Suggested Solutions

DUNMAN HIGH SCHOOL
Preliminary Examination
Year 6

H2 CHEMISTRY 9729/03

Paper 3 Free Response Questions

21 September 2023
2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your centre number, index number, name and class 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. If additional space is required, you should use the pages at the end of this booklet. The question number must be clearly shown.

Section A
Answer **all** questions.

Section B
Answer **one** question.

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

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

For Examiner's Use	
Section A	
1	**20**
2	**20**
3	**20**
Section B	
4 / 5	**20**
Total	**80**

This document consists of **25** printed pages and **1** blank page.

Section A

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

1 (a) Group 2 salts, such as carbonates, decompose when heated. Table 1.1 shows information of some Group 2 salts that undergo thermal decomposition.

Table 1.1

Group 2 salt	thermal decomposition temperature / °C
$MgCO_3$	350
$CaCO_3$	825

(i) Explain the difference in thermal decomposition temperature of $MgCO_3$ and $CaCO_3$.

[2]

The Ca^{2+} cation has a **lower charge density and hence lower polarising power** compared to the Mg^{2+} cation.

The **electron cloud of CO_3^{2-} anion is distorted/polarised** by Ca^{2+} to a **lesser extent** compared to Mg^{2+}. Hence the covalent bonds in CO_3^{2-} are weakened to a lesser extent by Ca^{2+} and **higher energy** is required for the thermal decomposition of $CaCO_3$.

(ii) Hence predict the thermal decomposition temperature for $SrCO_3$.

[1]

Any temperature higher than 825°C

(iii) Write an equation for the thermal decomposition of $CaCO_3$. Include state symbols in your answer.

[1]

$CaCO_3$ (s) → CaO (s) + CO_2 (g)

(iv) State and explain the sign of ΔS for the thermal decomposition of $CaCO_3$. Hence explain how spontaneity of the reaction changes as temperature increases.

[2]

$\Delta S > 0$ / is **positive** since there is an **increase in number of gaseous particles** from 0 to 1.
$\Delta G = \Delta H - T\Delta S$. Hence **$\Delta G$ becomes more negative** as temperature increases and **spontaneity increases**.

(v) Outline a suitable experiment to verify that the thermal decomposition of a sample of $Mg(OH)_2$ is complete.

No details regarding use of specific glassware are required.

[2]

1. Transfer the sample to a crucible.
2. **Weigh** the sample using an electronic mass balance.
3. **Heat** the sample for a few minutes.
4. Remove the sample from the flame and let it **cool**.
5. **Re-weigh** the sample.

6. **Repeat** until there is **negligible / no change in mass** of the sample upon further heat-cool-weigh cycles.

(b) Group 2 carbonates are sparingly soluble in water. Table 1.2 shows the solubility product, K_{sp}, of two Group 2 carbonates.

Table 1.2

Group 2 carbonate	K_{sp}
$MgCO_3$	2.61×10^{-3}
$CaCO_3$	5.83×10^{-5}

(i) Write an expression for K_{sp} of $MgCO_3$, giving its units.

[1]

$K_{sp} = [Mg^{2+}][CO_3^{2-}]$ mol^2 dm^{-6}

(ii) Describe and explain how the solubility of $MgCO_3$ is affected by the addition of ethanoic acid.

[2]

$MgCO_3(s) \rightleftharpoons Mg^{2+}(aq) + CO_3^{2-}(aq)$

Ethanoic acid undergoes **neutralisation / acid-base reaction / acid-carbonate reaction** with CO_3^{2-}, hence **decreases $[CO_3^{2-}]$**. **Position of equilibrium shifts to the right** to increase $[CO_3^{2-}]$, hence **solubility increases**.

Excess solid magnesium nitrate and calcium nitrate were added to a solution containing carbonate ions. The mixture was stirred and left to equilibrate at room temperature.

(iii) Calculate the $[Mg^{2+}]/[Ca^{2+}]$ ratio in the resulting mixture.

[1]

Both carbonate salts are saturated in the resulting mixture.

$$K_{sp} = [M^{2+}][CO_3^{2-}]$$
$$[M^{2+}] = \frac{K_{sp}}{[CO_3^{2-}]}$$

$$\frac{[Mg^{2+}]}{[Ca^{2+}]} = \frac{2.61 \times 10^{-3} \div [CO_3^{2-}]}{5.83 \times 10^{-5} \div [CO_3^{2-}]}$$

$$= \mathbf{44.8}$$

(c) Magnesium is also used in the pinacol coupling reaction. A new C–C bond is formed between two carbonyl compounds, as shown in Fig. 1.1.

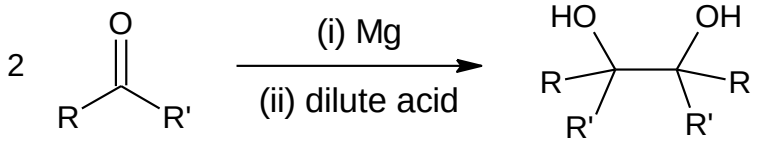
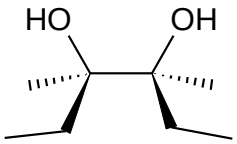


Fig. 1.1

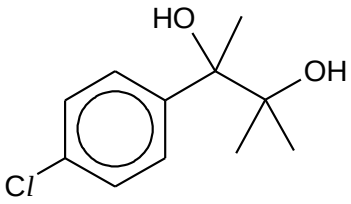
(i) When butanone undergoes the pinacol coupling reaction, a mixture of 3 stereoisomers are formed.

Draw the structure of the product that does **not** rotate plane-polarised light, showing the stereochemistry of the molecule clearly.

[1]



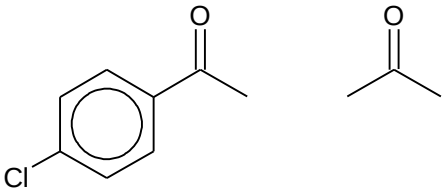
(ii) Phenaglycodol is a sedative. It can be synthesised from compounds **P** and **Q** using the pinacol coupling reaction.



Phenaglycodol

Suggest possible structures for **P** and **Q**.

[2]



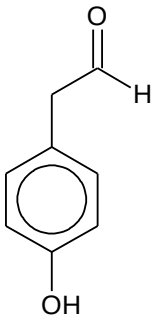
(d) Compound **R**, $C_8H_8O_2$, reacts with Fehling's reagent and aqueous bromine. It is also soluble in NaOH(aq). When **R** is heated with acidified potassium manganate(VII), $C_8H_8O_3$, is first formed. Further heating produces 4-hydroxybenzoic acid.

For each reaction, state the type of reaction described and explain what the information tells you about the functional groups present in **R**. Hence suggest a possible structure for **R**.

