EUNOIA JUNIOR COLLEGE
JC2 Preliminary Examination 2020
General Certificate of Education Advanced Level
Higher 2

CANDIDATE NAME	

CIVICS GROUP	1	9	–			INDEX NUMBER		

CHEMISTRY

Paper 3 Free Response

9729/03

17 September 2020

2 hours

Candidates answer on the Question Paper

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name, civics group, index number on all the work you hand in.
Write in dark blue or black pen.
You may use an HB pencil for any diagrams or graphs.
Do not use staples, paper clips, glue or correction fluid.

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

Section B
Answer **one** question.

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

At the end of the examination, fasten all your work securely together.
The number of marks is given in brackets [ ] at the end of each question or part question.

For Examiner's Use	
Paper 3	
1	/ 22
2	/ 19
3	/ 19
4	/ 20
5	/ 20
Total	/ 80

This document consists of **32** printed pages.

Section A

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

1 (a) Describe and explain the trend observed in the thermal stabilities of the carbonates of Group 2 elements. [3]

(b) (i) Elements in period 3 can react with chlorine gas to form different chlorides. State the types of bonding in the chlorides of sodium, aluminium and silicon. [1]

(ii) Write appropriate equations to illustrate the reactions, if any, when separate samples of sodium chloride, aluminium chloride and silicon chloride were added to excess water. [3]

(i) **Size of cations** increases down the group, leading to a decrease in **charge density** and **polarising power of the cations**. The **ability of cations to distort the electron cloud of** CO_3^{2-} decreases, weakening the **C–O bond** to a lesser extent. Hence, **thermal stability of Group 2 carbonates increases down the group**.

(ii) Sodium chloride: **ionic bonding**; Aluminium chloride and silicon chloride: **covalent bonding** (accept id-id)

(iii) Sodium chloride does not react with water but merely dissolves in it.

$NaCl$ (s) + aq → Na^+ (aq) + Cl^- (aq)

Aluminium chloride dissolves in water to give cations of high charge densities.

$AlCl_3$ (s) + $6H_2O$ → $[Al(H_2O)_6]^{3+}$ (aq) + $3Cl^-$ (aq)

The aqua complexes of these ions hydrolyse in water to give an acidic solution.

$[Al(H_2O)_6]^{3+}$ (aq) + H_2O (l) ⇌ $[Al(H_2O)_5(OH)]^{2+}$ (aq) + H_3O^+ (aq)

Silicon tetrachloride hydrolyses in water to give a strong acid:

$SiCl_4$ (aq) + $2H_2O$ (l) → SiO_2 (s) + 4HCl (aq)

(c) Acids, bases and buffers play important roles in balancing biological systems.

(i) Explain what is meant by the term *buffer solution*.
Write equations to explain how an aqueous solution of ammonia and an ammonium salt maintains the pH when a little acid or base is added into it. [3]

(ii) Calculate the pH of the solution formed when 48 cm^3 of gaseous ammonia (K_b of ammonia = 1.8×10^{-5} mol dm^{-3}) is channeled into 20 cm^3 of 0.05 mol dm^{-3} of sulfuric acid at room temperature and pressure.

Hence, predict the colour observed when a few drops of thymolphthalein is added to the resulting solution. [3]

(i) A buffer solution is one which is **able to resist pH change** when **a little acid or base is added**.

The buffer contains a large reservoir of NH_3 and NH_4^+.

When a little acid is added, the NH_3 will react with it to give NH_4^+, hence $[H^+]$ in the solution is maintained. **$NH_3 + H^+ \rightarrow NH_4^+$**

When a little base is added, the NH_4^+ will react with it to give NH_3 and H_2O, hence $[OH^-]$ in the solution is maintained. **$NH_4^+ + OH^- \rightarrow NH_3 + H_2O$**

(ii) amount of $NH_3 = \frac{48}{24000} = 0.002$ mol

amount of $H_2SO_4 = \frac{20}{1000} \times 0.05 = 0.001$ mol

$2NH_3 + H_2SO_4 \longrightarrow (NH_4)_2SO_4$

Hence, resulting solution only contains $(NH_4)_2SO_4$ salt.

$[NH_4^+] = 0.002 \div \frac{20}{1000} =$ **0.100 mol dm^{-3}**

salt hydrolysis: $NH_4^+ \overset{K_a}{\rightleftharpoons} NH_3 + H^+$

$$K_a = \frac{[NH_3][H^+]}{[NH_4^+]}$$

$$\frac{10^{-14}}{1.8 \times 10^{-5}} \approx \frac{[H^+]^2}{0.1}$$

$$[H^+] = 7.453 \times 10^{-6} \text{ mol dm}^{-3}$$

$$\text{pH} = -\log(7.453 \times 10^{-6}) = \mathbf{5.13}$$

Colour of thymolphthalein is **colourless**.

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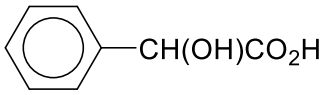
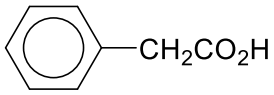
(d) The following questions concern oxygen-containing organic compounds and their derivatives.

(i) The structures of mandelic acid and phenylacetic acid are shown below.



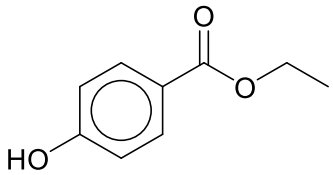
mandelic acid



phenylacetic acid

Suggest a simple chemical test that would distinguish mandelic acid from phenylacetic acid. State clearly the reagents and conditions used and write down the observations. [2]

(ii) Certain esters, like ethyl 4-hydroxybenzoate, are used as permitted anti-fungal preservatives.



ethyl 4-hydroxybenzoate

Draw the structures of the compounds formed when ethyl 4-hydroxybenzoate reacts with

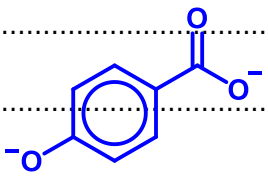
- dilute NaOH, heat
- dilute HNO_3 at room temperature [3]

(iii) **A**, $C_4H_6O_4$, is a neutral compound. When **A** is heated with reflux with aqueous sulfuric acid, it gives an organic acid **B**, $C_2H_2O_4$. On warming with concentrated sulfuric acid, **B** releases a mixture of a neutral toxic gas and an acidic gas which forms white precipitate with aqueous calcium hydroxide.
Suggest a possible identity of both **A** and **B**. Write balanced equations for the above reactions involving **A** and **B**. [4]

(i) Add **$K_2Cr_2O_7$, dilute sulfuric acid** to each of the unknowns and **heat** in a hot water bath.

