ST ANDREW'S JUNIOR COLLEGE

JC2 Preliminary Examinations

Higher 2

CANDIDATE NAME	
CLASS	1 9 S

CHEMISTRY 9729/02

Paper 2 Structured Questions **2 September 2020**

2 hours

Candidate answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name and class on all the work you hand in.

Write in dark blue or black pen.

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

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

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

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

A Data Booklet is provided.

At the end of the examination, fasten all your work securely together.

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

For Examiner's Use		
Q1		15
Q2		9
Q3		15
Q4		19
Q5		17
Total		75

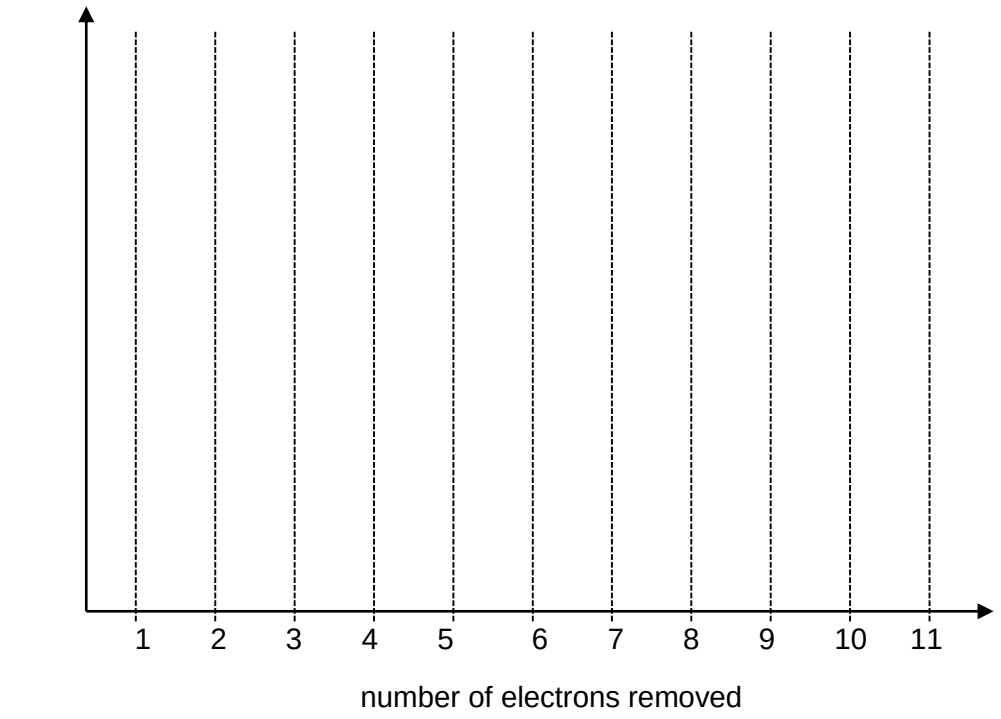
This document consists of **??** printed pages and ? blank page.

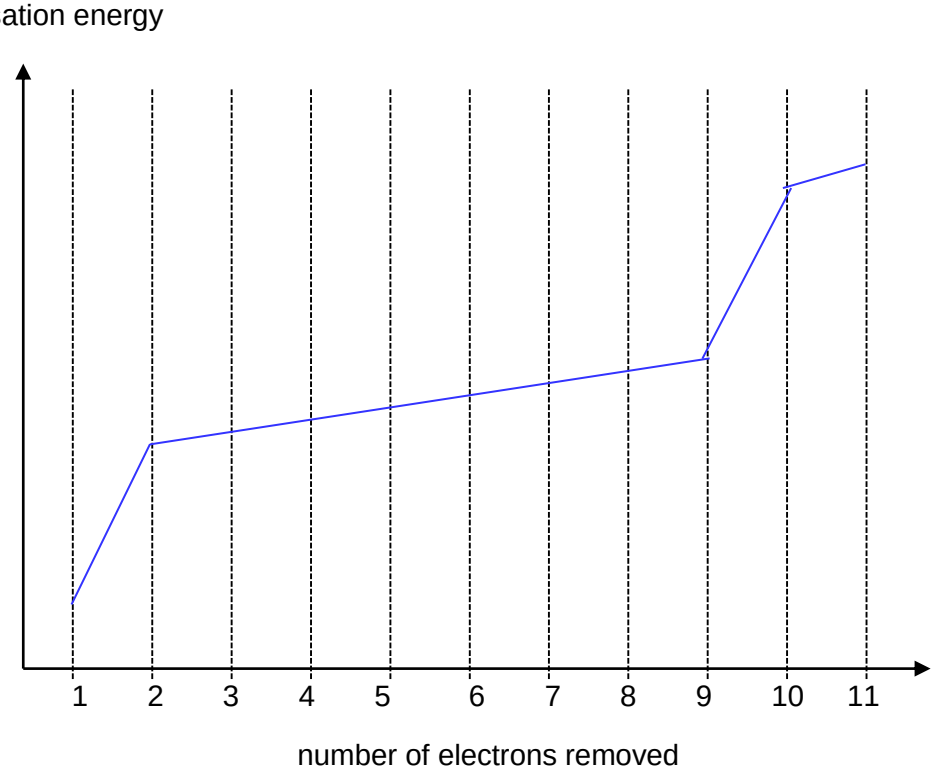
Answer **all** questions in the spaces provided.

1 (a) (i) On the axis below, sketch a graph to show the eleven ionisation energies for sodium.