[5]

Observations	Type of reaction	Deductions
R has the molecular formula $C_8H_8O_2$	-	The high C:H ratio indicates that a benzene ring is likely present
R reacts with Fehling's reagent.	Oxidation	**R** contains an aliphatic aldehyde
R reacts with aqueous bromine	Electrophilic addition or Electrophilic substitution	**R** contains a C=C bond / alkene group or **R** contains a phenol group
R is soluble in NaOH(aq)	Neutralisation	**R** contains a –COOH or phenol group.

		Since **R** only contains two oxygen atoms and must contain an aldehyde, it must also contain a phenol group.
When **R** is heated with acidic potassium manganate(VII), $C_8H_8O_3$ is first formed.	Oxidation	Aldehyde is oxidised to a carboxylic acid.
Further heating with acidic potassium manganate(VII) produces 4-hydroxybenzoic acid.	Side-chain oxidation	There are two substituents on the benzene ring with a 1,4-substitution pattern



[Total: 20]

2 (a) (i) State the two main assumptions of ideal gases.

[1]

Negligible intermolecular forces of attraction between gas particles.
Gas **particles** have **negligible volume** compared to volume of container/gas.

(ii) Explain why a real gas will deviate more from ideality at a lower temperature.

[1]

At lower temperature, the average **kinetic energy of the gas particles decreases** and they have less energy to overcome the intermolecular forces of attraction. Hence **intermolecular forces of attraction between particles become more significant**.

(b) Pure hydrogen iodide, HI, partially dissociates into hydrogen and iodine as shown in the equation below.

$$2HI(g) \rightleftharpoons H_2(g) + I_2(g)$$

The reaction was carried out at 500 K. At the start of the reaction, 9.0×10^{-4} mol of HI were introduced into a 2 dm^3 vessel. When equilibrium was established, it was found that 85% of the hydrogen iodide was left.

(i) Write an expression for the equilibrium constant, K_c, for the dissociation of HI.

[1]

$K_c = \frac{[H_2][I_2]}{[HI]^2}$

(ii) Determine the equilibrium constant, K_c, for this reaction at 500 K.

[2]

	$2HI(g) \rightleftharpoons H_2(g) + I_2(g)$		
Initial mole/ mol	9.0×10^{-4}	0	0
Change in mole / mol	-1.35×10^{-4}	$+6.75 \times 10^{-5}$	$+6.75 \times 10^{-5}$
Equilibrium mole / mol	7.65×10^{-4}	$+6.75 \times 10^{-5}$	$+6.75 \times 10^{-5}$
Equilibrium conc / mol dm^{-3}	3.825×10^{-4}	3.375×10^{-5}	3.375×10^{-5}

$K_c = \frac{[3.375\ x\ 10^{-5}]^2}{[3.825\ x\ 10^{-4}]^2} = 7.79 \times 10^{-3}$

(iii) When the temperature was increased to 700 K, it was found that only 70% of the hydrogen iodide was left.

Deduce from this information whether the forward reaction is endothermic or exothermic. Explain your reasoning.

[2]

When temperature was increased to 700 K, there were lesser hydrogen iodide left, indicating that the **position of equilibrium had shifted to the right**.
When temperature increases, position of equilibrium shifts to the right to favour endothermic reaction to **absorb more heat**.
Hence the **forward reaction is endothermic.**

(iv) Explain why gaseous hydrogen chloride does not undergo a similar dissociation like that of hydrogen iodide at 500 K.

[1]

Bond energy and hence covalent bond strength of H–C*l* is stronger than that of H–I

(c) 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]

Bubble Cl_2 gas into HC*l*(aq) and HBr(aq) separately.

With HC*l*(aq), solution **remains colourless**.
With HBr(aq), **colourless solution turns orange** due to the formation of Br_2.

(d) The chloro–alkali industry generates commercially useful substances such as chlorine, hydrogen and sodium hydroxide. Saturated sodium chloride solution, known as brine, is electrolysed in the diaphragm cell as shown in Fig. 2.1.

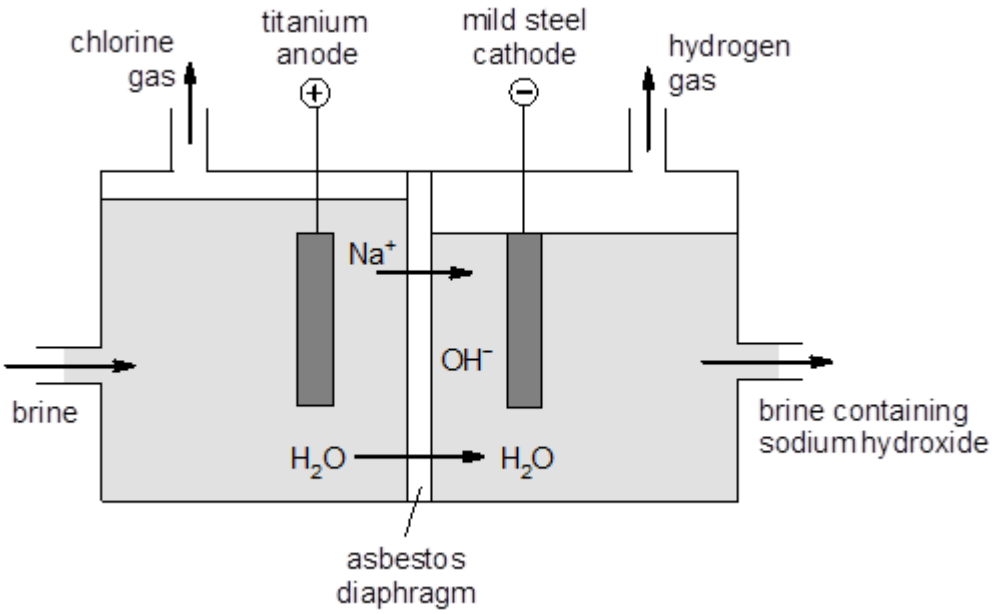


Fig. 2.1

During the electrolysis process, a steady current of 5000 A was passed through the cell. 8.30 x 10^5 cm^3 of chlorine gas was produced at 30 °C and 1.5 atm.

(i) Write ionic equations for the reactions occurring at the anode and at the cathode.

[2]

Anode: $2Cl^-(aq) \rightarrow Cl_2(g) + 2e^-$
Cathode: $2H_2O(l) + 2e^- \rightarrow 2OH^-(aq) + H_2(g)$

(ii) Determine the amount, in moles, of chlorine gas produced.

[1]

$pV = nRT$

$n = \frac{1.5 \; x \; 101325 \; x \; 0.830}{8.31 \; x \; 303}$

$= 50.1$ mol

(iii) Hence, calculate the time taken to produce the amount of chlorine gas in **(d)(ii)**.

[2]

Amount of electrons = 2 x (50.1) = 100.2 mol
$Q = nF = (100.2)(96500) = 9.669 \times 10^6$ C

$Q = It$

time taken = $\frac{9.669 \; x \; 10^6}{5000}$ = 1930 s

[Total: 15]

3 In this question, R and R' can be H or any alkyl group.

Terminal alkynes, R−C≡C−H, react with aldehydes, R'CHO, to form allenes, RCH=C=CHR'. An example of this reaction is shown in Fig. 3.1, which occurs in the presence of a weak base and copper(I) bromide.

