** Describe and explain the trend in thermal stability of the Group 2 carbonates. [3]

- **Down the group, charge of the cation remains constant but ionic radius increases. Hence charge density of the cation decreases.**
- **(CO_3^{2-} ion is a large anion so is easily polarised but) Polarising power of cation decreases resulting in less distortion of the electron cloud of CO_3^{2-} ion, weakening the C-O covalent bond less.**
- **More energy needed to decompose the carbonate, hence down the Group, carbonates become more stable to heat, therefore decomposition temperature increases and thermal stability increases down the group.**

(ii) Determine the minimum temperature for the spontaneous decomposition of calcium carbonate, given that $\Delta H = +178.5 \text{ kJ mol}^{-1}$ and $\Delta S = +163.2 \text{ J K}^{-1} \text{ mol}^{-1}$. [2]

$\Delta G = \Delta H - T\Delta S$
- **$\Delta H - T\Delta S < 0$**

$T > \Delta H / \Delta S$

$T > 178.5 \times 1000 / 163.2$
- **$T > 1090$ K (3 sig fig)**

(b) Limestone is predominantly calcium carbonate, a slightly soluble salt with a K_{sp} value of 3.3×10^{-9}. This rocky material began accumulating in the Earth over 400 million years ago. The Howe Caverns in the USA is a relatively young limestone cave which began forming 800 000 years ago.

(i) Determine the solubility of calcium carbonate. [1]

Let solubility of $CaCO_3$ be x.

$CaCO_3 \rightleftharpoons Ca^{2+} + CO_3^{2-}$

$K_{sp} = x^2$
- **$x = 5.74 \times 10^{-5} \text{ mol dm}^{-3}$**

The principal cave-forming process is explained below.

Gaseous CO_2 is in equilibrium with aqueous CO_2 in surface water.

$CO_2(g) \rightleftharpoons CO_2(aq)$ ----- **(1)**

As surface water trickles through cracks in the ground, it meets soil-trapped air which contains higher levels of CO_2 (P_{CO_2} = 100 Pa) and hence $[CO_2(aq)]$ increases.

When this CO_2-rich water contacts limestone, more $CaCO_3$ dissolves. As a result, more rock is carved out, more water flows in and over centuries a cave is formed.

$CaCO_3(s) + CO_2(aq) + H_2O(l) \rightleftharpoons Ca^{2+}(aq) + 2HCO_3^-(aq)$ ----- **(2)**

(ii) Show that the atmospheric partial pressure of CO_2, P_{CO_2}, is 40.5 Pa. You may assume air contains 0.04% by volume CO_2.

[1]

volume of gas α no of mole of gas (Avogadro's Law)

- **P_{CO_2} = 0.04/100 x 101325 = 40.5 Pa**

(iii) State and explain whether CO_2 in the atmosphere or soil-trapped air is behaving less ideally.

[2]

- **CO_2 in soil-trapped air will behave less ideally.**
- **As soil-trapped air will be under higher pressure the total volume occupied by the gas is reduced, the volume of the gas molecules becomes more significant compared with the total volume of the gas.**

Stalactites and stalagmites are rock formations that hang from ceiling of caves and rise from the floor of caves, respectively. They are formed when surface water seeps through rock and drips from the ceiling of a cave.

(iv) With reference to equilibria **(1)** and **(2)**, explain the formation of stalactites and stalagmites in limestone caves.

[3]

- **When the surface water drips from the ceiling, $CO_2(g)$ escape as it comes into contact with the atmosphere, which has a lower P_{CO_2}.**
- **By Le Chatelier's principle, equilibrium (1) shift to the left causing $[CO_2(aq)]$ to decrease. Equilibrium (2) will be be shifted to the left to counter the decrease in $[CO_2(aq)]$**
- **$CaCO_3$ will then be precipitated out on the ceiling or on the floor resulting in the formation of stalactites and stalagmites.**

(v) Suggest a reason why some of these rock formations can appear reddish brown or bluish green.

[1]

- **It is likely due to the presence of transition metal ions like Fe^{3+} and Cu^{2+}.**

Lakes bounded by limestone-rich soil are less likely to be impacted by acid rain. Limestone dissolves sufficiently in lake water to form a buffer system capable of mitigating the effect of acid rain.

(vi) Suggest, with the aid of an equation, how the buffer system will maintain the pH of the lake water.

[1]

- **$CO_3^{2-}(aq) + H^+(aq) \rightarrow HCO_3^-(aq)$**

As the carbonate ions neutralise the H^+ from acid rain, there is negligible change in pH.

Acidification due to acid rain of lakes and rivers poses a serious environmental problem. The concentration of carbonate ions in these water is small due to the high acidity, hence affecting the survivability of some marine organisms.

(vii) Suggest a reason why the survivability of some marine organisms is affected. [1]

- **Carbonate ions, together with calcium ions, are the building blocks of their shells and skeletons.**

(c) Emission from power stations using coal, which contains sulfur, as fuel has significant environmental consequences. One of the components is sulfur dioxide, which can be oxidised by atmospheric hydroxyl radical to sulfur trioxide.

(i) Write a balanced equation to explain how sulfur trioxide contribute to acid rain. [1]

- $SO_3(g) + H_2O(l) \rightarrow H_2SO_4(aq)$

Current power plants are fitted with flue-gas desulfurization devices. These devices heat powdered limestone in air to remove sulfur dioxide from the gases produced during coal combustion. One of the products is calcium sulfate.

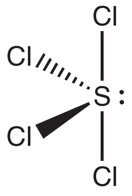
(ii) Write a balanced equation for the reaction that had taken place. [1]

- $CaCO_3(s) + \frac{1}{2}O_2(g) + SO_2(g) \rightarrow CaSO_4(s) + CO_2(g)$

(d) Sulfur and aluminium can both react with chlorine.

Aluminium chloride is a white solid that sublimes while sulfur tetrachloride, SCl_4, is an unstable pale yellow solid. Both react with water but formed different products.

(i) Predict the shape of sulfur tetrachloride, using a diagram where appropriate. Suggest the bond angle(s) in the molecule. [2]

- **See-saw, < 90° and < 120°**
- 

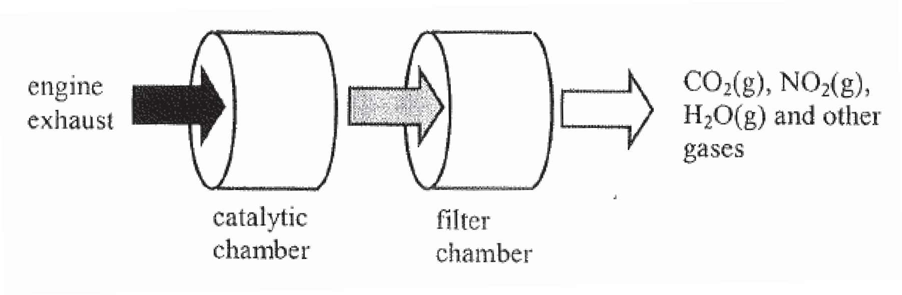
(ii) Describe and explain, with the aid of equations, the reaction of aluminium chloride with water. Suggest the pH of the resulting solution. [3]

- **Hydration:** $AlCl_3(s) + 6H_2O(l) \rightarrow [Al(H_2O)_6]^{3+}(aq) + 3Cl^-(aq)$
  Hydrolysis: $[Al(H_2O)_6]^{3+}(aq) \rightleftharpoons [Al(H_2O)_5OH]^{2+}(aq) + H^+(aq)$
- **Hydrolysis is possible because Al^{3+} has a high charge density (small in size and highly charged) hence a high polarising power. It draws electrons away from its surrounding water molecules and weakens the O-H bond. It is easier for a H^+ ion to leave the water molecule.**
- **pH = 3**

[Total: 22]

2 The exhaust of heavy-duty diesel engines contains a significant amount of particulate matter (PM) and harmful gases such as nitrogen oxides. A Continuous Regenerating Trap (CRT) is a device which is designed for use in exhaust systems of buses and lorries running on diesel to remove PM and some of the harmful gases. A second catalytic converter is usually installed to remove the oxides of nitrogen.

The diagram below shows how a CRT works:



(a) **(i)** Explain, with the aid of equations, why oxides of nitrogen are present in the engine exhaust.

[2]

- **Under the high temperature condition of the internal combustion engine, atmospheric nitrogen reacts with oxygen to from oxides of nitrogen.**
- **$N_2(g) + O_2(g) \rightarrow 2NO(g)$**
  $2NO(g) + O_2(g) \rightarrow 2NO_2(g)$

(ii) State one harmful effect of nitrogen oxides on the environment.

[1]

- **Acid rain OR photochemical smog**

(iii) State two harmful gases that are also present in the engine exhaust. Use chemical equations to show how these two gases can be removed in the catalytic chamber of a CRT.

[2]

- **CO and hydrocarbons**
- **$CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(g)$**
  $C_xH_y(g) + (x + y/4)\ O_2(g) \rightarrow xCO_2(g) + y/2\ H_2O(l)$

A CRT is an automated, self-regenerating device which does not require cleaning of the filter. In a CRT, the carbon, which is the most abundant element in PM, is trapped onto the filter and is then removed by one of the harmful gases.

(iv) Explain, with the aid of an equation, how the carbon trapped on the filter of a CRT can be removed. Hence explain why the filter need not be cleaned.

[2]

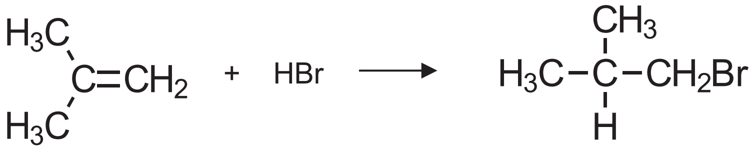
- **$C(s) + 2NO_2(g) \rightarrow CO_2(g) + 2NO(g)$ OR**
  $C(s) + 2NO(g) \rightarrow CO_2(g) + N_2(g)$ OR
  $2C(s) + 2NO_2(g) \rightarrow 2CO_2(g) + N_2(g)$
- **The carbon on the filter is oxidised by the oxides of nitrogen to form gaseous CO_2 and thus the filter need not be cleaned.**

(v) Suggest why buses and lorries equipped with CRT should not run on diesel with high sulfur content.

[1]

- **The sulfur will poison the catalyst rendering it ineffective.**

(b) In the reaction of HBr to alkenes such as methylpropene, scientists discovered that impurities such as peroxides, R-O-O-R, greatly increased the amount of anti-Markovnikov addition product as shown below.

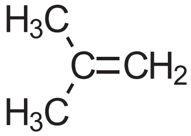


methylpropene 1-bromo-2-methylpropane

The above reaction is explained by the 4 step free radical addition mechanism as described below.

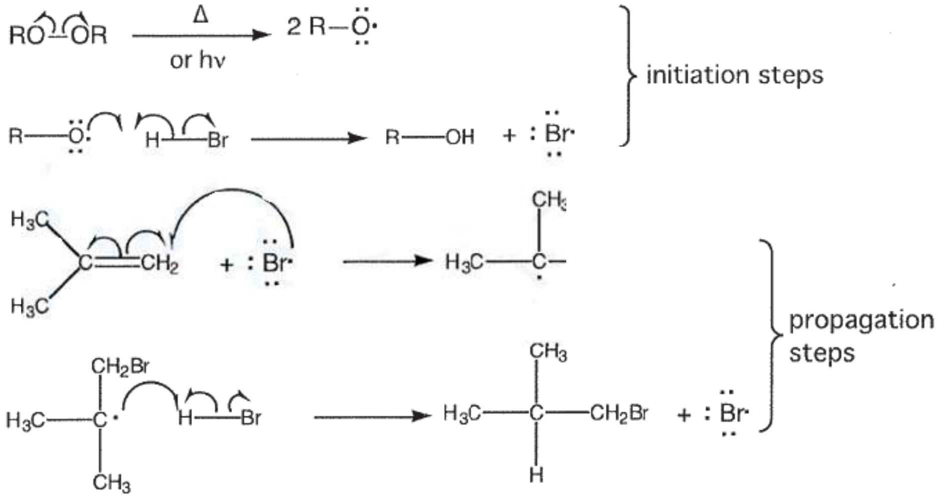
Step 1: The reaction is initiated by the formation of RO• radicals.
Step 2: This is followed by the reaction of the RO• radical with HBr to give bromine radical.
Step 3: The bromine radical adds to the alkene via the cleaving of the pi bond.
Step 4: The radical obtained from Step 3 reacts with HBr to form the anti-Markovnikov product.

(i) Use the information given above to draw out the full mechanism for the reaction. You are advised to use structural formulae for all species, such as



for methylpropene, so that it is clear which bonds are broken and which are formed. Indicate any unpaired electrons by a dot and use ↷ to represent movement of an electron.

[4]

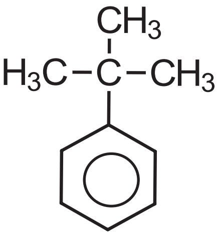


(ii) Unlike HBr, HC*l* does not undergo free radical addition to alkenes, even in the presence of peroxides. Explain this observation by quoting relevant values from the Data Booklet to substantiate your answer.

[2]

- **B.E H-Cl = 431 kJ mol^{-1}**
  B.E H-Br = 366 kJ mol^{-1}
- **The H—Cl bond is a stronger bond with better orbital overlap between H and Cl atoms. More energy is required to break the bond compared to HBr as shown by the bond energy values.**

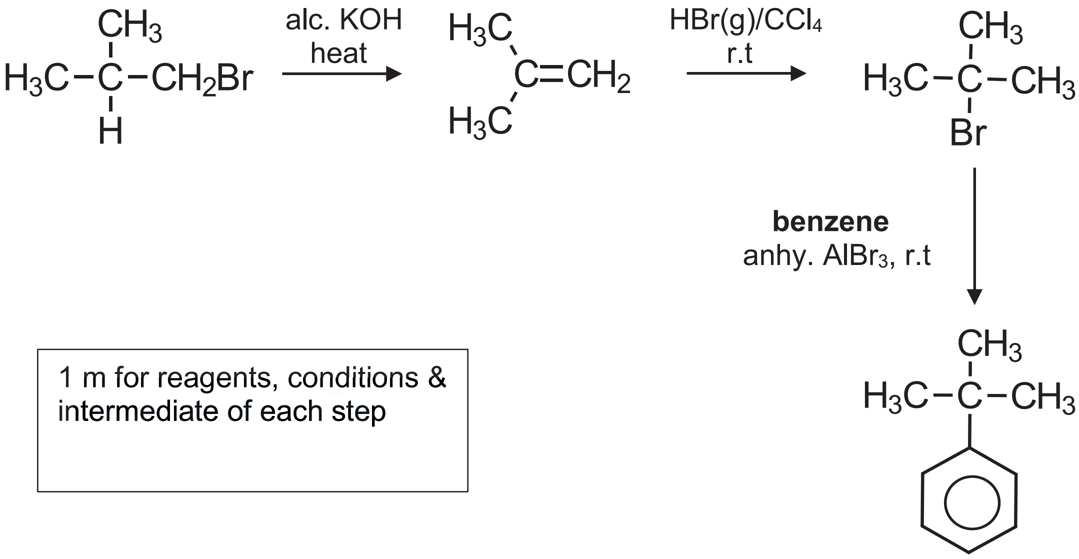
Tertiary butylbenzene is a colourless liquid widely used as a solvent for organic synthesis and also as a polymer linking agent.



t-butylbenzene

(iii) Using 1-bromo-2-methylpropane as the starting material, suggest a 3-stage synthesis of t-butylbenzene. You should state the reagents and conditions needed for each step, and show clearly the structure of any intermediate compounds.

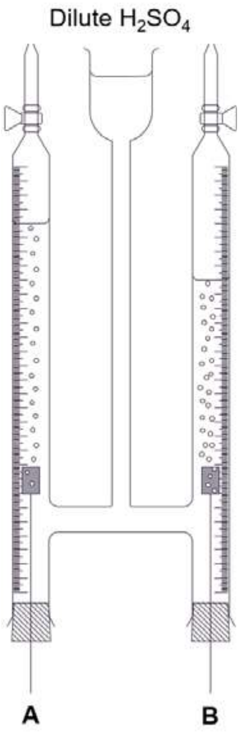
[3]



1 m for reagents, conditions & intermediate of each step

[Total: 17]

3 The following setup was carried out for the electrolysis of dilute sulfuric acid under room conditions, using platinum electrodes. A steady current of 2 A was applied for 1 minute through the circuit. The ratio of volume of gas produced at electrodes **A** and **B** is 1:2.



(a) **(i)** Write the half-equations for the reactions occurring at **A** and **B**. Label the polarity of each electrode clearly.

[2]

• Anode is A: $2H_2O \rightarrow O_2 + 4H^+ + 4e$ Polarity of electrode: +
• Cathode is B: $2H^+ + 2e \rightarrow H_2$ Polarity of electrode: -

(ii) Calculate the volume of gas produced at **A** after 1 minute.

[1]

Number of moles of electrons = It/F = 2x60/96500 = 1.24×10^{-3} mol
O_2 gas is produced at A. Since 4e ≡ O_2, amount of O_2 gas produced

= $1.24 \times 10^{-3} / 4 = 3.11 \times 10^{-4}$ mol
• Volume of O_2 gas = $3.11 \times 10^{-4} \times 24000 = 7.46$ cm^3

(iii) A student repeated the same experiment above, but using a copper electrode at **A** this time.

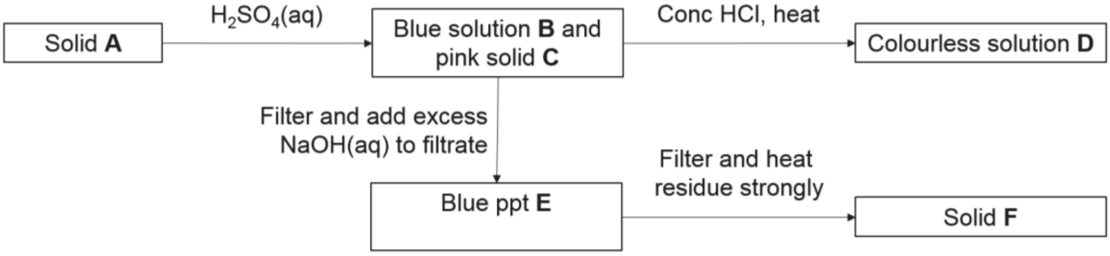
Suggest the volume of gas produced at **A** and explain your answer.

[2]

• Volume of gas at A = <u>0 cm^3</u>.
$E^{\ominus}_{Cu^{2+}/Cu} = +0.34$ V

$E^{\ominus}_{O2/H2O} = +1.23$ V
Since the • <u>standard reduction potential of Cu^{2+}/Cu is less positive than O_2/H_2O</u>, the copper electrode would be <u>preferentially oxidised</u> instead of water. Hence, no gas is produced at A.

(b) Solid **A,** which is formed when a copper complex reacts with an aldehyde, is subjected to the following reactions.



Suggest the identities of **A** to **F**. [6]

A: Cu_2O
B: $[Cu(H_2O)_6{}^{2+}]$(aq)
C: Cu
D: $[CuCl_2]^-$
E: $Cu(OH)_2$(s) OR $Cu(OH_2)(H_2O)_4$
F: CuO

(c) Compounds **V** and **W** are gaseous hydrocarbons of empirical formulae CH_2 and CH_3 respectively. When 10 cm^3 of **V** and 10 cm^3 of **W** were completely burnt in 150 cm^3 of oxygen, the total gaseous volume decreased by 55 cm^3. After shaking the residual gases with aqueous sodium hydroxide, the total gaseous volume decreased by another 60 cm^3. When compound **V** is heated with acidified potassium manganate(VII), compound **X**, C_3H_6O, is formed.

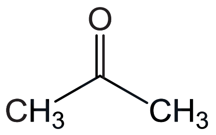
(i) Suggest the molecular formula of **W**. [1]

- **C_2H_6**

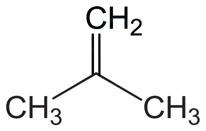
(ii) Suggest the structures of compounds **V** and **X**. Explain your answers. [4]

- **Since the total gaseous volume decreased by 60 cm^3 when shaken with NaOH, the volume of CO_2(g) is 60 cm^3. Compounds V and W contain a total of 6 carbon atoms.**
- **Since W is ethane, CH_3CH_3, V contains 4 carbons and is an alkene that undergoes strong oxidation with $KMnO_4$ to form X (C_3H_6O) and CO_2.**

- **X is**



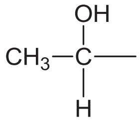
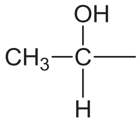
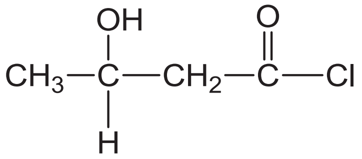
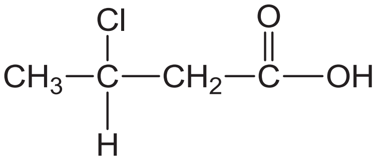
- **V is**



(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 warmed 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 HCl is formed.**
- **Compound Z is a carboxylic acid as it gives an acidic solution upon partial dissociation of H$^+$ ions in water.**
- **Since white precipitate of AgCl is formed when Y is added to aqueous silver nitrate, Y is an acyl chloride.**
- **When warmed with alkaline medium, chloroalkane Z undergoes nucleophilic substitution to form**  $\mathrm{CH_3-\overset{OH}{\underset{H}{C}}-}$ **.**
- **Y undergoes oxidation with alkaline aqueous iodine and contains**  $\mathrm{CH_3-\overset{OH}{\underset{H}{C}}-}$ **.**
- **Y is**  $\mathrm{CH_3-\overset{OH}{\underset{H}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-Cl}$
- **Z is**  $\mathrm{CH_3-\overset{Cl}{\underset{H}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-OH}$

[7 marking points, maximum 5 marks]

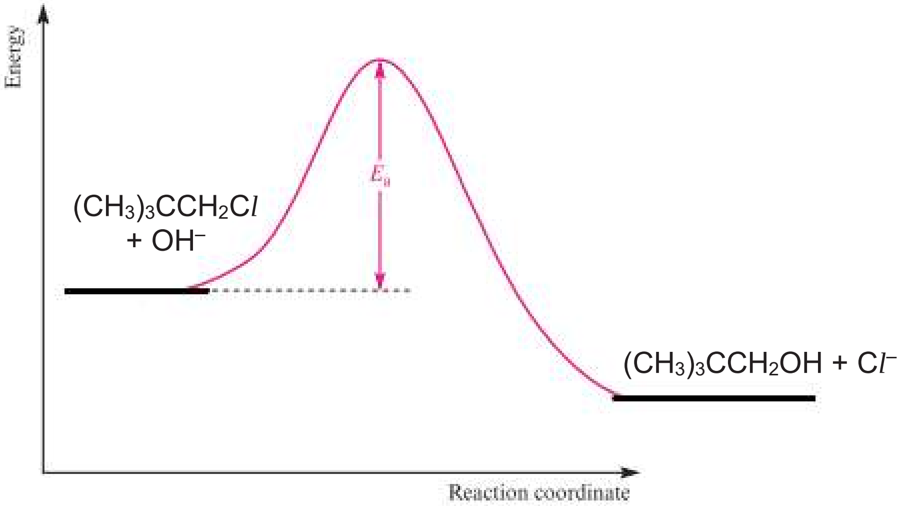
[Total: 21]

Section B

Answer **one** question from this section.

4 **(a)** Halogenoalkanes commonly undergo nucleophilic substitution reactions. On the basis of experimental observations developed over a 70-year period, two mechanisms for nucleophilic substitutions have been proposed.

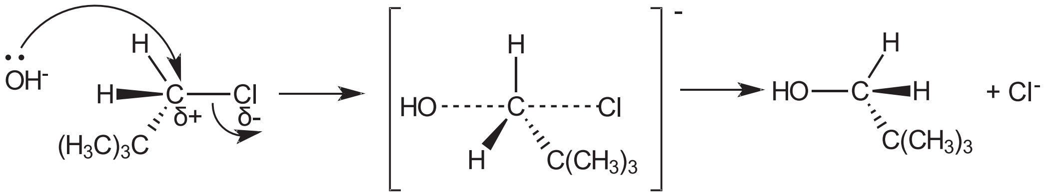
In the kinetics study of the hydrolysis of 1-chloro-2,2-dimethylpropane, $(CH_3)_3CCH_2Cl$, the energy-profile diagram of the reaction was proposed below:



(i) With reference to the energy profile diagram, describe the mechanism of the reaction between 1-chloro-2,2-dimethylpropane and hydroxide ions. The mechanism should include curly arrows to show the movement of electrons and all charges.

[2]

Energy profile diagram indicates S_N2 mechanism



•1m – shows inversion of configuration & correct transition state drawn
•1m – arrows, partial charges

(ii) A student decided to verify the mechanism deduced in **(a)(i)** for the hydrolysis reaction of 1-chloro-2,2-dimethylpropane.

The following results were obtained and you may consider the overall [NaOH(aq)] to remain virtually constant at 0.10 mol dm^{-3} throughout the experiment.

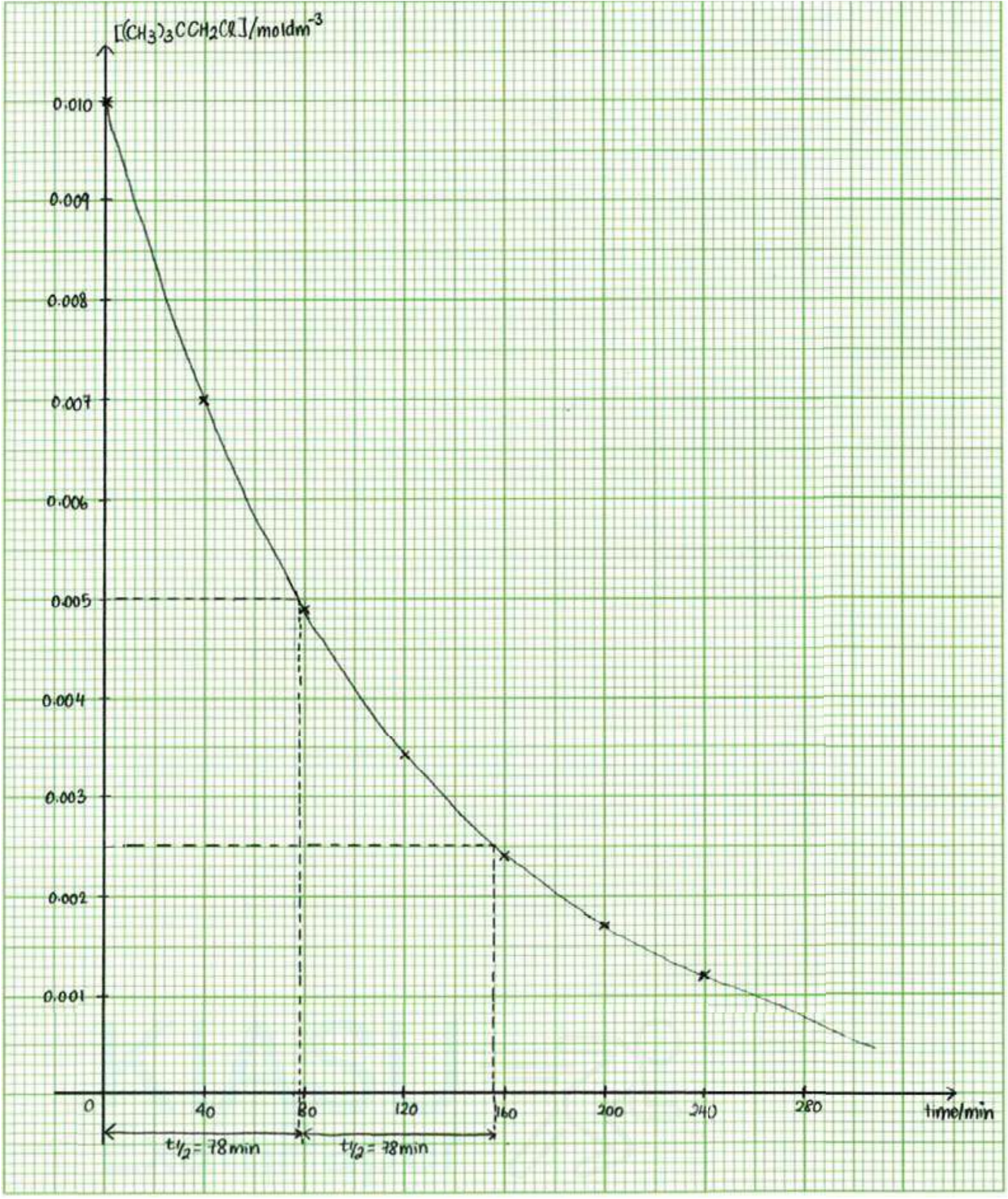
Time/ min	Experiment 1
	$[(CH_3)_3CCH_2Cl]$/ mol dm^{-3}
0	0.0100
40	0.0070
80	0.0049
120	0.0034

160	0.0024
200	0.0017
240	0.0012

Using appropriate axes, plot a graph of [$(CH_3)_3CCH_2Cl$] against time and use your graphs to deduce the order with respect to the concentration of the 1-chloro-2,2-dimethylpropane, showing your working clearly.

[4]

•appropriate axes
•smooth curve drawn with accurate points plotted



•1st t ½ = 78 min; 2nd t ½ = 78 min (with workings line drawn on graph)
•Since <u>t ½ is a constant</u>, order of reaction is <u>1st order with respect to [$(CH_3)_3CCH_2Cl$].</u>

(iii) Given the general rate equation as

$$\text{Rate} = k'\,[(CH_3)_3CCH_2Cl]^x$$

Using your answer in **(a)(ii),** calculate the rate constant k', stating its units.

[2]

$t_{1/2} = \frac{ln2}{k'}$ ●$k' = \frac{ln2}{t_{1/2}} = \frac{ln2}{78} = 0.00889\ min^{-1}$ (●correct units)

(iv) When the experiment was repeated at the same temperature, the concentration of NaOH was doubled and the concentration of 1-chloro-2,2-dimethylpropane was monitored against time. The same graph was obtained as Experiment 1.

Deduce the order of reaction with respect to the concentration of hydroxide ion.

[1]

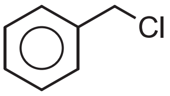
●When [OH⁻] doubles, the same graph was plotted means that the initial rate remains the same.
Since initial rate remains the same when concentration doubles, order of reaction is 0th order with respect to [OH⁻].

(v) Using your answers in **(a)(ii)** and **(a)(iv)**, explain if the student should agree with the proposed mechanism for the reaction in **(a)(i)**.

[1]

The student ●should not agree with the proposed mechanism as the rate equation is rate = k [$(CH_3)_3CCH_2Cl$], and thus only 1 molecule of $(CH_3)_3CCH_2Cl$ reacts in the rate-determining step.

(b) (Chloromethyl)benzene is a primary alkyl halide.



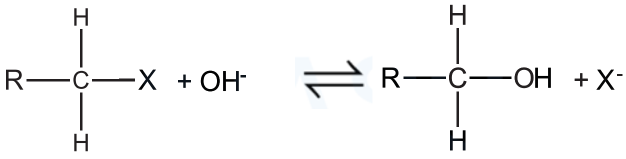
(Chloromethyl)benzene

Suggest a reason why (chloromethyl)benzene undergoes substitution via S_N1 mechanism.

[1]

● (chloromethyl)benzene favours substitution via S_N1 due to resonance stabilisation of the benzyl carbocation.

(c) Different alkyl halides would have different reactivity towards nucleophilic substitution.



$$RCH_2X + OH^- \rightleftharpoons RCH_2OH + X^-$$

where X⁻ is a leaving group

The difference in reactivity is dependent on the stability of the leaving group. The more stable the halide ion, the better the leaving group. The pK_a values of HX is given below.

Halide (X)	pK_a (HX)
F	+3
Cl	–7
Br	–9
I	–10

[Turn Over

(i) Suggest the relationship between pK_a of HX and the stability of the halide ion. [1]

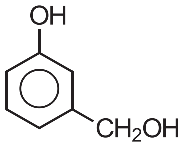
●The smaller the pK_a of HX, the more stable the halide ion.

(ii) Iodomethane and chloromethane are separately reacted with hydroxide ions. Using your answer in **(c)(i)**, explain why iodomethane reacts at a faster rate. [1]

As the pK_a of HI is the smallest, I^- is the most stable halide ion, and thus ●a better leaving group than Cl^-. Thus, iodomethane is more susceptible towards nucleophilic substitution.

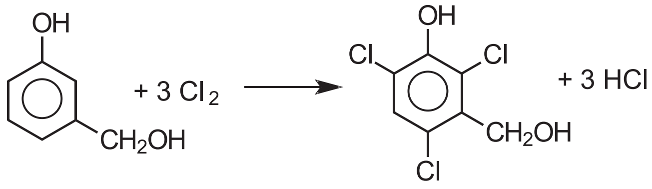
(d) Chlorinated phenols have gained an increasing use as fungicides, herbicides, insecticides, and precursors in the synthesis of other pesticides since the early 1930s.

It can be easily synthesised from its precursor **A** using aqueous chlorine.



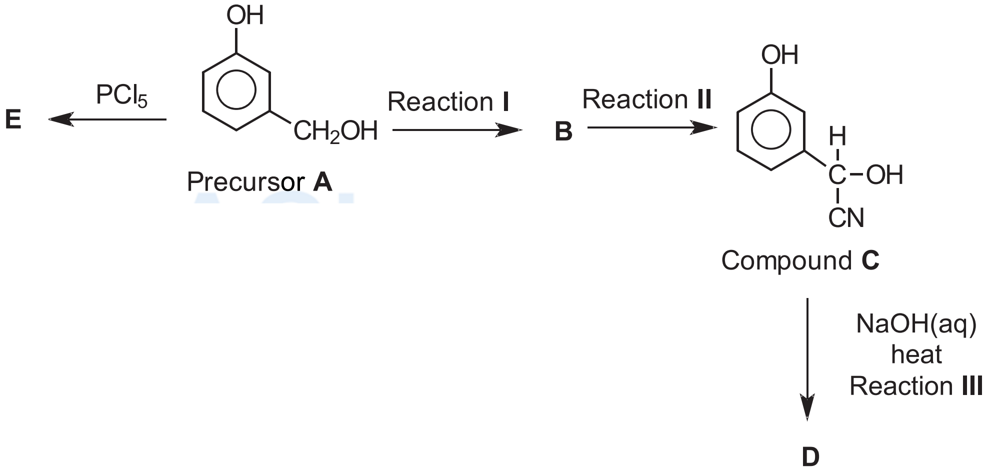
Precursor **A**

(i) Write a balanced equation for the reaction between precursor **A** and aqueous chlorine. [1]



●

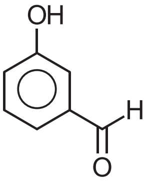
(ii) Precursor **A** undergoes a series of reactions shown in the reaction scheme below.



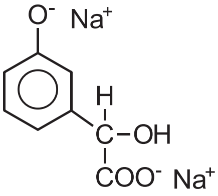
State the reagent and condition for Reaction **I** and **II**, and hence draw the structures of **B**, **D** and **E**. [5]

•Reaction I: acidified $K_2Cr_2O_7$, warm with immediate distillation
•Reaction II: HCN, in small amount of KCN, 10 – 20 °C

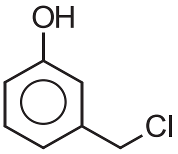
• B:



• D:



• E:



(iii) Reaction **III** can be used as a distinguishing test between compound **C** and precursor **A**. State the observation for this distinguishing test.

[1]

•NH_3 gas will be evolved for compound C. No gas evolved for precursor A.

[Total: 20]

5 **(a)** Describe and explain the relative thermal stabilities of the hydrogen halides down the group.

[2]

• Thermal stability decreases down the group: HF > HC*l* > HBr > HI
• This is because the atomic radius increases down the group, resulting in decreasing degree of effective overlap of orbitals and decreasing covalent bond strength and hence bond energy of HX decreases down the group.

(b) Potassium chlorochromate (VI), $KCrClO_3$, was made using concentrated hydrochloric acid and potassium dichromate(VI).

$$K_2Cr_2O_7 + 2HCl \rightarrow 2KCrClO_3 + H_2O$$

Chlorine gas may be evolved as a side product. It was found that chlorine gas will not be produced if dilute hydrochloric acid was used instead.

Use data from the *Data Booklet* to explain why this is so.

[2]

$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightleftharpoons 2Cr^{3+} + 7H_2O$ **E° = +1.33 V**
$Cl_2 + 2e^- \rightleftharpoons 2Cl^-$ **E° = +1.36 V**
• E°_{cell} = +1.33 – (+1.36) = - 0.03 V
Since E°_{cell} < 0, the reaction is not spontaneous and Cl^- will not be oxidised to form chlorine gas when dilute hydrochloric acid was used.
• When concentrated hydrochloric acid is used, [Cl^-] increases, the position of the above equilibrium shifts to the left by Le Chatelier's Principle and favours oxidation.
$E_{Cl2/Cl-}$ becomes less positive and E_{cell} becomes positive. Hence, the reaction is spontaneous, producing chlorine gas.

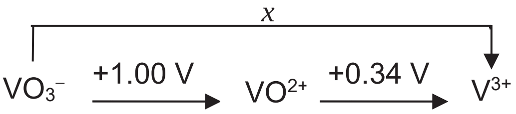
(c) **(i)** Vanadium is a transition element that exhibits variable oxidation states.

Explain why vanadium has the ability to form compounds with different oxidation states.

[1]

• Transition elements can exhibit a variety of oxidation states due to close proximity in energy of the 3d and 4s electrons. Thus both 3d and 4s electrons are available for bond formation (both ionic and covalent).

(ii) A Latimer diagram shown below summarises the standard electrode potential data of vanadium complexes in acidic medium.



x, the standard electrode potential of converting VO_3^- to V^{3+}, is **not** the summation of +1.00 V and +0.34 V. It can be calculated from $\Delta G^{\ominus}$.

Write a half-equation for the conversion of VO_3^- to V^{3+}.

[1]

• $VO_3^- + 6H^+ + 2e^- \rightarrow V^{3+} + 3H_2O$

(iii) Calculate x, given that $\Delta G^{\ominus}$ for the conversion of VO_3^- to V^{3+} is -129000 J mol^{-1}.

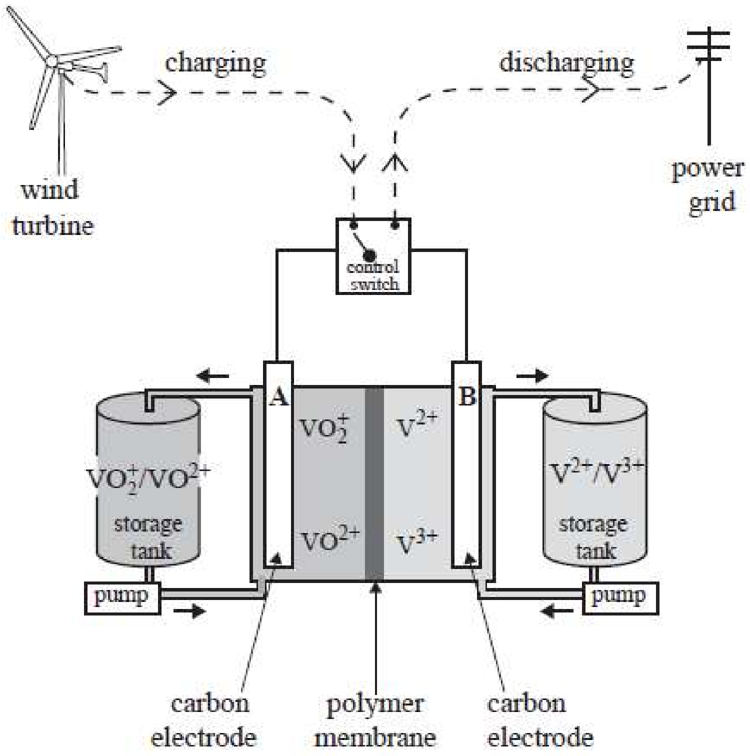
[1]

$\Delta G^{\ominus} = -nFE^{\ominus}$

• $E^{\ominus} = (-129 \times 10^3) / -(2 \times 96500) = +0.67$ V

(d) A vanadium redox battery is used to store electrical energy generated at a wind farm in Tasmania. The battery supplies electricity to the power grid as required through a control switch.

The diagram below shows the structure of a cell in a vanadium redox battery. The reactants are dissolved in an acidic solution, stored in large tanks and pumped through the cell. The cell is recharged using electricity generated by the wind turbines. A polymer membrane allows the movement of particular ions.



(i) State the polarity of electrode **A** when the cell is **discharging.** Explain your answer. [2]

$VO_2^+(aq) + 2H^+(aq) + e^- \rightleftharpoons VO^{2+}(aq) + H_2O(l)$ $\quad E^\ominus = +1.00$ V
$V^{3+}(aq) + e^- \rightleftharpoons V^{2+}(aq)$ $\quad E^\ominus = -0.26$ V
• When the cell is discharging, it is a galvanic cell. Since $E^\ominus$ VO_2^+/VO^{2+} is more positive than $E^\ominus$ V^{3+}/V^{2+}, VO_2^+ will undergo reduction.
• Therefore, electrode A is the cathode and is positive.

(ii) Write an equation for the reaction that occurs when the cell is being **recharged**. [1]

• $VO^{2+} + H_2O + V^{3+} \rightarrow VO_2^+ + V^{2+} + 2H^+$

(e) Nitrogen containing compounds such as ammonia and amines are common ligands found in transition metal complexes.

(i) Explain the relative basicities of ammonia, methylamine, dimethylamine and trimethylamine in the gaseous phase. [2]

● Basicity increases in the order of ammonia, methylamine, dimethylamine and trimethylamine.
●The greater the number of electron donating methyl group, the more available the lone pair on N for dative bonding with a proton.

(ii) Amides, such as ethanamide, are nitrogen containing compounds that do not exhibit basic properties like amines.

Explain why amides are neutral. [1]

- **Amides are neutral because the <u>lone pair of electrons on nitrogen atom</u> in amides is in a *p* orbital, and can <u>overlap with the π orbital of the adjacent carbonyl group</u>. Hence, <u>not available for donation to a proton</u>.**

(f) In 1893, Alfred Werner proposed the octahedral configuration of transition metal complexes. He was able to interpret isomeric properties using extensive studies on the octahedral cobalt complexes.

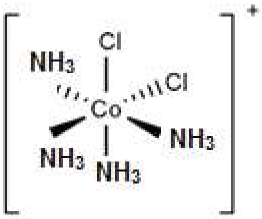
The following table gave information of two cobalt complexes **A** and **B** which are isomers of each other.

	Complex	Colour of solid	Does the complex have a dipole moment
A	$CoCl_2(NH_3)_4^+$	Violet	Yes
B	$CoCl_2(NH_3)_4^+$	Green	No

(i) Suggest structures for the cobalt complexes **A** and **B**.

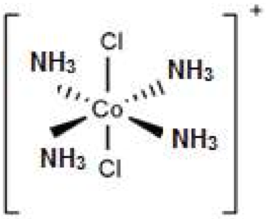
[2]

A



cis isomer

B

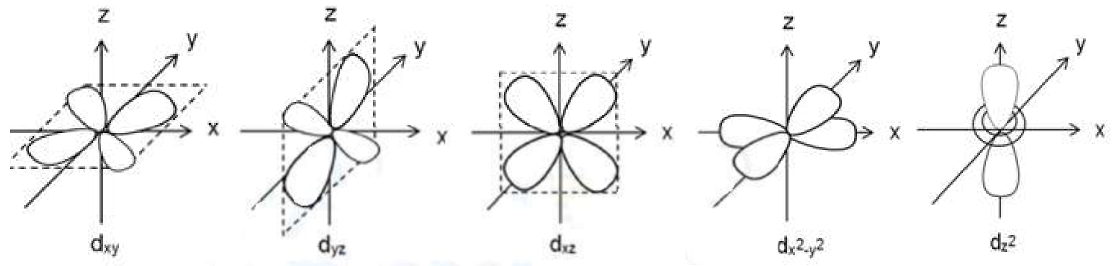


trans isomer hence no net dipole

(ii) The crystal field theory can be used to explain colour of transition metal complexes.

Describe, using the shape and orientation of the d orbitals, the splitting of degenerate d orbitals into two energy levels in octahedral complexes.

[3]

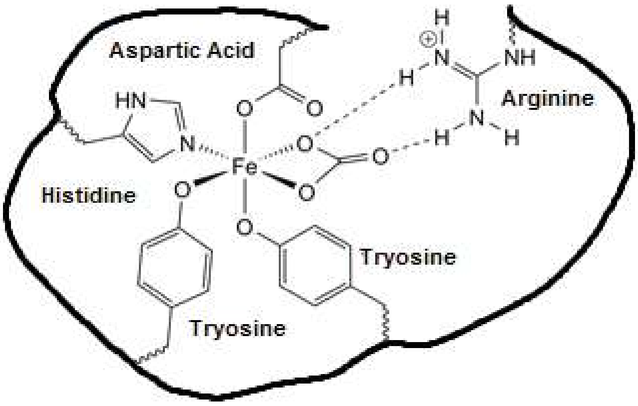


●

- **<u>d_{z^2} and $d_{x^2-y^2}$ orbitals experience stronger electronic repulsion with the negative charges as the orbital lobes</u> are in the region of the negative charges. Due to these stronger electronic repulsion, the d_{z^2} and $d_{x^2-y^2}$ orbitals are at a <u>higher energy level</u> and the degenerate d orbitals split into 2 different energy levels.**

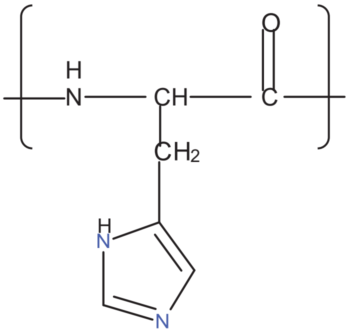
- **the <u>d_{xy}, d_{yz} and d_{xz} orbitals</u> have lobes that project <u>between the charges</u> hence are at a <u>lower energy level.</u>**

(g) R-groups on amino acids residues on protein act as ligands in biological systems. *Transferrin* is a protein in the blood that transports iron from food to the rest of the body.

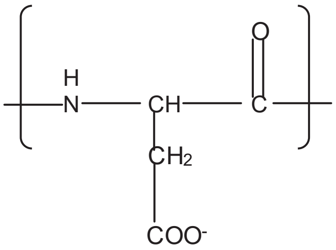


binding sites of *Transferrin*

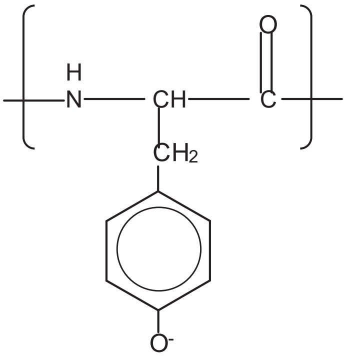
Transferrin binds to iron(III) via tryosine, histidine and aspartic acid residues as shown below.



Histidine residue
Side chain pK_a = 6.00



Aspartic acid residue
Side chain pK_a = 3.65

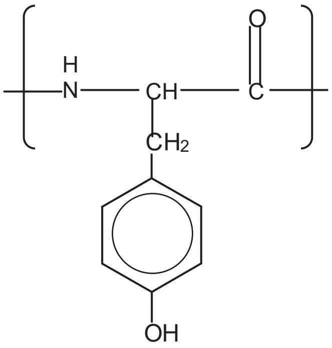


Tyrosine residue
Side chain pK_a = 10.07

The key to controlling uptake and release iron(III) is the change in pH. At pH 7.4, free transferrin binds to iron(III) to form the iron-transferrin complex. When the pH is lowered from 7.4 to 5.5, free iron(III) ions will be released from the protein binding site.

(i) Draw the structural formula of the tyrosine residue at its most stable state at pH 5.5.

[1]



- **tyrosine residue pronotated**

(ii) Suggest how the decrease in pH releases iron(III) from the protein complex. [1]

- **When pH decreases, tryrosine and histidine are protonated, it reduces the protein affinity to/ can no longer form dative bonds with Fe(III) thus releasing the free Fe(III).**

[Total: 20]

TEMASEK
JUNIOR COLLEGE

2017 JC2 PRELIMINARY EXAMINATIONS
HIGHER 2

CANDIDATE NAME	
CIVICS GROUP	/
CENTRE NO. / INDEX NO.	/

CHEMISTRY **9729/04**

Paper 4 Practical **28 August 2017**

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 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	/ 15
2	/ 24
3	/ 16
Total	/ 55

This document consists of 15 printed pages.

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

1 **Determination of change in oxidation number of a transition metal ion, M^{2+}**

You are to determine, by titration, the change in oxidation number of a transition metal ion, $\mathbf{M}^{2+}$, when reacted with acidified potassium manganate(VII).

FA 1 is 0.0200 mol dm^{-3} potassium manganate(VII), $KMnO_4$
FA 2 is 0.0470 mol dm^{-3} transition metal salt, $\mathbf{M}SO_4$
FA 3 is 1.00 mol dm^{-3} sulfuric acid, H_2SO_4

(a) Method

(i)

1. Fill the burette with **FA 1.**
2. Using a pipette, transfer 25.0 cm^3 of **FA 2** into the conical flask.
3. Using a measuring cylinder, transfer 25.0 cm^3 of **FA 3** to the same conical flask.
4. Carry out as many accurate titrations as necessary to obtain consistent results. Add **FA 1** until the contents of the conical flask turns a permanent pale pink colour.
5. Record below, in a table form, all of your burette readings and the volume of **FA 1** added in each accurate titration.

Results

Final burette reading /cm^3	**23.50**	**23.50**
Initial burette reading /cm^3	**0.00**	**0.00**
Volume of FA 1 /cm^3	**23.50**	**23.50**
	√	√

●Appropriate headings and units for accurate data where headings should match readings.
●All accurate burette readings recorded to 0.05 cm^3
●Has two uncorrected, accurate titres value within ±0.10cm^3
●●●3m – accuracy [6]

(ii) From your titrations, obtain a suitable volume of **FA 1** to be used in your calculations. Show clearly how you obtained this volume.

●**Average titre =** $\frac{23.50+23.50}{2}$

= 23.50 cm^3

25.0 cm^3 of **FA 2** required _**23.50**______________ cm^3 of **FA 1** [1]

(b) Calculations

Show your working and appropriate significant figures in the final answer to **each** step of your calculations.

(i) Calculate the amount of potassium manganate(VII) present in the volume of **FA 1** calculated in **(a)(ii)**.

●**Amount of MnO_4^-**
$= \frac{23.50}{1000} \times 0.02$
= 4.70 x 10^{-4} mol

amount of $KMnO_4$ = **4.70 x 10^{-4} mol** [1]

(ii) Determine the amount of **M**SO_4 in 25.0 cm^3 of **FA 2**.

●Amount of MSO_4 in 25.0 cm^3 of FA 2

= 0.0470 x $\frac{25}{1000}$

= 1.175 x 10^{-3} mol

= 1.18 x 10^{-3} mol (3sf)

amount of **M**SO_4 in 25.0 cm^3 = **1.18 x 10^{-3} mol** [1]

(iii) Use your answer to **(b)(i)** and **(b)(ii)** to calculate the number of moles of **M**SO_4 that react with 1 mole of $KMnO_4$

●Number of moles of MSO4 reacting with 1 mole of $KMnO_4$

= $\frac{1.175\times10^{-3}}{4.7\times10^{-4}} = 2.50$ mol

amount of **M**SO_4 = **2.50 mol** [1]

(iv) Two possible equations for the reaction of acidified $KMnO_4$ with **M**SO_4 are shown below:

Equation 1: $2KMnO_4 + 10MSO_4 + 8H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 5M_2(SO_4)_3 + 8H_2O$

Equation 2: $2KMnO_4 + 5MSO_4 + 8H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 5M(SO_4)_2 + 8H_2O$

State and explain which of the above two equations is consistent with your answer in **(b)(iii)**.

●Equation 2 as ratio of $KMnO_4$: MSO_4 is 2:5 OR 1:2.5
Hence it is 2.5 mol of MSO_4 reacting with 1 mol of $KMnO_4$

[1]

(v) Use your answer in **(b)(iv)** to state the oxidation number of the transition metal **M** in the product of the reaction.

●Oxidation state of M in product is +4

Workings: $M(SO_4)_2 \rightarrow x+2(-2) = 0 \rightarrow x= +4$

[1]

(c) **(i)** A student suggested that using a burette to measure 25.0 cm^3 of **FA 2** would give a more accurate result than using a pipette. The percentage error of a 25.0 cm^3 pipette is 0.24%.

Calculate the percentage error of using a burette and deduce if the above claim by the student is correct.

Using the burette to measure 25.0 cm^3 of FA 2 involve 2 readings, thus the max error would be 2x (±0.05) = ±0.10

●%error would be $\frac{0.10}{25} \times 100\% = 0.400\%$

●Since %error using burette > %error using pipette (0.24%). The claim is incorrect as it is less accurate to use a burette to measure the 25.0 cm^3 of FA2.

[2]

(ii) Another student decided to use a 25.0 cm^3 pipette instead of a measuring cylinder to measure the volume of **FA 3** in **Step 3**.

State and explain whether this alteration will improve the accuracy of the experimental results.

●No this alteration will not improve the accuracy of the experiment as the acid was used in excess.

[1]

[Total: 15]

2 Determination of the enthalpy change of neutralisation, ΔH_n

You are to determine the enthalpy change for the neutralisation reaction given below.

$$HA(aq) + NaOH(aq) \rightarrow NaA(aq) + H_2O(l)$$

FA 4 is 1.80 mol dm^{-3} HA
FA 5 is aqueous sodium hydroxide, NaOH

(a) Method

Read through the instructions carefully and prepare a table below for your results before starting any practical work.

1. Support the styrofoam cup in the 250 cm^3 beaker.
2. Rinse and fill the burette with **FA 4**.
3. Use the measuring cylinder to transfer 25 cm^3 of **FA 5** into the styrofoam cup.
4. Place the thermometer in the styrofoam cup and record the temperature of the solution. Tilt the cup if necessary to ensure the thermometer bulb is fully immersed.
5. Run 5.00 cm^3 of **FA 4** into the cup. Stir, and record the new temperature of the solution and the volume of **FA 4** added.
6. Run a second 5.00 cm^3 of **FA 4** into the cup. Stir and record the new temperature and the total volume of **FA 4** added.
7. Continue adding **FA 4** in 5.00 cm^3 portions. Stir and record each new temperature and total volume of **FA 4** until a total of 45.00 cm^3 has been added.