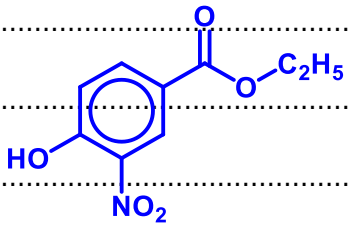
Mandelic acid **turns orange $K_2Cr_2O_7$ green** but phenylacetic acid **does not**.

(ii) with dilute NaOH (aq), heat:

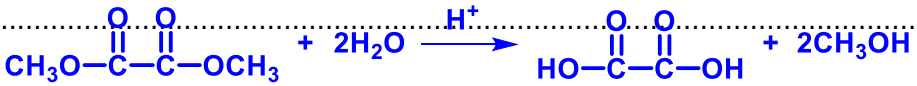


CH_3CH_2OH

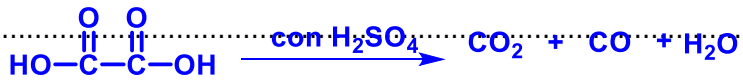
with dilute HNO_3 at room temp:



(iii) **A** is dimethyl ethandioate (**$CH_3OCOCOCH_3$**), a neutral compound.



B is ethanedioic acid (**HOOCCOOH**).



[Total: 22]

2 (a) The following method was used to determine the concentration of dissolved oxygen in water at 288 K.

Approximately 700 cm^3 of distilled water were shaken with air at 288 K for some time. 500 cm^3 of this water was then placed in a 500 cm^3 graduated flask.

1.00 cm^3 of concentrated aqueous sodium hydroxide was delivered into the flask below the surface of the liquid, followed by 1.00 cm^3 of concentrated aqueous manganese(II) chloride in the same way. The contents were gently agitated for a few minutes before allowing the precipitate to settle.

The stopper was then removed for the addition of potassium iodide crystals, followed by approximately 5 cm^3 of concentrated hydrochloric acid. The contents of the flask were then titrated against 0.0200 mol dm^{-3} of sodium thiosulfate solution using starch as an indicator.

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

(i) When sodium hydroxide and manganese(II) chloride were mixed, it caused the initial precipitation of manganese(II) hydroxide. This initial precipitate of manganese(II) hydroxide was oxidised by dissolved oxygen to form manganese(III) hydroxide as the only product.

Using oxidation states or otherwise, determine the number of moles of oxygen required to produce one mole of manganese(III) hydroxide. [2]

(ii) In the presence of hydrochloric acid, manganese(III) hydroxide oxidises iodide ions to form iodine while itself is reduced to manganese(II) ions. Write an equation for this reaction. [1]

(iii) The volume of aqueous thiosulfate required in the above titration was 30.00 cm^3. Calculate the concentration of dissolved oxygen in water in mol dm^{-3}. [3]

(i) Increase in oxidation no. of Mn = +3 – (+2) = **+1**

Decrease in oxidation no. of O = –2 – (0) = **–2**

In order for magnitude of change in oxidation no. to be same,

mole ratio of $Mn(OH)_3 : O_2 = 4 : 1$

amount of O_2 to form 1 mol of $Mn(OH)_3$ = **0.25 mol**

(ii) $2Mn(OH)_3 + 2I^- + 6H^+ \rightarrow 2Mn^{2+} + I_2 + 6H_2O$

(iii) amount of $S_2O_3^{2-} = \frac{30}{1000} \times 0.02 = 6.00 \times 10^{-4}$ mol

amount of $I_2 = \frac{1}{2} \times$ amount of $S_2O_3^{2-}$

$= \mathbf{3.00 \times 10^{-4}\ mol}$

amount of $Mn(OH)_3 = 2 \times$ amount of $I_2 = 6.00 \times 10^{-4}$ mol

amount of $O_2 = \frac{1}{4} \times$ amount of $Mn(OH)_3$

$= \mathbf{1.50 \times 10^{-4}\ mol}$

$[\text{dissolved } O_2] = \frac{1.50 \times 10^{-4}}{\frac{500}{1000}} = \mathbf{3.00 \times 10^{-4}\ mol\ dm^{-3}}$

(b) Explain why Co^{3+} is unstable in aqueous solution, but $[Co(NH_3)_6]^{2+}$ is stable. Support your answers with data from the *Data Booklet* where appropriate. [2]

Co^{3+} can be reduced to Co^{2+} by H_2O *or* **$4Co^{3+} + 2H_2O \rightarrow 4Co^{2+} + 4H^+ + O_2$**

$E^{\ominus}_{cell} = 1.89 - (+1.23) =$ **+0.66 V** (feasible)

$2[Co(NH_3)_6]^{2+} + 2H_2O \rightarrow 2Co + 6NH_3 + 4H^+ + O_2$

$E^{\ominus}_{cell} = -0.43 - (+1.23) =$ **−1.66 V** (not feasible)

(c) Copper minerals often contain copper sulfide mixed with sulfides of silver and zinc. After roasting in air to produce the oxides and reduction to the crude metals with carbon, the solid impure copper is purified with electrolysis.

With the aid of relevant data from the *Data Booklet*, describe the electrode reactions that take place during this electrolysis, and explain in detail how each of the two impurity metals is removed from the copper. [4]

Anode: **$Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$**

Cathode: **$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$**

From Data Booklet,

Reduction Half-Equation	$E^{\ominus}$/V
$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$	**+0.34**
$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s)$	**–0.76**
$Ag^+(aq) + e^- \rightleftharpoons Ag(s)$	**+0.80**

Zn will be oxidised preferably over Cu since its reduction potential, $E^{\ominus}$, is more negative than that of Cu. Hence, Zn will be oxidised to Zn^{2+}, followed by Cu to Cu^{2+}. However, **Zn^{2+} which will remain in the electrolyte** as reduction of Cu^{2+} to Cu at the cathode is preferred.

Ag will be **deposited as anodic sludge** and will not undergo any redox reaction as its reduction potential**, E°, is more positive than that of Cu**, so Ag will not be oxidized.

(d) Carbonyl compounds undergo many reactions involving different nucleophiles with the general equation shown in Fig 2.1, of which the formation of a cyanohydrin (where X = CN) is one.

