



ANDERSON SERANGOON JUNIOR COLLEGE

2021 JC 2 PRELIMINARY EXAMINATION

NAME: _____ () CLASS: 21 / _____

CHEMISTRY

Paper 2 Structured Questions

9729/02

14 September 2021

2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name, class and register 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, glue or correction fluid.

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

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

A Data Booklet is provided.

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

For Examiner's Use		
Paper 2	1	/21
	2	/10
	3	/13
	4	/10
	5	/11
	6	/10
	Total	/75

This document consists of **23** printed pages and **1** blank page.

- (iv) Explain the difference in size between the radius of the potassium ion and the radius of a potassium atom.

.....

[1]

- (c) Anodisation of aluminium is a process which coats an oxide layer on aluminium objects.

- (i) Draw a labelled diagram of the electrolysis cell used to anodise a small piece of aluminium object. Include details of the cathode, anode and electrolyte.

[1]

- (ii) Complete Table 1.1 to show the type of reaction occurring, with the relevant half-equations, during the anodisation of the aluminium object.

Table 1.1

	type of reaction occurring	half-equation(s)
anode		
cathode		

[2]

- (d) The molecules of alcohol **P**, $C_7H_{16}O$, are optically active and does not react with hot, acidified $Na_2Cr_2O_7(aq)$.

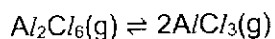
On treatment with Al_2O_3 , **P** produces a mixture of four different isomeric alkenes with the formula C_7H_{14} , **only two** of which are cis-trans isomers of each other.

Suggest the structural formula of compound **P** and the four alkenes.

[4]

Question 1 continues on the next page.

- (e) The following equilibrium exists in a sample of aluminium chloride vapour.



- (i) Draw a dot-and-cross diagram of the Al_2Cl_6 molecule, including its co-ordinate bonds.

[1]

When 1.50 g of aluminium chloride was introduced into an evacuated flask of 250 cm³ capacity and heated to 500 K, the pressure inside the flask rose to 1.16×10^5 Pa.

- (ii) Assuming the gaseous mixture behaves ideally, calculate the average M_r of the mixture. Give your answer to **four** significant figures.

[2]

- (iii) Using the following relationships, calculate the mole fraction of Al_2Cl_6 , x and the mole fraction of AlCl_3 , y , in the mixture.

$$\begin{aligned} x + y &= 1 \\ \text{average } M_r &= 267x + 133.5y \end{aligned}$$

[1]

(iv) Hence calculate the partial pressures of Al_2Cl_6 and $AlCl_3$ in this mixture.

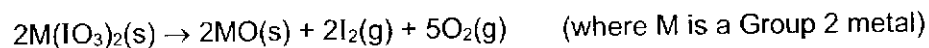
[1]

(v) Write an expression for K_p for the reaction, and calculate its value. Include units in your answer.

[2]

[Total: 21]

- 2 (a) When Group 2 iodates(V), $M(\text{IO}_3)_2$, is heated, it behaves in a similar way to the Group 2 carbonates. Upon heating, it decomposes as shown.



- (i) Using your knowledge of Group 2 carbonates, suggest and explain the trend in thermal stabilities of the Group 2 iodate(V).

.....

[2]

X, Y and Z are Group 2 metals (Mg to Ba, not necessarily in that order).

$X(\text{IO}_3)_2$, $Y(\text{IO}_3)_2$ and $Z(\text{IO}_3)_2$ are Group 2 iodates(V). The three graphs in Fig. 2.1 show the change in mass when 2.00 g each of $X(\text{IO}_3)_2$, $Y(\text{IO}_3)_2$ and $Z(\text{IO}_3)_2$ were heated separately at a temperature $T^\circ\text{C}$.

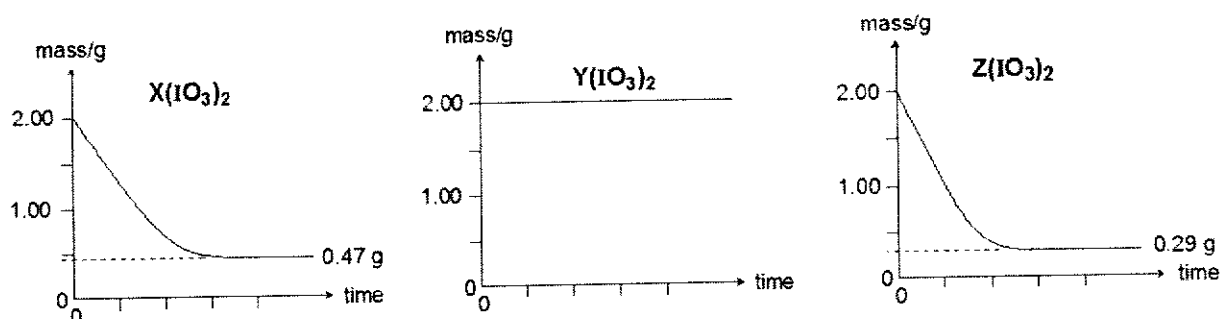


Fig. 2.1

- (ii) With reference to the information from Fig. 2.1, show, by calculations, that none of the above iodate(V) samples contains $\text{Mg}(\text{IO}_3)_2$.

[2]

- (iii) Hence, suggest the identities of the three iodates(V).
[No calculation is required.]

iodates(V)	X(IO ₃) ₂	Y(IO ₃) ₂	Z(IO ₃) ₂
identity			

[1]

- (b) When a salt such as a Group 2 sulfate dissolves in water, the lattice energy must be overcome.

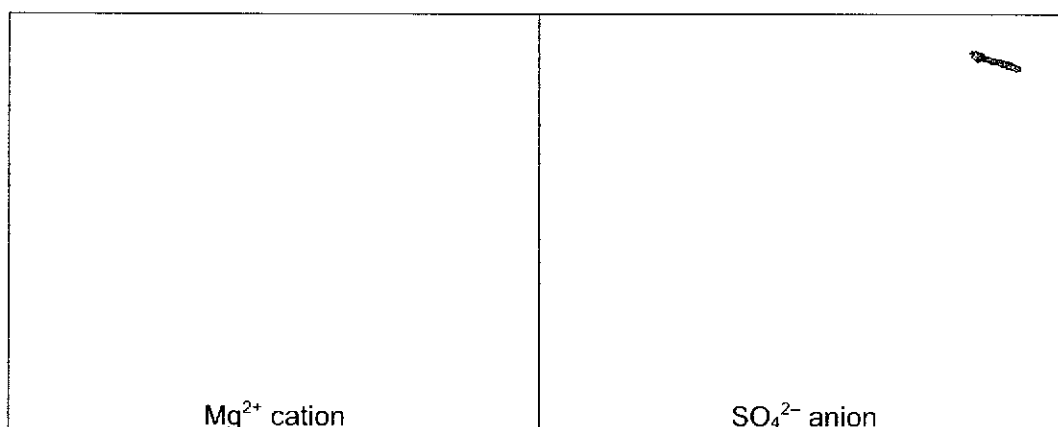
- (i) How will the **magnitude** of the lattice energy of Group 2 sulfates change from MgSO₄ to BaSO₄?

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

- (ii) Suggest a reason for this trend.

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

- (iii) Draw a simple diagram to show how a water molecule can be attached to a magnesium cation, and to a sulfate anion. Show the displayed structure of the sulfate anion in your answer and label each diagram to show the type of interaction involved.



[3]

[Total: 10]

Question 3 starts on the next page.

~~www.testpapersfree.com~~

(b) Fig. 3.1 illustrates the synthesis of trisoxazoline.