Results

Total Vol. FA 4 /cm^3	Temp./^{0}C
0.00	27.5
5.00	31.0
10.00	34.0
15.00	36.5
20.00	38.0
25.00	39.0
30.00	38.0
35.00	37.0
40.00	36.5
45.00	36.0

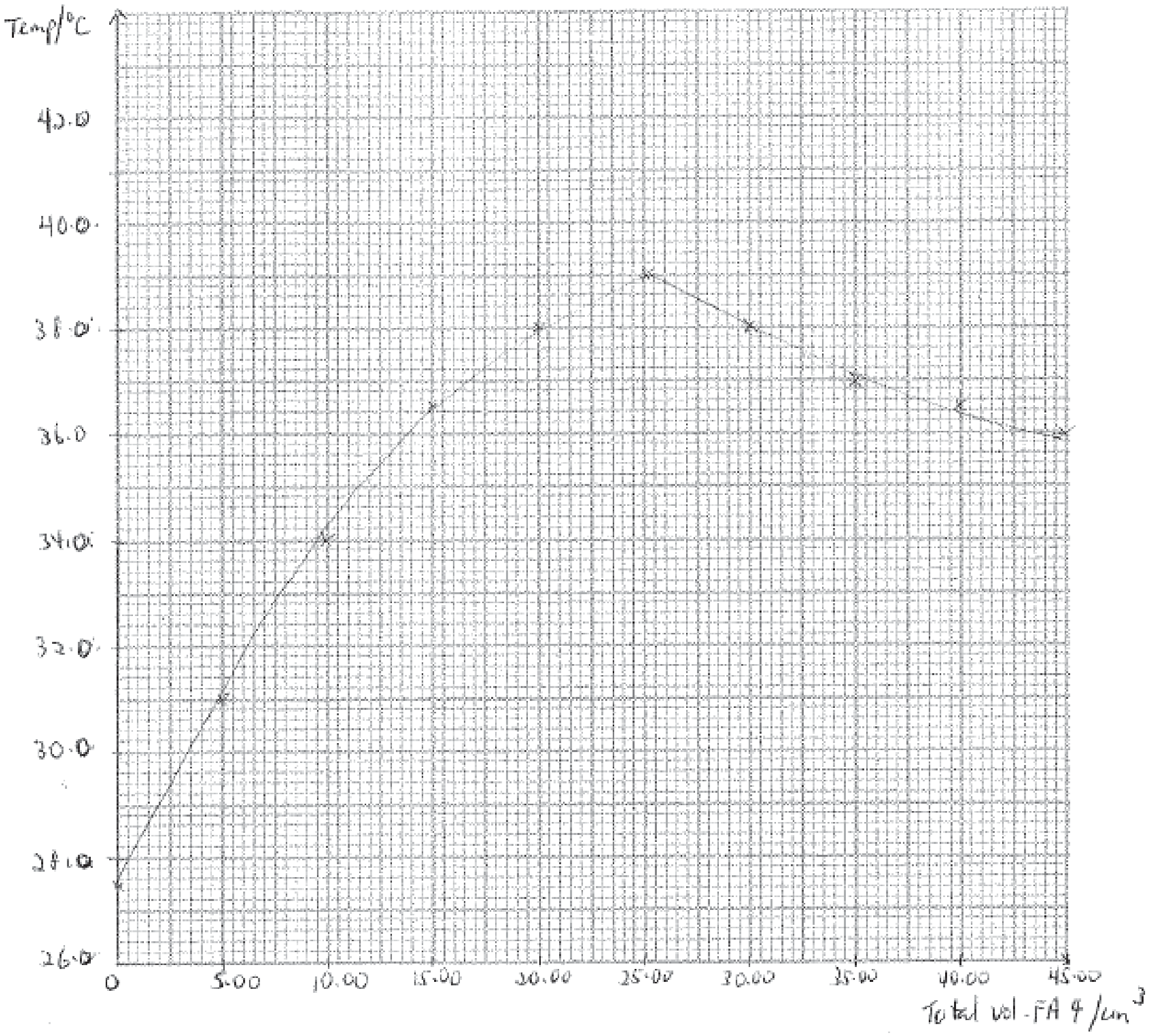
•Table with initial temp of solution and 9 sets of results with appropriate headers
•Record every volume to 2dp and temperature recorded to 1dp.

[2]

(b) (i) Plot a graph of temperature (*y*-axis) against total volume of **FA 4** added (*x*-axis) on the grid below. The temperature axis should allow you to include a point at least 2 °C greater than the maximum temperature recorded.

Draw two best-fit lines connecting all the plotted points with
- an increasing trend
- a decreasing trend.

Answer:



●Appropriate labels of the axis and appropriate scale of the graph

● All points accurately plotted (within ½ small square)

● Two lines of best fit drawn

[3]

(ii) Extrapolate the two lines until they cross.
The intersection gives the maximum temperature, T_{max}, at equivalence point.
Use your graph to determine the following and show clearly on your graph how you obtained these answers.

- Maximum temperature at the equivalence point, T_{max},
- Maximum temperature change at the equivalence point, ΔT_{max}.
- Total volume of **FA 4** added at the equivalence point, $V_{eq.}$

T_{max} = **39.0 ^{0}C**

ΔT_{max} = **11.5 ^{0}C**

$V_{eq.}$ = **25.25 cm^3**

[3]

(c) Explain the shapes of your graph lines before the equivalence point and after the equivalence point.

(i) Before the equivalence point

●Each 5 cm^3 addition of HA causes the temperature of the mixture to rise as the reaction between HA and NaOH is exothermic.

●Each rise in temperature is smaller than before because the same amount of heat is produced but the volume of mixture is larger. Thus the heat is distributed over an increasing volume of mixture.

**mark according to the students' graph – with ECF (1st mark for both (i) and (ii))*

[2]

(ii) After equivalence point

●NaOH has reacted completely and hence no more heat is produced. The temperature of the mixture falls with each 5 cm^3 addition of HA (at a lower temperature/room temperature).

[If students' answer is a downward-sloping curve]:

Each temperature fall is smaller than before as there is a smaller extent of cooling since the temperature of the mixture is now closer to temperature of the NaOH solution.

[1]

(d) **Calculations**

Show your working and appropriate significant figures in the final answer to **each** step of your calculations.

(i) Calculate the number of moles of HA present in the volume of **FA 4** recorded in **(b)**.

Amt of HA = 25.25/1000 x 1.80 mol

= 0.0455 mol

Amount of HA = **0.0455 mol**

(ii) Using your answers in **(b)**, calculate the heat energy produced when **FA 4** neutralised 25 cm^3 of sodium hydroxide.

(Assume that **4.2 J** of heat energy changes the temperature of 1.0 cm^3 of solution by 1 °C.)

Heat evolved = (25 + 25.25) x 4.2 x 11.5 J

= 2427 J

Heat energy produced = **2427 J**

(iii) Calculate the enthalpy change of neutralisation, in kJ mol^{-1}, for the reaction below.

$$HA(aq) + NaOH(aq) \rightarrow NaA(aq) + H_2O(l)$$

Enthalpy change of neutralisation = – 2427/(0.0455 x 1000) kJ mol^{-1}

= – 53.3 kJ mol^{-1}

Enthalpy change = **– 53.3 kJ mol^{-1}**

[6]

(e) Apart from using a thermometer calibrated to a greater level of precision, suggest one other improvement that could be made to the **method** carried out in **(a)**.

Use burette / pipette for FA 4 / instead of measuring cylinder.
or Use smaller volumes close to max T
or windshield *(but not* *lid* *because it's a titration)*

[1]

Planning

The enthalpy change of solution of solid NaOH can be calculated using the enthalpy change of neutralisation of aqueous NaOH with aqueous HC*l*, ΔH_1 and the enthalpy change of reaction of solid NaOH with aqueous HC*l*, ΔH_2.

(f) Given that the enthalpy change of neutralisation of aqueous NaOH with aqueous HC*l* is –57.0 kJ mol^{-1}, construct an energy cycle and show how it can be used to determine the enthalpy change of solution of NaOH.

$$\begin{tikzcd}
HCl(aq) + NaOH(s) \arrow[rr, "\Delta H_{sol}"] \arrow[dr, "\Delta H_2"'] & & HCl(aq) + NaOH(aq) \arrow[dl, "\Delta H_1 = -57\ kJmol^{-1}"] \\
& NaCl(aq) + H_2O(l) &
\end{tikzcd}$$

Using Hess' Law,

$\Delta H_{sol} = \Delta H_2 - \Delta H_1$

[1]

(g) You are to plan an experiment to determine the enthalpy change of reaction of solid NaOH with aqueous HC*l*, ΔH_2. You are provided with the following reagents and the usual laboratory apparatus.

Reagents : 50 cm^3 1 mol dm^{-3} HC*l* solution
sodium hydroxide solid

Your plan should include

- calculation to show the appropriate mass of solid sodium hydroxide to be used.
- a sequence of numbered steps, the details of the experimental procedure including the measurements to be taken and tabulation of measurements and results.
- calculation of the enthalpy change of reaction of solid NaOH with HC*l* (aq).

(Assume that **4.2 J** of heat energy changes the temperature of 1.0 cm^3 of solution by 1 °C.)
[Ar Na: 23.0, H:1.0; O:16.0]

Pre-calculation

Using 30 cm^3 of 1 mol dm^{-3} HCl solution to react completely with solid NaOH.
Amt of HCl used = 30/1000 x 1 mol = 3.00 x 10^{-2} mol
NaOH is the limiting reagent.
Let amount of NaOH used be 1.00 x 10^{-2} mol
Mass of solid NaOH = 1.00 x 10^{-2} x 40 g
= 0.400 g

Procedure

1. Using a measuring cylinder, place 30 cm^3 of 1 mol dm^{-3} HCl into the styrofoam cup.
2. Measure and record the initial temperature of the HCl solution.
3. Using the electronic weighing balance, weigh accurately about 0.4 g solid NaOH in a clean and dry weighing bottle.
4. Add the solid NaOH into the cup. Stir and record the highest temperature reached.
5. Reweigh the weighing bottle.

Results

Mass of empty dry weighing bottle/g	M
Mass of weighing bottle and solid NaOH/g	M_1
Mass of weighing bottle and residual NaOH/g	M_2
Mass of NaOH added/g	$M_1 – M_2$

Initial Temp/^{0}C	T_1
Highest Temp/^{0}C	T_2
Temperature rise/^{0}C	$T_2 – T_1$

Calculation

Heat evolved = mcΔT

= $(30 \times 4.2 \times T_2 – T_1)$ J

Amt of NaOH used = $(M_1 – M_2)$ / 40 mol

$\Delta H_2 = –(40)(30 \times 4.2 \times T_2 – T_1) / 1000(M_1 – M_2)$ kJ mol^{-1}

[5]

[Total:24]

3 You are provided with the solid **FA 6** and solution **FA 7**.

You are to perform the tests below and record your observations in the spaces provided. Your answers should include

- details of colour changes and precipitates formed;
- the names of any gases evolved **and** details of the test used to identify each one.

You should indicate clearly at what stage in a test a change occurs.

If it appears that no reaction has taken place this should be clearly recorded.

Rinse and reuse test-tubes where possible.

Marks are **not** given for chemical equations.

No additional or confirmatory tests for ions present should be attempted.

Candidates are reminded that definite deductions may be made from tests where there appears to be no reaction.

(a) **FA 6** contains one cation and one anion.

	Test	*Observation*
(i)	To half a spatula-full of **FA 6** in a test-tube add excess dilute sulfuric acid. Keep the solution for test **(iii)** and **(iv)**.	• **effervescence observed** • **colourless, odourless and acidic gas evolved which gives a white ppt with $Ca(OH)_2$** • **gas is CO_2** **green solid dissolved to give blue solution**
(ii)	Place a spatula-full of **FA 6** in a test-tube and heat strongly.	• **green solid turn black on heating** • **colourless, odourless and acidic gas evolved which gives a white ppt with $Ca(OH)_2$** **gas is CO_2**
(iii)	To 1 cm depth of the solution from **(i)** in a test-tube, add a few drops of aqueous sodium hydroxide Then add excess aqueous sodium hydroxide.	• **pale blue ppt formed** • **insoluble in excess NaOH**
(iv)	To 1 cm depth of the solution from **(i)** in a test-tube, add a few drops of aqueous ammonia. Then add excess aqueous ammonia.	• **blue ppt formed** • **soluble in excess NH_3 giving dark blue solution**

The cation present in **FA 6** is Cu^{2+}

The anion present in **FA 6** is CO_3^{2-}

FA 7 contains one cation and two anions.

	Test	*Observations*
(v)	To 1 cm depth of **FA 7** in a test-tube, add a few drops of aqueous sodium hydroxide. Then add excess aqueous sodium hydroxide. Warm the mixture.	• **no ppt formed** • **no gas (NH_3) evolved**
(vi)	To 1 cm depth of **FA 7** in a test-tube, add a few drops of aqueous ammonia Then add excess aqueous ammonia.	• **no ppt formed**
(vii)	To 1 cm depth of **FA 7** in a test-tube, add aqueous silver nitrate, followed by aqueous ammonia.	• **yellow ppt formed** **insoluble in excess NH_3**
(viii)	To half a spatula-full of **FA 6** in a test-tube, add 3 cm depth of **FA 7**.	• **effervescence observed** • **colourless, odourless and acidic gas evolved which gives a white ppt with $Ca(OH)_2$** • **gas is CO_2** • **brown solution formed** • **white/greyish white ppt formed**
	Then add 1 cm depth of aqueous sodium thiosulfate.	• **brown solution decolourise**

One anion present in **FA 7** is I^-

With reference to tests **(v)**, **(vi)** and **(viii)**, suggest the identity of the cation present in **FA 7**.

H^+

The second anion is suspected to be the sulfate ion.

(ix) Suggest a test to verify the presence of sulfate ion in **FA 7**. Carry out the test and record your results in the space below.

Test	*Observations*
- To 1 cm depth of **FA 7** in a test-tube, add aqueous barium nitrate, followed by aqueous nitric acid.	- **white ppt formed insoluble in excess nitric acid.**

[11]

(b) **FA 8** is a solution that contains the Cr^{3+}, Mg^{2+} and Cl^{-} ions.

Plan a sequence of steps by which the three ions could be separated so that each ion is present in a separate precipitate. For each of the steps, you are to specifiy the location of the ions.

You may assume that the usual bench reagents and apparatus are available for use.

1. **Add excess NaOH(aq). Carry out filtration to separate the insoluble ppt from the solution**
   Residue: Mg^{2+} as $Mg(OH)_2$
   Filtrate: Cr^{3+} as $[Cr(OH)_6]^{3-}$, Cl^-

2. **Add sufficient HNO_3 to regenerate the ppt which is soluble in excess NaOH. Carry out filtration to separate the insoluble ppt from the solution**
   Residue: Cr^{3+} as $Cr(OH)_3$
   Filtrate: Cl^-

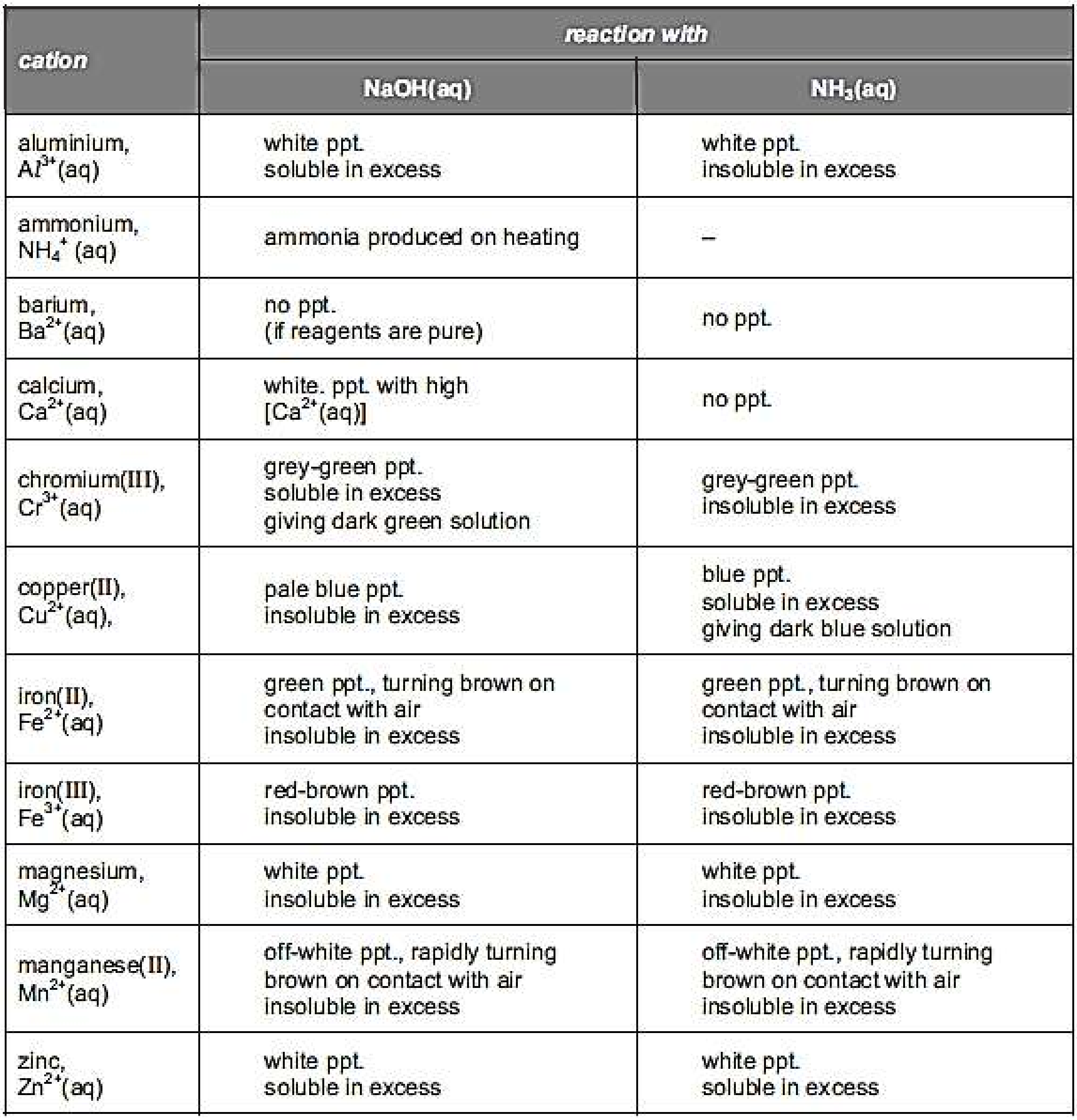
3. **Add excess acidified $AgNO_3$. Carry out filtration to separate the insoluble ppt (AgCl) from the solution**

[5]
[Total: 16]

Qualitative Analysis Notes

[ppt. = precipitate]

(a) Reactions of aqueous cations



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

(b) Reactions of anions

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

(c) Tests for gases

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

(d) 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

2 x burettes (50 cm^3);
1 x pipette (25.0 cm^3);
1 x pipette filler (students bring their own);
1 x retort stands and burette clamps;
1 x 25 cm^3 measuring cylinder;
2 x funnels (for filling burette);
2 x 250 cm^3 conical flasks;
1 x 250 cm^3 beaker
1 x white tile;
1 x thermometer with range -10 °C to +110 °C, graduated to 1 °C;
1 x Styrofoam cup
5 plastic dropping pipettes;
9 test-tubes (students bring their own);
1 x test-tube rack;
1 x test-tube holder;
1 x delivery-tube
1 x small spatula
1 x wash bottle containing deionised water;
1 x Bunsen burner;
1 x lighter (per bench)
wooden splinters
red and blue litmus paper
filter paper strips
paper towels

Additional pipette filler, test-tubes and dropping pipettes should be available.

Chemicals Required

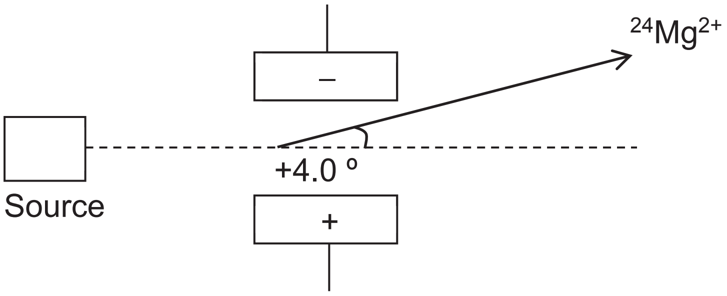
Question 1-3:

Label	**Per candidate**	**Identity**	**Notes (preparation)**
FA 1	120 cm^3	0.02 mol dm^{-3} potassium managanate (VII)	
FA 2	100 cm^3	0.940 mol dm^{-3} ammonium iron (II) sulfate	Dissolve 7.36g of $(NH_4)_2SO_4.FeSO_4.6H_2O$ in 200 cm^3 of solution made with 20% 1.0 mol dm^{-3} H_2SO_4 and 80% water mixture.
FA 3	100 cm^3	1.0 mol dm^{-3} sulfuric acid	
FA 4	100 cm^3	1.8 mol dm^{-3} HCl	
FA 5	70 cm^3	2.00 mol dm^{-3} NaOH	
FA 6	Solid	Solid basic copper (II) carbonate	About 4 spatula (spoonful) per candidate
FA 7	20 cm^3	HI (aq)	Freshly prepared (per shift) 1:1 portion of (1) 0.25 $moldm^{-3}$ of KI (41.5g/dm^3) (2) 0.5 $moldm^{-3}$ of H_2SO_4 (aq)

For each question there are four possible answers, **A**, **B**, **C**, and **D**. Choose the **one** you consider to be correct.

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

In an experiment, a sample containing 2 different species was vaporised, ionised and passed through an electric field. Analysis of the deflection occurring at the electric region revealed the following data for the sample. It was observed that a beam of $^{24}Mg^{2+}$ gives an angle of deflection of +4.0 °.



Which one of the following species will give the correct angle of deflection?

	isotope	no. of electrons	angle of deflection
A	^{16}O	6	–6.0 °
B	^{23}Na	10	+2.1 °
C	^{28}Si	10	–6.9 °
D	^{35}Cl	18	+1.4 °

2 Which one of the following corresponds to the electronic configuration of the 6 outermost electrons of a Group 6 element in its ground state?

A $3d^4 4s^2$

B $3d^5 4s^1$

C $4s^2 4p^4$

D $4p^6$

3 Which of the following have species arranged in increasing bond angle about the central atom?

1 ICl_4^- IO_3^-, I_3^-

2 XeF_4, XeO_3, XeF_2

3 N_2O, NO_3^-, NO_2^+

4 SO_4^{2-}, SO_3^{2-}, SO_2

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

4 The molar mass of ethanoic acid is 120.0 g mol^{-1} when dissolved in trichloromethane but 60.0 g mol^{-1} when dissolved in water.

Which one of the following statements best explains the phenomenon?

A Ethanoic acid is more soluble in trichloromethane than in water.

B Ethanoic acid molecules form strong covalent bonds with trichloromethane molecules.

C Ethanoic acid evaporates more readily in water.

D Ethanoic acid molecules form extensive hydrogen bonds with water molecules.

5 1.00 mol of gaseous molecules of a compound **A**, takes up a volume of 39 dm^3 when subjected to a pressure of 1.52 atm at a temperature of 70 ºC.

Which of the following statements explain the above observation?

1 Gaseous molecules of **A** experiences strong intermolecular forces of attractions.

2 Gaseous molecules of **A** have a significant molecular volume.

3 Gaseous molecules of **A** are in constant, rapid, random motion.

A **1**, **2** and **3**

B **1** and **2** only

C **2** and **3** only

D **1** only

6 **P**, **Q** and **R** are 3 consecutive elements in Period 3 of the Periodic Table.

- **R** has the highest melting point out of the 3 elements.
- The chloride of **P** gives a solution that is least acidic in water as compared to chlorides of **Q** and **R**.
- The 3rd ionisation energy of **Q** is much lower than that of **P**.

What can **P**, **Q** and **R** be?

A Na, Mg, A*l*

B Mg, A*l*, Si

C A*l*, Si, P

D Si, P, S

7 Which one of the following statements about Group 2 elements and their compounds is correct?

A Calcium hydroxide has a higher solubility than magnesium hydroxide.

B Calcium reacts with barium chloride to give calcium chloride.

C Strontium carbonate, on heating over a short period of time, decomposes to give more carbon dioxide gas than magnesium carbonate.

D Magnesium has a lower melting point than strontium.

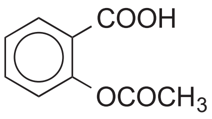
8 10 cm^3 of gaseous $C_xH_yO_z$ was burnt in excess oxygen. There was a contraction of 20 cm^3. When the gaseous mixture was passed through aqueous sodium hydroxide, there was a further contraction of 30 cm^3. All gas volumes were measured at room temperature and pressure.

Which one of the following could be $C_xH_yO_z$?

A $C_3H_2O_3$ **C** $C_3H_6O_2$

B $C_3H_4O_4$ **D** $C_3H_8O_2$

9 Aspirin is a medication used to treat pain, fever or inflammation.



Aspirin

25.0 cm^3 of 1.00 mol dm^{-3} NaOH was added to 25.0 cm^3 of solution containing aspirin. This resulting solution required 35.20 cm^3 of 0.325 mol dm^{-3} HC*l* to be fully neutralised.

What is the concentration of aspirin in the original 25.0 cm^3 solution?

A 0.229 mol dm^{-3} **C** 0.458 mol dm^{-3}

B 0.271 mol dm^{-3} **D** 0.542 mol dm^{-3}

10 Nitrogen monoxide, NO, is a pollutant that is formed in car exhausts and it can be oxidised as follows:

$$NO(g) + O(g) \rightarrow NO_2(g)$$

What is the enthalpy change of the above reaction given the following information?

$NO(g) + O_3(g) \rightarrow NO_2(g) + O_2(g)$ $\Delta H = -199$ kJ mol^{-1}

$O_3(g) \rightarrow \frac{3}{2}O_2(g)$ $\Delta H = -142$ kJ mol^{-1}

$O_2(g) \rightarrow 2O(g)$ $\Delta H = +495$ kJ mol^{-1}

A –94 kJ mol^{-1} **C** –552 kJ mol^{-1}

B –305 kJ mol^{-1} **D** –589 kJ mol^{-1}

11 A key step in the production of sulfuric acid is the oxidation of $SO_2(g)$ to $SO_3(g)$.

$$2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$$

At 25 °C, $\Delta G = -142$ kJ mol^{-1}, $\Delta H = -198$ kJ mol^{-1}, $\Delta S = -188$ J K^{-1} mol^{-1}.

Assuming ΔH and ΔS are constant with temperature, which of the following statements about this reaction are correct?

1 The reaction becomes less spontaneous with increasing temperature.

2 The reaction becomes spontaneous at 780 °C.

3 The reaction is spontaneous at 900 °C.

A **1**, **2** and **3**

B **1** and **2** only

C **2** and **3** only

D **1** only

12 An experiment was carried out to investigate the initial rate of reaction between ammonium peroxodisulphate, $(NH_4)_2S_2O_8$, an oxidising agent, and potassium iodide, KI.

The initial concentrations of the $(NH_4)_2S_2O_8$ and KI solutions in the mixture together with the time taken for the mixture to darken for the various experimental runs are given below.

initial concentration of $(NH_4)_2S_2O_8$ / mol dm^{-3}	initial concentration of KI / mol dm^{-3}	time taken to darken / s
0.10	0.20	35
0.05	0.20	70
0.10	0.067	105
0.02	0.75	?

What is the expected time taken (in s) to darken when the experiment is repeated using initial concentrations of $(NH_4)_2S_2O_8$ and KI to be 0.02 mol dm^{-3} and 0.75 mol dm^{-3} respectively?

A 40 **B** 47 **C** 60 **D** 72

13 Ammonia is a raw material used in the manufacture of fertilisers, explosives and cleaning fluids. It is produced in the Haber process as shown:

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

- A closed system initially containing 2.00 mol of nitrogen, 6.00 mol of hydrogen, and 2.40 mol of ammonia at 448 °C is allowed to reach equilibrium in a sealed vessel of volume 1 dm^3. At equilibrium, there was 2.32 mol of nitrogen present.
- The vessel is subsequently expanded to 2 dm^3 under constant temperature, and equilibrium re-established.

Which of the following statements about this reaction are correct?

1 The equilibrium constant, K_c, is 3.96×10^{-3} mol^{-2} dm^6.

2 The equilibrium will shift to the left when vessel is expanded to double its initial volume.

3 The equilibrium concentration of $NH_3(g)$ is lower after the second equilibrium is established.

A **1**, **2** and **3**

B **1** and **2** only

C **2** and **3** only

D **1** only

14 Common chlorine bleach is typically a 5 % sodium hypochlorite, Na*Cl*O solution.

A solution, made by adding solid NaC*l*O to 2 dm^3 of water, has a pH of 10.5.

How many moles of NaC*l*O was added to the water, given that chloric(I) acid, HC*l*O has a K_a of 3.03×10^{-8} mol dm^{-3} at 25 °C?

A 0.25 mol

B 0.31 mol

C 0.55 mol

D 0.62 mol

15 Hydroxyapatite, $Ca_5(PO_4)_3OH$, is the main constituent of tooth enamel. In the presence of saliva, which contains a buffer system, the following equilibria exist:

$$Ca_5(PO_4)_3OH(s) \rightleftharpoons 5Ca^{2+}(aq) + 3PO_4^{3-}(aq) + OH^-(aq)$$

$$HPO_4^{2-}(aq) \rightleftharpoons H^+(aq) + PO_4^{3-}(aq)$$

Which one of the following statements does **not** help to explain why tooth enamel is dissolved more readily when saliva is acidic?

A The phosphate ion PO_4^{3-} accepts H^+.

B The hydroxide ions are neutralised by the acid.

C The calcium ions can precipitate to form $Ca(OH)_2$.

D The concentration of PO_4^{3-} decreases in this medium.

16 A solution contains three anions with the following concentrations:

anion	concentration / mol dm^{-3}
CrO_4^{2-}	0.20
CO_3^{2-}	0.10
Cl^-	0.010

A dilute $AgNO_3$ solution is slowly added to the solution.

Which is the first compound to precipitate and what concentration of Ag^+ is necessary to begin its precipitation?

[Given: K_{sp} (Ag_2CrO_4) = 1.2 x 10^{-12} mol^3 dm^{-9}, K_{sp} (Ag_2CO_3) = 8.1 x 10^{-12} mol^3 dm^{-9}, K_{sp} ($AgCl$) = 1.8 x 10^{-10} mol^2 dm^{-6}]

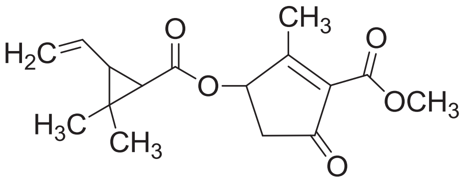
	first ppt	[Ag^+] to begin precipitation / mol dm^{-3}
A	Ag_2CrO_4	6.00×10^{-12}
B	Ag_2CrO_4	2.45×10^{-6}
C	Ag_2CO_3	9.06×10^{-6}
D	$AgCl$	1.80×10^{-8}

17 Species with the molecular formula CH_3 can act as an electrophile, a free radical or a nucleophile depending on the number of outer shell electrons on the central carbon atom.

How many outer shell electrons must be present for CH_3 to act in these different ways?

	as an electrophile	as a free radical	as a nucleophile
A	6	7	8
B	6	8	7
C	7	6	8
D	8	7	6

18 Pyrethrins such as jasmolin II, are a group of natural compounds synthesised by flowers of the genus Chrysanthemum to act as insecticides.



jasmolin II

How many stereoisomers are there for a molecule of jasmolin II?

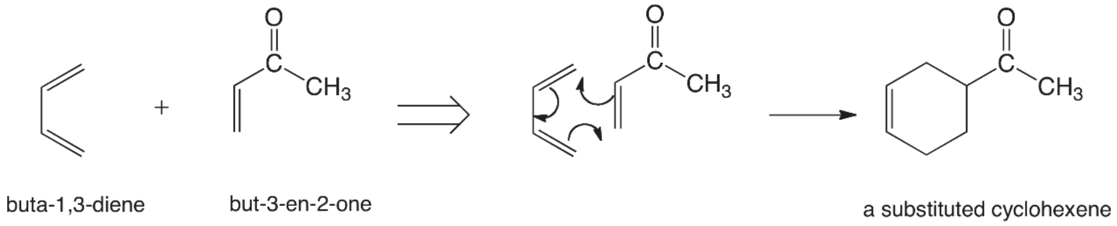
A 2 **B** 4 **C** 8 **D** 16

19 Compound **X** has molecular formula C_4H_{10}. **X** reacts with $Cl_2(g)$ in the presence of sunlight to produce only two different monosubstituted products. Both of these products give the same Compound **Y**, and no other organic products, when they are reacted with hot ethanolic KOH.

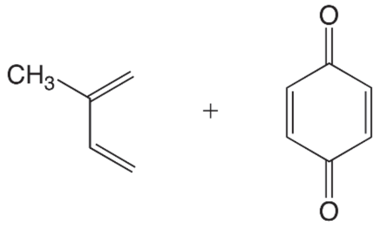
What is produced when **Y** is treated separately with hot acidified dichromate(VI) and cold alkaline manganate(VII)?

	hot acidified dichromate(VI)	cold alkaline manganate(VII)
A	CO_2 and $CH_3CH_2CO_2H$	$CH_2(OH)CH(OH)CH_2CH_3$
B	CO_2 and CH_3COCH_3	CH_3CO_2H only
C	$CH_2{=}CHCH_2CH_3$	$CH_2(OH)CH(OH)CH_2CH_3$
D	$CH_2{=}CHCH_2CH_3$	CO_2 and $CH_3CH_2CO_2H$

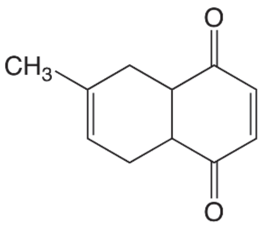
20 The Diels-Alder reaction is an organic reaction between a conjugated diene and a substituted alkene to form a substituted cyclohexene system. One such reaction between buta-1,3-diene and but-3-en-2-one is shown below:



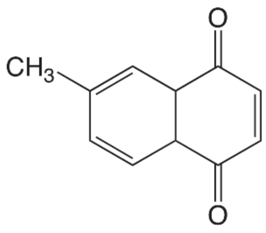
What would be the product formed when the following diene and substituted alkene reacts in a 1:1 ratio?



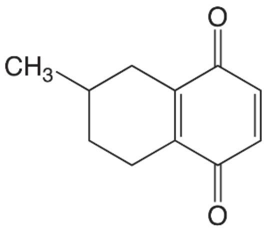
A



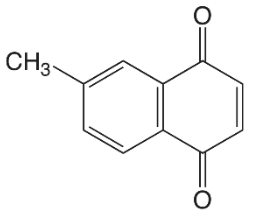
C



B

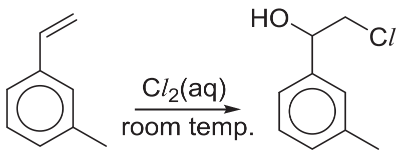


D

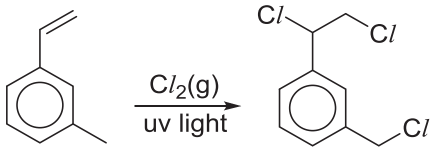


21 Which one of the following products is **unlikely** to be formed based on the given reagents and conditions?

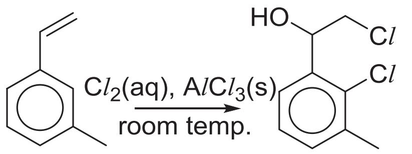
A



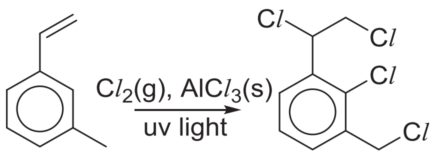
B



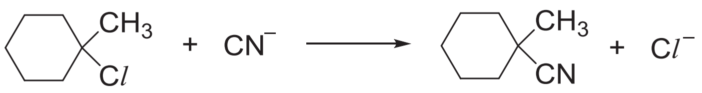
C



D



22 The reaction between 1–chloro–1–methylcyclohexane and alcoholic potassium cyanide is shown below:

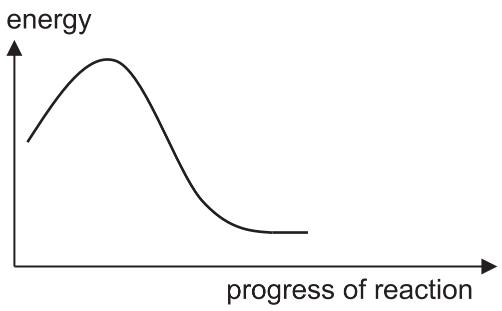


Which of the following statements regarding the reaction are likely to be true?

1 The rate equation of the reaction is overall first order.

2 The same mechanism will occur less readily if 1–chloro–1–methylhexane is used.

3 The energy profile diagram of the reaction is as shown below:



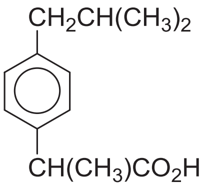
A **1**, **2** and **3**

B **1** and **2** only

C **2** and **3** only

D **3** only

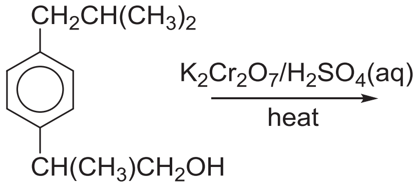
23 *Ibuprofen* is an anti-inflammatory drug.



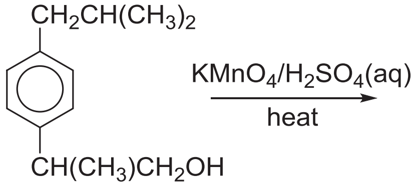
ibuprofen

Which one of the following reactions is **unlikely** to lead to its formation?

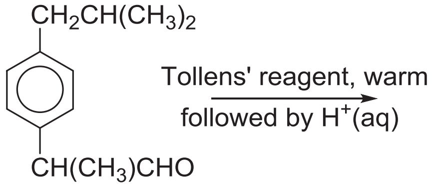
A



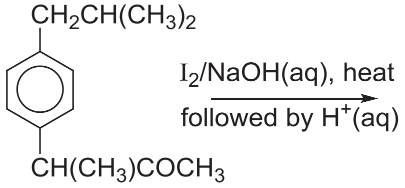
B



C

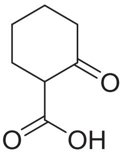
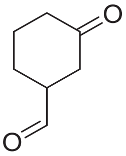
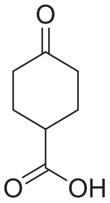


D



24 When compound **V** is first treated with an excess of a reducing agent, followed by heating with excess concentrated sulfuric acid, it gives **only one** final product with the molecular formula C_7H_{10}.

Which of the following options show a possible structure of compound **V** and the reducing agent?

	compound **V**	reducing agent
1		H_2/Ni
2		$NaBH_4$
3		$LiAlH_4$

A **1** and **2** only

B **2** and **3** only

C **1** only

D **3** only

25 The acid dissociation constants of ethanoic acid, peroxyethanoic acid, and ethanol are given in the table below.

name	formula	pK_a
ethanoic acid	CH_3CO_2H	4.8
peroxyethanoic acid	CH_3CO_3H	8.2
ethanol	CH_3CH_2OH	15.9

Which one of the following statements can best be inferred from the information given above?

A CH_3CO_3H can react with Na(s) but not with NaOH(aq).

B The K_b of the three conjugate bases decrease in the following order:

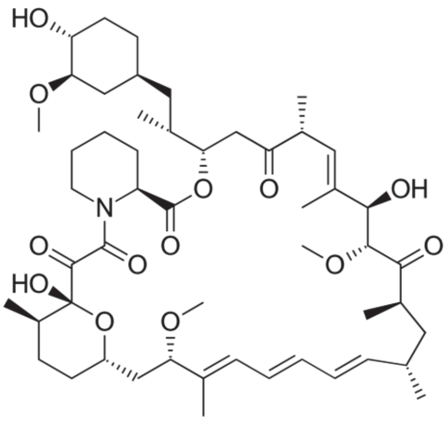
$$CH_3CO_2^- > CH_3CO_3^- > CH_3CH_2O^-$$

C The negative charge on $CH_3CO_2^-$ is less dispersed due to a smaller number of electron–withdrawing O atoms as compared to $CH_3CO_3^-$.

D The negative charge on $CH_3CO_2^-$ is stabilised by delocalisation of electrons over the C=O group but the negative charge on $CH_3CO_3^-$ is not.

26 *Use of Data Booklet is relevant to this question.*

The drug *Sirolimus* is used for treatment after kidney transplants.



Sirolimus

The reaction between *Sirolimus* and hot aqueous hydrochloric acid yields an equimolar mixture of two organic products.

What is the relative molecular mass of the nitrogen–containing organic product?

A 129.0 **B** 164.5 **C** 165.5 **D** 179.5

27 *Use of Data Booklet is relevant to this question.*

The calomel electrode was used extensively a reference electrode in the past. However, it has since been superseded by safer options such as the silver/silver chloride electrode and the standard hydrogen electrode (S.H.E.).

Calomel electrode: $\frac{1}{2}Hg_2Cl_2 + e^- \rightleftharpoons Hg + Cl^-$

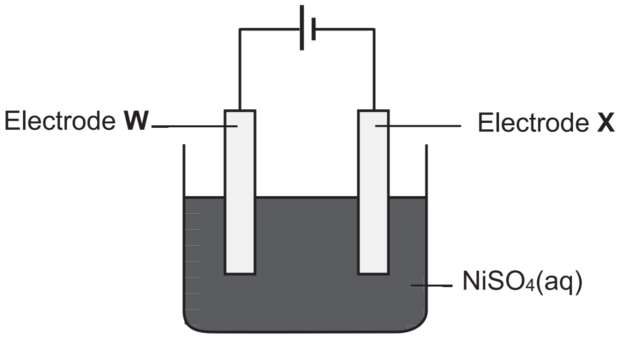
When measured with reference to the calomel electrode, a half–cell containing Zn^{2+}/Zn has a change in Gibbs' free energy of +199 kJ per mole of Zn^{2+}.

What is the standard electrode potential of the calomel electrode?

A +0.27 V **B** +1.30 V **C** –1.79 V **D** –2.82 V

28 *Use of Data Booklet is relevant to this question.*

An electrolytic cell is set up to obtain pure nickel from a nickel–chromium alloy.



The mass of the anode changes by 25 g during the process.

Which one of the following statements best describes the electrolysis process?

A The mass of the cathode changes by 25 g during the process.

B Chromium can be collected as anode sludge at the end of the process.

C Electrode **W** is pure nickel and electrode **X** is nickel–chromium alloy.

D The concentration of $Ni^{2+}(aq)$ in the electrolyte will decrease during the process.

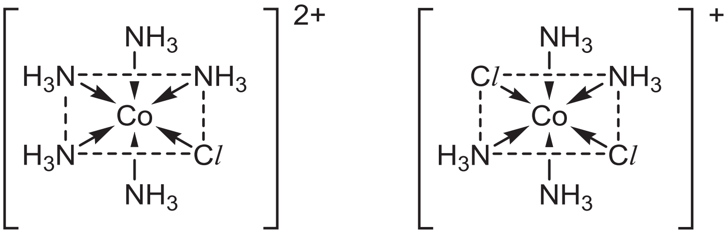
29 Two different complexes, **Y** and **Z**, can be obtained when aqueous cobalt(III) chloride undergoes ligand–exchange reaction with ammonia.

complex	co-ordination number	overall dipole moment	mole of AgCl ppt. per mole of complex
Y	6	yes	2
Z	6	no	1

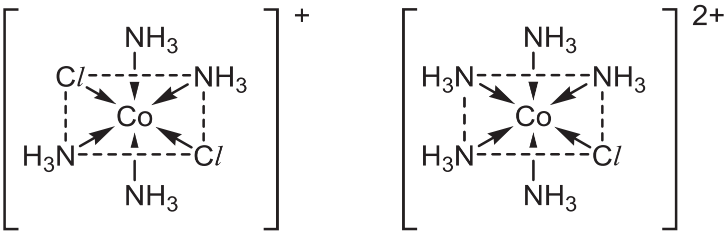
Which one of the following is likely to be the correct cationic structures of **Y** and **Z**?

Y **Z**

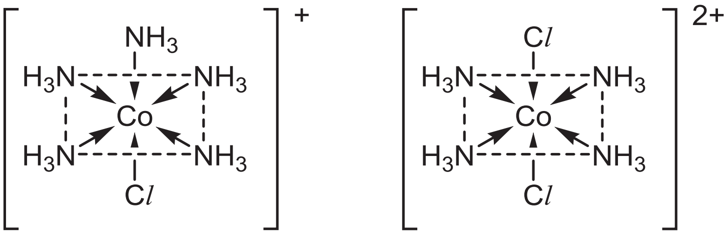
A



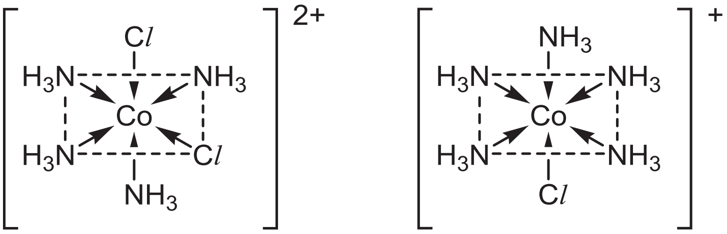
B



C

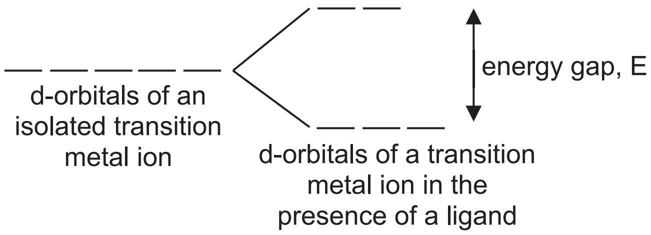


D



30 *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?

A Cu^{2+} **B** Cr^{3+} **C** Fe^{3+} **D** Ni^{2+}

1 This question concerns some unusual nitrogen compounds.

(a) Heating monomer **X** to 150 °C produces the trimer, melamine, $C_3H_6N_6$. Melamine is a cyclic planar molecule and is symmetrical.

(i) Suggest a structure for melamine.

[1]

(ii) The average C–N bond length is 0.145 nm and the average C=N bond is 0.125 nm. Suggest why all the carbon-nitrogen bonds in melamine are intermediate in length between the given C–N and C=N values.

…………………………………………………………………………………………

…………………………………………………………………………………………

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

(iii) Deduce the structure of **X**. Calculate the number of protons, neutrons and electrons in a monomer of **X**.

[2]

(b) Group 1 metal azides, **M**N_3, can be formed by passing heated dinitrogen oxide, N_2O over their corresponding amines, **M**NH_2.

(i) Explain why lattice energies of Group 1 azides become less exothermic down the group.

…………………………………………………………………………………………

…………………………………………………………………………………………

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

(ii) Suggest why the azides become thermally more stable down the group.

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

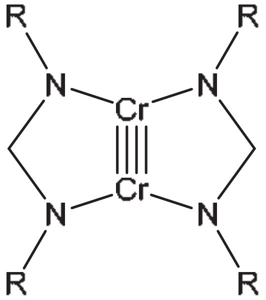
……………………………………………………………………………………………

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

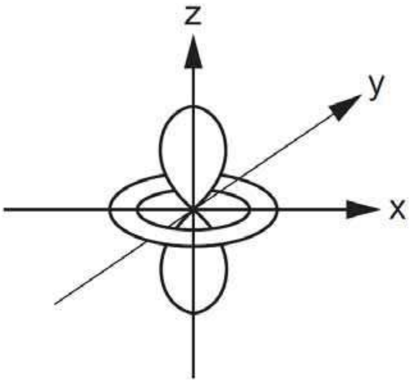
(c) Nitrogen has been used extensively in the research of compounds involving quadruple (bond order of 4) and quintuple (bond order of 5) bonds.

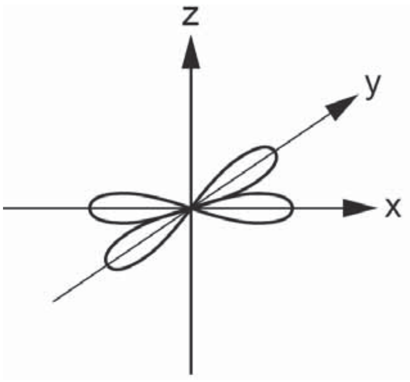
These compounds typically involve transition metal atoms that are able to form bonds between themselves using their d orbitals.

An example is given below:

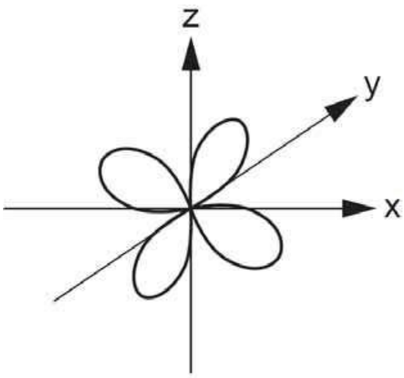


(i) Sketches of the shapes of the atomic orbitals from the d subshells are shown below, in random order. Name and label **each** orbital.

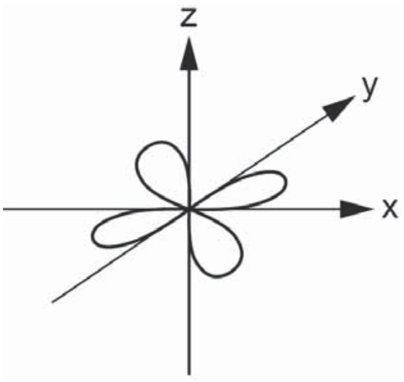




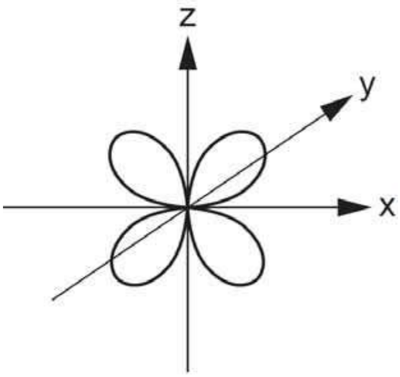
……………….. ………………..



………………



………………



………………

[2]

(ii) The d orbitals of an atom can overlap with d orbitals of the same type to form pi (π) and delta (δ) bonds. While a single sigma (σ) bond involves the overlap of two orbital lobes in total, and a single pi (π) bond four lobes, a single delta (δ) bond involves the overlap of eight lobes in total. When two atoms overlap, the z-axis is used to define the internuclear axis.

Suggest two different d orbitals that could be involved in delta bonds (δ).

………………………………………………………………………………………………

[1]

[Total: 10]

2 *Use of Data Booklet is relevant to this question.*

Aerozine 50 is a 50/50 mix of UDMH, $(CH_3)_2N_2H_2$ and hydrazine, N_2H_4. It is used as a rocket fuel, and is typically mixed with dinitrogen tetroxide, N_2O_4, as the oxidising agent.

The equation for the reaction between UDMH and dinitrogen tetroxide under standard conditions is given as follows:

$(CH_3)_2N_2H_2(l) + 2N_2O_4(g) \rightarrow 2CO_2(g) + 3N_2(g) + 4H_2O(l)$ ---------- **reaction 1**

(a) Suggest an equation, including state symbols, for the reaction between hydrazine and dinitrogen tetroxide under standard conditions.

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

[1]

(b) An experiment was set up such that hydrazine in a spirit burner was combusted beneath a copper can filled with water. It was found that 0.50 g of hydrazine was required to raise the temperature of 100 cm^3 of water in the can by 15 ºC.

Using relevant data from the *Data Booklet* and the information given below, calculate the efficiency of the system, expressed as a percentage.

- The heat capacity of the copper can be taken to be 96.0 J K^{-1}
- The density of water can be taken to be 1.00 g cm^{-3}.
- The standard enthalpy change of combustion of hydrazine, found using a bomb calorimeter, has a value of –628 kJ mol^{-1}.

[3]

Pure UDMH, $(CH_3)_2N_2H_2$, can be used as an alternative to *Aerozine 50* in thruster rockets.

(c) Using relevant data from the *Data Booklet* and the information given below, construct an energy cycle to calculate the enthalpy change for **reaction 1**.

$(CH_3)_2N_2H_2(l) + 4O_2(g) \rightarrow 2CO_2(g) + N_2(g) + 4H_2O(l)$	-1980 kJ mol^{-1}
$N_2O_4(g) \rightarrow 2N(g) + 4O(g)$	$+1930$ kJ mol^{-1}

[3]

(d) The total mass of propellant (UDMH and dinitrogen tetroxide, N_2O_4) used in the thruster rockets in the ascent stage of a lunar module was 366 kg.

Assuming that UDMH (M_r = 60.0) and dinitrogen tetroxide (M_r = 92.0) were mixed according to the stoichiometric ratio, calculate the mass of UDMH in the propellant mixture.

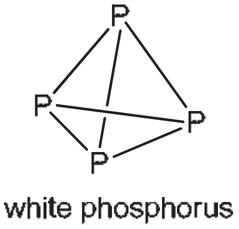
[1]

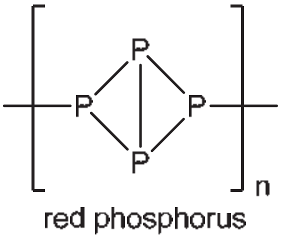
[Total: 8]

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

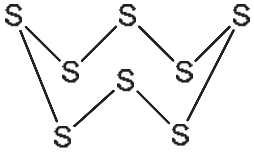
Phosphorus and sulfur are elements in Period 3 in the Periodic Table and each can exist in various allotropic forms.

Phosphorus can exist as white phosphorus and red phosphorus. White phosphorus exists as a tetrahedron with bond angle 60° while red phosphorus exists as a polymeric chain of regular tetrahedrons.


white phosphorus


red phosphorus

Sulfur, on the other hand is thermodynamically most stable at room temperature as rhombic sulfur, which consists of puckered S_8 rings.



Both elements form a wide range of compounds with the halogens.

(a) **(i)** By considering the bond angles involved, suggest why white phosphorus is less stable than red phosphorus.

……………………………………………………………………………………………..

……………………………………………………………………………………………..

……………………………………………………………………………………………..

[1]

(ii) The phosphorus halides fume in air because of reaction with water vapour.

