ST ANDREW'S JUNIOR COLLEGE

JC2 PRELIMINARY EXAMINATIONS

HIGHER 2

CANDIDATE NAME

2	**3**	**S**		

CLASS

CHEMISTRY **9729/03**

Paper 3 Free Response **9 September 2024**

Candidates answer on the Question Paper. **2 hours**

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name and class on all the work that 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.

If additional space is required, you should use the pages at the end of this booklet.

The question number must be clearly shown.

Section A

Answer **all** questions.

Section B

Answer **one** question.

A Data Booklet is provided.

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

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		**8**
Q2		**21**
Q3		**20**
Q4		**11**
Q5 **or** **Q6**		**20**
Total		**80**

This document consists of **32** printed pages (including this cover page).

Section A

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

1 **(a)** **(i)** Define the term *relative atomic mass*. **[1]**

Relative atomic mass of an element is the **average mass of 1 atom of the element relative to 1/12th the mass of 1 atom of ^{12}C**. **[1]**

OR

$$\frac{\text{average mass of one atom of an element}}{\frac{1}{12}\text{ the mass of one atom of carbon-12}} \textbf{ [1]}$$

OR

It refers to **mass of one mole of atoms** **relative/compared to 1/12 (the mass) of 1 mole of ^{12}C** or in which 1 mole ^{12}C (atom) has a mass of (exactly) 12g.

(ii) Diamond, which is made up of both ^{12}C and ^{13}C atoms, has a relative atomic mass of 12.011. With reference to Table 1.1, calculate the percentage abundance of ^{13}C in diamond. **[1]**

Table 1.1

	Relative isotopic mass
^{12}C	12.000
^{13}C	13.003

Let the percentage abundance of ^{13}C be y%.

$$\frac{(13.003)(y) + (12.000)(100-y)}{100} = 12.011$$

y = 1.096 ≈ **1.10 [1]**

(b) **(i)** Define the term *enthalpy change of atomisation* of $C_{(graphite)}$. **[1]**

It refers to the **enthalpy change/energy required** to **form one mole of gaseous C atoms from $C_{(graphite)}$.** **[1]**

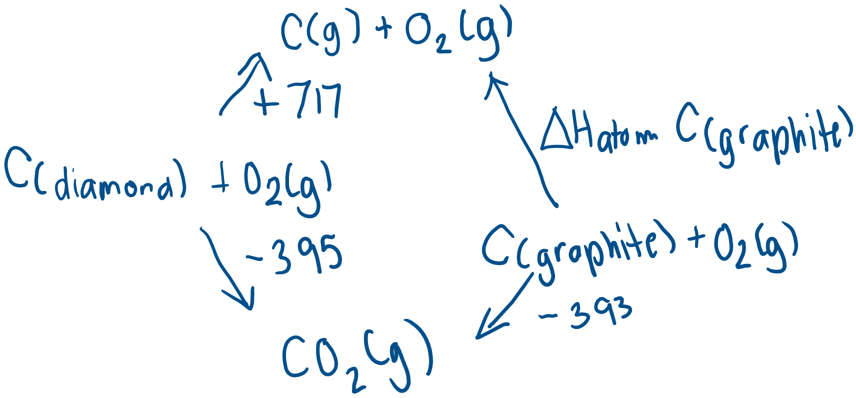
(ii) Some enthalpy change values are shown in Table 1.2.

Table 1.2

	value / kJ mol^{-1}
enthalpy change of atomisation of $C_{(diamond)}$	+717

enthalpy change of combustion of $C_{(diamond)}$	–395
enthalpy change of combustion of $C_{(graphite)}$	–393

Using the data in Table 1.2, construct a suitable energy cycle to show that the enthalpy change of atomisation of $C_{(graphite)}$ is +719 kJ mol^{-1}. **[3]**



[2]

ΔH_{atom} = **<u>-393 + 395 + 717</u>** = +719 kJ mol^{-1} **[1]**

(iii) Even though graphite and diamond are allotropes of carbon, they have different enthalpy change of atomisation.

With reference to hybridisation of the carbon atoms, explain this difference. **[2]**

Carbon atoms in graphite are **<u>sp^2 hybridised</u>** while the carbon atoms in diamond are **<u>sp^3 hybridised</u>**. As **<u>sp^3 hybrid orbitals have less s character</u>** than sp^2 hybrid orbitals, C-C in diamond will experience **<u>less effective orbital overlap</u>**, leading to **<u>weaker bond</u>** which requires less energy to overcome. Hence, the enthalpy change of atomisation of $C_{(diamond)}$ is less endothermic.

