Suggested Answers

TAMPINES MERIDIAN JUNIOR COLLEGE

JC2 PRELIMINARY EXAMINATION

CANDIDATE NAME	
CIVICS GROUP	

H2 CHEMISTRY

9729/03

Paper 3 Free Response

22 September 2021

2 hours

Candidates answer on Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name and Civics Group in the spaces at the top of the page.

Write in dark blue or black pen on the answer booklet.

You may use an HB pencil for any diagrams or graphs.

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

Section A
Answer **all** questions.

Section B
Answer **one** question.

A *Data Booklet* is provided.

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

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

For Examiners' Use		
Section A	Q1	/15
	Q2	/21
	Q3	/24
Section B	Q4	/20
	Q5	/20
Total		/80
Grade		

Section A

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

1 The *rate of reaction* between an unknown bromoalkane, RBr, and aqueous sodium hydroxide, NaOH, undergoing hydrolysis to form an alcohol can be investigated experimentally using phenolphthalein as an indicator.

A few drops of phenolphthalein were added to a sample of hot aqueous sodium hydroxide. An excess of bromoalkane was added to the mixture, shaken, and the relative rate was measured when the end of the reaction was observed.

The experiment was then repeated with various initial concentrations of the bromoalkane and aqueous sodium hydroxide. All experiments were carried out at the same temperature.

(a) (i) Explain what you understand by the term '*rate of reaction*'. [1]

(ii) Describe how the end of the experiment would be determined. [1]

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i) The rate of reaction is defined as the **change in the concentration of reactants or products per unit time.**

ii) When the **pink solution (phenolphathalein) turns colourless.**

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Table 1.1 below shows the results for the series of hydrolysis experiments.

Table 1.1

experiment	[RBr] / mol dm^{-3}	[NaOH] / mol dm^{-3}	relative rate
1	0.120	0.0400	0.0238
2	0.040	0.0400	0.00794
3	0.048	0.0800	0.00952
4	0.180	0.0200	***x***

(b) (i) Deduce the order of reaction for both RBr and NaOH. [2]

(ii) Hence write the overall rate equation for the reaction. [1]

(iii) Predict the relative rate, ***x***, for the reaction in experiment 4. [1]

(iv) It was determined that 20% of the RBr in experiment 1 was reacted in 4.6 s. Predict the time taken for the same percentage of RBr to be reacted in experiment 3, giving your reasoning. [2]

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i) Comparing **Experiments 1 & 2**, keeping **[NaOH] constant**,

When the **[bromoalkane] x 1/3, rate x 1/3, hence the order w.r.t. bromoalkane is 1.**

Comparing **Experiments 2 & 3,**

When the **[bromoalkane] x 6/5 & [NaOH] x 2, rate x 6/5.** Since the order of reaction w.r.t. bromoalkane is determined to be 1, **order w.r.t. NaOH is 0**.

(or use mathematical method for determination)

$$\frac{0.00794}{0.00952} = \frac{k[0.040]^1 \times [0.0400]^x}{k[0.048]^1 \times [0.0800]^x}$$

$x = 0$, **order w.r.t. NaOH is 0**

ii) Rate = k [bromoalkane]

iii) Comparing Experiments 1 & 4

Since [bromoalkane] x 1.5, relative rate = 0.0238 x 1.5 = **0.0357**

([NaOH] is ignored as it is independent of rate of reaction)

iv) The time taken for 20% of the bromoalkane to be reacted would **remain the same at 4.6 s** since the reaction is first order with respect to the bromoalkane, **half-life remains the same** and since the order of reaction with respect to NaOH is 0, changes to the **[NaOH] does not affect the rate of reaction**.

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(c) **(i)** Given that the identity of the bromoalkane is an aromatic chiral compound with the molecular formula C_8H_9Br, suggest a possible structure for the bromoalkane. [1]

(ii) The hydrolysis of the bromoalkane proceeds via a 2–step mechanism.

Name and describe the mechanism for the hydrolysis of the bromoalkane in aqueous sodium hydroxide. Show relevant lone pairs and dipoles, and use curly arrows to indicate the movement of electron pairs. [3]

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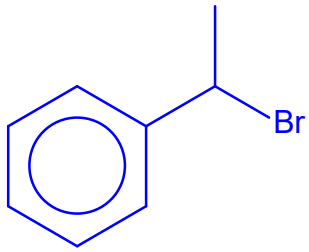
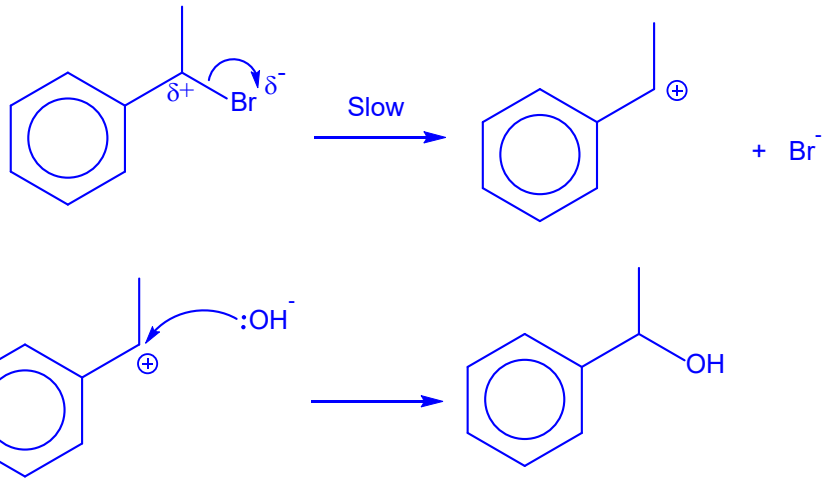
i)



ii) **Nucleophilic substation (S_N1)**



- **e⁻ movement for step 1**
- **e⁻ movement for step 2 + lone pair on OH^-**
- **Dipole for step 1**
- **Slow step**
- **Intermediate structure**
- **Balanced equations**

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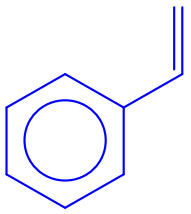
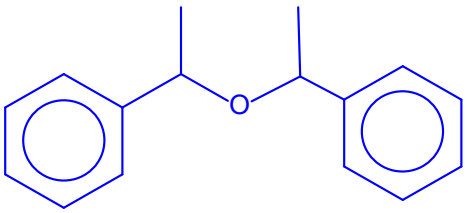
(iii) Based on the stability of the carbocation formed, suggest briefly why the bromoalkane proceeds via the mechanism proposed in **(c)(ii)**. [1]

(iv) Upon analysis of the final reaction mixture, it was found that the reaction mixture contained several organic side-products along with the production of the alcohol. One of the side-products was an alkene, while the other contained an ether (R–O–R) functional group.

Suggest the structures of these two side-products. [2]

iii) The **stability of the carbocation is increased** as the positive charge of the carbocation is dispersed **via delocalisation into the benzene ring.**

iv)  and 

[Total: 15]

2 *Ketamine* is a medication that is used to induce anaesthesia. It can relieve pain in humans and animals.

The following scheme shows a possible synthesis route of *Ketamine* from 1-bromo-2-chlorobenzene. Study Fig. 2.1 carefully and answer the questions that follow.