Explain briefly why phosphorus(V) chloride can react with water. Write a balanced equation for its reaction.

……………………………………………………………………………………………..

……………………………………………………………………………………………..

……………………………………………………………………………………………..

……………………………………………………………………………………………..

……………………………………………………………………………………………..

[2]

(b) When sulfur is heated under pressure with chlorine, the major product is SCl_2.

$$S_8(g) + 8Cl_2(g) \rightarrow 8SCl_2(g)$$

(i) Using data from the *Data Booklet*, calculate the enthalpy change, ΔH, for this reaction.

[2]

Under suitable conditions, SCl_2 reacts with water to produce a yellow precipitate and a solution **X**. Solution **X** contains a mixture of SO_2(aq) and compound **Y**.

(ii) By constructing an equation for the hydrolysis of SCl_2, work out how the oxidation number of sulfur changes during the reaction.

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

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

(iii) Hence, suggest a pH value of the resultant solution formed.

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

(iv) Using relevant data from the *Data Booklet*, suggest what would be observed when acidified potassium dichromate is added to a sample of solution **X**.

……………………………………………………………………………………………

……………………………………………………………………………………………

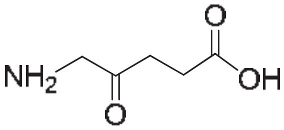
……………………………………………………………………………………………

……………………………………………………………………………………………

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

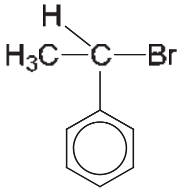
[Total: 10]

4 Aminolevulinic acid is involved in the synthesis of haemoglobin and chlorophyll.



aminolevulinic acid

(a) Aminolevulinic acid reacts readily with (1-bromoethyl)benzene.

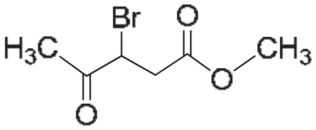


(1-bromoethyl)benzene

Name and outline the mechanism for the reaction of aminolevulinic acid with (1-bromoethyl)benzene.

[3]

(b) Compound **A** is a precursor in the synthesis of aminolevulinic acid.



compound **A**

Suggest a simple chemical test to distinguish between compound **A** and aminolevulinic acid. Include clearly the reagents, conditions and observations for each compound. Write a balanced equation for any positive test.

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

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

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

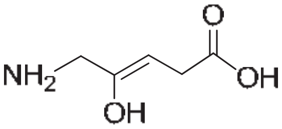
……………………………………………………………………………………………………

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

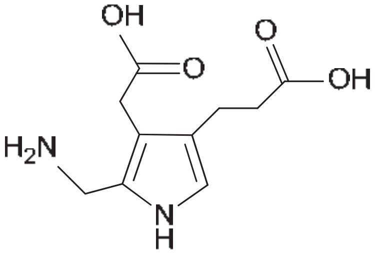
……………………………………………………………………………………………………

[3]

(c) Porphobilinogen is a pyrrole involved in porphyrin metabolism. It is generated from a reduced form of aminolevulinic acid, compound **B** by the enzyme ALA dehydratase.



compound **B**



porphobilinogen

Show how porphobilinogen may be formed from the condensation of two molecules of compound **B**, with the help of a balanced equation. Indicate clearly with dotted lines how the non-organic by-products are formed.

[2]

[Total: 8]

5 The formation of carbon-carbon bonds is important in the synthesis of large organic compounds. This question discusses the chemistry of some carbon-carbon bond forming reactions.

(a) Most of the starting reagents of such reactions typically involve a halogenoalkane. Halogenoalkanes can be obtained by reacting alkenes with hydrogen halides.

(i) Name and outline the mechanism of the reaction between 2-methylbut-2-ene and hydrogen chloride, showing the major product formed.

[2]

(ii) 2-methylbut-2-ene can also react with hydrogen bromide and hydrogen iodide to form its respective halogenoalkane.

Suggest and explain, with reference to the mechanism of the reaction, how the rate of reaction changes from HC*l* to HI.

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

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

(b) Depending on the conditions of the reaction, a nitrile group can be introduced into an organic compound through either a halogenoalkane or a carbonyl, forming carbon-carbon bonds in the process.

(i) Suggest why alkenes are unable to react to form nitriles in the same way as carbonyls.

…………………………………………………………………………………………

…………………………………………………………………………………………

…………………………………………………………………………………………

[1]

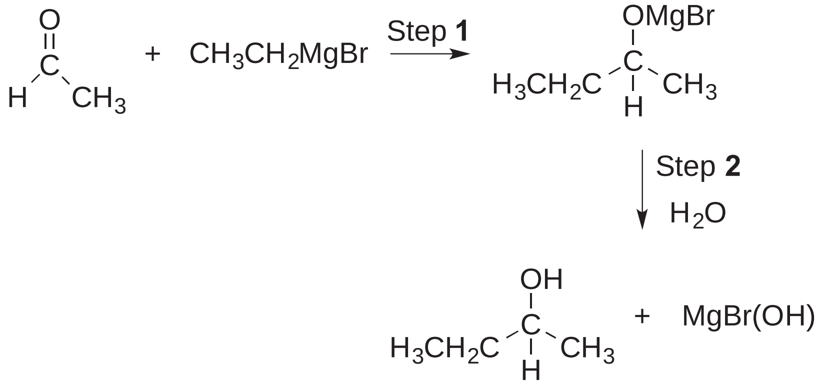
(ii) Propose a synthetic route that is **less than 5 steps** to convert butanal to pentanoic acid. State the reagents and conditions you would use for each step and draw the structures of the intermediate compounds.

[5]

(c) A classic carbon-carbon bond formation reaction is the Grignard reaction. First, the Grignard reagent, an alkylmagnesium halide, is formed by reacting a halogenoalkane with magnesium.

$$CH_3CH_2Br + Mg \rightarrow CH_3CH_2MgBr$$

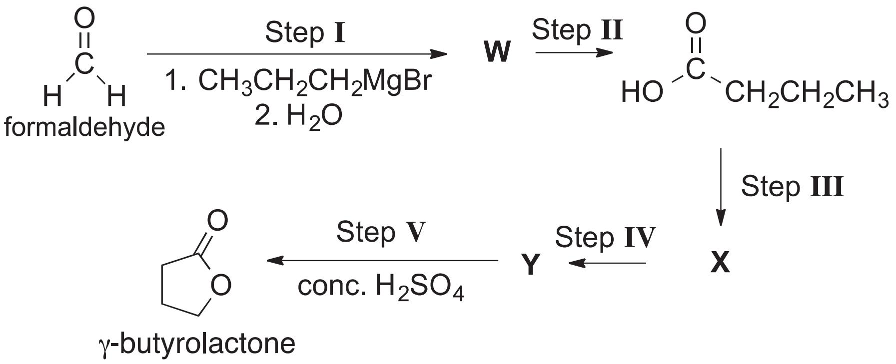
The reaction then proceeds with a reaction between the alkylmagnesium halide with a carbonyl to give an alcohol in a 2-step reaction.



(i) Suggest the type of mechanism for step **1**.

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

(ii) The synthesis of γ-butyrolactone, a common solvent from formaldehyde, involves the Grignard reaction as follows.



Propose structures of **W**, **X** and **Y**.

W	**X**

Y

[3]

(iii) State the reagents and conditions required for steps **II**, **III** and **IV**.

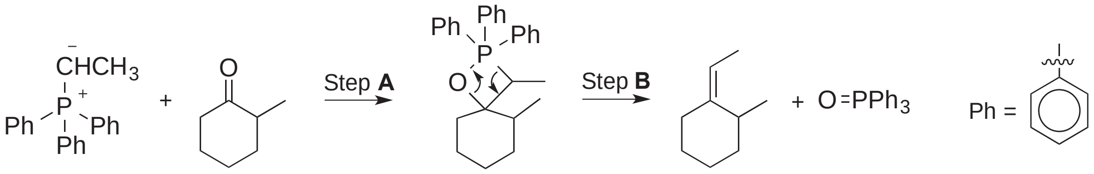
Step **II**: ……………………………………………………………………………..

Step **III**: ……………………………………………………………………………

Step **IV**: ……………………………………………………………………………

[3]

(d) Another common carbon-carbon bond formation reaction is the Wittig reaction. A phosphorus-containing reagent reacts with a carbonyl to form an intermediate, which then cleaves quickly to give an alkene.



(i) Identify, with the aid of a diagram, the type of stereoisomerism that the product can show.

[2]

(ii) By considering the hybridisation of relevant carbon atoms, suggest a reason why step **B** is a fast reaction.

…………………………………………………………………………………

…………………………………………………………………………………

…………………………………………………………………………………

…………………………………………………………………………………

[2]

[Total: 21]

6 **(a)** 1.0 cm^3 of 0.10 mol dm^{-3} solution of sodium iodide was added to 1.0 cm^3 of 0.050 mol dm^{-3} $AgNO_3(aq)$. 3.0 cm^3 of 1.0 mol dm^{-3} $NH_3(aq)$ was then added. The resulting precipitate formed is virtually insoluble.

(i) Show that the number of moles of $I^-(aq)$ that is **not** used to form the precipitate is 5.0×10^{-5} mol.

[1]

(ii) Show that under these conditions $[I^-(aq)] = 0.010$ mol dm^{-3} and hence $[Ag^+(aq)]$ which would just allow the precipitate to dissolve.

$K_{sp}(AgI) = 8.0 \times 10^{-17}$ mol^2 dm^{-6}

[1]

(iii) Under the conditions of the experiment, $[Ag^+(aq)] = 1.9 \times 10^{-9}$ mol dm^{-3}. Use your answer in **(a)(ii)** to justify why the precipitate is virtually insoluble.

…………………………………………………………………………………………

…………………………………………………………………………………………

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

(iv) When the above experiment is repeated using sodium chloride instead of sodium iodide, different observations were made. Briefly describe and explain the differences with the aid of equations. **No** calculations are required.

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

[3]

(b) The standard electrode potential values for reactions **(I)** and **(II)** are +1.21 V and +0.54 V respectively.

$IO_3^- + 6H^+ + 5e^- \rightleftharpoons \frac{1}{2}I_2 + 3H_2O$ **(I)**

$\frac{1}{2}I_2 + e^- \rightleftharpoons I^-$ **(II)**

(i) Find the standard Gibbs free energy change for **each** of the reactions **(I)** and **(II).**

[1]

(ii) Use your answers from **(b)(i)** to find the standard Gibbs free energy change for the following reaction, and hence its standard electrode potential.

$IO_3^- + 6H^+ + 6e^- \rightleftharpoons I^- + 3H_2O$

[2]

(c) When 0.530 g of potassium iodide was completely reacted with an aqueous solution of XeF_2, all the iodide is converted into the iodate anion. A student proposed that the anion could be either iodate(V), IO_3^-, or iodate(VII), IO_4^-.

(i) Show that the number of moles of iodate that were involved in the reaction is 3.19×10^{-3} mol.

[1]

(ii) The equation involving the reaction of iodate(VII), IO_4^- with excess acidified potassium iodide is given below:

$IO_4^- + 8H^+ + 7I^- \rightarrow 4I_2 + 4H_2O$

For the reaction involving iodate(V), IO_3^- with excess acidified potassium iodide, write the corresponding half equations and hence the overall **ionic** equation.

Reduction: …………………………………………………………………………………..

Oxidation: ………………………………………………………………………………….

Overall ionic equation:

…………………………………………………………………………………………………

[3]

(iii) 3.19 x 10^{-3} mol of iodate anion, which is either iodate(V), IO_3^-, or iodate(VII), IO_4^- is acidified, and added to excess potassium iodide solution where iodine is formed. It is found that 28.40 cm^3 of 0.900 mol dm^{-3} of $Na_2S_2O_3$ is required to discharge the colour of iodine.

It is given that $I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-}$.

By using the information and your answers in **(c)(ii)**, determine whether the anion is iodate(V), IO_3^-, or iodate(VII), IO_4^-.

[2]

(d) Nitrogen trifluoride was first prepared in the electrolysis of a molten mixture of ammonium fluoride and hydrogen fluoride using inert electrodes.

(i) It is given that at one of the electrodes, the following reaction occurs:
$NH_4^+ + 3F^- \rightarrow NF_3 + 4H^+ + 6e^-$

State the electrode that is involved in the above reaction and its polarity.

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

(ii) When the above electrolysis was set up using a current of 0.50 A, 0.276 g of nitrogen trifluoride was liberated. Calculate the time taken for the electrolysis to occur.

[2]

[Total: 18]

Section A

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

1 **(a)** Ethanoic acid and its salt, sodium ethanoate, is often used as an acid buffer to help extend the shelf-life of food products such as meat, fish and dairy.

A buffer solution of pH 5.5 was prepared by mixing 0.200 mol dm^{-3} of ethanoic acid and 0.200 mol dm^{-3} aqueous sodium ethanoate.

(K_a of ethanoic acid = 1.74×10^{-5} mol dm^{-3})

(i) What do you understand by the term *buffer solution*? [1]

(ii) Calculate the ratio of $\frac{[\text{ethanoate}]}{[\text{ethanoic acid}]}$ required to prepare the above buffer solution.

Hence deduce whether the above buffer is more effective in buffering against added acids or bases.

Write an equation to illustrate your answer. [3]

(iii) Calculate the volume of ethanoic acid and that of aqueous sodium ethanoate required to prepare 60 cm^3 of the above buffer. [1]

(iv) The boiling points of the components in the buffer are as shown.

Ethanoic acid	118 °C
Sodium ethanoate	881 °C

With reference to the structure and bonding present in the compounds, account for the difference in the boiling points. [3]

(b) The limestone that collects in kettles in hard water areas is mainly calcium carbonate. It can be removed fairly harmlessly by using a warm solution of vinegar, which contains ethanoic acid. The limestone dissolves with fizzing and a solution of calcium ethanoate remains.

(i) Write a balanced equation for the reaction between ethanoic acid and calcium carbonate. [1]

When the solution in **(b)** is evaporated and the resulting solid calcium ethanoate is heated strongly in a test-tube, an organic compound **Q** is formed, which condenses to a colourless liquid. The residue in the tube contains calcium carbonate.

When 0.10 g of compound **Q** was injected into a gas syringe at a temperature of 383 K and a pressure of 101 kPa, 55 cm^3 of vapour were produced.

(ii) Calculate the relative molecular mass of **Q**. [2]

(iii) Compound **Q** is neutral and water-soluble. **Q** does not react with sodium metal nor with Fehling's solution but it does react with alkaline aqueous iodine.

Suggest a structural formula for **Q.** Justify your answer by reference to these properties of **Q**. [4]

(iv) Construct a balanced equation for the formation of **Q** by the action of heat on calcium ethanoate. [1]

(v) The residue calcium carbonate can also undergo thermal decomposition when heated very strongly. Copper(II) carbonate behaves in a similar manner when heated.

State which carbonate, calcium or copper(II) will have a higher decomposition temperature. Explain your answer, with the help of relevant data from the *Data Booklet*. [3]

[Total: 19]

2 **(a)** In a closed reaction vessel maintained at a high temperature, 1 mol of Al_2Cl_6 dimers dissociate into $AlCl_3$ according to the following equation.

$$Al_2Cl_6(g) \rightleftharpoons 2AlCl_3(g)$$

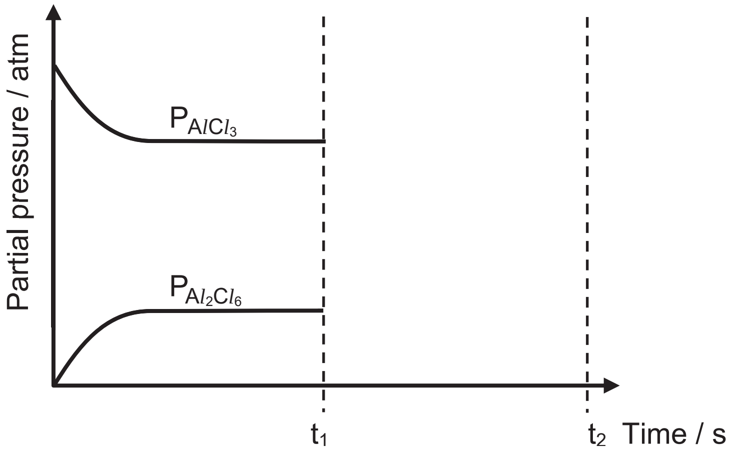
The average M_r of the equilibrium gas mixture is found to be 178.0.

(i) Given that the average M_r of the equilibrium gas mixture is the sum of the mole fractions of each gas, multiplied by the M_r of that gas, calculate the degree of dissociation of Al_2Cl_6, α. [3]

(ii) Write down the expression of K_p for the above equilibrium system. Hence, show that $K_p = K_cRT$. [2]

(iii) An experiment on the dissociation of Al_2Cl_6 was conducted in a closed container of a fixed volume and the partial pressures of all the components were plotted as shown in the figure below.

Copy and complete the diagram to show how the partial pressure of each gas changes when the volume of the container is halved at t_1 until t_2.



[2]

(b) Strontium chloride, $SrCl_2$ is a typical salt which forms neutral aqueous solutions. It emits a bright red colour in a flame and this allows it to be used as a source of redness in fireworks.

Use the data below to answer the questions that follow.

Standard Gibbs free energy change of solution of $SrCl_2$(s)	–41.6 kJ mol^{-1}
Standard enthalpy change of formation of $SrCl_2$(s)	–828.9 kJ mol^{-1}
Standard enthalpy change of formation of Sr^{2+}(aq)	–545.8 kJ mol^{-1}
Standard enthalpy change of formation of Cl^-(aq)	–167.5 kJ mol^{-1}
Standard enthalpy change of hydration of Sr^{2+}(g)	–1446 kJ mol^{-1}
Standard enthalpy change of hydration of Cl^-(g)	–378 kJ mol^{-1}

(i) Define the term *standard enthalpy change of formation* of strontium chloride. [1]

(ii) Calculate $\Delta H^{\ominus}_{sol}$ and $\Delta S^{\ominus}_{sol}$ of strontium chloride. [4]

(iii) Write an equation to show the relationship between the lattice energy of strontium chloride and $\Delta H^{\ominus}_{sol}$ of strontium chloride. Hence, calculate the lattice energy of strontium chloride. [2]

(iv) Predict with reasoning, how Gibbs free energy change of formation of strontium chloride, ΔG_f will change with increasing temperature. [2]

(c) Using the data given below, draw a labelled energy cycle to calculate the enthalpy change of combustion of solid carbon.

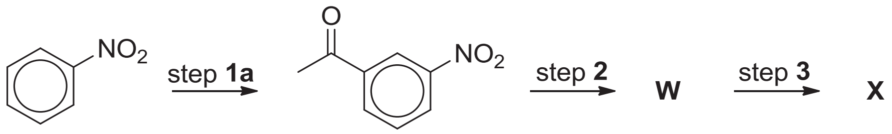
$2SrO(s) \rightarrow 2Sr(s) + O_2(g)$ $\Delta H = +1184$ kJ mol^{-1}

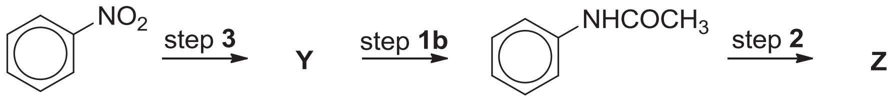
$SrO(s) + CO_2(g) \rightarrow SrCO_3(s)$ $\Delta H = -234$ kJ mol^{-1}

$2SrCO_3(s) \rightarrow 2Sr(s) + 2C(s) + 3O_2(g)$ $\Delta H = +2440$ kJ mol^{-1} [4]

[Total: 20]

3 **(a)** Consider the following synthesis pathways starting from nitrobenzene:





(i) Ethanoyl chloride (CH_3COCl) is used as a reactant for step **1a** and step **1b** but under different conditions. State the reaction mechanism that occurred for each step **1a** and **1b** and hence explain the difference in the conditions required. [3]

(ii) Identify the reagents and conditions required for **steps 2** and **3** and hence draw the structures of **W, X, Y** and **Z**.

[Note: **Steps 2** and **3** in both pathways each refers to the same set of reagents and conditions.] [6]

(iii) Compare the relative basicity of **Y** and **Z**. [2]

(b) In an isolated atom, the five d orbitals have the same energy. When a transition element ion is in an octahedral complex, the d orbitals are split into two groups of different energy levels.

(i) Draw an orbital energy diagram to show this, indicating the type of orbitals in each group. [2]

(ii) Use your diagram in **(b)(i)** to explain why transition element complexes like $Co(H_2O)_6^{2+}$ are often colored. [2]

(c) Aqueous cobalt(II) chloride, $CoCl_2$ is a pink solution which gives the following reactions.

$$CoCl_2(aq) \xrightarrow{NaOH(aq)} \text{blue ppt. insoluble in excess} \xrightarrow{H_2O_2} \text{blue ppt. turned brown}$$

$$CoCl_2(aq) \xrightarrow{HCl(aq)} \text{no observable change} \xrightarrow{H_2O_2} \text{no observable change}$$

(i) By using the data given below and appropriate values from the *Data Booklet*, calculate $E^\ominus_{cell}$ and explain the differences in the observations made between **acidic** and **alkaline** medium.

$$Co(OH)_3 + e^- \rightleftharpoons Co(OH)_2 + OH^- \qquad E^\ominus = +0.17\text{ V}$$

Write equations to account for the observations. [4]

(ii) When brine solution instead of HCl was added to $CoCl_2(aq)$, the solution turned from pink to blue. In this reaction, cobalt behaves like a transition element.
Suggest by means of an ionic equation, an explanation for this observation.
[2]

[Total: 21]

Section B

Answer **one** question from this section.

4 **(a)** The kinetics of the acid–catalysed hydrolysis of ethyl ethanoate may be investigated by analysing samples of the reaction mixture at different times.

$$CH_3CO_2CH_2CH_3 + H_2O \overset{H^+ \text{ (catalyst)}}{\rightleftharpoons} CH_3CO_2H + CH_3CH_2OH$$

In one such experiment, the reaction mixture was prepared by mixing solutions of ethyl ethanoate and hydrochloric acid. The concentration of hydrochloric acid, which serves as the catalyst, can be assumed to stay constant throughout the reaction.

At different times, 10.0 cm^3 portions of the reaction mixture were pipetted, quenched and titrated with 0.200 mol dm^{-3} NaOH(aq).

After all necessary samples have been drawn, the remaining reaction mixture is then heated for ½ h to ensure complete reaction. The volume of NaOH required for titrating a 10.0 cm^3 sample of the resulting solution is 30.00 cm^3.

The following experimental data were obtained:

Time / min	Volume of NaOH required for titration, V / cm^3	$30.00 - V$ / cm^3
0	20.00	10.00
10	24.40	5.60
20	26.90	3.10
30	28.20	1.80
40	29.00	1.00
50	29.40	0.60

(i) State how each of the quantities, V and $(30 - V)$, is related to the concentration of the components of the reaction mixture at any point in time. [1]

(ii) Hence, choose appropriate data from the above table to plot a graph that will allow you to determine the order with respect to ethyl ethanoate. [2]

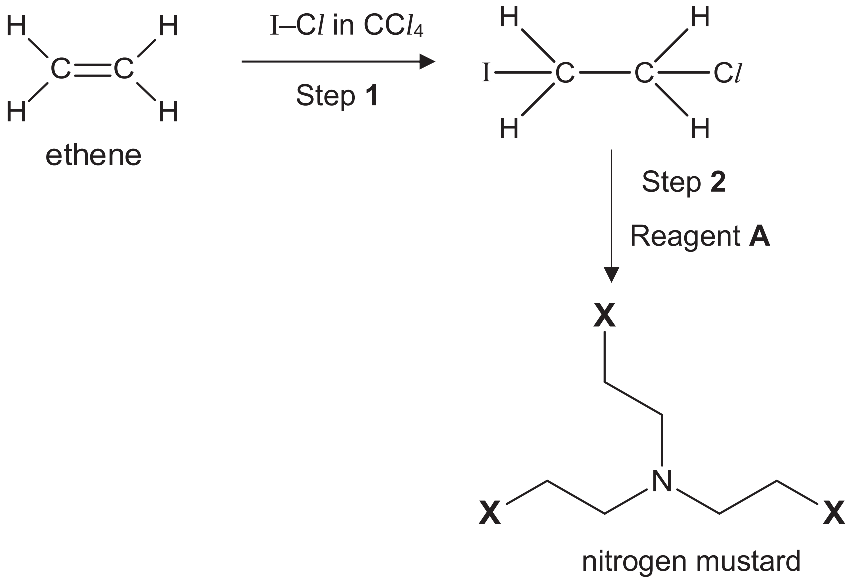
(iii) Deduce the order with respect to ethyl ethanoate, justifying your answer by showing construction lines clearly on your graph. [2]

(iv) Hydrolysis of $CH_3CO_2CH_2CH_3$ can also be catalysed by esterase, an enzyme found in the liver.

Sketch a graph to show how, for a constant [esterase], the rate of hydrolysis varies with [$CH_3CO_2CH_2CH_3$] and explain the shape of the graph. [2]

(b) Nitrogen mustard gas is commonly used in chemotherapy.

It was suggested that the synthesis of nitrogen mustard can be carried out via the following pathway:

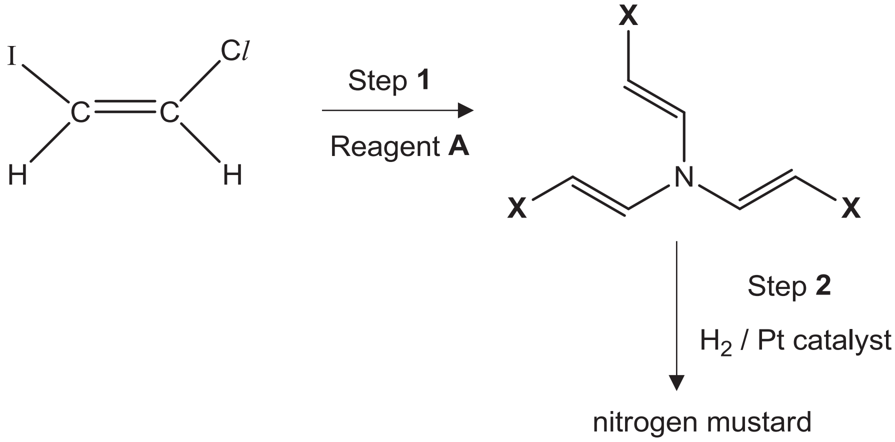


X in nitrogen mustard could be either C*l* or I.

(i) Suggest the identity of reagent **A** and the conditions necessary for an optimal yield in Step **2**. [1]

(ii) Is **X** in nitrogen mustard more likely to be C*l* or I? Explain your answer. [2]

(iii) Another reaction pathway was suggested for the synthesis of nitrogen mustard, with reagent **A** used for the first step:



Explain why this method of synthesis is likely to fail. [2]

(c) Compound **K** is a solid with the formula, $C_4H_9NO_3$. It dissolves in water to form a solution with high electrical conductivity. When **K** was warmed with aqueous sodium hydroxide, a colourless pungent gas was evolved. Acidification of the resulting solution gives **L**, $C_4H_6O_3$.

L gives an orange precipitate with 2,4-dinitrophenylhydrazine. When lithium aluminium hydride was added to **L**, **M**, $C_4H_{10}O_2$, was produced.
M can also be obtained from the oxidation of **N**, C_4H_8 by cold alkaline potassium manganate(VII).

Deduce the structures of compounds **K**, **L**, **M** and **N** and explain the reactions described. [8]

[Total: 20]

5 **(a)** The reaction between bromide and bromate(V) ions in acid solution is represented as follows:

$$5Br^- + BrO_3^- + 6H^+ \rightarrow 3Br_2 + 3H_2O$$

The reaction between Br^- and BrO_3^- is relatively fast, with Br_2 produced almost immediately after the reactants are mixed.

To measure the initial rate of the reaction, aqueous Br^- is added to acidified BrO_3^- solution containing a small amount of compound **A** and methyl orange indicator. The initial colour of the methyl orange is pink as the solution is acidic. After some time, the pink colour disappears due to the bleaching action of Br_2 as shown:

$$\underset{}{Br_2} + \underset{\text{pink}}{\text{methyl orange (acid form)}} \rightarrow \underset{\text{colourless}}{\text{bleached methyl orange}} + 2Br^-$$

The time taken for the pink colour to disappear is an indication of the initial rate.

(i) Compound **A** is added to delay the disappearance of the pink colour, which would otherwise take place too quickly for effective measurement of time.

Given that compound **A** is an acidic organic compound containing only **one** functional group, suggest a suitable identity for compound **A**. [1]

(ii) Explain, with the aid of an equation, why the compound mentioned in your answer to **(i)** would be effective in delaying the disappearance of the pink colour. [2]

(iii) To find the order of reaction with respect to H^+, a total of five experiments are conducted.

In all the experiments, 10.0 cm^3 of KBr(aq), 10.0 cm^3 of $KBrO_3$(aq), 5.0 cm^3 of Compound **A** solution and 2 drops of methyl orange indicator are used, with water added to keep the total volume constant. The volume of H_2SO_4(aq) used and other experimental data for each experiment are shown in the table below:

Experiment No.	Volume of H_2SO_4(aq), V / cm^3	V^2 / cm^6	Time taken for colour to change from pink to colourless, t / s	$\frac{1}{t}$ / s^{-1}
1	30.0	900	10.0	0.100
2	25.0	625	14.4	0.069
3	20.0	400	22.5	0.044
4	15.0	225	40.0	0.025
5	10.0	100	90.0	0.011

Choose appropriate data from the table above to plot a graph that will enable you to determine the order of reaction with respect to H^+. [2]

(iv) State, with justification, the order of reaction with respect to H^+. [1]

(b) Champagne is an example of *sparkling wine*, a term referring to wine with significant levels of carbon dioxide in it, making it fizzy. In the traditional method of production, wine is allowed to undergo a natural fermentation after bottling, which involves conversion of the malic acid present into lactic acid:

$$\underset{\text{malic acid}}{HO_2CCH_2CH(OH)CO_2H} \rightarrow \underset{\text{lactic acid}}{CH_3CH(OH)CO_2H} + CO_2$$

(i) A bottle typically has a total capacity of 1.5 dm^3 and contains 1.3 dm^3 of wine with a malic acid concentration of 0.05 mol dm^{-3}.

By means of the ideal gas equation, calculate the pressure exerted inside the air gap of the bottle by the carbon dioxide produced when all the malic acid present undergoes fermentation.

Assume that the temperature inside the bottle is 25°C. [2]

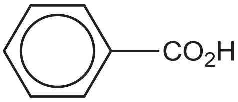
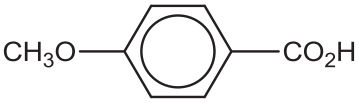
(ii) In fact, the pressure inside the bottle is much less under these conditions. Suggest why the actual pressure differs from the value calculated in **(i)**. [1]

(iii) Besides malic acid, many other organic acids also play an important role in our everyday life. For instance, acrylic acid, with the structure $CH_2{=}CHCO_2H$, is the starting material for the production of many plastics and adhesives industrially.

State the reagents and conditions that can be used to synthesize acrylic acid from lactic acid in the laboratory. [1]

(iv) Another example of an organic acid is benzoic acid which is commonly used as a food preservative.

The K_a values of benzoic acid and its substituted derivative, 4–methoxybenzoic acid are given below:

Compound	**K_a / mol dm^{-3}**
 Benzoic acid	6.5×10^{-5}
 4–methoxybenzoic acid	3.5×10^{-5}

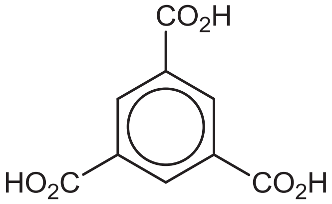
Explain the difference in the K_a values of the two acids. [2]

Need a home tutor? Visit smiletutor.sg

(c) Compound **P** is an aromatic compound with molecular formula $C_{12}H_{15}O_3Cl$. It reacts with exactly 2 mol of PCl_5 to form an organic product **Q**. **P** also gives a brick–red precipitate with Fehling's solution.

Upon heating **P** with alcoholic NaOH, only one of the products formed, **R**, has the molecular formula $C_{12}H_{14}O_3$.

On oxidation with hot acidified potassium manganate(VII) solution, **R** gives **S**, $C_2H_4O_2$, and the following compound:



Suggest the structures of **P**, **Q**, **R** and **S**, explaining the reactions involved. [8]

[Total: 20]

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

1 Determination of the M_r of a carbonate salt

FA 1 is a solid carbonate, **X**CO_3.

FA 2 is a solution containing 1.00 mol dm^{-3} of hydrochloric acid, HC*l*.

FA 3 is a solution of NaOH of concentration 0.100 mol dm^{-3}.

In this question, you will perform a titration. The data from this titration will be used to determine

- the amount of CO_3^{2-} ions in the mass of **FA 1** used,
- the M_r of **X**CO_3 and hence the identity of the metal **X**.

(a) Titration of FA 4 against FA 3

(i) You are to determine the amount of carbonate ions, CO_3^{2-}, in **FA 1,** by back titration after some **FA 2** has been added to it. Carry out the procedure as listed below.

1. Weigh accurately between 1.25 – 1.35 g of **FA 1** into a clean and dry 150 cm^3 beaker. If you have used the TARE facility on the balance, indicate clearly in your recording.
2. Record your weighing in an appropriate format in the space provided on the next page.
3. Measure out 50 cm^3 of **FA 2** into a measuring cylinder. Pour this into the beaker containing **FA 1.** Stir thoroughly to ensure all of **FA 1** has dissolved.
4. Quantitatively transfer the mixture into a 250 cm^3 volumetric flask. Make up to the mark with distilled water. Shake to obtain a homogeneous solution. Label this solution **FA 4.**
5. Pipette 25.0 cm^3 of **FA 4** into a conical flask and add 2 drops of methyl orange indicator.
6. Fill the burette with **FA 3.**
7. Titrate **FA 4** with **FA 3.**
8. Repeat the titration as many times as you consider necessary to obtain accurate results.
9. Record your titration results in the space provided on the next page. Make certain that your recorded results show the precision of your working.

Results:

*For weighing of **FA 1***

Titration

[6]

(ii) From your titrations, obtain a suitable volume of **FA 3** to be used in your calculations. Show clearly how you obtained this volume.

volume of **FA 3** = ………………….. [1]

(b) **(i)** Calculate the amount of excess acid pipetted into the conical flask.

amount of excess acid in the conical flask = …………………… [1]

(ii) Calculate the total amount of excess acid in the volumetric flask.

amount of excess acid in the volumetric flask = …………………… [1]

(iii) Hence calculate the amount of acid that has reacted with the carbonate that you have weighed out.

amount of acid reacted = …………………….. [1]

(iv) Use your answer in **b(iii)** to calculate the M_r of **X**CO_3.

M_r of **X**CO_3 = ……………………..

Deduce the identity of metal **X**.
Show your working.

[A_r: C, 12.0; O, 16.0; H, 1.0; Be, 9.0; Mg, 24.3; Ca, 40.1; Sr, 87.6; Ba, 137.3]

X is ………………………………… [3]

(c) Planning

Sodium carbonate, Na_2CO_3, does **not** decompose on heating with a Bunsen burner. Sodium hydrogencarbonate, $NaHCO_3$, decomposes on heating.

$$2NaHCO_3(s) \rightarrow Na_2CO_3(s) + H_2O(g) + CO_2(g)$$

You are to design an experiment in which the percentage by mass of $NaHCO_3$ in a mixture of $NaHCO_3$ and Na_2CO_3 can be determined by heating and weighing alone.

The only apparatus available consists of:

a boiling tube and holder
a chemical balance
a Bunsen burner
a heat proof mat

You are to show how you would use the results of this experiment to determine the percentage by mass of $NaHCO_3$ in the mixture.

(i) Outline, step by step, the practical sequence for the method you would use to:

- make appropriate weighings,
- decompose the sodium hydrogencarbonate in the mixture by heating,
- ensure that the decomposition was complete.

…………………………………………………………………………………………

…………………………………………………………………………………………

…………………………………………………………………………………………

…………………………………………………………………………………………

…………………………………………………………………………………………

…………………………………………………………………………………………

…………………………………………………………………………………………

…………………………………………………………………………………………

…………………………………………………………………………………………

…………………………………………………………………………………………

…………………………………………………………………………………………

…………………………………………………………………………………………

…………………………………………………………………………………………

…………………………………………………………………………………………

……………………………………………………………………………………… [3]

(ii) By considering the products of the decomposition, suggest a reason why a crucible, without a lid, might be more appropriate than a boiling tube for this experiment.

………………………………………………………………………………………….

……………………………………………………………………………………… [1]

(iii) Prepare a table to show the masses you would measure and record during the experiment. Include in your table any other masses you would calculate from the experimental results to enable you to determine the percentage by mass of $NaHCO_3$ in the mixture.

Insert in your table the letters **A**, **B**, **C** etc. to represent each mass. Use these letters to show how your calculated masses are obtained e.g. **B** – **A**.

[2]

(iv) Use the letters you have entered in **(c)(iii)** to show how you would process the results to find:

- the mass of $NaHCO_3$ in the mixture,

[A_r: C, 12.0; H, 1.0; O, 16.0; Na, 23.0]

- the percentage by mass of $NaHCO_3$ in the mixture.

[2]

[Total: 21]

2 Determination of the concentration of a mixture of acids and the enthalpy change of neutralization

FA 5 is an aqueous solution prepared by mixing equal volumes of y mol dm^{-3} hydrochloric acid, HC*l*, and y mol dm^{-3} sulfuric acid, H_2SO_4.

FA 6 is 1.60 mol dm^{-3} sodium hydroxide, NaOH.

Take care as aqueous solutions of sodium hydroxide are corrosive.

When an acid is run into an alkali, an exothermic reaction takes place and the temperature of the mixture increases until the end–point is reached. If acid is added beyond the end–point, the temperature will decrease as no further reaction takes place and the acid is at a lower temperature than the mixture.

You are to follow the neutralisation of the acids in **FA 5** by measuring the temperature as volumes of **FA 5** are added in regular portions from a burette to a fixed volume of **FA 6** placed in a Styrofoam cup.

The data obtained will enable you to determine the value of y and the enthalpy change of neutralization, ΔH_{neut}, of this acid–base 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 5**:

- Total volume of **FA 5** added from the burette up to the point in time
- Total volume of solution in the cup (V_{cup})
- Temperature measured (T)

You also need to calculate the corresponding values of:

- $\Delta T = T - T_0$, where T_0 is the initial temperature of **FA 6**
- ($V_{cup} \times \Delta T$) to 3 significant figures

1. Fill the burette to 0.00 cm^3 with **FA 5**.
2. Place the Styrofoam cup in a 250 cm^3 beaker to provide support for the cup. Use the measuring cylinder to place 40.0 cm^3 of **FA 6** into the cup and measure the steady temperature of the alkali, T_0.
3. Run 5.00 cm^3 of **FA 5** from the burette into the cup, stir the solution with the thermometer and record the maximum temperature, T.
4. **Immediately** run a further 5.00 cm^3 of **FA 5** from the burette into the cup, stir and record the maximum temperature as before.
5. Continue the addition of **FA 5** in 5.00 cm^3 portions 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) Experimental results

[3]

(ii) On the grid provided below, plot (V_{cup} × ΔT) against the total volume of **FA 5** added.

Draw a line of best fit for the points before the maximum value of (V_{cup} × ΔT).

Draw a second line of best fit for the points after the maximum value.

Extrapolate both lines until they meet.

[2]

(iii) Read from your graph the maximum value of (V_{cup} × ΔT) and the end–point volume of the titration.

maximum value of (V_{cup} × ΔT) = ……………………..

end–point volume = …………………….. [3]

(b) **(i)** Calculate the concentration of hydrogen ions in **FA 5**.

concentration of hydrogen ions = …………………….. [1]

(ii) Hence, determine the value of y, which is the concentration of either HCl or H_2SO_4 used to prepare **FA 5**.

y = ……………………… [1]

(c) **(i)** Determine the enthalpy change of neutralization of this reaction, ΔH_{neut}.

You should assume that the specific heat capacity of the final solution is 4.18 J g^{-1} K^{-1}, and that its density is 1.00 g cm^{-3}.

ΔH_{neut} = …………………….. [3]

(ii) Student **A** carefully performed the same experiment and correctly processed the data using the same method. His calculated value of ΔH_{neut} is –65.0 kJ mol^{-1} while the published value for this enthalpy change is –57.7 kJ mol^{-1}.

The specific heat capacity of the Styrofoam cup has not been taken into consideration in calculating ΔH_{neut}. Explain whether this omission could have been the reason for the discrepancy between the value obtained by Student **A** and the one published.

……………………………………………………………………………………..

……………………………………………………………………………………..

……………………………………………………………………………………..

……………………………………………………………………………………..

……………………………………………………………………………………..

…………………………………………………………………………………… [2]

(iii) Student **B** performed the same experiment but chose to plot ΔT instead of ($V_{cup} \times \Delta T$) on the y–axis.

He also drew and extrapolated two straight lines through the plotted points to do the calculations.

Suggest why his method is likely to yield **less** accurate results.

……………………………………………………………………………………..

……………………………………………………………………………………..

……………………………………………………………………………………..

…………………………………………………………………………………… [1]

[Total: 16]

3 Inorganic Analysis

(a) You are provided with the solid **FA 7** which contains one cation and one anion from the ions listed in the **Qualitative Analysis Notes**, and the solution **FA 8**.

You are to perform the tests below to identify the ions present in **FA 7** and to suggest the nature of the compound in **FA 8**.

If the evolution of a gas is observed at any stage, the gas should be tested and identified. Details of the test carried out, the observations of the test and the identity of the gas should be given with the observations.

If it appears that no reaction has taken place this should be clearly recorded.

Carry out the following tests on **FA 7** and **FA 8** and complete the table to show your observations.

	Test	Observations
(i)	To a spatula–full of **FA 7** in a test–tube add 3 cm depth of dilute sulfuric acid. Warm, and when the reaction has stopped, filter the mixture. Retain the filtrate for tests **(iii)** and **(iv)**.	
(ii)	Place a spatula–full of **FA 7** in a test–tube and heat strongly. Leave the tube to cool. Retain the residue for test **(viii)**.	
(iii)	To a 1 cm depth of the filtrate from **(i)** in a test–tube, add aqueous sodium hydroxide drop by drop until 1 cm depth of the reagent has been added. Then add a further 1 cm depth of the aqueous sodium hydroxide.	
	Swirl the test-tube and leave to stand for 2–3 minutes.	
(iv)	To a 1 cm depth of the filtrate from **(i)** in a test–tube, add aqueous ammonia drop by drop until 1 cm depth of the reagent has been added. Then add a further 1 cm depth of the aqueous ammonia.	
	Then **cautiously** add 1 cm depth of **FA 8**.	

(v)	Place 2 cm depth of aqueous potassium iodide in a test–tube and add 2 cm depth of **FA 8**.	
	Then add 2 cm depth of dilute sulfuric acid.	
(vi)	To a 1 cm depth of **FA 8** in a test–tube, add 1 cm depth of dilute sulfuric acid and 2 cm depth of potassium manganate(VII). Observe for 2 minutes or until no further change occurs.	
(vii)	To a 1 cm depth of aqueous sodium sulfite in a test–tube, add a few drops of aqueous barium nitrate.	
	Then add 2 cm depth of dilute nitric acid.	
	Immediately add 1 cm depth of **FA 8**.	
(viii)	Transfer a portion of the residue from test **(ii)** into a test–tube and add 2 cm depth of **FA 8**.	

[9]

(b) **(i)** From your observations, identify the cation and anion present in **FA 7**. Quote evidence from the table to support your conclusions.

Cation ………………………………

Evidence ……………………………………………………………………..

……………………………………………………………………..

Anion ………………………………

Evidence ……………………………………………………………………..

…………………………………………………………………… [2]

(ii) In tests **(a)(v)** and **(vii)**, **FA 8** behaves as ……………………………………...

In test **(a)(vi)**, **FA 8** behaves as …………………………………………….. [1]

(c) **Planning**

One of the transition metals, vanadium, was named after the Scandinavian goddess of beauty and fertility, Vanadis (Freya) due to the wide range of colours found in vanadium compounds.

Starting with an aqueous solution of VO_2^+, you are to devise a plan which will enable you to determine the colour exhibited by two other ions containing vanadium, VO^{2+} and V^{3+}. Your plan should only involve simple test–tube reactions.

The standard electrode potentials of the following ions are as shown:

$VO_2^+ + 2H^+ + e^- \rightleftharpoons H_2O + VO^{2+}$ $E^\ominus = +1.00$ V
$VO^{2+} + 2H^+ + e^- \rightleftharpoons H_2O + V^{3+}$ $E^\ominus = +0.34$ V
$V^{3+} + e^- \rightleftharpoons V^{2+}$ $E^\ominus = -0.26$ V

There are four reducing agents available as shown:

$Zn^{2+} + 2e^- \rightleftharpoons Zn$ $E^\ominus = -0.76$ V
$Sn^{2+} + 2e^- \rightleftharpoons Sn$ $E^\ominus = -0.14$ V
$O_2 + 2H^+ + 2e^- \rightleftharpoons H_2O_2$ $E^\ominus = +0.68$ V
$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$ $E^\ominus = +0.77$ V

(i) Explain which reducing agent(s) will **not** be suitable for determining the colours exhibited by VO^{2+} and V^{3+}.

……………………………………………………………………………………..

……………………………………………………………………………………..

……………………………………………………………………………………..

……………………………………………………………………………………..

…………………………………………………………………………………… [2]

(ii) Complete the table by choosing a suitable reducing agent for determining the colour exhibited by VO^{2+} and V^{3+} respectively. Justify your choice by calculating relevant $E^{\ominus}_{cell}$ values.

	Reducing agent	Justification
$VO_2^+ \rightarrow VO^{2+}$		
$VO_2^+ \rightarrow V^{3+}$		

[4]

[Total: 18]

VICTORIA JUNIOR COLLEGE
2017 JC2 PRELIMINARY EXAMINATIONS
H2 CHEMISTRY PAPER 1 ANSWERS

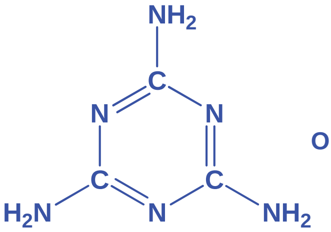
1	**B**	6	**B**	11	**B**	16	**D**	21	**C**	26	**C**
2	**B**	7	**A**	12	**B**	17	**A**	22	**B**	27	**A**
3	**A**	8	**D**	13	**A**	18	**C**	23	**B**	28	**D**
4	**D**	9	**D**	14	**D**	19	**C**	24	**D**	29	**A**
5	**C**	10	**B**	15	**C**	20	**A**	25	**D**	30	**C**

Victoria Junior College
2017 H2 Chemistry Prelim Exam 9729/2
Suggested Answers

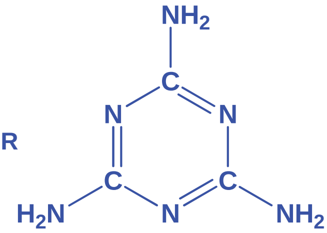
1 This question concerns some unusual nitrogen compounds.

(a) Heating monomer **X** to 150 °C produces the trimer, melamine, $C_3H_6N_6$. Melamine is a cyclic planar molecule and is symmetrical.

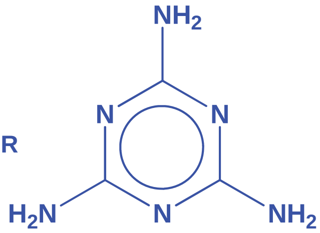
(i) Suggest a structure for melamine.



OR



OR



[1]

(ii) The average C–N bond length is 0.145 nm and the average C=N bond is 0.125 nm. Suggest why all the carbon-nitrogen bonds in melamine are intermediate in length between the given C–N and C=N values.

The structure of melamine is resonance–stabilised due to delocalisation of p orbital electrons between carbon and nitrogen atoms. Hence all carbon-nitrogen double bonds are partial double bonds.

[1]

(iii) Deduce the structure of **X**. Calculate the number of protons, neutrons and electrons in a monomer of **X**.

$H_2N{-}C{\equiv}N$

22p, 20n, $22e^-$

[2]

(b) Group 1 metal azides, $\mathbf{M}N_3$, can be formed by passing heated dinitrogen oxide, N_2O over their corresponding amines, $\mathbf{M}NH_2$.

(i) Explain why lattice energies of Group 1 azides become less exothermic down the group.

Lattice energy $\propto |q^+.q^- / (r^+ + r^-)|$. Down Group 1, cationic radius increases, thus lattice energy becomes less exothermic.

[1]

(ii) Suggest why the azides become thermally more stable down the group.

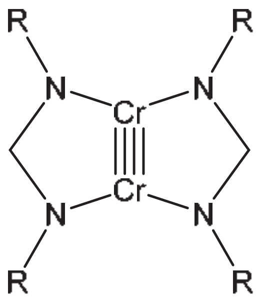
Down Group 1, cationic radius increases while charge remains the same. The charge density and polarising power of cations decrease. Extent of polarisation of anionic charge cloud N_3^- is less. More energy is required to decompose and break the N-N bonds within N_3^- down Group 1. Hence azides become more stable to heat.

[2]

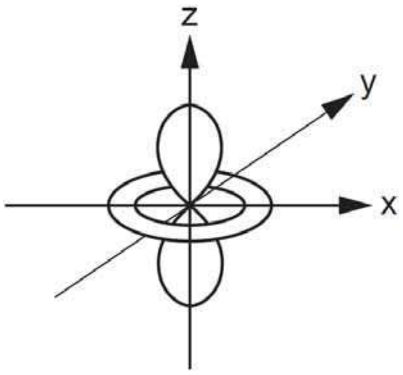
(c) Nitrogen has been used extensively in the research of compounds involving quadruple (bond order of 4) and quintuple (bond order of 5) bonds.

These compounds typically involve transition metal atoms that are able to form bonds between themselves using their d orbitals.

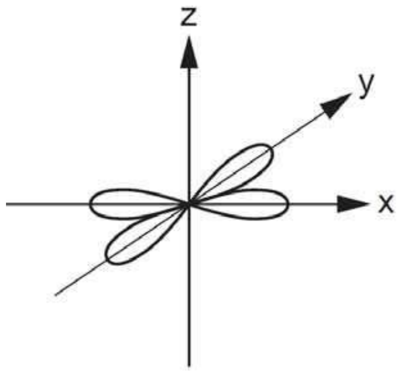
An example is given below:



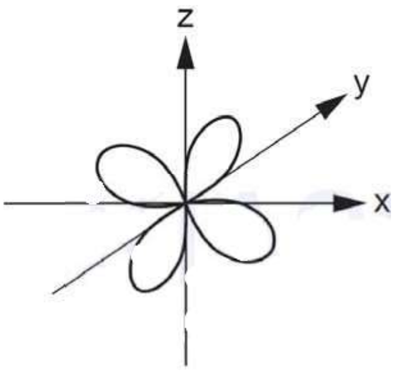
(i) Sketches of the shapes of the atomic orbitals from the d subshells are shown below, in random order. Name and label **each** orbital.



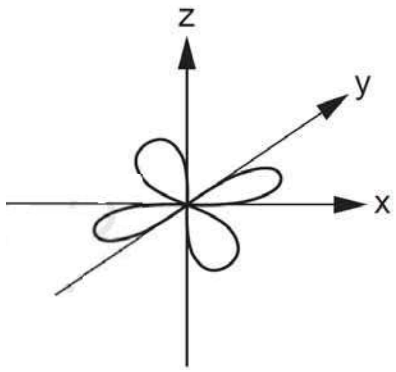
d_{z^2}



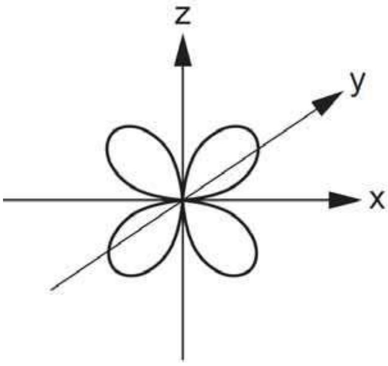
$d_{x^2-y^2}$



d_{yz}



d_{xy}



d_{xz}

[2]

(ii) The d orbitals of an atom can overlap with d orbitals of the same type to form pi (π) and delta (δ) bonds. While a single sigma (σ) bond involves the overlap of two orbital lobes in total, and a single pi (π) bond four lobes, a single delta (δ) bond involves the overlap of eight lobes in total. When two atoms overlap, the z-axis is used to define the internuclear axis.

Suggest two different d orbitals that could be involved in delta bonds (δ).

$d_{x^2-y^2}$ and d_{xy}

[1]

[Total: 10]

2 *Use of Data Booklet is relevant to this question.*

Aerozine 50 is a 50/50 mix of UDMH, $(CH_3)_2N_2H_2$ and hydrazine, N_2H_4. It is used as a rocket fuel, and is typically mixed with dinitrogen tetroxide, N_2O_4, as the oxidising agent.

The equation for the reaction between UDMH and dinitrogen tetroxide under standard conditions is given as follows:

$$(CH_3)_2N_2H_2(l) + 2N_2O_4(g) \rightarrow 2CO_2(g) + 3N_2(g) + 4H_2O(l) \quad \text{---------- } \textbf{reaction 1}$$

(a) Suggest an equation, including state symbols, for the reaction between hydrazine and dinitrogen tetroxide under standard conditions.

$$2N_2H_4(l) + N_2O_4(g) \rightarrow 3N_2(g) + 4H_2O(l)$$

[1]

(b) An experiment was set up such that hydrazine in a spirit burner was combusted beneath a copper can filled with water. It was found that 0.50 g of hydrazine was required to raise the temperature of 100 cm^3 of water in the can by 15 ^oC.

Using relevant data from the *Data Booklet* and the information given below, calculate the efficiency of the system, expressed as a percentage.

- The heat capacity of the copper can be taken to be 96.0 J K^{-1}
- The density of water can be taken to be 1.00 g cm^{-3}.
- The standard enthalpy change of combustion of hydrazine, found using a bomb calorimeter, has a value of –628 kJ mol^{-1}.

$Q_{aborbed}$ = (100)(4.18)(15) + (96.0)(15)
= 7710 J
$Q_{released}$ = 628000 x (0.5/32.0)
= 9813 J
Efficiency = 7710/9813 x 100 %
= 78.6 %

[3]

Pure UDMH, $(CH_3)_2N_2H_2$, can be used as an alternative to *Aerozine 50* in thruster rockets.

(c) Using relevant data from the *Data Booklet* and the information given below, construct an energy cycle to calculate the enthalpy change for **reaction 1**.