[Total: 8]

2 This question is on the chemistry of main group elements and their compounds.

(a) **(i)** The melting point of beryllium and magnesium are shown in Table 2.1.

Table 2.1

	melting point / °C
beryllium	1287
magnesium	650

Explain, in terms of structure and bonding, the difference in melting point between beryllium and magnesium. **[2]**

Both Be and Mg are **giant metallic lattices** with **strong electrostatic forces of attraction between the respective cations and sea of delocalised electrons / metallic bonds**.

Be^{2+} has a smaller cationic radius / higher charge density than Mg^{2+} and therefore, the **metallic bond in Be is stronger** and will require more energy to overcome. As such, Be has a higher melting point.

(ii) Explain why beryllium is a weaker reducing agent than magnesium in terms of shielding and nuclear charge. **[2]**

Down the group from Be to Mg, the number of protons increases and hence, **nuclear charge increases**. As the **number of** filled **electron shells / inner shells increase**, the **valence electrons are further away from nucleus** and experience **stronger shielding effect**. Therefore, the **valence electrons experience weaker nuclear attraction** and require less energy to be removed.

(iii) Explain why the radius of beryllium ion is smaller than the radius of beryllium atom. **[2]**

Both Be and Be^{2+} have the same number of protons and therefore, **same nuclear charge**. **Be^{2+} has 1 less shell of electrons** than Be. Therefore, the **valence electrons of Be^{2+} will experience lower shielding effect** and **stronger nuclear attraction**.

(iv) Unlike other Group 2 carbonates, beryllium carbonate is unstable as it will quickly decompose to form beryllium oxide and carbon dioxide.

On Fig. 2.1, draw the mechanism for the decomposition of beryllium carbonate. Show the relevant lone pair and movement of electron pairs by using curly arrows on the carbonate ion.

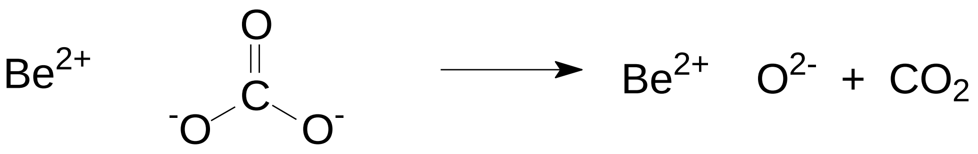
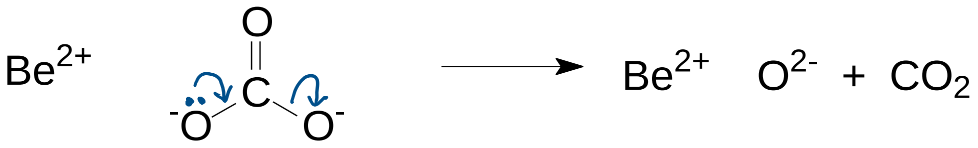


Fig 2.1

[1]



[1]

(b) Beryllium can be extracted from ores. An ore containing beryllium is first heated to a very high temperature to form beryllium fluoride, BeF_2, before it is dissolved in water. KOH pellets are then added to 1 mol dm^{-3} of aqueous BeF_2 to precipitate $Be(OH)_2$. The pH of the resultant solution is 12.4.

$Be(OH)_2$ is sparingly soluble in water. The K_{sp} of $Be(OH)_2$ is 2.55×10^{-4} at 25 °C.

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

$\underline{K_{sp} = [Be^{2+}][OH^-]^2 \text{ mol}^3 \text{ dm}^{-9}}$ [1]

(ii) Calculate the percentage of Be^{2+} that has been precipitated. **[2]**

pOH = 14 – 12.4 = 1.6

$[OH^-] = 10^{-1.6}$

$2.55 \times 10^{-4} = [Be^{2+}][0.025118]^2$

$[Be^{2+}]$ = **$\underline{0.40415 \text{ mol dm}^{-3}}$**

% precipitated = (1 - 0.40415) / 1 x 100% = **<u>59.6%</u>**

(iii) HC*l*(aq) and NaOH(aq) are added to separate saturated solutions containing $Be(OH)_2$, which is a white solid. The observations are recorded in Table 2.2.

Table 2.2

procedures	observations
HC*l*(aq) is added to $Be(OH)_2$.	White solid dissolves to form colourless solution.
NaOH(aq) is added to $Be(OH)_2$.	White solid dissolves to form colourless solution.