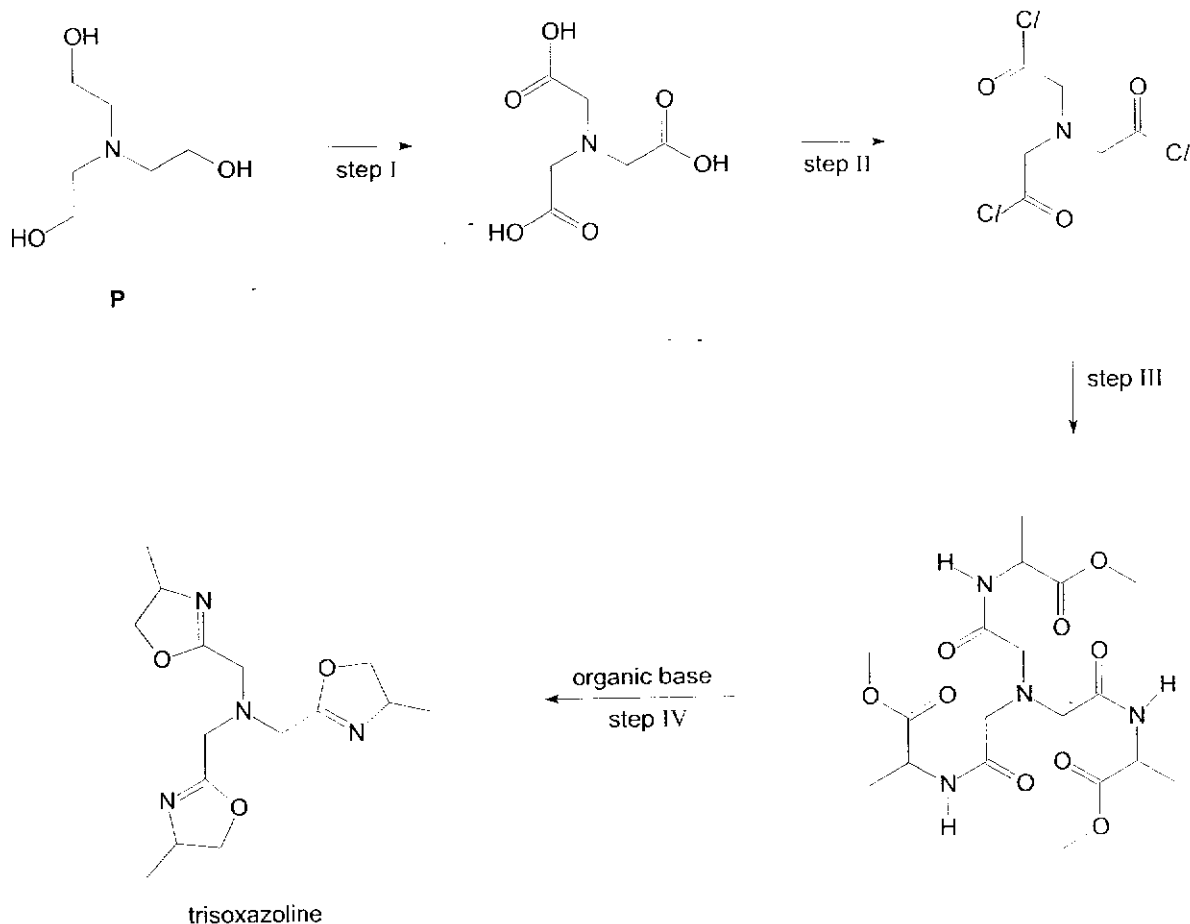


Fig. 3.1

(i) State the *types of reaction* that occur during each of the steps I and II.

step I:

step II: [2]

(ii) Suggest, with reason, the pH of the solution when the resultant product from step II is dissolved in water.

..... [1]

(iii) Suggest the reagents and conditions required for steps II and III.

step II:

step III: [2]

- (iv) Compound **P** in Fig. 3.1 can be synthesised from ethene via a two-step reaction scheme shown below.



Suggest the reagents required for each step.

step a:

step b:

[2]

- (c) Other than copper(II) ions, it was found that copper(I) ions are also able to form complexes with trisoxazoline.

Complete the full electronic configuration of copper(I) ions.

copper(I) ion: $1s^2$

[1]

- (d) Copper is in increasing demand for use in electric vehicles, consumer electronics and other energy efficient targets. Most current copper extraction processes burn sulfide minerals in air which produces sulfur dioxide which is harmful to the environment.

Describe and explain with the aid of suitable equations, the role of NO_2 in the oxidation of atmospheric sulfur dioxide.

.....

[2]

[Total: 13]

- 4 (a) A 2.00 g sample of an organic substance **Z** containing only C, H and O was burned completely. The only combustion products were 2.90 g of carbon dioxide and 1.20 g of water.

(i) Define the term *relative molecular mass*.

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

(ii) Given that the relative molecular mass of the organic substance **Z** is 90.0, show that the molecular formula is $C_3H_6O_3$.

[2]

(iii) Draw two constitutional isomers of **Z** which can react with sodium carbonate.

[2]

- (b) Complete the reaction scheme in Fig. 4.1 to show how compound **E** could be synthesised from ethylbenzene in **three** steps using suitable reagents.

Show the structures of the intermediate compounds and state the reagents and conditions for each step.

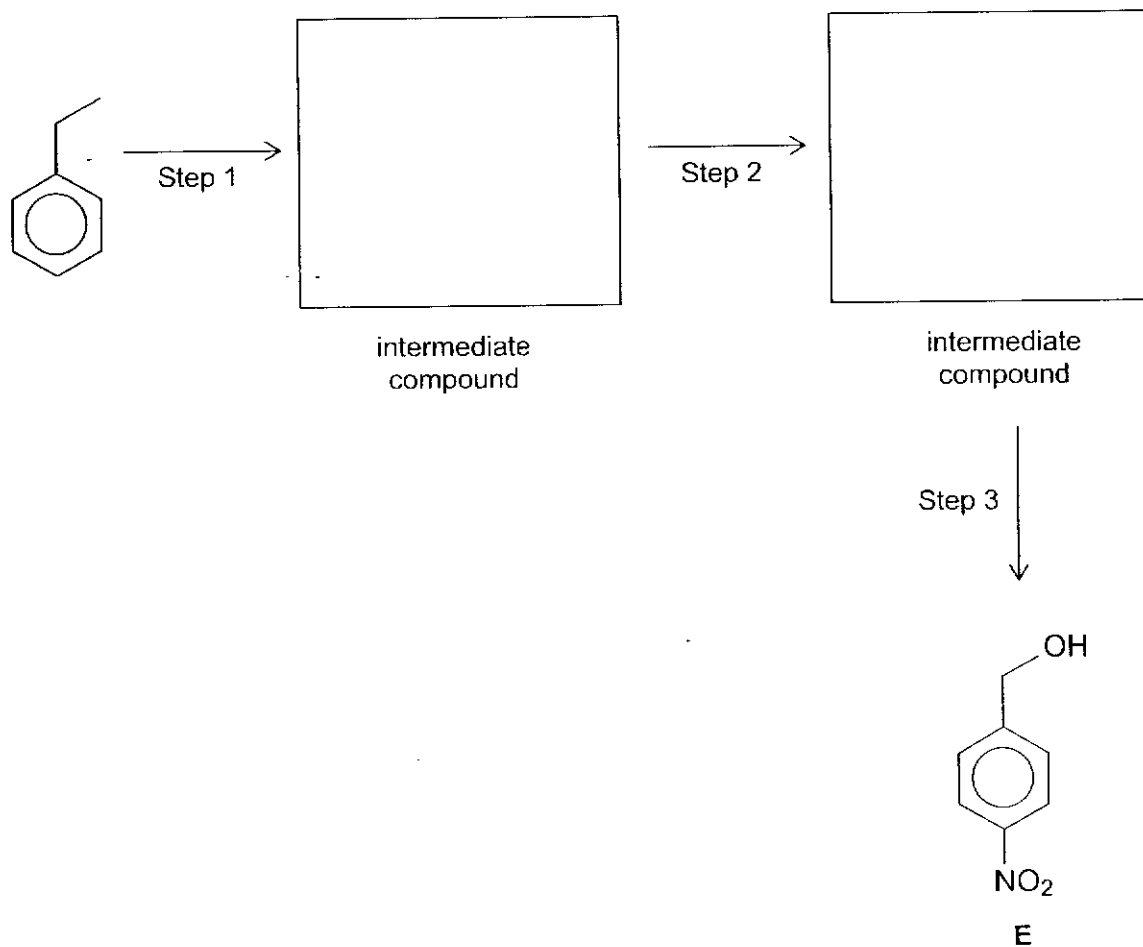


Fig. 4.1

Step 1:

Step 2:

Step 3:

[5]

[Total: 10]

Question 5 starts on the next page.

5 This question is about the chemistry of compounds containing halogen.

- (a) Bromoalkane can undergo two different mechanisms for nucleophilic substitution – S_N1 and S_N2 .

Experiments were conducted in two different set-ups to measure the relative rates of nucleophilic substitution for three bromoalkanes. Set-up 1 and 2 use different nucleophiles.

Table 5.1 summarises the relative rates of the three bromoalkanes in the experiments.

Table 5.1

bromoalkane	$\text{CH}_3\text{CH}_2\text{Br}$	$(\text{CH}_3)_2\text{CHBr}$	$(\text{CH}_3)_3\text{CBr}$
relative rate in set-up 1	4×10^{-2}	1	4×10^6
relative rate in set-up 2	30	1	5×10^{-5}

- (i) Predict the predominant mechanism for set-up 2. Explain your answer.

.....

.....

.....

.....

.....

.....[2]

- (ii) Explain the relative rate of $(\text{CH}_3)_3\text{CBr}$ in set-up 1.

.....

.....

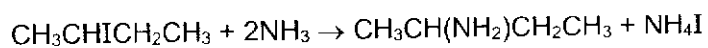
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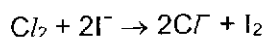
.....[1]

- (b) 2-iodobutane can be readily converted into 2-aminobutane using ethanolic ammonia.