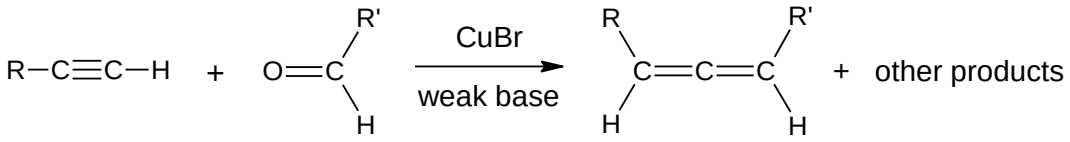


Fig. 3.1

(a) By reference to the electronic configuration of the relevant ion, explain how copper(I) bromide acts as a Lewis acid catalyst for this reaction.

[2]

Cu^+: **$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10}$**
Cu(I) ion has **energetically accessible or low-lying empty** (4s) **orbital** available to **accept a pair of electrons**.

(b) **(i)** State the hybridisation of the central carbon atom in the C=C=C group of the allene product. Hence describe the orbital overlap involved in the formation of the sigma bonds in the C=C=C group.

[1]

hybridisation of central C: **sp**
orbital overlap involved in sigma bond: **head-on** overlap of **sp^2 and sp** orbitals

(ii) Fig. 3.2 shows the plane in which the carbon atoms in the C=C=C group of the allene product lie.

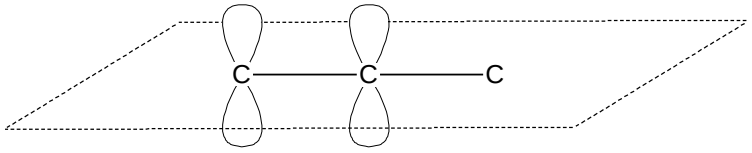
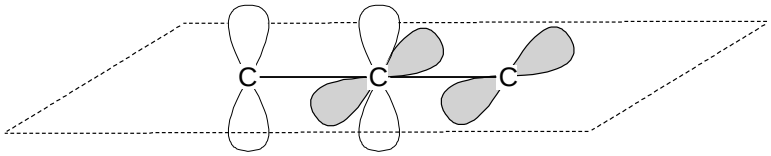


Fig. 3.2

By considering your answer in **(b)(i)**, complete Fig. 3.2 to show the arrangement of the *p* orbitals in the C=C=C group.

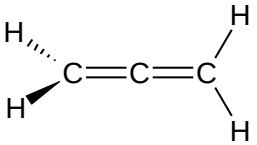
[1]



(iii) By considering your answer in **(b)(ii)**, draw the 3-dimensional structure of the allene, $H_2C=C=CH_2$.

Show the carbon atoms in the C=C=C bond in the plane of the paper and use wedged ◄ and dashed ····· bonds to the relevant hydrogen atoms to show the stereochemistry.

[1]



(iv) Predict and explain the relative rate of reaction of the allene, C*l*CH=C=CHC*l*,

and 1,3−dichloropropane with excess NaOH(aq).

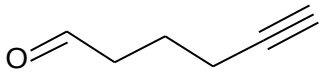
[2]

Relative rate of reaction: **1,3−dichloropropane > C*l*CH=C=CHC*l***

In the allene, the ***p* orbital of each C*l* atom overlaps side-on with the *p* orbitals of the adjacent C=C bond**, allowing the **lone pair of electrons on C*l* to delocalise into the adjacent C=C bond**. This results in **partial double character** of the C−C*l* bond. The **strengthened C−C*l* requires more energy to break** and thus rate of reaction with NaOH(aq) is slower than that of 1,3−dichloropropane.

OR
[Alternative answer]
Electron rich C=C double bond
Repels OH- nucleophile
Causing allene to be less susceptible to nucleophilic attack
Resulting in a slower rate of reaction.

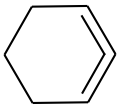
(c) **(i)** Compound **E** has the following structure. When **E** alone undergoes a reaction similar to that in Fig. 3.1, it forms a cyclic allene product.



E

Predict the cyclic allene product formed in this reaction.

[1]



(ii) The cyclic allene product formed in **(c)(i)** is highly strained. Suggest an explanation for this using the Valence Shell Electron Pair Repulsion theory.

[2]

By the VSEPR theory, there are **two bond pairs and no lone pairs of electrons around the central C** of the C=C=C group, and the two bond pairs **should be 180° apart / adopt a linear shape to minimise repulsion**.

The two bond pairs around the central C in the C=C=C group are **less than 180° apart in a hexagonal ring** and thus there is **significant repulsion between the bonding electrons** which makes the cyclic allene unstable.

(d) The weak base used in Fig. 3.1 is diisopropylamine, $(CH_3)_2CHNHCH(CH_3)_2$.

(i) Using the Brønsted-Lowry theory, explain what is meant by the term *weak base*.

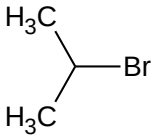
[1]

A weak base is a **proton acceptor** that **partially dissociates in water**.

(ii) Diisopropylamine is one of the organic products formed when an excess of a compound **X** (M_r = 122.9) is heated with ammonia in a sealed tube.

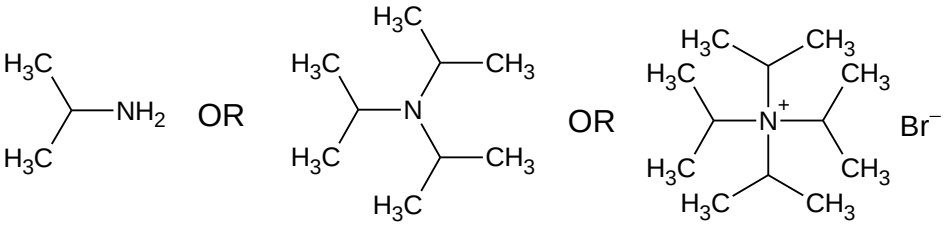
Draw the structure of **X** and suggest the identity of one other organic product formed in the reaction.

[2]



compound **X**

One other organic product:



Diisopropylamine, $(CH_3)_2CHNHCH(CH_3)_2$, has a pK_b of 3.43 at 298 K.

You may use **R_2NH** to represent diisopropylamine.

(iii) Calculate the percentage of diisopropylamine molecules that are dissociated in 0.25 mol dm^{-3} diisopropylamine.

[2]

	R_2NH + H_2O ⇌	$R_2NH_2^+$ +	OH^-
Initial [ ] / mol dm^{-3}	0.25	0	0
Change in [ ] / mol dm^{-3}	–x	+x	+x
Eqm [ ] / mol dm^{-3}	0.25–x	x	x

$K_b = \frac{x^2}{0.25 - x} \approx \frac{x^2}{0.25}$

$\Rightarrow x = \sqrt{K_b \times 0.25} = \sqrt{10^{-3.43} \times 0.25} = \underline{\mathbf{0.0096376}}$ mol dm^{-3}

% dissociation $= \frac{x}{0.25} \times 100\% = \frac{0.0096376}{0.25} \times 100\% = \underline{\mathbf{3.86\ \%}}$

(iv) Some HNO_3 is added to 1 dm^3 of the diisopropylamine solution in **(d)(iii)**.

