H

TEMASEK JUNIOR COLLEGE

2022 JC2 PRELIMINARY EXAMINATION

Higher 2

CANDIDATE NAME	ANSWERS

CENTRE NUMBER	S					INDEX NUMBER					

Chemistry **9729/02**

Paper 2 Structured Questions **23 August 2023**

2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your Centre number, index number, name and CG in the spaces at the top of this page.
Write in dark blue or black pen.
You may use an HB pencil for any diagrams or graphs.
Do not use staples, paper clips, glue or correction fluid.

Answer **all** the questions in the spaces provided on the Question Paper.
The use of an approved scientific calculator is expected, where appropriate.

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

For Examiner's Use		
Paper 1		**/30**
Paper 2	**Q1**	
	Q2	
	Q3	
	Q4	
	Q5	
	Q6	
	Total	**/75**
Paper 3		**/80**
TOTAL (%)		**/100**

This document consists of **17** printed pages and **3** blank page.

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

1 Atoms and ions of elements are made up of the three subatomic particles, protons, electrons and neutrons, in varying amounts.

(a) Complete the following table to show the number of each particle in $^{7}Li^{+}$ and $^{14}C^{2-}$.

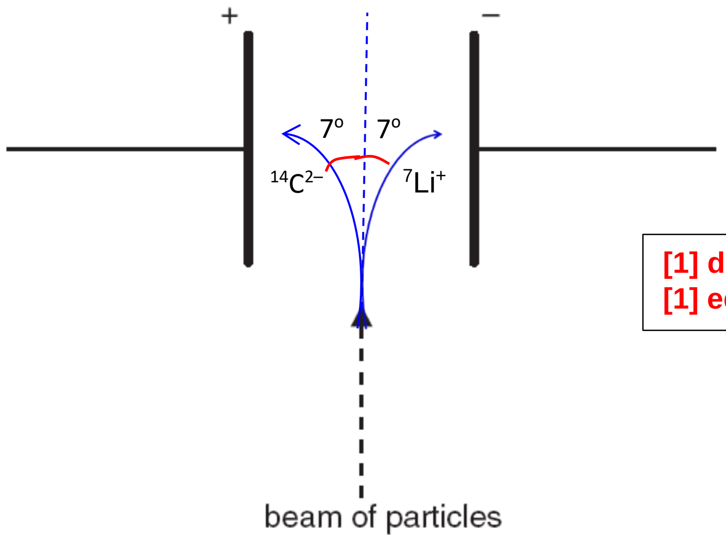
Ion	protons	electrons	neutrons
[1] $^{14}C^{2-}$	**6**	**8**	**8**
[1] $^{7}Li^{+}$	**3**	**2**	**4**

[2]

(b) Separate beams of $^{14}C^{2-}$ and $^{7}Li^{+}$ ions are passed through an electric field in the set-up below. The angle of deflection of the $^{14}C^{2-}$ beam is 7.0°.

Sketch on the diagram below, the paths taken by beams of $^{7}Li^{+}$ and $^{14}C^{2-}$ ions in the presence of an electric field. Label your sketch clearly.

[2]



[1] direction
[1] equal angle

[Total: 4]

2 **(a)** **(i)** Explain what is meant by the term 'electronegativity', and how it relates to the concept of bond polarity. [2]

[1] Electronegativity refers to the **ability of an atom to attract the shared electron pair** in a **covalent molecule/bond**

[1] Bond polarity is a measure of **how equally the electrons are shared between the two bonded atoms.** Bonded atoms with **different electronegativities** will result in a **polar bond.**

(ii) State and explain the change in electronegativity across a period in the Periodic Table. [2]

Across a Period

- ✓ **Nuclear charge increases** as number of protons increases.
- ✓ **Screening effect remains approximately constant** as electrons are added to the same electronic shell.
- ✓ **Increase in the attractive force** between the nucleus and the bonding electrons in the outer shell and atomic radius decreases.
- ✓ **Trend: Electronegativity increases across the period.**

2✓ : 1m

(iii) Explain, in terms of electronegativity why the bonding in Na*Cl* is different from the bonding in P*Cl*$_5$. [1]

[1] **Difference in electronegativity between Na and C*l* is greater than between P and C*l*.** Hence transfer of electrons occur between Na and C*l* resulting in an **ionic compound** whereas sharing of electrons occur between P and C*l* resulting in a **covalent compound.**

(b) Period 3 elements react with chlorine gas, C*l*$_2$ (g), to form chlorides. The chlorides of the elements in the third period behave in different ways when added to water, depending on their structure and bonding.

The table shows the differences in observations which occur when three Period 3 chlorides are added to water.