Explain how the solubility of $Be(OH)_2$ is affected by the addition of HC*l* and NaOH. **[2]**

$Be(OH)_2 \rightleftharpoons Be^{2+} + 2OH^-$

When HC*l*(aq) is added, **[OH^-] decreases due to neutralisation** and by Le Chatelier's Principle, **position of equilibrium shifts right** to produce more OH^-, resulting in $Be(OH)_2$ to dissolve.

OR

$Be(OH)_2$ reacts with HC*l* via **neutralisation** to form a **soluble salt BeC*l*$_2$.**

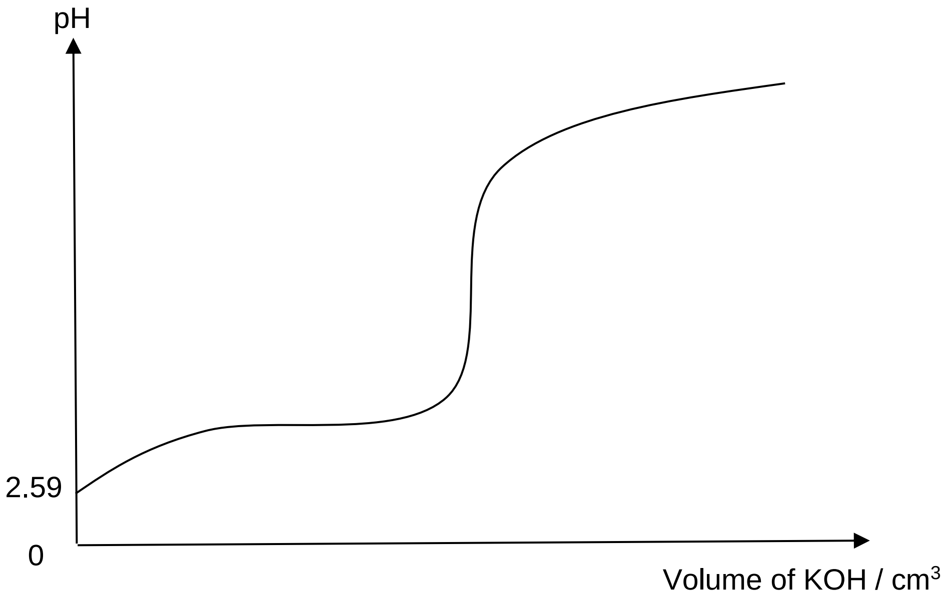
When NaOH(aq) is added, the white solids dissolve due to the **formation of complex ion $[Be(OH)_4]^{2-}$**.

(iv) In the gaseous state, BeF_2 has the same number of σ and π bonds as CO_2.

Draw the structure of BeF_2 in the gaseous state. **[1]**

[1]

(c) 25.0 cm^3 of 0.100 mol dm^{-3} of benzoic acid, C_6H_5COOH, was titrated with 0.100 mol dm^{-3} of KOH. The change in pH was monitored and shown in the graph below.



(i) Show that K_a of benzoic acid is 6.61 x 10^{-5} mol dm^{-3}. **[1]**

$[H^+] = 10^{-2.59} = 2.5704 \times 10^{-3}$ mol dm^{-3}

$K_a = \frac{(2.5704 \times 10^{-3})^2}{0.1} = 6.61 \times 10^{-5}$ mol dm^{-3}

(ii) Calculate the pH of the solution when 12.5 cm^3 of KOH was added. **[1]**

When 12.5 cm^3 of KOH was added, $[C_6H_5COOH]$ and $[C_6H_5COO^-]$ were the same. In other words, there is maximum buffering capacity.

$pH = pK_a = -\lg(6.61 \times 10^{-5}) =$ **4.18** (to 3 sf) **[1]**

(iii) Calculate the pH at equivalence point. **[3]**

Amount of sodium benzoate formed at equivalence point

= 0.025 x 0.1 = 0.0025 mol

[sodium benzoate] = 0.0025 / 0.05 = 0.05 mol dm^{-3}

$C_6H_5COO^- + H_2O \rightleftharpoons C_6H_5COOH + OH^-$

$K_b = K_w/K_a = 10^{-14} / (6.61 \times 10^{-5}) =$ **1.5129×10^{-10}** mol dm^{-3}

$1.5129 \times 10^{-10} = \frac{[OH^-]^2}{0.0500}$

$[OH^-] =$ **2.7503×10^{-6}** mol dm^{-3}

$pOH = -\lg(2.75 \times 10^{-6}) = 5.5606$

pH = 14 - 5.5606 = **8.44**

(iv) Table 2.3 shows some data on six indicators.