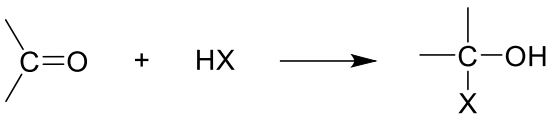
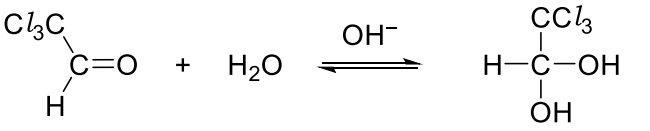


Fig 2.1

Chloral reacts in a similar way with water to give chloral hydrate as shown by the equilibrium in Fig 2.2. Chloral hydrate is a geminal diol, which is an organic compound that has two hydroxyl functional groups bonded to the same carbon atom.



chloral chloral hydrate

Fig 2.2

(i) Both water and OH^- can act as nucleophiles. Explain why OH^- is a stronger nucleophile. [1]

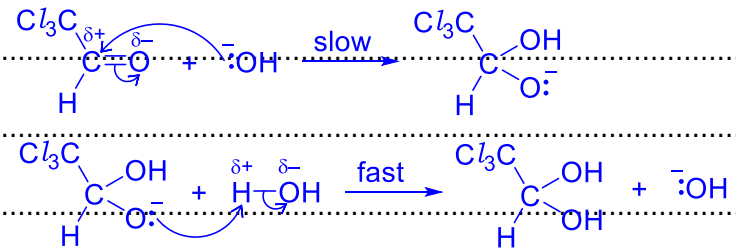
(ii) Given that OH^- acts as both a nucleophile and catalyst, suggest a mechanism for the reaction with chloral, showing clearly the flow of electrons. [3]

(iii) Using your answer in **(d)(ii)**, explain why the reaction shown in Fig 2.2 is faster when chloral is used as compared to CCl_3COCH_3. [1]

(iv) State the type of reaction undergone by chloral with 2,4-dinitrophenylhydrazine and give the structural formula of the product formed. [2]

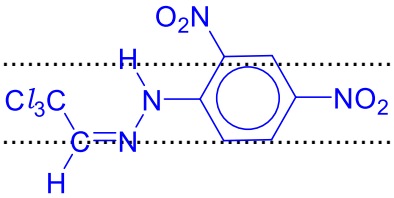
(i) OH^- is an **anion** hence it is more **electron-rich**, making the **lone pair more available for donation**.

(ii) Name of mechanism: **Nucleophilic addition**



(iii) CCl_3COCH_3 has **one more electron-donating alkyl group** which makes the carbonyl carbon in the ketone **less electron-deficient** OR CCl_3COCH_3 has **one more alkyl group attached to the carbonyl carbon**, which **hinders the approach of nucleophiles**. Hence, the reaction is slower with CCl_3COCH_3.

(iv) Type of reaction: **Condensation/Addition-Elimination**



[Total: 19]

PLEASE TURN OVER.

3 Henry's law is a gas law that states that, at a constant temperature, the amount of a given gas that dissolves in a given type and volume of liquid, is directly proportional to the partial pressure of that gas, in equilibrium with that liquid. The proportionality factor is called Henry's law constant.

Suppose gaseous A is in equilibrium with a solution of A in water:

$$\mathrm{A(g)} \overset{\mathrm{H_2O}}{\rightleftharpoons} \mathrm{A(aq)} \qquad\qquad \Delta H_{\mathrm{sol}}^{\ominus}$$

The Henry's law solubility constant, K_{H}, of A in water, is given by

$$K_{\mathrm{H}} = \frac{[\mathrm{A(aq)}]}{p_{\mathrm{A(g)}}}$$

where $p_{\mathrm{A(g)}}$ is the partial pressure of A in the gaseous phase

$[\mathrm{A(aq)}]$ is the concentration of A, in mol $\mathrm{dm^{-3}}$, in the aqueous phase

(a) Soda manufacturers often inject cold liquid with pressurised carbon dioxide, then can the drink under high pressure.

On the average, a typical 355 $\mathrm{cm^3}$ soda can possesses an internal pressure of 120 kPa when canned at 4 ºC, and 250 kPa when stored at room temperature.

The Henry's law constant, K_{H}, of $\mathrm{CO_2}$ in water is 3.4×10^{-7} mol $\mathrm{dm^{-3}}$ $\mathrm{Pa^{-1}}$ at room temperature.

(i) Explain why the internal pressure is so much higher than what is predicted by the ideal gas equation when the temperature is raised during storage. [1]

(ii) Calculate the concentration of $\mathrm{CO_2}$ dissolved in a typical soda can at room temperature, in mol $\mathrm{dm^{-3}}$. [1]

After opening a can of soda, the drink eventually goes flat when the dissolved $\mathrm{CO_2}$ escapes into the atmosphere.

(iii) Assume that ambient air contains 0.04% by volume of $\mathrm{CO_2}$, and that the volume of a gas is proportional to the amount of the gas at the same pressure and temperature.

Calculate the partial pressure of $\mathrm{CO_2}$ in air at room temperature and pressure, and hence the concentration of $\mathrm{CO_2}$ in the can of flat soda. [2]

(iv) Using your answers to **(a)(ii)** and **(a)(iii)**, calculate the mass of $\mathrm{CO_2}$ gas that has escaped into the atmosphere from the opened can of soda at room temperature, giving your answer to 4 decimal places. [1]

(i) The **solubility** of CO_2 gas in water **decreases** with increase in temperature, hence **increasing the partial pressure of CO_2.**

(ii) $\frac{[CO_2(aq)]}{p_{CO_2}} = K_H$

$\frac{[CO_2(aq)]}{250 \times 10^3} = 3.4 \times 10^{-7}$

$[CO_2(aq)] = \mathbf{0.0850\ mol\ dm^{-3}}$

(iii) $p_{CO_2} = \frac{0.04}{100} \times 101325\ Pa$

$= \mathbf{40.5\ Pa}$

$\frac{[CO_2(aq)]}{p_{CO_2}} = K_H$

$\frac{[CO_2(aq)]}{40.53} = 3.4 \times 10^{-7}$

$[CO_2(aq)] = 1.378 \times 10^{-5}\ mol\ dm^{-3} \approx \mathbf{1.38 \times 10^{-5}\ mol\ dm^{-3}}$

(iv) n_{CO_2} escaped $= \left(0.0850 - 1.378 \times 10^{-5}\right) \times \frac{355}{1000}$

$= 0.03017\ mol$

$m_{CO_2} = 0.03017 \times 44.0$

$= \mathbf{1.3275\ g}$

Glyoxal, OCHCHO, is the smallest dialdehyde. It is a crystalline solid, white at low temperatures and yellow near the melting point (15 ºC). The liquid is yellow, and the vapor is green.

The plot of $\ln\left(K_H / \text{mol dm}^{-3}\ \text{Pa}^{-1}\right)$ against $\frac{1}{T} \Big/ 10^{-3}\ \text{K}^{-1}$ for glyoxal over the temperature range between 278 K and 318 K is given in Fig. 3.1 below.