Period 3 chloride	Observations when added to excess water	pH of solution formed with water
Na*Cl*	White solid disappears. Colourless solution obtained.	7
P*Cl*$_5$	Colourless solution obtained.	1
Liquid Q	Vigorous reaction with cold water. White solid and pale yellow solution obtained.	1

(i) Explain in terms of bonding, why Na*Cl* and P*Cl*$_5$ behave differently when added to water. Write equation for any reaction that occurs. [2]

[1] **Na*Cl* is ionic** and it undergoes **hydration** in water. **P*Cl*$_5$ is covalent** and it undergoes **hydrolysis** in water to form an acidic solution.
[1] $PCl_5(s) + 4H_2O(l) \rightarrow H_3PO_4(aq) + 5HCl(aq)$

[Turn over

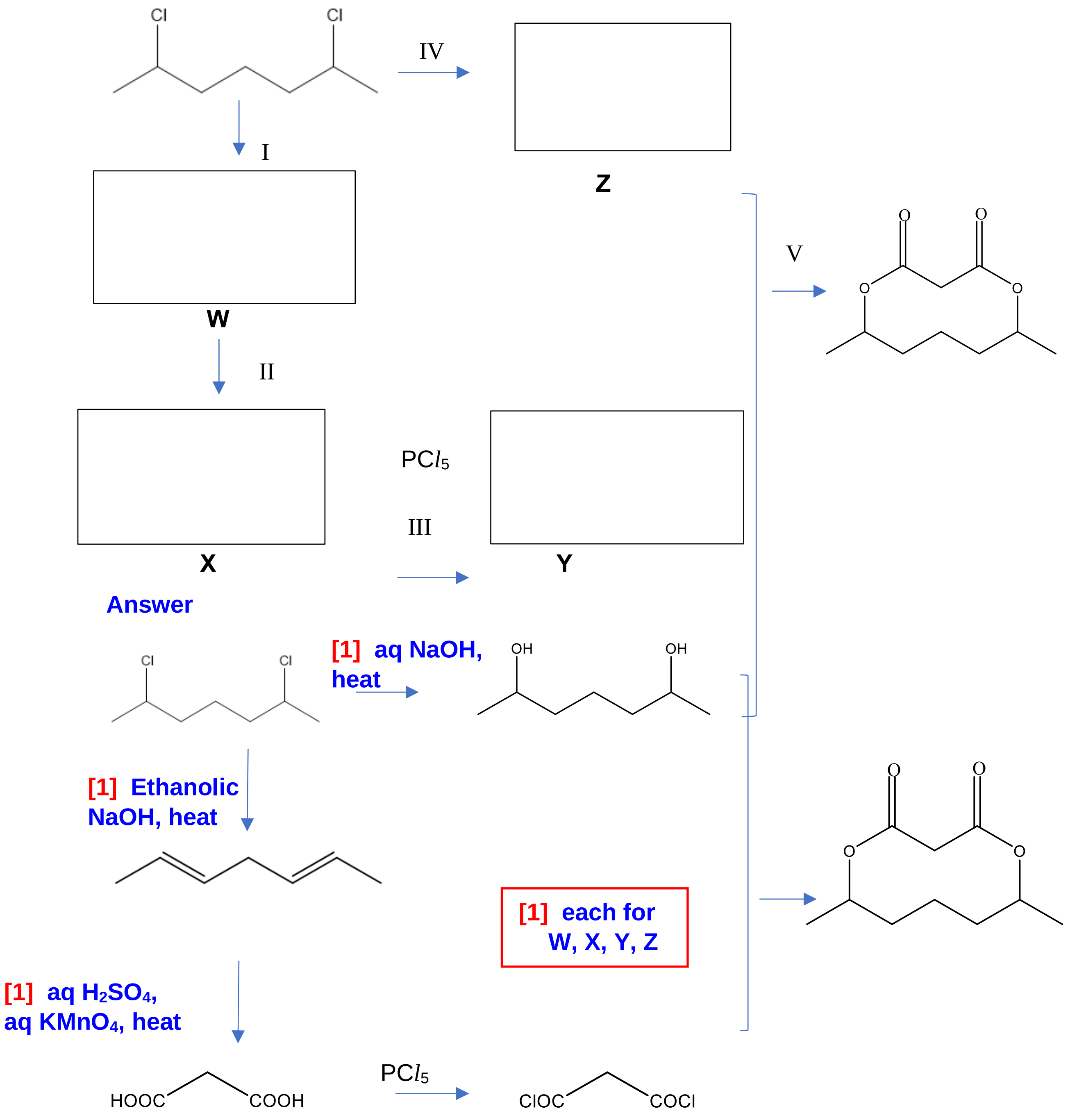
(ii) PCl_5 also reacts with limited amount of water. Write the equation for the reaction. [1]