Table 2.3

indicator	colour in acid	colour in alkali	pH range of colour change
methyl orange	red	yellow	3.2 – 4.4
methyl red	red	yellow	4.8 – 6.0
bromocresol purple	yellow	purple	5.2 – 6.6
bromocresol blue	yellow	blue	6.0 – 7.6
phenolphthalein	colourless	pink	8.2 – 10.0
thymolphthalein	colourless	blue	8.8 – 10.5

With reference to your answer in **(c)(iii)** and Table 2.3, state and explain which indicator is the most suitable for the neutralisation of benzoic acid by potassium hydroxide. **[2]**

Phenolphthalein [1]

pH of 8.44 at the equivalence point **falls within the working range of phenolphthalein, which is from 8.2 – 10.0**. **[1]**

(v) A primary standard is a reagent which can be used to accurately determine the concentration of an analyte. A potassium hydroxide solution with unknown concentration can be standardised by carrying out acid-base titration with the primary standard, benzoic acid.

Suggest a property of benzoic acid which makes it suitable for use as a primary standard. **[1]**

Any one of the following **[1]**:

- Benzoic acid is **pure**.
- Benzoic acid **reacts rapidly with KOH**.
- Benzoic acid is **not hygroscopic / does not absorb moisture**.
- Benzoic acid **reacts with KOH in a 1:1 mole ratio**.
- Benzoic acid has a **relatively large molar mass**, which helps to minimise weighing error.
- Benzoic acid is **stable**.

[Total: 21]

3 This question is on the chemistry and application of transition metals and their compounds.

(a) Fig. 3.1 illustrates a cell used to purify copper. The impure copper electrode contains zinc and silver impurities.

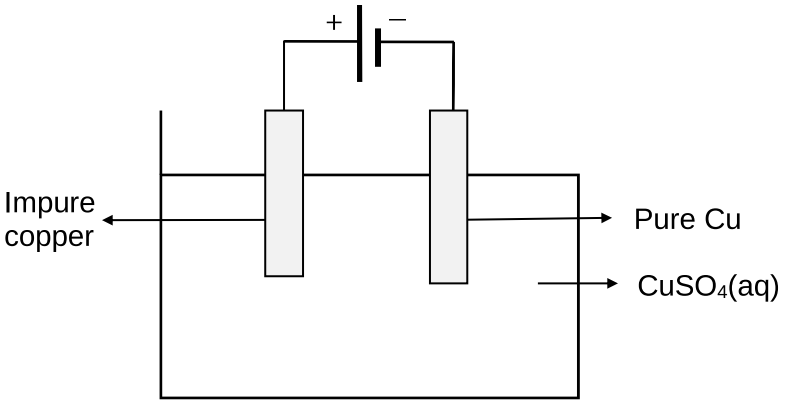


Fig. 3.1

Describe, with reference to relevant E^θ values, the electrode reactions that take place during this electrolysis. Explain how each of the two impurity metals is removed from the impure copper electrode. **[3]**

$Ag^+ + e^- \rightleftharpoons Ag$	**$E^\theta = +0.80V$**
$Cu^{2+} + 2e^- \rightleftharpoons Cu$	**$E^\theta = +0.34V$**
$Zn^{2+} + 2e^- \rightleftharpoons Zn$	**$E^\theta = -0.76V$**

[1] for E^θ only (no need half-equation)

$E^\theta(Zn^{2+}/Zn)$ is more negative than $E^\theta(Cu^{2+}/Cu)$. Hence, **at the impure copper** (which is the anode), **copper and zinc metals will be oxidised to form Cu^{2+} and Zn^{2+}**. **Ag will not be oxidised due to its more positive E^θ** than $E^\theta(Cu^{2+}/Cu)$ and will drop to the bottom as **anodic sludge**. **[1]**

Cu^{2+} and Zn^{2+} will migrate to the **pure copper** (cathode) but **only Cu^{2+} will be reduced to Cu as it has a more positive E^θ** than $E^\theta(Zn^{2+}/Zn)$. **[1]**

(b) A solution of $[Cu(NH_3)_4(H_2O)_2]^{2+}$ is made by dissolving $CuSO_4 \cdot 5H_2O$ in an excess of aqueous ammonia.

This solution of $[Cu(NH_3)_4(H_2O)_2]^{2+}$ is heated gently so that NH_3 is released. Some NH_3 remains in solution and some forms NH_3 gas. The colour of the solution changes; a precipitate of $Cu(OH)_2$ forms and is collected. The precipitate is divided into two portions.