In order to determine the rate equation for this reaction, an investigation was carried out at a constant temperature. 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 aliquot and excess chlorine gas was subsequently removed. Iodine is liberated by the following reaction.



The iodine was then titrated with $0.0250 \text{ mol dm}^{-3}$ sodium thiosulfate in the presence of an indicator.

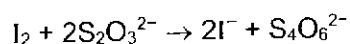


Fig. 5.1 shows the volume of sodium thiosulfate used against time for this experiment.

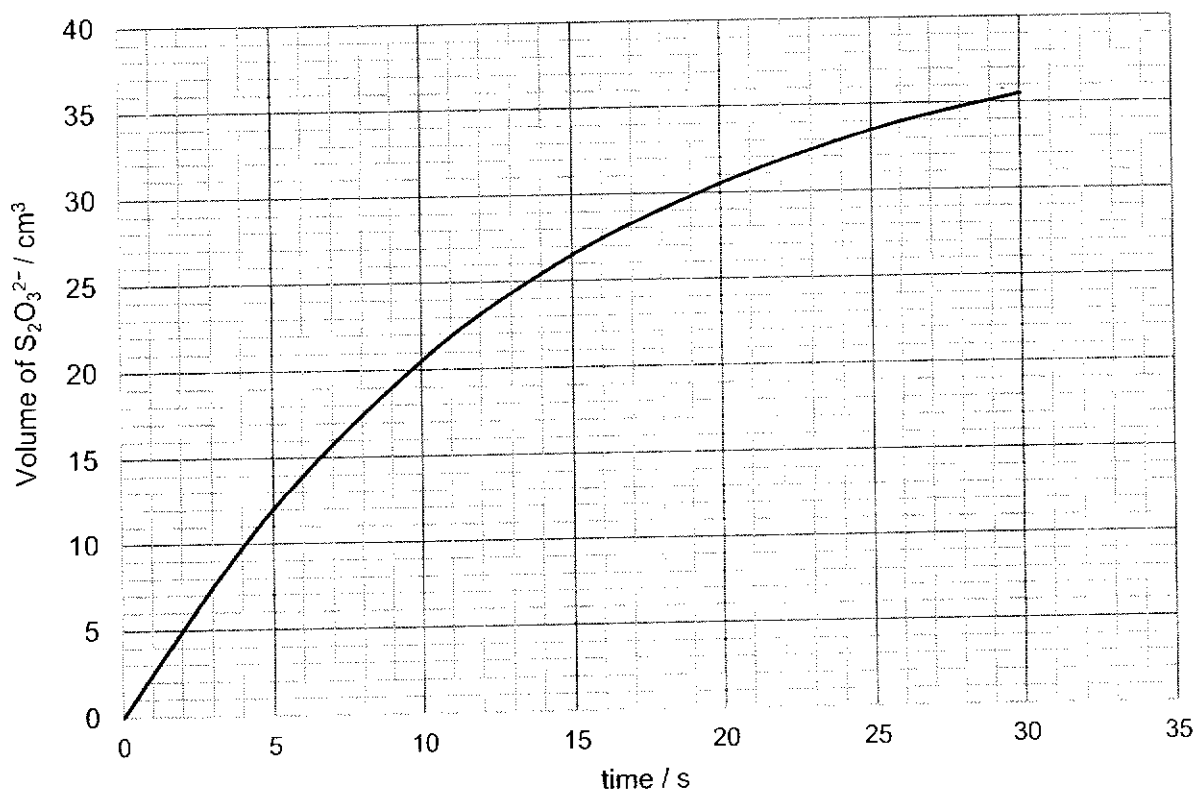


Fig. 5.1

- (i) Prove that the volume of $S_2O_3^{2-}$ required when the reaction between 2-iodobutane and ethanolic ammonia goes to completion in this investigation is 40 cm^3 .

[1]

- (ii) Hence, use Fig. 5.1 to deduce the order of reaction with respect to 2-iodobutane.

order =[2]

- (iii) The concentration of ethanolic ammonia is halved and a new series of experiments was carried out at the same temperature.

It is known that that the order of reaction with respect to ethanolic ammonia is one.

Suggest how the gradient at each point will change when a similar graph like the one in Fig. 5.1 was plotted.

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

- (iv) Hence, construct the rate equation for the reaction between 2-iodobutane and ethanolic ammonia.

.....[1]

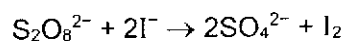
- (v) Calculate the value of the rate constant for the reaction between equal volumes of 0.20 mol dm^{-3} 2-iodobutane and 4.00 mol dm^{-3} ethanolic ammonia and state its units.

value of rate constant =

units =

[2]

- (c) Iodide ions, I^- , can react with peroxodisulfate, $S_2O_8^{2-}$.



A student wanted to investigate the effect of changes in volume used on the rate of this reaction.

Table 5.2 shows the results obtained when a series of experiments was carried out using different volumes of the two reagents, each solution being made up to the same total volume with water, where necessary.

Table 5.2

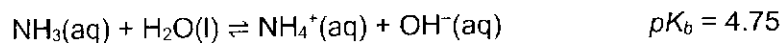
experiment	volume of KI / cm^3	volume of $Na_2S_2O_8$ / cm^3	volume of water / cm^3	initial rate / $mol\ dm^{-3}\ s^{-1}$
1	10	20	10	0.0200
2	5	20	15	0.0100
3	30	10	0	0.0303

Given that the order of reaction with respect to I^- is 1, determine the order of reaction with respect to $S_2O_8^{2-}$.

order =[1]

[Total: 11]

- 6 (a) Ammonia can act as a weak base.



$(\text{NH}_4)_2\text{SO}_4$ is a weak acid. Calculate the pH of $0.10 \text{ mol dm}^{-3} (\text{NH}_4)_2\text{SO}_4(\text{aq})$.

[2]

- (b) A buffer solution with a pH 8.90 is made by adding 150 cm^3 of solution **B** containing ammonium chloride to 100 cm^3 of $0.0200 \text{ mol dm}^{-3}$ aqueous NH_3 .

Calculate the concentration of ammonium chloride in solution **B**.

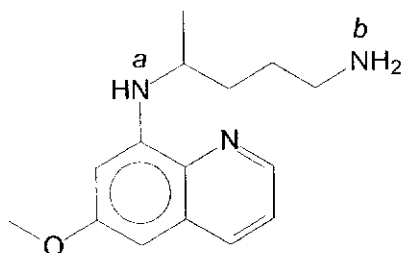
[3]

- (c) Write equations to explain how the $\text{NH}_3(\text{aq})/\text{NH}_4^+(\text{aq})$ buffer system helps to maintain the pH.

.....

 [2]

- (d) Malaria is a serious and sometimes fatal mosquito-borne disease. *Primaquine* is an antimalaria drug used to prevent relapse of malaria infections.



primaquine

Two of the pK_b values associated with *primaquine* are 4.1 and 9.8.

- (i) Using this information, write the pK_b values for the nitrogen-containing groups *a* and *b* in *primaquine*.

nitrogen-containing	group <i>a</i>	group <i>b</i>
pK_b		

[1]

- (ii) Suggest an explanation for your assignment of the pK_b values in (d)(i).

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.....[2]

[Total: 10]

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Anderson Serangoon Junior College
2021 JC2 Preliminary Examination
H2 Chemistry (9729) Paper 2 Suggested Solutions

- 1 (a) Describe and explain the trend in the electronegativity of elements across Period 3 from sodium to chlorine. [2]

Electronegativity increases across Period 3.

- Nuclear charge increases across Period 3.
- Shielding effect between nucleus and valence electrons are similar since successive elements in the period have an additional electron in the same valence shell/same no. of inner shells.
- There are stronger (electrostatic) forces of attraction between the nucleus and the electron pair in a covalent bond.

- (b) Some ionic radii are listed in the *Data Booklet*.

- (i) Explain the trend in ionic radius down Group 2. [2]

Ionic radius increases down the group.

- Nuclear charge increase but number of (inner) electronic shells increases.
- Outer electrons experienced greater shielding effect and are further from the nucleus.
- there are weaker electrostatic forces of attraction between the nucleus and the outer electrons.

- (ii) Explain the differences between the ionic radii of P^{3-} , Cl^- and Ca^{2+} . [1]

Ionic radius decreases from P^{3-} to Cl^- to Ca^{2+} .

- P^{3-} , Cl^- and Ca^{2+} are isoelectronic/same number of electrons and
- number of protons / nuclear charge increases from P^{3-} to Ca^{2+} while the shielding effect remains the same,
- resulting in an increasing attraction between the nucleus and outer electrons.

(accept there is an increasing attraction between the increasing number of protons and the same number of electrons.)

- (iii) Hence, suggest a value for the ionic radius of a potassium ion, K^+ . [1]

0.138 nm (any value between 0.099 and 0.181)

K^+ is isoelectronic with the ions in (b)(ii) and its nuclear charge is between that of Cl^- and Ca^{2+} . Hence, its ionic radius will be between 0.099 and 0.181 nm.