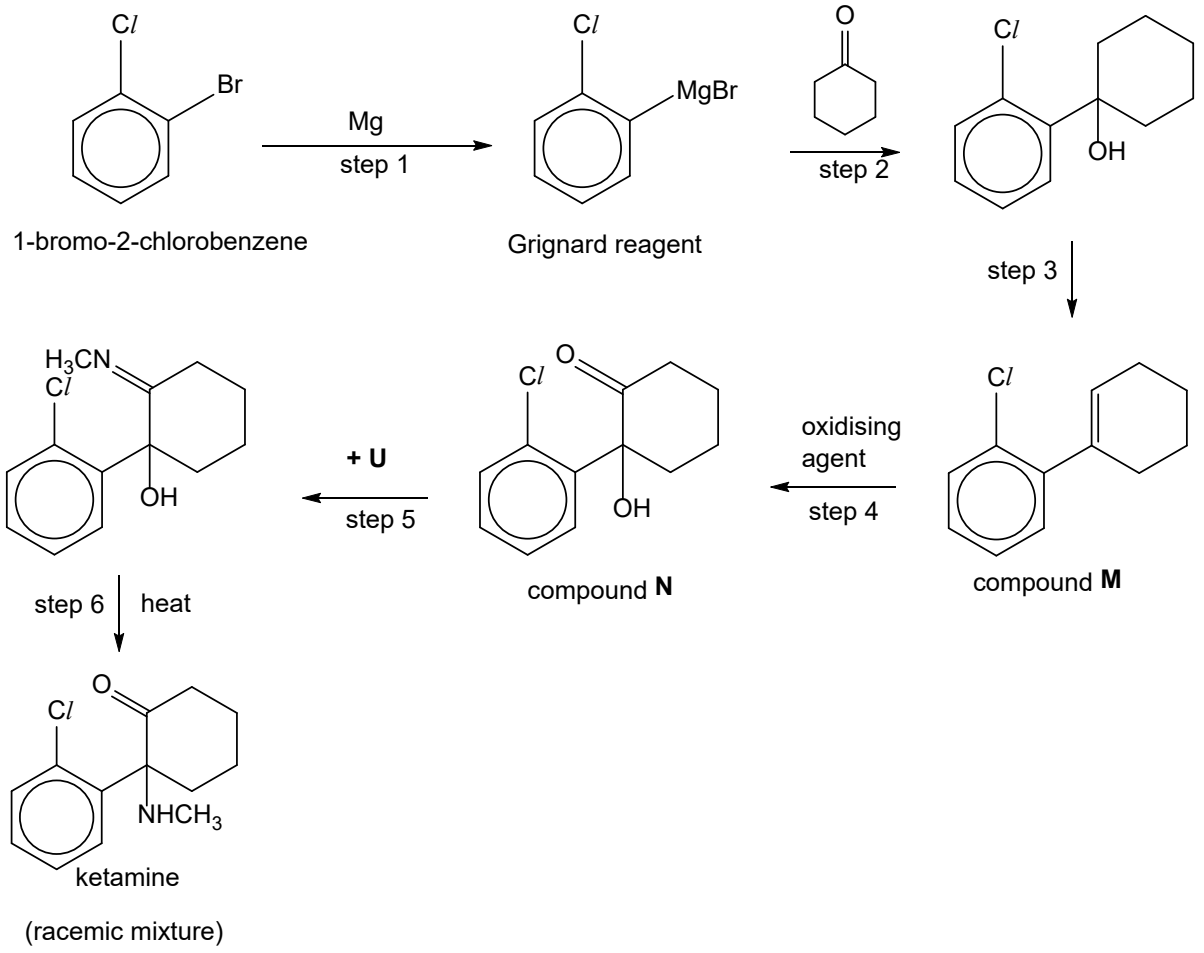


Fig. 2.1

(a) **(i)** Suggest the type of reaction that occurs in steps 2, 3 and 5. [3]

(ii) Suggest the identity of reagent **U** in step 5. [1]

i) **Step 2 – Nucleophilic addition**
Step 3 – elimination
Step 5 – condensation

ii) **CH_3NH_2**

(b) 1-bromo-2-chlorobenzene can be made from chlorobenzene and Br_2 with $AlBr_3$ as the catalyst.

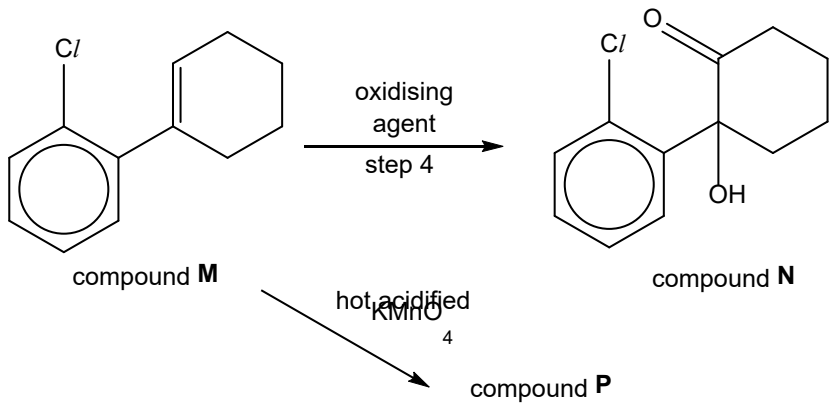
(i) Aside from acting as a catalyst, state and explain the other role of $AlBr_3$ in this reaction. [2]

(ii) Suggest why the reaction must be carried out using a dry solvent. [1]

i) **It is acting as the Lewis acid as it is acting as the electron pair acceptor to generate the electrophile, Br^+.**

ii) ii) $AlBr_3$ **dissolves in water** to form Fe^{3+} & Br^- and **destroy the catalyst** to generate the electrophile, Br^+.

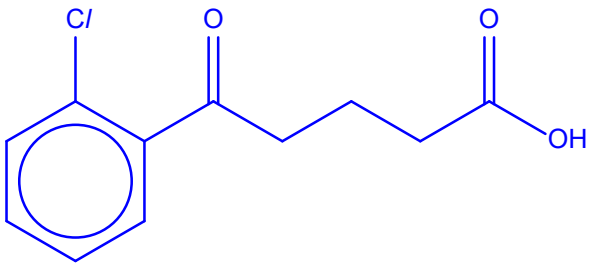
(c) If the oxidising agent used in Step 4 of Fig. 2.1 is hot acidified $KMnO_4$, compound **P** will be formed instead of compound **N** as shown below. Compound **P** gives white fumes with PCl_5.



(i) Draw the skeletal formula of compound **P**. [1]

(ii) Describe a simple chemical test to distinguish compounds **N** and **P**. State clearly the observations for each compound in the test. [2]

i)

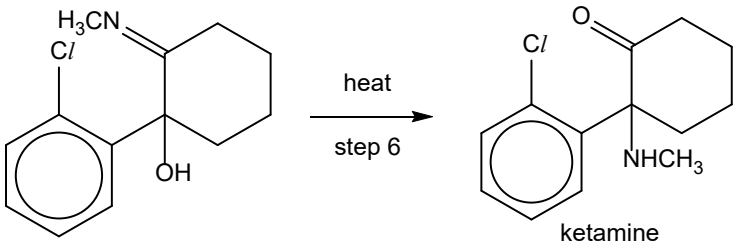


ii) **Test**: Add **aqueous or solid sodium carbonate** to the unknown compound.

Observation for compound P: Effervescence of CO_2 observed that forms a white ppt with $Ca(OH)_2$.

Observation for compound N: No effervescence of CO_2 observed, no white ppt with $Ca(OH)_2$.