[1] $PCl_5(s) + H_2O(l) \rightarrow POCl_3(l) + 2HCl(g)$

(iii) State the identity of Q. [1]

[1] Q is $SiCl_4$

(c) Phosphorus(V) chloride, PCl_5, is involved in the following reaction scheme. Suggest the reagents and conditions for steps I, II and IV and the products **W** to **Z** in the synthetic scheme below. [7]



[Total: 16]

3 Group 2 elements of the Periodic Table are also known as the *alkaline earth metals*. The metals are named after their oxides, the alkaline earths. "Earth" was a term applied by early chemists to non-metallic substances that are insoluble in water and resistant to heating.

Fig. 3.1 shows some reactions of the Group 2 element magnesium and its compounds.

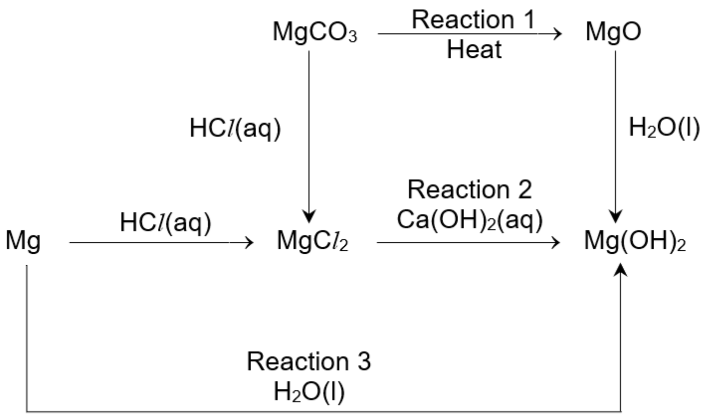


Fig. 3.1

(a) $MgCO_3(s)$ undergoes thermal decomposition in Reaction 1.

Describe and explain the trend in thermal stability of Group 2 carbonates in terms of the charge density of the cation and polarizability of the large anion. [2]

[2] 3√ = 1 mark

Down the Group, charge of the cation remains constant but ionic radius of cation increases. Hence √ charge density of the cation decreases. √ Polarising power of cation decreases resulting in √ less distortion of the electron cloud of the large anion CO_3^{2-}, √ weakening the C–O covalent bond less.

√ More energy (or higher temperature) needed to decompose the carbonate. √ Carbonates become more stable to heat down the Group.

(b) Write an equation for Reaction 3.

Explain the relative reactivity of the Group 2 elements (magnesium, calcium and barium) with water, and relate this reactivity to relevant $E^{\ominus}$ values. [3]

[1] $Mg(s) + 2H_2O(l) \rightarrow Mg(OH)_2(aq) + H_2(g)$

$E_{H_2O/H_2}^{\ominus} = -0.83$ V

√ $E_{Mg^{2+}/Mg}^{\ominus} = -2.38$ V
$E_{Ca^{2+}/Ca}^{\ominus} = -2.87$ V
$E_{Ba^{2+}/Ba}^{\ominus} = -2.90$ V

Down the Group, √ atomic radius increases. √ Attraction of the nucleus for the valence electrons decreases OR electrons can be removed more easily. √ Reactivity increases OR more readily oxidised down the Group.

[2] 2 √ = 1 mark

(c) In Reaction 2, $Mg(OH)_2(s)$ is precipitated when $Ca(OH)_2(aq)$ is added to $MgCl_2(aq)$. No precipitate is observed when $Ca(OH)_2(aq)$ is added to $BaCl_2(aq)$

Explain the difference in observations in terms of lattice energy. [2]

Solubility of Group 2 hydroxides increases down the Group.

√ $|\text{Lattice energy}| \propto \left|\frac{q_+q_-}{r_+ + r_-}\right|$**. q_+, q_-, r_- are the same, since √ Mg^{2+} has a smaller ionic radius (r_+) than Ba^{2+}, √ $Mg(OH)_2$ has a larger magnitude of lattice energy, stronger ionic bonds and √ lower solubility than $Ba(OH)_2$.**

[2] 2 √ = 1 mark

(d) Describe and deduce from $E^{\ominus}$ values, the relative reactivity of Group 17 elements (chlorine to iodine) as oxidising agents.