Explain the following features shown in your graph

- the general trend in ionisation energy
- significant change in values between ionisation energies





IE generally increases as it is **more difficult/more energy required to remove an e from an increasingly positively charged species**.

There are 2 large increase in IE. The **next electron is removed form an inner shell which is closer to the nucleus**. Hence, it experiences **stronger nuclear attraction** and **more energy is required to remove it**.

(ii) State one similarity and one difference (other than difference in energy) between the lowest and highest energy occupied orbital in sodium.

Similarity	
Difference	

[1]

Similarity: **spherical shape** OR **both are s orbitals**

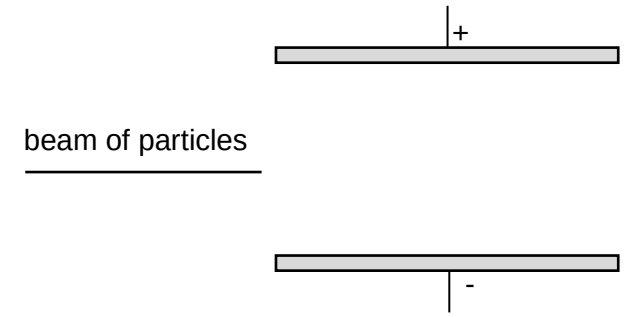
Difference: **Orbital from outermost shell/highest energy occupied orbital is more diffuse/larger** OR **orbital from innermost shell/lowest energy occupied orbital is less diffuse/smaller**.

(b) **(i)** State two factors that affect the behaviour of beams of positively charged particles in an electric field.

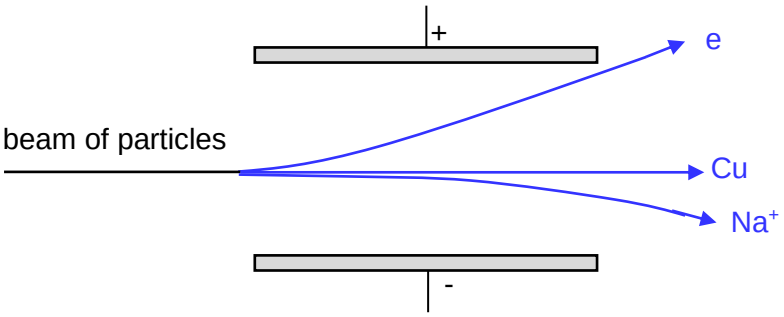
…… [1]

Charge and **mass**

(ii) On the diagram below, show how a beam of particles containing sodium ions, copper atoms and electrons deflects as they pass through an electric field at the same speed. Label your answer clearly.



[2]



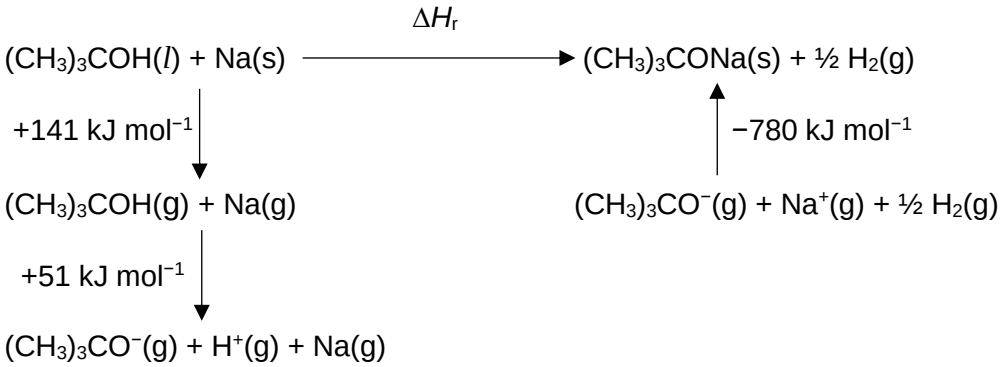
(c) Sodium and tert-butanol reacts to give sodium tert-butoxide and hydrogen gas.

$$(CH_3)_3COH(l) + Na(s) \longrightarrow (CH_3)_3CONa(s) + \tfrac{1}{2}H_2(g) \quad \Delta H_r$$

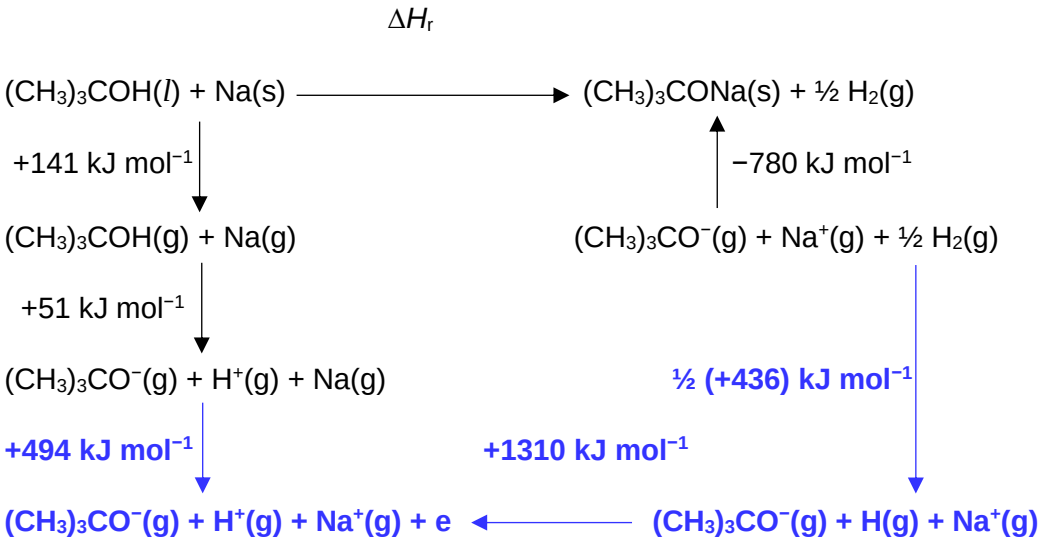
tert-butanol sodium tert-butoxide

(i) Complete the energy cycle below to calculate the enthalpy change of this reaction, ΔH_r.