(d) A *racemic mixture* of *Ketamine* is formed in step 6.



ketamine

(racemic mixture)

(i) Describe what is meant by the term *racemic mixture*. [1]

(ii) Draw the isomers of *Ketamine* formed in step 6. [2]

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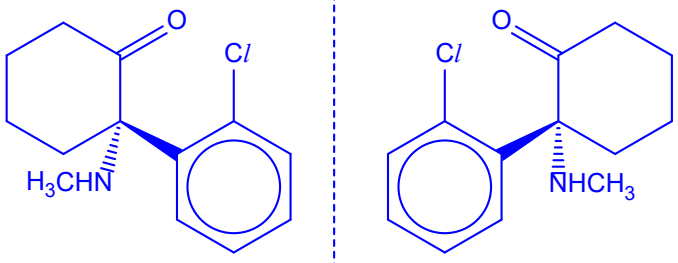
i) A **racemic mixture** is a mixture containing **equal amounts** of **each enantiomer**.



ii)

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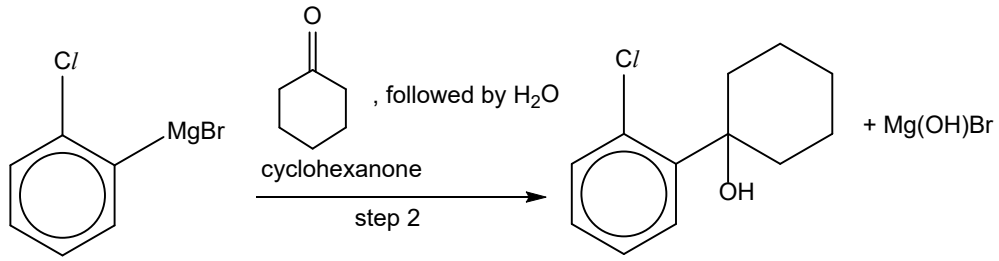
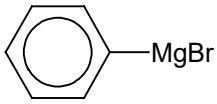
(e) Step 2 of the reaction involves the use of a Grignard reagent (organomagnesium halide) on cyclohexanone to generate the tertiary alcohol via a nucleophilic addition mechanism.



Grignard reagent

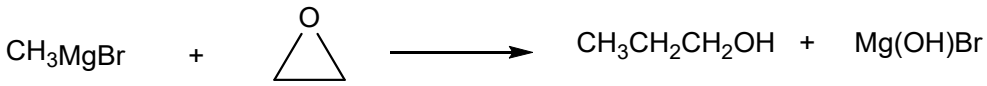
(i) Suggest the structural formula of the final organic product formed when

1. $(CH_3)_2CHMgBr$ reacts with CH_3CHO

2. 

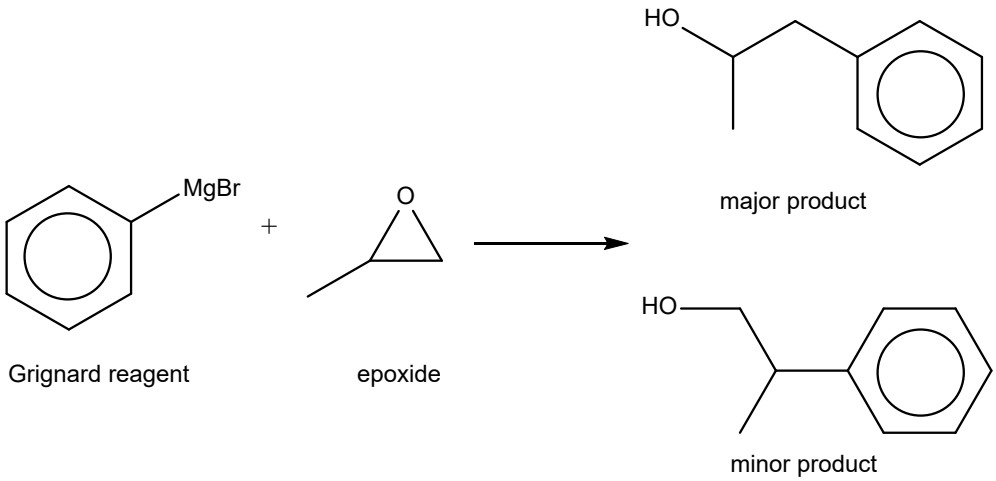
reacts with CO_2 [2]

(ii) It is also possible for a Grignard reagent to react with epoxides (3-membered cyclic ethers) via a substitution reaction.



Grignard reagent epoxide

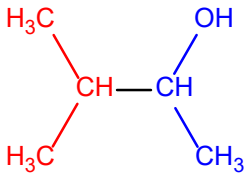
Suggest an explanation for the major product formed in the reaction below.

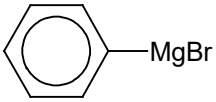


[1]

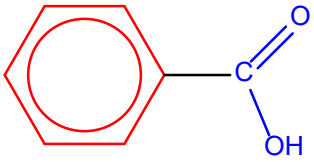
(iii) Draw the mechanism between cyclohexanone and HCN with cold NaOH. Show relevant lone pairs and dipoles, and use curly arrows to indicate the movement of electron pairs. [2]

i) **1.** $(CH_3)_2CHMgBr$ with CH_3CHO



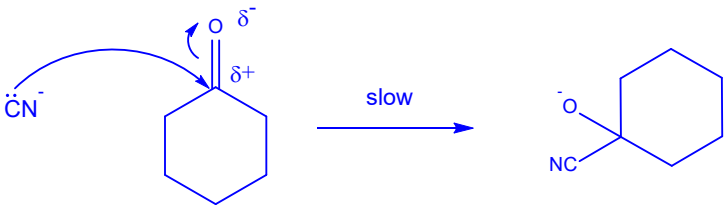
2. 

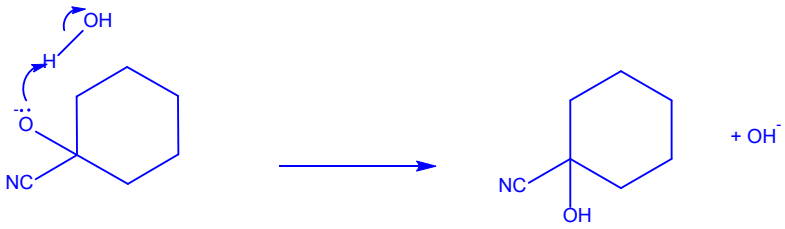
with CO_2



ii) There is **less steric hindrance** to attack **the less substituted side of** the epoxide.

iii)





(f) Table 2.2 shows the pK_b values of four nitrogen containing compounds, including *ketamine*.

Table 2.2

compound	pK_b
ethylamine	3.20
ammonia	4.75
ketamine	6.50
phenylamine	9.30

(i) Give an explanation for the different pK_b value for ethylamine, ammonia and phenylamine. [2]

(ii) Suggest a reason why the pK_b value for *ketamine* is so much higher than that for ethylamine. [1]

i) For ethylamine, the **electron-donating** (ethyl) group **increases** the **electron density of the lone electron pair on N atom**. Hence, the **lone electron pair on N atom** is **more available to accept a proton**. Hence ammonia has a larger pK_b value than ethylamine.

For phenylamine, the **lone pair of electrons** on the **nitrogen atom is delocalised into the benzene ring**. Hence **the lone pair on N atom** is **less available** to **accept a proton**. Hence phenylamine has a larger pK_b value than ammonia.

ii) For *ketamine*, the **electron withdrawing C=O or carbonyl group decreases the electron density of the lone pair on N atom**. Hence, **the lone pair on N atom is less available to accept a proton**. Hence *ketamine* has a larger pK_b value than ethylamine.

Or the **bulky R group** attach to nitrogen atom can cause **steric hindrance** and hence **the lone pair of electrons on N atom will be less available to accept protons**. Hence *ketamine* has a larger pK_b value than ethylamine.

[Total: 21]

3 The organisation of the Periodic Table can be used to derive relationships between various element properties. It is also used to predict chemical properties and behaviours of undiscovered elements.

(a) Fig. 3.1 shows the third ionisation energy of eight consecutive elements (**A** to **H**) in Periods 2 and 3 of the Periodic Table.