Identify the two major organic species present in this solution when the pH is 10.3. Hence determine the amount, in moles, of HNO_3 added.

[3]

two major organic species:
$\underline{R_2NH \text{ and } R_2NH_2^+}$

Let the amount of HNO_3 added be x mol.
$R_2NH + H^+ \rightarrow R_2NH_2^+$

Initial moles of $(CH_3)_2CHNHCH(CH_3)_2 = 0.25$ mol
pH = 10.3 $\Rightarrow$ pOH = 14 – 10.3 = 3.7

$pOH = pK_b + \lg\left(\frac{\frac{n(salt)}{V}}{\frac{n(base)}{V}}\right)$

$3.7 = 3.43 + \lg\left(\frac{x}{0.25 - x}\right)$

$\lg\left(\frac{x}{0.25 - x}\right) = 0.27$
$\left(\frac{x}{0.25 - x}\right) = 10^{0.27}$
x = **0.163 mol**

Diisopropylamine and heptane have similar molar masses.

(v) Explain why the boiling point of diisopropylamine is lower than that of heptane.

molecule	structural formula	boiling point
diisopropylamine	$(CH_3)_2CHNHCH(CH_3)_2$	357
heptane	$CH_3(CH_2)_5CH_3$	371

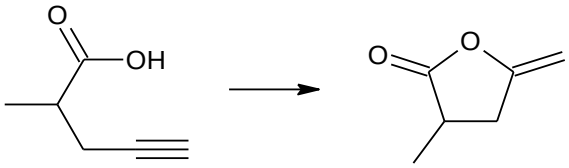
[2]

Diisopropylamine forms predominantly instantaneous dipole−induced dipole interactions between molecules due to the presence of two large non-polar alkyl (isopropyl) groups.

The **branched alkyl groups** result in **smaller surface area of contact between diisopropylamine molecules** as compared to the **linear heptane molecules**.

Less energy is required to overcome the **weaker / less extensive instantaneous dipole−induced dipole interactions** between diisopropylamine molecules.

Under suitable conditions, alkynes react with carboxylic acids to form esters. An example is shown in Fig. 3.3.



P

Fig. 3.3

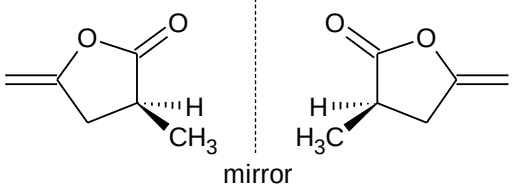
(e) **(i)** Identify the type(s) of stereoisomerism that product **P** exhibits and hence, state the number of stereoisomers that **P** has.

[1]

type of stereoisomerism: **enantiomerism**
number of stereoisomers: **2**

(ii) Draw the stereoisomers of **P**.

[1]



P undergoes a two−step reaction as shown in Fig. 3.4.

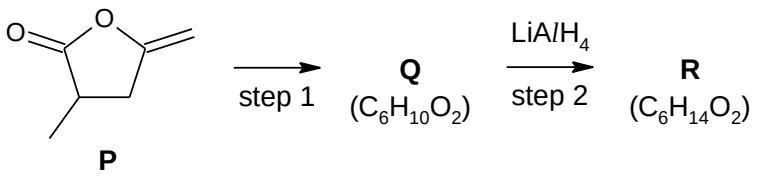
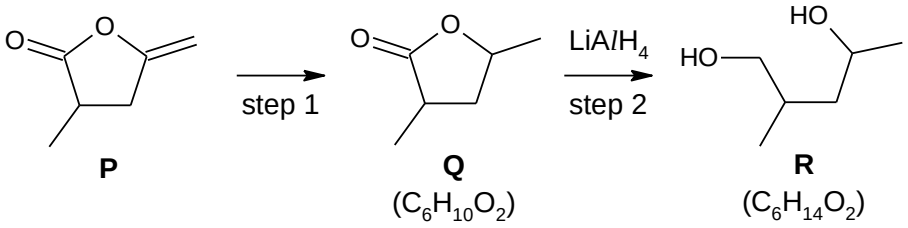


Fig. 3.4

(f) Predict the structures of **Q** and **R**. Suggest reagents and conditions for step 1.

[3]



reagents and conditions for step 1: **H_2, Ni, heat**

[Total: 25]

Section B

Answer **one** question from this section.

4 (a) Magnesium, aluminium and phosphorous are three elements in period 3 of the periodic table.

(i) Describe what you would observe when water is added to separate samples of the oxides of these three elements, MgO, Al_2O_3 and P_4O_{10}.

Suggest the pH of the resulting solutions and write equations where appropriate.

[3]

$MgO + H_2O \rightleftharpoons Mg(OH)_2$

MgO is **sparingly soluble** in water, forming weakly alkaline solution.

pH of resulting solution = 9

Al_2O_3 is **insoluble in water**.

pH of resulting solution = 7

P_4O_{10} (s) + $6H_2O$ (l) → $4H_3PO_4$ (aq)

P_4O_{10} **dissolves readily in water** to form an **acidic solution**.

pH of resulting solution = 2

(ii) By quoting data from the *Data Booklet*, explain in detail the differences in the reactions of water with magnesium oxide and with aluminium oxide.

[3]

Magnitude of Lattice Energy $\propto \left|\frac{q_+ q_-}{r_+ + r_-}\right|$

From the Data Booklet,
cationic radius of Mg^{2+} = 0.065 nm
cationic radius of Al^{3+} = 0.050 nm

Since anionic change and anionic radius of both oxides are the same and
Cationic charge : **$Al^{3+} > Mg^{2+}$,**
Cationic ionic radius : **$Al^{3+} < Mg^{2+}$,**
Magnitude of lattice energy: $Al_2O_3 > MgO$

Hence, ion–dipole interactions formed between ions (**Al^{3+}** and **O^{2-}**) and water molecules **does not release sufficient energy** to overcome the **larger magnitude of lattice energy in Al_2O_3** / for the **detachment of ions** from the ionic lattice of **Al_2O_3** for hydration to occur.

(b) **(i)** 0.80 g of liquid **T**, $C_{10}H_{18}$, was burned under a container filled with 100 cm^3 of water. The container of water has an initial temperature of 25 °C. The process is known to be 80% efficient and the enthalpy change of combustion of **T** is −5500 kJ mol^{-1}.

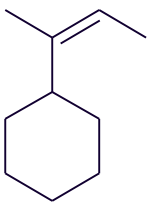
Using the *Data Booklet*, calculate the final temperature of water when 0.80 g of liquid **T** is completely burnt.