$(CH_3)_2N_2H_2(l) + 4O_2(g) \rightarrow 2CO_2(g) + N_2(g) + 4H_2O(l)$	–1980 kJ mol^{-1}
$N_2O_4(g) \rightarrow 2N(g) + 4O(g)$	+1930 kJ mol^{-1}

$$\begin{tikzcd}
4O_2(g) + (CH_3)_2N_2H_2(l) + 2N_2O_4(g) \arrow[r, "\Delta H_r"] \arrow[d, "-1980"'] & 2CO_2(g) + 3N_2(g) + 4H_2O(l) + 4O_2(g) \arrow[ddl, "\begin{array}{l}4BE(O{=}O) + 2BE(N{\equiv}N)\\ = 4(496) + 2(944)\end{array}"] \\
2CO_2(g) + N_2(g) + 4H_2O(l) + 2N_2O_4(g) \arrow[d, "2(+1930)"'] & \\
2CO_2(g) + N_2(g) + 4H_2O(l) + 4N(g) + 8O(g) &
\end{tikzcd}$$

By Hess Law
$\Delta H_r + 4(496) + 2(944) = -1980 + 2(+1930)$
$\Delta H_r = -1990$ kJ mol^{-1}

[3]

(d) The total mass of propellant (UDMH and dinitrogen tetroxide, N_2O_4) used in the thruster rockets in the ascent stage of a lunar module was 366 kg.

Assuming that UDMH (M_r = 60.0) and dinitrogen tetroxide (M_r = 92.0) were mixed according to the stoichiometric ratio, calculate the mass of UDMH in the propellant mixture.

Let amount of UDMH be x mol and amount of N_2O_4 be 2x mol
$x(60.0) + 2x(92.0) = 366000$
$x = 1500$ mol
$m_{UDMH} = 1500 \times 60.0$
$= 90000$ g
$= 90$ kg

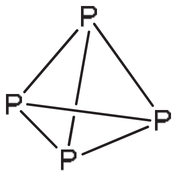
[1]

[Total: 8]

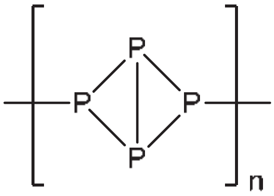
3 Use of the *Data Booklet* is relevant to this question.

Phosphorus and sulfur are elements in Period 3 in the Periodic Table and each can exist in various allotropic forms.

Phosphorus can exist as white phosphorus and red phosphorus. White phosphorus exists as a tetrahedron with bond angle 60° while red phosphorus exists as a polymeric chain of regular tetrahedrons.

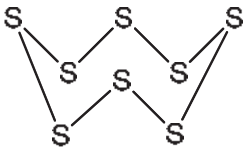


white phosphorus



red phosphorus

Sulfur, on the other hand is thermodynamically most stable at room temperature as rhombic sulfur, which consists of puckered S_8 rings.



Both elements form a wide range of compounds with the halogens.

(a) **(i)** By considering the bond angles involved, suggest why white phosphorus is less stable than red phosphorus.

The bond angle of 60° in white phosphorus, P_4 is smaller than 107° in red phosphorus. Hence there will be high angular strain in the bonding / strong electronic repulsion between the bond pairs. Thus, white phosphorus is less stable than red phosphorus.

[1]

(ii) The phosphorus halides fume in air because of reaction with water vapour.

Explain briefly why phosphorus(V) chloride can react with water. Write a balanced equation for its reaction.

PCl_5 undergoes hydrolysis in water due to the presence of energetically accessible vacant 3d orbitals on phosphorus which can accommodate lone pair of electrons from oxygen atoms of water molecules.

$PCl_5 + 4H_2O \rightarrow H_3PO_4 + 5HCl$

[2]

(b) When sulfur is heated under pressure with chlorine, the major product is SCl_2.

$$S_8(g) + 8Cl_2(g) \rightarrow 8SCl_2(g)$$

(i) Using data from the *Data Booklet*, calculate the enthalpy change, ΔH, for this reaction.

ΔH = Bonds broken – Bonds formed
= 8 x BE(S-S) + 8 x BE (Cl-Cl) – 16 x BE(S-Cl)
= (8 × 264) + (8 × 244) – (16 × 250)
= +64 kJ mol^{-1}

[2]

Under suitable conditions, SCl_2 reacts with water to produce a yellow precipitate and a solution **X**. Solution **X** contains a mixture of SO_2(aq) and compound **Y**.

(ii) By constructing an equation for the hydrolysis of SCl_2, work out how the oxidation number of sulfur changes during the reaction.

$2SCl_2 + 2H_2O \rightarrow S + SO_2 + 4HCl$
Oxidation number of sulfur increases from +2 (in SCl_2) to +4 (in SO_2), and also decreases from +2 (in SCl_2) to 0 (in S).

[2]

(iii) Hence, suggest a pH value of the resultant solution formed.

pH = 1 [OR 2]

[1]

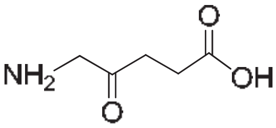
(iv) Using relevant data from the *Data Booklet*, suggest what would be observed when acidified potassium dichromate is added to a sample of solution **X**.

$E^\ominus(Cr_2O_7^{2-} | Cr^{3+}) = +1.33$ V > $E^\ominus(SO_4^{2-} | SO_2) = +0.17$ V
$E^\ominus_{cell} = +1.33 - 0.17 = +1.16$ V (spontaneous)
Thus $K_2Cr_2O_7$(aq), solution changes from orange to green.

[2]

[Total: 10]

4 Aminolevulinic acid is involved in the synthesis of haemoglobin and chlorophyll.

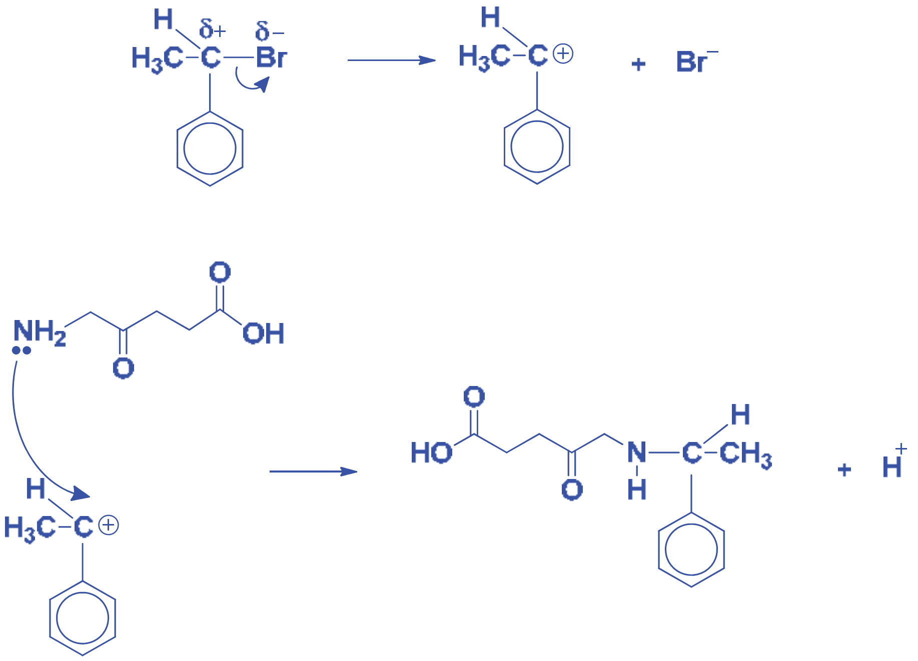


aminolevulinic acid

(a) Aminolevulinic acid reacts readily with (1-bromoethyl)benzene.

Name and outline the mechanism for the reaction of aminolevulinic acid with **(**1-bromoethyl**)**benzene.

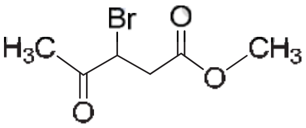
S_N1 mechanism



Note:
Dipole on C-Br and lone pair on N
Carbocation intermediate
Arrow drawn from lone pair on N to C+ AND arrow indicating heterolytic fission of C-Br bond
Product

[3]

(b) Compound **A** is a precursor in the synthesis of aminolevulinic acid.



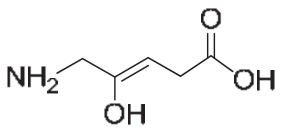
compound **A**

Suggest a simple chemical test to distinguish between compound **A** and aminolevulinic acid. Include clearly the reagents, conditions and observations for each compound. Write a balanced equation for any positive test.

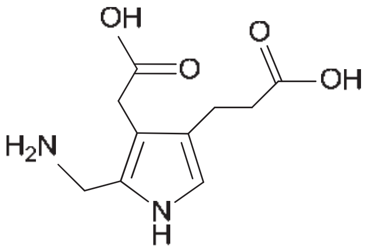
I_2(aq)/NaOH(aq), heat < 70°C
Observation for compound A: pale yellow ppt formed
$CH_3CO_2CH_2CH(Br)COCH_3 + 3I_2 + 6OH^- \rightarrow$
$^-O_2CCH_3CH_2CH(OH)CO_2^- + CHI_3 + 3I^- + 3H_2O + CH_3OH + Br^-$
Observation for aminolevulinic acid: no ppt formed
[Alternative tests accepted: Na_2CO_3 OR Na OR $KMnO_4/H_2SO_4$]

[3]

(c) Porphobilinogen is a pyrrole involved in porphyrin metabolism. It is generated from a reduced form of aminolevulinic acid, compound **B** by the enzyme ALA dehydratase.

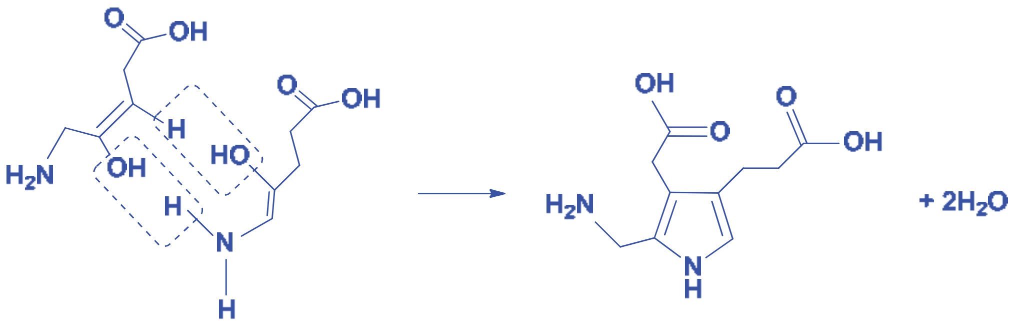


compound **B**



porphobilinogen

Show how porphobilinogen may be formed from the condensation of two molecules of compound **B**, with the help of a balanced equation. Indicate clearly with dotted lines how the non-organic by-products are formed.



Note:
2 molecules of A aligned as above
2 x dotted lines showing formation of $2H_2O$

[2]

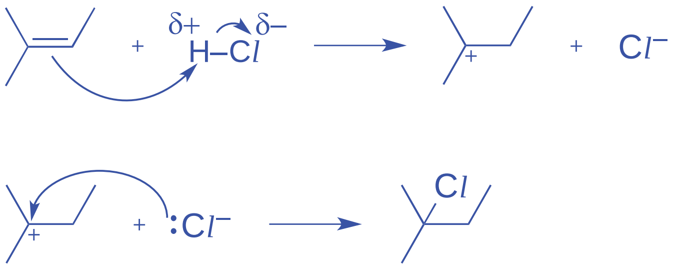
[Total: 8]

5 The formation of carbon-carbon bonds is important in the synthesis of large organic compounds. This question discusses the chemistry of some carbon-carbon bond forming reactions.

(a) Most of the starting reagents of such reactions typically involve a halogenoalkane. Halogenoalkanes can be obtained by reacting alkenes with hydrogen halides.

(i) Name and outline the mechanism of the reaction between 2-methylbut-2-ene and hydrogen chloride, showing the major product formed.

Electrophilic Addition



pair of arrows and partial charges (step 1)
correct intermediate & major product
balanced equations

[2]

(ii) 2-methylbut-2-ene can also react with hydrogen bromide and hydrogen iodide to form its respective halogenoalkane.

Suggest and explain, with reference to the mechanism of the reaction, how the rate of reaction changes from HC*l* to HI.

The **first step of the mechanism is the rate-determining step**.

From C*l* to I, **atomic radius increases**, **H–X bond length increases due to less effective overlap of orbitals**. **Bond strength decreases** and **less energy is required** to break H–X bond.

Hence rate of reaction increases in the following order.
Rate of reaction: HC*l* < HBr < HI

[2]

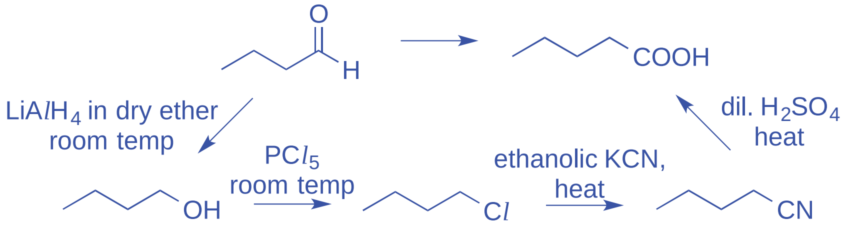
(b) Depending on the conditions of the reaction, a nitrile group can be introduced into an organic compound through either a halogenoalkane or a carbonyl, forming carbon-carbon bonds in the process.

(i) Suggest why alkenes are unable to react to form nitriles in the same way as carbonyls.

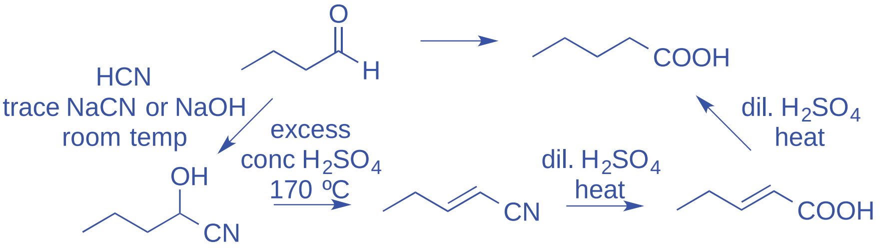
CN^- acts as a nucleophile due to the presence of a lone pair of electrons available for donation. **Alkenes have high electron density in the C=C** and hence **would repel CN^-**.

[1]

(ii) Propose a synthetic route that is **less than 5 steps** to convert butanal to pentanoic acid. State the reagents and conditions you would use for each step and draw the structures of the intermediate compounds.



OR



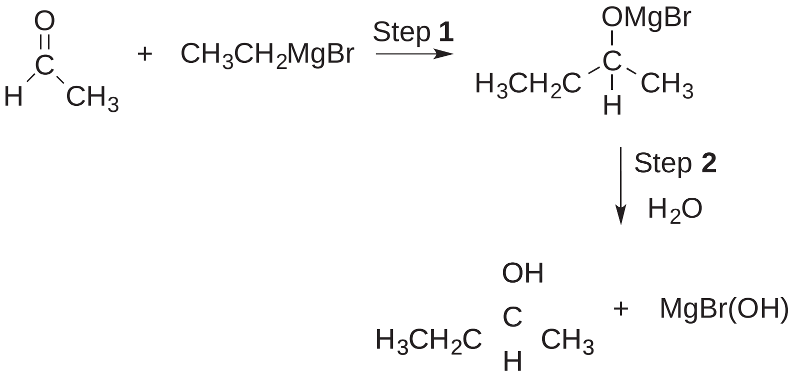
note: elimination of water and hydrolysis of nitrile are interchangeable

[5]

(c) A classic carbon-carbon bond formation reaction is the Grignard reaction. First, the Grignard reagent, an alkylmagnesium halide, is formed by reacting a halogenoalkane with magnesium.

$$CH_3CH_2Br + Mg \rightarrow CH_3CH_2MgBr$$

The reaction then proceeds with a reaction between the alkylmagnesium halide with a carbonyl to give an alcohol in a 2-step reaction.

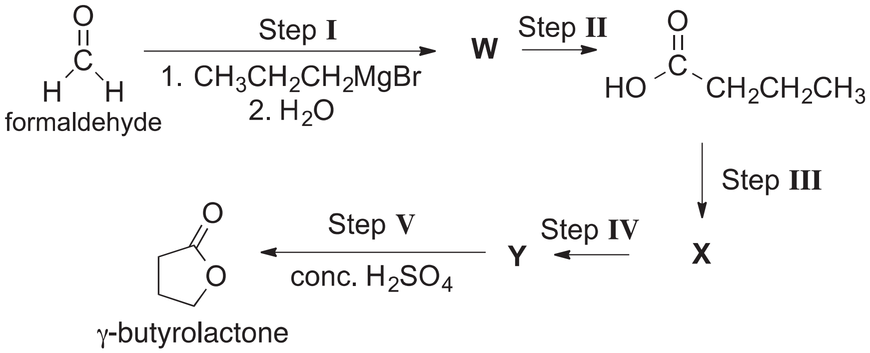


(i) Suggest the type of mechanism for Step **1**.

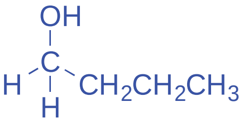
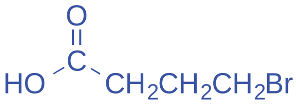
<u>**Nucleophilic addition**</u>

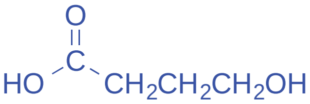
[1]

(ii) The synthesis of γ-butyrolactone, a common solvent from formaldehyde, involves the Grignard reaction as follows.



Propose structures of **W**, **X**, **Y** and **Z**.

 $HOCH_2CH_2CH_2CH_3$	 $HOOCCH_2CH_2CH_2Br$
W	**X**

 $HOOCCH_2CH_2CH_2OH$
Y

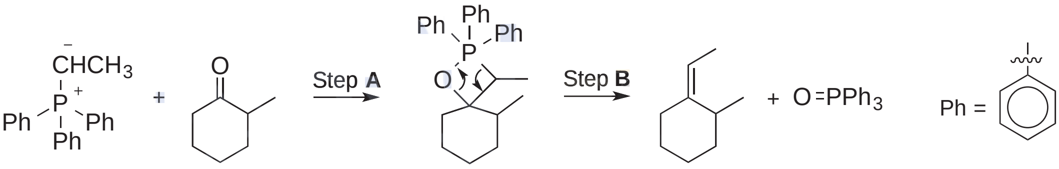
[3]

(iii) State the reagents and conditions required for steps **II**, **III** and **IV**.

Step **II**: **$KMnO_4$, H_2SO_4(aq), heat**
Step **III**: **Br_2, excess $CH_3CH_2CH_2CO_2H$, uv light**
Step **IV**: **NaOH(aq), heat**

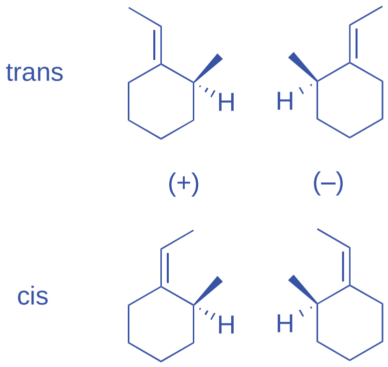
[3]

(d) Another common carbon-carbon bond formation reaction is the Wittig reaction. A phosphorus-containing reagent reacts with a carbonyl to form an intermediate, which then cleaves quickly to give an alkene.



(i) Identify, with the aid of a diagram, the type of stereoisomerism that the product can show.

cis-trans isomerism (OR enantiomerism)



Note: since the question asked for “can show”, students only need to identify one, even though there were 2

[2]

(ii) By considering the hybridisation of relevant carbon atoms, suggest a reason why step **B** is a fast reaction.

The carbon centres in the 4-membered cyclic ring are **sp^3 hybridised**. There is **high ring strain** due to angles being less than the ideal 109.5º. This results in the ring being **unstable**, which will then collapse quickly.

[2]

[Total: 21]

6 **(a)** 1.0 cm^3 of 0.10 mol dm^{-3} solution of sodium iodide was added to 1.0 cm^3 of 0.050 mol dm^{-3} $AgNO_3$(aq). 3.0 cm^3 of 1.0 mol dm^{-3} NH_3(aq) was then added. The resulting precipitate formed is virtually insoluble.

(i) Show that the number of moles of I^-(aq) that is **not** used to form the precipitate is 5.0 x 10^{-5} mol.

Amount of I^- originally = 1.0 / 1000 x 0.10 = 1.0 x 10^{-4} mol
Amount of Ag^+ originally = 1.0 / 1000 x 0.050 = 5.0 x 10^{-5} mol
Amount of I^- left = 1.0 x 10^{-4} – 5.0 x 10^{-5} mol
= 5.0 x 10^{-5} mol (the rest of I^-has been precipitated as AgI)

[1]

(ii) Show that under these conditions [I^-(aq)] = 0.010 mol dm^{-3} and hence [Ag^+(aq)] which would just allow the precipitate to dissolve.

K_{sp}(AgI) = 8.0 x 10^{-17} mol^2 dm^{-6}

[I^-(aq)]
= (5.0 x 10^{-5}) / (1.0 + 1.0 + 3.0) x 1000 = 0.010 mol dm^{-3}

For AgI to just dissolve, ionic product < K_{sp}(AgI)
[Ag^+(aq)] = 8.0 x 10^{-17} / 0.010 = 8.0 x 10^{-15} mol dm^{-3}

[1]

(iii) Under the conditions of the experiment, [Ag^+(aq)] = 1.9 x 10^{-9} mol dm^{-3}. Use your answer in **(a)(ii)** to justify why the precipitate is virtually insoluble.

The value of [Ag^+] calculated in (a)(ii) is less than 1.9 x 10^{-9} mol dm^{-3}, Hence ionic product > K_{sp}(AgI), precipitation still occurs and will not be soluble.

[1]

(iv) When the above experiment is repeated using sodium chloride instead of sodium iodide, different observations were made. Briefly describe and explain the differences with the aid of equations. **No** calculations are required.

$Ag^+(aq) + X^-(aq) \rightleftharpoons AgX(s)$ X = Cl or I ……… (1)

$Ag^+(aq) + 2NH_3(aq) \rightleftharpoons Ag(NH_3)_2^+(aq)$
Formation of white ppt of silver chloride and yellow ppt of silver iodide
Silver chloride will dissolve in aqueous NH_3 but silver iodide will not.
Aqueous NH_3 will form a complex with Ag^+ ions,
thus equilibrium (1) will shift left to restore the Ag^+ ions that were removed.
Hence ionic product of [Ag^+][Cl^-] < K_{sp} (AgCl) so ppt dissolves
AgI is less soluble with a much lower K_{sp} hence ionic product of [Ag^+][I^-] > K_{sp}(AgI) so ppt remains.

[3]

(b) The standard electrode potential values for reactions **(I)** and **(II)** are +1.21 V and +0.54 V respectively.

$IO_3^- + 6H^+ + 5e^- \rightleftharpoons \frac{1}{2}I_2 + 3H_2O$ **(I)**

$\frac{1}{2}I_2 + e^- \rightleftharpoons I^-$ **(II)**

(i) Find the standard Gibbs free energy change for **each** of the reactions **(I)** and **(II).**

For reaction (I),
$\Delta G^\ominus = -5 \times 96\,500 \times 1.21 = -5.84 \times 10^5$ **J mol^{-1}**
For reaction (II),
$\Delta G^\ominus = -1 \times 96\,500 \times 0.54 = -5.21 \times 10^4$ **J mol^{-1}**

[1]

(ii) Use your answers from **(b)(i)** to find the standard Gibbs free energy change for the following reaction, and hence its standard electrode potential.

$IO_3^- + 6H^+ + 6e^- \rightleftharpoons I^- + 3H_2O$

$\Delta G^\ominus = -5.21 \times 10^4 + (-5.84 \times 10^5) = -6.36 \times 10^5$ **J mol^{-1}**
$E^\ominus(IO_3^-/I^-) = -6.36 \times 10^5 / (-6 \times 96\,500) = +1.10$ **V**

[2]

(c) When 0.530 g of potassium iodide was completely reacted with an aqueous solution of XeF_2, all the iodide is converted into the iodate anion. A student proposed that the anion could be either iodate(V), IO_3^-, or iodate(VII), IO_4^-.

(i) Show that the number of moles of iodate that were involved in the reaction is 3.19×10^{-3} mol.

Amount of iodate = Amount of KI
= 0.530 / 166.0
= 3.19×10^{-3} mol

[1]

(ii) The equation involving the reaction of iodate(VII), IO_4^- with excess acidified potassium iodide is given below:

$IO_4^- + 8H^+ + 7I^- \rightarrow 4I_2 + 4H_2O$

For the reaction involving iodate(V), IO_3^- with excess acidified potassium iodide, write the corresponding half equations and hence the overall **ionic** equation.

Reduction: $2IO_3^- + 12H^+ + 10e^- \rightarrow I_2 + 6H_2O$
Oxidation: $2I^- \rightarrow I_2 + 2e^-$
Overall ionic equation: $IO_3^- + 6H^+ + 5I^- \rightarrow 3I_2 + 3H_2O$

[3]

(iii) 3.19×10^{-3} mol of iodate anion, which is either iodate(V), IO_3^-, or iodate(VII), IO_4^- is acidified, and added to excess potassium iodide solution where iodine is formed. It is found that 28.40 cm^3 of 0.900 mol dm^{-3} of $Na_2S_2O_3$ is required to discharge the colour of iodine.

It is given that $I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-}$.

By using the information and your answers in **(c)(ii)**, determine whether the anion is iodate(V), IO_3^-, or iodate(VII), IO_4^-.

Since $I_2 : S_2O_3^{2-} = 1 : 2$,
assuming anion is IO_3^-, $IO_3^- : S_2O_3^{2-} = 1 : 6$
assuming anion is IO_4^-, $IO_4^- : S_2O_3^{2-} = 1 : 8$

If anion is IO_3^-,

volume of $S_2O_3^{2-}$ required = $\dfrac{6 \times 3.19 \times 10^{-3} \times 10^{3}}{0.900} = 21.30$ **cm^3**

If anion is IO_4^-,

volume of $S_2O_3^{2-}$ required = $\dfrac{8 \times 3.19 \times 10^{-3} \times 10^{3}}{0.900} = 28.40$ **cm^3**

(or any reasonable method of elimination is accepted)
Hence the anion is IO_4^-.

[2]

(d) Nitrogen trifluoride was first prepared in the electrolysis of a molten mixture of ammonium fluoride and hydrogen fluoride using inert electrodes.

(i) It is given that at one of the electrodes, the following reaction occurs:
$NH_4^+ + 3F^- \rightarrow NF_3 + 4H^+ + 6e^-$

State the electrode that is involved in the above reaction and its polarity.

Anode
positive

[1]

(ii) When the above electrolysis was set up using a current of 0.50 A, 0.276 g of nitrogen trifluoride was liberated. Calculate the time taken for the electrolysis to occur.

Amount of NF_3 collected = 0.276 / (14.0 + 19.0 x 3) = 3.89×10^{-3} mol
Amount of electrons needed to liberate NF_3
= $3.89 \times 10^{-3} \times 6 = 2.33 \times 10^{-2}$ mol

Total quantity of charge used = $2.33 \times 10^{-2} \times 96\,500$ = 2250 C

Time taken = 2250 / 0.50 = 4500 s = 75 min

[2]

[Total: 18]

Victoria Junior College
2017 H2 Chemistry Prelim Exam 9729/3
Suggested Answers

Section A

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

1 **(a)** Ethanoic acid and its salt, sodium ethanoate, is often used as an acid buffer to help extend the shelf-life of food products such as meat, fish and dairy.

A buffer solution of pH 5.5 was prepared by mixing 0.200 mol dm^{-3} of ethanoic acid and 0.200 mol dm^{-3} aqueous sodium ethanoate.

(K_a of ethanoic acid = 1.74 x 10^{-5} mol dm^{-3})

(i) What do you understand by the term *buffer solution*? [1]

A buffer solution can maintain a fairly constant pH when a small amount of acid or base is added to it.

(ii) Calculate the ratio of $\frac{[\text{ethanoate}]}{[\text{ethanoic acid}]}$ required to prepare the above buffer solution.

Hence deduce whether the above buffer is more effective in buffering against added acids or bases.

Write an equation to illustrate your answer. [3]

$K_a = \frac{[H^+][A^-]}{[HA]}$ **= 1.74 x 10^{-5} where A$^-$ is ethanoate and HA is ethanoic acid.**

$$\frac{[A^-]}{[HA]} = \frac{1.74 \times 10^{-5}}{10^{-5.5}} = \frac{1.74 \times 10^{-5}}{3.16 \times 10^{-6}} = \frac{5.51}{1}$$

As higher [ethanoate] is present, buffer is better at removing added acids.

$CH_3CO_2^- + H^+ \rightarrow CH_3CO_2H$

(iii) Calculate the volume of ethanoic acid and that of aqueous sodium ethanoate required to prepare 60 cm^3 of the above buffer. [1]

Let x cm^3 be volume of ethanoate and (60 – x) cm^3 to be volume of ethanoic acid.

$$\frac{x}{60 - x} = \frac{5.51}{1}$$

x = 50.8 cm^3

Hence 50.8 cm^3 of sodium ethanoate and (60- 50.8) = 9.20 cm^3 of ethanoic acid will be required.

(iv) The boiling points of the components in the buffer are as shown.

Ethanoic acid	118°C
Sodium ethanoate	881°C

With reference to the structure and bonding present in the compounds, account for the difference in the boiling points. [3]

Ethanoic acid has a simple molecular structure with hydrogen bonding between the polar molecules.
Sodium ethanoate has a giant ionic structure with very strong electrostatic attractions between the oppositely charged ions. Hence a lot of heat energy is required to overcome the ionic attractions compared to the much weaker hydrogen bonding between acid molecules.

(b) The limestone that collects in kettles in hard water areas is mainly calcium carbonate. It can be removed fairly harmlessly by using a warm solution of vinegar, which contains ethanoic acid. The limestone dissolves with fizzing and a solution of calcium ethanoate remains.

(i) Write a balanced equation for the reaction between ethanoic acid and calcium carbonate. [1]

$$2CH_3COOH + CaCO_3 \rightarrow Ca(CH_3COO)_2 + CO_2 + H_2O$$

When the solution in **(b)** is evaporated and the resulting solid calcium ethanoate is heated strongly in a test-tube, an organic compound **Q** is formed, which condenses to a colourless liquid. The residue in the tube contains calcium carbonate.

When 0.10 g of compound **Q** was injected into a gas syringe at a temperature of 383 K and a pressure of 101 kPa, 55 cm^3 of vapour were produced.

(ii) Calculate the relative molecular mass of **Q**. [2]

$$PV = nRT = \frac{mRT}{M}$$

Rearranging gives $M = \frac{mRT}{PV} = \frac{0.10 \times 8.31 \times 383}{101 \times 10^3 \times 55 \times 10^{-6}}$

$= 57.3$

(iii) Compound **Q** is neutral and water-soluble. **Q** does not react with sodium metal nor with Fehling's solution but it does react with alkaline aqueous iodine.

Suggest a structural formula for **Q.** Justify your answer by reference to these properties of **Q**. [4]

Reaction	Deduction
Neutral	Absence of acidic and basic groups
No reaction with Na metal	Absence of –OH group so not alcohol ad carboxylic acid
No reaction with Fehling's solution	Absence of aliphatic aldehyde

Positive test with alkaline aqueous iodine	**Presence of $CH_3CO–$ group**

Mass of $CH_3CO–$ group = 43.0 hence remaining group has a mass of 57.9 – 43.0 = 14.9 ≈ 15.0
$\Rightarrow$ $–CH_3$ group present
Q is propanone CH_3COCH_3

(iv) Construct a balanced equation for the formation of **Q** by the action of heat on calcium ethanoate. [1]

$(CH_3COO)_2 \rightarrow CaCO_3 + CH_3COCH_3$

(v) The residue calcium carbonate can also undergo thermal decomposition when heated very strongly. Copper(II) carbonate behaves in a similar manner when heated.

State which carbonate, calcium or copper(II) will have a higher decomposition temperature. Explain your answer, with the help of relevant data from the *Data Booklet*. [3]

$CaCO_3$ will have a higher decomposition temperature.
Ionic radius of Ca^{2+} = 0.099 nm; Cu^{2+} = 0.073 nm

Size of Ca^{2+} is larger so its charge density is lower. Polarising power of Ca^{2+} is thus lower and less able to distort the electron cloud of CO_3^{2-} ion. Hence, $CaCO_3$ is more stable to heat and has a higher decomposition temperature.

[Total: 19]

2 **(a)** In a closed reaction vessel maintained at a high temperature, 1 mol of Al_2Cl_6 dimers dissociate into $AlCl_3$ according to the following equation.

$$Al_2Cl_6(g) \rightleftharpoons 2AlCl_3(g)$$

The average M_r of the equilibrium gas mixture is found to be 178.0.

(i) Given that the average M_r of the equilibrium gas mixture is the sum of the mole fractions of each gas, multiplied by the M_r of that gas, calculate the degree of dissociation of Al_2Cl_6, α. [3]

	$Al_2Cl_6(g)$ ⇌	$2AlCl_3(g)$
initial amt / mol	**1**	**0**
change	**–x**	**+2x**
eqm amt / mol	**1– x**	**2x**

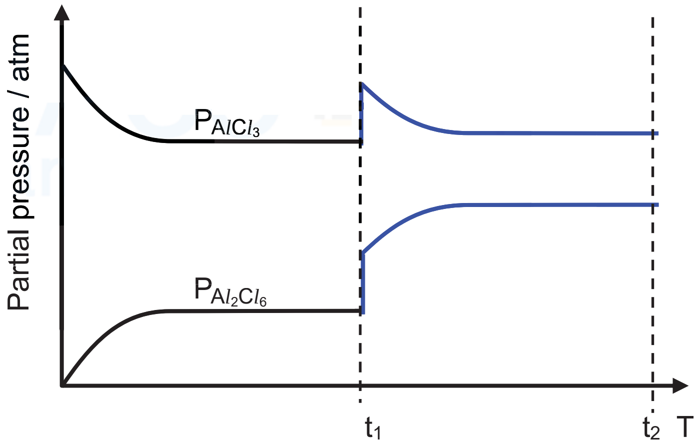
Total amt of gases present at eqm
= 1– x + 2x
= (1 + x) mol
Average $M_r = [(1-x)/(1+x)]\, M_r(Al_2Cl_6) + [2x/(1+x)]\, M_r(AlCl_3)$
$= 178.0$
$178.0 = [(1-x)/(1+x)](267.0) + [2x/(1+x)](133.5)$
$x = 0.50$
Hence, $\alpha = x / 1$
$= 0.50$

(ii) Write down the expression of K_p for the above equilibrium system. Hence, show that $K_p = K_cRT$. [2]

$K_p = (P_{AlCl_3})^2 / P_{Al_2Cl_6}$
Using $PV = nRT$; $P = (n/V)RT = CRT$
Hence, $K_p = ([AlCl_3]RT)^2 / [Al_2Cl_6]RT$
$= [AlCl_3]^2RT / [Al_2Cl_6]$
$= K_cRT$

(iii) An experiment on the dissociation of Al_2Cl_6 was conducted in a closed container of a fixed volume and the partial pressures of all the components were plotted as shown in the figure below.

Copy and complete the diagram to show how the partial pressure of each gas changes when the volume of the container is halved at t_1 until t_2.



[2]

Need a home tutor? Visit smiletutor.sg

Note:
Sudden increase in P of each gas at t_1
Increase in P_{Al2Cl6} and decrease in P_{AlCl3} after t_1 with eqm reached before t_2
Final eqm P_{AlCl3} is higher than the original eqm P before t_1

(b) Strontium chloride, $SrCl_2$ is a typical salt which forms neutral aqueous solutions. It emits a bright red colour in a flame and this allows it to be used as a source of redness in fireworks.

Use the data below to answer the questions that follow.

Standard Gibbs free energy change of solution of $SrCl_2$(s)	–41.6 kJ mol^{-1}
Standard enthalpy change of formation of $SrCl_2$(s)	–828.9 kJ mol^{-1}
Standard enthalpy change of formation of Sr^{2+}(aq)	–545.8 kJ mol^{-1}
Standard enthalpy change of formation of Cl^-(aq)	–167.5 kJ mol^{-1}
Standard enthalpy change of hydration of Sr^{2+}(g)	–1446 kJ mol^{-1}
Standard enthalpy change of hydration of Cl^-(g)	–378 kJ mol^{-1}

(i) Define the term *standard enthalpy change of formation* of strontium chloride. [1]

Standard enthalpy change of formation of $SrCl_2$ is the heat change when one mole of $SrCl_2$(s) is formed from its constituent elements, Sr(s) and Cl_2(g) under standard conditions of 298 K and 1 bar.

(ii) Calculate $\Delta H^\ominus_{sol}$ and $\Delta S^\ominus_{sol}$ of strontium chloride. [4]

$$\Delta H^\ominus_{sol}(SrCl_2) = \Delta H^\ominus_f(Sr^{2+}_{(aq)}) + 2\Delta H^\ominus_f(Cl^-_{(aq)}) - \Delta H^\ominus_f(SrCl_{2(s)})$$
$$= -545.8 + 2(-167.5) - (-828.9)$$
$$= -51.9 \text{ kJ mol}^{-1}$$

$$\Delta G^\ominus_{sol} = -41.6$$
$$= \Delta H^\ominus_{sol} - T\Delta S^\ominus_{sol}$$
$$= -51.9 - 298(\Delta S^\ominus_{sol})$$
$$\Delta S^\ominus_{sol} = -34.6 \text{ J mol}^{-1} \text{ K}^{-1}$$

(iii) Write an equation to show the relationship between the lattice energy of strontium chloride and $\Delta H^\ominus_{sol}$ of strontium chloride. Hence, calculate the lattice energy of strontium chloride. [2]

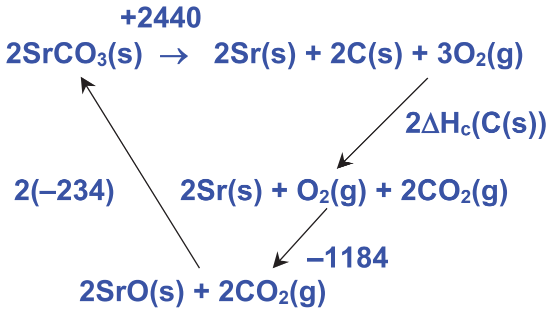
$$\Delta H^\ominus_{sol}(SrCl_2) = -LE + \Delta H^\ominus_{hyd}(Sr^{2+}_{(g)}) + 2\Delta H^\ominus_{hyd}(Cl^-_{(g)})$$
$$-51.9 \text{ kJ mol}^{-1} = -LE + (-1446) + 2(-378)$$
$$LE = -2150 \text{ kJ mol}^{-1}$$

(iv) Predict with reasoning, how Gibbs free energy change of formation of strontium chloride, ΔG_f will change with increasing temperature. [2]

ΔS_f of strontium chloride is negative as there a decrease in number of gaseous molecules in the reaction. While ΔH_f of strontium chloride is negative, when temperature increases until $|T\Delta S_f| > |\Delta H_f|$ (or $-T\Delta S_f$ becomes more positive), based on $\Delta G_f = \Delta H_f - T\Delta S_f$, ΔG_f will become more positive at higher temperature and the reaction will become less spontaneous with increasing temperature.

(c) Using the data given below, draw a labelled energy cycle to calculate the enthalpy change of combustion of solid carbon.

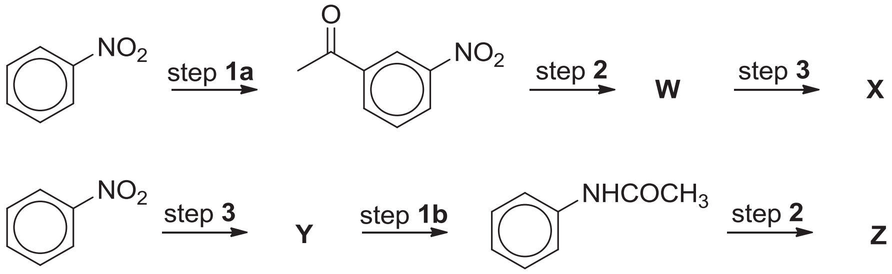
$2SrO(s) \rightarrow 2Sr(s) + O_2(g)$ $\Delta H = +1184 \text{ kJ mol}^{-1}$
$SrO(s) + CO_2(g) \rightarrow SrCO_3(s)$ $\Delta H = -234 \text{ kJ mol}^{-1}$
$2SrCO_3(s) \rightarrow 2Sr(s) + 2C(s) + 3O_2(g)$ $\Delta H = +2440 \text{ kJ mol}^{-1}$ [4]



By Hess Law:
$+2440 + 2\Delta H_c(C(s)) + (-1184) = -2(-234)$
$\Delta H_c(C(s)) = -394 \text{ kJ mol}^{-1}$

[Total: 20]

3 **(a)** Consider the following synthesis pathways starting from nitrobenzene:



(i) Ethanoyl chloride (CH_3COCl) is used as a reactant for step **1a** and step **1b** but under different conditions. State the reaction mechanism that occurred for each step **1a** and **1b** and hence explain the difference in the conditions required. [3]

Step 1a: Electrophilic substitution

Step 1b: Nucleophilic substitution or condensation

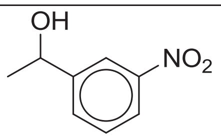
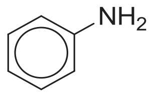
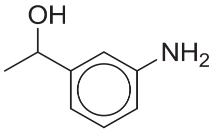
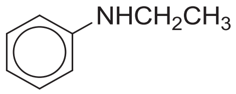
Lewis acid catalyst such as anhydrous $FeCl_3$ is required for step 1a to generate a strong electrophile for reaction.

(ii) Identify the reagents and conditions required for **steps 2** and **3** and hence draw the structures of **W, X, Y** and **Z**.

[Note: **Steps 2** and **3** in both pathways each refers to the same set of reagents and conditions.] [6]

Step 2: $LiAlH_4$ in dry ether, room temp

Step 3: Sn, conc. HCl, heat under reflux, followed by NaOH(aq), room temperature

 OH NO₂ **W**	 NH₂ **Y**
 OH NH₂ **X**	 NHCH₂CH₃ **Z**

(iii) Compare the relative basicity of **Y** and **Z**. [2]

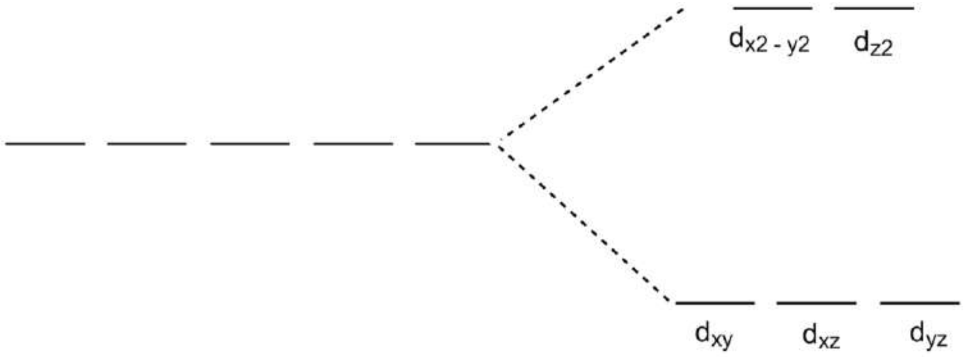
The basicity of a base depends on the availability of the lone pair of electrons on N for donation to acid.

Compound Z has an ethyl group which exerts an electron-donating inductive effect, causing the lone pair on electrons on N to be more available for donation to acid.

Hence compound Z is more basic than compound Y.

(b) In an isolated atom, the five d orbitals have the same energy. When a transition element ion is in an octahedral complex, the d orbitals are split into two groups of different energy levels.

(i) Draw an orbital energy diagram to show this, indicating the type of orbitals in each group. [2]



(ii) Use your diagram in **(b)(i)** to explain why transition element complexes like $Co(H_2O)_6^{2+}$ are often colored. [2]

For $Co(H_2O)_6^{2+}$, 3*d* electrons from the lower energy level are promoted to the upper energy level by absorbing a photon of light from the visible region of the electromagnetic spectrum. This effect is known as *d-d* transition which is possible due to partially filled d-subshell.
The colour seen is the complement of those absorbed in the visible region of the spectrum.

(c) Aqueous cobalt(II) chloride, $CoCl_2$ is a pink solution which gives the following reactions.

$$CoCl_2(aq) \xrightarrow{NaOH(aq)} \text{blue ppt. insoluble in excess} \xrightarrow{H_2O_2} \text{blue ppt. turned brown}$$

$$CoCl_2(aq) \xrightarrow{HCl(aq)} \text{no observable change} \xrightarrow{H_2O_2} \text{no observable change}$$

(i) By using the data given below and appropriate values from the *Data Booklet*, calculate $E^\ominus_{cell}$ and explain the differences in the observations made between **acidic** and **alkaline** medium.

$Co(OH)_3 + e^- \rightleftharpoons Co(OH)_2 + OH^-$ $E^\ominus = +0.17$ V

Write equations to account for the observations. [4]

In alkaline medium,
precipitation takes place as ionic product of blue ppt. $Co(OH)_2$, exceeds its K_{sp} value which is insoluble in excess.
$Co^{2+}(aq) + 2OH^-(aq) \rightleftharpoons Co(OH)_2(s)$
$Co(OH)_2(s)$ undergoes redox reaction with H_2O_2 (HO_2^- in alkaline medium) to give brown ppt of $Co(OH)_3$.
$HO_2^- + H_2O + 2e^- \rightleftharpoons 3OH^-$ $E^\ominus = +0.88$ V
$Co(OH)_3 + e^- \rightleftharpoons Co(OH)_2 + OH^-$ $E^\ominus = +0.17$ V
$2Co(OH)_2 + HO_2^- + H_2O \rightarrow 2Co(OH)_3 + OH^-$
$E^\ominus_{cell} = +0.88 - (+0.17)$
$= 0.71$ V which is feasible

In acidic medium,

Co^{2+}(aq) does not undergo redox reaction with H_2O_2 and hence no observable change.

$H_2O_2 + 2H^+ + 2e^- \rightleftharpoons 2H_2O$ $E^\ominus = +1.77$ V

$Co^{3+} + e^- \rightleftharpoons Co^{2+}$ $E^\ominus = +1.89$ V

$2Co^{2+} + H_2O_2 + 2H^+ \rightarrow 2Co^{3+} + 2H_2O$

$E^\ominus_{cell} = +1.77 - (+1.89)$

$= -0.12$ V which is not feasible

(ii) When brine solution instead of HC*l* was added to $CoCl_2$(aq), the solution turned from pink to blue. In this reaction, cobalt behaves like a transition element.
Suggest by means of an ionic equation, an explanation for this observation.

[2]

When brine solution is added to an aqueous solution of Co^{2+}, ligand exchange occurs where Cl^- displaces H_2O ligands, forming the blue $[CoCl_4]^{2-}$.

$[Co(H_2O)_6]^{2+} + 4Cl^- \rightleftharpoons [CoCl_4]^{2-} + 6H_2O$

[Total: 21]

Section B

Answer **one** question from this section.

4 **(a)** The kinetics of the acid–catalysed hydrolysis of ethyl ethanoate may be investigated by analysing samples of the reaction mixture at different times.

$$CH_3CO_2CH_2CH_3 + H_2O \overset{H^+ \text{ (catalyst)}}{\rightleftharpoons} CH_3CO_2H + CH_3CH_2OH$$

In one such experiment, the reaction mixture was prepared by mixing solutions of ethyl ethanoate and hydrochloric acid. The concentration of hydrochloric acid, which serves as the catalyst, can be assumed to stay constant throughout the reaction.

At different times, 10.0 cm^3 portions of the reaction mixture were pipetted, quenched and titrated with 0.200 mol dm^{-3} NaOH(aq).

After all necessary samples have been drawn, the remaining reaction mixture is then heated for ½ h to ensure complete reaction. The volume of NaOH required for titrating a 10.0 cm^3 sample of the resulting solution is 30.00 cm^3.

The following experimental data were obtained:

Time / min	Volume of NaOH required for titration, V / cm^3	$30.00 - V$ / cm^3
0	20.00	10.00
10	24.40	5.60
20	26.90	3.10
30	28.20	1.80
40	29.00	1.00
50	29.40	0.60

(i) State how each of the quantities, V and $(30 - V)$, is related to the concentration of the components of the reaction mixture at any point in time. [1]

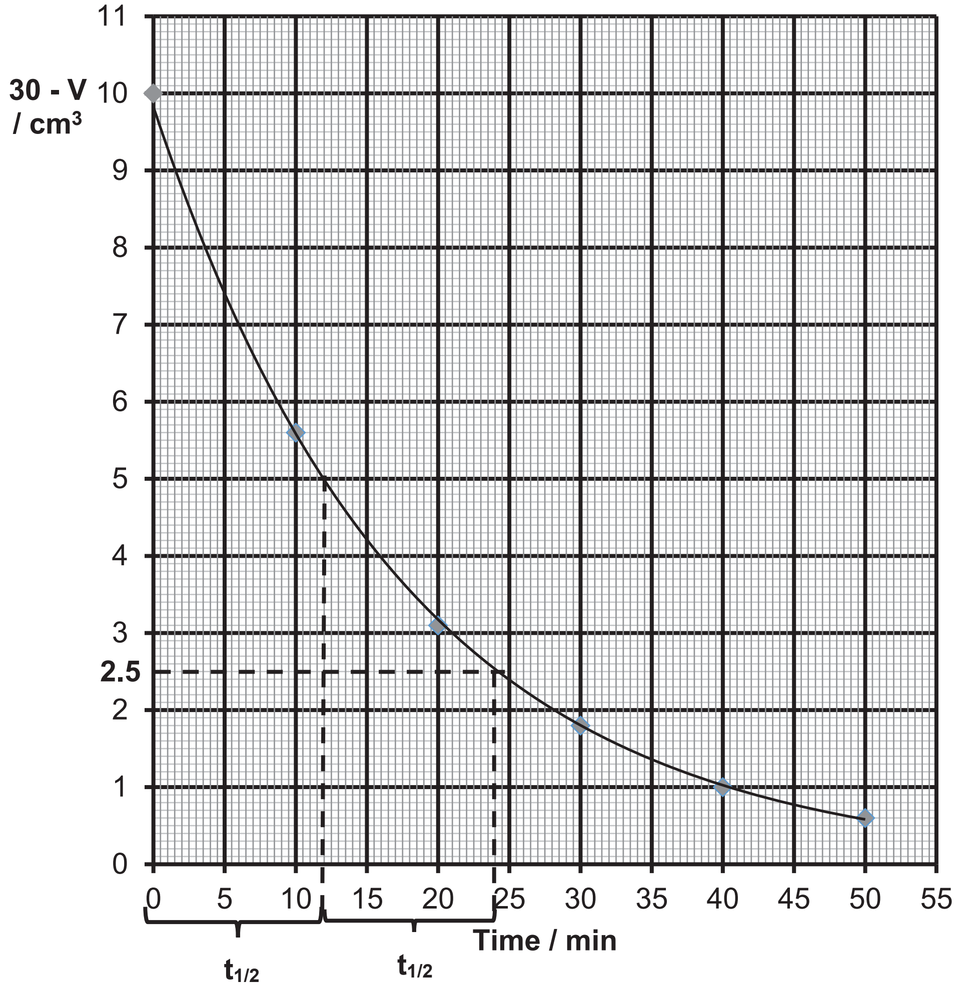
NaOH in titration neutralizes the CH_3CO_2H product and HC*l* catalyst. Hence, volume of NaOH, $\underline{V \propto [CH_3CO_2H] + [HCl]}$.

When hydrolysis reaction is completed, 30.00 cm^3 of NaOH is used to neutralize HC*l* and the maximum $[CH_3CO_2H]$ formed. Hence,

$$\begin{aligned} 30.00 - V &\propto [CH_3CO_2H]_{end} + [\cancel{HCl}] - \{[CH_3CO_2H] + [\cancel{HCl}]\} \\ &\propto [ester]_{initial} - [ester]_{reacted} = [ester] \end{aligned}$$

Hence $\underline{30.00 - V \propto [ester]}$

(ii) Hence, choose appropriate data from the above table to plot a graph that will allow you to determine the order with respect to ethyl ethanoate. [2]



Chooses to plot 30 – V against t
Large scale (at least ½ of grid) and axes properly labelled with units stated
All points correctly plotted
Smooth curve drawn through most of the points

(iii) Deduce the order with respect to ethyl ethanoate, justifying your answer by showing construction lines clearly on your graph. [2]

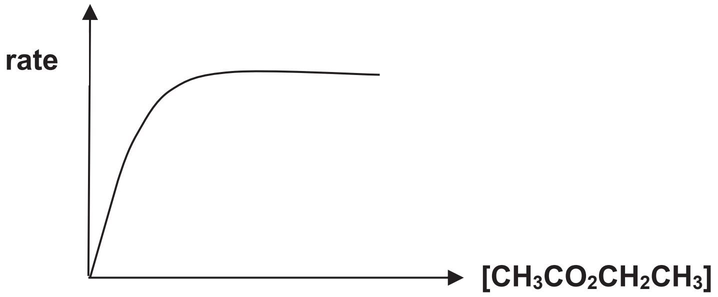
Show clearly two half–lives on graph

Since $t_{1/2}$ is constant at 12 min, reaction is first order w.r.t. ethyl ethanoate.

(iv) Hydrolysis of $CH_3CO_2CH_2CH_3$ can also be catalysed by esterase, an enzyme found in the liver.

Sketch a graph to show how, for a constant [esterase], the rate of hydrolysis varies with [$CH_3CO_2CH_2CH_3$] and explain the shape of the graph. [2]

Graph

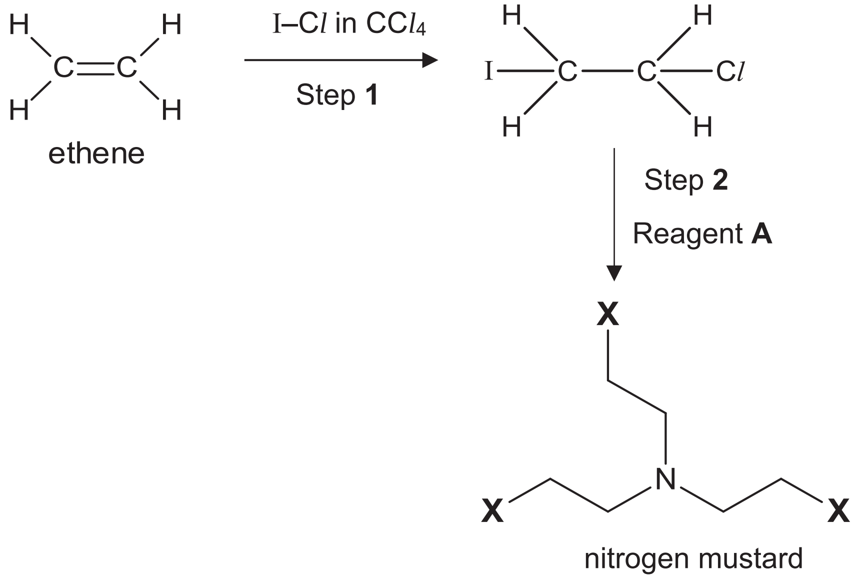


At low [substrate], rate is α [substrate] (OR 1st order rxn) since active sites are not fully occupied.