Hence, state the colour of the resultant solution when 1 cm^3 of $MgCl_2(aq)$ is added to 1 cm^3 of $Br_2(aq)$ in a test-tube. [3]

√ $E_{Cl_2/Cl^-}^{\ominus} = +1.36$ V

$E_{Br_2/Br^-}^{\ominus} = +1.07$ V

$E_{I_2/I^-}^{\ominus} = +0.54$ V

Down the Group, $E_{X_2/X^-}^{\ominus}$ becomes less positive.
√ size of atom increases or electron affinity decreases
√ lower tendency for X_2 to be reduced to X^-
√ oxidising power of halogens decreases/reactivity decreases down the group
[2] 2 √ = 1 mark

[1] The solution remains orange. *[Can be quoted from Data Booklet]*

(e) Element **X** is a Period 5 element.

X reacts with oxygen to form an insoluble white oxide that has a melting point of 1900 °C. The oxide of **X** conducts electricity only when in liquid state.

The chloride of **X** acts as a Lewis acid. It forms an acidic solution when dissolved in water.

(i) Suggest the structure of the oxide of **X**. Explain your answer. [2]

[1] Oxide of X has giant ionic structure.
[1] Molten oxide of X contains mobile ions as charge carriers to conduct electricity.

(ii) Suggest the structure shown by the chloride of **X** and identify **X**. [2]

[1] Chloride of X has simple molecular structure. Chloride of X is covalent and undergoes hydrolysis with water to give an acidic solution.
[1] X is indium.

[Total: 14]

4 **(a)** When bromine and sodium hydroxide are mixed, sodium bromide and sodium bromate(V), $NaBrO_3$, are formed.

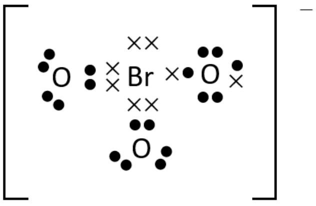
(i) Write a balanced equation for this reaction. [1]

[1] $6NaOH + 3Br_2 \rightarrow 5NaBr + NaBrO_3 + 3H_2O$

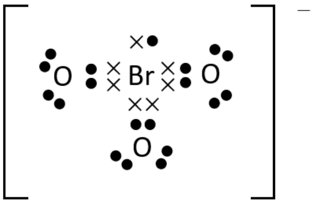
Working
[O] $Br_2 + 2e^- \rightarrow 2Br^-$ (x5)
[H] $Br_2 + 12OH^- \rightarrow 2BrO_3^- + 6H_2O + 10e^-$

(ii) Draw the dot-and-cross diagram for the bromate(V) ion, BrO_3^-. [1]

[1]



or



(b) A student is given three unlabelled bottles separately containing pentane, pent-1-ene and pent-2-ene.

(i) Suggest a chemical test to distinguish between the three compounds. [2]

[1] Heat the three compounds with dilute H_2SO_4, $KMnO_4$

[1] Pent-1-ene: Purple $KMnO_4$ decolorise and CO_2 evolved
Pent-2-ene: Purple $KMnO_4$ decolorise
Pentane: No decolorisation of purple $KMnO_4$

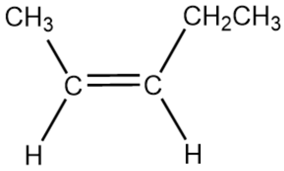
(ii) Infra-red absorptions can be used to identify functional groups in organic compounds.

With reference to the table of characteristic infra-red absorption frequencies in the *Data Booklet*, suggest how pentane can be distinguished from the other two compounds. [1]

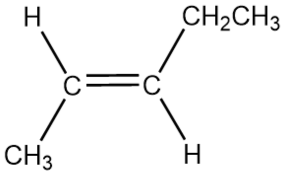
[1] As pent-1-ene and pent-2-ene are alkenes, an absorption at 1635 to 1690 cm^{-1} (for C=C group) will be observed, which is not observed for pentane.

(iii) One of the three compounds exhibits cis-trans isomerism. Draw and label the two cis-trans isomers. [1]

[1]



cis



trans

[Total: 6]

5 Monoprotic acids are acids that donate one H^+ per molecule.

(a) Benzoic acid, C_6H_5COOH, is a monoprotic acid, with a pK_a value of 4.20.

Calculate the pH of 0.010 mol dm^{-3} sodium benzoate. [2]

**** sodium benzoate is a salt of weak acid, so will undergo salt hydrolysis to give OH⁻ → find pK_b ****

$C_6H_5COO^- + H_2O\ (l) \rightleftharpoons C_6H_5COOH + OH^-$

pK_a + pK_b =14

pK_b = 14 – 4.20 = 9.80

$K_b = 10^{-9.8} = 1.58 \times 10^{-10}$ mol dm^{-3}

$[OH^-] = \sqrt{c \times K_b} = \sqrt{0.010 \times (1.58 \times 10^{-10})} = 1.26 \times 10^{-6}$ mol dm^{-3} [1]

pH = 8.10 (pH > 7) [1]

(b) Phenylboronic acid, $C_6H_5B(OH)_2$, can act as a Lewis acid due to the electron deficient B atom.