The first portion is added to concentrated hydrochloric acid and a coloured copper complex, **X**, is formed. The second portion is added to dilute sulfuric acid to form a different coloured copper complex, **Y**.

(i) Explain why a solution of $[Cu(NH_3)_4(H_2O)_2]^{2+}$ is coloured. **[3]**

In the **presence of ligands** like H_2O and NH_3, the **partially filled 3d orbitals split into 2 energy levels** with a small energy gap between them. **[1]**
An electron from the lower energy d orbital absorbs energy from the visible region of the electromagnetic spectrum with wavelength corresponding to the energy gap and **gets promoted to a higher energy d orbital**. **[1]**
The light energy/blue colour **not absorbed is reflected and observed as the colour of the complex.** **[1]**

(ii) Suggest an equation for the heating of $[Cu(NH_3)_4(H_2O)_2]^{2+}$ solution. **[1]**

$[Cu(NH_3)_4(H_2O)_2]^{2+} \rightarrow Cu(OH)_2 + 2NH_4^+ + 2NH_3$ **[1]**

OR

$[Cu(NH_3)_4(H_2O)_2]^{2+} \rightarrow Cu(OH)_2 + 2H^+ + 4NH_3$ **[1]**

(iii) State the identify of complexes **X** and **Y**. **[2]**

X: $[CuCl_4]^{2-}$ **[1]**
Y: $[Cu(H_2O)_6]^{2+}$ **[1]**

(iv) The enthalpy change for the following reactions are similar.

Reaction 1 $\quad [Cu(H_2O)_6]^{2+} + 2en \rightleftharpoons [Cu(en)_2(H_2O)_2]^{2+} + 4H_2O$

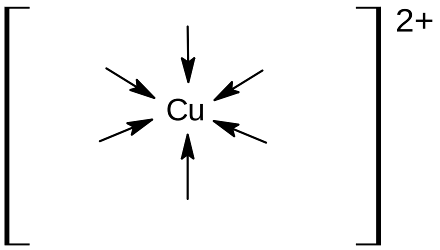
Reaction 2 $\quad [Cu(H_2O)_6]^{2+} + 4NH_3 \rightleftharpoons [Cu(NH_3)_4(H_2O)_2]^{2+} + 4H_2O$

However, reaction 1 occurs to a larger extent than reaction 2. Explain this observation. **[1]**

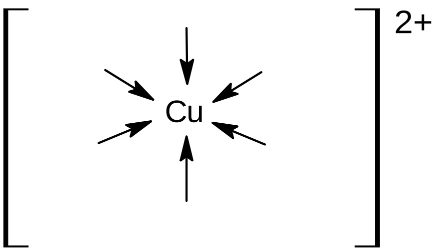
Reaction 1 occurs to a larger extent because it is **entropically driven** / **the system becomes more disordered** as the number of moles of products are more than the number of moles of reactants. ΔG will thus be more negative. **[1]**

(v) $[Cu(en)_2(H_2O)_2]^{2+}$ is able to exhibit cis-trans isomerism, where H_2O ligands can be found on either the same side or opposite sides.

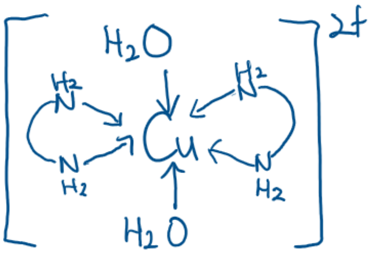
On the diagram below, suggest structures of the cis and trans isomers of $[Cu(en)_2(H_2O)_2]^{2+}$. You may use $H_2N \frown NH_2$ to represent en. **[2]**



cis isomer

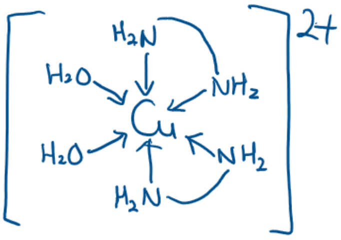


trans isomer



trans

[1]



cis

[1]

(c) The decomposition of hydrogen peroxide can be catalysed by transition metal ions, such as Fe^{3+}.

$$2H_2O_2 \rightarrow 2H_2O + O_2$$

With the aid of relevant data from the *Data Booklet*, show how Fe^{3+} can catalyse the decomposition of H_2O_2.