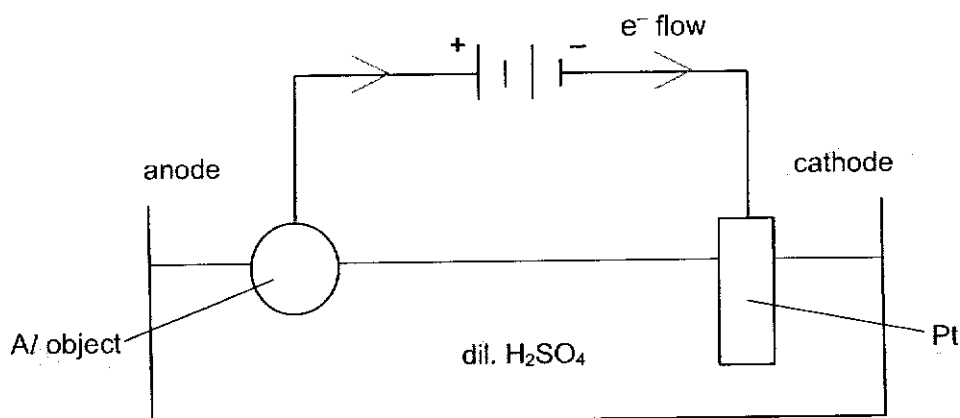
- (iv) Explain the difference in size between the radius of potassium ion and the radius of a potassium atom. [1]

Radius of K^+ ion is smaller than that of K atom

- nuclear charge remains the same.
- the cation has one less electronic shell than the atom.
- the outer electrons in the cation are less shielded and closer to the nucleus.
- there are stronger electrostatic forces of attraction between the nucleus and the outer electrons in cation.

- (c) Anodisation of aluminium is a process which coats an oxide layer on aluminium objects.

- (i) Draw a labelled diagram of the electrolysis cell used to anodise a small piece of aluminium object. Include details of the cathode, anode and electrolyte. [1]



- (ii) Complete Table 1.1 to show the type of reaction occurring, with the relevant half-equations, during the anodisation of the aluminium object. [2]

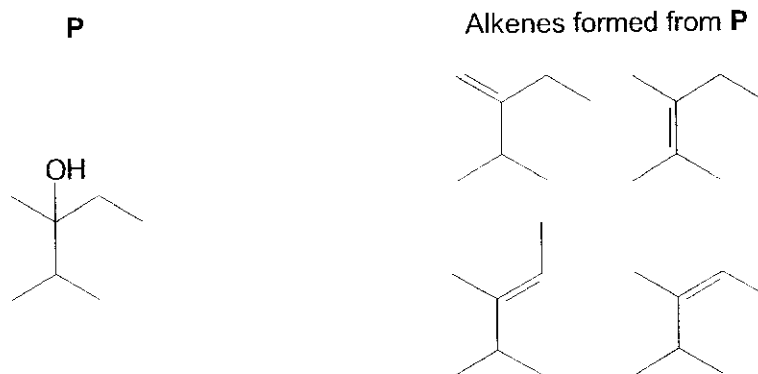
Table 1.1

	type of reaction occurring	half-equation(s)
anode	oxidation	$2Al + 3H_2O \rightarrow Al_2O_3(s) + 6H^+ + 6e^-$
cathode	reduction	$2H^+ + 2e^- \rightarrow H_2$

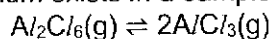
- (d) The molecules of alcohol **P**, $C_7H_{16}O$, are optically active and does not react with hot, acidified $Na_2Cr_2O_7(aq)$.

On treatment with Al_2O_3 , **P** 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.

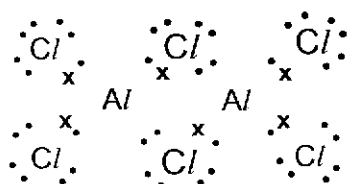
Suggest the structural formula of compound **P** and the four alkenes. [4]



(e) The following equilibrium exists in a sample of aluminium chloride vapour.



(i) Draw a dot-and-cross diagram of the Al_2Cl_6 molecule, including its co-ordinate bonds. [1]



When 1.50 g of aluminium chloride was introduced into an evacuated flask of 250 cm³ capacity and heated to 500 K, the pressure inside the flask rose to 1.16×10^5 Pa.

(ii) Assuming the gaseous mixture behaves ideally, calculate the average M_r of the mixture. Give your answer to **four** significant figures. [2]

$$M = \frac{mRT}{pV}$$

$$M = \frac{(1.50)(8.31)(500)}{(1.16 \times 10^5)(250 \times 10^{-6})}$$

$$= 214.9 \text{ g mol}^{-1}$$

Average M_r of mixture = 214.9

(iii) Using the following relationships, calculate the mole fraction of Al_2Cl_6 , x and the mole fraction of $AlCl_3$, y , in the mixture. [1]

$$x + y = 1$$

$$\text{average } M_r = 267x + 133.5y$$

Given the mole fraction of Al_2Cl_6 be x
and mole fraction of $AlCl_3$ be y .

$$[2(27.0) + 6(35.5)]x + [27.0 + 3(35.5)]y = 214.9 \text{ and } x + y = 1$$

$$267x + 133.5(1 - x) = 214.9$$

$$133.5x = 214.9 - 133.5$$

$$x = \underline{0.610}$$

$$y = \underline{0.390}$$

- (iv) Hence calculate the partial pressures of Al_2Cl_6 and $AlCl_3$ in this mixture. [1]

$$\text{partial pressure (p.p.) of } Al_2Cl_6 = 0.610 \times 1.16 \times 10^5 \\ = \underline{70729 \text{ Pa}}$$

$$\text{p.p. of } AlCl_3 = 0.390 \times 1.16 \times 10^5 \text{ (or } 1.16 \times 10^5 - 70729) \\ = \underline{45240 \text{ Pa}}$$

- (v) Write an expression for K_p for the reaction, and calculate its value. Include units in your answer. [2]

$$K_p = \frac{p_{AlCl_3}^2}{p_{Al_2Cl_6}} \\ = \frac{(45240)^2}{70729} \\ = \underline{28900 \text{ Pa}}$$

- 2 (a) When Group 2 iodates(V), $M(\text{IO}_3)_2$, is heated, it behaves in a similar way to the Group 2 carbonates. Upon heating, it decomposes as shown.



- (i) Using your knowledge of Group 2 carbonates, suggest and explain the trend in thermal stabilities of the Group 2 iodate(V). [2]

Down the group, ionic radius of M^{2+} increases.

As a result, the charge density of the M^{2+} decreases, the M^{2+} becomes less polarising.

The electron cloud of IO_3^- anion is less distorted.

The I–O covalent bond within the IO_3^- anions is less weakened down the group.

Thermal stability of Group 2 iodate increases down the group.

X, Y and Z are Group 2 metals (Mg to Ba, not necessarily in that order).

$X(\text{IO}_3)_2$, $Y(\text{IO}_3)_2$ and $Z(\text{IO}_3)_2$ are Group 2 iodates(V). The three graphs in Fig. 2.1 show the change in mass when 2.00 g each of $X(\text{IO}_3)_2$, $Y(\text{IO}_3)_2$ and $Z(\text{IO}_3)_2$ were heated separately at a temperature $T^\circ\text{C}$.

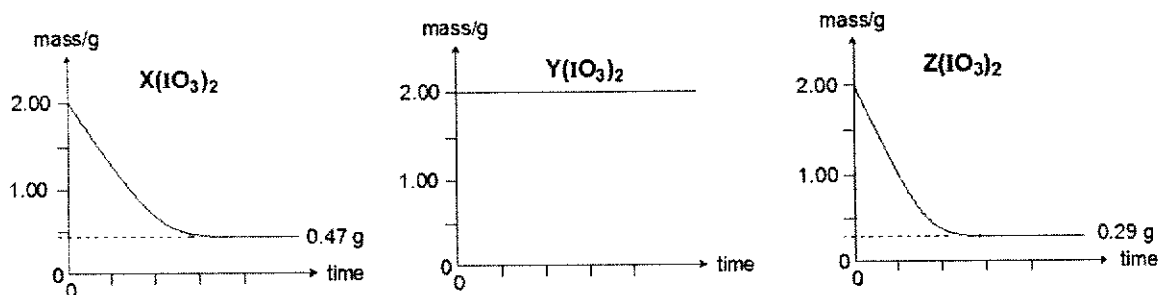


Fig 2.1

- (ii) With reference to the information from Fig. 2.1, show, by calculations, that none of the above iodate(V) samples contains $\text{Mg}(\text{IO}_3)_2$. [2]

Assume one iodate(V) given is $\text{Mg}(\text{IO}_3)_2$.