Define what is meant by a Lewis acid and give the balanced equation which represents phenylboronic acid acting as a Lewis acid in aqueous solution. [2]

Electron pair acceptor [1]

Dissociation equation in water [1]

$C_6H_5B(OH)_2 + H_2O \rightleftharpoons C_6H_5B^-(OH)_3 + H^+$

$C_6H_5B(OH)_2 + H_2O \rightleftharpoons [C_6H_5B(OH)_3]^- + H^+$

$C_6H_5B(OH)_2 + 2H_2O \rightleftharpoons C_6H_5B(OH)_3]^- + H_3O^+$

(c) Phenylboronic acid is a monoprotic acid with a pK_a value of 8.86.

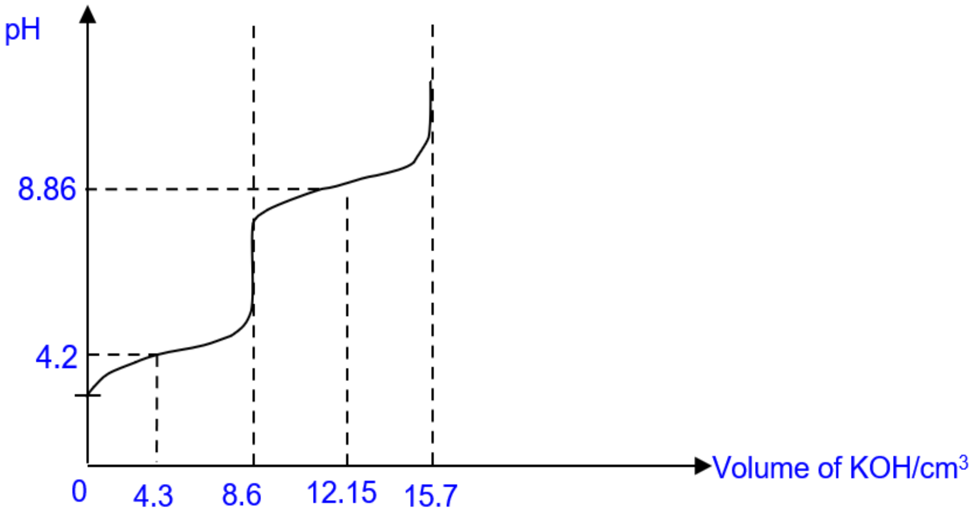
Benzoic acid has a pK_a value of 4.20.

10.0 cm^3 sample of **T**, a solution containing both benzoic acid and phenylboronic acid was titrated against 0.050 mol dm^{-3} KOH using a mixture of two indicators, bromothymol blue and phenolphthalein.

It was found that 8.6 cm^3 was needed to change the colour of the first indicator and a **further** 7.1 cm^3 was needed to change the colour of the second indicator.

(i) Sketch the shape of the pH curve during the titration on the given axes.

Label your graph clearly including the information in **(c)** as well as relevant pK_a values and the corresponding volumes. [2]



[1] graph shape with two equivalence point.

[1] labelling 4 volumes and 2 p*K*a values

(ii) Calculate the concentration of **each** of the two acids in sample **T**. [3]

<u>C_6H_5COOH is the stronger acid</u> and is neutralised <u>first</u> when 8.6 cm^3 KOH was added.

<u>To calculate [C_6H_5COOH]</u>

Amt of KOH in 8.6 cm^3 = $0.05 \times \frac{8.6}{1000}$ = 4.30×10^{-4} mol [✓]

KOH ≡ C_6H_5COOH

[C_6H_5COOH] = $\frac{4.30 \times 10^{-4}}{0.01}$ = <u>0.0430 mol dm^{-3}</u> [1]

<u>To calculate [phenylboronic acid]</u>

Amt KOH in 7.1 cm^3 = $0.05 \times \frac{7.1}{1000}$ = 3.55×10^{-4} mol [✓]

KOH ≡ $C_6H_5B(OH)_2$

[$C_6H_5B(OH)_2$] = $\frac{3.55 \times 10^{-4}}{0.01}$ = <u>0.0355 mol dm^{-3}</u> [1]

2[✓] = [1]

(d) Phenylethanol, $C_6H_5CH_2CH_2OH$, reacts with benzoic acid. However, phenol does not react directly with benzoic acid.