In your answer, give relevant equations for the reactions that occur. **[3]**

Step 1

$O_2 + 2H^+ + 2e^- \rightleftharpoons H_2O_2$ $E^\theta = +0.68$ V

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

$\underline{\mathbf{H_2O_2 + 2Fe^{3+} \rightarrow O_2 + 2H^+ + 2Fe^{2+}}}$

$E^\theta_{cell} = +0.77 - (+0.68) = \underline{\mathbf{+0.09\ V}}$

Step 2

$H_2O_2 + 2H^+ + 2e^- \rightleftharpoons 2H_2O$ $E^\theta = +1.77$

$\underline{\mathbf{H_2O_2 + 2H^+ + 2Fe^{2+} \rightarrow 2H_2O + 2Fe^{3+}}}$

$E^\theta_{cell} = +1.77 - (+0.77) = \underline{\mathbf{+1.00\ V}}$

(d) An alkaline manganese electrochemical cell is used to generate electricity.

The half-equations for the cell are as given.

$$ZnO(s) + H_2O(l) + 2e^- \rightleftharpoons Zn(s) + 2OH^-(aq) \qquad E^\theta = -1.28V$$

$$2MnO_2(s) + H_2O(l) + 2e^- \rightleftharpoons Mn_2O_3(s) + 2OH^-(aq) \qquad E^\theta = +0.15V$$

(i) Construct a balanced equation for the reaction that takes place when the cell is discharged. **[1]**

$\underline{\mathbf{Zn(s) + 2MnO_2(s) \rightarrow ZnO(s) + Mn_2O_3(s)}}$ **[1]**

State symbols are not required.

(ii) Calculate the standard Gibbs free energy change, ΔG^θ, for this electrochemical reaction. **[2]**

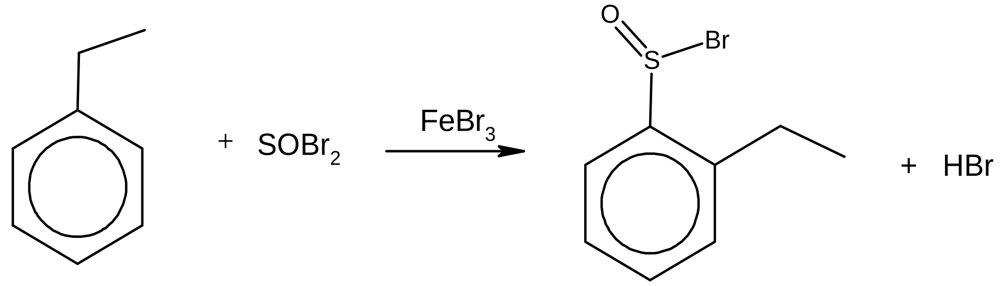
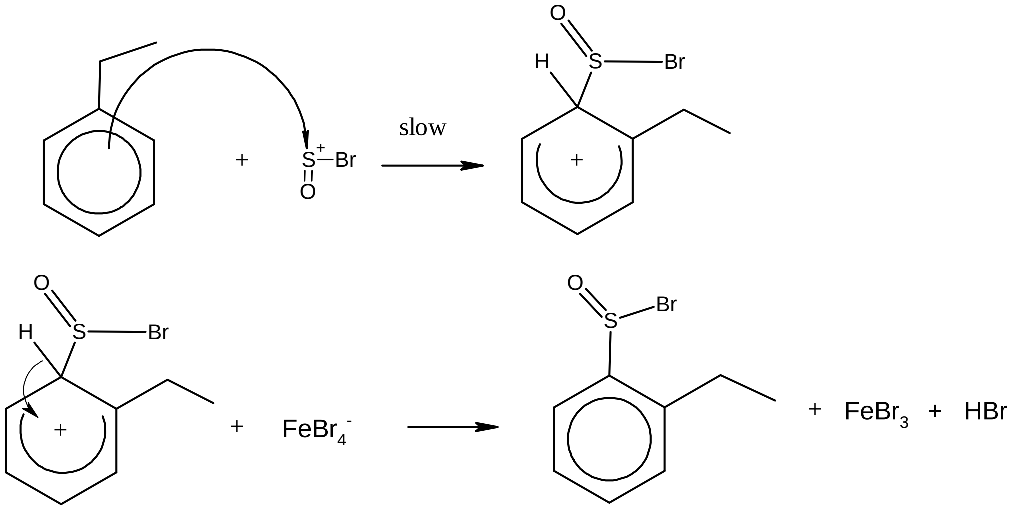
$E^\theta_{cell} = +0.15 - (-1.28)$