Molar mass of $\text{Mg}(\text{IO}_3)_2 = 374.1 \text{ g mol}^{-1}$

Amount of $\text{Mg}(\text{IO}_3)_2 = \frac{2.00}{374.3} = 5.346 \times 10^{-3} \text{ mol}$

Amount of MgO formed = $5.346 \times 10^{-3} \text{ mol}$

Molar mass of $\text{MgO} = 40.3 \text{ g mol}^{-1}$

Mass of MgO formed = $(5.346 \times 10^{-3})(40.3)$
= 0.215 g

Since the mass of the oxide calculated does not correspond to that of either XO, YO or ZO, $\text{Mg}(\text{IO}_3)_2$ is not among the given iodate(V).

- (iii) Hence, suggest the identities of the three iodates(V).

[No calculation is required.]

[1]

iodates(V)	$X(\text{IO}_3)_2$	$Y(\text{IO}_3)_2$	$Z(\text{IO}_3)_2$
identity	$\text{Sr}(\text{IO}_3)_2$	$\text{Ba}(\text{IO}_3)_2$	$\text{Ca}(\text{IO}_3)_2$

(b) When a salt such as a Group 2 sulfate dissolves in water, the lattice energy must be overcome.

(i) How will the **magnitude** of the lattice energy of Group 2 sulfates change from MgSO_4 to BaSO_4 ? [1]

Magnitude decreases from MgSO_4 to BaSO_4 .

(ii) Suggest a reason for this trend. [1]

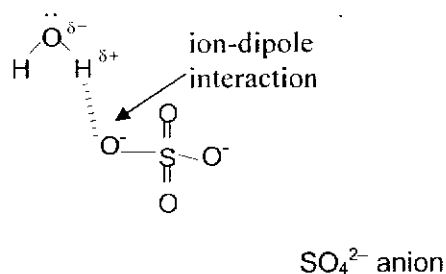
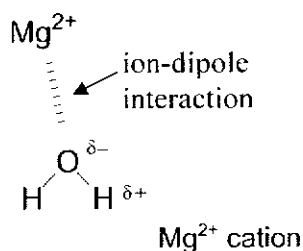
$$|\Delta H_{\text{latt}}| \propto \left| \frac{q^+ \times q^-}{r^+ + r^-} \right|$$

charges of cation and anion and anionic radius remain unchanged

Cationic radius increases from Mg^{2+} to Ba^{2+}

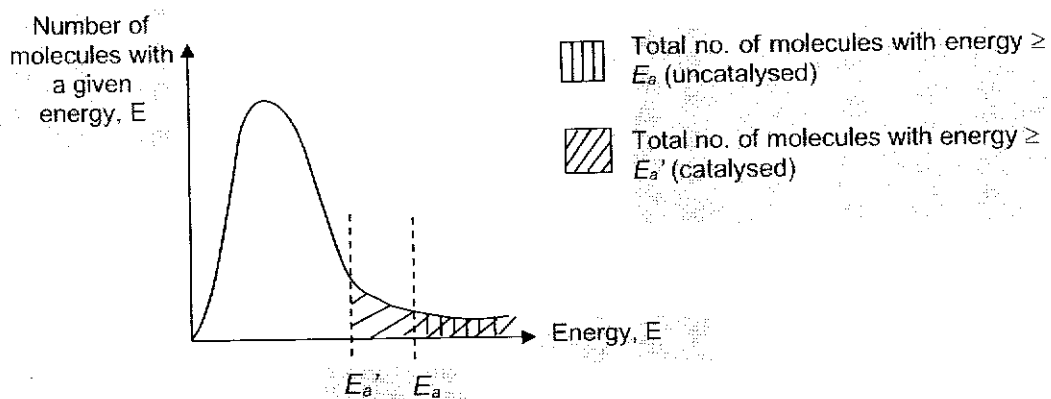
Interionic distance increases thus electrostatic forces of attraction between the metal cation and SO_4^{2-} becomes weaker

(iii) Draw a simple diagram to show how a water molecule can be attached to a magnesium cation, and to a sulfate anion, Label each diagram to show the type of interaction involved and show the displayed structure of the sulfate anion. [3]



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) With an aid of the Boltzmann distribution, explain how a catalyst increases the rate of reaction. [3]



As shown on the diagram, in the **presence of a catalyst**, at a certain temperature T ,

- Catalyst provides an alternative pathway of a lower activation energy ($E_a' < E_a$).
- More molecules have energies greater than or equal to the lowered activation energy E_a' .
- This results in an increase in the frequency of effective collisions.
- The rate constant, k , increases and hence rate of reaction increases

(b) Fig 3.1 illustrates the synthesis of trisoxazoline.

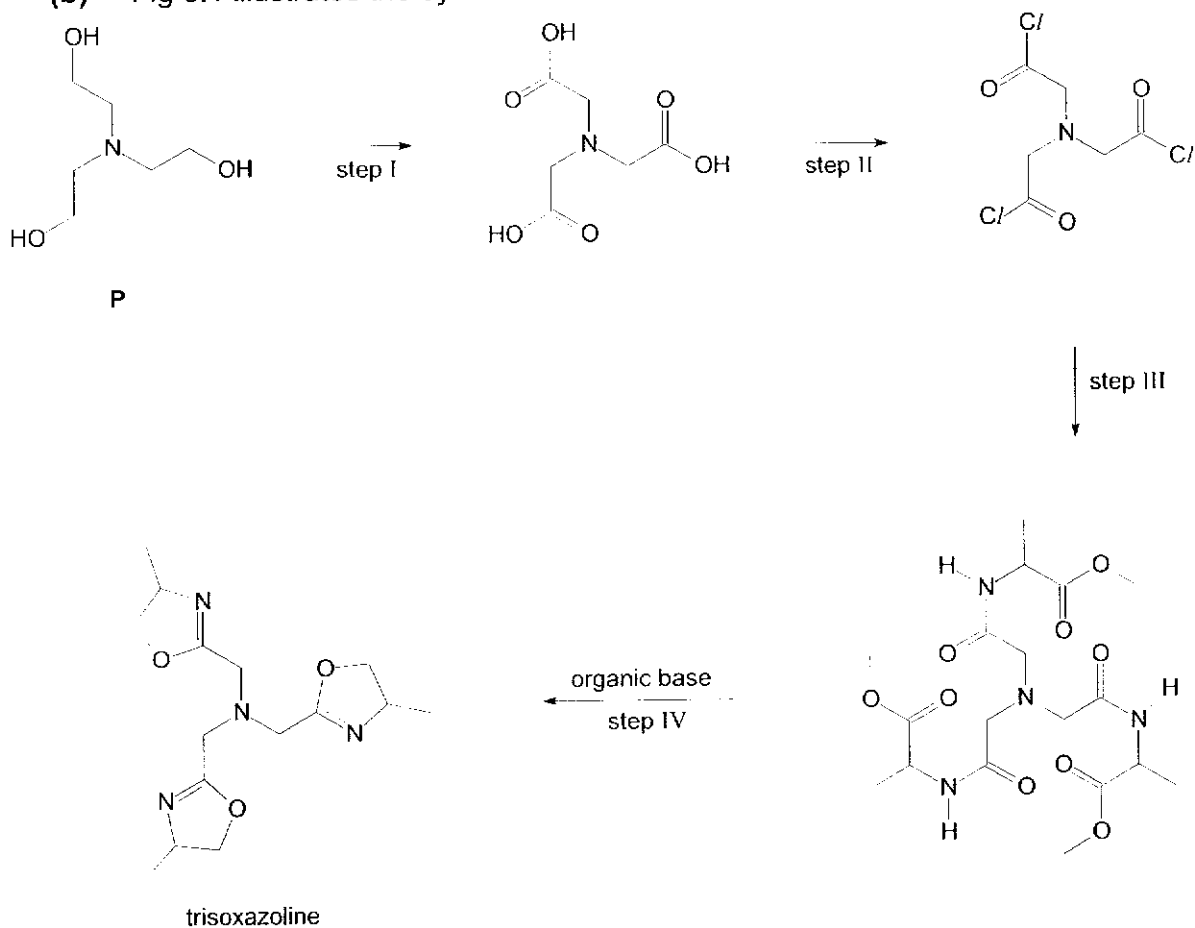


Fig 3.1

(i) State the *types of reaction* that occur during each of the steps I and II. [2]

I: oxidation

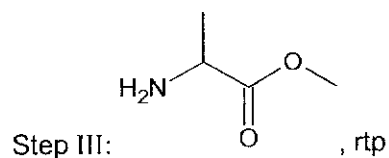
II: nucleophilic substitution

(ii) Suggest, with reason, the pH of the solution when the resultant product from step II is dissolved in water. [1]

pH: 1

reason: as hydrolysis occur, strong acid HCl was formed.