Suggest and explain why phenol does not react with benzoic acid. [2]

<u>Phenol is a weak nucleophile</u> [1]

<u>Lone pair electrons on O in phenol can delocalise into the benzene ring</u> [1], making it less available to act as a nucleophile to attack the electron deficient carbon atom in benzoic acid.

(e) In a separate experiment, 200 cm^3 of sodium hydroxide was added to 800 cm^3 of 0.3 mol dm^{-3} of propanoic acid to make a buffer solution of pH 5.00. The pK_a value of propanoic acid is 4.90.

(i) Explain what is meant by a *buffer* solution. [1]

A buffer solution resists pH changes when small amount of acid / H^+ or base / ^-OH are added. [1]

(ii) Write an equation to show what happens when a small amount of OH^- is added to the buffer solution. [1]

$CH_3CH_2CO_2H + OH^- \rightarrow CH_3CH_2CO_2^- + H_2O$ [1]

(iii) Calculate the concentration of the sodium hydroxide solution added to make the buffer solution. [2]

Let the conc of NaOH be a mol dm^{-3}.

Amt of NaOH added = 200/1000 x a = 0.2a mol

Amt of RCOOH added = 800/1000 x 0.3 = 0.24 mol

	RCOOH	NaOH	RCOONa
Initial / mol	0.24	0.2a	0
Change / mol	– 0.2a	– 0.2a	+ 0.2a
Final / mol	0.24 – 0.2a	0	0.2a

$$pH = pK_a + \log\frac{[salt]}{[acid]}$$

$$5 = 4.90 + \log\frac{0.2a}{0.24 - 0.2a}\ [1]$$

$$a = \underline{0.669\ mol\ dm^{-3}}\ [1]$$

[Total: 15]

6 Ethylamine, $CH_3CH_2NH_2$, is commonly used in the production of herbicides.

(a) To determine the standard enthalpy change of neutralisation, 60 cm^3 of 0.370 mol dm^{-3} aqueous ethylamine was placed in a polystyrene cup. Constant volume of dilute HC*l* was added. The mixture was stirred after each addition and the maximum temperature was recorded.

The following graph of (V_T × ΔT) against volume of HC*l* added was obtained in Figure 6.1. V_T represents the total volume of the mixture. The intersection of the 2 extrapolated lines corresponds to the equivalence point.

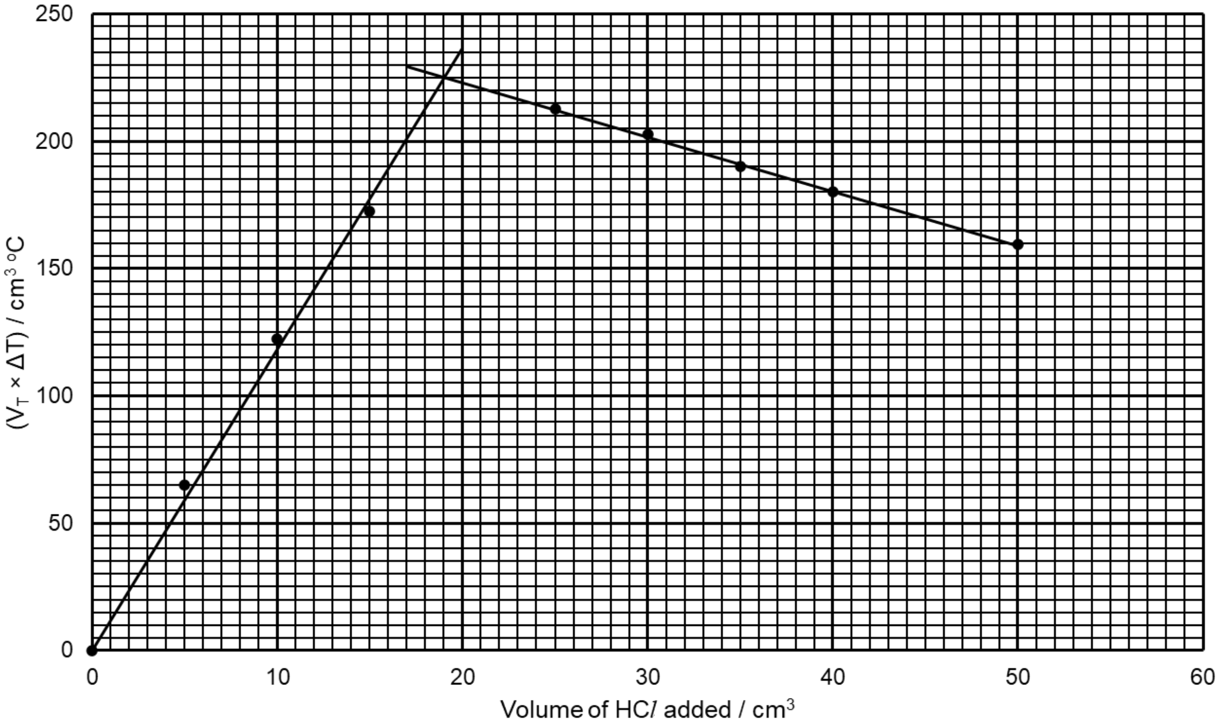


Figure 6.1

(i) Define the term *standard enthalpy change of neutralisation*. [1]