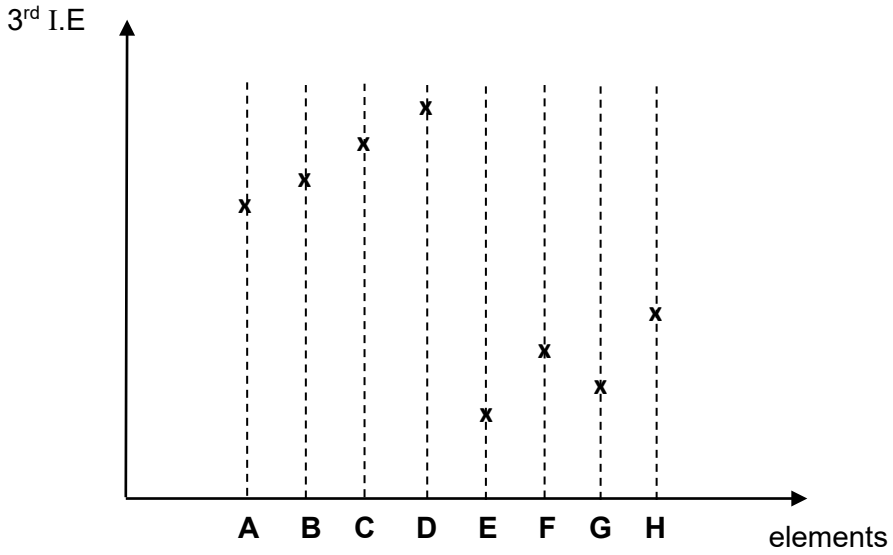


Fig. 3.1

(i) Write an equation for the third ionisation energy of element **B**. [1]

(ii) Using information from Fig. 3.1, identify element **E** and write its electronic configuration. [1]

(iii) Based on the electronic configuration of the species, explain the difference in the third ionisation energies of element **F** and element **G**. [1]

(iv) Draw and label the orbital in which the third electron is removed from in element **G**. [1]

The Periodic Table shows helium is placed at the top of Group 18.

(v) Suggest why helium could be placed at the top of Group 2. [1]

(vi) Suggest why helium is not placed at the top of Group 2, by comparing **one** physical property related to its structure. [1]

(a)(i) $B^{2+}(g) \rightarrow B^{3+}(g) + e$

(ii) **E** is aluminium / Al

$1s^2 2s^2 2p^6 3s^2 3p^1$

(iii) Electronic configuration:

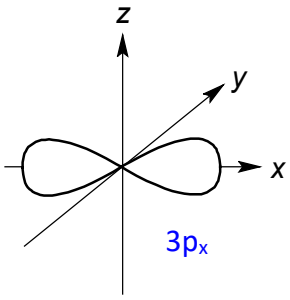
F^{2+} $[Ne]3s^2$ **G^{2+} $[Ne]3s^2 3p^1$**

A <u>smaller</u> amount of energy is required to remove the **<u>3p</u>** electron in **<u>G^{2+}</u>** which is of **<u>higher energy</u>** than **<u>3s</u>** electron in **<u>F^{2+}</u>**.

OR <u>3p</u> electron in **<u>G^{2+}</u>** is **<u>further away</u>** from the nucleus and **<u>experiences weaker electrostatic attraction to the nucleus</u>** than **<u>3s</u>** electron in **<u>F^{2+}</u>**.

Hence 3rd ionisation energy of **G** is lower than that of **F.**

(iv)



(v) Helium has $2s^2$ electron configuration. Like the Group 2 elements, helium has **<u>2 valence electrons</u>**.

(vi) Unlike **<u>Group 2 metals</u>** which are **<u>solids</u>** while **<u>helium</u>** is a **<u>gas</u>** at room temperature since **<u>helium</u>** has a much **<u>lower low melting point (or boiling point)</u>** than group 2 metals. (or Group 2 metals have **<u>higher melting point (or boiling point)</u>**.

(b) In an experiment, an impure copper strip containing only nickel and silver impurities was placed at the anode of an electrolytic cell, with a pure copper strip at the cathode and aqueous copper(II) sulfate as the electrolyte.

A current of 2.35 A was passed through the cell for 30.0 min, and the electrodes removed and weighed. It was found that the anode had lost 1.59 g of mass.

After filtration of the electrolyte, the deposit underneath the anode weighed 0.09 g. On adding an excess of dimethylglyoxime to the electrolyte, 0.68 g of a bright red solid complex with the formula $Ni(C_4H_7N_2O_2)_2$ was precipitated.

[M_r of $Ni(C_4H_7N_2O_2)_2$ is 288.7]

(i) Calculate the expected increase in mass of copper at the cathode. [2]

(ii) Calculate the actual mass of copper removed from the impure copper strip. [2]

(iii) Hence, or otherwise, determine the percentage purity by mass of the copper strip at the anode. [1]

(iv) Suggest how the experimental procedure for collection of the solids after the filtration of the electrolyte can be improved to increase the accuracy of the value calculated in **(b)(iii)**. [2]

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(b) (i)

Amount of Cu expected to be discharged $= \frac{I \times t}{n_e F} = \frac{2.35 \times 30 \times 60}{2 \times 96500}$

$= 0.02192$ mol

Increase mass of copper expected at the cathode = **0.02192** x 63.5

= **1.39 g**

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(b)(ii)

Amount of Ni oxidised at anode = no of moles of $Ni(C_4H_7N_2O_2)_2$

$$= \frac{0.68}{58.7+2(4\times12+7+2\times14+2\times16)} = \frac{0.68}{288.7}$$

$$= \mathbf{2.35 \times 10^{-3}\ mol}$$

Mass of Ni in alloy (anode) = $2.35 \times 10^{-3} \times 58.7$ = **0.138 g**

Mass of Ag = 0.09 g (given)

Mass of Cu = 1.59 – 0.09 – 0.138 = **1.36 g**

(iii) % purity of copper = $\frac{1.36}{1.59} \times 100$ = **85.5%**

(iv)

Any one of the suggestion below is acceptable for mass measurement:

- **Ag (sludge) and $Ni(C_4H_7N_2O_2)_2$** collected could be **heated to consistent mass** to ensure **all water is driven off**. This will ensure that the **mass of solid measured is that of dry mass** of Ag and $Ni(C_4H_7N_2O_2)_2$.
- Since the **mass of Ag** (sludge) is rather **small**, use **electronic balance of higher precision** in order to **reduce % uncertainty in mass measurement.**

(c) Copper is an unreactive metal that does not react directly with dilute acids. Thus, the enthalpy change of reaction, ΔH_r, as shown below, cannot be determined directly.

$$Cu(s) + H_2SO_4(aq) \longrightarrow CuSO_4(aq) + H_2(g) \quad \Delta H_r$$

In order to determine a value for ΔH_r, the enthalpy change of reaction for two reactions are needed. One of these reactions involves adding a reactive metal M to dilute sulfuric acid.

$$nM(s) + H_2SO_4(aq) \longrightarrow M_nSO_4(aq) + H_2(g) \quad \Delta H_1$$

The other reaction is a displacement of copper from aqueous copper(II) sulfate, $CuSO_4(aq)$, using metal M.

$$nM(s) + CuSO_4(aq) \longrightarrow M_nSO_4(aq) + Cu(s) \quad \Delta H_2$$

The value for the enthalpy change of the displacement reaction ΔH_2 can be determined using a simple calorimeter shown in Fig 3.2. The following experiment was carried out and the metal M used in this experiment can be assumed to be in excess.

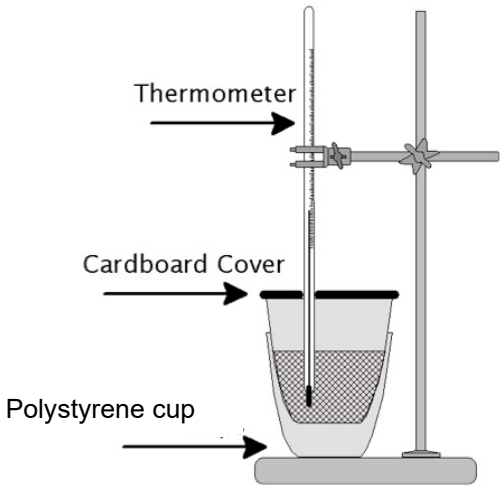


Fig 3.2

In the experiment, 15.9 g of metal M was added into 50.9 cm^3 of 0.300 mol dm^{-3} $CuSO_4(aq)$ in a polystyrene cup. The temperature of the resulting solution increased from 25.0 °C to 60.0 °C.