Your cycle should include relevant data from the *Data Booklet*.



[3]



ΔH_r + ½ (+436) + (+1310) = (+141) + (+51) + (+494) + (−780)

ΔH_r = −1622 kJ mol^{-1}

(ii) The standard enthalpy change of vapourisation of butanol, tert-butanol and butanone are given below

compound	$\Delta H_{vap}^{\ominus}$/ kJ mol^{-1}
$CH_3CH_2CH_2CH_2OH$	+46
$(CH_3)_3COH$	+44
$CH_3CH_2COCH_3$	+32

By considering the type of interactions involved, suggest reasons for the

- difference in $\Delta H_{vap}^{\ominus}$ between tert-butanol and butanone, and
- similarity in $\Delta H_{vap}^{\ominus}$ between butanol and tert-butanol.

…… [3]

They are simple covalent polar molecules.

Difference:

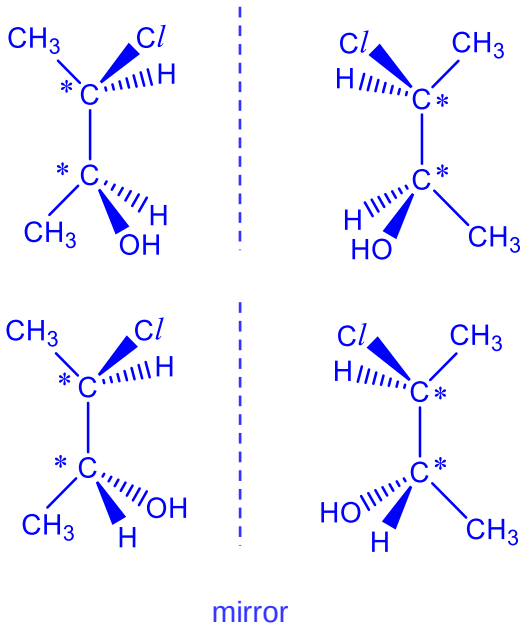
More energy is required to break the **stronger hydrogen bonding between tert-butanol molecules**, than the **permanent dipole-permanent dipole interactions between butanone molecules**. Hence, $H_{vap}^{\ominus}$ for butanone is the most endothermic.

Similarity:

Both tert-butanol and butanol have **similar number of electrons**. They experience **similar strength of instantaneous dipole-induced dipole interactions between molecules**, which requires the same amount of energy to overcome. Hence, $H_{vap}^{\ominus}$ for tert-butanol and butanol is similar.

(d) Compound **A** is a constitutional isomer of tert-butanol, $(CH_3)_3COH$. **A** exhibits stereoisomerism. It reacts with chlorine in the presence of UV light to form a mono-chlorinated compound **B**, which has four stereoisomers. Draw the four stereoisomers of **B**.

[2]


CH3
Cl
H
OH
CH3
Cl
H
CH3
HO
CH3
CH3
Cl
H
OH
CH3
H
Cl
H
CH3
HO
CH3
H
mirror

[Total: 15]

2 **(a)** Explain why benzene prefers to undergo substitution reactions rather than addition reactions.

…… [1]

Unlike addition reaction, substitution reaction helps to **retain the delocalised π electron cloud** of the benzene ring, which gives it **resonance stabilisation**.

(b) The reaction of phenylamine with nitrosonium ion, NO^+, produces benzenediazonium, which is a very useful intermediate in the synthesis of many aromatic compounds.

The mechanism is shown in Fig. 2.1.