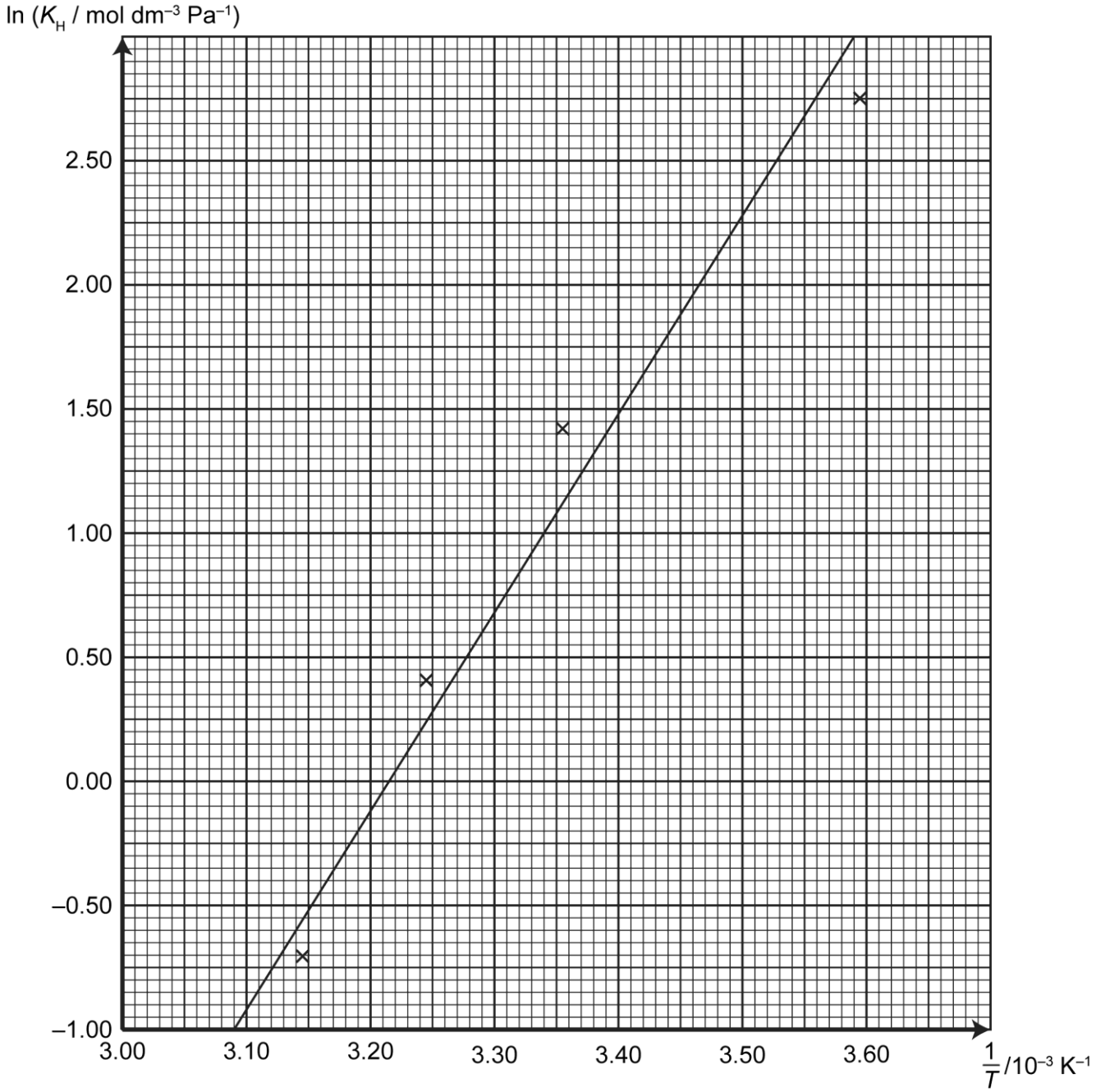


Fig. 3.1

(b) Given that the standard Gibbs free energy change of solution, $\Delta G_{sol}^{\ominus}$, is related to the K_H, by the relationship

$$\Delta G_{sol}^{\ominus} = -RT \ln K_H$$

(i) Determine using Fig. 3.1, a value for the standard enthalpy change of solution, $\Delta H_{sol}^{\ominus}$, of glyoxal. [2]

(ii) Explain the significance of the sign of $\Delta H_{sol}^{\ominus}$ you have obtained in **(b)(i)** in terms of structure and bonding. [1]

(i) $\Delta G_{sol}^{\ominus} = -RT \ln K_H$

$\Delta H_{sol}^{\ominus} - T\Delta S_{sol}^{\ominus} = -RT \ln K_H$

$\ln K_H = -\frac{\Delta H_{sol}^{\ominus}}{R}\left(\frac{1}{T}\right) + \frac{\Delta S_{sol}^{\ominus}}{R}$

$\text{gradient} = \frac{3.00 - (-1.00)}{(3.59 - 3.09) \times 10^{-3}}$

$= 8000$

$-\frac{\Delta H_{sol}^{\ominus}}{R} = \text{gradient}$

$\Delta H_{sol}^{\ominus} = -8000 \times 8.31$

$= -66480$

$\approx$ **$-66.5\ \text{kJ mol}^{-1}$**

(ii) The negative sign means that **heat is given out** when glyoxal dissolves in water. This is due to the ability of glyoxal to form **hydrogen bonding** with water, which more than compensates for the **weaker permanent dipole-permanent dipole (solute-solute) interaction** between glyoxal molecules.

(c) Glyoxal can be converted into CO_2.

(i) State the reagents and conditions for the conversion of glyoxal into CO_2. [1]

(ii) Using Fig. 3.1, determine the Henry's law constant, K_H, for glyoxal at room temperature, in mol dm^{-3} Pa^{-1}. [1]

(iii) Glyoxal is sold in bottles containing 40% of glyoxal by weight, which is approximately 11.5 mol dm^{-3}. Using your answer to **(c)(ii)**, explain whether an opened bottle of glyoxal will rapidly lose glyoxal, like in the case of CO_2 in soda drinks. [1]

(i) $KMnO_4(aq)$, $H_2SO_4(aq)$, (prolonged) heating

(ii) When $T = 20\,^{o}C = 293$ K, $\frac{1}{T} = 3.413 \times 10^{-3}$ K^{-1}, from the graph,

$$\ln\left(K_H / \text{mol dm}^{-3}\ \text{Pa}^{-1}\right) = 1.60$$

$$K_H = e^{1.60} = \mathbf{4.95\ mol\ dm^{-3}\ Pa^{-1}}$$

(iii) **No**. This is because the partial pressure of gaseous glyoxal in equilibrium with 11.5 mol dm^{-3} of glyoxal is $\frac{11.5}{4.95} \approx 2.32$ Pa , which is $\frac{2.32}{101325} \times 100 \approx 0.00229\%$ by volume of air. Hence the loss of glyoxal from solution will be negligible.

Glyoxal is used in the synthesis of CL-20, a nitroamine explosive with the formula $C_6H_6O_{12}N_{12}$. One synthesis of CL-20 is shown in Fig. 3.2.