At high [substrate], rate becomes constant (OR zero order xn) since active sites fully occupied.

(b) Nitrogen mustard gas is commonly used in chemotherapy.

It was suggested that the synthesis of nitrogen mustard can be carried out via the following pathway:



X in nitrogen mustard could be either C*l* or I.

(i) Suggest the identity of reagent **A** and the conditions necessary for an optimal yield in Step **2**. [1]

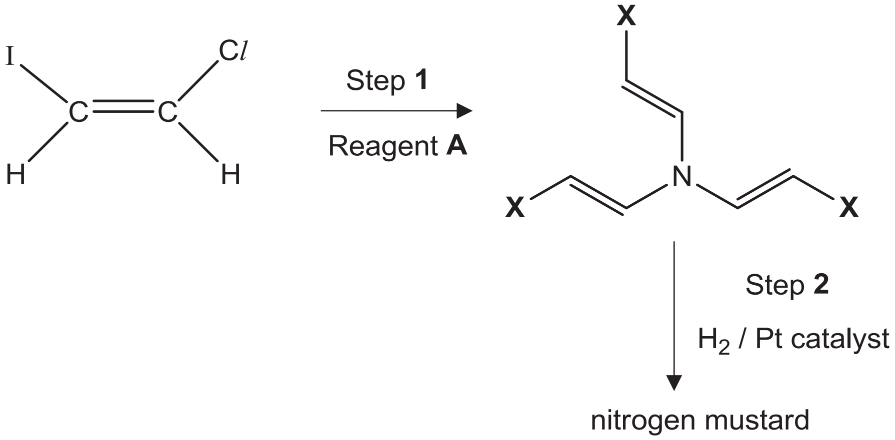
NH_3 dissolved in ethanol in limited amount, heat under pressure in a sealed tube

(ii) Is **X** in nitrogen mustard more likely to be C*l* or I? Explain your answer. [2]

X is likely to be C*l*.

In Step 2, iodine in CH_2ICH_2Cl is more likely to react with NH_3. As iodine atom is bigger than C*l*, the C–I bond is weaker and hence breaks more easily than C–C*l* bond.

(iii) Another reaction pathway was suggested for the synthesis of nitrogen mustard, with reagent **A** used for the first step:



Explain why this method of synthesis is likely to fail. [2]

Step 1 is not likely to occur as <u>$CH_2I{=}CH_2Cl$ is unreactive</u> towards reagent A. This is because the <u>p–orbital of the halogen atom overlaps with those of the C=C group</u> [OR lone pair on C*l* is delocalized into the ring], causing the C–halogen bond to acquire <u>partial double bond character</u> and hence <u>breaks less easily</u>.

(c) Compound **K** is a solid with the formula, $C_4H_9NO_3$. It dissolves in water to form a solution with high electrical conductivity. When **K** was warmed with aqueous sodium hydroxide, a colourless pungent gas was evolved. Acidification of the resulting solution gives **L**, $C_4H_6O_3$.

L gives an orange precipitate with 2,4-dinitrophenylhydrazine. When lithium aluminium hydride was added to **L**, **M**, $C_4H_{10}O_2$, was produced.

M can also be obtained from the oxidation of **N**, C_4H_8 by cold alkaline potassium manganate(VII).

Deduce the structures of compounds **K**, **L**, **M** and **N** and explain the reactions described. [8]

	Rxn type	**Structural feature**
High electrical conductivity of K	**---**	**K is an ionic compound.**
K + hot NaOH(aq)	**Acid–base reaction**	**Pungent gas is <u>NH_3</u>. This shows that <u>K contains NH_4^+</u>.** **Anion in solution is likely to be carboxylate which is acidified to give <u>carboxylic acid, L</u>.**
L + 2, 4–DNPH	**Condensation**	**<u>L is a carbonyl</u> compound.**
L + LiA*l*H4 → M	**Reduction**	**Loss of one oxygen confirms carboxylic acid in L which is reduced to <u>primary alcohol</u> while carbonyl group is reduced to either <u>primary or secondary alcohol</u> in M.**

Need a home tutor? Visit smiletutor.sg

N + cold MnO_4^- /OH^- → M	Oxidation (given in qn)	The two alcohol groups in M are adjacent to one another. Since M contains a primary alcohol, N has a $=CH_2$ group (or terminal alkene). Since the other alcohol group in M is primary or secondary, the other alkene C has at least one H attached.

Hence, N is $CH_3CH_2CH=CH_2$.

M is $CH_3CH_2CH(OH)CH_2OH$.

L is $CH_3CH_2COCO_2H$.

K is $CH_3CH_2COCO_2^- NH_4^+$

[Total: 20]

5 **(a)** The reaction between bromide and bromate(V) ions in acid solution is represented as follows:

$$5Br^- + BrO_3^- + 6H^+ \rightarrow 3Br_2 + 3H_2O$$

The reaction between Br^- and BrO_3^- is relatively fast, with Br_2 produced almost immediately after the reactants are mixed.

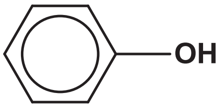
To measure the initial rate of the reaction, aqueous Br^- is added to acidified BrO_3^- solution containing a small amount of compound **A** and methyl orange indicator. The initial colour of the methyl orange is pink as the solution is acidic. After some time, the pink colour disappears due to the bleaching action of Br_2 as shown:

$$\underset{\text{pink}}{Br_2 + \text{methyl orange (acid form)}} \rightarrow \underset{\text{colourless}}{\text{bleached methyl orange} + 2Br^-}$$

The time taken for the pink colour to disappear is an indication of the initial rate.

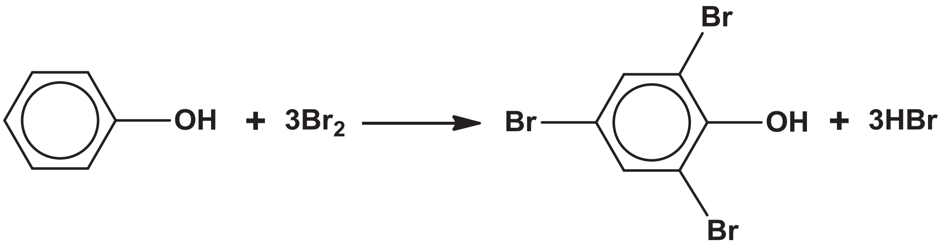
(i) Compound **A** is added to delay the disappearance of the pink colour, which would otherwise take place too quickly for effective measurement of time.

Given that compound **A** is an acidic organic compound containing only **one** functional group, suggest a suitable identity for compound **A**. [1]



(ii) Explain, with the aid of an equation, why the compound mentioned in your answer to **(i)** would be effective in delaying the disappearance of the pink colour. [2]

The lone pair on O of phenol is delocalized into the ring, causing the ring to be strongly activated. Hence, any Br_2 initially formed reacts readily with phenol in the following manner:



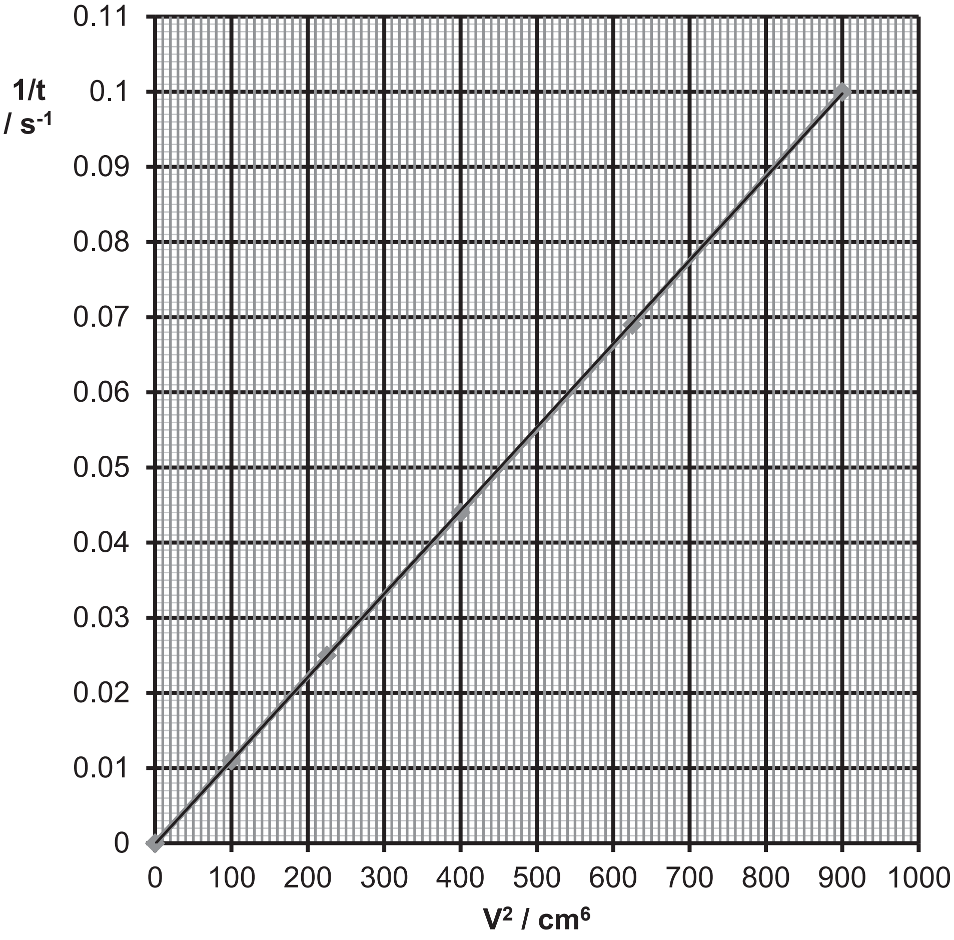
Br_2 is hence prevented from bleaching the methyl orange too soon.

(iii) To find the order of reaction with respect to H^+, a total of five experiments are conducted.

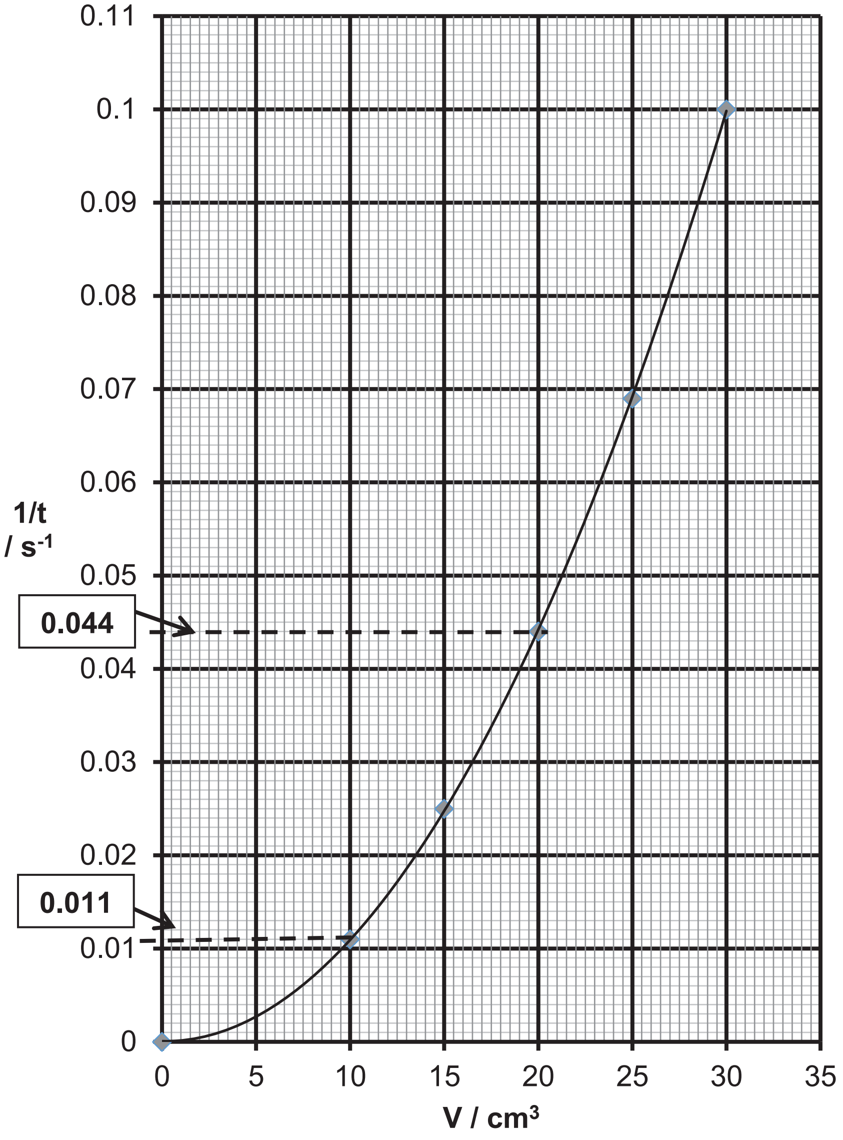
In all the experiments, 10.0 cm^3 of KBr(aq), 10.0 cm^3 of $KBrO_3$(aq), 5.0 cm^3 of Compound **A** solution and 2 drops of methyl orange indicator are used, with water added to keep the total volume constant. The volume of H_2SO_4(aq) used and other experimental data for each experiment are shown in the table below:

Experiment No.	Volume of H_2SO_4(aq), V / cm^3	V^2 / cm^6	Time taken for colour to change from pink to colourless, t / s	$\frac{1}{t}$ / s^{-1}
1	30.0	900	10.0	0.100
2	25.0	625	14.4	0.069
3	20.0	400	22.5	0.044
4	15.0	225	40.0	0.025
5	10.0	100	90.0	0.011

Choose appropriate data from the table above to plot a graph that will enable you to determine the order of reaction with respect to H^+. [2]


1/t
/ s^{-1}
0.11
0.1
0.09
0.08
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0
0
100
200
300
400
500
600
700
800
900
1000
V^2 / cm^6

OR



Chooses to plot 1/t vs V^2 or V
Large scale (at least ½ of grid) and axes properly labelled with units stated
All points correctly plotted
Straight line / smooth curve drawn through origin and most of the points

(iv) State, with justification, the order of reaction with respect to H$^+$. [1]

Using graph of 1/t vs V^2
Since the graph obtained is a <u>straight line passing through the origin</u>, rate ∝ [H$^+$]^2. Hence, order with respect to H$^+$ is 2.

OR Using graph of 1/t vs V
A curve passing through the origin is obtained, whereby as [H$^+$] (or V) increases by <u>*n* times</u>, rate (or 1/t) increases by <u>*n*^{2} times</u>.
<u>[show any two points with co–ordinates on the graph</u> to illustrate this relationship]

Hence, order with respect to H$^+$ is <u>2</u>.

(b) Champagne is an example of *sparkling wine*, a term referring to wine with significant levels of carbon dioxide in it, making it fizzy. In the traditional method of production, wine is allowed to undergo a natural fermentation after bottling, which involves conversion of the malic acid present into lactic acid:

$$\underset{\text{malic acid}}{HO_2CCH_2CH(OH)CO_2H} \rightarrow \underset{\text{lactic acid}}{CH_3CH(OH)CO_2H} + CO_2$$

(i) A bottle typically has a total capacity of 1.5 dm^3 and contains 1.3 dm^3 of wine with a malic acid concentration of 0.05 mol dm^{-3}.

By means of the ideal gas equation, calculate the pressure exerted inside the air gap of the bottle by the carbon dioxide produced when all the malic acid present undergoes fermentation.

Assume that the temperature inside the bottle is 25°C. [2]

$n_{CO_2} = n_{\text{malic acid}}$
$= 1.3 \times 0.05$
$= 0.065$ mol

$PV = nRT$
$P = (0.065)(8.31)(25 + 273) / (0.2 \times 10^{-3})$
$= \underline{8.05 \times 10^5 \text{ Pa}}$

(ii) In fact, the pressure inside the bottle is much less under these conditions. Suggest why the actual pressure differs from the value calculated in **(i)**. [1]

Intermolecular attractive forces are not negligible. This causes the gas molecules to strike the walls of the container with less force, leading to lower pressure.

OR

Carbon dioxide can dissolve in aqueous solution. Thus less CO_2 occupies the empty space.

[Molecular volume not accepted as this would lead to actual pressure being higher.]

(iii) Besides malic acid, many other organic acids also play an important role in our everyday life. For instance, acrylic acid, with the structure $CH_2{=}CHCO_2H$, is the starting material for the production of many plastics and adhesives industrially.

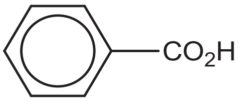
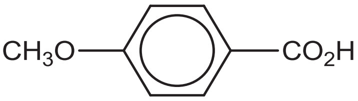
State the reagents and conditions that can be used to synthesize acrylic acid from lactic acid in the laboratory. [1]

Excess concentrated H_2SO_4, heat to 170°C

(iv) Another example of an organic acid is benzoic acid which is commonly used as a food preservative.

The K_a values of benzoic acid and its substituted derivative, 4–methoxybenzoic acid are given below:

Need a home tutor? Visit smiletutor.sg

Compound	K_a / mol dm^{-3}
 Benzoic acid	6.5 × 10^{-5}
 4–methoxybenzoic acid	3.5 × 10^{-5}

Explain the difference in the K_a values of the two acids. [2]

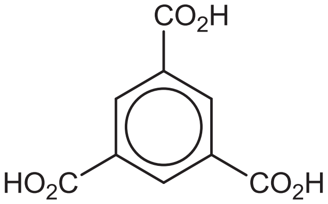
$RCO_2H \rightleftharpoons RCO_2^- + H^+$

4–methoxybenzoic acid is a weaker acid as shown by its lower K_a value. This is due to delocalization of the lone pair of O into the benzene ring, leading to intensification of the negative charge of the anion, which is hence destabilized.

(c) Compound **P** is an aromatic compound with molecular formula $C_{12}H_{15}O_3Cl$. It reacts with exactly 2 mol of PCl_5 to form an organic product **Q**. **P** also gives a brick–red precipitate with Fehling's solution.

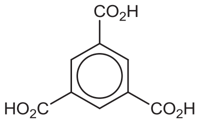
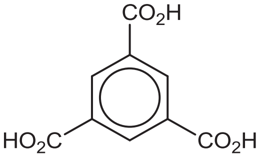
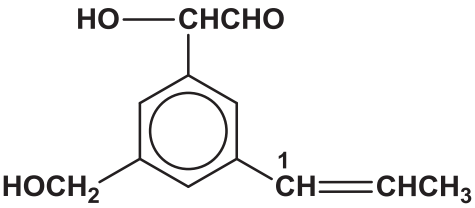
Upon heating **P** with alcoholic NaOH, only one of the products formed, **R**, has the molecular formula $C_{12}H_{14}O_3$.

On oxidation with hot acidified potassium manganate(VII) solution, **R** gives **S**, $C_2H_4O_2$, and the following compound:



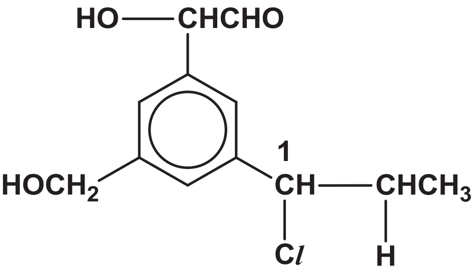
Suggest the structures of **P**, **Q**, **R** and **S**, explaining the reactions involved. [8]

	Rxn type	**Structural feature**
P + 2PCl_5 → Q	**Nucleophilic substitution**	**P contains 2 alcohol or –CO_2H groups. Hence, Q is a halogenoalkane or –COC*l* group.**
P + Fehling's soln	**Oxidation**	**Brick red ppt is Cu_2O.** **P has an aliphatic aldehyde group.** **Since P has only 3 oxygen atoms, it cannot contain –COOH. Hence, P must be alcohol and Q is a halogenoalkane.**
P + NaOH(alc) → R	**Elimination**	**P has H and C*l* atoms attached to adjacent C atoms.** **R is an alkene.**

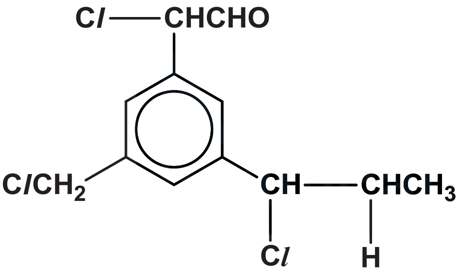
R + hot MnO_4^- / H^+ → S + 	Oxidative cleavage (given in qn)	Since S is an oxidation product, it must be a carboxylic acid or ketone. Based on its molecular formula, S is CH_3CO_2H. Hence, R has a $CH_3CH=$ group. The positions of the –COOH groups in  correspond to those of the side-chains in R. Hence, R is 

Since P only forms one alkene with alcoholic NaOH, C*l* atom is on C1.

Hence, P is



and Q is



[Total: 20]

Victoria Junior College

2017 H2 Chemistry Prelim Exam 9729/4

Suggested Answers

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

1 Determination of the M_r of a carbonate salt

FA 1 is a solid carbonate, **X**CO_3.

FA 2 is a solution containing 1.00 mol dm^{-3} of hydrochloric acid, HC*l*.

FA 3 is a solution of NaOH of concentration 0.100 mol dm^{-3}.

In this question, you will perform a titration. The data from this titration will be used to determine

- the amount of CO_3^{2-} ions in the mass of **FA 1** used,
- the M_r of **X**CO_3 and hence the identity of the metal **X**.

(a) Titration of FA 4 against FA 3

(i) You are to determine the amount of carbonate ions, CO_3^{2-}, in **FA 1,** by back titration after some **FA 2** has been added to it. Carry out the procedure as listed below.

1. Weigh accurately between 1.25 – 1.35 g of **FA 1** into a clean and dry 150 cm^3 beaker. If you have used the TARE facility on the balance, indicate clearly in your recording.
2. Record your weighing in an appropriate format in the space provided on the next page.
3. Measure out 50 cm^3 of **FA 2** into a measuring cylinder. Pour this into the beaker containing **FA 1.** Stir thoroughly to ensure all of **FA 1** has dissolved.
4. Quantitatively transfer the mixture into a 250 cm^3 volumetric flask. Make up to the mark with distilled water. Shake to obtain a homogeneous solution. Label this solution **FA 4.**
5. Pipette 25.0 cm^3 of **FA 4** into a conical flask and add 2 drops of methyl orange indicator.
6. Fill the burette with **FA 3.**
7. Titrate **FA 4** with **FA 3.**
8. Repeat the titration as many times as you consider necessary to obtain accurate results.
9. Record your titration results in the space provided on the next page. Make certain that your recorded results show the precision of your working.

Results:

*For weighing of **FA 1***

Mass of beaker and FA 1 / g	5.125
Mass of empty beaker / g	3.825
Mass of FA 1 used / g	1.300

OR if TARE is used:

Mass of beaker only / g	TARE
Mass of FA1 / g	1.300

✓✓Table with appropriate headers / units
AND all readings to 3 dp
AND mass used within 1.25 – 1.35 g

Titration

Experiment	1	2
Final burette reading / cm^3	25.90	36.00
Initial burette reading / cm^3	0.00	10.00
Volume of FA 3 used / cm^3	25.90	26.00

✓✓Table with appropriate headers and units
✓✓Record all burette readings to 2 dp
✓✓At least two consistent readings ±0.10 cm^3
Accuracy:
[2m] M_r within ± 4 units of supervisor's answer (108)
[1m] M_r within ± 8 units of supervisor's answer (108)

[5m]

[6]

(ii) From your titrations, obtain a suitable volume of **FA 3** to be used in your calculations. Show clearly how you obtained this volume.

✓✓Average volume of FA 3 = (25.90 + 26.00) / 2 = 25.95 cm^3

volume of **FA 3** = 25.95 cm^3 [1]

(b) **(i)** Calculate the amount of excess acid pipetted into the conical flask.

✓✓Amount of acid pipetted in 25.0 cm^3
= (25.95 / 1000) x 0.100 = 2.60×10^{-3} mol

Amount of excess acid in conical flask = 2.60×10^{-3} mol [1]

(ii) Calculate the total amount of excess acid in the volumetric flask.

✓✓Total amount of excess acid
= (250 / 25.0) x 2.60×10^{-3} mol = 2.60×10^{-2} mol

amount of excess acid in the volumetric flask = 2.60×10^{-2} mol [1]

(iii) Hence calculate the amount of acid that has reacted with the carbonate that you have weighed out.

✓✓Amount of acid reacted
= $(1.00 \times 50/1000) - 2.60 \times 10^{-2} = 0.0240$ mol

Amount of acid reacted = **0.0240 mol** [1]

(iv) Use your answer in **b(iii)** to calculate the M_r of **X**CO_3.

$XCO_3 + 2HCl \rightarrow XCl_2 + CO_2 + H_2O$

✓✓Amount of XCO_3 = $(0.0240 / 2) = 0.0120$ mol

✓✓M_r of XCO_3 = $(1.30 / 0.0120) = 108.3$

M_r of **X**CO_3 = **108.3**

Deduce the identity of metal **X**. Show your working.
[A_r: C, 12.0; O, 16.0; H, 1.0; Be, 9.0; Mg, 24.3; Ca, 40.1; Sr, 87.6; Ba, 137.3]

A_r of X + 12.0 + 3(16.0) = 108.3
A_r of X = 48.3

✓✓Hence X is Ca (calculated value closest to A_r of Ca)

X is **Ca** [3]

[Total: 13]

(c) **Planning**

Sodium carbonate, Na_2CO_3, does **not** decompose on heating with a Bunsen burner. Sodium hydrogencarbonate, $NaHCO_3$, decompose on heating.

$$2NaHCO_3(s) \rightarrow Na_2CO_3(s) + H_2O(g) + CO_2(g)$$

You are to design an experiment in which the percentage by mass of $NaHCO_3$ in a mixture of $NaHCO_3$ and Na_2CO_3 can be determined by heating and weighing alone.

The only apparatus available consists of:

a boiling tube and holder
a chemical balance
a Bunsen burner
a heat proof mat

You are to show how you would use the results of this experiment to determine the percentage by mass of $NaHCO_3$ in the mixture.

(i) Outline, step by step, the practical sequence for the method you would use to:

- make appropriate weighings,
- decompose the sodium hydrogencarbonate in the mixture by heating,
- ensure that the decomposition was complete.

1. **Weigh the clean and dry boiling tube.**

2. **Add all the sample into the boiling tube. Weigh the mass of the boiling tube with the sample.**

3. **Heat the boiling tube gently at first (~1 min) and then strongly (~5 min) to decompose the sodium hydrogencarbonate. Heat the whole length of the tube to ensure even heating of the mixture and to prevent condensation.**

4. **Cool the boiling tube on a heat proof mat, and weigh the mass of the boiling tube and its residue.**

5. **Repeat heating, cooling and weighing steps [steps 3 and 4] until constant mass is achieved (OR consecutive mass difference within ±0.050 g is achieved) to ensure complete decomposition. Record all masses.**

Mark Scheme

[1m]: weigh empty boiling tube, sample and boiling tube before and after heating

[1m]: give details such as dry boiling tube, heat strongly, heat whole length of tube, use of heat proof mat for cooling

[1m]: heat until constant mass (OR within ±0.050 g) to ensure complete decomposition

[3]

(ii) By considering the products of the decomposition, suggest a reason why a crucible, without a lid, might be more appropriate than a boiling tube for this experiment.

The crucible has a ✓✓wider surface area for the volatile substances such as water vapour and carbon dioxide to escape more readily which lowers the risk of breakage due to condensation.

[OR It can withstand high temperature during heating which reduces the risk of breakage.]

[1]

(iii) Prepare a table to show the masses you would measure and record during the experiment. Include in your table any other masses you would calculate from the experimental results to enable you to determine the percentage by mass of $NaHCO_3$ in the mixture.

Insert in your table the letters **A**, **B**, **C** etc. to represent each mass. Use these letters to show how your calculated masses are obtained e.g. **B** – **A**.

Mass of empty boiling tube / g	**A**
Mass of boiling tube and sample before heating / g	**B**
Mass of boiling tube and residue after heating / g	**C**
Mass of sample used / g	**B – A**
Mass loss due to H_2O and CO_2 / g	**B – C**

Mark Scheme

[1m]: Tabulation with headers and units as well as raw data recorded (first 3 rows)

[1m]: Processed data of mass of sample used and mass loss due to heating (last 2 rows)

[2]

(iv) Use the letters you have entered in **(c)(iii)** to show how you would process the results to find:

- the mass of $NaHCO_3$ in the mixture,

[A_r: C, 12.0; H, 1.0; O, 16.0; Na, 23.0]

✓✓Mass of $NaHCO_3$ in the mixture

$= (B - C) \times \frac{168.0}{62.0}$ g = R g

- the percentage by mass of $NaHCO_3$ in the mixture.

✓✓Percentage of $NaHCO_3$ in the mixture = [R / (B – A)] x 100 %

[2]

[Total: 8]

2 Determination of the concentration of a mixture of acids and the enthalpy change of neutralization

FA 5 is an aqueous solution prepared by mixing equal volumes of y mol dm^{-3} hydrochloric acid, HC*l*, and y mol dm^{-3} sulfuric acid, H_2SO_4.

FA 6 is 1.60 mol dm^{-3} sodium hydroxide, NaOH.

Take care as aqueous solutions of sodium hydroxide are corrosive.

When an acid is run into an alkali, an exothermic reaction takes place and the temperature of the mixture increases until the end–point is reached. If acid is added beyond the end–point, the temperature will decrease as no further reaction takes place and the acid is at a lower temperature than the mixture.

You are to follow the neutralisation of the acids in **FA 5** by measuring the temperature as volumes of **FA 5** are added in regular portions from a burette to a fixed volume of **FA 6** placed in a Styrofoam cup.

The data obtained will enable you to determine the value of y and the enthalpy change of neutralization, ΔH_{neut}, of this acid–base 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 5**:

- Total volume of **FA 5** added from the burette up to the point in time
- Total volume of solution in the cup (V_{cup})
- Temperature measured (T)

You also need to calculate the corresponding values of:

- $\Delta T = T - T_0$, where T_0 is the initial temperature of **FA 6**
- ($V_{\text{cup}} \times \Delta T$) to 3 significant figures

1. Fill the burette to 0.00 cm^3 with **FA 5**.
2. Place the Styrofoam cup in a 250 cm^3 beaker to provide support for the cup. Use the measuring cylinder to place 40.0 cm^3 of **FA 6** into the cup and measure the steady temperature of the alkali, T_0.
3. Run 5.00 cm^3 of **FA 5** from the burette into the cup, stir the solution with the thermometer and record the maximum temperature, T.
4. **Immediately** run a further 5.00 cm^3 of **FA 5** from the burette into the cup, stir and record the maximum temperature as before.
5. Continue the addition of **FA 5** in 5.00 cm^3 portions 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) Experimental results

Total volume of FA 5 / cm^3	Total volume of solution in the cup (V_{cup}) / cm^3	Temperature (T) / °C	$\Delta T = T - T_0$ / °C	($V_{cup} \times \Delta T$) / cm^3 °C
0.00	40.0	31.0	0.0	0.00
5.00	45.0	35.0	4.0	180
10.00	50.0	38.5	7.5	375
15.00	55.0	41.0	10.0	550
20.00	60.0	43.0	12.0	720
25.00	65.0	44.0	13.0	845
30.00	70.0	45.0	14.0	980
35.00	75.0	44.0	13.0	975
40.00	80.0	43.0	12.0	960
45.00	85.0	42.0	11.0	935

✓✓Clear headers with units
AND table populated up to 45.00 cm^3 of FA 5
✓✓Correct computation of V_{cup}, ΔT and ($V_{cup} \times \Delta T$)
✓✓Correct precision: 2 d.p. for FA 5, 1 d.p. for V_{cup}, 1 d.p. for temperature and 3 s.f. for ($V_{cup} \times \Delta T$)

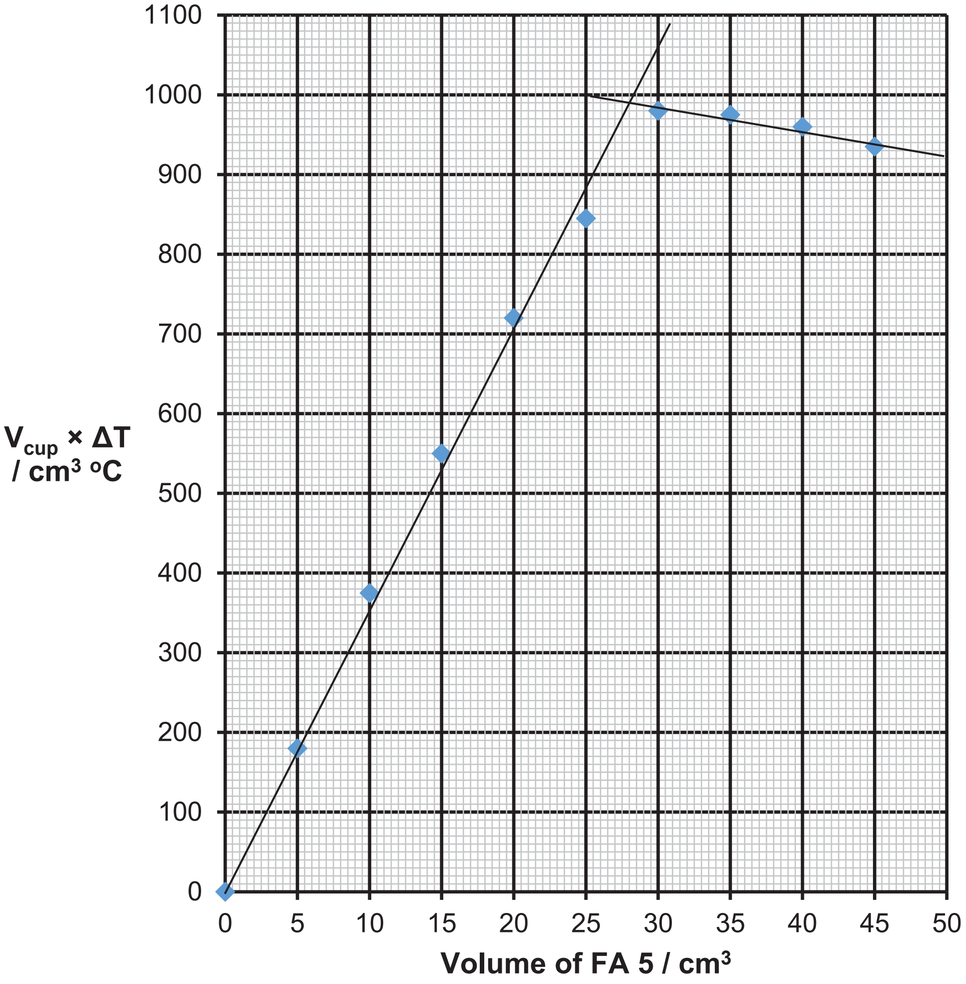
[3]

(ii) On the grid provided below, plot (V_{cup} × ΔT) against the total volume of **FA 5** added.

Draw a line of best fit for the points before the maximum value of (V_{cup} × ΔT).

Draw a second line of best fit for the points after the maximum value.

Extrapolate both lines until they meet.



✓✓Axes labelled with units AND scale large enough to cover at least ½ of given grid
✓✓Points correctly plotted to ± ½ a small square AND two lines of best fit drawn and extrapolated to meet

[2]

(iii) Read from your graph the maximum value of (V_{cup} × ΔT) and the end–point volume of the titration.

maximum value of (V_{cup} × ΔT) = **990 cm^3 °C**
end–point volume = **28.0 cm^3** [3]

✓✓Vol of FA5 AND V_{cup} × ΔT correctly read to ± ½ a small square
Accuracy:
Supervisor's value = 28.0 cm^3
[2m] End–point volume within 3.0 cm^3 of supervisor's value
[1m] End–point volume within 5.0 cm^3 of supervisor's value

(b) **(i)** Calculate the concentration of hydrogen ions in **FA 5**.

$H^+ + OH^- \rightarrow H_2O$

$n_{OH^-} = (40.0 / 1000) \times 1.60 = 0.0640 \text{ mol} = n_{H^+}$

✓✓ $[H^+] = (0.0640 / \frac{28.0}{1000})$

$= 2.29 \text{ mol dm}^{-3}$

concentration of hydrogen ions = **2.29 mol dm^{-3}** [1]

(ii) Hence, determine the value of *y*, which is the concentration of either HC*l* or H_2SO_4 used to prepare **FA 5**.

If V cm^3 of HC*l* and V cm^3 of H_2SO_4 were mixed to prepare FA 5,

$[H^+] = [n_{H^+}$ from HC*l* + n_{H^+} from $H_2SO_4] / 2V$

$2.29 = [V \times y + V \times 2y] / 2V$

$= 3y / 2$

✓✓ y = 1.53 [accept with or without mol dm^{-3}]

y = **1.53** [1]

(c) **(i)** Determine the enthalpy change of neutralization of this reaction, ΔH_{neut}.

You should assume that the specific heat capacity of the final solution is 4.18 J g^{-1} K^{-1}, and that its density is 1.00 g cm^{-3}.

✓✓Heat evolved = $(V_{cup} \times \Delta T) \times c = 990 \times 4.18 = 4140$ J

$n_{H_2O} = n_{OH^-} = 0.0640$ mol

✓✓$\Delta H_{neut} = -4140 / 0.0640 = -64700 \text{ J mol}^{-1} = -64.7 \text{ kJ mol}^{-1}$

✓✓Correct units for 1(a)(ii), 1(b), 2(a)(iii), 2(b) and 2(c)(i)

AND

1 d.p. for A_r / M_r, 3 sf for other answers, clear statements and working for 1(b), 2(b) and 2(c)(i)

ΔH_{neut} = **$-64.7 \text{ kJ mol}^{-1}$** [3]

(ii) Student **A** carefully performed the same experiment and correctly processed the data using the same method. His calculated value of ΔH_{neut} is -65.0 kJ mol^{-1} while the published value for this enthalpy change is -57.7 kJ mol^{-1}.

The specific heat capacity of the Styrofoam cup has not been taken into consideration in calculating ΔH_{neut}. Explain whether this omission could have been the reason for the discrepancy between the value obtained by Student **A** and the one published.

Omission of the specific heat capacity of the cup ✓✓could not have been the reason for the discrepancy because this would result in a ✓✓less exothermic ΔH_{neut} since the cup would also absorb heat.

[2]

(iii) Student **B** performed the same experiment but chose to plot ΔT instead of $(V_{cup} \times \Delta T)$ on the y–axis.

He also drew and extrapolated two straight lines through the plotted points to do the calculations.

Suggest why his method is likely to yield **less** accurate results.

$V_{cup} \times \Delta T \propto$ heat evolved
$\propto$ moles of limiting reagent
$\propto$ volume of FA 5 added before the end–point

✓✓However, total volume in the cup is not constant. Hence, ΔT is not proportional to volume of FA 5 added [OR vary less linearly with volume of FA 5]

[1]

[Total: 16]

3 Inorganic Analysis

(a) You are provided with the solid **FA 7** which contains one cation and one anion from the ions listed in the **Qualitative Analysis Notes**, and the solution **FA 8**.

You are to perform the tests below to identify the ions present in **FA 7** and to suggest the nature of the compound in **FA 8**.

If the evolution of a gas is observed at any stage, the gas should be tested and identified. Details of the test carried out, the observations of the test and the identity of the gas should be given with the observations.

If it appears that no reaction has taken place this should be clearly recorded.

Carry out the following tests on **FA 7** and **FA 8** and complete the table to show your observations.

	Test	Observations
(i)	To a spatula–full of **FA 7** in a test-tube add 3 cm depth of dilute sulfuric acid. Warm, and when the reaction has stopped, filter the mixture. Retain the filtrate for tests **(iii)** and **(iv)**.	• **Effervescence of CO_2 which** • **forms white ppt. in limewater** • **Colourless filtrate**
(ii)	Place a spatula–full of **FA 7** in a test-tube and heat strongly. Leave the tube to cool. Retain the residue for test **(viii)**.	• **CO_2 gas evolved which** • **forms white ppt. in limewater** • **Black residue (OR dark brown)**
(iii)	To a 1 cm depth of the filtrate from **(i)** in a test–tube, add aqueous sodium hydroxide drop by drop until 1 cm depth of the reagent has been added. Then add a further 1 cm depth of the aqueous sodium hydroxide.	• **Off-white ppt. insoluble in excess**
	Swirl the test-tube and leave to stand for 2–3 minutes.	• **Off-white ppt., rapidly turning brown on contact with air**
(iv)	To a 1 cm depth of the filtrate from **(i)** in a test-tube, add aqueous ammonia drop by drop until 1 cm depth of the reagent has been added. Then add a further 1 cm depth of the aqueous ammonia.	• **Off-white ppt. insoluble in excess**

	Then **cautiously** add 1 cm depth of **FA 8**.	- **Off-white ppt., rapidly turning (dark) brown** - **Effervescence of O_2** - **relights a glowing splint**
(v)	Place 2 cm depth of aqueous potassium iodide in a test–tube and add 2 cm depth of **FA 8**.	- **Solution turns (pale) yellow**
	Then add 2 cm depth of dilute sulfuric acid.	- **Yellow solution turns brown** - **Black solid forms**
(vi)	To a 1 cm depth of **FA 8** in a test–tube, add 1 cm depth of dilute sulfuric acid and 2 cm depth of potassium manganate(VII). Observe for 2 minutes or until no further change occurs.	- **Purple solution decolourises** - **Effervescence of O_2** - **relights a glowing splint**
(vii)	To a 1 cm depth of aqueous sodium sulfite in a test-tube, add a few drops of aqueous barium nitrate.	- **White ppt**
	Then add 2 cm depth of dilute nitric acid.	- **White ppt soluble in acid**
	Immediately add 1 cm depth of **FA 8**.	- **White ppt reforms**
(viii)	Transfer a portion of the residue from test **(ii)** into a test–tube and add 2 cm depth of **FA 8**.	- **Effervescence of O_2** - **relights a glowing splint**

[Mark Scheme: 20-23: 9m, 18-19: 8m, 16-17: 7m, 14-15: 6m, 12-13: 5m, 10-11: 4m, 8-9: 3m, 6-7: 2m, 4-5: 1m]

[9]

(b) **(i)** From your observations, identify the cation and anion present in **FA 7**. Quote evidence from the table to support your conclusions.

Cation	**✓Mn^{2+}**
Evidence	**✓Test (iii): off-white ppt., rapidly turning brown on contact with air, insoluble in excess [OR test (iv)]**
Anion	**✓CO_3^{2-}**
Evidence	**✓Test (i): Effervescence of CO_2 that forms white ppt. in limewater [OR test (ii)]**

[2]

(ii) In tests **(a)(v)** and **(vii)**, **FA 8** behaves as **✓oxidising agent**

In test **(a)(vi)**, **FA 8** behaves as **✓reducing agent** [1]

[Total: 12]

(c) Planning

One of the transition metals, vanadium, was named after the Scandinavian goddess of beauty and fertility, Vanadis (Freya) due to the wide range of colours found in vanadium compounds.

Starting with an aqueous solution of VO_2^+, you are to devise a plan which will enable you to determine the colour exhibited by two other ions containing vanadium, VO^{2+} and V^{3+}. Your plan should only involve simple test–tube reactions.

The standard electrode potentials of the following ions are as shown:

$$VO_2^+ + 2H^+ + e^- \rightleftharpoons H_2O + VO^{2+} \qquad E^\ominus = +1.00\text{ V}$$
$$VO^{2+} + 2H^+ + e^- \rightleftharpoons H_2O + V^{3+} \qquad E^\ominus = +0.34\text{ V}$$
$$V^{3+} + e^- \rightleftharpoons V^{2+} \qquad E^\ominus = -0.26\text{ V}$$

There are four reducing agents available as shown:

$$Zn^{2+} + 2e^- \rightleftharpoons Zn \qquad E^\ominus = -0.76\text{ V}$$
$$Sn^{2+} + 2e^- \rightleftharpoons Sn \qquad E^\ominus = -0.14\text{ V}$$
$$O_2 + 2H^+ + 2e^- \rightleftharpoons H_2O_2 \qquad E^\ominus = +0.68\text{ V}$$
$$Fe^{3+} + e^- \rightleftharpoons Fe^{2+} \qquad E^\ominus = +0.77\text{ V}$$

(i) Explain which reducing agent(s) will **not** be suitable for determining the colours exhibited by VO^{2+} and V^{3+}.

✓✓Zinc will reduce VO_2^+ to V^{2+} and hence will not be able to observe the colour exhibited by VO^{2+} and V^{3+}.
✓✓Fe^{2+} is coloured and thus will affect the final colour observed.
[OR The reaction between Fe^{2+} and VO_2^+ is unlikely to occur as both reactants are positively charged and hence will not be kinetically feasible.]

[2]

(ii) Complete the table by choosing a suitable reducing agent for determining the colour exhibited by VO^{2+} and V^{3+} respectively. Justify your choice by calculating relevant $E^\ominus_{cell}$ values.

	Reducing agent	Justification
$VO_2^+ \rightarrow VO^{2+}$	**✓✓H_2O_2**	**$VO_2^+ + 2H^+ + e^- \rightleftharpoons H_2O + VO^{2+}$ $E^\ominus = +1.00$ V** **$O_2 + 2H^+ + 2e^- \rightleftharpoons H_2O_2$ $E^\ominus = +0.68$ V** **$E^\ominus_{cell} = 1.00 - (0.68)$** **$=$ ✓✓$+0.32$ V > 0** **Reaction is feasible.** **$VO^{2+} + 2H^+ + e^- \rightleftharpoons H_2O + V^{3+}$ $E^\ominus = +0.34$ V** **$O_2 + 2H^+ + 2e^- \rightleftharpoons H_2O_2$ $E^\ominus = +0.68$ V** **$E^\ominus_{cell} = 0.34 - (0.68)$** **$=$ ✓✓-0.34 V < 0** **Reaction is not feasible.** **H_2O_2 can only reduce VO_2^+ to VO^{2+}.**

$VO_2^+ \rightarrow V^{3+}$	✓✓Sn	$VO_2^+ + 2H^+ + e^- \rightleftharpoons H_2O + VO^{2+}$ $E^\ominus = +1.00$ V $Sn^{2+} + 2e^- \rightleftharpoons Sn$ $E^\ominus = -0.14$ V $E^\ominus_{cell} = 1.00 - (-0.14)$ $=$ ✓✓ $+1.14$ V > 0 Reaction is feasible. $VO^{2+} + 2H^+ + e^- \rightleftharpoons H_2O + V^{3+}$ $E^\ominus = +0.34$ V $Sn^{2+} + 2e^- \rightleftharpoons Sn$ $E^\ominus = -0.14$ V $E^\ominus_{cell} = 0.34 - (-0.14)$ $=$ ✓✓ $+0.48$ V > 0 Reaction is feasible. $V^{3+} + e^- \rightleftharpoons V^{2+}$ $E^\ominus = -0.26$ V $Sn^{2+} + 2e^- \rightleftharpoons Sn$ $E^\ominus = -0.14$ V $E^\ominus_{cell} = -0.26 - (-0.14)$ $=$ ✓✓ -0.12 V < 0 Reaction is not feasible. Sn can only reduce VO_2^+ to V^{3+}.

[Mark Scheme: 6-7: 4m, 5: 3m, 3-4: 2m, 1-2: 1m]

[4]

[Total: 6]

CANDIDATE'S NAME: ________________________________ CTG: ____________

YISHUN JUNIOR COLLEGE

2017 JC2 PRELIMINARY EXAMINATION

CHEMISTRY **9729/01**

HIGHER 2

Paper 1 Multiple Choice Questions **FRIDAY 15 SEPTEMBER 2017**

0800hrs − 0900hrs

(1 hour)

Additional Materials: Optical Mark Sheet (OMS)
Data Booklet

READ THESE INSTRUCTIONS FIRST

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

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

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

Read the instructions on the Answer Sheet very carefully.

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

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

This question paper consists of **13** printed pages.

1 An element R can exist in a few oxidation states. 0.01 mol of R^{2+} requires 0.004 mol of acidified $KMnO_4$ for complete reaction. The half equation for reduction of MnO_4^- is

$$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$$

What is the final oxidation state of R?

A +4 **B** +3 **C** 0 **D** −1

2 Which equation corresponds to the third ionisation energy of titanium (Ti)?

A $Ti(g) \rightarrow Ti^{3+}(g) + 3e^-$

B $Ti^{2+}(s) \rightarrow Ti^{3+}(g) + e^-$

C $Ti^{2+}(g) \rightarrow Ti^{3+}(g) + e^-$

D $Ti^{3+}(g) + e^- \rightarrow Ti^{2+}(g)$

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

Which of the following particles would, on gaining an electron, have a half-filled set of p orbitals?

1 B^- 2 C 3 N 4 N^+

A 1, 2 and 3

B 1, 2 and 4

C 3 only

D 2 and 4

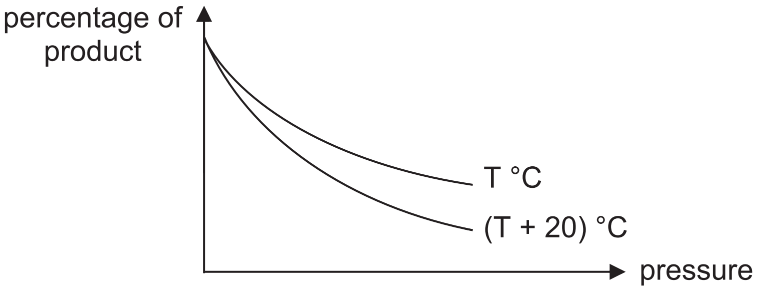
4 Which gas shows the greatest deviation from ideality?

A CH_4 **B** SO_3 **C** C_2H_2 **D** O_2

5 A gas at a pressure of 4.50 atm is heated from 25 °C to 480 °C and simultaneously compressed to one-third of its original volume. What will be the final pressure?

A 3.79 atm **B** 34.1 atm **C** 86.4 atm **D** 259 atm

6 The graph below shows how the percentage of product present at equilibrium varies with temperature and pressure for a reaction.



Which reaction could the graph represent?

A $4Fe(s) + 3O_2(g) \rightleftharpoons 2Fe_2O_3(s)$ $\Delta H = -1644\ \text{kJ mol}^{-1}$

B $N_2O_4(g) \rightleftharpoons 2NO_2(g)$ $\Delta H = +57\ \text{kJ mol}^{-1}$

C $2C(s) + O_2(g) \rightleftharpoons 2CO(g)$ $\Delta H = -222\ \text{kJ mol}^{-1}$

D $CO(g) + Cl_2(g) \rightleftharpoons COCl_2(s)$ $\Delta H = +86\ \text{kJ mol}^{-1}$

7 Values for the ionic product of water, K_w, at two different temperatures are given below.

Temperature / °C	K_w / mol^2 dm^{-6}
25	1.00×10^{-14}
50	5.48×10^{-14}

What is correct for pure water at 50 °C?

A $[H^+] > [OH^-]$

B pH = 2.34×10^{-7}

C pH > 7

D pH < 7

8 What is a satisfactory indicator for the titration of 0.10 mol dm^{-3} aqueous methylamine with 0.10 mol dm^{-3} ethanoic acid?

A methyl red (pH range 4.2 − 6.3)

B bromothymol blue (pH range 6.0 − 7.6)

C thymol blue (pH range 8.0 − 9.6)

D there is no suitable indicator

9 The uncatalysed reaction between SO_2 and O_2 is slow.

$$2SO_2 + O_2 \rightarrow 2SO_3$$

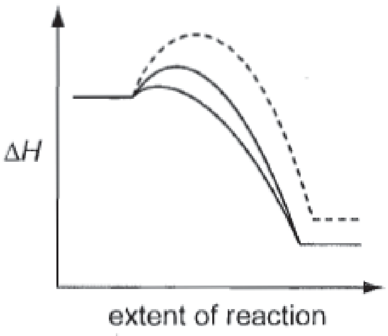
The reaction is speeded up in the presence of the homogeneous catalyst NO, which participates as follows.

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

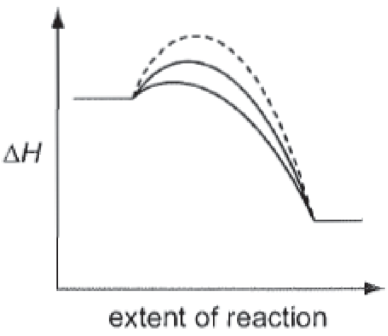
$$2NO_2 + 2SO_2 \rightarrow 2NO + 2SO_3$$

Which reaction pathway diagram is most appropriate for describing the enthalpy changes occurring during the catalysed reaction? In each case the reaction pathway for the uncatalysed reaction is shown as a dashed line.

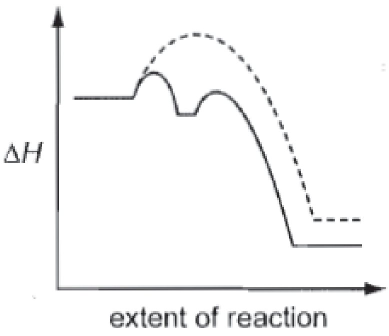
A



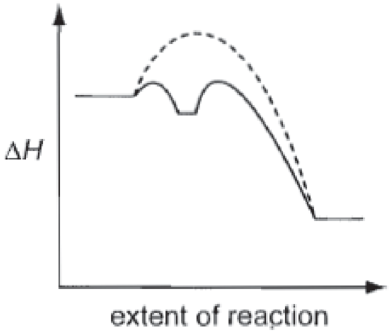
B



C



D



10 The enthalpy change of formation of rubidium bromide, RbBr, can be calculated using a Born-Haber cycle.

The relevant enthalpy changes are shown in the table.