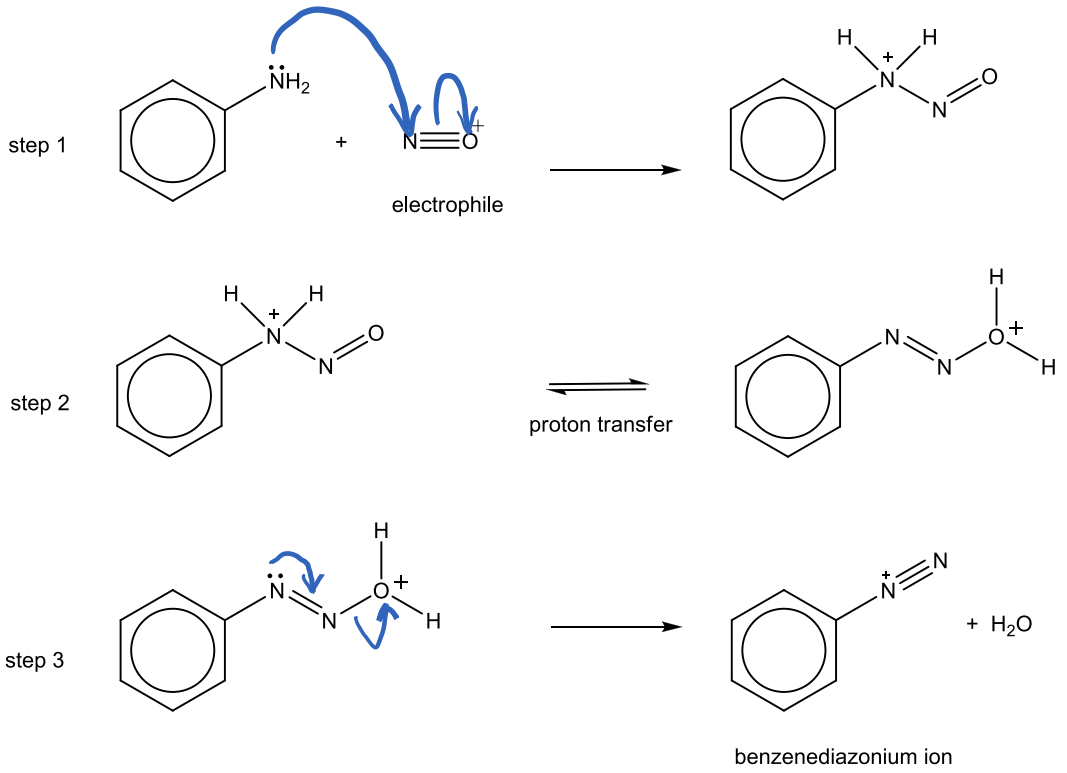


Fig. 2.1

(i) The electrophile, nitrosonium ion, is formed from the reaction between nitrite, NO_2^-, and acid, H^+.

Write an ionic equation for this reaction.

…… [1]

$NO_2^- + 2H^+ \rightarrow NO^+ + H_2O$ OR

$NO_2^- + H^+ \rightarrow NO^+ + OH^-$

(ii) By considering the bonds formed and broken, show the movement of electron pairs using curly arrows for steps 1 and 3 **on Fig. 2.1**. [2]

- curly arrow from N of NH_2 to N of NO^+
- curly arrow from π bond to O of NO^+
- curly arrow from N to π bond of N=N
- curly arrow from N-O bond to O

(iii) Using appropriate data from the *Data Booklet*, estimate the bond energy of the π bond in N=N.

…….. [1]

BE of π bond in N=N = 410 – 160 = **+250 kJ mol^{-1}**

(iv) Given that the bond energy of the π bond in N=O is +405 kJ mol^{-1}, use your answer in **(iii)** and relevant data from the *Data Booklet* to calculate the enthalpy change of reaction for step 2.

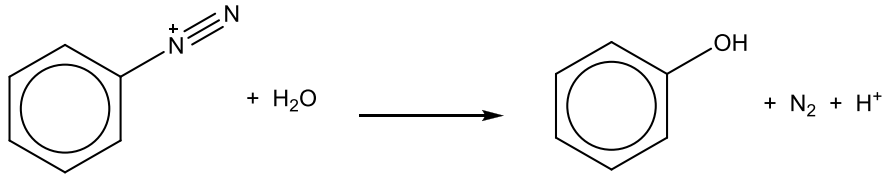
Hence, by considering the effect on the equilibrium, suggest whether a high or low temperature would favour the proton transfer in step 2.

…….. [2]

ΔH = [2(+390) + (405)] – [(+250) + 2(460)] = **+15 kJ mol^{-1}** [1] *(ecf **(iii)**)*

A **high temperature** favours proton transfer because the **equilibrium position would shift right** to favour the endothermic reaction so as to **absorb the additional heat**. *(ecf ΔH)*

(c) Benzenediazonium ion reacts with water to form phenol readily.



(i) Deduce whether water is acting as an electrophile or nucleophile in the reaction. Explain your answer.

…….. [1]

Water is the **nucleophile**. It has **lone pair of electrons on O** that can attack the electrophilic benzenediazonium ion.

(ii) The reaction of benzenediazonium ion with KI(aq) forms phenol and another carbon-containing side product. Name this carbon-containing side product.

…….... [1]

iodobenzene

[Total: 9]

3 Benzyl bromide, $C_6H_5CH_2Br$, is a strong irritant that affects skin and mucous membranes. It exists as a colourless liquid under standard conditions and is used in military chemical warfare training due to its irritating but non-lethal nature.

(a) **(i)** The standard enthalpy change of formation of $C_6H_5CH_2Br$ is +22.5 kJ mol^{-1}.

Write an equation that illustrates the standard enthalpy change of formation of $C_6H_5CH_2Br$.

…… [1]

$7C\ (s) + 7/2H_2\ (g) + 1/2Br_2\ (l) \rightarrow C_6H_5CH_2Br\ (l)$

(ii) Predict the sign of Δ*S* for the reaction in **(a)(i)**.

…… [1]

ΔS is negative. There is a **decrease in the number of gaseous particles**. The system is less disordered due to fewer ways of arranging the system.

(iii) Hence, predict whether the formation of $C_6H_5CH_2Br$ is spontaneous under standard conditions.

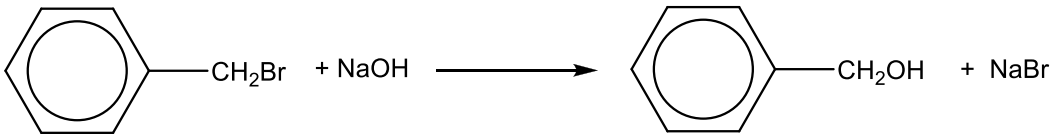
…… [1]

$\Delta G = \Delta H - T\Delta S$

Since **ΔH is positive and ΔS is negative**, **ΔG>0**. The reaction is **not spontaneous.** (ecf**(ii)**)

(b) For safety reasons, benzyl bromide has to be hydrolysed before disposal.