[3]

Energy evolved from burning 0.8 g of **T** = 5500 x 10^3 x $\frac{0.80}{138}$ = **31884 J**

Let the final temperature of water be y.
$\frac{80}{100}$ × **31884** = m c (y - 25)
$\frac{80}{100}$ × 35484 = 100 x 4.18 x (y - 25)
y - 25 = 61.0
y = 86.0 °C

(ii) Compound **U** is an isomer of **T** and its skeletal structure is shown below.



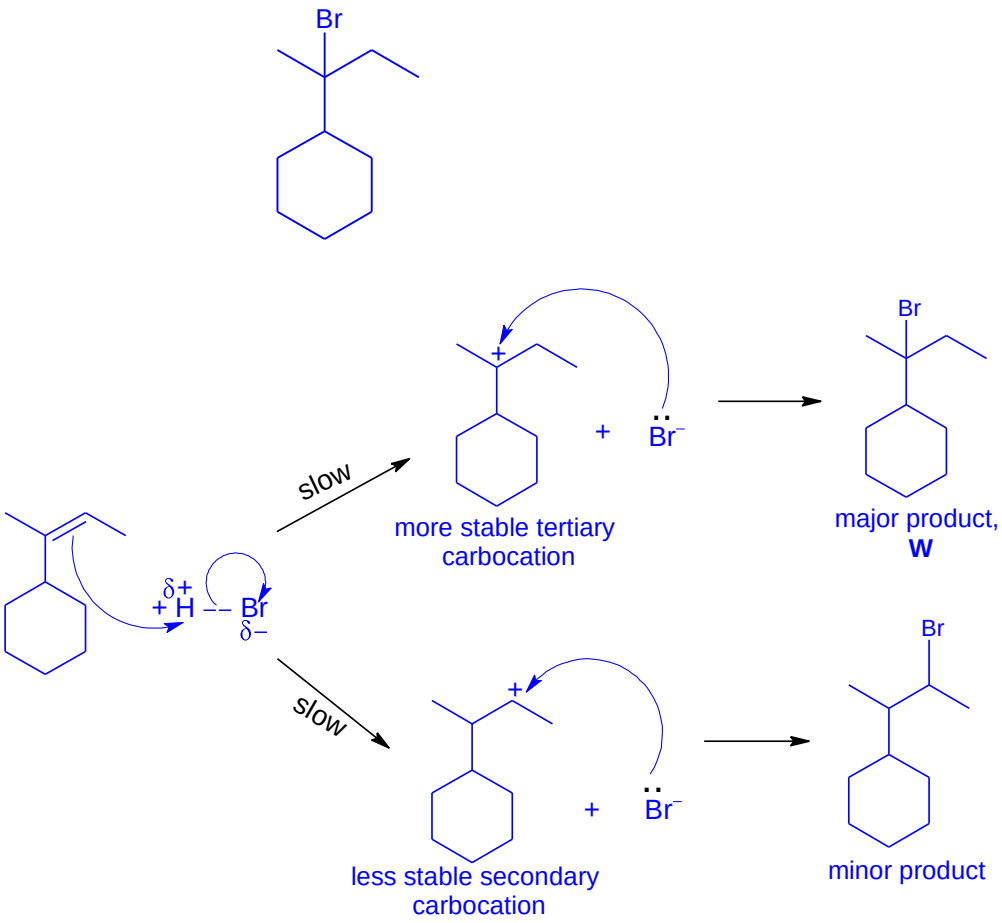
U

The major product, **W**, is formed when compound **U** is mixed with dry hydrogen bromide gas.

Draw the skeletal structure of **W** and explain why **W** is the major product of this reaction.

[3]

Skeletal structure of **W** :



The tertiary carbocation leading to W has **more electron-donating alkyl groups that disperse the positive charge** on C **to a greater extent** than the secondary carbocation leading to minor product.

Hence, the tertiary carbocation intermediate is **more stable** than the secondary carbocation intermediate and **W** is the major product.

(c) Compound **V** has the molecular formula C_6H_{12}. Aqueous bromine remained orange when added to **V**. However, **V** forms three different mono-brominated products when reacted with bromine in UV light.

(i) Deduce the structure of **V**. Explain your reasoning.

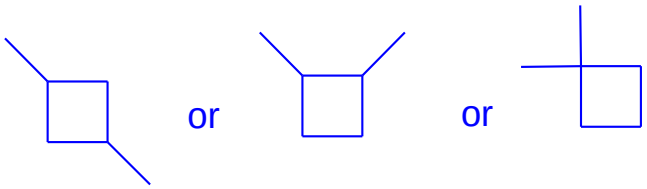
[3]

V does not undergo **electrophilic addition** with Br_2 (aq).
- There is **no C=C double** / **alkene** in **V**

V undergoes **free radical substitution** with Br_2 in UV light.
- **V** is **an alkane**

Since **V** has a molecular formula of C_6H_{12}
- **V is a cycloalkane**

For **V** to be able to form only three mono-brominated products after free radical substitution, its structure must be



V

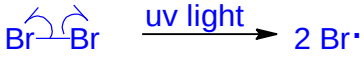
(ii) Using the structure you have deduced in **(c)(i)**, draw the mechanism of the reaction between **V** and bromine in UV light.

You should show how a secondary alkyl bromide is formed in your mechanism.

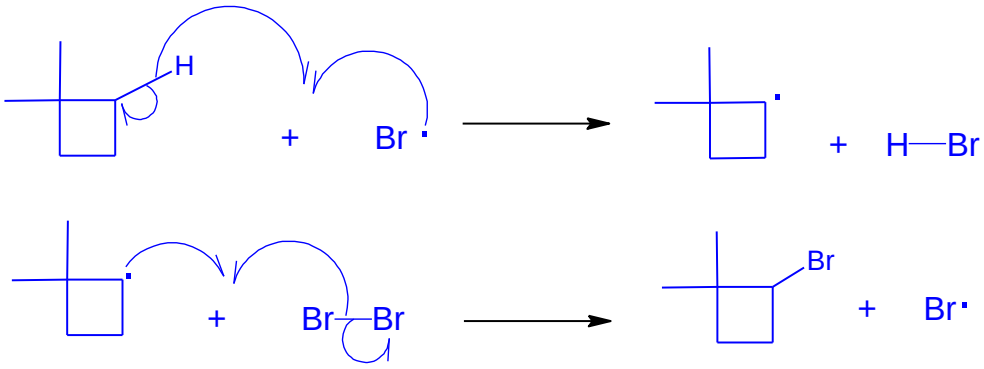
[3]