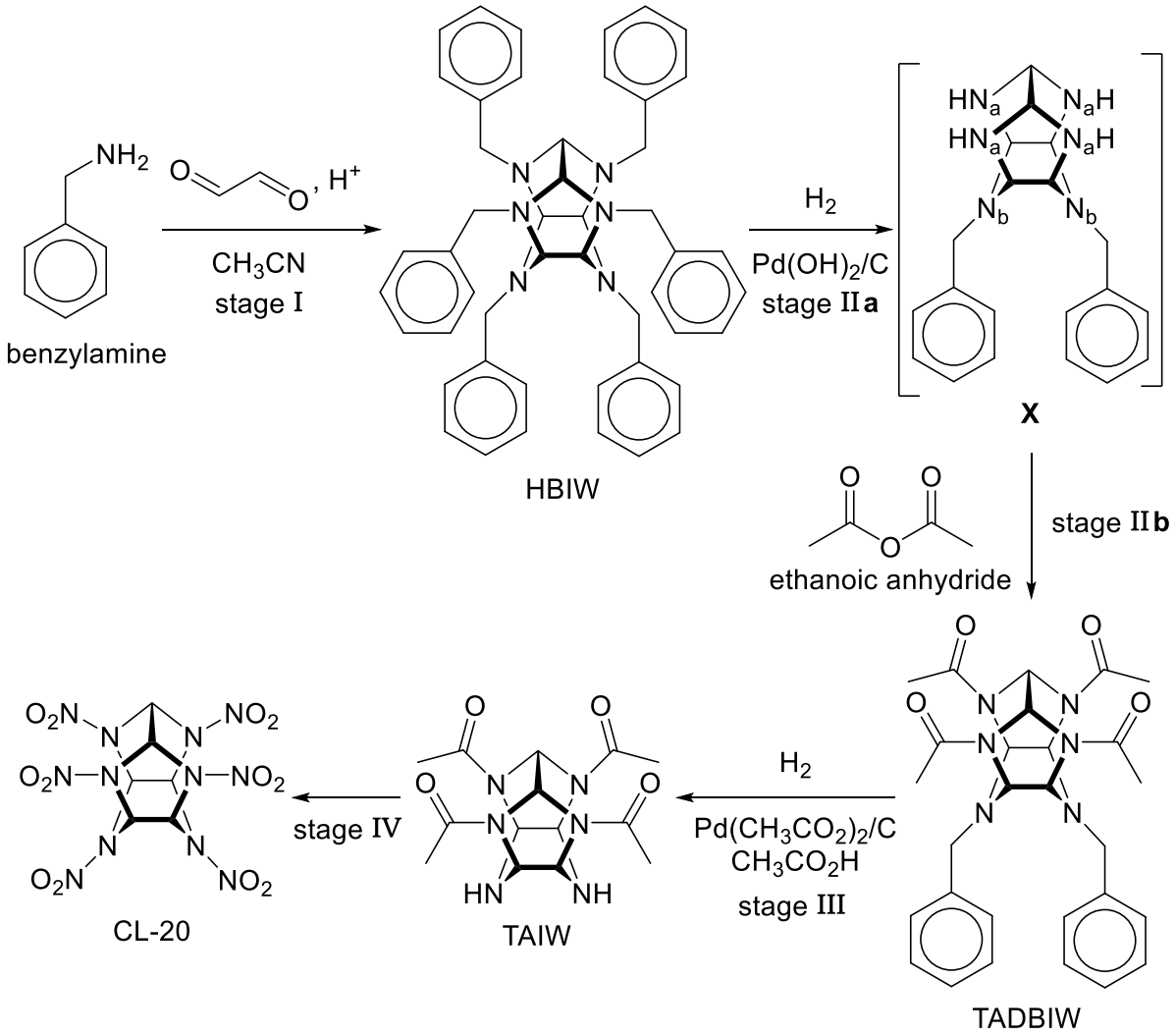
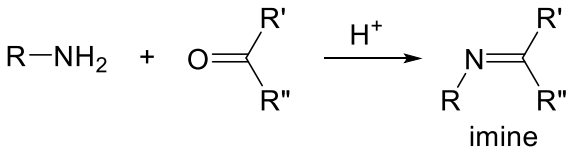


Fig. 3.2

(d) Stage **I** involves the reaction of glyoxal with benzylamine to give HBIW.
There are two types of reactions taking place in this stage, one involving the condensation between a primary amine and a carbonyl group to give an imine:



Name the **second** type of reaction involved, which results in the formation of the N–C–N linkage. [1]

Nucleophilic addition

(e) Stage **II** of the synthesis involves hydrogenation of HBIW in the presence of a palladium(II) catalyst, using ethanoic anhydride as the solvent, to give TADBIW.
The reaction can be thought to proceed *via* the intermediate **X** which reacts with ethanoic anhydride *in situ*, to give TADBIW.

(i) Explain why N_b is the more basic nitrogen atom among the two types of nitrogen atom, N_a and N_b, present in **X**. [1]

(ii) Ethanoic anhydride is an ethanoylating agent like ethanoyl chloride. Explain why despite N_b being more basic than N_a, only N_a reacts with ethanoic anhydride in stage **IIb**. [1]

(i) N_a is a **secondary amine**, attached to **two electron-donating alkyl chains**, while N_b is a **tertiary amine**, attached to **three electron-donating alkyl chains**. Hence the **lone pair of electrons** on N_b is **more available** for donation to a proton, and is more basic.

(ii) There is **no N–H hydrogen** on N_b which can be **eliminated** upon reaction with ethanoic anhydride (to give ethanoic acid).

(f) Methylbenzene is a by-product in stages **IIa** and **III**. State the type of reaction involved in these two stages. [1]

Reduction

(g) Stage **IV** involves the reaction of TAIW with the nitronium ion, NO_2^+, to give CL-20. Suggest the reagents used. [1]

Concentrated nitric acid and concentrated sulfuric acid

(h) (i) The detonation of solid CL-20, $C_6H_6O_{12}N_{12}(s)$, leads to the formation of oxides of nitrogen, CO_2 and HCN, among other products:

$$C_6H_6O_{12}N_{12}(s) \rightarrow NO(g) + HNO_2(g) + 5HCN(g) + CO_2(g) + N_2O(g) + 3NO_2(g)$$

Determine the standard enthalpy change of detonation of CL-20 using the data in Table 3.1.

Table 3.1

compound	$\Delta H_f^{\ominus}$ / kJ mol^{-1}
CL-20(s)	+377.4
NO(g)	+91.3
HNO_2(g)	–79.5
HCN(g)	+135.1
CO_2(g)	–393.5
N_2O(g)	+81.6
NO_2(g)	+33.1

[2]

(ii) By considering your answer in **(h)(i)** and the information given above, explain why the detonation of solid CL-20 is spontaneous. [1]

(i) $\Delta H^{\ominus}_{detonation}(\text{CL-20}) = \sum \Delta H_f^{\ominus}(\text{products}) - \sum \Delta H_f^{\ominus}(\text{reactants})$

$= \Delta H_f^{\ominus}(\text{NO}) + \Delta H_f^{\ominus}(\text{HNO}_2) + 5\Delta H_f^{\ominus}(\text{HCN}) + \Delta H_f^{\ominus}(\text{CO}_2)$

$+ \Delta H_f^{\ominus}(\text{N}_2\text{O}) + 3\Delta H_f^{\ominus}(\text{NO}_2) - \Delta H_f^{\ominus}(\text{CL-20})$

$= 91.3 + (-79.5) + 5(135.1) + (-393.5) + 81.6 + 3(33.1)$

$- 377.4$

$= \mathbf{+97.3\ kJ\ mol^{-1}}$

(ii) It is spontaneous as the detonation of 1 mole of solid CL-20 gives 12 moles of gaseous product, thus the **large increase in no. of moles of gas** leads to a **very large increase in the entropy**, which **compensates for the positive enthalpy change**, giving a **negative ΔG**.