The polystyrene cup used in the experiment can also absorb heat, hence a separate experiment was performed and the heat capacity of the polystyrene cup was found to be 9.7 J K^{-1}.

(i) Based on the given information, calculate the value of ΔH_2 in kJ mol^{-1}.

You may take the density of the solution to be 1.00 g cm^{-3}, and the specific heat capacity of the solution to be 4.18 J g^{-1} K^{-1}. [2]

(ii) Hence, or otherwise, determine the value of ΔH_r, given that ΔH_1 is –466.9 kJ mol^{-1}. [2]

(c)(i) Amount of heat evolved = $mc\Delta T + C\Delta T$

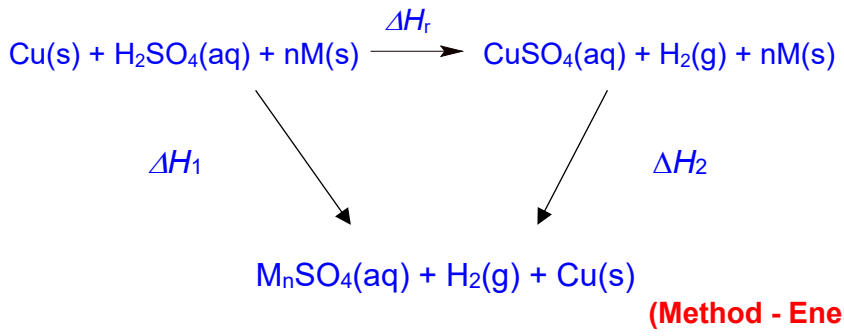
= **(50.9 x 4.18 x (60.0 – 25.0)) + (9.7 x (60.0 – 25.0))**

= **7786.17 J**

$n(CuSO_4)$ = 50.9/1000 x 0.3 = 0.01527 mol

$$\Delta H_2 = -\frac{7786.17}{0.01527 \times 1000} = \underline{\textbf{–509.9 kJ mol}^{-1}}$$

(ii)



(Method - Energy cycle)

OR Algebra method

(1) $nM(s) + H_2SO_4(aq) \longrightarrow M_nSO_4(aq) + H_2(g)$ ΔH_1

(2) $nM(s) + CuSO_4(aq) \longrightarrow M_nSO_4(aq) + Cu(s)$ ΔH_2

Equation (1) - (2)

$Cu(s) + H_2SO_4(aq) + nM(s) \longrightarrow CuSO_4(aq) + H_2(g) + nM(s)$ ΔH_r

By Hess' law,

$\Delta H_r = \Delta H_1 - \Delta H_2$

= – 466.9 – (–509.9) = – 43.0 kJ mol^{-1}

(iii) The $E^{\ominus}$ values of some redox reactions are shown below in Table 3.3.

Table 3.3

reaction	$E^{\ominus}$ / V
$Ag^+ + e^- \rightleftharpoons Ag$	+0.80
$Na^+ + e^- \rightleftharpoons Na$	–2.71
$Cu^{2+} + 2e^- \rightleftharpoons Cu$	+0.34
$2H^+ + 2e^- \rightleftharpoons H_2$	+0.00
$Mg^{2+} + 2e^- \rightleftharpoons Mg$	–2.38

Based on the list above, magnesium was chosen to be the most suitable metal M in both reactions to find ΔH_1 and ΔH_2. Give two reasons to explain why magnesium was chosen instead of silver and sodium. [2]

(c)(iii)
Na and Mg can undergo both reactions but **Ag cannot**.

Ag is not suitable as it cannot be oxidised by Cu^{2+} and H^+ since

- **$E^{\ominus}(Ag^+/Ag)$ is more positive** than **$E^{\ominus}(H^+/H_2)$ and $E^{\ominus}(Cu^{2+}/Cu)$** in both reactions 1 and 2.
  (Accept $E^{\ominus}_{cell}$ calculation to prove that reactions are not feasible.)

Ag & H^+
$E^{\ominus}_{cell} = E^{\ominus}_{Red} – E^{\ominus}_{ox}$
$= 0 – 0.80$
$= – 0.80 < 0$ (not feasible)

Ag & Cu^{2+}
$E^{\ominus}_{cell} = E^{\ominus}_{Red} – E^{\ominus}_{ox}$
$= 0.34 – 0.80$
$= – 0.46 < 0$ (not feasible)

- The **$E^{\ominus}(Na^+/Na)$ and $E^{\ominus}(Mg^{2+}/Mg)$ values** are **more negative/less positive** than **$E^{\ominus}(H^+/H_2)$ and $E^{\ominus}(Cu^{2+}/Cu)$**, hence they can be oxidised in both reactions 1 and 2.
  (Accept $E^{\ominus}_{cell}$ calculation to prove that reactions are feasible.)

Na & H^+
$E^{\ominus}_{cell} = E^{\ominus}_{Red} – E^{\ominus}_{ox}$
$= 0 – (-2.71)$
$= + 2.71 > 0$ (feasible)

Na & Cu^{2+}
$E^{\ominus}_{cell} = E^{\ominus}_{Red} – E^{\ominus}_{ox}$
$= 0.34 – (-2.71)$
$= +3.05 > 0$ (feasible)

Mg & H^+
$E^{\ominus}_{cell} = E^{\ominus}_{Red} – E^{\ominus}_{ox}$
$= 0 – (-2.38)$
$= + 2.38 > 0$ (feasible)

Mg & Cu^{2+}
$E^{\ominus}_{cell} = E^{\ominus}_{Red} – E^{\ominus}_{ox}$
$= 0.34 – (-2.38)$
$= +2.72 > 0$ (feasible)

- Although $E^{\ominus}(Na^+/Na)$ is more negative/less positive than $E^{\ominus}(Mg^{2+}/Mg)$ implying oxidation of Na is more favourable, **Na is not suitable as it reacts too vigorously with acid** but reaction of Mg with acid is slow.

Hence, Mg is the most suitable metal.

(d) Nickel naturally exists as mineral ores in the crust of the Earth. One such mineral is gaspéite, which contains mainly nickel(II) carbonate, $NiCO_3$, with impurities such as oxides and carbonates of zinc and magnesium.

To extract the nickel from gaspéite, the mineral is first heated strongly to convert metal carbonates to metal oxides. The enthalpy change for the thermal decomposition of metal carbonates can be determined using the *lattice energy* of the ionic solids.

The enthalpy change of some reactions are given in Table 3.4.

Table 3.4

$CO_2(g) + O^{2-}(g) \rightarrow CO_3^{2-}(g)$	-1148 kJ mol^{-1}
lattice energy of NiO(s)	-3870 kJ mol^{-1}
lattice energy of $NiCO_3$(s)	-2980 kJ mol^{-1}

(i) Define the term *lattice energy*. [1]

(ii) Explain why the lattice energy of NiO is more exothermic than that of $NiCO_3$. [1]

(iii) Construct a fully labelled energy cycle and hence calculate the standard enthalpy change of thermal decomposition of $NiCO_3$. [3]

.....

(d)(i)
The lattice energy of an ionic compound is **the energy released** when **one mole** of the **solid ionic compound** is formed from its **constituent gaseous ions** at **298 K and 1 bar**.

(ii)

|Lattice energy| $\propto \left|\frac{q_+q_-}{r_+ + r_-}\right|$

Ionic radius : O^{2-} < CO_3^{2-} where r^+ , q^+ and q^- are constant

Hence, the lattice energy of NiO is more exothermic.