Free radical substitution

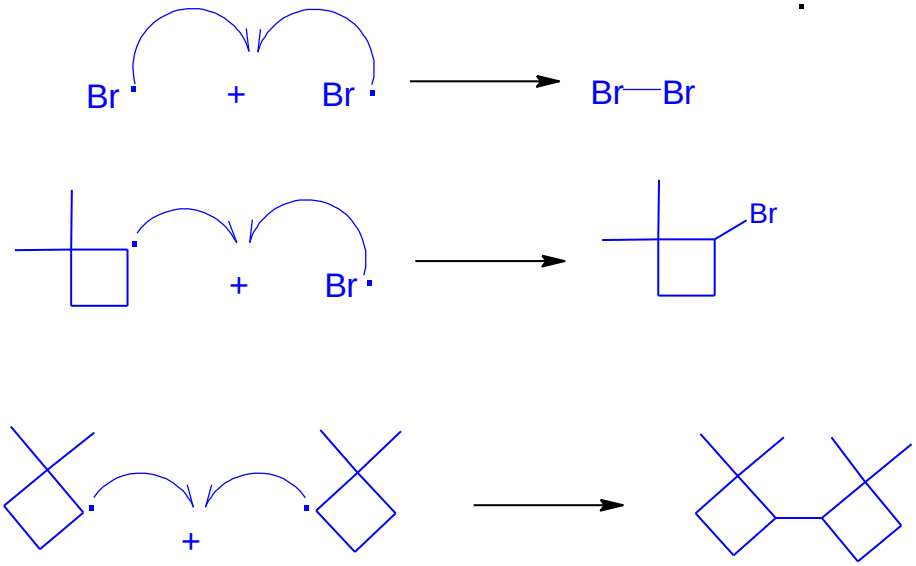
Initiation:



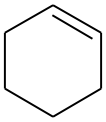
Propagation:



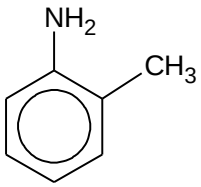
Termination:



(d) The structures of compound **X** and **Y** are shown below.



X



Y

Suggest the reagents and conditions for a reaction that could be used to distinguish between compounds **X** and **Y**. Describe the observations in each case.

[2]

Add **cold $KMnO_4$ (aq) in dilute KOH** to each sample.

Positive Observations: Compound X undergoes mild oxidation and **decolourises purple alkaline $KMnO_4$**. **Brown ppt of MnO_2** seen.

Negative Observations: $KMnO_4$ remains purple and **no brown ppt seen** for Compound **Y**.

[Total: 20]

5 Iron is a lustrous, ductile, malleable, silver-grey metal. It is the most used of all metals and it exists in more than one oxidation state.

(a) Pale yellow aqueous iron(III) chloride undergoes the following reactions shown in Fig. 5.1.

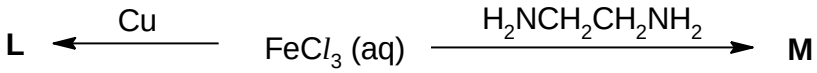


Fig. 5.1

(i) Explain why aqueous iron (III) chloride is coloured.

[3]

In aqueous solutions, each Fe^{3+} ion is surrounded by six H_2O ligands in an octahedral complex, $[Fe(H_2O)_6]^{3+}$.

- The **d orbitals of Fe^{3+} are split into two groups of different energy levels** by H_2O **ligands**.

- When white light shines on the complex, **a d electron undergoes d–d transition** and is **promoted to a higher energy vacant or partially filled d orbital.**

- During the transition, the d electron **absorbs light from the visible spectrum**. The colour observed is the **complementary colour of the wavelength absorbed**.

(ii) Solution **L** is formed when copper metal is added to iron(III) chloride solution.

By selecting appropriate $E^{\ominus}$ values from the *Data Booklet*, explain why the reaction occurs.

Hence, write a balanced ionic equation for this reaction.

[2]

From Data Booklet,

$Cu^{2+} + 2e^- \rightleftharpoons Cu$ $\quad E^\ominus = +0.34$ V

$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$ $\quad E^\ominus = +0.77$ V

$E^\ominus_{cell} = E^\ominus_{cathode} - E^\ominus_{anode} = +0.77 - (+0.34) = +0.43$ V > 0 (reaction is spontaneous)

$2Fe^{3+} + Cu \rightarrow 2Fe^{2+} + Cu^{2+}$

Fig. 5.2 shows how the colour intensity of a solution containing 0.01 mole of iron(III) chloride varies as increasing amounts of $H_2NCH_2CH_2NH_2$ is added.

The colour intensity due to the complex ion **M** formed is measured with a colorimeter. The colour intensity is directly proportional to the concentration of **M**.

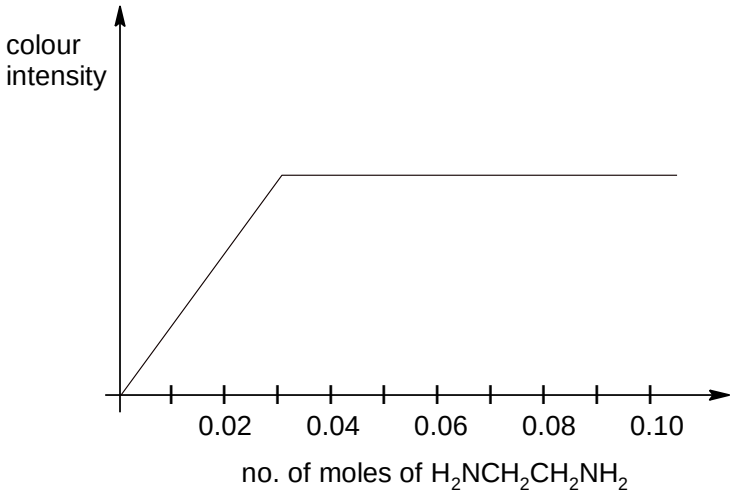


Fig. 5.2

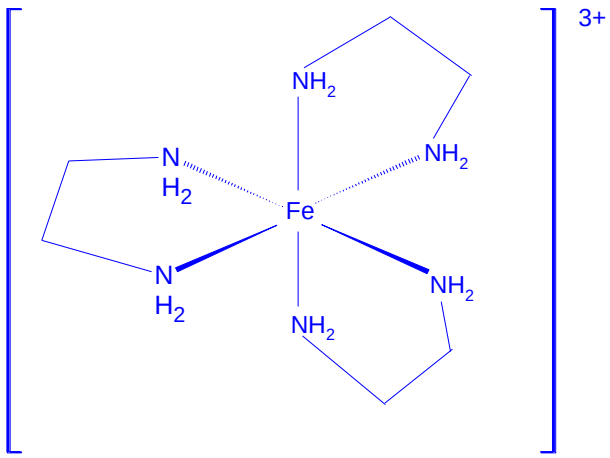
(iii) Use Fig. 5.2 to deduce the mole ratio of Fe^{3+} and $H_2NCH_2CH_2NH_2$ in complex **M**.

[1]

mole ratio of Fe^{3+} and $H_2NCH_2CH_2NH_2$ = **1: 3**

(iv) Draw the structure of complex **M.**

[1]



(b) Fig. 5.3 shows two reactions of benzylamine, one of which involves the use of solid $FeCl_3$ as a catalyst.