The hydrolysis of benzyl bromide is shown in the equation below.



In the first experiment, 25 cm^3 of 0.1 mol dm^{-3} sodium hydroxide solution was added to 25 cm^3 of 0.0050 mol dm^{-3} of benzyl bromide solution.

Fig. 3.1 shows the concentration of $C_6H_5CH_2OH$ produced against time for this experiment.

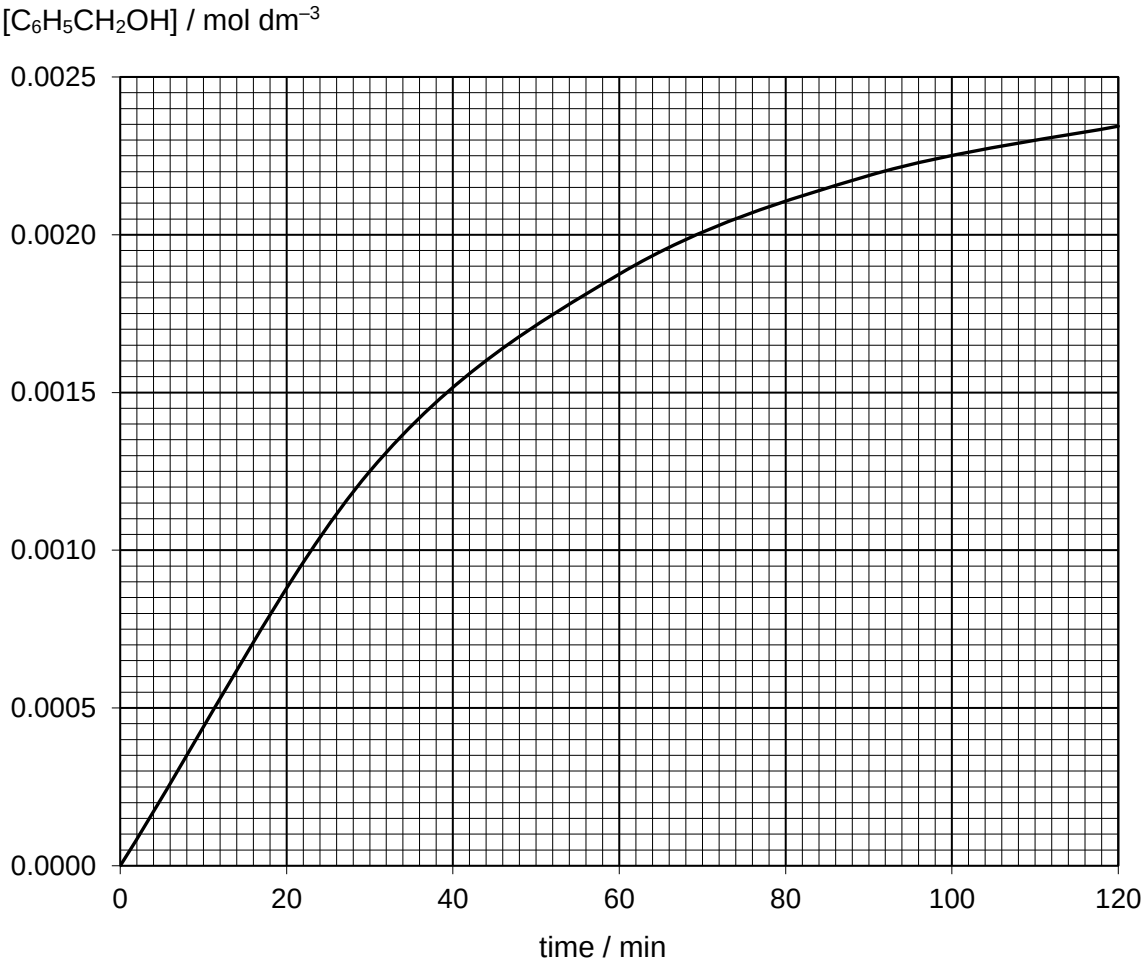


Fig. 3.1

The experiment was repeated to find the order of reaction with respect to sodium hydroxide. The total volume was kept constant and the concentration of benzyl bromide was kept the same. The concentration of sodium hydroxide used was 0.20 mol dm^{-3}.

The same graph as Fig. 3.1 was obtained in this second experiment.

(i) Using Fig. 3.1 and the information given, show that the hydrolysis reaction has the following rate equation:

rate = k[benzyl bromide]

…… [3]

Show two $t_{½}$ on graph clearly and $t_{½}$ = 30 min

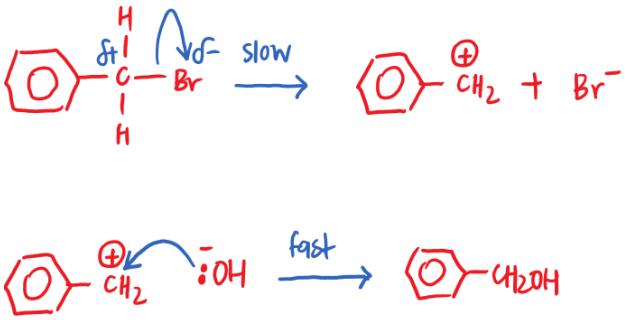
Since **$t_{½}$ is constant at 30 min**, reaction is **first order with respect to [$C_6H_5CH_2Br$]**.