[1] The enthalpy change when acid and base react under infinitely dilute concentration to form one mole of water at 298 K and 1 bar.

(ii) Using the definition in **(a)(i)**, show that $\frac{V_T\Delta T}{n_{water}}$ is a constant value before equivalence point, where n_{water} is the amount of water produced during neutralisation.

Hence, explain the shape of the graph in Figure 6.1 before equivalence point. [2]

[1] explanation using equation

Before equivalence point

$$\Delta H^{\ominus}_{neu} = -\frac{mc\Delta T}{n_{water}} = -\frac{V_T c\Delta T}{n_{water}}$$

Since $\Delta H^{\ominus}_{neu}$ is a constant value for the same acid and base used and c is constant,

$$\frac{V_T\Delta T}{n_{water}} = constant$$

Since HC*l* added is the limiting reagent before equivalence point, $n_{water} \propto$ Vol of HC*l*

$$\frac{V_T\Delta T}{Vol\ of\ HCl} = constant$$

[1] Hence as volume of HC*l* increases before equivalence point, more water is produced, more heat is evolved, $V_T\Delta T$ increases proportionally.

(iii) Explain the shape of the graph in Figure 6.1 after equivalence point. [1]

Reaction is complete, so no more heat is given out. [1] Heat is lost to the surroundings, so ΔT drops and $V_T\Delta T$ decreases proportionally.

Alternative answer : Same amount of heat released but dispersed over a larger volume as volume of HC*l* increases.

(iv) Determine the maximum temperature change using relevant data from Figure 6.1. [1]

When volume of HC*l* = 19 cm^3, max $V_T\Delta T$ = 225

Total volume at equivalence point = 60 + 19 = 79 cm^3

Hence ΔT = 225 / 79 = 2.85 °C [1]

(v) Calculate the concentration of HC*l* used in the experiment. [1]

$1CH_3CH_2NH_2 \equiv 1HCl$

Conc of HC*l* used = $\frac{60\times0.370}{19}$ = 1.17 mol dm^{-3} [1]

(vi) Calculate the enthalpy change of neutralisation, $\Delta H_n^{\ominus}$, for the reaction between HC*l* and ethylamine. [2]

Assuming that the density of all aqueous solution is 1.00 g cm^{-3}.

Amt of water produced at equivalence point = 60/1000 x 0.37 = 0.0222 mol [1]

$$\Delta H^{\circ}_{neu} = -\frac{mc\Delta T}{n_{water}} = -\frac{V_T c\Delta T}{n_{water}} = -\frac{225\times4.18}{0.0222} = -42326 \text{ J mol}^{-1} = -42.3 \text{ kJ mol}^{-1} \text{ [1]}$$

ECF from (iv)

(b) The experiment was repeated with aqueous KOH and butylamine of identical concentration as ethylamine.

The table below shows the absolute theoretical values of the standard change of neutralisation, $|\Delta H_n^{\ominus}|$ with HC*l* of various bases.

Base	Theoretical $|\Delta H_n^{\ominus}|$
butylamine	x
ethylamine	40.7
KOH	57.9

Suggest a value for x, and hence explain your answer fully. [3]

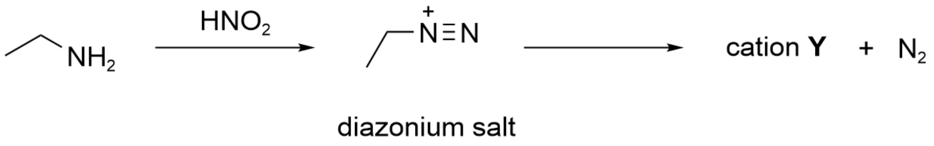
[1] x = 45 (any value in between 40.7 and 57.9)

[✓] Butylamine is a weaker base than KOH, so part of the heat evolved from the neutralisation process is absorbed back [✓] to dissociate the weak base for further neutralisation reaction, resulting in a less exothermic enthalpy change.