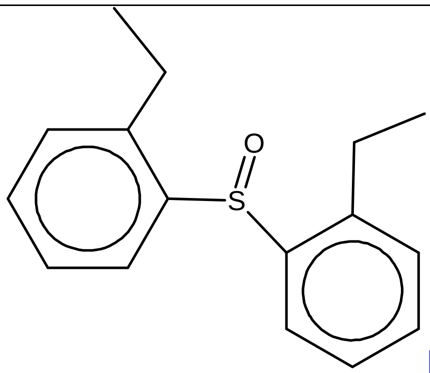
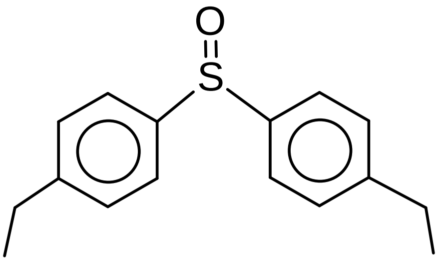
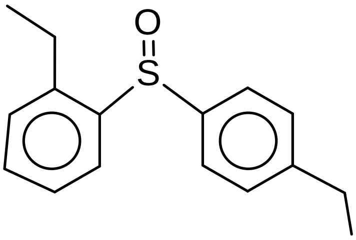
$= \underline{+1.43V}$ [1]

$\Delta G^\theta = -(2 \times 96500 \times 1.43)$

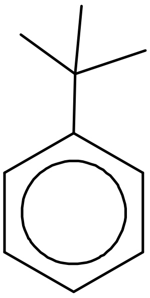
$= \underline{\mathbf{-276000\ J\ mol^{-1}}}$ (3sf) [1]

		(iii)	State and explain what happens to the cell potential, E_{cell}, when Mg^{2+} ions are added to the ZnO/Zn half-cell.	**[2]**
			When Mg^{2+} ions are added, $Mg(OH)_2$ will be precipitated causing **[OH⁻] to decrease**. $ZnO(s) + H_2O(l) + 2e^- \rightleftharpoons Zn(s) + 2OH^-(aq)$ As such **position of equilibrium shifts to the right**. E(ZnO/Zn) becomes **more positive/less negative**. E_{cell} become **less positive**.	
			[Total: 20]	

4	**(a)**	The reaction of ethylbenzene with thionyl bromide, $SOBr_2$, in the presence of $FeBr_3$ catalyst is as shown. The mechanism of this reaction is similar to that of the bromination of benzene.  		
		(i)	The first step of the mechanism involves the generation of electrophile from the reaction between thionyl bromide and catalyst. Write an equation to represent the generation of electrophile.	**[1]**
			$FeBr_3 + SOBr_2 \rightarrow SOBr^+ + [FeBr_4]^-$ [1]	
		(ii)	Describe the mechanism for the reaction between ethylbenzene and thionyl bromide, showing the structure of the intermediate and the movement of electron pairs by using curly arrows.	**[2]**
			Electrophlic substitution  	
		(iii)	The reaction between ethylbenzene and thionyl bromide produces a by-product with the molecular formula $C_{16}H_{18}SO$. Suggest a structure of this by-product.	**[1]**

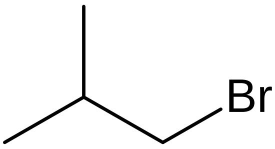
			 [1] **OR**  [1] **OR**  [1]	
		(iv)	Benzene also undergoes the same type of reaction with thionyl bromide but is less reactive than methylbenzene. Explain why benzene is less reactive in reacting with thionyl bromide.	**[1]**
			Benzene **does not have the electron-donating/ ring activating alkyl group.** Hence, it is **less electron rich** and attracts electrophile less readily than methyl benzene. **[1]**	

(b) t-Butylbenzene is a colourless liquid widely used as a solvent for organic synthesis.



t-butylbenzene

(i) t-Butylbenzene may be synthesised from compound **X** in 3 steps.