When $[OH^-]$ x 2, the same graph is obtained. This shows that the **rate is independent on $[OH^-]$**. Hence, reaction is **zero order with respect to $[OH^-]$**.

(ii) Draw the mechanism of the hydrolysis reaction between benzyl bromide and hydroxide ion

[2]

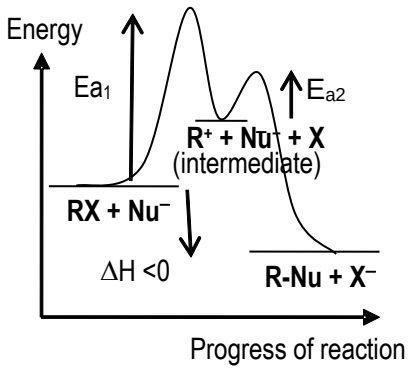
Nucleophilic substitution (S_N1).



(iii) Hence, draw a fully labelled reaction pathway diagram for the hydrolysis of benzyl bromide.

…… [2]

Energy Profile of S_N1 reaction



Accept endothermic or exothermic, but arrow must point from reactants to products

*ecf from **(ii)** if students gave S_N2 mechanism*

(iv) Unlike most straight chain primary bromoalkanes, such as 1-bromoheptane, the hydrolysis of benzyl bromide is zero order with respect to hydroxide ions.

Suggest **two** reasons why benzyl bromide undergoes the mechanism in **(b)(ii)**.

……..... [2]

Bulky benzene ring causes **steric hinderance**, preventing S_N2.

The **carbocation intermediate is stable**. The p orbital of the positively charged C can overlap with the p orbitals of the benzene ring. As the **positive charge is delocalised** into π electron cloud of the **benzene ring**, the positive charge is more dispersed.

In the third experiment, the same experiment was conducted using 25 cm^3 of 0.1 mol dm^{-3} sodium hydroxide solution and 25 cm^3 of 0.0050 mol dm^{-3} of benzyl chloride solution.

(v) **On Fig. 3.1**, sketch how the graph would look like when $C_6H_5CH_2C\mathit{l}$ was used instead of $C_6H_5CH_2Br$.

Explain your answer.

……..... [3]

Atomic size of C*l* < Br. **C-C*l* bond** is shorter and **stronger** due to **more effective orbital overlap**. Hence, more energy is required to break the bond and the **reaction is slower**.

[Total: 15]

4 Calcium carbonate, $CaCO_3$, is one of nature's most abundant raw materials. It is found as a component of seashells, eggshells, corals and pearls. In terms of applications, it has been used in cave paintings, paper, plastics and construction.

(a) (i) Explain why Ca^{2+} has a larger ionic radius than Na^+.

……..…….... [1]

Ca^{2+} has **one more shell of electrons** compared to Na^+ and the valence electrons are **further away from the nucleus** / **experience greater shileding effect**. and. Hence, there is **weaker attraction** between the nucleus and the valence electrons in Ca^{2+}.

(ii) Despite Ca^{2+} having a larger ionic radius than Na^+, the magnitude of the lattice energy of calcium carbonate is still larger than that of sodium carbonate.

Explain why this is so.

……..…….... [1]

$|LE| \alpha |(q^+.q^-)/(r_+ + r_-)|$

Ca^{2+} has a **higher charge** than Na^+. The higher charge of Ca^{2+} **outweighs its increase in ionic radius**, such that the |LE| is still higher.

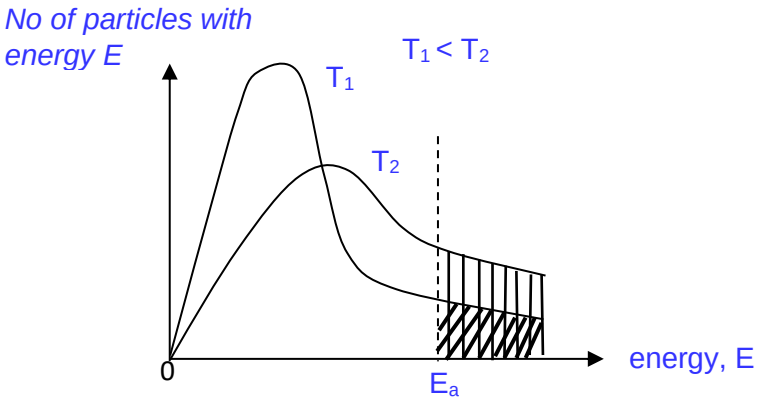
Limestone is a type of calcium carbonate-containing rock found naturally. In industry, large quantities of limestone are heated to form calcium oxide. The equation for this thermal decomposition is as shown.

$$CaCO_3(s) \longrightarrow CaO(s) + CO_2(g)$$

(b) (i) The heating of calcium carbonate takes place over a range of temperatures from 1200 K to 1500 K.

With the aid of a Boltzmann distribution diagram, explain the effect of a high temperature range on the rate of thermal decomposition of calcium carbonate.

……..…….... [3]



At high temperature, the reacting **particles gain kinetic energy**. There are **more particles with energy greater than or equal to the activation energy**. Hence**, frequency of effective collision increases** and the thermal decomposition of $CaCO_3$ happens **faster**.

(ii) Under the influence of the calcium cation, the carbonate ion in calcium carbonate undergoes thermal decomposition to form oxide and carbon dioxide in one step. In this mechanism, a σ bond breaks and a π bond forms simultaneously. [2]

Draw the mechanism for the thermal decomposition of the carbonate ion. Show all charges and relevant lone pairs and show the movement of electron pairs by using curly arrows.