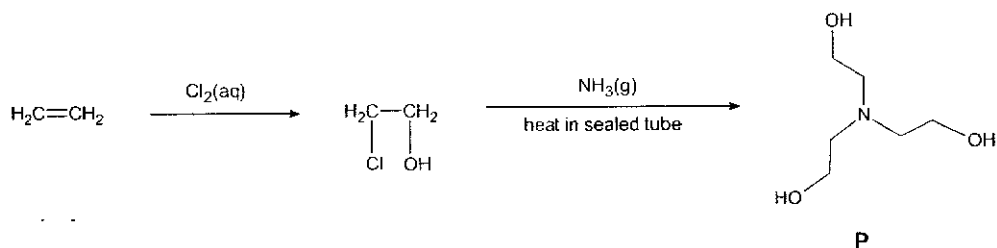
(iii) Suggest the reagents and conditions required for steps II and III. [2]
 Step II: anhydrous $\text{PCl}_5(\text{s})$, rtp or anhydrous PCl_3 , rtp or anhydrous SOCl_2 , rtp



- (iv) Compound **P** in Fig 3.1 can be synthesised from ethane via a two-step reaction scheme show below.



Suggest the reagents required for each step. [2]

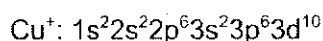
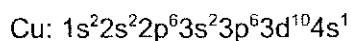


Step a: aqueous chlorine

Step b: (limited) alcoholic NH_3 , (heat in sealed tube)

- (c) Other than copper(II) ions, it was found that copper(I) ions are also able to form complexes with trisoxazoline.

Complete the full electronic configuration of copper(I) ions. [1]

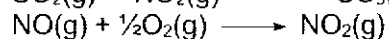
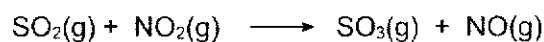


- (d) Copper is in increasing demand for use in electric vehicles, solar energy, consumer electronics and other energy efficient targets. Most current copper extraction processes burn sulfide minerals in air which produces sulfur dioxide which is harmful to the environment.

Describe and explain with the aid of suitable equations, the role of NO_2 in the oxidation of atmospheric sulfur dioxide. [2]

$\text{NO}_2(\text{g})$ is a homogeneous catalyst.

($\text{NO}_2(\text{g})$ oxidises SO_2 to SO_3 , and itself reducing to NO , hence reducing the $[\text{SO}_2]$ in the atmosphere.)



- 4 (a) A 2.00 g sample of an organic substance **Z** containing only C, H and O was burned completely. The only combustion products were 2.90 g of carbon dioxide and 1.20 g of water.

(i) Define the term *relative molecular mass*. [1]

The *average mass of one molecule of the substance* relative to $\frac{1}{12}$ the mass of one atom of ^{12}C .

(ii) Given that the relative molecular mass of the organic substance **Z** is 90.0, show that the molecular formula is $\text{C}_3\text{H}_6\text{O}_3$. [2]

$$\text{Amount of CO}_2 \text{ in 2.90 g} = \frac{2.9}{44} = 0.06591 \text{ mol}$$

Since $\text{CO}_2 \equiv \text{C}$

$$\text{Amount of C in 2.90 g} = 0.06591 \text{ mol}$$

$$\text{Mass of C in compound} = 0.06591 \times 12.0 = 0.7909 \text{ g}$$

$$\text{Amount of H}_2\text{O in 1.2 g} = \frac{1.2}{18} = 0.06667 \text{ mol}$$

Since $\text{H}_2\text{O} \equiv 2\text{H}$

$$\text{Amount of H in 1.2 g} = 0.06667 \times 2 = 0.1333 \text{ mol}$$

$$\text{Mass of H in compound} = 0.1333 \times 1.0 = 0.1333 \text{ g}$$

$$\text{Mass of O in compound} = 2.00 - 0.7909 - 0.1333 = 1.076 \text{ g}$$

	C	H	O
Mass	0.7909	0.1333	1.076
Amount in mole (i.e. mass/Ar)	$\frac{0.7909}{12.0} = 0.06591$	$\frac{0.1333}{1.0} = 0.1333$	$\frac{1.076}{16.0} = 0.06725$
Simplest mole ratio	$\frac{0.06591}{0.06591} = 1.0$	$\frac{0.1333}{0.06591} = 2.0$	$\frac{0.06725}{0.06591} = 1.0$

Empirical formula of compound: **CH₂O**

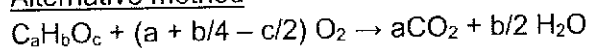
Let molecular formula be $(\text{CH}_2\text{O})_n$.

$$n(12.0 + 2 + 16.0) = 90.0$$

$$n = 3$$

Molecular formula: **C₃H₆O₃**

Alternative method



$$\text{Amount of CO}_2 \text{ in 2.90 g} = \frac{2.9}{44} = 0.06591 \text{ mol}$$

$$\text{Amount of H}_2\text{O in 1.2 g} = \frac{1.2}{18} = 0.06667 \text{ mol}$$

$$\text{Amount of Z in 2.0 g} = \frac{2.0}{90} = 0.02222 \text{ mol}$$

$$\frac{a}{1} = \frac{n(\text{CO}_2)}{n(\text{Z})}$$

$$\frac{a}{1} = \frac{0.065909}{0.02222}$$

$$a = 3$$

$$\frac{b}{2} = \frac{n(\text{H}_2\text{O})}{n(\text{Z})}$$

$$\frac{b}{2} = \frac{0.06667}{0.02222}$$

$$b = 6$$

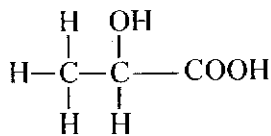
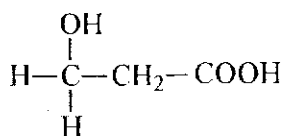
$$M_r \text{ C}_3\text{H}_6\text{O}_c = 90.0$$

$$3(12.0) + 6(1.0) + c(16.0) = 90.0$$

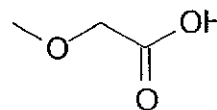
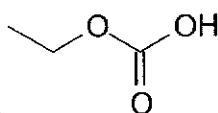
$$c = 3$$

Molecular formula: **C₃H₆O₃**

(iii) Draw all constitutional isomers of **Z** which can react with sodium carbonate. [2]



Any two structures



Accept either structures:

- (b) Complete the reaction scheme in Fig. 4.1 to show how compound **E** could be synthesised from ethylbenzene in **three** steps using suitable reagents. Show the structures of the intermediate compounds and state the reagents and conditions for each step.

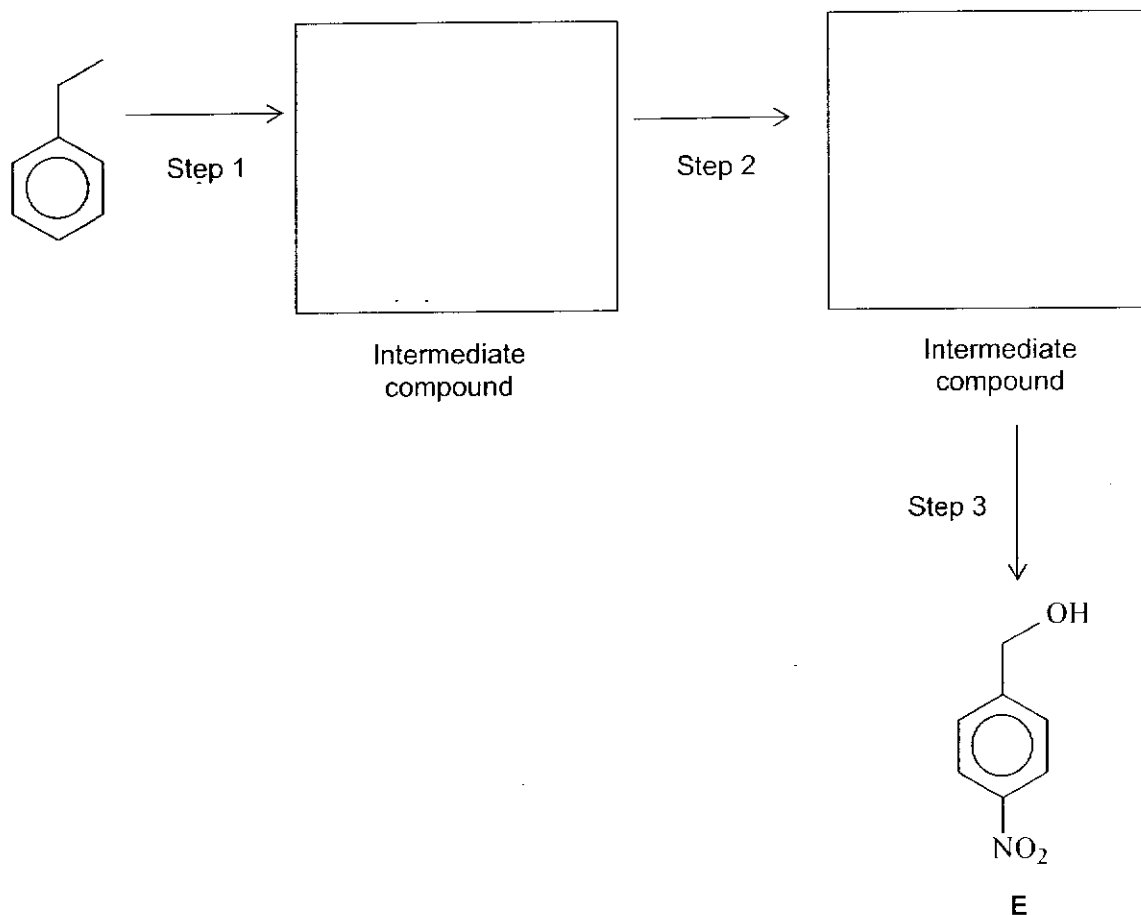
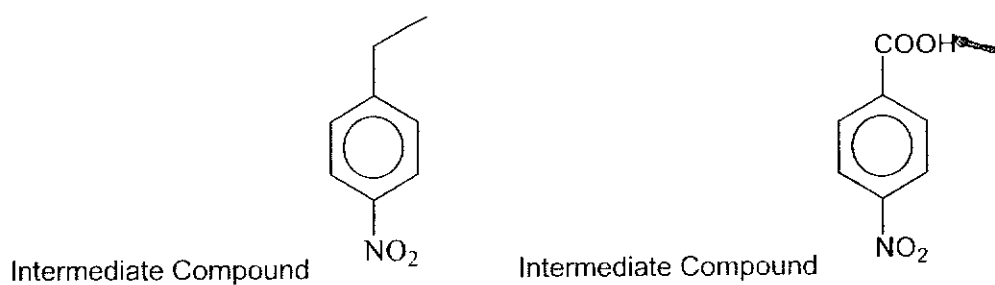