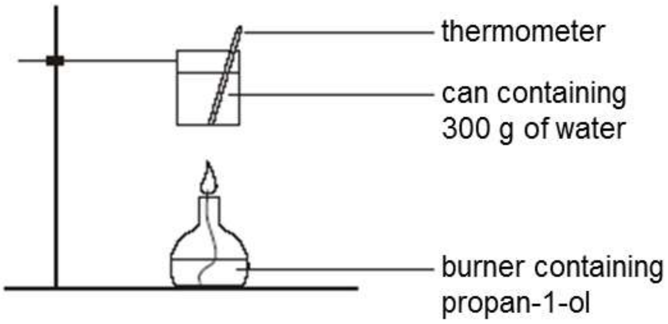
	enthalpy change / kJ mol^{-1}
$Rb(s) \rightarrow Rb(g)$	+81
$Br_2(l) \rightarrow 2Br(g)$	+224
$Rb(g) \rightarrow Rb^+(g) + e^-$	+403
$Br(g) + e^- \rightarrow Br^-(g)$	−324
$Rb^+(g) + Br^-(g) \rightarrow RbBr(s)$	−687

What is the enthalpy change of formation of RbBr?

A −303 kJ mol^{-1} **B** −415 kJ mol^{-1}

C −577 kJ mol^{-1} **D** −627 kJ mol^{-1}

11 A student used the set-up below to heat a can containing 300 g of water.



The following data were recorded:
mass of propan-1-ol burnt = m g
change in temperature of water = ΔT °C

Given that:
relative molecular mass of propan-1-ol = 60.0
enthalpy change of combustion of propan-1-ol = -2021 kJ mol^{-1}
specific heat capacity of water = c J g^{-1} K^{-1}

What is the efficiency of this heating process?

A $\dfrac{m \times 2021 \times 1000}{300 \times c \times \Delta T \times 60.0} \times 100\%$

B $\dfrac{m \times c \times \Delta T \times 60.0}{300 \times 2021 \times 1000} \times 100\%$

C $\dfrac{300 \times c \times \Delta T \times 60.0}{m \times 2021} \times 100\%$

D $\dfrac{300 \times c \times \Delta T \times 60.0}{m \times 2021 \times 1000} \times 100\%$

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

Peroxodisulfate(VI), $S_2O_8^{2-}$, is capable of oxidising iodide as shown in the following equation.

$$2I^- + S_2O_8^{2-} \rightarrow I_2 + 2SO_4^{2-}$$

Which metal ion can be a suitable catalyst for this reaction?

1 Cu^{2+} 2 Co^{2+} 3 Mn^{2+} 4 V^{2+}

A 1, 2 and 3

B 2 and 3

C 2 only

D 4 only

13 Consider the reaction $2A + 2B \rightarrow A_2B_2$.
The mechanism involves the following steps:

$2A \rightleftharpoons C$	fast
$B + C \rightarrow D$	slow
$B + D \rightarrow A_2B_2$	fast

Based on the information, what is the rate equation for this reaction?

A rate = $k\,[A]^2\,[B]^2$

B rate = $k\,[B]\,[C]$

C rate = $k\,[A]^2\,[B]$

D rate = $k\,[A]\,[B]^2$

14 Element J is in Period 3 of the Periodic Table. The following four statements were made about the properties of element J or its compounds.

Three statements are correct descriptions and one is false.

Which statement does **not** fit with the other three?

A Adding NaOH(aq) to the solution resulting from the reaction of a chloride of J with water produces a white precipitate which is soluble in an excess of NaOH(aq).

B Element J is a solid at room temperature.

C Element J has the highest melting point among the period 3 elements.

D The oxide of element J is soluble in hydrochloric acid.

15 A student was given a sample of strontium carbonate that was mixed with strontium nitrate. He carried out two separate experiments using the same mass of the solid mixture.

Strontium nitrate decomposes according to the following equation.

$$Sr(NO_3)_2(s) \rightarrow SrO(s) + 2NO_2(g) + \tfrac{1}{2}O_2(g)$$

Experiment 1: The sample was heated strongly to constant mass and the volume of gas evolved was found to be 200 cm^3.

Experiment 2: Excess dilute sulfuric acid was added to the sample and the volume of gas evolved was found to be 75 cm^3.

All volumes were measured at the same temperature and pressure.

What is the mole ratio of strontium carbonate to strontium nitrate in the sample?

A 3 : 2 **B** 3 : 5 **C** 6 : 5 **D** 8 : 5

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

By using the relevant $E^\ominus$ values, what are the vanadium containing products formed when chlorine is passed through a solution that contains $VO^{2+}(aq)$?

A V^{3+}

B VO_2^+

C VO_2^+, VO_3^- and V^{3+}

D VO_2^+ and VO_3^-

17 Element Y has the following electronic configuration.

$$1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^7\,4s^2$$

Which compounds do **not** exist?

1 YO_2Cl_2

2 $[Y(C_2O_4)_2(H_2O)_2]Cl$

3 $Na_2[Y(CN)_6]$

4 YCl_2

A 1 only

B 1, 2 and 3

C 2 and 3

D 2, 3 and 4

18 Platinum(IV) chloride is combined with ammonia to form a single product. The product is a different platinum(IV) compound which contains a cation with a 2+ charge and has a co-ordination number of 6.

What is the formula of this product?

A $Pt(NH_3)_6Cl_2$

B $Pt(NH_3)_3Cl_4$

C $Pt(NH_3)_4Cl_4$

D $Pt(NH_3)_6Cl_4$

19 The C−H bond lengths of three hydrocarbons are given in the table below.

compound	structural formula	C−H bond length / nm
ethane	CH_3CH_3	0.110
ethene	$CH_2{=}CH_2$	0.108
ethyne	$CH{\equiv}CH$	0.106

Which statement best explains the shortest C−H bond length observed in ethyne?

A The carbon-carbon triple bond in ethyne has the greatest bond energy.

B The bond angle around the carbon atom in ethyne is the largest.

C The orbital that carbon used in formation of the C−H bond in ethyne has the greatest s orbital character.

D A sp-sp overlap occurs between the two carbon atoms in ethyne.

20 Which statements best describe the reaction mechanism involved in the conversion of chloroethane to ethanol?

1 The reaction mechanism involves a carbocation.

2 The reaction mechanism involves nucleophilic attack of OH^- in an overall second order reaction.

3 The reaction mechanism involves heterolytic fission of the C−C*l* bond, followed by a reaction with OH^-.

4 The activation energy of the first step of the mechanism is greater than the activation energy of the second step of the mechanism.

A 1 and 3 only

B 2 only

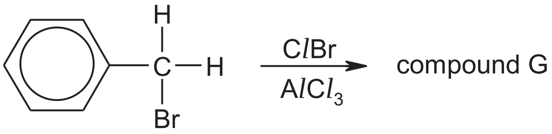
C 1, 3 and 4 only

D 2 and 4 only

21 How many constitutional isomers can C_4H_9Cl form?

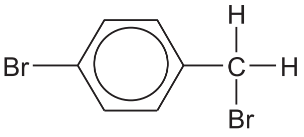
A 3 **B** 4 **C** 5 **D** 6

22 Bromine, in the presence of anhydrous aluminium chloride, undergoes a substitution reaction with benzene forming bromobenzene. When bromomethylbenzene reacts with C*l*Br, in the presence of anhydrous aluminium chloride, a similar reaction occurs and compound G is formed.

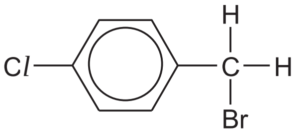


What could compound G be?

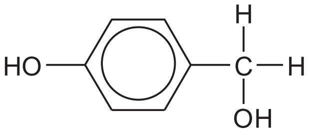
A



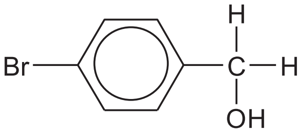
B



C



D



23 An alcohol D has the molecular formula of $C_5H_{11}OH$. On heating D with concentrated sulfuric acid, two products E and F are formed, E being the minor product. On heating E with hot acidified potassium manganate(VII), one of the products gives a pale yellow precipitate with alkaline aqueous iodine.

What could D be?

A $CH_3CH(OH)CH_2CH_2CH_3$

B $CH_3CH_2CH(OH)CH_2CH_3$

C $CH_3CH(CH_3)CH(OH)CH_3$

D $(CH_3)_2C(OH)CH_2CH_3$

24 Which of the following reagents **cannot** be used to distinguish between ethanol and propanone?

A alkaline aqueous iodine

B acidified potassium dichromate(VI)

C 2,4-dinitrophenylhydrazine

D sodium metal

25 Which reaction yields a carbon compound containing deuterium, D? [D = ^2H]

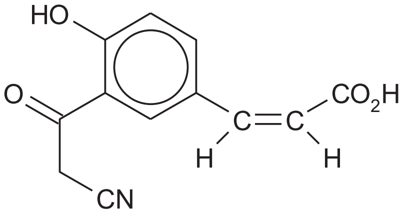
A $CH_3CH_2CN \xrightarrow{\substack{NaOD \\ D_2O}}$

B $CH_3CH(OH)CH_3 \xrightarrow{\substack{KMnO_4 \\ D_2SO_4(aq)}}$

C $CH_3CO_2H \xrightarrow{\substack{C_2H_5OD \\ \text{conc } D_2SO_4}}$

D $C_6H_5ONa \xrightarrow{D_2O}$

26 Which statements about compound P are correct?



compound P

1 4 moles of hydrogen gas will react completely with 1 mole of compound P in the presence of platinum metal.

2 It will exist as a pair of stereoisomers.

3 It reacts with ethanoic acid in the presence of concentrated sulfuric acid to form a sweet-smelling product.

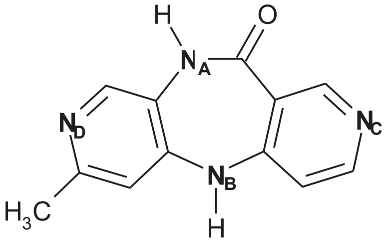
A 1, 2 and 3

B 2 only

C 1 and 2 only

D 2 and 3 only

27 An analogue of Nevirapine which is a synthetic antiviral drug is shown below.



The four nitrogen atoms are labelled as N_A, N_B, N_C and N_D.

N_c and N_D are part of the pyridine rings where the lone pair of electrons on the nitrogen atoms are not delocalised into the pyridine rings.

Which sequence shows the four nitrogen atoms in decreasing order of basicity?

A $N_B > N_D > N_C > N_A$

B $N_D > N_C > N_A > N_B$

C $N_C > N_D > N_B > N_A$

D $N_D > N_C > N_B > N_A$

28 Which statement about 2-aminopropanoic acid extracted from silkworms is correct?

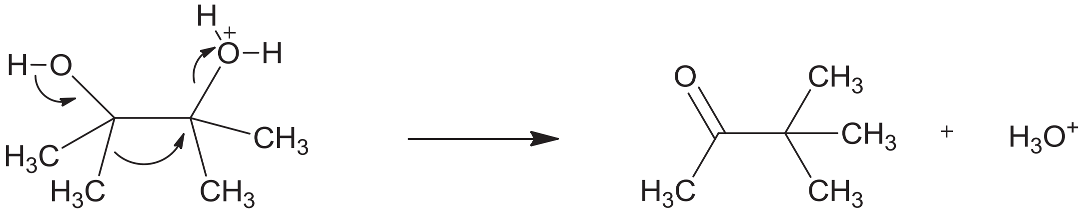
A It is able to rotate plane polarised light.

B It reacts with ethanoic acid to form an amide.

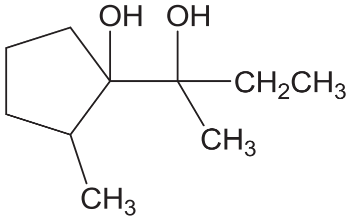
C pH of its aqueous solution drops drastically when a small amount of hydrochloric acid is added.

D It decolourises orange aqueous bromine.

29 When a 1, 2–diol is treated with a dilute acid, the protonated diol undergoes pinacol rearrangement as shown.

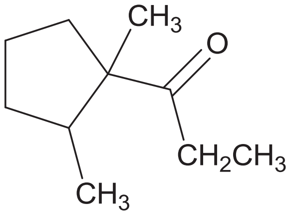


Which of the following products is **not** formed via pinacol rearrangement by adding dilute acid to diol Z?

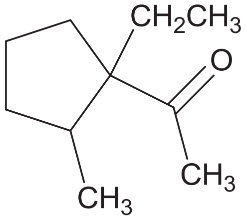


diol Z

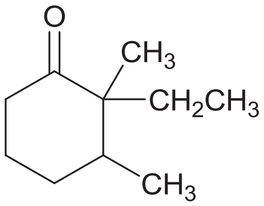
A



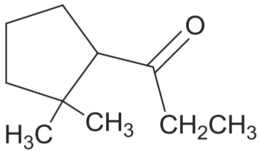
B



C



D



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

An experiment was conducted to compare the rate of hydrolysis of four halogen-containing compounds. 1 mole of the 4 compounds K, L, M and N are each heated separately with excess NaOH(aq) for 30 seconds and then acidified with HNO_3(aq). Excess $AgNO_3$(aq) is added and the precipitate formed is filtered, dried and weighed.

CH_3CH_2COCl	C_6H_5Cl	$(CH_3)_3CCl$	$(CH_3)_3CBr$
K	L	M	N

71.1 g of the precipitate is obtained from compound M. What are the possible masses of the precipitates obtained from the other three halogen-containing compounds?

	mass of precipitate from K / g	mass of precipitate from L / g	mass of precipitate from N / g
A	128.1	0	112.9
B	120.2	0	60.7
C	126.2	40.2	112.9
D	65.2	0	57.3

~ END OF PAPER ~

Parent's Signature:

CANDIDATE'S NAME: ______________________________ **CTG:** _________

YISHUN JUNIOR COLLEGE

2017 JC2 PRELIMINARY EXAMINATION

CHEMISTRY HIGHER 2

9729/02

Paper 2 Structured Questions

THURSDAY 24 AUGUST 2017
1400 hrs − 1600hrs
(2 hours)

Candidates answer on the Question Paper
Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

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

Answer **all** questions.
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 1	
Total	**/ 30**
Paper 2	
1	/ 15
2	/ 12
3	/ 10
4	/ 19
5	/ 19
Total	**/ 75**
Paper 3	
Total	**/ 80**
Paper 4	
Total	**/ 55**

This document consists of **18** printed pages.

Answer **all** the questions.

1 Antacids neutralise stomach acid and relieve the symptoms of indigestion, heartburn or stomach ulcer. One of the active ingredient in antacid is calcium carbonate, $CaCO_3$. There are also other ingredients such as binders present in each tablet. On average, a 1.3 g tablet contains 0.5 g of $CaCO_3$.

Calcium carbonate undergoes neutralisation reaction with hydrochloric acid as shown in the following equation.

$$CaCO_3(aq) + 2HCl(aq) \rightarrow CaCl_2(aq) + H_2O(l) + CO_2(g)$$

A student was given an antacid tablet. She was asked to determine the volume of stomach acid that can be neutralised by 1 tablet. She crushed the antacid tablet and dissolved it with 50.0 cm^3 of 0.100 mol dm^{-3} of HC*l* in a 50.0 cm^3 graduated flask. She pipetted 25.0 cm^3 of this sample and boiled gently for 5 minutes. She then titrated the boiled sample with 20.0 cm^3 of 0.0500 mol dm^{-3} sodium hydroxide for complete neutralisation.

(a) Suggest a reason why the 25.0 cm^3 sample was boiled before titrating with NaOH.

....[1]

(b) **(i)** Calculate the amount of HC*l* present initially in the graduated flask.

[1]

(ii) Calculate the amount of HC*l* reacted with NaOH.

[1]

(iii) Using your answer in **(b)(i)** and **(b)(ii),** calculate the amount of HC*l* neutralised by one antacid tablet.

[2]

(iv) A patient with a hyperacidic stomach has a HC*l* concentration of 0.0300 mol dm^{-3}. The volume of liquid in the stomach is 375 cm^{3}.

Using your answer in **(b)(iii)**, calculate the minimum number of antacid tablets that the patient with hyperacidic stomach would have to take to bring the concentration of HC*l* in the stomach to the normal level of 0.000300 mol dm^{-3}.

[2]

(c) The following diagram shows the nutrition fact label of the antacid used for the student's analysis.

Drug Facts

Active ingredient (in each tablet)	***Purpose***
Calcium carbonate 500 mg..........................	Antacid

Uses relieves ■ heartburn ■ sour stomach ■ acid indigestion

Warnings

Ask a doctor or pharmacist before use if you are now taking a prescription drug. Antacids may interact with certain prescription drugs.

When using this product do not exceed 15 tablets daily or use the maximum dosage for more than 2 weeks

Keep out of reach of children.

Directions chew 2 to 4 tablets as symptoms occur

Other information

- ■ **each tablet contains:** calcium 215 mg and magnesium 5 mg
- ■ store at 20°-25°C (68°-77°F)

Inactive ingredients adipic acid, dextrose, FD&C blue #1 aluminum lake, FD&C red #40 aluminum lake, FD&C yellow #5 aluminum lake (tartrazine), FD&C yellow #6 aluminum lake, flavors, maltodextrin, mineral oil, polyethylene glycol, powdered cellulose, talc

Verify by calculation if there are 500 mg of $CaCO_3$ in each antacid tablet.

[2]

(d) Magnesium oxide, MgO and aluminium oxide, Al_2O_3 can also act as antacids. The oxides MgO and Al_2O_3 have the melting points 2852°C and 2072°C respectively.

(i) Both MgO and Al_2O_3 have giant ionic structure. Explain the difference between the melting points of MgO and Al_2O_3.

....

....

....

....[2]

(ii) Describe the reactions of MgO and Al_2O_3 with water. Give the approximate pH of any solution formed.

…………………………………………………………………………………………

…………………………………………………………………………………………

…………………………………………………………………………………………[2]

(iii) When NaOH(aq) is added to separate solutions containing Mg^{2+}(aq) and Al^{3+}(aq), a white precipitate is formed in each case. When an excess of NaOH(aq) is added, **one** of these precipitates dissolves.

Construct ionic equations, with state symbols, for the formation of the white precipitate, and its subsequent dissolving.

…………………………………………………………………………………………

…………………………………………………………………………………………

…………………………………………………………………………………………[2]

[Total: 15]

2 The halogens, found in group 17 of the Periodic Table, and their compounds are useful laboratory reagents.

The table below shows some properties of the halogens and their compounds.

halogen	chlorine	bromine	iodine
standard enthalpy change of vapourisation ($\Delta H_v^\ominus$) of X_2 / kJ mol^{-1}	0	+15	+30
electronegativity	3.2	3.0	2.7
standard enthalpy change of reaction ($\Delta H_r^\ominus$) for thermal decomposition of HX / kJ mol^{-1}	+183	+103	+11
solubility of $PbX_2(s)$ / g dm^{-3}	4.7	4.3	0.6

(a) Describe and explain the trend in the volatility of the halogens.

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

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

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

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

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

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

(b) By quoting relevant data from the *Data Booklet*, explain the relative thermal stabilities of the hydrides of the Group 17 elements.

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

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

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

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

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

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

(c) **(i)** Write an expression for K_{sp} of $PbCl_2$, stating the units.

K_{sp} = ……………………………………………… units ………………………… [1]

(ii) Using relevant data from the table and your expression for K_{sp} in **(c)(i)**, calculate the solubility product of $PbCl_2$.

Give your answer to **two** significant figures.

[2]

(d) Astatine, At, is found below iodine in group 17 of the Periodic Table. Using your knowledge of the chemistry of group 17, predict the changes (if any) that you may observe when the following reagents are mixed.

If nothing is formed, write "no reaction" and where there is a reaction predicted, write an ionic equation with state symbols.

(i) aqueous bromine and aqueous sodium astatide

…………………………………………………………………………………………

…………………………………………………………………………………………

…………………………………………………………………………………………

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

(ii) astatine and aqueous sodium chloride

…………………………………………………………………………………………

…………………………………………………………………………………………

…………………………………………………………………………………………

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

(e) In 1886, Henri Moissan succeeded in obtaining fluorine by the electrolysis of molten potassium hydrogen difluoride, KHF_2, which is an ionic compound containing **one** cation and **one** anion.

(i) Write the formulae of the ions present in KHF_2.

cation: ……………………………………….

anion: ………………………………………

[1]

(ii) Draw the structure for the anion and indicate the types of bonding that occur within it in your diagram.

[2]

[Total: 12]

3 **(a)** **(i)** Describe and explain how the thermal stability of magnesium carbonate might compare to calcium carbonate.

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

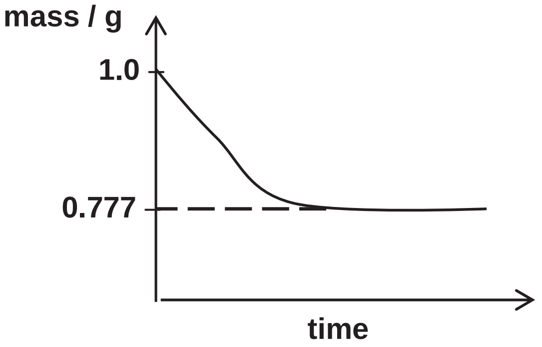
……………………………………………………………………………………………

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

(ii) Write an equation for the decomposition of $MgCO_3$.

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

(b) The graph represents the change in mass that occurs when 1.0 g of powdered carbonate of another group 2 element, **Z,** is decomposed at a temperature T.



Using the above graph, calculate and determine the identity of **Z**.

Identity of **Z** : ……………………….. [3]

(c) Beryllium, the first member of the group 2 elements was discovered in 1798 by a chemist named Vaquelin when he was working with emeralds. Cutting edge computers require an alloy of beryllium and copper to meet the demands placed on microprocessor connectors.

(i) Beryllium chloride reacts with ammonia in a 1:2 ratio to form a product. Draw dot–and–cross diagrams showing the bonding in beryllium chloride and ammonia.

beryllium chloride

ammonia

[1]

(ii) Draw a diagram to illustrate the shape of the product around the Be atom formed from the reaction between beryllium chloride and ammonia.

[2]

[Total: 10]

4 Energy density is the amount of energy that can be stored in a given mass of a substance or system. The higher the energy density of a substance or system, the greater the amount of energy stored in its mass. In fuel, energy density can be measured as the amount of energy released in megajoules per gram of fuel (MJ/g).
(1 MJ = 10^3 kJ)

The table below provides information on the standard enthalpy change of combustion of some commonly used fuel today.

fuel	formula	standard enthalpy change of combustion ($\Delta H_c^\ominus$) / kJ mol^{-1}
hydrogen	H_2	– 286
coal	C	– 393
ethanol	CH_3CH_2OH	– 1367
ethene	$CH_2{=}CH_2$	– 1410

(a) An average household was found to consume an average energy of 108 MJ per day.

(i) Using relevant data from the table above, determine the mass of the coal required to supply energy for an average household a day.

Hence, determine the energy density of coal.

[2]

(ii) The energy density of ethanol was found to be 0.0297 MJ/g. With reference to your answer in **(a)(i)**, state and explain which fuel is more efficient in supplying energy to the average household.

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

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

(iii) Ethanol, ethene and liquid hydrogen are possible alternative sources of fuel that may be used in replacement of coal as the burning of coal releases toxic carbon monoxide gas into the atmosphere.

Explain why carbon monoxide gas, CO, is toxic.

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

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

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

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

(b) **(i)** Using relevant data from the table, determine the standard enthalpy change of formation of liquid ethanol.

[1]

(ii) Using relevant data from the *Data Booklet*, determine the standard enthalpy change of combustion of liquid ethanol.

[2]

(iii) Suggest a reason for the discrepancy between the value in **(b)(ii)** and the one given in the table.

…………………………………………………………………………………………………

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

(c) The direct oxidation of alcohols such as ethanol in a fuel cell represents potentially the most efficient method of obtaining useful energy from a renewable fuel.

(i) Given that carbon dioxide is formed at the anode while water is produced at the cathode, construct the relevant half-equations for the reactions occurring at the electrodes and hence the equation for the overall reaction, assuming acidic conditions.

cathode: ………………………………………………………………………………

anode: ………………………………………………………………………………

overall: ……………………………………………………………………………...

[2]

(ii) The value for the $E^\ominus$ for the reaction occurring at the anode was determined to be +0.08 V. Using suitable data from the *Data Booklet*, determine the e.m.f produced by the ethanol fuel cell.

[2]

(iii) Hence, determine the value of $\Delta G^\ominus$ of the ethanol fuel cell.

[1]

(d) Ethanol can be readily synthesised from ethene industrially.

(i) State the reagents and conditions for the industrial synthesis of ethanol from ethene.

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

(ii) Identify the type of hybridisation that exists in the carbon atoms of ethene and hence explain the bonding that occurs in a molecule of ethene in terms of orbitals overlap.

Type of hybridization in C: ………………….

Explanation of bonding:

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

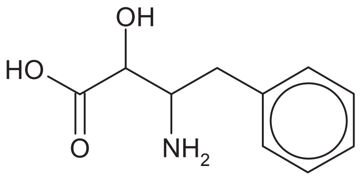
……………………………………………………………………………………………

……………………………………………………………………………………………

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

[Total: 19]

5 **(a)** Compound **Y** is an intermediate in the production of a drug which is being developed to reduce the effects of the HIV virus.



compound **Y**

(i) Name three functional groups in compound **Y**, other than the phenyl group.

……………………………………………………………………………………………

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

(ii) On the structure above, indicate with an asterisk (*) any chiral carbon present, and state the total possible number of stereoisomers that compound **Y** can have.

total possible number of stereoisomers = ……………… [2]

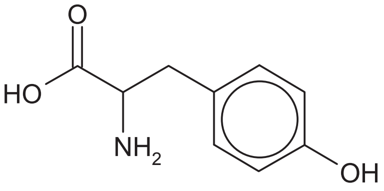
(iii) Draw the structural formula of the organic products that will be formed when compound **Y** is treated with

- hot acidified $K_2Cr_2O_7(aq)$

- anhydrous $PBr_3(l)$

[3]

(b) Compound **Y** is similar in structure to tyrosine, one of the twenty α-amino acids found in proteins.



tyrosine

At pH = 5.7, compound **Y** exists as a *zwitterion*.

(i) Define the term *zwitterion*.

…………………………………………………………………………………………

…………………………………………………………………………………………[1]

(ii) Draw the structural formula of the zwitterionic form of tyrosine.

[1]

Another potential anti-HIV drug can be synthesised by combining tyrosine with another α-amino acid, glycine, $H_2NCH_2CO_2H$.

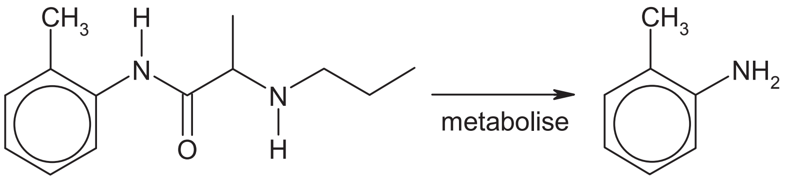
(iii) State the type of linkage that will be formed between tyrosine and glycine.

…………………………………………………………………………………………[1]

(iv) Draw the structures of two different dipeptides that could be formed when one molecule of tyrosine reacts with one molecule of glycine.

[2]

(c) Prilocain, a widely used local anaesthetic, is metabolised in the liver by enzymes to form 2-methylphenylamine.



prilocain 2-methylphenylamine

(i) State the reagents and conditions required to produce 2-methylphenylamine from prilocain in the laboratory.

....[1]

In the aqueous medium, 2-methylphenylamine is a weak Bronsted base.

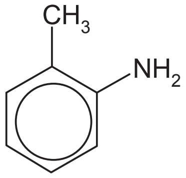
(ii) Write an expression for the base dissociation constant, K_b, for 2-methylphenylamine.

[1]

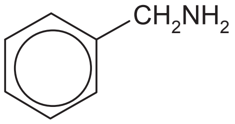
(iii) The pK_b value for 2-methylphenylamine is 9.6. Use this value to calculate the pH of a 0.10 mol dm^{-3} solution of 2-methylphenylamine.

[2]

(d) 2-methylphenylamine and benzylamine are isomers.



2-methylphenylamine



benzylamine

Suggest how the pK_b value of benzylamine might compare to that of 2-methylphenylamine.

Explain your answer in terms of their structures.

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

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

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

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

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

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

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

[Total: 19]

~ END OF PAPER ~

CANDIDATE'S NAME: ________________________________ **CTG:** ____________

YISHUN JUNIOR COLLEGE

2017 JC2 PRELIMINARY EXAMINATION

CHEMISTRY
HIGHER 2

9729/03

Paper 3 Free Response Questions

MONDAY 11 SEPTEMBER 2017
1400hrs − 1600hrs
(2 hours)

Candidates answer in separate paper.

Additional Materials: Writing Papers
Data Booklet

READ THESE INSTRUCTIONS FIRST

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

Section A
Answer **all** questions.

Section B
Answer **one** question.

The use of an approved 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.

At the end of the examination, fasten all your work for Section A **separately** from Section B with the respective cover sheet on top.

This question paper consists of **12** printed pages.

Section A

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

1 **(a)** Copper often occurs in the Earth's crust as copper(I) sulfide, Cu_2S, associated with the sulfides of zinc, ZnS, and silver, Ag_2S. The first stage of the extraction of copper from its ore involves the partial air-oxidation to copper(I) oxide, Cu_2O, and sulfur dioxide, SO_2, followed by the reaction between this copper(I) oxide and unreacted copper(I) sulfide to give copper and more sulfur dioxide.

(i) Write balanced chemical equations for these two reactions. [2]

(ii) Suggest how the melting point of copper(I) sulfide might compare to that of copper(I) oxide. Explain your answer. [2]

(iii) This first stage produces copper containing some zinc and silver as impurities. The solid impure copper is purified by electrolysis.

Describe, with reference to the $E^\ominus$ values, the electrode reactions that take place during this electrolysis, and explain in detail how each of the two impurity metals is removed from the copper. [3]

(iv) Using inert electrodes, a current was passed through two beakers containing aqueous silver nitrate and aqueous copper(II) sulfate, connected in series. After 30 minutes, 0.100 g of silver was deposited from the first solution.

Calculate the current passed and the mass of copper deposited from the aqueous copper(II) sulfate. [2]

(b) When KI(aq) is added to a solution containing Cu^{2+}(aq), a white precipitate of the highly insoluble copper(I) iodide and a brown solution is formed.

(i) By selecting appropriate $E^\ominus$ values from the *Data Booklet*, explain why it would be expected that this redox reaction would **not** occur. [1]

(ii) Suggest a possible reason for why it does in fact occur. [1]

(c) Copper(I) iodide is used in the synthesis of Gilman reagents, $R_2Cu^-Li^+$, which are very useful in organic synthesis because larger molecules can be prepared from smaller ones.

$$2RLi + CuI \rightarrow \underset{\text{Gilman reagent}}{R_2Cu^-Li^+} + LiI$$

For example, lithium dimethylcopper reacts with 1-chlorodecane to give undecane.

$$(CH_3)_2Cu^-Li^+ + CH_3(CH_2)_8CH_2Cl \rightarrow CH_3(CH_2)_8CH_2CH_3 + LiCl + CH_3Cu$$

The above reaction is called organometallic coupling reaction.

Similarly, organometallic coupling reaction can be used to synthesise ketones by reacting suitable Gilman reagents and acid chlorides.

Suggest a suitable Gilman reagent and an acid chloride that can be used to synthesise 5,6-dimethyldecan-3-one. [2]

(d) Carbonyl compounds can be converted into alkanes by reacting the carbonyl compounds with hydrazine, H_2NNH_2, in the presence of KOH. This reaction is named as the Wolff-Kishner reaction, which is named by the two chemists, Ludwig Wolff and N.M. Kishner, who discovered it in 1911.

$$RCOR' + H_2NNH_2 \xrightarrow{OH^-} RCH_2R' + N_2 + H_2O$$

For example, ethane can be synthesised from ethanal and hydrazine, according to the following equation.

$$\underset{\text{ethanal}}{CH_3CHO(g)} + H_2NNH_2(l) \longrightarrow \underset{\text{ethane}}{CH_3CH_3(g)} + N_2(g) + H_2O(l)$$

For this reaction, $\Delta S^{\ominus} = +191.5\ \text{J K}^{-1}\ \text{mol}^{-1}$ at 298 K.

(i) Explain what is meant by the term *entropy* of a chemical system. [1]

(ii) Suggest what is the significance of the sign of the entropy change with respect to the reaction between ethanal and hydrazine. [1]

The following table lists some $\Delta H_f^{\ominus}$ values.

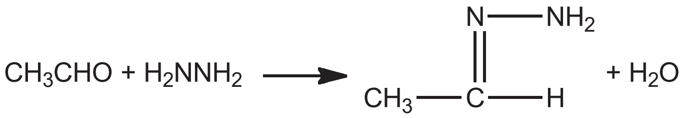
compound	$\Delta H_f^{\ominus}$ / kJ mol^{-1}
$CH_3CHO(g)$	−196.4
$H_2NNH_2(l)$	+50.6
$CH_3CH_3(g)$	−84.7
$H_2O(l)$	−285.8

(iii) Use the data above to calculate $\Delta H^{\ominus}$ for the reaction between ethanal and hydrazine.

Hence calculate the $\Delta G^{\ominus}$ for the reaction between ethanal and hydrazine.

Leave all your answers to one decimal place. [2]

(iv) The first step of the Wolff-Kishner reaction involves the formation of a hydrazone intermediate.



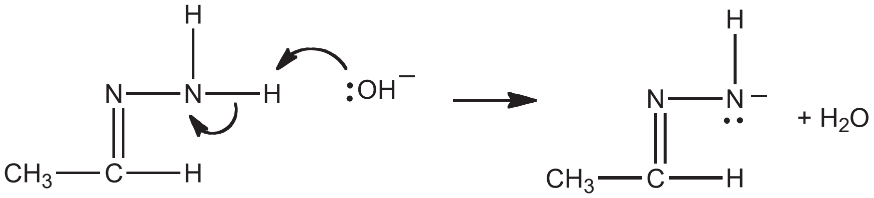
$$CH_3CHO + H_2NNH_2 \longrightarrow CH_3C(H){=}N{-}NH_2 + H_2O$$

hydrazone

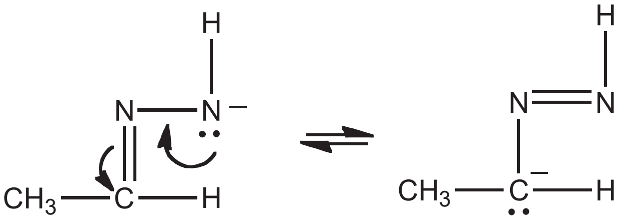
State the type of reaction that has occurred. [1]

(v) After the formation of the hydrazone, the reaction occurs via a five-step mechanism to obtain ethane as the product.

step 1: abstraction of one of the weakly acidic protons from the $-NH_2$ group by OH^-, to form a hydrazone anion.



step 2: the hydrazone anion has a resonance form that places the negative charge on the carbon atom and has a double bond between the two nitrogen atoms.



step 3: protonation of the carbon atom of the resonance form of the hydrazone anion by H_2O to yield a neutral intermediate.

step 4: abstraction of a proton from the neutral intermediate by OH^- to form N_2, an ethyl anion, $CH_3CH_2^-$, and H_2O.

step 5: protonation of the carbon atom of the ethyl anion by H_2O to yield ethane and OH^-.

Using the information given above, suggest the mechanism for steps 3, 4 and 5.

Show any relevant lone pairs and charges, and indicate the movement of electron pairs with curly arrows. [3]

[Total: 21]

2 Manganate(VII) and dichromate(VI) ions are oxidising agents that are commonly used in organic synthesis.

(a) In aqueous solution, dichromate(VI) ions exist in equilibrium with chromate(VI) ions.

$$\underset{\text{orange}}{Cr_2O_7^{2-}(aq)} + H_2O(l) \rightleftharpoons \underset{\text{yellow}}{2CrO_4^{2-}(aq)} + 2H^+(aq)$$

(i) State Le Chatelier's Principle. [1]

(ii) Explain why a solution of potassium chromate turns from yellow to orange on the addition of dilute hydrochloric acid. [1]

Following the addition of dilute hydrochloric acid, the solution was warmed. This caused the colour to change from orange back to yellow.

(iii) State whether the forward reaction is exothermic or endothermic.

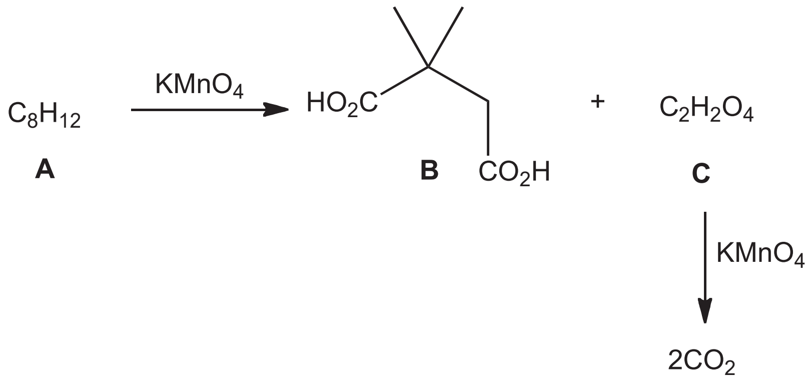
Explain your answer. [2]

At 25 °C, the equilibrium constant, K_c, for the above equilibrium has a value of 1.31×10^{-13}.

(iv) Calculate a value for the ratio $\frac{[CrO_4^{2-}]^2}{[Cr_2O_7^{2-}]}$ at pH 8. [1]

(v) Use your answer for **(a)(iv)** to deduce the colour of the solution at pH 8. [1]

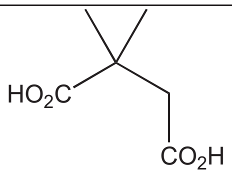
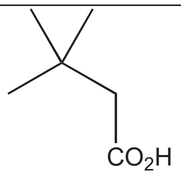
(b) Hot, acidified concentrated potassium manganate(VII) can oxidise various functional groups to ketones, carboxylic acids and carbon dioxide, allowing the structures to be determined. The following scheme shows the reaction of compound **A**.



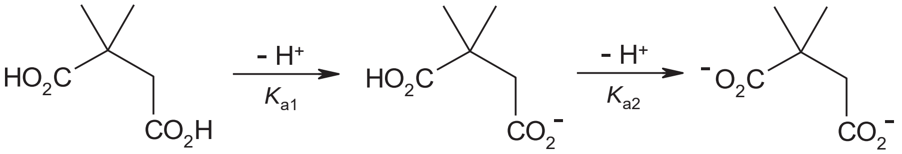
(i) Suggest the structures of compounds **A** and **C**. [2]

(ii) Explain why compound **A** does not exhibit *cis−trans* isomerism. [1]

(iii) Compound **B** and 3,3-dimethylbutanoic acid and are both weak acids.

acid	formula
compound **B**	
3,3-dimethylbutanoic acid	

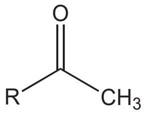
Compound **B** is a dicarboxylic acid which ionises in two stages.



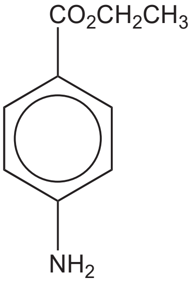
Suggest a reason why the K_{a1} value of compound **B** is much higher than the K_a value of 3,3-dimethylbutanoic acid. [1]

(c) Hydroxynitriles can be synthesised from ketones, and they are useful intermediates in the synthesis of amino acids.

Name and outline the mechanism for the synthesis of hydroxynitrile from a ketone. In your answer, show any relevant lone pairs, dipoles and charges, and use curly arrows to indicate the movement of electron pairs.

You may use  to represent a ketone. [3]

(d) Benzocaine is well known for its local anaesthetic properties and is commonly used in antiseptic creams and sunburn remedies.



benzocaine

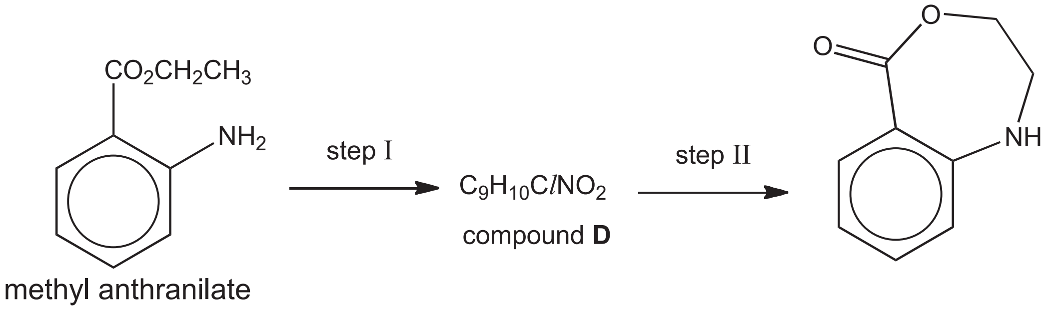
The preparation of benzocaine from methylbenzene involves the use of potassium manganate(VII) in one of the steps.

(i) *Use of the Data Booklet is relevant to this question.*

Suggest how methylbenzene can be converted to benzocaine. Give reagents, conditions and the structural formulae of the compounds obtained for each stage of the conversion. [4]

(ii) Describe a simple chemical test that could be used to distinguish methylbenzene from benzocaine, other than the use of $KMnO_4$. State your observations clearly. [2]

(e) Methyl anthranilate is an isomer of benzocaine and it is used as a bird repellent to protect crops. It can be used in the following organic synthesis.



(i) Suggest the reagents and conditions needed for step I. [1]

(ii) Suggest the structure of compound **D**. [1]

[Total: 21]

3 This question is about reactions involving some *d*-block elements and their ions.

(a) Ammonia is a reagent commonly used to react with copper and silver ions. The metal ions can be precipitated from their solutions in some instances.

With the aid of relevant equations, explain the following observations as fully as you can.

(i) When aqueous ammonia is added to a solution containing copper(II) ions, a pale blue precipitate is obtained. This precipitate dissolves to form a deep blue solution when excess ammonia is added. [3]

(ii) When aqueous ammonia is added to $AgCl$, the precipitate dissolves. However, if aqueous ammonia is added to $AgBr$, the precipitate remains insoluble. [3]

(b) Iron forms compounds mainly in the +2 and +3 oxidation states. Iron complexes are usually coloured.

(i) Explain why iron exhibits variable oxidation states. [2]

(ii) State the full electronic configuration of an iron(III) ion and draw fully-labelled diagrams of **all** the orbitals in the 3*d*-subshell of an iron(III) ion. [3]

(iii) Using your diagrams in **(b)(ii)**, briefly explain why splitting of the *d*-subshell occurs in an octahedral complex.

Hence, explain why iron(III) complexes are usually coloured. [3]

(iv) In 2012, a group of scientists synthesised two iron(III) complexes with different colours. The iron(III) complex bonded to N,N-diethylethylenediamine ligands is red in colour and the one bonded to N-ethylethylenediamine ligands is blue in colour. The energy gap between the *d*-orbitals is inversely proportional to the wavelength of the light absorbed.

Given that red light has a longer wavelength than blue light, deduce whether the red complex or the blue complex has a larger energy gap between the *d*-orbitals. [2]

(v) The arrangement of electrons in the *d*-orbitals depends on the spin states of complexes.

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.

It was found that the two iron(III) complexes in **(b)(iv)** have different 'spin' state for the Fe^{3+} ion.

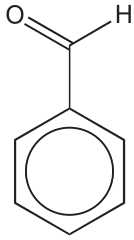
Use appropriate diagrams and your answer to **(b)(iv)** to show the electronic configuration of a Fe^{3+} ion in the red complex and the blue complex respectively. Your diagrams should indicate clearly the relative size of the energy gap for each complex. [2]

[Total: 18]

Section B

Answer **one** question from this section.

4 Benzaldehye contains an aromatic benzene ring and has the following structure.



(a) Benzaldehyde undergoes disproportionation reaction in the presence of a strong base such as potassium hydroxide to produce potassium benzoate and phenylmethanol. Potassium benzoate can be acidified to obtain benzoic acid as one of the final products.

The disproportionation reaction is as follows:

$$2C_6H_5CHO + KOH \rightarrow C_6H_5CH_2OH + C_6H_5CO_2K$$

The rate of disappearance of potassium hydroxide was measured for several different concentrations of benzaldehyde and potassium hydroxide at a certain temperature.

experiment number	$[C_6H_5CHO]$ / mol dm^{-3}	[KOH] / mol dm^{-3}	rate of disappearance of KOH / mol dm^{-3} s^{-1}
1	0.300	0.050	5.7×10^{-5}
2	0.300	0.100	1.1×10^{-4}
3	0.600	0.200	9.2×10^{-4}

(i) With reference to the above reaction, explain why it is a disproportionation reaction. [1]

(ii) From the experimental data given in the table, determine the order of reaction with respect to C_6H_5CHO and KOH. Explain your reasoning. [2]

(iii) Hence write the rate equation for the disproportionation of benzaldehyde, and calculate the rate constant, giving its units. [2]

(iv) Calculate the half-life of the reaction when the concentration of C_6H_5CHO is increased to 1.60 mol dm^{-3}. [2]

(v) With the aid of a sketch of the Boltzmann distribution, explain the effect of increasing temperature on the rate of reaction. [3]

(b) The disproportionation reaction in **(a)** produces a low yield of phenylmethanol and benzoic acid.

Two other separate reactions could be carried out to convert benzaldehyde to phenylmethanol and to benzoic acid.

State the reagents and conditions needed to convert benzaldehyde to

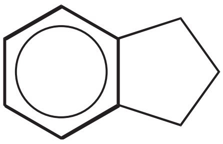
(i) phenylmenthanol, and [1]

(ii) benzoic acid. [1]

(c) Suggest a chemical test that could be used to distinguish between benzaldehyde and phenylmethanol. You should state what you would observe for **each** compound. [2]

(d) Aromatic hydrocarbon **R** and **S** are structural isomers, with molecular formula C_9H_{10}.

The structure of **S** is shown below.



S

R is found to exhibit stereoisomerism. When aqueous bromine was added to both **R** and **S** separately, only **R** decolourised orange aqueous bromine. When hot acidified potassium manganate(VII) solution was added to **R** and **S** separately, both decolourised purple potassium manganate(VII) to form compounds **T** and **U** respectively.

1.0 mol of compound **T** reacts with exactly 0.5 mol of sodium carbonate while 1.0 mol of compound **U** reacts with exactly 1.0 mol of sodium carbonate.

Deduce the structures of compounds **R**, **T** and **U**. Explain the chemistry of the reactions described. [6]

[Total: 20]

5 This question is about reactions involving acids and bases.

(a) **(i)** Draw a dot-and-cross diagram to show the bonding in a carbonate anion, CO_3^{2-}.

You should distinguish carefully between electrons originating from the central atom and those from the outermost atoms.

Include all lone pairs in your diagram. [1]

(ii) Use the VSEPR (valence shell electron pair repulsion) theory to predict the shape of the carbonate ion, giving a reason for your answer. [2]

(b) The carbonate ion is a diacidic base. When sodium carbonate reacts with hydrochloric acid, the neutralisation reaction occurs in two stages.

Stage 1: $Na_2CO_3 + HCl \rightarrow NaHCO_3 + NaCl$

Stage 2: $NaHCO_3 + HCl \rightarrow CO_2 + NaCl + H_2O$

(i) Explain why **Stage 1** is considered to be a Bronsted-Lowry acid-base reaction. [1]

(ii) Explain, with the help of an equation, why the pH at the end of **stage 1** is slightly higher than 7. [2]

(c) The major buffer system that is used to control the pH of blood is the carbonic acid, H_2CO_3, and hydrogen carbonate, HCO_3^-, buffer system.

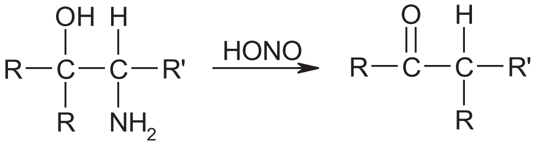
Explain, with the aid of relevant equations, how the pH of blood is maintained when a small amount of acid or alkali is added. [2]

(d) **(i)** State **two** assumptions of the kinetic theory of gases. [2]

(ii) When excess hydrochloric acid is added to a 20.0 cm^3 sample of aqueous sodium carbonate, 56.0 cm^3 of carbon dioxide gas was collected at 1.1 atm and 30 °C.

Determine the concentration of the sample of aqueous sodium carbonate. [2]

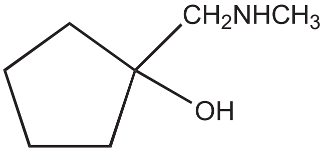
(e) A carbonyl compound, **H**, $C_6H_{10}O$, can be synthesised from 1-aminoalcohol, **G**, $C_6H_{13}ON$, in the presence of nitrous acid, HONO, via Tiffeneau-Demjanov Rearrangement. The simplified illustration of the rearrangement is illustrated below.



H produces a yellow precipitate with iodine in alkaline solution. Treatment of **H** with hot acidified solution of potassium manganate(VII) produces **J,** $C_5H_8O_3$, along with a gas that forms white precipitate in limewater. **H** was also observed to decolourise bromine in tetrachloromethane readily.

Explain the chemistry of the reactions described and deduce the structures of **G**, **H** and **J**. [5]

(f) Starting from a suitable carbonyl compound of your choice, devise a 3-step synthesis of the compound below.



Suggest reagents and conditions for each step, and draw the structural formula of every intermediate compound. [3]

[Total: 20]

~ END OF PAPER ~

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

1 Determination of the concentration of sodium thiosulfate in solution Z

Sodium thiosulfate is commonly used in an alternative method for the extraction of gold from its ores, through the formation of a stable and soluble complex of gold(I) ions, $[Au(S_2O_3)_2]^{3-}$. One of your tasks is to determine the concentration of sodium thiosulfate in a commercially produced solution **Z** used in the extraction process.

Solution **Z** contains sodium thiosulfate in deionised water. You are not provided with solution **Z**, as it is too concentrated for use in this experiment. A diluted solution of **Z** has been prepared for you. This diluted solution is **FA 5**.

FA 1 is 0.0230 mol dm^{-3} of aqueous potassium iodate(V), KIO_3
FA 2 is 0.50 mol dm^{-3} potassium iodide, KI
FA 3 is 0.75 mol dm^{-3} sulfuric acid, H_2SO_4
FA 4 is a solution of sodium thiosulfate, $Na_2S_2O_3$ of an unknown concentration
FA 5 a diluted solution of **Z**, in which 31.00 cm^3 of solution **Z** was made up to 250 cm^3 with deionised water in a volumetric flask

You are also provided with starch solution.

In acidic medium, iodate(V) ions oxidise iodide ions to iodine

$$IO_3^-(aq) + 5I^-(aq) + 6H^+(aq) \rightarrow 3I_2(aq) + 3H_2O(l) \qquad \textbf{reaction 1}$$

If an excess of sodium thiosulfate is present in the reaction mixture, the iodine produced in **reaction 1** is immediately reduced back to iodide ions, as shown in **reaction 2**, and the dark brown colour of iodine does not form.

$$I_2(aq) + 2S_2O_3^{2-}(aq) \rightarrow 2I^-(aq) + S_4O_6^{2-}(aq) \qquad \textbf{reaction 2}$$

In the experiments that you will perform, insufficient volumes of the first sodium thiosulfate solution will be added initially, and some iodine will remain in the solution. The amount of iodine left-over can be determined by titration with the second solution of sodium thiosulfate, as shown in **reaction 2**.

You will prepare a number of reaction mixtures, each of which will contain:

- a fixed volume of **FA 1**,
- excess amounts of **FA 2** and **FA 3**,
- a different volume of **FA 4**.

All reaction mixtures will contain some iodine, produced in **reaction 1**, that will be titrated against the **FA 5** solution.

You are required to use a graphical method to determine the concentrations of sodium thiosulfate in **FA 4**, **FA 5** and solution **Z**.

(a) Titration of iodine produced against FA 5

Note: You will perform each titration only **once**. Great care must be taken to ensure that you do not overshoot the end-point.

You will be using two burettes in this task, and each of the burette will contain different sodium thiosulfate solutions, so care must be taken that the right one is used each time.

(i) Experiment 1

1. Fill the burette labelled "**FA 4**" with **FA 4** solution.
2. Fill the burette labelled "**FA 5**" with **FA 5** solution.
3. Using a pipette, transfer 25.0 cm^3 of **FA 1** into a 250 cm^3 conical flask.
4. From the burette labelled "**FA 4**", transfer 9.50 cm^3 of **FA 4** to the same conical flask.

If you accidentally added an incorrect volume of **FA 4** for any of your titrations, record the actual volume of **FA 4** added in your table on the next page, and use that volume for the plotting of the graph later

5. Use appropriate measuring cylinders to add to this flask:
   - 10 cm^3 of **FA 2**,
   - 10 cm^3 of **FA 3**.
6. Titrate the iodine liberated with **FA 5** until the solution fades to a pale yellow colour.
7. Add about 1 cm^3 of starch indicator to this flask. Continue adding **FA 5** until the blue-black colour **just** disappears.
8. Record your titration results in the section "Table of results" on page 3. Make sure that your recorded results show the precision of your working.

(ii) Experiment 2

9. Repeat steps 3 to 8 but add 22.00 cm^3 of **FA 4** at step 4.

(iii) Experiment 3 to 5

10. Choose three further volumes of **FA 4** between 9.50 cm^3 and 22.00 cm^3.
11. Repeat steps 3 to 8 using each of your chosen volumes of **FA 4** at step 4.

Recording

Prepare a table in the space provided on the next page to record:

- the volumes of **FA 4** added for each experiment.
- the burette readings and the volumes of **FA 5** used for each experiment.

Table of results

[4]

(b) **Graphical determination of the concentration of sodium thiosulfate in FA 4, FA 5 and solution Z.**

(i) Plot a graph of the volume of **FA 5** added (*y-axis*) against the volume of **FA 4** added (*x-axis*) on the grid below. When choosing the scale, you should ensure that the graph line can be extrapolated to intersect both the *x-axis* and the *y-axis*.

Draw a straight line of best fit, taking into account all of your plotted points.

Extrapolate your graph line so that it intersects both the *x-axis* and the *y-axis*.

[3]

(ii) It is possible to react all the iodine produced by the reaction between 25.0 cm^3 of **FA 1** and 10 cm^3 of **FA 2** and **FA 3** by using **FA 4** only.

From your graph, determine the volume of **FA 4** required to do this.

volume of **FA 4** required = ... [3]

(iii) Calculate the gradient of your graph line, showing clearly how you did this.

gradient = ... [1]

(c) Calculations

(i) The amount of iodate(V) ions, IO_3^-, present in 25.0 cm^3 of **FA 1** is 5.75×10^{-4} mol.