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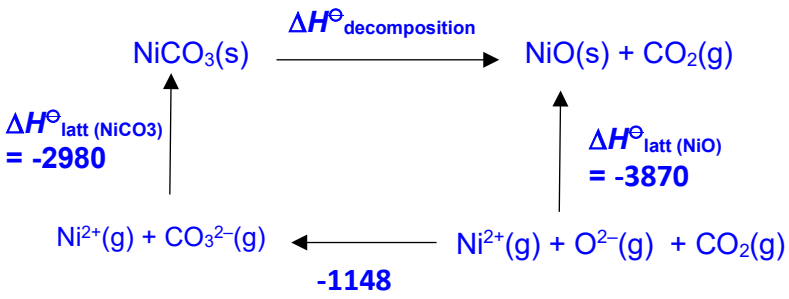
(d)(iii)



Energy cycle

- cycle shows all correctly linked balanced equations with state symbols
- cycle shows correctly assigned enthalpy changes (denote either with symbol or values)

By Hess' law

$-1148 - 2980 + \Delta H^{\ominus}_{decomposition} = -3870$

$\Delta H^{\ominus}_{decomposition} = -3870 + 2980 + 1148$

$= \mathbf{+258\ kJ\ mol^{-1}}$

[Total: 24]

Section B

Answer **one** question from this section.

4 Dinitrogen tetroxide, N_2O_4, and nitrogen dioxide, NO_2, exist in dynamic equilibrium with each other.

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

(a) (i) Explain what is meant by *dynamic equilibrium*. [1]

(ii) 0.0500 mol of N_2O_4 was placed in a sealed vessel of volume 1.00 dm^3 and at a temperature of 50 °C. The resultant equilibrium mixture had a pressure of 1.68×10^5 Pa, and a mass of 4.600 g.

Calculate the average relative molecular mass, M_r, of the resulting equilibrium mixture. [2]

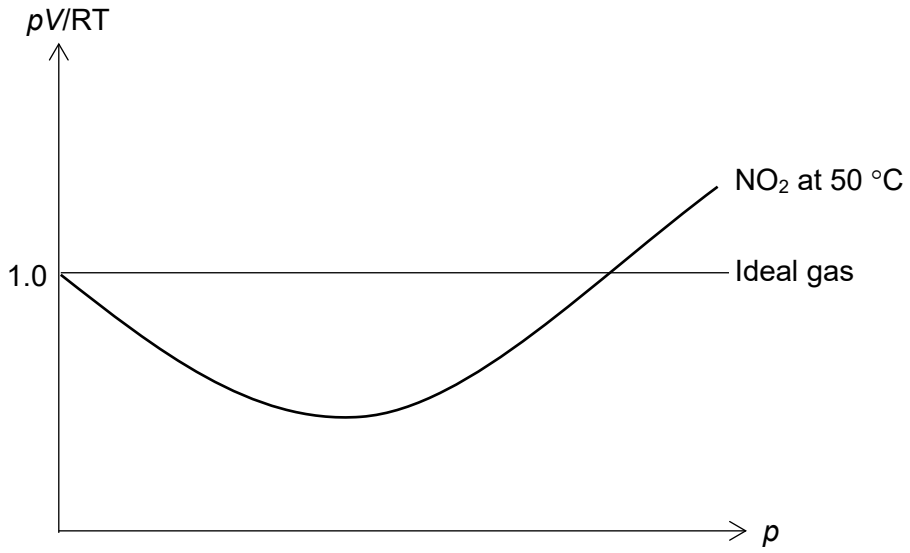
(iii) In this equilibrium mixture, the mole fraction of NO_2 is 0.400. Determine the degree of dissociation, α, of the N_2O_4 sample at equilibrium. [2]

(iv) Write the expression for the equilibrium constant, K_p, for this equilibrium. [1]

(v) Calculate the equilibrium constant, K_p at 50 °C. [2]

(vi) 0.0500 mol of N_2O_4 was placed in in a larger vessel at the same temperature, and allowed to reach equilibrium. Suggest, with reasoning, whether there will be any change to the equilibrium composition compared to the original system. [1]

(vii) The value of pV/RT is plotted against p for one mole of an ideal gas and one mole of NO_2 gas at 50 °C, where p is the pressure and V is the volume of the gas.



On the same axes, sketch the variation of pV/RT against p for one mole of NO_2 at 100 °C. Briefly explain your answer. [2]

i) Dynamic equilibrium is reached when the **rate of forward reaction equals the rate of backward reaction** in a **reversible reaction.**

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

$(1.68 \times 10^5)(1.00 \times 10^{-3}) = \frac{4.606}{M}(8.31)(273 + 50)$

$M = 73.58$

M_r = **73.6**

iii) Let the degree of dissociation be ***a***.

	$N_2O_4(g) \rightleftharpoons 2NO_2(g)$	
Initial moles	0.0500	0
Change in moles	$-0.0500a$	$+2(0.0500a)$
Eqm moles	$0.0500 - 0.05a$	$0.1a$

Total moles = $(0.0500 - 0.05a) + a = 0.0500 + 0.05a$

Since mole fraction of NO_2 is 0.400,

$\frac{0.1a}{0.0500 + 0.05a} = 0.400$

$0.1a = 0.0200 + 0.02a \Rightarrow a = 0.250$

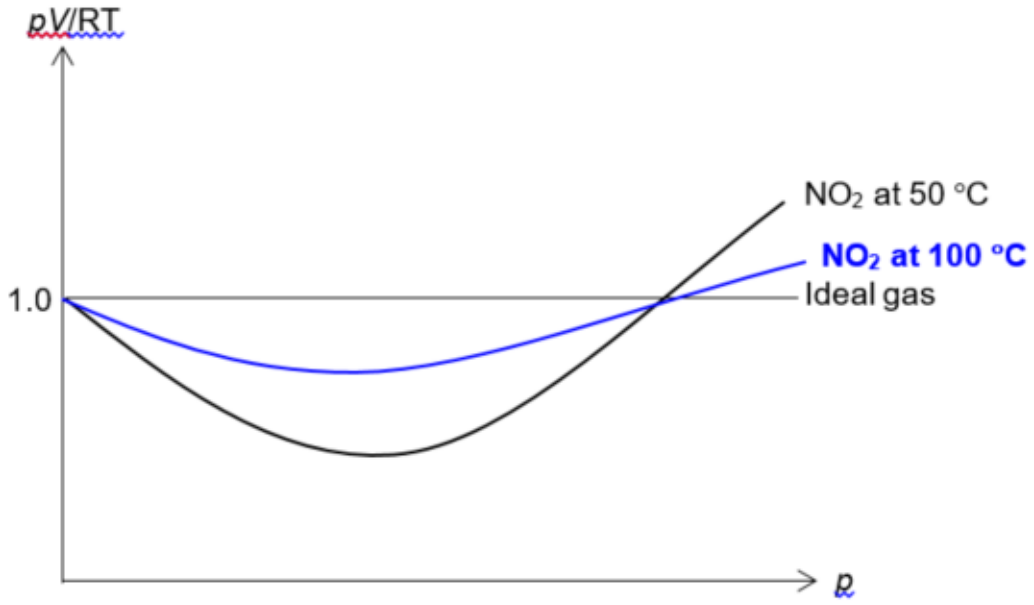
iv) $K_p = \frac{(p_{NO_2})^2}{p_{N_2O_4}}$

v) $K_p = \frac{(0.400 \times 1.68 \times 10^5)^2}{(1 - 0.400) \times 1.68 \times 10^5}$