(iii) The thermal decomposition of both calcium carbonate and calcium ethanedioate, CaC_2O_4, involve the weakening and breaking of the same bond. Despite this, the temperature for thermal decomposition required for both calcium salt is different.

Predict which calcium salt requires a higher temperature for thermal decomposition. Explain your answer by making reference to the bond which is weakened and broken.

……..…….... [3]

Thermal decomposition of **calcium carbonate** requires a higher temperature. **CO_3^{2-} has a smaller electron cloud than $C_2O_4^{2-}$** and so, the **former is less easily distorted / polarised** by Ca^{2+}. Thus, a **lower energy** is required to **weaken and break the C-O bond** in CaC_2O_4.

(iv) Lithium carbonate behaves like calcium carbonate during thermal decomposition. Suggest an explanation for this.

……..……..... [2]

Li^+ has a much **smaller ionic radius** despite having a smaller charge than Ca^{2+}. Hence, it has a similarly **high charge density** and hence high polarising power. It will **polarise / distort the electron cloud of carbonate**, weakening C-O and thus requiring a small amount of energy to break it.

(c) The Solvay Process is a continuous process that uses limestone to produce sodium carbonate.

The Solvay process comprises of the following key steps.

I $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$

II $NaCl(aq) + CO_2(g) + NH_3(g) + H_2O(l) \rightleftharpoons NH_4Cl\,(aq) + NaHCO_3(s)$

III $2NaHCO_3(s) \rightarrow Na_2CO_3(s) + H_2O(l) + CO_2(g)$

IV $CaO(s) + H_2O(l) \rightarrow Ca(OH)_2\,(aq)$

V $Ca(OH)_2(aq) + 2NH_4Cl(aq) \rightarrow CaCl_2(aq) + 2NH_3(g) + 2H_2O(l)$

The Solvay Process operates as two cycles, an ammonia cycle and a carbon dioxide cycle, where both ammonia and carbon dioxide can be recycled.

(i) With reference to the above equations, explain how ammonia and carbon dioxide are recycled.

……..……..... [1]

The **NH_3 produced in step V** can be **used in Step II**.

The **CO_2 produced in steps I and III** can be **used in step II**.

(ii) Give one advantage and one disadvantage of recycling these gases.

……..……..... [2]

Advantage: Ammonia and carbon dioxide are **pollutants/greenhouse gases**. By recycling them, they are **not released into the environment**.

Disadvantage: **Expensive process** as it would be **necessary to separate the gases from the reaction mixture.**

Any other appropriate answers.

$NaHCO_3$ is soluble in water. However, the use of high concentration of sodium chloride results in the precipitation of $NaHCO_3$ in step **II**.

(iii) State Le Chatelier's Principle and explain how it can be used to explain why $NaHCO_3$ precipitates in step **II**.

…… [2]

When a system at dynamic **equilibrium is subjected to a change**, the system will react to **reduce/counteract** the effect of the change and re-establish equilibrium.

High [NaC*l*] causes the **equilibrium position to shift right** to **decrease the [NaC*l*]**, This results in **more $NaHCO_3$(s)**.

In step **III**, sodium hydrogen carbonate is heated to obtain sodium carbonate.

(iv) Suggest an experimental method to confirm the completion of this reaction.

…… [1]

Heat the product mixture, cool and then weigh its mass. **Constant mass** suggest the reaction is completed. OR

Measure the **volume of CO_2 produced** until it is **constant**.

(v) The sodium carbonate is eventually passed through a dryer and collected as crystals. Suggest a physical method to determine the purity of the sodium carbonate crystals.

…… [1]

Determine its **melting point**. The crystal is pure if it has similar melting point to pure sodium carbonate.

[Total: 19]

5 Copper is used globally in electrical wiring, printed circuit boards, generators and electric motors. Copper is also used in cars in various electronic devices, such as batteries and motors.

(a) State the electronic configuration of Cu^+.

$1s^2$…… [1]

$1s^2\mathbf{2s^2 2p^6 3s^2 3p^6 3d^{10}}$

(b) The following electrochemical cell was set up.

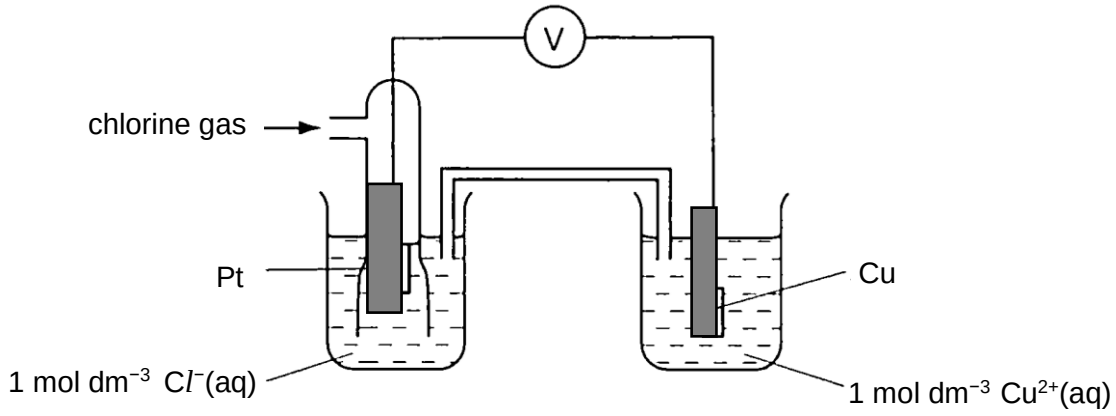


Fig. 5.1

(i) Construct a balanced equation for the cell reaction and use the *Data Booklet* to calculate the $E^{\ominus}_{cell}$ of this cell.