[✓] Butylamine is a stronger base than ethylamine due to [✓] greater electron donating effect by the longer alkyl chain which increases the electron density on N atom. Hence the neutralisation with HC*l* produces more heat and a higher $|\Delta H_n^{\ominus}|$.

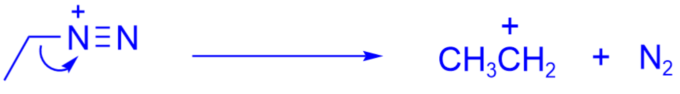
Every 2[✓] = [1]

(c) Primary aliphatic amines such as ethylamine react with nitrous acid, HNO_2, to form diazonium salts which *spontaneously decompose* by losing N_2, forming cation **Y**.



Illustrate, using curly arrows, the formation of cation **Y** and N_2 gas from the diazonium salt. [1]

[1]



(d) **(i)** Explain the general unreactivity of alkanes. [2]

[1] Alkanes have only carbon and hydrogen atoms which have similar electronegativity, hence there is no electron rich or electron poor region around the molecule which reacts with nucleophiles or electrophiles. In addition, the [1] C-C and C-H bond has high bond strength and require high energy to break.

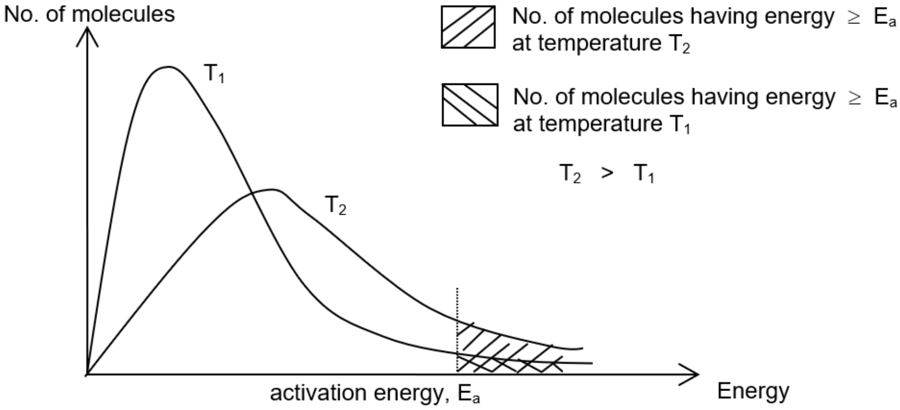
(ii) Alkanes undergo free radical substitution with halogens in ultraviolet light. The propagation step is found to be affected by temperature.

Sketch the Boltzmann distribution and explain how an increase in temperature affects the rate of reaction. [3]

[✓] The increase in the average kinetic energy of the reacting molecules leads to an increase in the collision frequency.

[✓] The number of reactant molecules having energy greater than or equal to the activation energy, E_a, is significantly increased when the temperature is increased.

[✓] The frequency of effective collisions increases. [✓] The rate constant, k increases and hence the rate increases.



[1] correct Boltzmann curve + legends + labels

2 [✓] = [1]

(e) Alkanes with high number of carbons are produced from the Wurtz reaction, whereby 2 alkyl halides are treated with sodium metal.

$$2\ CH_3\text{–}Cl + 2\ Na \rightarrow CH_3\text{–}CH_3 + 2NaCl$$

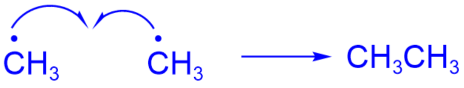
The reaction was first believed to follow a free radical mechanism.

In step 1, alkyl radicals are formed in the presence of sodium. In step 2, the radicals combine to form a larger chain alkane.

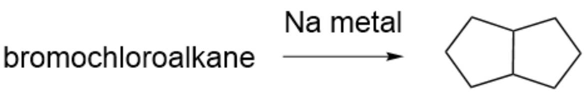
(i) Write balanced equations for step 1 and step 2 of the Wurtz reaction, for the formation of ethane using chloromethane. [2]

[1] $CH_3\text{–}Cl + Na \rightarrow NaCl + \bullet CH_3$

[1]



(ii) Bicyclic alkanes such as compound **X**, can be produced from the Wurtz reaction, using a bromochloroalkane.

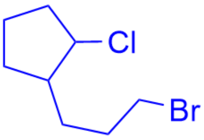


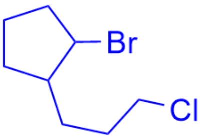
X

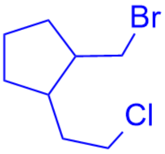
Deduce the structure of the bromochloroalkane used to produce **X**. [1]

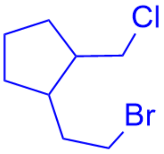
[1]

Alternative structures include:









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