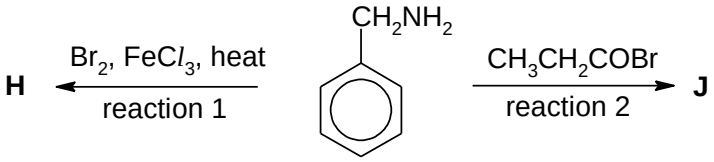
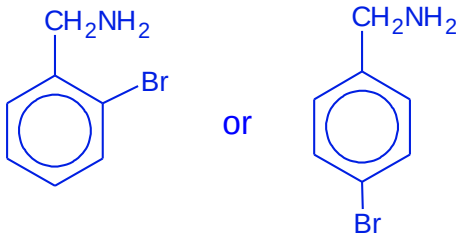


Fig. 5.3

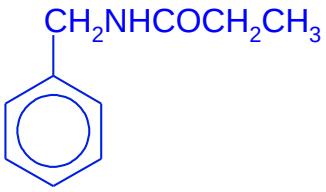
(i) Suggest the structures of compounds **H** and **J**.

[2]

H :



J :



(ii) Name the type of reaction for reaction 2.

[1]

Reaction 2 : Condensation

(iii) Name and draw a mechanism for reaction 1. Show clearly

- any intermediates that may be formed
- the movement of electron pairs by using curly arrows
- how $FeCl_3$ acts as a catalyst

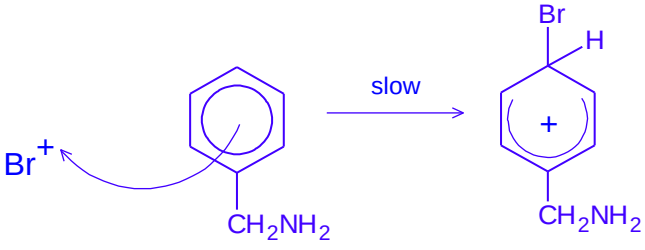
[3]

Name: Electrophilic Substitution

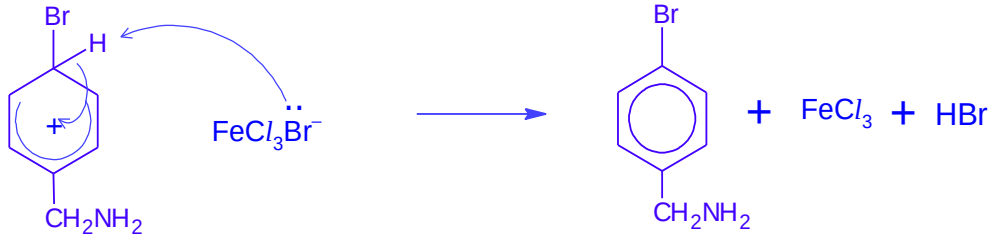
Generation of the electrophile, Br^+

$Br_2 + FeCl_3 \rightarrow FeCl_3Br^- + Br^+$

Step1



Step 2



(c) Hydrogen peroxide decomposes slowly in aqueous solution according to the following equation:

$$2H_2O_2(aq) \rightarrow 2H_2O(l) + O_2(g)$$

A H_2O_2 solution of original concentration of 4.66 mol dm^{-3} was placed in a bottle contaminated with Fe^{3+} ions for some time. The Fe^{3+} ions catalyse the decomposition of H_2O_2.

10 cm^3 of H_2O_2 is withdrawn from the contaminated bottle and the rate of decomposition is measured by collecting the oxygen gas produced over time at room temperature and pressure.

Fig. 5.4 shows the volume of oxygen gas produced recorded against time for this experiment.