[Total: 19]

Section B

Answer **one** question from this section.

4 (a) Nucleophilic substitution reactions can proceed via bimolecular or unimolecular mechanisms, which is often dependent on whether the halogenoalkane is primary, secondary, or tertiary.

Fig. 4.1 shows the experimental data for a kinetics study for the reaction between aqueous sodium hydroxide and a solution of benzyl bromide, $C_6H_5CH_2Br$, which is carried out at constant temperature.

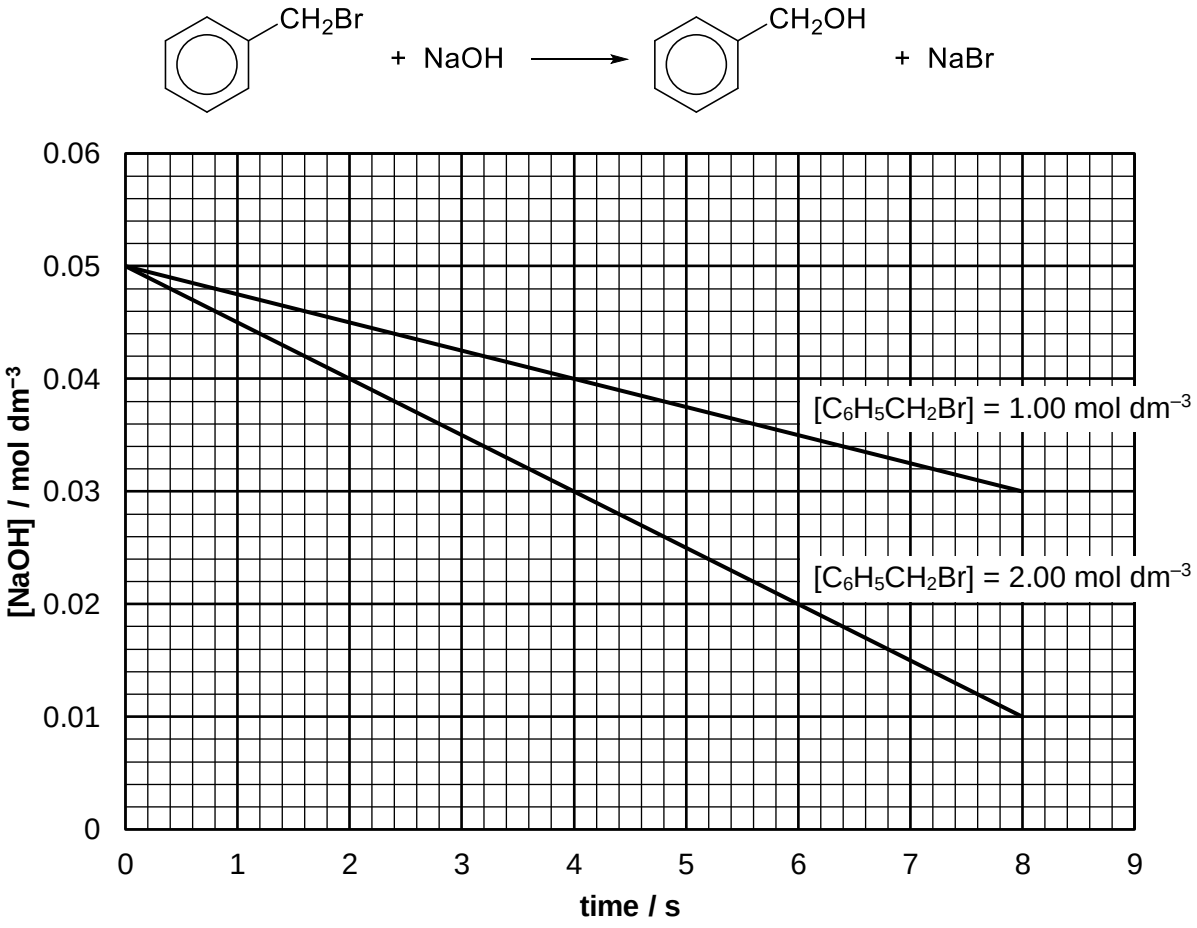


Fig. 4.1

(i) With reference to the graph shown in Fig 4.1, determine the orders of reaction with respect to NaOH and $C_6H_5CH_2Br$. [2]

(ii) Hence, construct a rate equation for the reaction between NaOH and $C_6H_5CH_2Br$. [1]

(iii) State and explain the type of mechanism for the reaction. Suggest how the structure of $C_6H_5CH_2Br$ favours the type of mechanism you have stated. [2]

(iv) Suggest and explain how the rate of reaction would change if aqueous potassium hydroxide of the same concentration was used in place of aqueous sodium hydroxide. [1]

(i) The graph shown for [NaOH] against time is **linear**, and hence the reaction is **zero order with respect to NaOH**. Since the gradient of the graph **increases by twice in magnitude when [$C_6H_5CH_2Br$] is doubled**, the order of reaction with respect to $C_6H_5CH_2Br$ is **first order**.

(ii) rate = $k[C_6H_5CH_2Br]$

(iii) The reaction between $C_6H_5CH_2Br$ and NaOH(aq) **follows S_N1 reaction**, as the reaction is independent of the concentration of $[OH^-]$ and **dependent only on [$C_6H_5CH_2Br$]**, which suggests that the rate determining step is the breaking of C–Br bond in $C_6H_5CH_2Br$ to yield the intermediate $C_6H_5CH_2^+$.

The carbon atom in the carbocation is sp^2 hybridised, leaving an unhybridised p orbital that can overlap side-on with the π electron cloud of the benzene ring. The allows for **resonance stabilisation of the benzylic carbocation OR** the **positive charge on the carbocation can be better** dispersed, **allowing for a more stable reaction intermediate** to be formed, hence favouring a S_N1 mechanism.

(iv) As the rate law is independent of the hydroxide concentration, the rate of reaction remains the same.

(b) The concentration of Br^- ions in an aqueous sample of drinking water may be determined via a technique known as the Mohr method.