…… [1]

$\mathbf{Cu + Cl_2 \rightarrow Cu^{2+} + 2Cl^-}$

$E^{\ominus}_{cell}$ = +1.36 – (+0.34) = **+1.02 V**

(ii) Draw **on Fig. 5.1** the direction of electron flow when the reaction in **(b)(i)** is occurring. [1]

e- flow from Cu half cell (Cu electrode) to Cl_2 half cell (Pt electrode) (ecf from equation in **(i)**)

(iii) Using your answer in **(b)(i)**, calculate $\Delta G^{\ominus}$ for the reaction.

…… [1]

Overall 2 mol of electrons are transferred.

$\Delta G = - nFE_{cell} = - 2 \times 96500 \times (1.02) =$ **– 196 860 J mol^{-1} ≈ – 197 kJ mol^{-1}**

(ecf from equation in **(i)**)

(iii) Predict how the voltage of this cell would change, if at all, when a small amount of aqueous silver nitrate was accidentally spilled into the Cl_2/Cl^- half-cell. [2]

$Cl_2 + 2e \rightleftharpoons 2Cl^-$ $\quad E^{\theta} = +1.36V$

At the cathode, **Ag^+ reacts with Cl^- to form insoluble $AgCl$ solid**. This **decreases [Cl^-]**. The **position of equilibrium shifts right to increase [Cl^-]**. As more Cl_2 is reduced, **$E_{cathode}$ becomes more positive**. Hence, **E_{cell} is more positive and voltage increases**.

(c) A car motor is electroplated with copper to replace its worn copper coating. The total surface area to be electroplated is 0.1m x 0.2m.

A current of 5.0A is used to electroplate one side of the car motor with new copper for 2h. The electrolyte is copper (II) sulfate.

(i) Calculate the number of copper atoms electroplated on the car motor. [2]

Amount of charge = 5.0 x 60 x 60 x 2 = 36000 C

Amount of e = 36000/96500 = 0.37305 mol

Cu^{2+} : e = 1: 2

Amt of Cu = 0.37305 / 2 = 0.18652 mol

No of Cu atoms electroplated = 0.18652 x 6.02 x 10^{23} = **1.13 x 10^{23} atoms**

(ii) Assume that each copper atom occupies a cube of length 2.98 x 10^{-12} m and that there is a uniform coverage. [1]

Calculate the depth of copper electroplated in metres, m.

Vol of Cu atoms = 1.13 x 10^{23} x $(2.98 \times 10^{-12})^3$ = 2.9904 x 10^{-12} m^3

Depth of Cu (atoms) = 2.9904 x 10^{-12} / (0.1 x 0.2) = **1.49 x 10^{-10} m** (3sf) (ecf from **(i)**)

Copper (II) iodate, $Cu(IO_3)_2$, (M_r = 413.5) is sparingly soluble in water.

The solubility of copper (II) iodate in water is 1.36 g dm^{-3}.

(d) (i) Calculate the solubility product, K_{sp}, of copper (II) iodate, stating its units

[2]

Solubility of $Cu(IO_3)_2$ = 1.36 / 413.5 = 3.2889×10^{-3} mol dm^{-3}

$K_{sp} = [Cu^{2+}][IO_3^-]^2$

$K_{sp} = (3.2889 \times 10^{-3})(2 \times 3.2889 \times 10^{-3})^2$ = **1.42×10^{-7} mol^3 dm^{-9}**

(ii) Copper (II) bromide is a greyish solid that is highly soluble in water.

Copper (II) bromide solid was added to 500 cm^3 of 0.100 mol dm^{-3} potassium iodate solution. Determine minimum mass of copper (II) bromide solid that can be added to the solution for a precipitate to form.

[2]

$1.42 \times 10^{-7} = [Cu^{2+}] (0.100)^2$

$[Cu^{2+}]$ = **1.42×10^{-5} mol dm^{-3}** *(ecf Ksp from **(ii)**)*

Minimum mass of $CuBr_2$ = $1.42 \times 10^{-5} \times 0.5 \times (63.5 + 79.9 \times 2)$ = **0.00159 g** *(ecf $[Cu^{2+}]$)*

(e) (i) Write an equation which describes the standard enthalpy change of hydration of $Cu^{2+}(g)$.

…… [1]

Cu^{2+} (g) + aq → Cu^{2+} (aq)

(ii) Hence, by considering the type of interactions involved, explain why the standard enthalpy change of hydration is always negative.

Explain how the interactions arise.

…… [2]

In hydration of a gaseous cation, there is **formation of ion-dipole interactions** between the **positively charged cation with the δ− O atom of water molecules**. Bond formation is exothermic.

(iii) The following data is useful in this question

enthalpy change of hydration of $Cu^{2+}(g)$	= −1650 kJ mol^{-1}
enthalpy change of hydration of iodate ions (g)	= −460 kJ mol^{-1}
enthalpy change of solution of copper (II) iodate	= −16.2 kJ mol^{-1}

Calculate the lattice energy of copper (II) iodate using data from the above list.

[1]

$\Delta H_{soln}^{o} = \Delta H_{hyd}^{o} - L.E.$

LE = [(−1650) + 2(−460)] – (−16.2) = -2553.8 = **-2550 kJ mol^{-1}**

[Total: 17]