Use this value, together with data obtained from your graph in **(b)(i)**, to calculate the concentration of thiosulfate ions in **FA 4**.

$[S_2O_3^{2-}]$ in **FA 4** = ... [2]

(ii) The concentration of $S_2O_3^{2-}$ in **FA 4** and **FA 5** are related to the gradient of the graph obtained in **(b)(iii)** by the following equation:

$$[S_2O_3^{2-}]_{\textbf{FA 5}} = \frac{[S_2O_3^{2-}]_{\textbf{FA 4}}}{|\text{gradient}|}$$

Using the equation, or otherwise, calculate the concentration of thiosulfate ions in **FA 5**.

$[S_2O_3^{2-}]$ in **FA 5** = ... [1]

(iii) Calculate the concentration of thiosulfate ions in the commercially produced solution **Z**.

$[S_2O_3^{2-}]$ in solution **Z** = ... [1]

(d) A student suggested using burettes, rather than using measuring cylinders, to measure the volume of **FA 2** and **FA 3** used in **(a)** so as to improve on the accuracy of the titration data.

State whether you agree with the student and briefly explain why.

....

....

....

.... [1]

(e) In a private institution, a laboratory assistant made the mistake in the preparation of the **FA 5** solution by diluting 21.00 cm^3 of solution **Z** to 250 cm^3, rather than the specified volume of 31.00 cm^3.

State and explain how using this incorrect sample of **FA 5** will affect the gradient of your graph.

....

....

....

.... [1]

[Total: 17]

2 Determination of the enthalpy change for the thermal decomposition of sodium hydrogen carbonate

FA 6 is solid anhydrous sodium carbonate, Na_2CO_3
FA 7 is solid sodium hydrogen carbonate, $NaHCO_3$

You will need access to the **FA 3** solution that you have used earlier.

Sodium hydrogen carbonate is commonly used as a raising agent in baking, as it undergoes thermal decomposition at temperatures above 80 °C, according to the equation:

$$2NaHCO_3(s) \rightarrow Na_2CO_3(s) + CO_2(g) + H_2O(l) \qquad \textbf{reaction 1}$$

Due to the high temperature involved, the enthalpy change of this reaction cannot be measured directly using a coffee-cup calorimeter.

In the experiments that you will perform, the coffee-cup calorimeter will be used to determine the enthalpy change, ΔH_2, for the reaction:

$$Na_2CO_3(s) + H_2SO_4(aq) \rightarrow Na_2SO_4(aq) + CO_2(g) + H_2O(l) \qquad \textbf{reaction 2}$$

and the enthalpy change, ΔH_3, for the reaction:

$$2NaHCO_3(s) + H_2SO_4(aq) \rightarrow Na_2SO_4(aq) + 2CO_2(g) + 2H_2O(l) \qquad \textbf{reaction 3}$$

You will then use your results of your experiments to calculate the enthalpy change, ΔH_1, for the thermal decomposition of sodium hydrogen carbonate.

(a) **Determining enthalpy change for the reaction between Na_2CO_3 and H_2SO_4, ΔH_2**

1. Place the styrofoam cup inside a 250 cm^3 beaker to prevent it from toppling over.
2. Using a measuring cylinder, place 40 cm^3 of **FA 3** into the styrofoam cup.
3. Stir the solution in the cup gently with the thermometer, and measure its temperature. Record the initial temperature of **FA 3** in your table.
4. Weigh the weighing bottle labelled "**FA 6**" and its contents using a weighing scale, without the cap. The bottle has been pre-weighed to contain between 4.50 g and 5.00 g of solid sodium carbonate.
5. Pour **FA 6** from the weighing bottle into the styrofoam cup, place the lid onto the cup, and insert the thermometer through the lid.
6. Stir the mixture using the thermometer and record the maximum temperature reached.
7. Reweigh the weighing bottle.

(i) In an appropriate format in the space below, record:

- all mass readings, including the mass of **FA 6** added to the styrofoam cup
- all temperatures measured and the temperature rise.

[1]

(ii) Calculate the heat change for **reaction 2**.

Assume that the specific heat capacity of the final solution is 3.75 J g^{-1} K^{-1} and that its density is 1.00 g cm^{-3}.

heat change = ... [1]

(iii) By calculating the number of moles of each reagent that was added to the styrofoam cup, and with reference to the equation for the reaction, show which of the reagents, **FA 3** or **FA 6**, is added in excess.

[A_r: Na, 23.0; C, 12.0; O, 16.0]

reagent added in excess = ... [1]

(iv) Calculate enthalpy change for **reaction 2**, ΔH_2:

$$Na_2CO_3(s) + H_2SO_4(aq) \rightarrow Na_2SO_4(aq) + CO_2(g) + H_2O(l)$$

ΔH_2 = ... [1]

(b) **Determining enthalpy change for the reaction between $NaHCO_3$ and H_2SO_4, ΔH_3**

1. Empty and rinse the styrofoam cup used in **(a)**, and place the cup back in the 250 cm^3 beaker.
2. Using the same measuring cylinder used in **(a)**, place 40 cm^3 of **FA 3** into the styrofoam cup.
3. Wash and dry the thermometer used in **(a)**, before using it to stir the solution in the cup gently, and measure its temperature. Record the initial temperature of **FA 3** in your table.
4. Weigh the weighing bottle labelled "**FA 7**" and its contents using a weighing scale, without the cap. The bottle has been pre-weighed to contain between 3.50 g and 4.00 g of solid sodium hydrogen carbonate.
5. Pour **FA 7** from the weighing bottle into the styrofoam cup, place the lid onto the cup, and insert the thermometer through the lid.
6. Stir the mixture using the thermometer and record the minimum temperature reached.
7. Reweigh the weighing bottle.

(i) In an appropriate format in the space below, record:

- all mass readings, including the mass of **FA 7** added to the styrofoam cup
- all temperatures measured and the temperature fall.

[3]

(ii) Calculate the heat change for **reaction 3**.

Assume that the specific heat capacity of the final solution is 3.75 J g^{-1} K^{-1} and that its density is 1.00 g cm^{-3}.

heat change = ... [1]

(iii) By calculating the number of moles of each reagent that was added to the styrofoam cup, and with reference to the equation for the reaction, show which of the reagents, **FA 3** or **FA 7**, is added in excess.

[A_r: Na, 23.0; H, 1.0; C, 12.0; O, 16.0]

reagent added in excess = ... [1]

(iv) Calculate enthalpy change for **reaction 3**, ΔH_3:

$$2NaHCO_3(s) + H_2SO_4(aq) \rightarrow Na_2SO_4(aq) + 2CO_2(g) + 2H_2O(l)$$

ΔH_3 = ... [1]

(c) Use your answer to **(a)(iv)** and **(b)(iv)** to calculate enthalpy change for **reaction 1**, ΔH_1:

$$2NaHCO_3(s) \rightarrow Na_2CO_3(s) + CO_2(g) + H_2O(l)$$

ΔH_1 = ... [4]

(d) In **(a)**, one of the significant sources of errors that will affect the accuracy of the enthalpy change for the reaction between Na_2CO_3 and H_2SO_4, ΔH_2, is that the heat capacity of the styrofoam cup is not taken into account.

Explain the effect of this error on your calculated value of ΔH_2.

[1]

[Total: 15]

3 Planning

A sample of solid anhydrous sodium carbonate is believed to be contaminated with sodium chloride, Na*Cl*.

The percentage purity of sodium carbonate in the sample can be determined by measuring the volume of carbon dioxide formed when sodium carbonate is reacted with an excess of sulfuric acid.

$$Na_2CO_3(s) + H_2SO_4(aq) \rightarrow Na_2SO_4(aq) + CO_2(g) + H_2O(l)$$

You are to plan an experiment that will enable you to:

- react a pre-weighed impure sample of sodium carbonate with a pre-determined volume of the **FA 3** solution that you have used earlier for Question 1 and 2,
- collect and measure the volume of the carbon dioxide gas evolved.

(a) Draw a diagram of the apparatus that you would use to carry out this experiment.

[2]

(b) By considering the capacity of the apparatus that you have drawn in **(a)** to measure the volume of the carbon dioxide gas, calculate the maximum mass of the impure sample of sodium carbonate that you would use in your experiment.

[A_r: Na, 23.0; C, 12.0; O, 16.0 and 1 mole of gas occupies a volume of 24.0 dm^3 under the conditions present in the laboratory]

maximum mass of impure sample of sodium carbonate used = ... [2]

(c) A student suggested that 40.0 cm^3 of **FA 3** solution is sufficient for the experiment.

State whether you agree with the student, and explain your answer.

....

....

.... [1]

(d) State how you would ensure that all the carbon dioxide gas given off in the reaction between the impure sample of sodium carbonate and **FA 3** solution was collected and that none escaped from the apparatus.

....

....

.... [1]

(e) Other than this method that involves the collection of carbon dioxide gas, the percentage purity of sodium carbonate in the sample can also be determined using a titration.

In a typical experiment, a pre-weighed mass of the impure sample of sodium carbonate is dissolved in water and made up to 250 cm^3 in a volumetric flask, and 25.0 cm^3 of this solution is titrated against a standard solution of hydrochloric acid using methyl orange as indicator.

State which of the two methods you would expect to give the more accurate results. Explain your choice.

....

....

....

....

.... [2]

[Total: 8]

4 Inorganic Qualitative Analysis

You are provided with **FA 8**, which is a mixture of two solids, **FA 9**, which is soluble in water and **FA 10**, which is insoluble in water. Each contains **one cation** and **one anion** from the lists on page 17 and 18.

In this question you will perform a series of test-tube reactions, make observations and deduce the identities of the cations and anions present in **FA 9** and **FA 10**.

If the evolution of a gas is observed at any stage, the gas should be tested and identified.

You are advised that the reagent should be added gradually in all tests, with shaking after each addition.

(a) Tests on FA 8

Perform the test-tube experiments described below and record your observations in the spaces provided in the table.

	Test	Observations
(i)	Place all of the solid, **FA 8**, into a 100 cm^3 beaker. Add 25 cm^3 of distilled water and warm to dissolve the **FA 9**. Filter the mixture and use the filtrate for tests **(a)(ii)** to **(a)(iv)**. Wash the residue, **FA 10**, and use it for tests **(a)(v)** to **(a)(vii)**.	

Tests on Filtrate, FA 9

	Test	Observations
(ii)	Place about 1 cm depth of **FA 9** into a test-tube. Add a few drops of dilute sulfuric acid.	
(iii)	Place about 1 cm depth of **FA 9** into a test-tube. Add a few drops of aqueous barium chloride, followed by a few drops of dilute hydrochloric acid.	
(iv)	Place about 1 cm depth of **FA 9** into a test-tube. Add a few drops of aqueous silver nitrate. followed by a few drops of aqueous ammonia.	

Tests on Residue, FA 10

	Test	**Observations**
(v)	Using a spatula, transfer as much of the residue on the filter paper as you can into a test-tube. Add dilute sulfuric acid drop-wise into the test-tube to dissolve the residue. Filter if necessary. Use the resultant solution for test **(a)(vi)** and **(a)(vii)**.	
(vi)	Place about 1 cm depth of the **filtrate** from **(a)(v)** in a test-tube. Add aqueous sodium hydroxide drop-wise with shaking, until no further change is seen.	
(vii)	Place about 1 cm depth of the **filtrate** from **(a)(v)** into a test-tube. Add aqueous ammonia, drop-wise with shaking, until no further change is seen.	

[5]

(b) Based on your observations to **(a)(ii)**, suggest a possible identity of the cation in **FA 9**.

cation in **FA 9**: .... [1]

(c) From your remaining observations, state the identities of the one anion in both **FA 9** and **FA 10**, and the one cation in **FA 10**.

In each case, give evidence to support your conclusion.

	identity		evidence
FA 9	anion:		
FA 10	cation:		
	anion:		

[3]

[Total: 9]

5 Planning

In this question, you will devise a plan, using test-tube reactions, to distinguish between four organic compounds, so that each is identified.

Consider 4 unlabelled bottles and each bottle contains one of the following colourless liquids:

ethanal propanone propan-2-ol ethanoic acid

Plan an investigation, using test tube reactions, which would allow you to identify each of these organic compounds.

Each compound should be identified by at least one positive test. 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.

[Total: 6]

Qualitative Analysis Notes
[ppt. = precipitate]

(a) Reactions of aqueous cations

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

(b) Reactions of anions

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

(c) Test for gases

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

(d) Colour of halogens

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

END OF PAPER 4

Paper 1 Worked Solutions

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

1 $MnO_4^- + 8H^+ + 5e^- \rightleftharpoons Mn^{2+} + 4H_2O$
0.004 mol MnO_4^- gains 0.004 × 5
= 0.020 mol of e^-.
0.01 mol $\mathbf{R}^{2+}$ loses 0.020 mol of e^-.
$\Rightarrow$ 1 mol $\mathbf{R}^{2+}$ loses 2 mol of e^-.
O.S. of **R** increases from +2 to +4.

Ans: A

2 **A**: Incorrect. The equation corresponds to the sum of 1st, 2nd and 3rd I.E.

B: Incorrect. Ti^{2+} needs to be in gaseous state, not solid state.

C: Correct. Third ionisation of Ti is the energy required to remove one mole of electrons from one mole of $Ti^{2+}(g)$ to form one mole of $Ti^{3+}(g)$.

D: Incorrect. The equation corresponds to the reverse of 3rd I.E.

Ans: C

3 **1**: Correct. B^{2-} has an electronic configuration of $1s^2\ 2s^2\ 2p^3$.

2: Correct. C^- has an electronic configuration of $1s^2\ 2s^2\ 2p^3$.

3: Incorrect. N^- has an electronic configuration of $1s^2\ 2s^2\ \mathbf{2p^4}$.

4: Correct. N has an electronic configuration of $1s^2\ 2s^2\ 2p^3$.

Ans: B

4 As all four gases consist of non-polar molecules (the dipole moments cancel out completely in SO_3 as it has a trigonal planar shape), only id-id interactions exist between their respective molecules.

Since SO_3 has the biggest and most polarisable electron cloud, the id-id interaction between its molecules is the strongest (and the volume of its molecules will be the most significant compared to the volume of the container), and so SO_3 shows the greatest deviation from ideality among the 4 gases.

Ans: B

5 $p_1V_1 = nRT_1$
$p_2V_2 = nRT_2$
Rearranging,

$$\frac{p_1V_1}{T_1} = nR = \frac{p_2V_2}{T_2}$$

$$\Rightarrow \frac{(4.50)V}{298} = \frac{P_2(\frac{1}{3}V)}{753}$$

$\Rightarrow P_2 = 34.1$ atm

Ans: B

6 As pressure increases, equilibrium position will shifts to the side with a smaller number of moles of gas to reduce pressure; and as seen from the graph, percentage of the product decreases. This implies that the reactants contain fewer moles of gas than the products (option **B** or **C**).

When temperature is increased from T °C to (T + 20) °C, the endothermic reaction will occur to a greater extent to remove heat; and as seen from the graph, percentage of the product decreases. This implies that the forward reaction is exothermic (option **A** or **C**).

Ans: C

7 $K_w = [H^+]\,[OH^-]$ (by definition)

At 50 °C, $K_w = 5.48 \times 10^{-14}$ mol^2 dm^{-6}
$\Rightarrow [H^+]\,[OH^-] = 5.48 \times 10^{-14}$ mol^2 dm^{-6}

Since $[H^+] = [OH^-]$ for pure water,
$\Rightarrow [H^+]^2 = 5.48 \times 10^{-14}$ mol^2 dm^{-6}
$\Rightarrow [H^+] = 2.34 \times 10^{-7}$ mol dm^{-3}

pH = $-\log [H^+] = -\log (2.34 \times 10^{-7}) = 6.63$ (< 7)

Answer: **D**

8 For a weak acid-weak base (methylamine) titration, the pH will change gradually as the titrant is added to the aliquot even when it is near to the equivalence point (i.e.no sharp colour change will be observed), and so there is no suitable indicator that can be used for the titration.

Answer: **D**

9 In the presence of the homogeneous catalyst NO, the reaction proceed via a two-step mechanism (i.e. the reaction pathway diagram has two humps) with lower activation energy (option **C** and **D**).

In addition, the use of a catalyst <u>does not alter the energy level of the reactants and the products</u> (options **B** and **D**).

Answer: **D**

10

$$\begin{tikzcd}
\text{Rb(s)} \arrow[d, "+81"] & + & \frac{1}{2}\text{Br}_2(l) \arrow[d, "\frac{1}{2}(+224)"] \arrow[r, "\Delta H_f"] & \text{RbBr(s)} \\
\text{Rb(g)} \arrow[d, "+403"] & + & \text{Br(g)} \arrow[d, "-324"] & \\
\text{Rb}^+\text{(g)} & + & \text{Br}^-\text{(g)} \arrow[r, dash] & {} \arrow[uu, "-687"']
\end{tikzcd}$$

$\Delta H_f = +81 + \frac{1}{2}(+224) + 403 + (-324) + (-687)$

$= -415 \text{ kJ mol}^{-1}$

Answer: **B**

11 Heat evolved = (300 x c x ΔT) J

No. of moles of propan-1-ol = (m / 60.0) mol

Maximum amount of heat evolved
= (2021 x 1000 x m / 60.0) J

Efficiency of heating process

$$= \frac{300 \times c \times \Delta T \times 60.0}{m \times 2021 \times 1000} \times 100\%$$

Ans: D

12 From the Data Booklet,

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

$I_2 + 2e^- \rightleftharpoons 2I^-$ $E^\ominus = +0.54$ V

In order for the metal ion to catalyse the reaction, $E^\ominus_{cell}$ must be positive. Hence the $E^\ominus$ value should be between +0.54 V and +2.01 V.

1: Incorrect. $E^\ominus(Cu^{2+}/Cu^+) = +0.15$ V

2: Correct. $E^\ominus(Co^{3+}/ Co^{2+}) = +1.89$ V

3: Correct. $E^\ominus(Mn^{3+}/ Mn^{2+}) = +1.54$ V

4: Incorrect. $E^\ominus(V^{3+}/ V^{2+}) = -0.26$ V

Ans: B

13 The rate of the reaction depends on the rate of the slow step.
⇒ rate = k [B] [C]

However, the rate equation for the overall reaction should be in terms of concentrations of only the reactants (note that C and D are reaction intermediates).

Since step 1 of the mechanism is an equilibrium, $2A \rightleftharpoons C$, we can write an expression for the equilibrium constant:

$$K = \frac{[C]}{[A]^2}$$

rearranging, we get: $[C] = K[A]^2$

The rate equation then becomes
Rate = k [B] K $[A]^2$
= k' $[A]^2$ [B]

Ans: C

14. Option **A** suggest that element J is A*l*. Since in the aqueous solution Al^{3+} first form a white ppt with OH^-: $Al(OH)_3$ which dissolves in excess NaOH due to the formation of $Al(OH)_4^-$

Options **B** and **D** agrees with the suggestion that element J is A*l*.

Option **C** is **incorrect** as Si has the highest melting point among the period 3 elements.

Answer: C

15 Expt 1:
$SrCO_3(s) \rightarrow SrO(s) + CO_2(g)$
$Sr(NO_3)_2(s) \rightarrow SrO(s) + 2NO_2(g) + \frac{1}{2}O_2(g)$

Expt 2:
$SrCO_3(s) + H_2SO_4 \rightarrow SrSO_4(s) + CO_2(g) + H_2O(l)$

No. of moles of $CO_2(g) = \frac{75}{V_m}$ mol

(where V_m = molar volume at a certain temperature and pressure)

Let amount of $SrCO_3$ be a mol and amount of $Sr(NO_3)_2$ be b mol.

From expt 1, $a + 2.5b = 200/V_m$ ----- eqn 1
From expt 2, $a = 75/V_m$

Subst $a = 75/V_m$ into eqn 1 gives
$b = 50/V_m$ mol

⇒ Mole ratio of $SrCO_3 : Sr(NO_3)_2$
$= 75/V_m : 50/V_m = 3 : 2$

Ans: A

16

	$E^\ominus$
$\mathbf{Cl_2} + 2e^- \rightleftharpoons 2Cl^-$	+1.36
$VO_3^- + 4H^+ + e^- \rightleftharpoons \mathbf{VO^{2+}} + 2H_2O$	+1.00
$VO_2^+ + 2H^+ + e^- \rightleftharpoons \mathbf{VO^{2+}} + H_2O$	+1.00
VO_2^+ + 2H+ + $e^- \rightleftharpoons V^{3+}$ + H2O	+0.34

Cl_2 can only be reduced and VO^{2+} can only be oxidised.

Hence, VO^{2+} can be oxidised to either VO_3^- or VO_2^+ since the $E^\ominus$ values of $E^\ominus(Cl_2/Cl^-)$ is more positive than $E^\ominus(VO_2^+/VO^{2+})$ and $E^\ominus(VO_3^-/VO^{2+})$.

Answer: **D**

17 **Highest oxidation state = number of 4s electrons + number of unpaired 3d electrons**

Given electronic configuration to be:
$1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^7\,4s^2$

There are a total of two 4s electrons and three unpaired 3d electrons. Hence maximum oxidation state is +5.

O.S of Y in compound 1 is +6.
O.S of Y in compound 2 is +5.
O.S of Y in compound 1 is +4.
O.S of Y in compound 1 is +2.

Ans: A

18 Since the product is a platinum(IV) compound which contains a cation with a 2+ charge and has a co-ordination number of 6, this means that the cation contains two $\mathrm{C}l^-$ ligands and four NH_3 ligands, i.e. $[\mathrm{Pt(NH_3)_4C}l_2]^{2+}$.

Since the reaction is between $\mathrm{PtC}l_4$ and NH_3 only, and so the anion of the product is $\mathrm{C}l^-$ ions, i.e. the product is made up of $[\mathrm{Pt(NH_3)_4C}l_2]^{2+}$ & $2\mathrm{C}l^-$.

Hence the formula of the product is: $\mathrm{Pt(NH_3)_4C}l_4$.

Ans: C

19 The shortest C−H bonds are associated with those carbon hybrid orbitals with the greatest s character. With greater s character, the hybrid orbital can pull the electron density closer to the nucleus and results in shorter bond length.

A, **B** and **D** are correct statements but do not explain the C-H bond length.

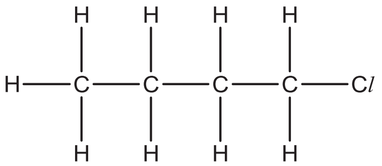
Ans: C

20 Chloroethane undergoes the S_N2 mechanism to give ethanol as it is a primary halogenoalkane. The mechanism involves an OH^- nucleophilic attack from the opposite end of the C*l* leaving group and it is an overall second order reaction.

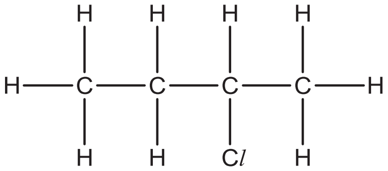
1, 3 and 4 are statements which describes S_N1 mechanism.

Ans: B

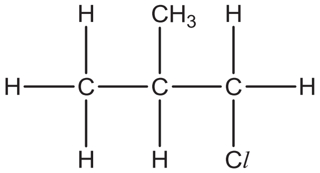
21 In total, there are 4 constitutional isomers that $\mathrm{C_4H_9C}l$ can form. The isomers are as follows:



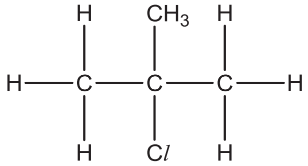
1-chlorobutane



2-chlorobutane



1-chloro-2-methylpropane



2-chloro-2-methylpropane

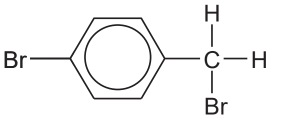
Ans: B

22 Since Br is less electronegative than C*l*, the δ+ charge will reside on the Br-atom in the C*l*−Br molecule. The molecule will therefore react with $\mathrm{A}l\mathrm{C}l_3$ to produce the electrophile Br^+:

$$\mathrm{C}l\mathrm{-Br} + \mathrm{A}l\mathrm{C}l_3 \rightarrow \mathrm{Br}^+ + \mathrm{A}l\mathrm{C}l_4^-$$

Br^+ then acts as the electrophile to attack the benzene ring.

Structure of G is therefore:



Ans: A

23 D undergoes dehydration to give alkenes E and F. E being the minor product as it is the less substituted alkene (i.e. less stable). Upon oxidation, E gives a ketone with −$COCH_3$ group.

A: Minor product obtained upon dehydration is $CH_2=CHCH_2CH_2CH_3$. It is oxidised to give CO_2, H_2O and $CH_3CH_2CH_2CO_2H$.

B: The only product obtained upon dehydration is $CH_3CH=CHCH_2CH_3$. It is oxidised to give CH_3CO_2H and $CH_3CH_2CO_2H$.

C: Minor product obtained upon dehydration is $CH_3CH(CH_3)CH=CH_2$. It is oxidised to give $CH_3CH(CH_3)CO_2H$, CO_2 and H_2O.

D: Minor product obtained upon dehydration is $CH_2=C(CH_3)CH_2CH_3$. It is oxidised to give CO_2, H_2O and $CH_3COCH_2CH_3$. $CH_3COCH_2CH_3$ gives yellow ppt with I_2/OH^-

Ans: D

24 **A**: Both ethanol (−$CH(OH)CH_3$) and propanone (−$COCH_3$) give yellow ppt with aqueous alkaline iodine.

B: Ethanol will be oxidised to ethanoic acid and turns acidified potassium dichromate(VI) from orange to green. Propanone cannot be oxidised and so acidified potassium dichromate (VI) will remain orange.

C: Propanone will give a yellow or orange ppt with 2,4 DNPH and ethanol will not give a ppt with 2,4 DNPH.

D: Effervescence of H_2 gas which 'pops' with lighted splint will be observed for ethanol reacting with sodium metal. No gas will be evolved when sodium metal is added to propanone.

Ans: A

25

A: $CH_3CH_2CN \xrightarrow[D_2O]{NaOD} CH_3CH_2CO_2^-Na^+$

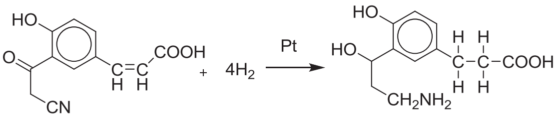
B: $CH_3CH(OH)CH_3 \xrightarrow[D_2SO_4(aq)]{KMnO_4} CH_3COCH_3$

C: $CH_3CO_2H \xrightarrow[\text{conc } D_2SO_4]{C_2H_5OD} CH_3CO_2C_2H_5$

D: $C_6H_5ONa \xrightarrow{D_2O} C_6H_5OD$

Ans: D

26 1: **Correct**



1 mole of compound **P** reacts completely with 4 moles of H_2 gas.

2: **Correct**
It has 1 C=C which can exhibit cis-trans isomerism and no chiral carbon.
Total number of stereoisomers = $2^1 = 2$

3: **Incorrect**
Phenol does not react with ethanoic acid in the presence of concentrated sulfuric acid. Acid chloride is needed to react with phenol to form ester.

Ans: C

27 N_D is the most basic as it has an electron donating methyl group on the adjacent carbon which makes the lone pair of electrons more available for donation to a proton. Hence, N_D is more basic than N_C.

Lone pair of electrons on N_B is delocalised into the pyridine rings (similar to phenylamine) which makes the lone pair of electron less available for donation to a proton. Hence, N_B is less basic than N_C and N_D where the lone pair of electrons are not delocalised into the pyridine rings.

N_A is an amide nitrogen with the lone pair of electron being delocalised into the adjacent carbonyl group. Hence the lone pair is not available for donation to a proton. Amide is neutral.

Order of basicity is $N_D > N_C > N_B > N_A$

Ans: **D**

28 **A**: Correct. 2-aminopropanoic acid isolated from silkworm has a chiral centre and is optically pure and is able to rotate plane polarised light.

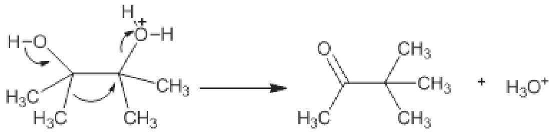
B: Incorrect. Amine cannot react with ethanoic acid to form an amide. Acyl chloride which is more reactive has to be used to react with amine.

C: Incorrect. An aqueous solution of 2-aminopropanoic acid exists as zwitterions and has buffering capacity.

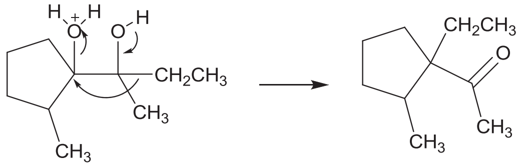
D: Incorrect. Aqueous bromine is decolourised only when alkene, phenol or phenylamine is present (and is absent in 2-aminopropanoic acid)

Ans: A

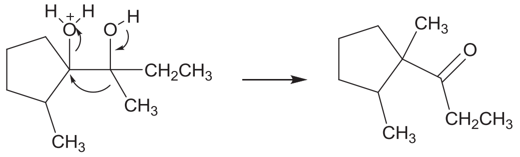
29 The pinacol rearrangement works via the mechanism as shown.



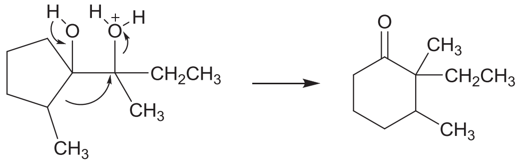
A:



B:



C:



Compound **A**, **B** and **C** can be obtained via pinacol rearrangement.

Ans: D

30 Rate of hydrolysis is in the following order:

K > N > M > L

K is acid chloride and undergoes hydrolysis most readily due to the presence of 2 electronegative atoms (Cl and O atoms) attached to the carbon.

For halogenoalkane, rate of hydrolysis depends on the strength of the C−Hal bond. C−Br bond is weaker than C−Cl bond and hence is broken more readily.

L is a chlorobenzene and the C−Cl bond is not broken in the presence of NaOH(aq). The lone pair of electrons on Cl is partially delocalised into the benzene ring, leading to partial double character and strengthen the C−Cl bond.

71.1 g of $AgCl$ is equivalent to 0.5 mol of $AgCl$. W will give more $AgCl$ as it is more reactive than M.

N will give more than 0.5 mol of AgBr which is equivalent to 93.9 g of AgBr.

L will not give any precipitate.

Ans: A

2017 H2 Chemistry 9729 Preliminary Examinations Suggested solutions

Paper 2: Structured Questions

1 (a) To drive off the CO_2

(b) (i) Amount of $HCl = 50.0 \times 10^{-3} \times 0.100 = 5.00 \times 10^{-3}$ mol

(ii) Amount of $HCl = 20.0 \times 10^{-3} \times 0.0500 = 1.00 \times 10^{-3}$ mol

(iii) Amount of HCl unreacted in graduated flask = $2 \times 1.00 \times 10^{-3} = 2.00 \times 10^{-3}$mol
Amount of HCl neutralised = $5.00 \times 10^{-3} - 2.00 \times 10^{-3} = 3.00 \times 10^{-3}$ mol

(iv) Amount of excess stomach acid
= $(375 \times 10^{-3} \times 0.0300) - (375 \times 10^{-3} \times 0.000300) = 0.011138$ mol

1 tablet is able to neutralise 3.00×10^{-3} mol of HCl.
To neutralise 0.011138 mol of HCl, minimum of 4 tablets is needed.

(c) Amount of $CaCO_3$ in 1 tablet = $\frac{1}{2} \times 3.00 \times 10^{-3} = 1.50 \times 10^{-3}$ mol

Mass of $CaCO_3$ in 1 tablet = $1.50 \times 10^{-3} \times 100.1 = 0.150$ g = 150 mg.

There are only 150 mg of $CaCO_3$ in 1 tablet.

(d) **(i)** For Al_2O_3, there is a **decrease** in **ionic character/ increase in covalent character**

due to the **high polarising power of Al^{3+} ion** which distorts the electron cloud of O^{2-} ion to a greater extent compared to Mg^{2+} ion. Thus the melting point is lower than MgO.

(ii) MgO is only **slightly soluble in water.** pH = 9 (accepts 8 to 10)

Al_2O_3 remains **insoluble** in water. pH = 7.

(iii) $Al^{3+}(aq) + 3OH^-(aq) \rightarrow Al(OH)_3(s)$
$Al(OH)_3(s) + OH^-(aq) \rightarrow Al(OH)_4^-(aq)$

2 **(a)** The volatility of the halogens **decreases** down the group.

The halogens have simple molecular structure and are non-polar.

The **instantaneous dipole-induced dipole interactions between the molecules of each halogen become stronger** due to the **increasing size and polarisability of the electron cloud of the halogens down the group.**

Hence more energy is required to overcome the stronger instantaneous dipole-induced dipole interactions between the molecules of each halogen.

(b)

hydrogen halides	H−C*l*	H−Br	H−I
bond energy / kJ mol^{-1}	431	366	299

The thermal stability of the hydrides of the Group 17 elements **decreases** down the group as the **H−X bond strength decreases** down the group. Hence less energy is required to overcome the H−X covalent bond.

(c) **(i)** $K_{sp} = [Pb^{2+}][Cl^{-}]^2$ mol^3 dm^{-9}

correct expression and units

(ii) $[PbCl_2] = 4.7 \div 278.2 =$ **0.016894 mol dm^{-3}**

$K_{sp} = (0.016894) \times (2 \times 0.016894)^2 =$ **1.9×10^{-5}** mol^3 dm^{-9}

[1] for correct calculation of solubility in mol dm^{-3}
[1] for correct numerical answer and leave the answer to 2 significant figures

(d) **(i)** Decolourisation of orange/yellow/reddish brown $Br_2(aq)$ and a black solid is formed.

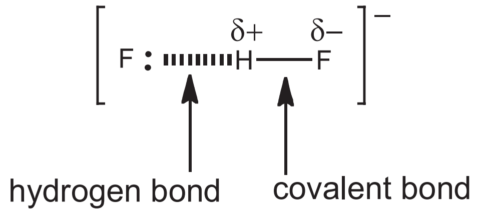
$Br_2(aq) + 2At^-(aq) \rightarrow 2Br^-(aq) + At_2(s)$

(ii) no reaction

(e) **(i)** cation: K^+

anion: HF_2^-

(ii)



[1] for covalent bond; [1] for hydrogen bond

[Total:12]

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

- Mg^{2+} has a smaller ionic radii and thus a higher charge density and polarising power.
- Ease of distortion of electron cloud of carbonate increases, weakening of C–O covalent bond occurs to a greater extent.
- thermal stability of magnesium carbonate is lower than calcium carbonate.

(ii) $MgCO_3 \rightarrow MgO + CO_2$

(b)

$$Mass\ of\ CO_2 = 1.00 - 0.777 = 0.223g$$

$$n_{CO_2} = \frac{0.223}{(12 + 16 \times 2)} = 5.0682 \times 10^{-3} mol$$

$$n_{ZCO_3} = 5.0682 \times 10^{-3} mol$$

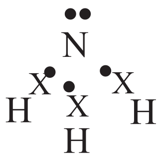
$$5.0682 \times 10^{-3} = \frac{1.0}{M_{MCO3}} \quad \Rightarrow \quad M_{ZCO_3} = 197.3 gmol^{-1}$$

$$M_Z + (12 + 16 \times 3) = 197.3$$

$$M_Z = 137.3 gmol^{-1}$$

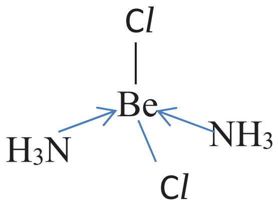
Identity of **Z** : **Barium**

(c) **(i)**



Both correct [1]

(ii)



Tetrahedral shape around Be.

[Total:10]

4 **(a)** **(i)** Amount of coal required

$$= \frac{108 \text{x} 10^3}{393}$$

$= 274.81$mol

Mass of coal required

$= 274.81$x12.0

$= 3297.7$g

Energy density of coal

$$= \frac{108}{3297.7}$$

$= 0.0327$ MJ/g

(ii)

- Coal is a **more efficient fuel.**
- The energy density of coal (0.0327 MJ/g) **is larger than the energy of density of ethanol.** Thus for the **same amount of energy supplied**, **lesser amount of coal is required.**

(iii)

- CO undergoes **ligand exchange reaction** and **binded more strongly via dative bond** **to haemoglobin than O_2**.
- Thus, this **displaces O_2 from oxyhaemoglobin** and **reduces the amount of haemoglobin available for carrying O_2.**

(b) **(i)** $2C (s) + 3H_2 (g) + ½ O_2 (g) \rightarrow CH_3CH_2OH (l)$

$\Delta H^{\ominus}_{f}$ □ =□$\Delta H^{\ominus}_{c}$ (C) + 3□$\Delta H^{\ominus}_{c}$ (H_2) + ½ $\Delta H^{\ominus}_{c}$ (O_2) – $\Delta H^{\ominus}_{c}$ (CH_3CH_2OH)

= 2 x (–393) + 3(–286) + 0 – (–1367)

= **–277 kJmol^{-1}** [1]

(ii) $\Delta H^{\ominus}_r$= Energy absorbed to break bonds + Energy released to form bonds

$CH_3CH_2OH\ (l) + 3\ O_2\ (g) \rightarrow 2\ CO_2\ (g) + 3\ H_2O\ (l)$

bonds broken	(endothermic)	bonds formed	(exothermic)
5 × C–H	**5 × (+410)**	**4 × C=O**	**4 × (−805)**
1 × C–O	**1 × (+360)**	**6 × O–H**	**6 x (<u>−460</u>)**
1 × C–C	**1 x (+350)**		
1 × O–H	**1 x (+460)**		
3 O=O	**3 × (+496)**		
total energy absorbed	**+4708**	**total energy evolved**	**− 5980**

$\Delta H^{\ominus}_c = +4708 - 5980$
$\Delta H^{\ominus}_c = \mathbf{-1272\ kJ\ mol^{-1}}$

- ✓ Bond energy data from data booklet [1]
- ✓ Final answer + units [1]

(iii) ✓ **Bond energy values in the Data Booklet are averages**, so it would not apply exactly to a particular compound.

Or

✓ In the calculation in **(b)(ii)**, it is assumed that all the reactants and products are in the gaseous state. However, **ethanol is a liquid at standard conditions**

(c) **(i)**
Anode: $\mathbf{CH_3CH_2OH + 3H_2O \rightarrow 2CO_2 + 12H^+ + 12e^-}$
Cathode: $\mathbf{O_2 + 4H^+ + 4e^- \rightarrow 2H_2O}$
Overall: $\mathbf{CH_3CH_2OH + 3O_2 \rightarrow 2CO_2 + 3H_2O}$

(ii) $E^{\ominus}_{cell} = E^{\ominus}_{cathode} - E^{\ominus}_{anode}$
$= +\underline{\mathbf{1.23}} - (+0.08)$
$= \mathbf{+\ 1.15V}$

✓ Correct value for $E^{\ominus}_{cathode}$ [1]
(allow for e.c.f if student wrote the wrong equation at the anode as :
$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$, $E^{\ominus}_{cathode} = +0.40$)

✓ Correct value for $E^{\ominus}_{cell}$ [1]

(iii) $\Delta G^{\ominus} = -nFE^{\ominus}_{cell}$
$= -12 \times 96500 \times 1.15$
$= -1.33 \times 10^6\ J mol^{-1}$

= –1.33 x 10^3 kJmol^{-1} (correct units)

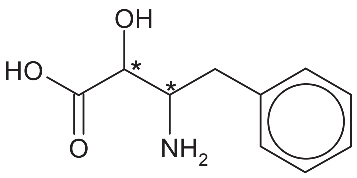
(d) (i) **$H_2O(g)$ (steam), H_3PO_4 catalyst, heat, high pressure**

(ii)

1. In ethene, each of the carbon atom is **sp^2 hybridised**.
2. Each carbon atoms forms **two σ-bonds with hydrogen atoms** through **the head on overlap** of two of **its sp^2 orbitals with the 1s orbitals** of the **hydrogen atoms**.
3. Another **σ-bond** is formed when the remaining **sp^2 orbital of the two carbon atoms overlap with each other**.
4. The **remaining unhybridised p orbital** of the two carbon atoms, which is perpendicular to the plane of sp^2 hybrid orbitals, **overlaps laterally or sideways to form a π bond.**

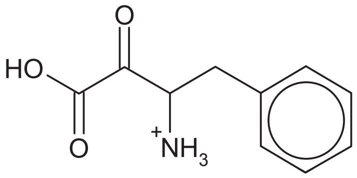
5 (a) (i) carboxylic acid , (secondary) alcohol , and (primary) amine .

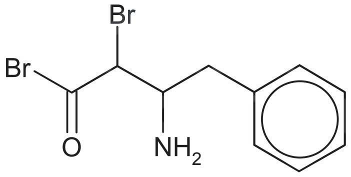
(ii)



total possible number of stereoisomers = 2^2 = **<u>4</u>**

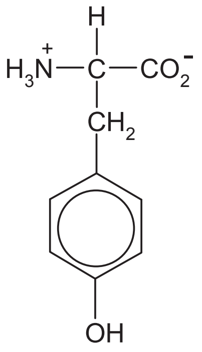
(iii)





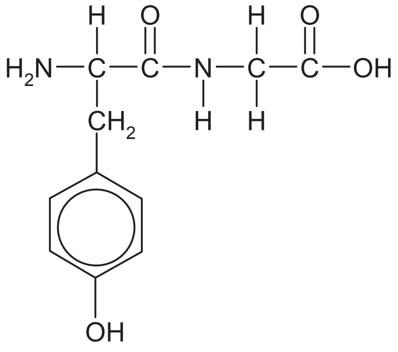
(b) **(i)** A zwitterion is a molecule that is **<u>neutral overall</u>**, but **<u>contains a positive charge</u>** on one part of the molecule (usually $-NH_3^+$) **<u>and a negative charge</u>** on another part of the molecule (usually $-CO_2^-$).

(ii)

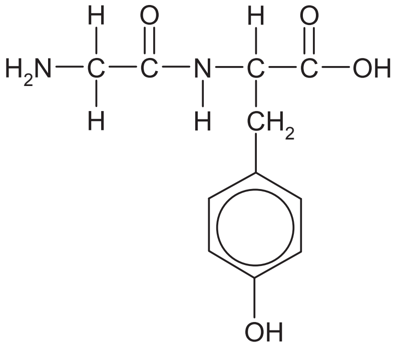


(iii) peptide or amide linkage

(iv)

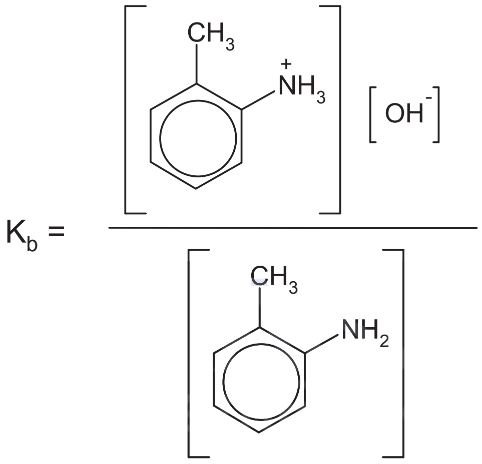


and



(c) **(i)** NaOH(aq), reflux
or
HC*l*(aq), reflux, followed by NaOH(aq)

(ii)



(iii) $K_b = 10^{-pK_b} = 10^{-9.6} = 2.5119 \times 10^{-10}\ \text{mol dm}^{-3}$

$[OH^-] = \sqrt{K_b \times c_{base}} = \sqrt{2.5119 \times 10^{-10} \times 0.10} = 5.0119 \times 10^{-6}\ \text{mol dm}^{-3}$

$pOH = -\log[OH^-] = -\log(5.0119 \times 10^{-6}) = 5.30$

$pH = 14.0 - 5.30 = 8.70$

(d) The pK_b of benzylamine will be **lower** than that for 2-methylphenylamine

Benzylamine is a stronger base as **the phenylmethyl group is electron donating**, **making the lone pair of electrons on N more available for donation** to a proton (or H^+ ion).

2-methylphenylamine is a weaker base as the **lone pair of electrons on the N** of the amine is **delocalised into the benzene ring**, making them **less available for donation** to a proton (or H^+ ion).

Worked solutions for 2017 9729 H2 Chemistry Preliminary Examination Paper 3

1 **(a)** **(i)** $2Cu_2S + 3O_2 \rightarrow 2Cu_2O + 2SO_2$

$2Cu_2O + Cu_2S \rightarrow 6Cu + SO_2$

(ii) Both compounds have giant ionic lattice structure. While the charge and size of the cation as well as the charge of the anion are the same in both ionic compounds, **S^{2-} is bigger than O^{2-}**.

Consequently, **the electrostatic forces of attraction between Cu^+ and S^{2-} are weaker than that between Cu^+ and O^{2-}**. Hence, **lesser amount of energy is required** to overcome the weaker ionic bonds in Cu_2S. The melting point of **Cu_2S will be lower than that of Cu_2O**.

[1]: correct comparison of the size of S^{2-} and O^{2-}
[1]: Cu_2S has a lower melting point than Cu_2O

(iii) anode: impure copper
cathode: pure copper
electrolyte: $CuSO_4(aq)$

$Ag^+ + e^- \rightleftharpoons Ag$ $E^\ominus = +0.80V$
$Cu^{2+} + 2e^- \rightleftharpoons Cu$ $E^\ominus = +0.34V$
$Zn^{2+} + 2e^- \rightleftharpoons Zn$ $E^\ominus = -0.76V$

reaction at the anode
By controlling the voltage, when the current runs through the circuit, copper and zinc metals will be oxidised to form aqueous cations at the anode.

$Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$
$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$

Ag will not be oxidised due to its more positive $E^\ominus$ reduction potential (compared to Cu), and will drop to the bottom as sludge.

reaction at the cathode
Subsequently both Cu^{2+} and Zn^{2+} will migrate to the cathode but only Cu^{2+} will be reduced to Cu as it has a more positive $E^\ominus$ reduction potential than Zn.

$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$

Hence, the copper cathode would grow in size with pure copper deposited, while Zn^{2+} remains in solution.

[1]: description of anode, cathode and electrolyte
[1]: correct electrode reactions (both anode and cathode) with reference to relevant $E^\ominus$ values (correct state symbols must be given for the equations)
[1]: Ag dropping to the bottom as sludge and Zn^{2+} remaining in the solution

(iv) Amount of Ag deposited = 0.100 ÷ 107.9 = 9.2678×10^{-4} mol

$Ag^+(aq) + e^- \rightarrow Ag(s)$

Amount of electrons = 9.2678×10^{-4} mol

$Q = (9.2678 \times 10^{-4}) \times 96500 = 89.436$ C

$I = 89.436 \div (30 \times 60) = 0.0497$ A

$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$

Amount of copper deposited = ½ × $(9.2678 \times 10^{-4}) = 4.6339 \times 10^{-4}$ mol
Mass of copper deposited = $(4.6339 \times 10^{-4}) \times 63.5 = 0.029425 = 0.0294$ g

---

(b) **(i)** $2Cu^{2+}(aq) + 4I^{-}(aq) \rightarrow 2CuI(s) + I_2(aq)$

$E^{\ominus}_{cell} = +0.15 - (+0.54) = \mathbf{-0.39V}$

Since the ***E*°cell is negative, the reaction is not feasible**.

(ii) The precipitation of CuI reduces the concentration $Cu^{+}(aq)$, shifting the Cu^{2+}/Cu^{+} equilibrium ($Cu^{2+} + e^{-} \rightleftharpoons Cu^{+}$) to the right, favouring the reduction process and hence making the reduction potential of Cu^{2+}/Cu^{+} more positive.
As such, $E^{\ominus}_{cell}$ becomes positive and the redox reaction becomes spontaneous.

(c) CH_3CH_2COCl and $(CH_3CH_2CH_2CH(CH_3)CH(CH_3)CH_2)_2Cu^{-}Li^{+}$
or
$CH_3CH_2CH_2CH(CH_3)CH(CH_3)CH_2COCl$ and $(CH_3CH_2)_2Cu^{-}Li^{+}$

[1] for a suitable Gilman reagent, and [1] for the corresponding acid chloride

(d) **(i)** Entropy (S) is a measure of the degree of disorder or randomness in a system.

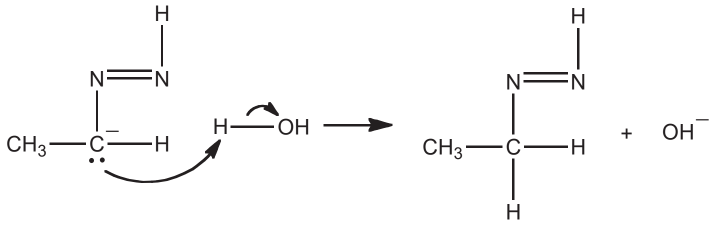
(ii) ΔS is **positive** as the forward reaction is **accompanied by an increase in the number of moles of gases**. Hence, there is an increase in the number of ways of distributing the gaseous particles and entropy increases.

(iii) $\Delta H^{\ominus} = [(-84.7) + (-285.8)] - [(-196.4) + 50.6] = -224.7 \text{ kJ mol}^{-1}$

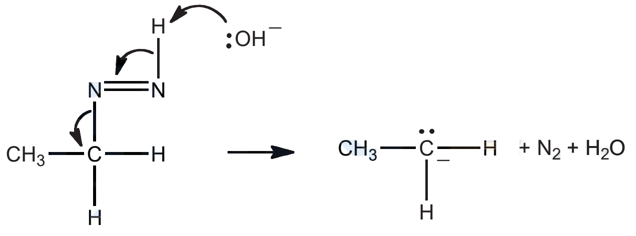
$\Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus} = -224.7 - (298)(0.1915) = -281.8 \text{ kJ mol}^{-1}$

(iv) condensation (or addition-elimination) reaction

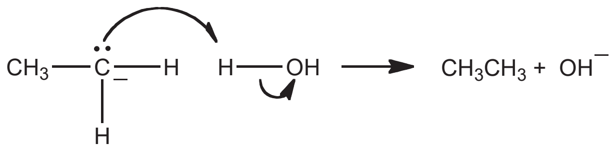
(v) step 3:



step 4:



step 5:



[Total: 21]

2 **(a)** **(i)** Le Chatelier's principle states that when a **system at equilibrium** is subjected to **external disturbance**, the **position of equilibrium will shift** to **counteract the change** imposed to re−establish the equilibrium.

(ii) As [H$^+$] is increased, the **position of equilibrium shifts to the left** to **reduce [H$^+$]**, producing **higher concentration of $Cr_2O_7^{2-}$** and turning the solution orange.

(iii) The colour change implies that the **position of equilibrium has shifted** to the **right** to **absorb** some of the **added heat.**

Hence, the forward reaction is **endothermic**.

(iv)

$$K_c = \frac{[CrO_4^{2-}]^2[H^+]^2}{[Cr_2O_7^{2-}]}$$

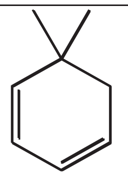
$$= \frac{[CrO_4^{2-}]^2(10^{-8})^2}{[Cr_2O_7^{2-}]} = 1.31\times10^{-13}$$

$$\frac{[CrO_4^{2-}]^2}{[Cr_2O_7^{2-}]} = 1310$$

(v) The high ratio of $\frac{[CrO_4^{2-}]^2}{[Cr_2O_7^{2-}]}$ indicates a much **higher proportion of CrO_4^{2-}** compared to $Cr_2O_7^{2-}$.
The solution will appear **yellow**.

(allow for ecf from **(iii)**)

(b) **(i)**

	$(COOH)_2$
A	**C**

(ii) **A** does **not** exhibit ***cis-trans*** **isomerim** because only the *cis*-form can exist due to **ring strain**.

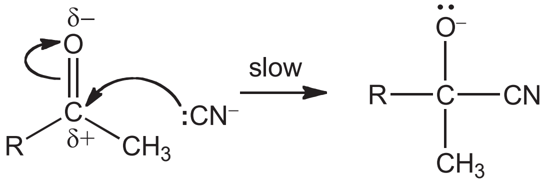
(iii) Compound **B** is a stronger acid than 3,3-dimethylbutanoic acid, because the conjugate base of compound **B** is **more stable** than the conjugate base of 3,3-dimethylbutanoic acid due to the **additional stabilisation of the hydrogen bond formed between the −COO$^-$ group of the mono-anion with the unionised –COOH group.**

(c) nucleophilic addition

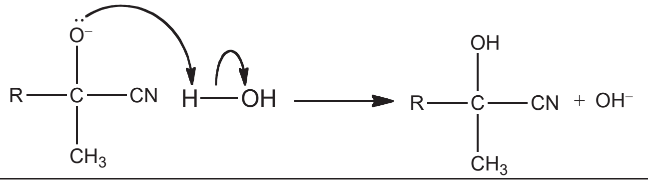
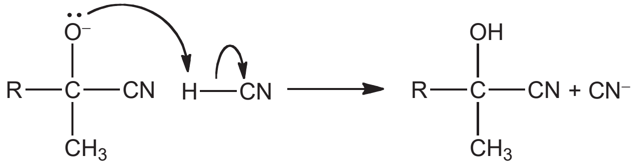
step 1:

NaOH(aq) used	$HCN + OH^- \rightarrow H_2O + CN^-$
NaCN(s) used	$NaCN(s) + aq \rightarrow Na^+(aq) + CN^-(aq)$

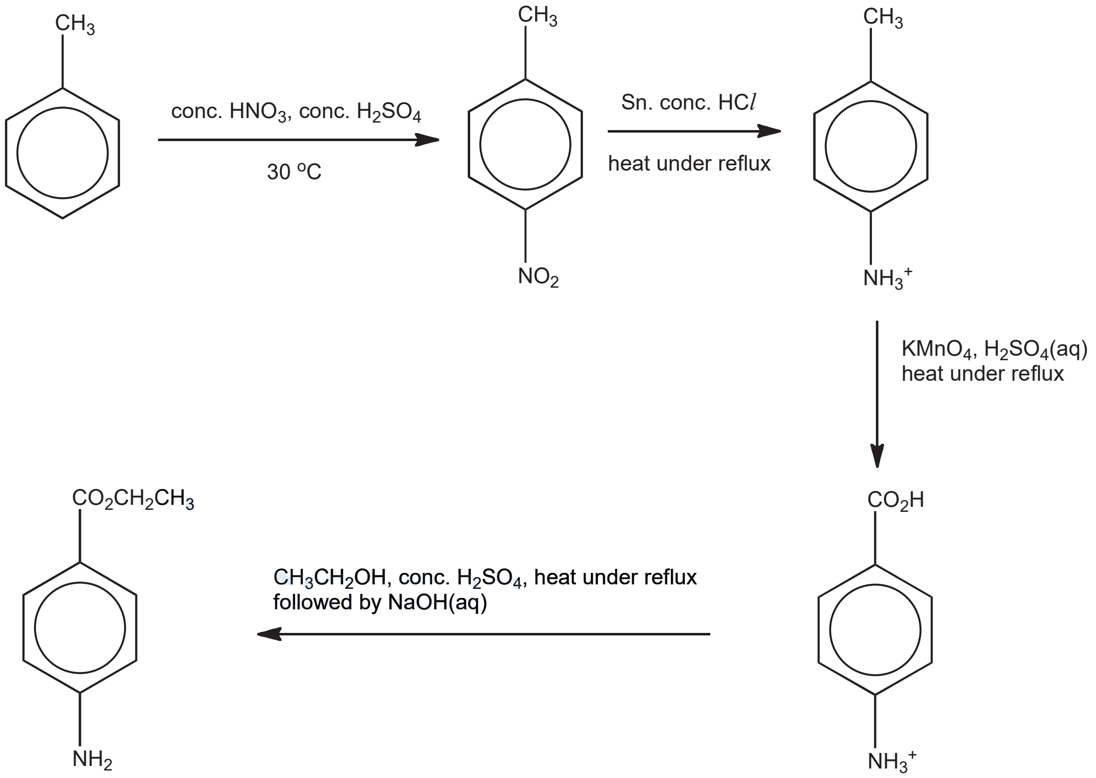
step 2:



step 3:

NaOH(aq) used	
NaCN(s) used	

(d) (i)

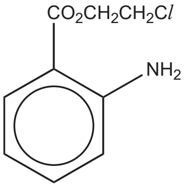


(ii) To a sample of the unknown in a test−tube, add **Br_2(aq)** until in excess.