The Mohr method uses $AgNO_3$ as a titrant and K_2CrO_4 as an end point indicator. When $AgNO_3$ is first added, the Br^- ions precipitate as AgBr. The end point is indicated by the precipitation of the brick-red Ag_2CrO_4.

At 298 K, the numerical values of the solubility product of AgBr and Ag_2CrO_4 are 5.40×10^{-13} and 3.01×10^{-12} respectively.

A 25.0 cm^3 of an analyte solution containing Br^- ions was titrated against 0.100 mol dm^{-3} $AgNO_3$ solution. Before the titration, 0.100 cm^3 of 0.200 mol dm^{-3} of K_2CrO_4 solution was added to the analyte. 24.55 cm^3 of $AgNO_3$ was required to reach the end point of reaction.

(i) By determining the concentration of CrO_4^{2-} ions present at the end-point of the titration, calculate the concentration of Br^- remaining in the solution at the end point. [3]

(ii) Hence, calculate the concentration of the Br^- ions present initially in the analyte solution. Assume that the precipitation of Ag_2CrO_4 causes a negligible change in the concentration of Ag^+ ions. [2]

(iii) State and explain the effect of increasing pH on the accuracy of the titre value for the determination of Br^- ions obtained via the Mohr method. [1]

(i) $\left[CrO_4^{2-}\right]$ at end-point $= \dfrac{0.100 \times 0.200}{25.0 + 24.55 + 0.100}$

$= \mathbf{4.028 \times 10^{-4}\ mol\ dm^{-3}}$

IP of Ag_2CrO_4 = K_{sp} of Ag_2CrO_4 = $\left[Ag^+\right]^2\left[CrO_4^{2-}\right]$

$3.01 \times 10^{-12} = \left[Ag^+\right]^2 \times 4.028 \times 10^{-4}$

$\left[Ag^+\right] = \mathbf{8.644 \times 10^{-5}\ mol\ dm^{-3}}$

IP of AgBr = K_{sp} of AgBr = $\left[Ag^+\right]\left[Br^-\right]$

$\left[Br^-\right] = \dfrac{5.40 \times 10^{-13}}{8.644 \times 10^{-5}}$

$= \mathbf{6.25 \times 10^{-9}\ mol\ dm^{-3}}$

(ii) $[Br^-]$ present in analyte solution $= \frac{n_{Br^-}}{0.025}$

$= \frac{0.02455 \times 0.100 + 6.247 \times 10^{-9} \times (0.025 + 0.02455 + 0.0001) - 8.644 \times 10^{-5} \times (0.025 + 0.02455 + 0.0001)}{0.025}$

$= \mathbf{0.0980\ mol\ dm^{-3}}$

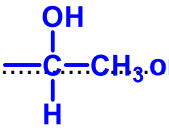
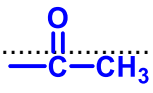
(iii) An increasing pH value signifies that the $[OH^-]$ increases. As the $[OH^-]$ increases, AgOH selectively precipitates out instead due to the higher $[OH^-]$, and **causes the titre value obtained to be increasingly higher and inaccurate**, as more silver nitrate is required for the titration.

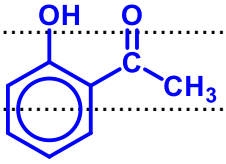
(c) Compound **Q**, $C_8H_8O_2$ is formed when phenyl ethanoate, $CH_3COOC_6H_5$ is warmed with aluminum chloride. It is known that:

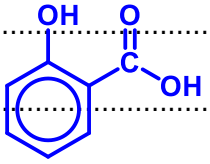
- Compound **Q** forms an orange precipitate with 2,4-DNPH, but does not produce a red precipitate with Fehling's solution.
- Compound **Q** reacts with alkaline aqueous iodine, followed by acidification, to produce compound **R**, $C_7H_6O_3$, which reacts with aqueous sodium hydroxide in a 1:2 mole ratio.
- Compound **Q** produces compound **S**, $C_8H_6O_2Br_2$, in bromine water.

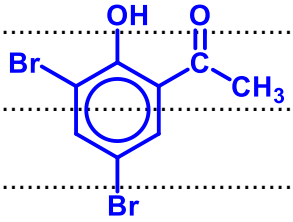
Deduce the structures of compound **Q**, **R** and **S**, explaining the chemistry of the reactions described.

(There is no need to explain the chemistry of the formation of compound **Q** from phenyl ethanoate.) [8]

- Since the **ratio of C to H atoms** in the molecular formula of **Q** is approximately **1:1**, and the **number of C atoms is more than 6 (✓)**, a **benzene ring (✓)** is likely present in **Q**.
- **Q** undergoes a **condensation reaction (✓)** with 2,4-DNPH but **no reduction (✓)** reaction with Fehling's solution suggesting the **presence of** at least one **an aromatic carbonyl group** (accept aromatic aldehyde or ketone) **(✓)**.
- **Q** undergoes **mild oxidation (✓)** with alkaline aqueous iodine to produce a carboxylic acid, suggesting the presence of either **a**  **or**  group **(✓)**. **R** is a **carboxylic acid** formed from the iodoform reaction **(✓)**.
- As **R** undergoes **acid-base reaction (✓)** with NaOH in a **1:2 mole ratio**, R is **dibasic (✓)**. As **R** already contains 1 carboxylic acid functional group, the other oxygen atom present signifies the presence of an acidic **phenol group (✓)**.
- **Q** undergoes **electrophilic substitution (✓)** with bromine water, as it contains a strongly activated benzene ring due to the **presence of phenol group (✓)**.
- **Q** is a **2- or 4- substituted phenol (✓)**, as it **only has 2 H atoms substituted** with 2 Br atoms **(✓)**. **[**1 mark per 2 ticks, max **5 marks]**

Q: 

R: 

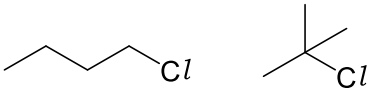
S: 

[1] per correct structure

[Total: 20]

5 Halocarbon compounds are compounds in which one or more carbon atoms are covalently bonded to one or more halogen atoms. They are important precursors in organic chemistry laboratories as they can be converted to many other different compounds.

(a) By means of a simple chemical test, distinguish between compounds **J** and **K**. You should include the reagents and conditions used, and the observations for each test compound.



J **K**

[2]

Heat separate portions of the two compounds in **$KMnO_4$(aq) and NaOH(aq)** **[1]**.

Compound **J** will **decolourise $KMnO_4$ and brown ppt will be formed** while **brown ppt will form but no decolourisation** will be observed with compound **K** **[1]**.

(b) The Finkelstein reaction is another method that can be used to distinguish between primary and tertiary chloroalkanes. In this reaction, the test compounds are treated with NaI dissolved in acetone, $(CH_3)_2CO$.

$$RCl + NaI \rightleftharpoons RI + NaCl$$

The reaction conditions lead to an S_N2 reaction. The NaCl produced is insoluble in acetone, so a white precipitate will be observed if the chloroalkane tested undergoes a reaction.