= **44800 Pa**

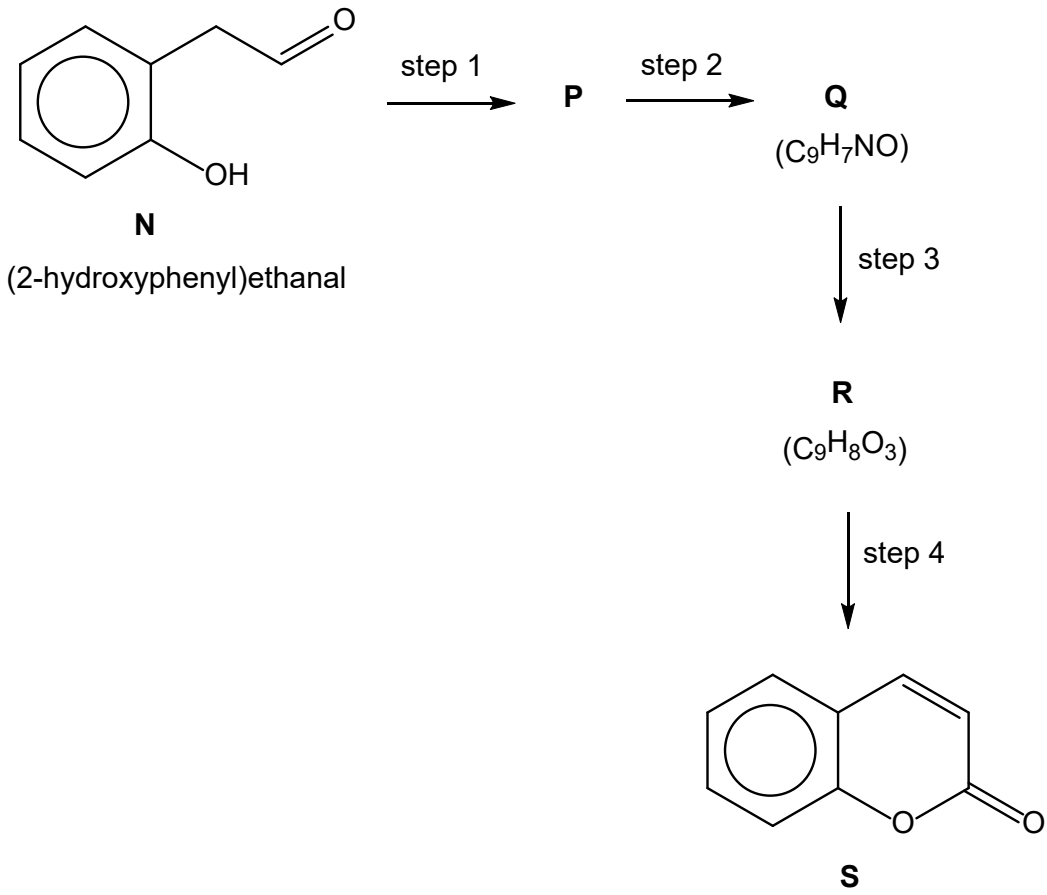
vi) When a larger vessel is used, **pressure of system decreases**. By Le Chatelier's Principle, the position of **equilibrium shifts to the right** to **increase the moles of gaseous particles**. Hence, the **equilibrium mixture** will have **more NO_2 and less N_2O_4** compared to the original system.

vii)



At 100°C, **NO_2 molecules have more energy** and **experiences weaker** (**OR** able to overcome) **intermolecular instantaneous dipole-induced dipole attractions**, Hence, NO_2 **deviate less from the ideal gas assumption** that gaseous particles have negligible intermolecular forces of interaction.

(b) Compound **S** can be synthesised from compound **N**, (2-hydroxyphenyl)ethanal, by a four-step synthesis route shown in Fig. 4.1.



N
(2-hydroxyphenyl)ethanal

S

Fig. 4.1

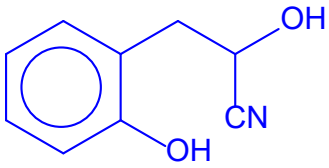
(i) State the reagents and conditions required for each step and suggest structures for the organic compounds **P**, **Q** and **R**. [7]

(ii) A chemist carried out step 1 of the synthesis. After leaving the reactants to react for several hours, he wanted to determine whether the reaction had reached completion.

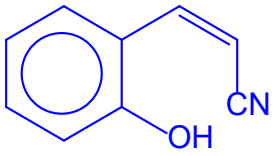
Suggest a simple chemical test that could be carried out for this purpose. State the expected observation if the reaction is complete. [2]

i) Step 1: **HCN, trace NaCN** (or NaOH), **cold**
Step 2: **Al_2O_3, heat** (or excess conc. H_2SO_4, heat)
Step 3: **H_2SO_4(aq), heat**
Step 4: anhydrous **PCl_5** (or **$SOCl_2$**)

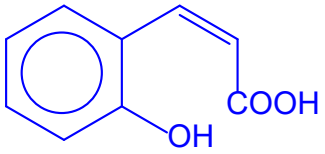
P:



Q:



R:



ii) To a sample of the reaction mixture, add **2,4-DNPH** and **warm**.
If the reaction is complete, **no orange precipitate** will be observed.

[Total: 20]

5 Three separate samples of white powder containing MgO, Al_2O_3 and SiO_2 were incorrectly labelled.

(a) (i) State the pH of the resultant solution when MgO is dissolved in water. [1]

(ii) Describe **two** simple chemical tests that could be used to distinguish the three oxides from one another. State the expected observation for each oxide in each test. [3]

i) **pH 9**

ii) Test 1: Add **aq NaOH** to each of the 3 samples.
Observation:
The sample that **dissolved to form colourless solution is Al_2O_3**.
The samples that **did not dissolve are MgO and SiO_2**.
(SiO_2 only dissolves if hot conc NaOH is used)

Test 2: Add **aq HCl or H_2SO_4/ HNO_3** to each of the 2 remaining samples that did not dissolve in aq NaOH.
Observation:
The samples that **dissolved to form colourless solution is MgO**
The sample that **did not dissolve/react is SiO_2.**

Or can present in table format.

	MgO	Al_2O_3	SiO_2
aq NaOH	**did not dissolve**	**dissolved to form colourless solution**	**did not dissolve**
aq HCl /H_2SO_4/ HNO_3	**dissolved to form colourless solution**	**dissolved to form colourless solution**	**did not dissolve**

Understanding that:
MgO only dissolves in aqueous acid
SiO_2 does not dissolve in both aqueous acid and base
Al_2O_3 dissolves in both aqueous acid and base

(b) Magnesium hydroxide, $Mg(OH)_2$, is sparingly soluble in water and is used in suspension as either an antacid or a laxative.

$$Mg(OH)_2(s) \rightleftharpoons Mg^{2+}(aq) + 2OH^-(aq)$$

(i) Write an expression for the K_{sp} of $Mg(OH)_2$ stating its units. [1]

(ii) The pH of a saturated aqueous solution of $Mg(OH)_2$ at 25 °C is 10.35. Calculate the solubility of $Mg(OH)_2$ at 25 °C. [2]

(iii) Hence, or otherwise, calculate the value of K_{sp} of $Mg(OH)_2$ at 25 °C. [1]

(iv) State and explain how the solubility of $Mg(OH)_2$ is affected by the addition of a small amount of HC*l* solution. [2]

(v) The thermal decomposition of Group 2 metal hydroxides is similar to the carbonates, producing metallic oxides and water. Table 5.1 shows the minimum temperature required to thermally decompose three Group 2 hydroxides.

Table 5.1

	decomposition temperature / °C
$Mg(OH)_2$	332
$Ca(OH)_2$	512
$Ba(OH)_2$	800

Explain the trend in the thermal decomposition temperatures shown in Table 5.1. [2]

i) $K_{sp} = [Mg^{2+}][OH^-]^2$ mol^3 dm^{-9}

ii) pOH= 14 –10.35 = 3.65

$[OH^-] = 10^{-3.65} = 2.239 \times 10^{-4}$ mol dm^{-3}

$Mg(OH)_2(s) \rightleftharpoons Mg^{2+}(aq) + 2OH^-(aq)$

s s 2s

$2s = 2.239 \times 10^{-4}$ mol dm^{-3}

Solubility of $Mg(OH)_2$ = s $= \frac{2.239 \times 10^{-4}}{2}$

$= 1.119 \times 10^{-4}$

$= 1.12 \times 10^{-4}$ mol dm^{-3}

iii) K_{sp} $= [Mg^{2+}][OH^-]^2$
$= (1.119 \times 10^{-4}) (2.239 \times 10^{-4})^2$
$= \underline{5.61 \times 10^{-12}}$ $mol^3\ dm^{-9}$

iv) $Mg(OH)_2(s) \rightleftharpoons Mg^{2+}(aq) + 2OH^-(aq)$ (1)

When HC*l* is added, the **$\underline{H^+}$** ions undergoes **neutralisation** (or reacts) with **$\underline{OH^-}$** thus $[OH^-]$ decreases. **Equilibrium position of (1) shifts to the right,** thus **solubility of $Mg(OH)_2$ will increase** .

v) Down Group 2 from Mg^{2+} to Ba^{2+},

- **Cation size increases**.
- **Charge density and polarising of cation decreases**,
- **Ability of cation to distort OH^- electron cloud and weaken O–H bond decreases**,
- Thus **thermal stability** and thus decomposition temperature of Group 2 hydroxides **increases**.