Fig. 4.1

[5]



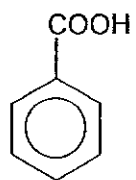
Step 1: concentrated nitric acid, concentrated sulfuric acid, heat

Step 2: KMnO₄, H₂SO₄(aq), heat

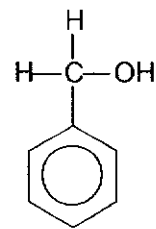
Step 3: LiAlH₄ in dry ether

Or

13



Intermediate Compound



Intermediate Compound

Step 1: KMnO₄, H₂SO₄(aq), heat

Step 2: LiAlH₄ in dry ether

Step 3: concentrated nitric acid, concentrated sulfuric acid, heat

5 This question is about the chemistry of compounds containing halogen.

- (a) Bromoalkane can undergo two different mechanisms for nucleophilic substitution – S_N1 and S_N2 .

Experiments were conducted in two different set-ups to measure the relative rates of nucleophilic substitution for three bromoalkanes. Set-up 1 and 2 use different nucleophiles.

Table 5.1 summarises the relative rates of three bromoalkanes in the two experiments.

Table 5.1

bromoalkane	$\text{CH}_3\text{CH}_2\text{Br}$	$(\text{CH}_3)_2\text{CHBr}$	$(\text{CH}_3)_3\text{CBr}$
relative rate in set-up 1	4×10^{-2}	1	4×10^6
relative rate in set-up 2	30	1	5×10^{-5}

- (i) Predict the predominant mechanism for set-up 2. Explain your answer. [2]

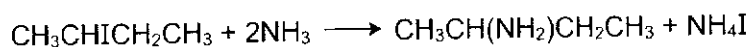
S_N2 .

The rate of reaction is fastest for the primary bromoalkane ($\text{CH}_3\text{CH}_2\text{Br}$). This favors S_N2 as the C bonded to Br is less sterically hindered which allows the nucleophile to approach it more easily.

- (ii) Explain the relative rate of $(\text{CH}_3)_3\text{CBr}$ in set-up 1. [1]

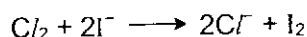
The rate is fastest for $(\text{CH}_3)_3\text{CBr}$ as it forms the most stable carbocation. The three electron donating alkyl group bonded to the C+ dispersed the positive charge on the carbocation to a larger extent and stabilises the carbocation to a larger extent. This favors the S_N1 mechanism in set-up 1.

- (b) 2-iodobutane can be readily converted into 2-aminobutane using ethanolic ammonia.



In order to determine the rate equation for this reaction, an investigation was carried out at a constant temperature. 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 aliquot and excess chlorine gas was subsequently removed. Iodine is liberated by the following reaction.



The iodine was then titrated with $0.0250 \text{ mol dm}^{-3}$ sodium thiosulfate in the presence of an indicator.

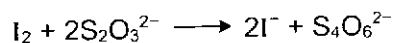


Fig 5.1 shows the volume of sodium thiosulfate used against time for this experiment.

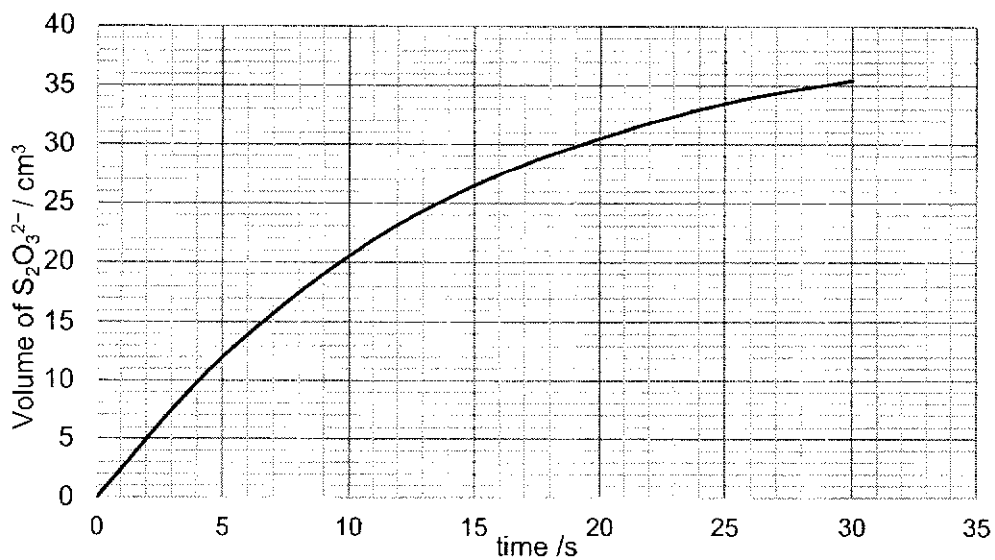


Fig 5.1

- (ii) Prove that the volume of $S_2O_3^{2-}$ required when the reaction between 2-iodobutane and ethanolic ammonia goes to completion in this investigation is 40 cm^3 . [1]

$$[2\text{-iodobutane}] = 0.20 \div 2 = 0.10\text{ mol dm}^{-3}$$

$$n(2\text{-iodobutane}) = 10/1000 \times 0.10 = 0.001000\text{ mol}$$

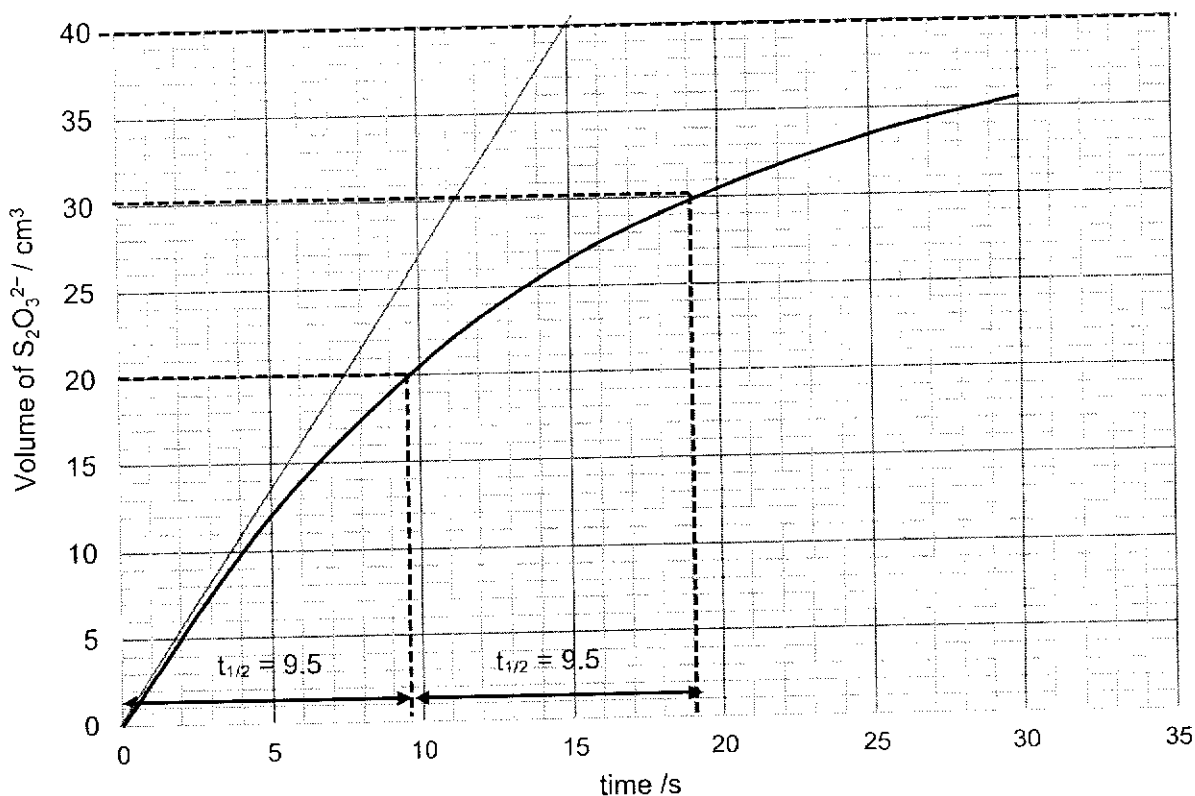
$$\text{When the reaction goes to completion, } n(I^-) \text{ formed} = 0.001000\text{ mol}$$