(i) Explain how the Finkelstein reaction can be used to distinguish between primary and tertiary chloroalkanes. [1]

(ii) Describe the mechanism of the Finkelstein reaction with compound **J**.

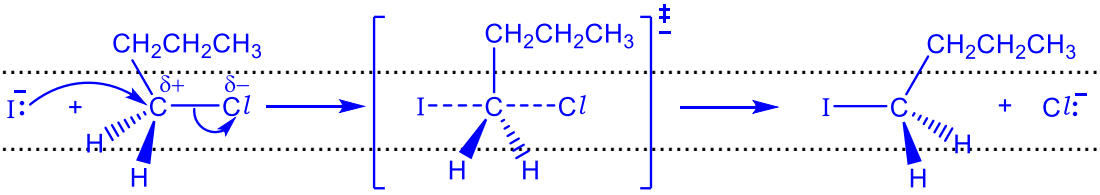
Show all charges and relevant lone pairs and show the movement of electron pairs by using curly arrows. [2]

(iii) Explain, with the aid of suitable diagrams, how NaI is able to dissolve in acetone. [2]

(iv) Explain why the equilibrium position lies largely to the right in the Finkelstein reaction. [1]

(i) **Tertiary** chloroalkanes **do not undergo S_N2 substitution** due to the presence of the **three groups** on the α-carbon which leads to **steric hindrance** towards the **attacking nucleophile**. Hence, **no white precipitate of NaC*l*** will be formed **[1]**.

(ii) Type of reaction: **S_N2 Nucleophilic substitution**

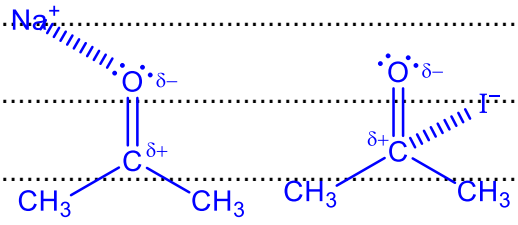


[2]

- ✓ Nucleophile shown with lp and charge
- ✓ Arrows for backside attack and breaking of C–C*l* bond
- ✓ Indication of dipoles on C and C*l*
- ✓ Transition state with correct structure and bonding and overall charge
- ✓ Indication of inversion of configuration in product
- ✓ Balanced equation with C*l*$^-$

Any one missing/wrong; 1 mark; any three or more missing/wrong; 0 mark

(iii) **Favourable ion-dipole interactions** can be formed between the ions of NaI and acetone which results in the **release** of sufficient energy to **overcome the ionic bonds** in the giant ionic lattice structure of NaI **[1]**.



ıııııııı : ion-dipole interactions

[1 for both diagrams with correct indication of dipoles**]**

(iv) **NaC*l*** produced is **insoluble in acetone**, and is hence **continuously removed** from the solution via precipitation **[1]**.

(c) To differentiate between a chloroalkane and an iodoalkane, separate portions of the two compounds can be heated with ethanolic silver nitrate. The respective insoluble silver halides will be produced.

(i) The silver chloride formed from the chloroalkane dissolves upon addition of dilute ammonia, while the silver bromide formed from the bromoalkane does not.

Using relevant equations, account for the difference in the solubilities of the two halides in aqueous ammonia. [3]

(ii) Given that the numerical value of the K_{sp} of silver chloride is 1.8×10^{-10}, show with the necessary calculations that the solubility of silver chloride is lower in a 0.200 mol dm^{-3} solution of aqueous sodium chloride, as compared to water. [2]

(i) $AgX(s) \rightleftharpoons Ag^+(aq) + X^-(aq)$ ---------- (1)

$Ag^+(aq) + 2NH_3(aq) \rightleftharpoons [Ag(NH_3)_2]^+(aq)$ --------- (2) **[1** for both eqn**]**

Addition of NH_3 **shifts the position of equilibrium (2) to the right**, causing a **decrease in [Ag^+]**, and consequently a **decrease in the ionic product** of AgX **[1]**.

For AgC*l*, the addition of dilute NH_3 is **sufficient** to lower [Ag^+] such that the **ionic product becomes smaller than K_{sp} of AgC*l***. The **K_{sp} of AgBr is lower**, and the addition of dilute NH_3 is **not sufficient** to lower [Ag^+] such that the **ionic product becomes smaller than K_{sp} of AgBr [1]**. Hence, the AgC*l* precipitate dissolves while the AgBr precipitate does not.

(ii) Let s be the solubility of AgC*l* in water

$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$

$K_{sp} = [Ag^+][Cl^-]$

$1.8 \times 10^{-10} = s^2$

$s = \sqrt{1.8 \times 10^{-10}}$

$= \mathbf{1.342 \times 10^{-5}\ mol\ dm^{-3}}$ **[1]**

Let s' be the solubility of AgC*l* in 0.200 mol dm^{-3} NaC*l*(aq)

$K_{sp} = [Ag^+][Cl^-]$

$1.8 \times 10^{-10} = [0.200 + s'][s']$

Assume that s' << 0.200

1.8×10^{-10}

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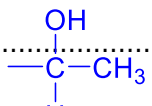
(d) **L** is an achiral molecule with the molecular formula $C_8H_{16}O$. It decolourises aqueous bromine, produces white fumes with phosphorus pentachloride, but does not form a yellow precipitate with alkaline aqueous iodine. When heated with acidified $KMnO_4$, **L** is oxidised to produce **M** and carbon dioxide gas. When **M** is heated with a small amount of concentrated sulfuric acid, only a sweet-smelling cyclic compound **N** with the molecular formula $C_7H_{12}O_2$ is formed.

Deduce the structures of compounds **L**, **M** and **N**, giving reasons for your answer. [7]

- **L** is an optically inactive molecule, hence it either **does not have a chiral carbon**, or **does not have chiral carbons with an internal plane of symmetry (✓)**.
- **L** has a **C : H ratio of 1 : 2**, hence it is **unlikely to have a benzene ring (✓)**.
- **L** undergoes **electrophilic addition (✓)** with aqueous bromine, hence it is likely to be an **alkene (✓)**.
- **L** undergoes **nucleophilic substitution (✓)** with PCl_5, hence it is likely to be an **alcohol (✓)**.
- **L** does not undergo **oxidation (✓)** with alkaline aqueous iodine, hence it **does not have the**  **(✓)**.
- **L** produces carbon dioxide gas upon vigorous oxidation, hence **L** has a **terminal alkene (✓)**.
- **M** undergoes **condensation (✓)** to form **N**, hence **N** is likely to be an **ester (✓)**. **M** must have a **tertiary alcohol** which is not oxidised by $KMnO_4$ **(✓)**.

[1] for every two **(✓)**, max 4 marks

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[Total: 20]

Additional answer space

If you use the following pages to complete the answer to any question, the question number must be clearly shown.

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