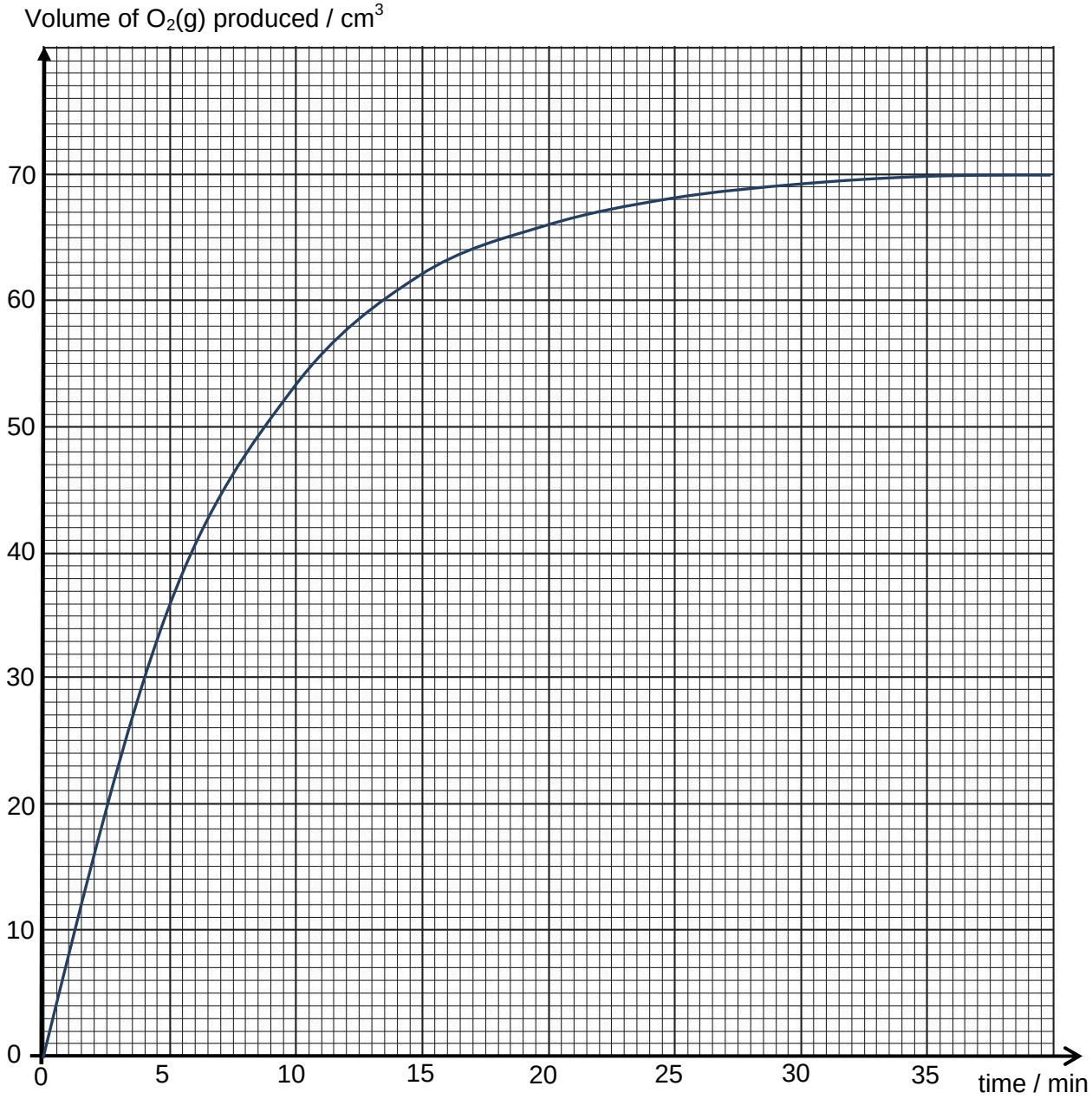


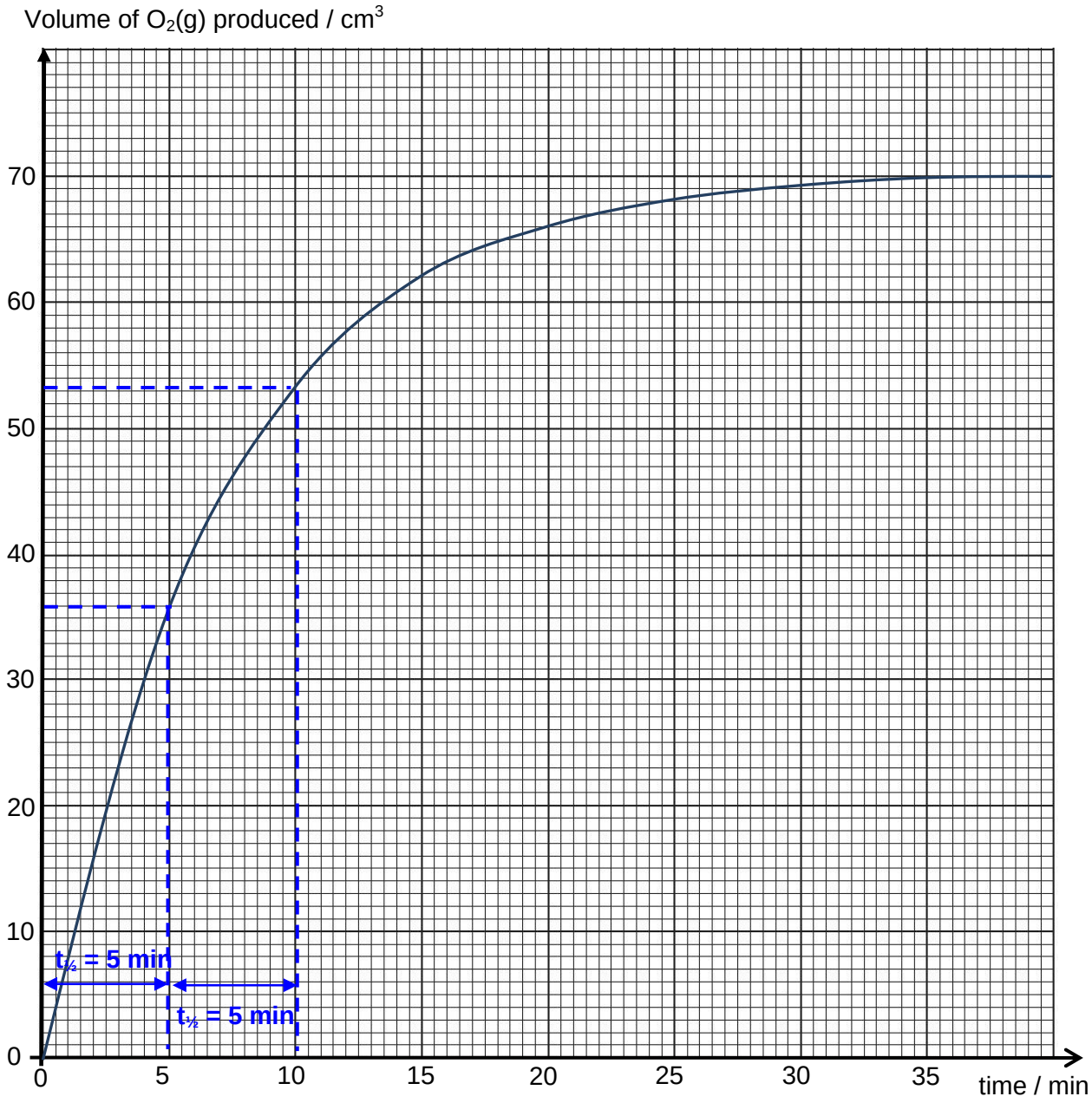
Fig. 5.4

(i) Using Fig. 5.4, prove that the reaction is first order with respect to hydrogen peroxide. Show your working clearly.

[2]

From Fig. 5.4, **half life is constant** at **5 min**, the reaction is first order w.r.t. H_2O_2.

Note: a total of 70 cm^3 of O_2(g) was produced, hence V_{max} = 70 cm^3.
The first half life is the time taken for volume of O_2(g) to increase from 0 cm^3 to ½ V_{max} = 35 cm^3; and the second half life is the time taken for volume of O_2(g) to increase from ½ V_{max} = 35 cm^3 to ¾ V_{max} = 52.5 cm^3.



(ii) Using your answer in **(c)(i)**, calculate the rate constant for the catalysed decomposition of hydrogen peroxide.

[1]

$t_{1/2} = \frac{\ln 2}{k}$

$k = \frac{\ln 2}{5} = 0.139\ min^{-1}$

(iii) Using Fig. 5.4, calculate the concentration of hydrogen peroxide at the start of this experiment. Hence, calculate how long the hydrogen peroxide had been in the contaminated bottle.

[3]

From Fig. 5.4,
a total of **70 cm^3 of O_2** gas has evolved.

No of moles of O_2 gas evolved at r.t.p = $\frac{70}{1000}$ **÷24 = 0.00292 mol**

No of moles of H_2O_2 in contaminated bottle = 0.00292 x 2 = 0.00583 mol
$[H_2O_2]$ withdrawn from contaminated bottle / at the start of experiment
$= 0.00583 \div \frac{10}{1000} =$ **$\underline{0.583\ mol\ dm^{-3}}$**

Since $[H_2O_2]_{before\ contamination} = 4.66\ mol\ dm^{-3}$

$$4.66\ mol\ dm^{-3} \xrightarrow{1^{st}\ t_{1/2}} 2.33\ mol\ dm^{-3} \xrightarrow{2^{nd}\ t_{1/2}} 1.165\ mol\ dm^{-3} \xrightarrow{3^{rd}\ t_{1/2}} 0.5825\ mol\ dm^{-3}$$

OR

Let *n* be the number of half–lives
$\left(\frac{1}{2}\right)^n = \frac{0.583}{4.66}$
n = 3

Time which the hydrogen peroxide had been in the contaminated bottle
= 5 x 3 = **$\underline{15\ min}$**

(iv) Suggest a method whereby the shelf-life of uncontaminated hydrogen peroxide solution could be increased.

[1]

Keep the **$\underline{hydrogen\ peroxide\ solution\ at\ low\ temperature}$** such as keeping them in the refrigerator. This will reduce the rate of decomposition of H_2O_2 by reducing rate constant.

[Total: 20]