$$n(I_2) = 0.001000 \div 2 = 0.0005\text{ mol}$$

$$n(S_2O_3^{2-}) \text{ required} = 0.0005 \times 2 = 0.001000\text{ mol}$$

$$V(S_2O_3^{2-}) \text{ required} = \frac{0.001000}{0.0250} = 0.04000\text{ dm}^3 = 40.00\text{ cm}^3$$

- (ii) Hence, use Fig 5.1 to deduce the order of reaction with respect to 2-iodobutane. [2]



Time taken when volume of sodium thiosulfate increases from 0 to $20\text{ cm}^3 = 9.5\text{ min}$.
 Time taken when volume of sodium thiosulfate increases from 20 to $30\text{ cm}^3 = 9.5\text{ min}$.

Since $t_{1/2}$ is constant, it is 1st order with respect to 2-iodobutane

- (iii) The concentration of ethanolic ammonia is halved and a new series of experiments was carried out at the same temperature.

It is known that the order of reaction with respect to ethanolic ammonia is one.

Suggest how the gradient at each point will change when a similar graph like the one in Fig. 5.1 was plotted. [1]

Since the reaction is first order with respect to ethanolic ammonia, when concentration of ethanolic ammonia is halved, rate will be halved as well. Thus, the gradient at each point will be halved.

- (iv) Hence, construct the rate equation for the reaction between 2-iodobutane and ethanolic ammonia. [1]

$$\text{rate} = k[2\text{-iodobutane}][\text{ammonia}]$$

- (v) Calculate the value of the rate constant for the reaction between equal volumes of 0.20 mol dm^{-3} 2-iodobutane and 4.00 mol dm^{-3} ethanolic ammonia and its units. [2]

$$\text{rate} = k[2\text{-iodobutane}][\text{ethanolic ammonia}]$$

Since ethanolic ammonia is in large excess,
 $\text{rate} = k' [2\text{-iodobutane}]$, where $k' = k [\text{ethanolic ammonia}]$

$$t_{1/2} = \frac{\ln 2}{k'} = \frac{\ln 2}{k [\text{ethanolic ammonia}]}$$

$$[\text{ethanolic ammonia}] \text{ in the reaction mixture} = 4.00 \div 2 = 2.00$$

$$9.5 = \frac{\ln 2}{k (2.00)}$$

$$k = \underline{0.0365 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}}$$

OR

Initial rate of disappearance of 2-iodobutane

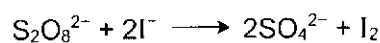
$$= [40 \times 0.025 / 10] / 15$$

$$= 6.67 \times 10^{-3}$$

$$k = 6.67 \times 10^{-3} / (0.1 \times 2.00)$$

$$= \underline{0.0333 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}}$$

- (c) Iodide ions, I^- , can react with peroxydisulfate, $S_2O_8^{2-}$.



A student wanted to investigate the effect of changes in volume used on the rate of this reaction.

Table 5.2 shows the results obtained when a series of experiments was carried out using different volumes of the two reagents, each solution being made up to the same total volume with water, where necessary.

Table 5.2

experiment	volume of KI / cm^3	volume of $Na_2S_2O_8$ / cm^3	volume of water / cm^3	initial rate / $mol\ dm^{-3}\ s^{-1}$
1	10	20	10	0.0200
2	5	20	15	0.0100
3	30	10	0	0.0303

Given that the order of reaction with respect to I^- is 1, determine the order of reaction with respect to $S_2O_8^{2-}$. [1]

$$\text{Let rate} = k[I^-][S_2O_8^{2-}]^n$$

Comparing experiment 1 and 3,

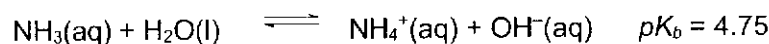
$$\frac{0.0200}{0.0303} = \frac{k(10)(20)^n}{k(30)(10)^n}$$

$$n = 0.985$$

$$n \approx 1$$

Order = 1

- 6 (a) Ammonia can act as a weak base.



$(\text{NH}_4)_2\text{SO}_4$ is a weak acid. Calculate the pH of $0.10 \text{ mol dm}^{-3} (\text{NH}_4)_2\text{SO}_4(\text{aq})$. [2]

$$[\text{NH}_4^+] = 2 \times 0.10 = 0.20 \text{ mol dm}^{-3}$$

$$pK_a \text{ of } \text{NH}_4^+ = 14 - 4.75 = 9.25$$

$$K_a = \frac{[\text{NH}_3][\text{H}^+]}{[\text{NH}_4^+]} = \frac{[\text{H}^+]^2}{(2 \times 0.10)} = 10^{-9.25}$$

$$[\text{H}^+]^2 = 1.124 \times 10^{-10}$$

$$[\text{H}^+] = 1.060 \times 10^{-5} \text{ mol dm}^{-3}$$

$$\text{pH} = -\lg(1.060 \times 10^{-5}) = 4.97$$

- (b) A buffer solution with a pH 8.90 is made by adding 150 cm^3 of solution **B** containing ammonium chloride to 100 cm^3 of $0.0200 \text{ mol dm}^{-3}$ aqueous NH_3 . Calculate the concentration of ammonium chloride in solution **B**. [3]

$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = \frac{\left(\frac{0.15x}{0.100 + 0.150}\right)(10^{-5.1})}{\left(\frac{0.100 \times 0.02}{0.100 + 0.150}\right)} = 10^{-4.75} = 1.778 \times 10^{-5}$$

$$x = 0.0298 \text{ mol dm}^{-3}$$

Or

$$pOH = pK_b + \lg \frac{[\text{salt}]}{[\text{base}]}$$

$$5.1 = 4.75 + \lg \frac{150x}{100 \times 0.02}$$

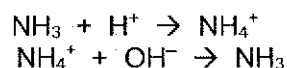
$$x = 0.0298 \text{ mol dm}^{-3}$$

Or

$$K_a = \frac{[\text{NH}_3][\text{H}^+]}{[\text{NH}_4^+]} = \frac{\left(\frac{0.100 \times 0.02}{0.100 + 0.150}\right)(10^{-8.90})}{\left(\frac{0.15x}{0.100 + 0.150}\right)} = 10^{-9.25} = 5.623 \times 10^{-10}$$

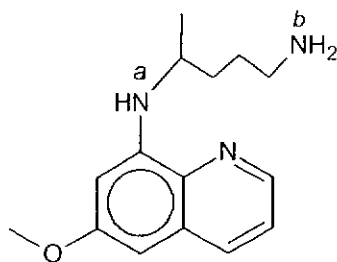
$$x = 0.0298 \text{ mol dm}^{-3}$$

- (c) Write equations to explain how the $\text{NH}_3(\text{aq})/\text{NH}_4^+(\text{aq})$ buffer system helps to maintain the pH. [2]



Therefore pH remains fairly constant

- (d) Malaria is a serious and sometimes fatal mosquito-borne disease. Primaquine is an antimalaria drug used to prevent relapse of malaria infections.



primaquine

Two of the pK_b values of primaquine are 4.1 and 9.8.

- (i) Using the information, write the pK_b values for the nitrogen-containing groups *a* and *b* in primaquine. [1]

nitrogen-containing	group a	group b
pK_b	9.8	4.1

- (ii) Suggest an explanation for the for your assignment of pK_b values in (d)(i). [2]

The alkyl group in group b exerts an electron-donating effect. This makes the lone pair on N atom more available to accept a proton.

The lone pair of electrons on N in group a is delocalised into the π electron cloud of the benzene ring. This makes the lone pair on N atom less available to accept a proton.