If the sample is benzocaine, **orange Br_2** will be **decolourised** and a **white precipitate** is formed.
If the sample is methylbenzene, orange Br_2 will **not be decolourised** and **no white precipitate** is formed.

(e) (i) (limited) Cl_2, uv

(ii)



[Total: 21]

3 (a) (i) $NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$
$Cu^{2+}(aq) + 2OH^-(aq) \rightleftharpoons Cu(OH)_2(s)$ -------- (1)

NH_3(aq) undergoes **hydrolysis in water** to form OH^-. When a **small amount of NH_3** is added, a **blue precipitate** of **$Cu(OH)_2$** is formed.

$[Cu(H_2O)_6]^{2+}(aq) + 4NH_3(aq) \rightleftharpoons [Cu(NH_3)_4(H_2O)_2]^{2+}(aq) + 4H_2O(l)$

Addition of **excess ammonia** causes the formation of the more stable **deep blue $[Cu(NH_3)_4(H_2O)_2]^{2+}$** complex ion through a **ligand-exchange reaction**.

The reaction **lowers the concentration of Cu^{2+}(aq)** causing $Cu(OH)_2$ to dissolve. The **position of equilibrium (1) shifts to the left** and the **ionic product < K_{sp}**.

(ii) When NH_3(aq) is added, it reacts with Ag^+ to form $[Ag(NH_3)_2]^+(aq)$.
$Ag^+(aq) + 2NH_3(aq) \rightleftharpoons [Ag(NH_3)_2]^+(aq)$

The concentration of Ag^+(aq) decreases and the equilibrium position shifts left and ionic product $[Ag^+][Cl^-]$ becomes lower than K_{sp} (AgCl)

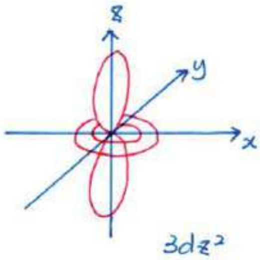
$Ag^+(aq) + Cl^-(aq) \rightleftharpoons AgCl(s)$

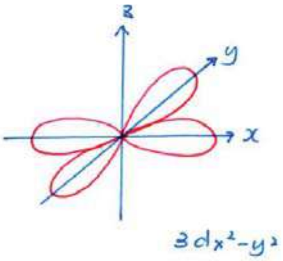
As the **K_{sp} of AgBr is lower than K_{sp} of AgCl**, the **ionic product $[Ag^+][Br^-]$ remains higher than K_{sp} of AgBr** upon addition of NH_3(aq). Hence, the precipitate remains insoluble.

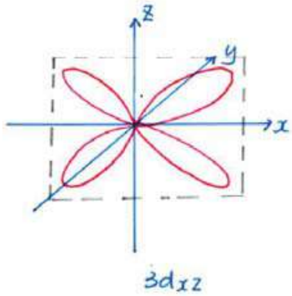
(b) (i) The **energy difference between the 3d and 4s subshells in Fe is relatively small**.

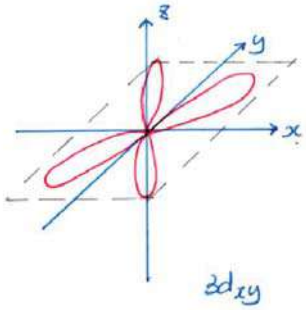
This means with sufficient energy, **both the 4s and some / all of the inner 3d electrons can be removed** to form stable compounds and ions of various oxidation states.

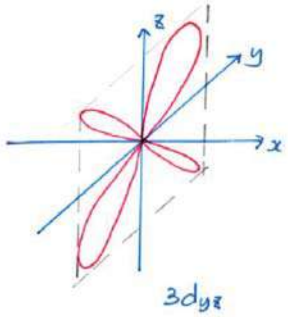
(ii) Fe^{3+}: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5$











(iii) As the lobes of the $3d_{x^2-y^2}$ and $3d_{z^2}$ orbitals lie along the axes, the electrons in these two d-orbitals are pointing towards the lone pairs of electrons of the ligands in an octahedral complex.
Repulsion between the lone pair of electrons of the ligands and the 3*d* electrons in these orbitals is stronger. Thus, $3d_{x^2-y^2}$ and $3d_{z^2}$ orbitals form the higher energy set.

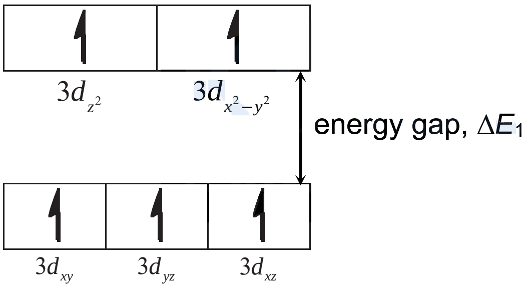
As the 3d orbitals in Fe^{3+} are **partially filled**, d-d transition, where the **electron is promoted from a lower energy orbital to a higher energy orbital**, is possible.

Energy that corresponds to the frequency of light in the visible region of the electromagnetic spectrum is absorbed. Colours that are complementary to those frequency of light absorbed are seen.

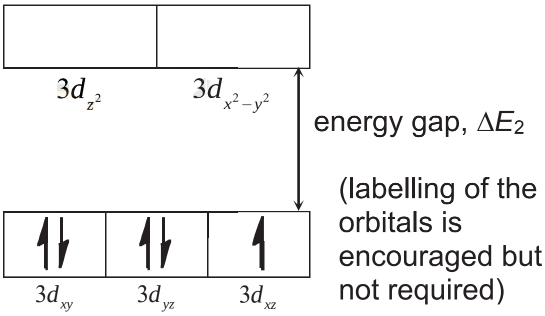
(iv) The **red complex absorbs visible light in the blue region** while the blue complex absorbs in the red region,

i.e. the red complex absorbs light with a shorter wavelength, and so **the red complex has a larger energy gap** between the d-orbitals.

(v) high spin state for the blue complex



low spin state for the red complex



(labelling of the orbitals is encouraged but not required)

- [1] for each correctly drawn spin state
- [1] for indicating the energy gap size in the diagram such that $\Delta E_1 < \Delta E_2$

[Total: 18]

4 **(a)** **(i)** Benzaldehyde is simultaneously oxidised to benzoic acid and reduced to phenylmethanol.

(Or carbon is simultaneously oxidised as its oxidation state is increased from +1 in benzaldehyde to +3 in benzoic acid and reduced, as its oxidation state is decreased from +1 in benzaldehyde to −1 in phenylmethanol.)

(ii) Comparing experiments 1 and 2, concentration of C_6H_5CHO is kept constant, when concentration of KOH doubles, the rate doubles. Hence order of reaction with respect to KOH is 1.

Comparing experiments 2 and 3, as the order w.r.t. KOH is one, when the concentration of KOH is doubled, the rate should be doubled. However, when both the concentration of KOH and C_6H_5CHO is doubled, the rate increased by 8 times. This means that when the concentration of C_6H_5CHO is doubled, the rate is quadrupled. Hence order of reaction with respect to C_6H_5CHO is 2.

(iii) rate = $k\,[C_6H_5CHO]^2[KOH]$

For experiment 1: k = **0.0127 $mol^{-2}\ dm^6\ s^{-1}$**
For experiment 2: k = **0.0122 $mol^{-2}\ dm^6\ s^{-1}$**
For experiment 3: k = **0.0128 $mol^{-2}\ dm^6\ s^{-1}$**

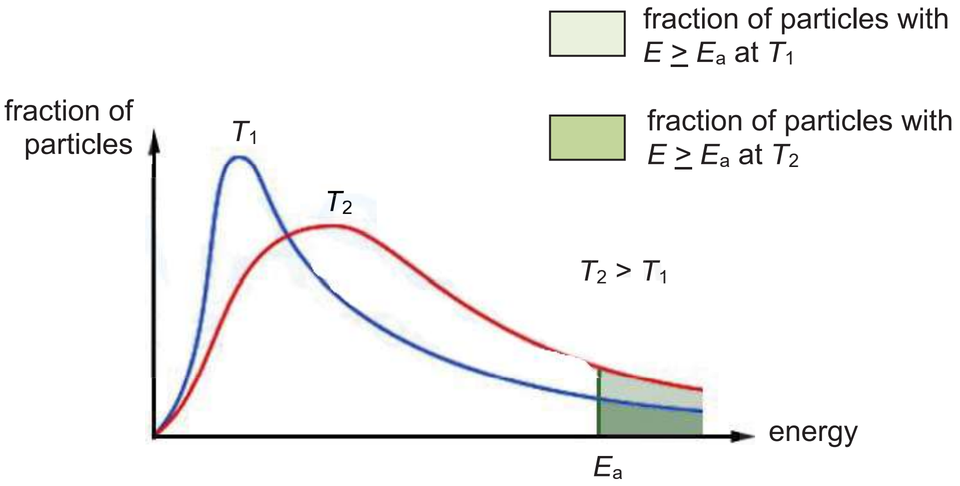
- [1] for any one out of the three

(iv) rate = k' [KOH] where $k' = k[C_6H_5CHO]^2$

$$t_{\frac{1}{2}} = \frac{\ln 2}{k[C_6H_5CHO]^2} = \frac{\ln 2}{(0.012667)(1.60)^2} = 21.4\ \text{s}$$

(v) When temperature increases, **molecular speed and average kinetic energies of reactant particles increases.** Hence, there will be a **higher frequency of collisions and** a **greater fraction** of the particles will have energy **greater than the activation energy** required for reaction. This will lead to a **higher frequency of effective collisions**.

The **rate constant *k* increases** as the temperature increases, hence **rate of reaction increases.**



(b) **(i)** LiA/H$_4$ in dry ether / $NaBH_4$ in methanol, room temperature

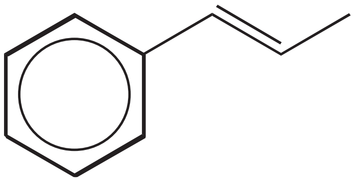
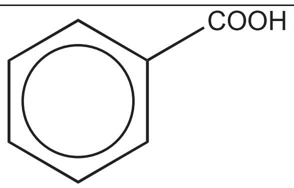
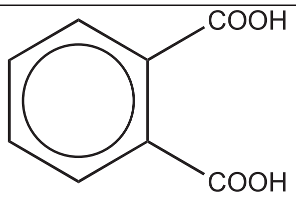
(ii) $KMnO_4$ / $K_2Cr_2O_7$, dilute H_2SO_4, reflux

(c)

test	benzaldehyde	phenylmethanol
anhydrous PCl_5 / $SOCl_2$	no white fumes	white fumes
Tollens' regent, warm	silver mirror	no silver mirror
2,4-DNPH	orange precipitate	no orange precipitate
Na	no effervescence	effervescence and the gas evolved 'pops' with a lighted splint

[1] for correct reagents and conditions, and [1] for correct observations for both benzaldehyde and phenylmethanol

(d)

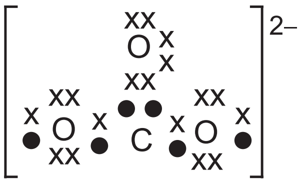
		
R	**T**	**U**

[1] for each correct structure

information	deduction
R exhibits stereoisomerism.	**R** exhibits **cis-trans isomerism** (it cannot exhibit enantiomerism as the side chain contains only three C-atoms). **R contains C=C group** (with two different groups attached to each C-atom)
R is found to decolourise orange aqueous bromine but **S** does not.	**R** undergoes **electrophilic addition** with aqueous bromine. **R contains C=C group**
When hot acidified potassium managate solution is added to 1 mol of **R** and **S,** both decolourised the purple potassium managate to form compound **T** and **U** respectively.	**R** and **S** undergoes **oxidation** Presence of benzylic H on both **R** and **S** both **T** and **U contains −COOH group**
1.0 mol of compound **T** exactly reacts with 0.5 mol of sodium carbonate while compound 1.0 mol of compound **U** reacts with exactly 1.0 mol of sodium carbonate to give out carbon dioxide gas.	**T** and **U** undergoes **neutralisation** reaction with sodium carbonate. **T** contains **one −COOH group** **U** contains **two −COOH groups**

[Total: 20]

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



(ii) trigonal planar

the **3 bond pairs and 0 lone pair** of electrons **will space themselves out as far apart as possible to minimise repulsion**.

(b) **(i)** The reaction between Na_2CO_3 and HC*l* is an acid-base reaction as HC*l* functions as a **Bronsted acid** and **donates** a **proton** to Na_2CO_3. Hence, Na_2CO_3 functions as a **Bronsted base** and **accepts** a **proton** from HC*l*.

(ii) $HCO_3^- + H_2O \rightleftharpoons H_2CO_3 + OH^-$

The pH is weakly basic as HCO_3^- undergoes hydrolysis in water to produce OH^-.

(c) When **a small amount of acid** is added,
$HCO_3^-(aq) + H_3O^+(aq) \rightarrow H_2CO_3(aq) + H_2O(l)$

When **a small amount of alkali** is added:
$H_2CO_3(aq) + OH^-(aq) \rightarrow HCO_3^-(aq) + H_2O(l)$

(d) **(i)** Ideal gas particles take up zero (or negligible) volume (as compared to the volume of the container)

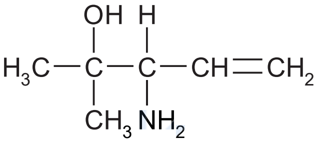
There are no (or negligible) intermolecular forces of attraction between the particles of an ideal gas.

(ii) pV = nRT
$1.1 \times 101325 \times 56.0 \times 10^{-6} = n \times 8.31 \times (30 + 273)$
No. of moles of CO_2 produced = $\mathbf{2.4789 \times 10^{-3}}$ **mol**

No. of moles of Na_2CO_3 = 2.4789×10^{-3} mol
$[Na_2CO_3] = [(2.4789 \times 10^{-3}) \div 0.02]$ = **0.124 mol dm**$^{\mathbf{-3}}$

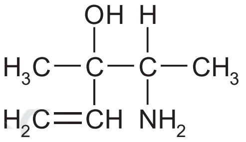
(e)

G is:



$H_3C-\underset{CH_3}{\overset{OH}{C}}-\underset{NH_2}{\overset{H}{C}}-CH=CH_2$

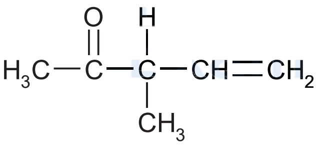
(but also accept:



$H_3C-\underset{H_2C=CH}{\overset{OH}{C}}-\underset{NH_2}{\overset{H}{C}}-CH_3$

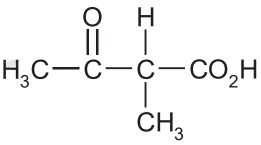
)

H is:



$H_3C-\overset{O}{\overset{\|}{C}}-\underset{CH_3}{\overset{H}{C}}-CH=CH_2$

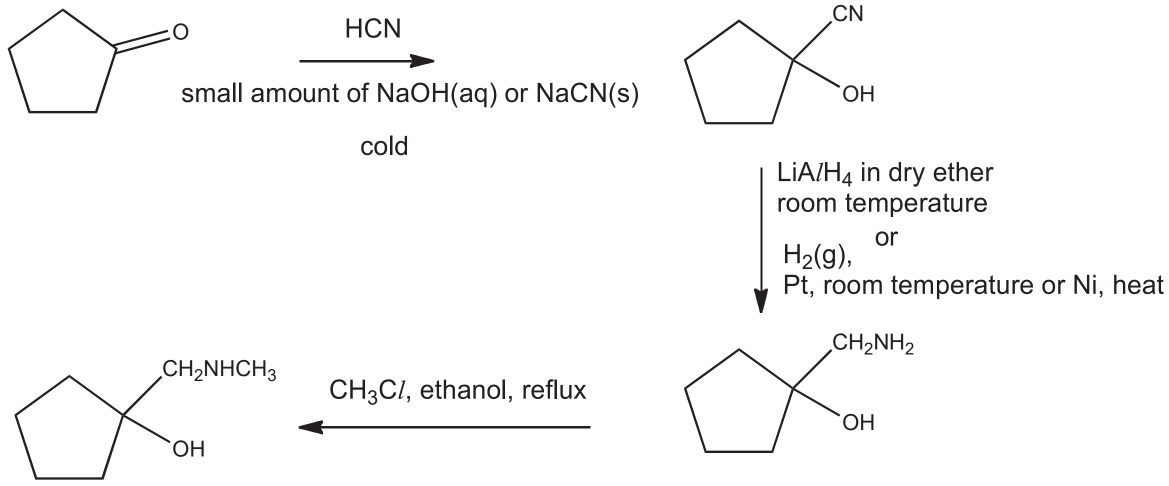
J is:



$H_3C-\overset{O}{\overset{\|}{C}}-\underset{CH_3}{\overset{H}{C}}-CO_2H$

information	deduction
H produces a yellow precipitate with iodine in alkaline solution.	**H** undergoes **oxidation**. **H** contains **CH_3CO- group**.
Treatment of **H** with hot acidified solution of potassium maganate(VII) produces **J,** $C_5H_8O_3$, along with a gas that forms white precipitate in limewater.	**H** undergoes **oxidation (or oxidative cleavage)** with hot acidified potassium maganate(VII) to produce CO_2(g) **H** contains a **terminal alkene**
H was also observed to be able to readily decolourise bromine in tetrachloromethane	**H** undergoes **electrophilic addition** with Br_2 in CCl_4 **H** contains a **alkene**

(f)



[Total: 20]

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

1 Determination of the concentration of sodium thiosulfate in solution Z

Sodium thiosulfate is commonly used in an alternative method for the extraction of gold from its ores, through the formation of a stable and soluble complex of gold(I) ions, $[Au(S_2O_3)_2]^{3-}$. One of your tasks is to determine the concentration of sodium thiosulfate in a commercially produced solution **Z** used in the extraction process.

Solution **Z** contains sodium thiosulfate in deionised water. You are not provided with solution **Z**, as it is too concentrated for use in this experiment. A diluted solution of **Z** has been prepared for you. This diluted solution is **FA 5**.

FA 1 is 0.0230 mol dm^{-3} of aqueous potassium iodate(V), KIO_3
FA 2 is 0.50 mol dm^{-3} potassium iodide, KI
FA 3 is 0.75 mol dm^{-3} sulfuric acid, H_2SO_4
FA 4 is a solution of sodium thiosulfate, $Na_2S_2O_3$ of an unknown concentration
FA 5 a diluted solution of **Z**, in which 31.00 cm^3 of solution **Z** was made up to 250 cm^3 with deionised water in a volumetric flask

You are also provided with starch solution.

In acidic medium, iodate(V) ions oxidise iodide ions to iodine

$$IO_3^-(aq) + 5I^-(aq) + 6H^+(aq) \rightarrow 3I_2(aq) + 3H_2O(l) \qquad \textbf{reaction 1}$$

If an excess of sodium thiosulfate is present in the reaction mixture, the iodine produced in **reaction 1** is immediately reduced back to iodide ions, as shown in **reaction 2**, and the dark brown colour of iodine does not form.

$$I_2(aq) + 2S_2O_3^{2-}(aq) \rightarrow 2I^-(aq) + S_4O_6^{2-}(aq) \qquad \textbf{reaction 2}$$

In the experiments that you will perform, insufficient volumes of the first sodium thiosulfate solution will be added initially, and some iodine will remain in the solution. The amount of iodine left-over can be determined by titration with the second solution of sodium thiosulfate, as shown in **reaction 2**.

You will prepare a number of reaction mixtures, each of which will contain:

- a fixed volume of **FA 1**,
- excess amounts of **FA 2** and **FA 3**,
- a different volume of **FA 4**.

All reaction mixtures will contain some iodine, produced in **reaction 1**, that will be titrated against the **FA 5** solution.

You are required to use a graphical method to determine the concentrations of sodium thiosulfate in **FA 4**, **FA 5** and solution **Z**.

(a) Titration of iodine produced against FA 5

Note: You will perform each titration only **once**. Great care must be taken to ensure that you do not overshoot the end-point.

You will be using two burettes in this task, and each of the burette will contain different sodium thiosulfate solutions, so care must be taken that the right one is used each time.

(i) Experiment 1

1. Fill the burette labelled "**FA 4**" with **FA 4** solution.
2. Fill the burette labelled "**FA 5**" with **FA 5** solution.
3. Using a pipette, transfer 25.0 cm^3 of **FA 1** into a 250 cm^3 conical flask.
   From the burette, transfer 9.50 cm^3 of **FA 4** to the same conical flask.

   If you accidentally added an incorrect volume of **FA 4** for any of your titrations, record the actual volume of **FA 4** added in your table on the next page, and use that volume for the plotting of the graph later
4. Use appropriate measuring cylinders to add to this flask:
   - 10 cm^3 of **FA 2**,
   - 10 cm^3 of **FA 3**.
5. Titrate the iodine liberated with **FA 5** until the solution fades to a pale yellow colour.
6. Add about 1 cm^3 (about 10 drops) of starch indicator to this flask. Continue adding **FA 5** until the blue-black colour **just** disappears.
7. Record your titration results in the section "Recording" on page 3. Make sure that your recorded results show the precision of your working.

(ii) Experiment 2

8. Repeat steps 3 to 8 but add 22.00 cm^3 of **FA 4** at step 4.

(iii) Experiment 3 to 5

9. Choose three further volumes of **FA 4** between 9.50 cm^3 and 22.00 cm^3.
10. Repeat steps 3 to 8 using each of your chosen volumes of **FA 4** at step 4.

Recording

Prepare a table in the space provided on the next page to record:

- the volumes of **FA 4** added for each experiment.
- the burette readings and the volumes of **FA 5** used for each experiment.

Table of results

Titration number	1	3	4	5	2
Volume of **FA 4** /cm^3	**9.50**	**12.50**	**15.50**	**18.50**	**22.00**
Final burette reading /cm^3	31.30	28.75	24.10	44.90	46.80
Initial burette reading /cm^3	0.10	1.00	0.00	24.10	30.00
Volume of **FA 5** added /cm^3	31.20	27.75	24.10	20.80	16.80

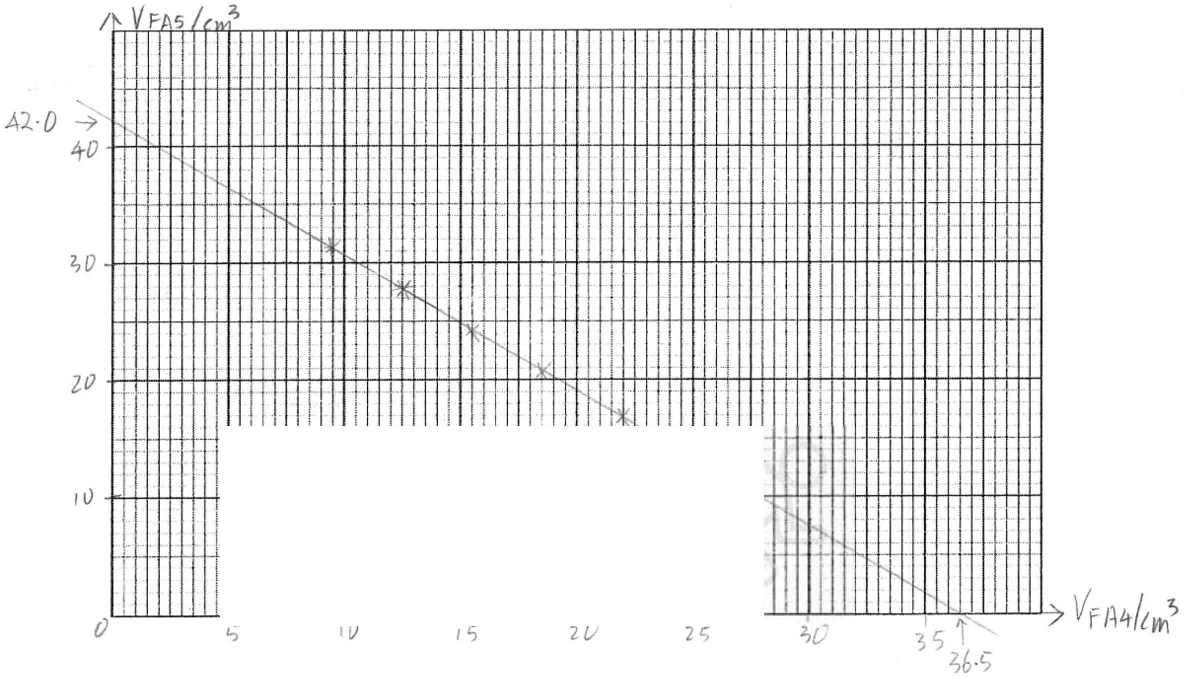
[4]

(b) **Graphical determination to determine concentration of sodium thiosulfate in FA 4, FA 5 and solution Z.**

(i) Plot a graph of the volume of **FA 5** added (*y-axis*) against the volume of **FA 4** added (*x-axis*) on the grid below. When choosing the scale, you should ensure that the graph line can be extrapolated to intersect both the *x-axis* and the *y-axis*.

Draw a straight line of best fit, taking into account all of your plotted points.

Extrapolate your graph line so that it intersects both the *x-axis* and the *y-axis*.



[3]

(ii) It is possible to react all the iodine produced by the reaction between 25.0 cm^3 of **FA 1** and 10 cm^3 of **FA 2** and **FA 3** by using **FA 4** only.

From your graph, determine the volume of **FA 4** required to do this.

volume of **FA 4** required = 36.5 cm^3 [3]

(iii) Calculate the gradient of your graph line, showing clearly how you did this.

gradient = $\frac{0-42.0}{36.5-0} = -1.1507 = -1.15$

gradient = −1.15 [1]

(c) Calculations

(i) The amount of iodate(V) ions, IO_3^-, present in 25.0 cm^3 of **FA 1** is 5.75×10^{-4} mol.

Use this value, together with data obtained from your graph, to calculate the concentration of thiosulfate ions in **FA 4**.

Number of moles of iodine produced = $3 \times n_{IO_3^-} = 3 \times 5.75 \times 10^{-4} = 1.725 \times 10^{-3}$ mol

Number of moles of $S_2O_3^{2-}$ required = $2 \times n_{I_2} = 2 \times 1.725 \times 10^{-3} = 3.45 \times 10^{-3}$ mol

concentration of $S_2O_3^{2-}$ in **FA4** = $\frac{n_{S_2O_3^{2-}}}{V_{\mathbf{FA4}}} = \frac{3.45 \times 10^{-3}}{36.5 \times 10^{-3}} = 0.094521 = 0.0945 \text{ mol dm}^{-3}$

$[S_2O_3^{2-}]$ in **FA 4** = 0.0945 mol dm^{-3} [2]

(ii) The concentration of $S_2O_3^{2-}$ in **FA 4** and **FA 5** are related to the gradient of the graph obtained in **(b)(iii)** by the following equation:

$$[S_2O_3^{2-}]_{\mathbf{FA\,5}} = \frac{[S_2O_3^{2-}]_{\mathbf{FA\,4}}}{|\text{gradient}|}$$

Using the equation, or otherwise, calculate the concentration of thiosulfate ions in **FA 5**.

$$[S_2O_3^{2-}]_{\mathbf{FA5}} = \frac{[S_2O_3^{2-}]_{\mathbf{FA4}}}{|\text{gradient}|} = \frac{0.094521}{1.1507} = 0.082142 = 0.0821 \text{ mol dm}^{-3}$$

$[S_2O_3^{2-}]$ in **FA 5** = 0.0821 mol dm^{-3} [1]

(iii) Calculate the concentration of thiosulfate ions in the commercially produced solution **Z**.

$$[S_2O_3^{2-}]_z \times 31.00\times10^{-3} = [S_2O_3^{2-}]_{\mathbf{FA5}} \times 250\times10^{-3}$$

$$\Rightarrow [S_2O_3^{2-}]_{\mathbf{z}} = \frac{[S_2O_3^{2-}]_{\mathbf{FA5}} \times 250\times10^{-3}}{31.00\times10^{-3}} = \frac{0.082142\times250\times10^{-3}}{31.00\times10^{-3}} = 0.662 \text{ mol dm}^{-3}$$

$[S_2O_3^{2-}]$ in solution **Z** = 0.622 mol dm^{-3} [1]

(d) A student suggested using burettes, rather than using measuring cylinders, to measure the volume of **FA 2** and **FA 3** used in **(a)** so as to improve on the accuracy of the titration data.

State whether you agree with the student and briefly explain why.

No. Since both solutions are in excess, using a burette (which has a higher precision than measuring cylinders) does not improve the accuracy of the experiment.

[1]

(e) In a private institution, a laboratory assistant made the mistake in the preparation of the **FA 5** solution by diluting 21.00 cm^3 of solution **Z** to 250 cm^3, rather than the specified volume of 31.00 cm^3.

State and explain how using this incorrect sample of **FA 5** will affect the gradient of your graph.

As the concentration of $S_2O_3^{2-}$ in the incorrect sample of **FA 5** will be **<u>lower</u>** than the intended value, and since $[S_2O_3^{2-}]_{\mathbf{FA\,5}} = \frac{[S_2O_3^{2-}]_{\mathbf{FA\,4}}}{|\text{gradient}|}$, the **<u>magnitude of the gradient</u>** will be **<u>larger</u>**.

<u>Or</u>

As the concentration of $S_2O_3^{2-}$ in the incorrect sample of **FA 5** will be lower than the intended value, a larger volume of **FA 5** would be required for each titration, leading to a larger magnitude for the gradient.

[1]

[Total: 17]

2 Determination of the enthalpy change for the thermal decomposition of sodium hydrogen carbonate

FA 6 is solid anhydrous sodium carbonate, Na_2CO_3
FA 7 is solid sodium hydrogen carbonate, $NaHCO_3$

You will need access to the **FA 3** solution that you have used earlier.

Sodium hydrogen carbonate is commonly used as a raising agent in baking, as it undergoes thermal decomposition at temperatures above 80 °C, according to the equation:

$$2NaHCO_3(s) \rightarrow Na_2CO_3(s) + CO_2(g) + H_2O(l) \qquad \textbf{reaction 1}$$

Due to the high temperature involved, the enthalpy change of this reaction cannot be measured directly using a coffee-cup calorimeter.

In the experiments that you will perform, the coffee-cup calorimeter will be used to determine the enthalpy change, ΔH_2, for the reaction:

$$Na_2CO_3(s) + H_2SO_4(aq) \rightarrow Na_2SO_4(aq) + CO_2(g) + H_2O(l) \qquad \textbf{reaction 2}$$

and the enthalpy change, ΔH_3, for the reaction:

$$2NaHCO_3(s) + H_2SO_4(aq) \rightarrow Na_2SO_4(aq) + 2CO_2(g) + 2H_2O(l) \qquad \textbf{reaction 3}$$

You will then use your results of your experiments to calculate the enthalpy change, ΔH_1, for the thermal decomposition of sodium hydrogen carbonate.

(a) Determining enthalpy change for the reaction between Na_2CO_3 and H_2SO_4, ΔH_2

1. Place the styrofoam cup inside a 250 cm^3 beaker to prevent it from toppling over.
2. Using a measuring cylinder, place 40 cm^3 of **FA 3** into the styrofoam cup.
3. Stir the solution in the cup gently with the thermometer, and measure its temperature. Record the initial temperature of **FA 3** in your table.
4. Weigh the weighing bottle labelled "**FA 6**" and its contents using a weighing scale, without the cap. The bottle has been pre-weighed to contain between 4.50 g and 5.00 g of solid sodium carbonate.
5. Pour **FA 6** from the weighing bottle into the styrofoam cup, place the lid onto the cup, and insert the thermometer through the lid.
6. Stir the mixture using the thermometer and record the maximum temperature reached.
7. Reweigh the weighing bottle.

(i) In an appropriate format in the space below, record:

- all mass readings, including the mass of **FA 6** added to the styrofoam cup
- all temperatures measured and the temperature rise.

Mass of weighing bottle and **FA 6**	/ g	8.104
Mass of weighing bottle and residual **FA 6**	/ g	3.542
Mass of **FA 6** added to the styrofoam cup	/ g	4.562
Initial temperature of **FA 3**	/ °C	30.2
Maximum temperature reached	/ °C	39.2
Temperature rise	/ °C	9.0

[1]

(ii) Calculate the heat change for **reaction 2**.

Assume that the specific heat capacity of the final solution is 3.75 J g^{-1} K^{-1} and that its density is 1.00 g cm^{-3}.

$$q = (40.0 \times 1.00) \times 3.75 \times 9.0 = 1350 \text{ J} = 1.35 \text{ kJ}$$

heat change = 1.35 kJ [1]

(iii) By calculating the number of moles of each reagent that was added to the styrofoam cup, and with reference to the equation for the reaction, show which of the reagents, **FA 3** or **FA 6**, is added in excess.

[A_r: Na, 23.0; C, 12.0; O, 16.0]

$$n_{H_2SO_4} = 0.75 \times 40.0 \times 10^{-3} = 0.0300 \text{ mol}$$

$$n_{Na_2CO_3} = \frac{4.562}{2(23.0) + 12.0 + 3(16.0)} = \frac{4.562}{106.0} = 0.043038 \text{ mol}$$

From the balanced equation, $\frac{n_{H_2SO_4}}{n_{Na_2CO_3}} = \frac{1}{1}$,

0.0300 mol of H_2SO_4 will require only 0.0300 mol of Na_2CO_3 for complete reaction, and since the number of moles of Na_2CO_3 added is more than 0.0300 mol, Na_2CO_3 is added in excess.

reagent added in excess = Na_2CO_3 [1]

(iv) Calculate enthalpy change for **reaction 2**, ΔH_2:

$$Na_2CO_3(s) + H_2SO_4(aq) \rightarrow Na_2SO_4(aq) + CO_2(g) + H_2O(l)$$

$$\Delta H_{rxn} = -\frac{1.35}{0.0300} = -45.0 \text{ kJ mol}^{-1}$$

ΔH_2 = −45.0 kJ mol^{-1} [1]

(b) **Determining enthalpy change for the reaction between $NaHCO_3$ and H_2SO_4, ΔH_2**

1. Empty and rinse the styrofoam cup used in **(a)**, and replace the cup in the 250 cm^3 beaker.
2. Using the same measuring cylinder used in **(a)**, place 40 cm^3 of **FA 3** into the styrofoam cup.
3. Wash and dry the thermometer used in **(a)**, before using it to stir the solution in the cup gently, and measure its temperature. Record the initial temperature of **FA 3** in your table.
4. Weigh the weighing bottle labelled "**FA 7**" and its contents using a weighing scale, without the cap. The bottle has been pre-weighed to contain between 3.50 g and 4.00 g of solid sodium hydrogen carbonate.
5. Pour **FA 7** from the weighing bottle into the styrofoam cup, place the lid onto the cup, and insert the thermometer through the lid.
6. Stir the mixture using the thermometer and record the minimum temperature reached.
7. Reweigh the weighing bottle.

(i) In an appropriate format in the space below, record:

- all mass readings, including the mass of **FA 7** added to the styrofoam cup
- all temperatures measured and the temperature fall.

Mass of weighing bottle and **FA 7**	/ g	7.428
Mass of weighing bottle and residual **FA 7**	/ g	3.463
Mass of **FA 7** added to the styrofoam cup	/ g	3.965
Initial temperature of **FA 3**	/ °C	30.2
Minimum temperature reached	/ °C	37.8
Temperature fall	/ °C	7.6

[3]

(ii) Calculate the heat change for **reaction 3**.

Assume that the specific heat capacity of the final solution is 3.75 J g^{-1} K^{-1} and that its density is 1.00 g cm^{-3}.

$$q = (40.0 \times 1.00) \times 3.75 \times 7.6 = 1140 \text{ J} = 1.14 \text{ kJ}$$

heat change = 1.14 kJ [1]

(iii) By calculating the number of moles of each reagent that was added to the styrofoam cup, and with reference to the equation for the reaction, show which of the reagents, **FA 3** or **FA 7**, is added in excess.

[A_r: Na, 23.0; H, 1.0; C, 12.0; O, 16.0]

$$n_{H_2SO_4} = 0.75 \times 40.0 \times 10^{-3} = 0.0300 \text{ mol}$$

$$n_{NaHCO_3} = \frac{3.965}{23.0 + 1.0 + 12.0 + 3(16.0)} = \frac{3.965}{84.0} = 0.047202 \text{ mol}$$

From the balanced equation, $\frac{n_{H_2SO_4}}{n_{NaHCO_3}} = \frac{1}{2}$,

0.0300 mol of H_2SO_4 will require 0.0600 mol of $NaHCO_3$ for complete reaction, and since the number of moles of $NaHCO_3$ added is less than 0.0600 mol, H_2SO_4 is added in excess.

reagent added in excess = H_2SO_4 [1]

(iv) Calculate enthalpy change for **reaction 3**, ΔH_3:

$$2NaHCO_3(s) + H_2SO_4(aq) \rightarrow Na_2SO_4(aq) + 2CO_2(g) + 2H_2O(l)$$

$$\Delta H_{rxn} = +\frac{1.14}{0.047202} \times 2 = +48.303 = +48.3 \text{ kJ mol}^{-1}$$

ΔH_3 = +48.3 kJ mol^{-1} [1]

(c) Use your answer to **(a)(iv)** and **(b)(iv)** to calculate enthalpy change for **reaction 1**, ΔH_1:

$$2NaHCO_3(s) \rightarrow Na_2CO_3(s) + CO_2(g) + H_2O(l)$$

$$\begin{tikzcd}
2NaHCO_3(s) \arrow[rr, "\Delta H_1"] \arrow[dr, swap, "\Delta H_3"] \arrow[dr, "+ H_2SO_4(aq)"] & & Na_2CO_3(s) + CO_2(g) + H_2O(l) \arrow[dl, swap, "\Delta H_2"] \arrow[dl, "+ H_2SO_4(aq)"] \\
& Na_2SO_4(aq) + 2CO_2(g) + 2H_2O(l) &
\end{tikzcd}$$

Hence, $\Delta H_1 = \Delta H_3 - \Delta H_2 = +48.303 - (-45.0) = +93.303 = +93.3$ kJ mol^{-1}

ΔH_1 = +93.3 kJ mol^{-1} [4]

(d) In **(a)**, one of the significant sources of errors that will affect the accuracy of the enthalpy change for the reaction between Na_2CO_3 and H_2SO_4, ΔH_2, is that the heat capacity of the styrofoam cup is not taken into account.

Explain the effect of this error on your calculated value of ΔH_2.

As some of the **heat produced** in the reaction **is absorbed** by the styrofoam cup, the **maximum temperature** measured is **lower** than expected, and so the **magnitude** of ΔH_2 calculated will be **lower** than the theoretical value

[1]

[Total: 15]

3 Planning

A sample of solid anhydrous sodium carbonate is believed to be contaminated with 5 to 10% of sodium chloride, Na*Cl*.

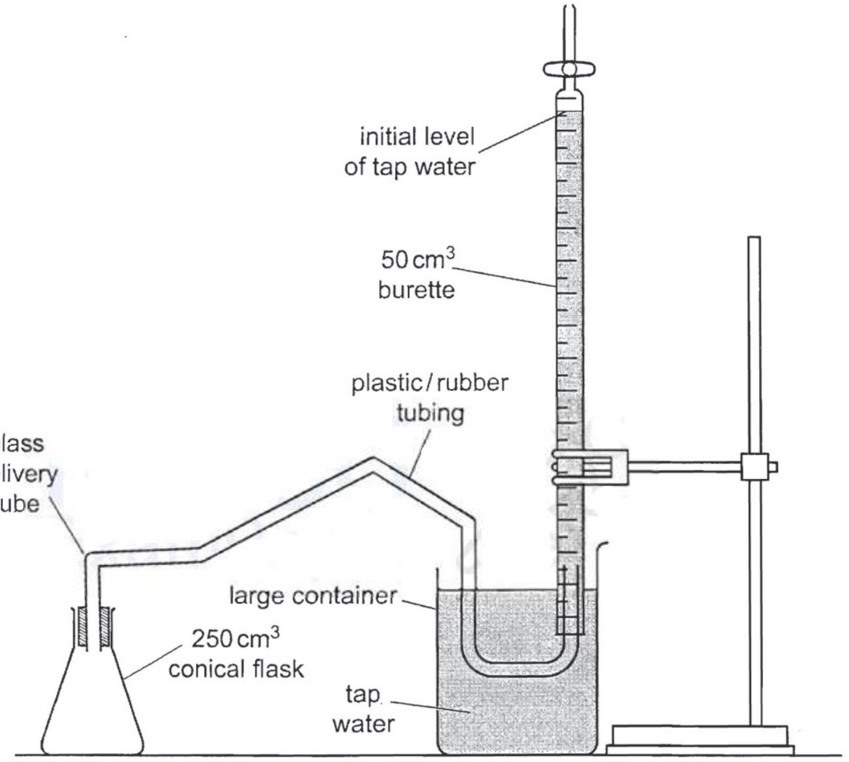
The percentage purity of sodium carbonate in the sample can be determined by measuring the volume of carbon dioxide formed when sodium carbonate is reacted with an excess of sulfuric acid.

$$Na_2CO_3(s) + H_2SO_4(aq) \rightarrow Na_2SO_4(aq) + CO_2(g) + H_2O(l)$$

You are to plan an experiment that will enable you to:

- react a pre-weighed impure sample of sodium carbonate with a pre-determined volume of the **FA 3** solution that you have used earlier for Question 1 and 2,
- collect and measure the volume of the carbon dioxide gas evolved.

(a) Draw a diagram of the apparatus that you would use to carry out this experiment.



[2]

(b) By considering the capacity of the apparatus that you have drawn in **(a)** to measure the volume of the carbon dioxide gas, calculate the maximum mass of the impure sample of sodium carbonate that you would use in your experiment.

[A_r: Na, 23.0; C, 12.0; O, 16.0 and 1 mole of gas occupies a volume of 24.0 dm^3 under the conditions present in the laboratory]

Taking the maximum volume of $CO_2(g)$ collected to be 50 cm^3,

$$n_{CO_2} = \frac{50}{24000} = 2.0833 \times 10^{-3} \text{ mol}$$

$$\Rightarrow n_{Na_2CO_3} = 2.0833 \times 10^{-3} \text{ mol}$$

$$m_{Na_2CO_3} = 2.0833 \times 10^{-3} \times \{2(23.0) + 12.0 + 3(16.0)\} = 2.0833 \times 10^{-3} \times \{106.0\} = 0.22083 = 0.221 \text{ g}$$

maximum mass of impure sample of sodium carbonate used = 0.221 g [2]

(c) A student suggested that 40.0 cm^3 of **FA 3** solution is sufficient for the experiment.

State whether you agree with the student, and explain your answer.

Yes, I agree with the student. The number of moles of H_2SO_4 present in 40.0 cm^3 of **FA 3** {0.0300 mol, calculated in **2(a)(iii)** and **2(b)(iii)**} is more than enough to react with the amount of Na_2CO_3 calculated in **3(b)**.

[1]

(d) Describe briefly how you would ensure that all the carbon dioxide gas given off in the reaction between the impure sample of sodium carbonate and **FA 3** solution was collected and that none escaped from the apparatus.

Place the weighed sample of sodium carbonate in the conical flask, and stopper the flask. Introduce the measured volume of **FA 3** solution using a thistle funnel (the volume of **FA 3** introduced need to be subtracted from the volume of gas collected).

or

Place the weighing bottle that contains the weighed sample of sodium carbonate (carefully) into the conical flask that contains the measured volume of **FA 3** solution. Stopper the conical flask. Tilt the conical flask such that the weighing bottle is tipped over in order to start the reaction.

[1]

(e) Other than this method that involves the collection of carbon dioxide gas, the percentage purity of sodium carbonate in the sample can also be determined using a titration.

In a typical experiment, a pre-weighed mass of the impure sample of sodium carbonate is dissolved in water and made up to 250 cm^3 in a volumetric flask, and 25.0 cm^3 of this solution is titrated against a standard solution of hydrochloric acid using methyl orange as indicator.

State which of the two methods you would expect to give the more accurate results. Explain your choice.

Titration method.

Source of error for the collection of CO_2 gas method:

- The volume of the CO_2 gas may not be measured under standard conditions (the volume collected will be lower than the actual volume produced, as the gas syringe may not be perfectly frictionless; or the volume measured will be higher than the actual volume as the water level inside the burette is higher than the water level in the beaker for the downward displacement of water).

Other sources of errors if downward displacement of water method was used:

- CO_2 gas is slightly soluble in water (the volume collected will be lower than the actual volume produced, as some of the CO_2 produced may be dissolved in the water used for downward displacement of water).
- The rubber tubing contains a certain volume of water at the start of the experiment that must first be displaced before the CO_2 gas can be collected (the volume collected will be lower than the actual volume produced).

[2]

[Total: 8]

4 Inorganic Qualitative Analysis

You are provided with **FA 8**, which is a mixture of two solids, **FA 9**, which is soluble in water and **FA 10**, which is insoluble in water. Each contains **one cation** and **one anion** from the lists on page 16 and 17.

In this question you will perform a series of test-tube reactions, make observations and deduce the identities of the cations and anions present in **FA 9** and **FA 10**.

If the evolution of a gas is observed at any stage, the gas should be tested and identified.

You are advised that the reagent should be added gradually in all tests, with shaking after each addition.

If it appears that no reaction has taken place, this should be clearly recorded.

(a) Tests on FA 8

Perform the test-tube experiments described below and record your observations in the spaces provided in the table.

	Test	**Observations**
(i)	Place all of the solid, **FA 8**, into a 100 cm^3 beaker. Add 25 cm^3 of distilled water and warm to dissolve the **FA 9**. Filter the mixture and use the filtrate for tests **(a)(ii)** to **(a)(iv)**. Wash the residue, **FA 10**, and use it for tests **(a)(v)** to **(a)(vii)**.	A green residue **[✓1]** and a colourless filtrate was obtained **[✓2]**.

Tests on Filtrate, FA 9

	Test	**Observations**
(ii)	Place about 1 cm depth of **FA 9** into a test-tube. Add a few drops of dilute sulfuric acid.	A white ppt is formed **[✓3]**.
(iii)	Place about 1 cm depth of **FA 9** into a test-tube. Add a few drops of aqueous barium chloride,	No ppt is formed **[✓4]**.
	followed by a few drops of dilute hydrochloric acid.	No ppt is formed / no gas is produced **[✓5]**.
(iv)	Place about 1 cm depth of **FA 9** into a test-tube. Add a few drops of aqueous silver nitrate.	A white ppt is formed **[✓6]**.
	followed by a few drops of aqueous ammonia.	The ppt dissolves to give a colourless solution **[✓7]**.

Tests on Residue, FA 10

	Test	**Observations**
(v)	Using a spatula, transfer as much of the residue on the filter paper as you can into a test-tube. Add dilute sulfuric acid drop-wise into the test-tube to dissolve the residue. Filter if necessary. Use the resultant solution for test **(a)(vi)** and **(a)(vii)**.	Effervescence produced **[✓8]**, the gas gives white ppt with limewater **[✓9]**. A pale green / blue solution is produced **[✓10]**.
(vi)	Place about 1 cm depth of the **filtrate** from **(a)(v)** in a test-tube. Add aqueous sodium hydroxide drop-wise with shaking, until no further change is seen.	A (pale) blue ppt is formed that is insoluble in excess NaOH(aq) **[✓11]**.
(vii)	Place about 1 cm depth of the **filtrate** from **(a)(v)** into a test-tube. Add aqueous ammonia, drop-wise with shaking, until no further change is seen.	A blue ppt is formed **[✓12]** that is soluble in excess NH_3(aq) to form a dark blue solution **[✓13]**.

[5]

(b) Based on your observations to **(a)(ii)**, suggest a possible identity of the cation in **FA 9**.

cation in **FA 9**: Ba^{2+} [1]

(c) From your remaining observations, state the identities of the one anion in both **FA 9** and **FA 10**, and the one cation in **FA 10**.

In each case, give evidence to support your conclusion.

	identity		evidence
FA 9	anion:	Cl^-	A white ppt is formed with $AgNO_3$(aq), that is soluble in NH_3(aq) in **(a)(iv)**.
FA 10	cation:	Cu^{2+}	A (pale) blue ppt is formed with NaOH(aq) that is insoluble in excess in **(a)(vi)**. **Or** A blue ppt is formed with NH_3(aq) that is soluble in excess to form a dark blue solution in **(a)(vii)**.
	anion:	CO_3^{2-}	CO_2(g) produced with H_2SO_4(aq) in **(a)(v)**.

[3]

[Total: 9]

5 Planning

In this question, you will devise a plan, using test-tube reactions, to distinguish between four organic compounds, so that each is identified.

Consider 4 unlabelled bottles and each bottle contains one of the following colourless liquids:

ethanal propanone propan-2-ol ethanoic acid

Plan an investigation, using test tube reactions, which would allow you to identify each of these organic compounds.

Each compound should be identified by at least one positive test. 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.

	Test	**Expected Observations**
1	Place about 1 cm depth of each of the four samples into four separate test tubes. Add a few drops aqueous sodium carbonate.	If effervescence is produced, and the gas gives a white ppt with limewater, the sample is ethanoic acid. If no effervescence is produced, the sample is ethanal, propanone or propan-2-ol.
2	Place about 1 cm depth of a fresh sample for each of the three remaining samples into three separate test tubes. Add a few drops of Tollen's reagent, and warm in a hot water bath.	If a grey ppt or a silver mirror is formed, the sample is ethanal. If no grey ppt or silver mirror is obtained, the sample is propanone or propan-2-ol.
3	Place about 1 cm depth of a fresh sample for each of the two remaining samples into two separate test-tubes. Add a few drops of 2,4-dinitrophenylhydrazine.	If a yellow / orange ppt is formed, the sample is propanone If no ppt is formed, the same is probably propan-2-ol.
4	Place about 1 cm depth of a fresh sample for the last sample in a test-tube. Add 10 drops of dilute sulfuric acid, followed by 2 drops of potassium manganate(VII) and warm in the water bath.	If the purple $KMnO_4$ is decolourised, the sample is propan-2-ol.

[Total: 6]

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

END OF PAPER 4

Preparation list

Chemicals:

FA 1 is 0.0230 mol dm^{-3} of potassium iodate(V), KIO_3 (about 150 cm^3 per student)
FA 2 is 0.500 mol dm^{-3} potassium iodide, KI (about 70 cm^3 per student)
FA 3 is 0.750 mol dm^{-3} dilute sulfuric acid (about 230 cm^3 per student)
FA 4 is 0.100 mol dm^{-3} sodium thiosulfate, $Na_2S_2O_3$ (about 120 cm^3 per student)
FA 5 is 0.0869 mol dm^{-3} sodium thiosulfate, $Na_2S_2O_3$ (about 180 cm^3 per student)

starch solution containing 20 g dm^{-3} of soluble starch (about 10 cm^3 per student)

FA 6 is solid anhydrous sodium carbonate, Na_2CO_3 (preweighed 4.50 − 5.00 g)
FA 7 is solid sodium hydrogen carbonate, $NaHCO_3$ (preweighed 3.50 − 4.00 g)

FA 8 is a 10 : 1 solid mixture of $CuCO_3 \cdot Cu(OH)_2 \cdot H_2O$ and $BaCl_2 \cdot 2H_2O$
(preweighed 2.00 − 2.50 g, mixture should be thoroughly mixed)

Apparatus:

1 × 50 cm^3 burette labelled **FA 4**
1 × 50 cm^3 burette labelled **FA 5**
1 × 25.0 cm^3 pipette with pipette filler
2 × 250 cm^3 conical flask
1 × 10 cm^3 measuring cylinder
1 × 25 cm^3 measuring cylinder
1 × 50 cm^3 measuring cylinder
1 × 100 cm^3 beaker
1 × 250 cm^3 beaker
1 × 250 cm^3 beaker labelled “waste”

2 × glass filter funnel
1 × Styrofoam cup with lid
1 × thermometer (0.2 °C graduation)
1 × distilled water bottle (with access to additional supplies of deionised water)
1 × retort stand with double clamps
1 × paper towel

6 × test-tubes
2 × small test-tubes
1 × boiling tube
6 × dropper / teat pipette
1 × glass rod and spatula
1 × set of blue / red litmus paper + filter paper strips and box of filter paper
1 × tripod stand, wire gauze, and heat-proof mat
1 × bunsen burner and lighter

weighing scale (for weighing / reweighing of **FA 6** & **FA 7**, about 1 per 8-12 candidates)

Bench Reagents:

aqueous sodium hydroxide (approximately 2.0 mol dm^{-3})
aqueous ammonia (approximately 2.0 mol dm^{-3})
hydrochloric acid (approximately 2.0 mol dm^{-3})
nitric acid (approximately 2.0 mol dm^{-3})
sulfuric acid (approximately 1.0 mol dm^{-3})
aqueous silver nitrate (approximately 0.05 mol dm^{-3})
aqueous barium chloride (approximately 0.2 mol dm^{-3})
limewater (saturated solution of calcium hydroxide)