(c) Chloramphenicol is an antibiotic used for the treatment of bacterial infections. The following scheme shows possible reactions involving chloramphenicol. Study Fig. 5.2 carefully and answer the questions that follow.

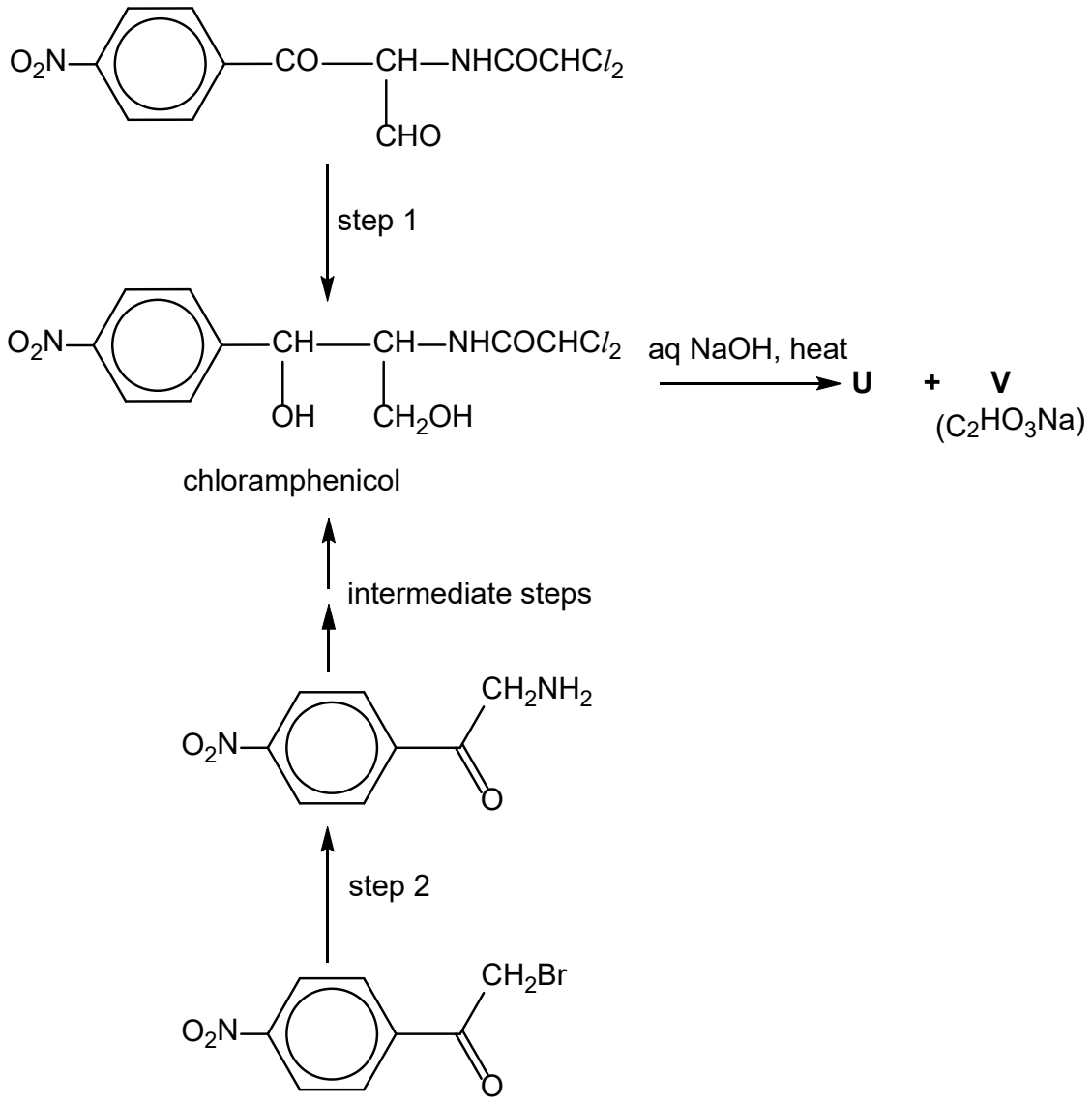


Fig. 5.2

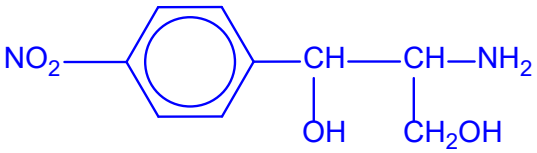
(i) Suggest reagents and conditions for step 1. [1]

(ii) Suggest the structures of organic products **U** and **V**. [2]

(iii) Step 2 represents one of the possible initial steps in the synthesis of chloramphenicol. State the type of reaction in step 2. [1]

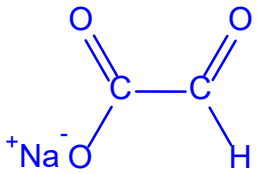
i) $NaBH_4$ in ethanol (cannot use LiA/H_4 as it will reduce the amide)
Or H_2 with Pd
Or H_2 with Ni and heat

ii)



U

and



V

iii) Nucleophilic Substitution

(d) **W** ($C_9H_{11}NO_2$) is soluble in dilute HC*l* but insoluble in dilute NaOH. When heated with I_2 in aqueous NaOH, **W** formed 2 organic salts **X** ($C_7H_6NO_2Na$) and **Y,** together with a yellow precipitate **Z**. Acidification of **Y** formed CH_2O_2. 1 mol of **X**, reacts with 3 mol of aqueous bromine. Suggest the structures of **W**, **X**, **Y** and **Z**. [4]

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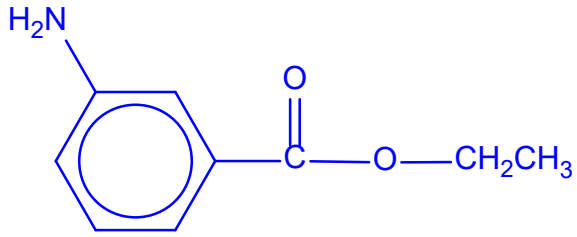
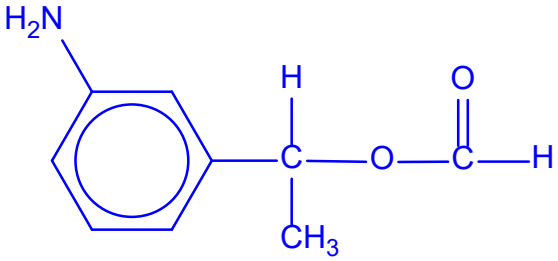
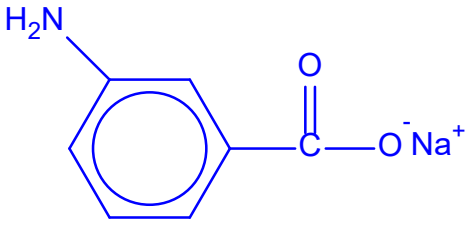
W



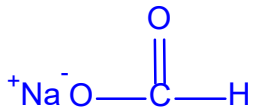


Alternative structure:

X



Y



Z CHI_3

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[Total: 20]