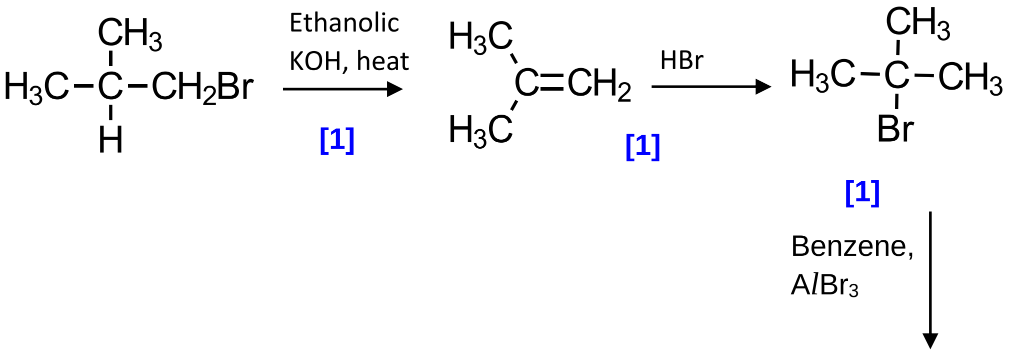
Compound **X**

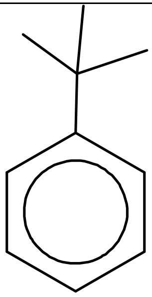
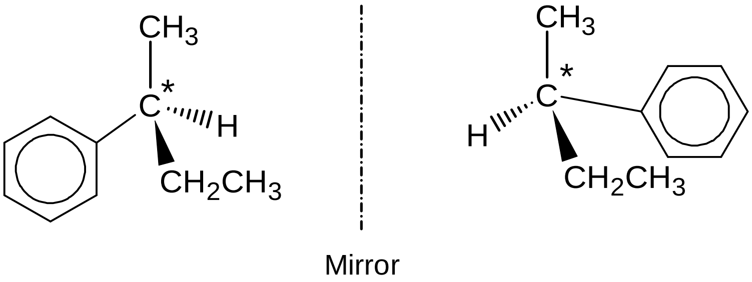
Give the systematic name of compound **X**. **[1]**

1-bromo-2-methylpropane **[1]**

(ii) Using compound **X** as the starting material, suggest a 3-step synthesis of t-butylbenzene.

You should state the reagents and conditions needed for each step and show clearly the structure of any intermediate compounds. **[3]**



				
		(iii)	A constitutional isomer of t-butylbenzene has a chiral carbon and no internal plane of symmetry. Draw this structure as a pair of enantiomers.	**[2]**
				
			[Total: 11]	

Section B

Answer **one** question from this section.

5 Potassium iodide, KI, is used as a reagent in both inorganic and organic chemistry.

(a) **(i)** *Use of the Data Booklet is relevant to this question.*

The cubic unit cell is the smallest repeat unit in an ionic lattice structure. An example of a cubic unit cell is the simple cubic unit, as shown in Fig. 5.1.

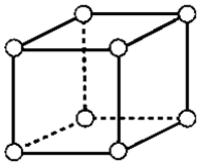


Fig. 5.1

The density of an ionic compound can be calculated using the following formula

$$\text{density} = \frac{Z \times M}{a^3 \times N_A}$$

Z = number of ions in one cubic unit cell

a = edge length of cubic unit cell in cm

M = formula mass of one mole of ionic compound

N_A = Avogadro's constant

Given that potassium iodide has an edge length of 705 pm and there are four ions in one cubic unit cell, calculate the density of potassium iodide in g cm^{-3}.

1 pm = 10^{-10} cm **[2]**

$$\text{Density} = \frac{4 \times (39.1+126.9)}{(705 \times 10^{-10})^3 \times (6.02 \times 10^{23})} = \underline{\mathbf{3.15\ g\ cm^{-3}}}$$

(ii) Potassium iodide can be synthesised by heating iodine with concentrated potassium hydroxide. Besides potassium iodide, potassium iodate(V), KIO_3, and water are produced.

Construct a balanced equation for this reaction. State the type of reaction. **[2]**

$\underline{\mathbf{3I_2 + 6KOH \rightarrow 5KI + KIO_3 + 3H_2O}}$ **[1]**

Disproportionation **[1]**

(iii) Iodine is known to sublime easily. A mass of 1.00 g of I_2 solid was placed into a gas syringe at 79 °C. The volume of iodine gas collected was 67 cm^3. The temperature was kept constant at 79 °C and the pressure was 1 bar.

Calculate the percentage of iodine that sublimed. **[2]**

$pV = nRT$

$(1 \times 10^5) \times (67 \times 10^{-6}) = n \times 8.31 \times (79 + 273)$

$n = 2.2905 \times 10^{-3}$ mol **[1]**

Mass of $I_2 = 2.2894 \times 10^{-3} \times (126.9 \times 2) = 0.58132$ g

% sublimation = 0.58105/1.0 x 100% = **58.1%** **[1]**

(iv) Predict the colour of the solution that would be observed when the following pairs of solutions are mixed.

- KI(aq) is added to Cl_2(aq),
- KC*l*(aq) is added to I_2(aq).

Write equations for any reactions that occur. Explain your answer using E^θ values from the Data Booklet. **[2]**

$Cl_2 + 2e \rightleftharpoons 2Cl^-$ **$E^\theta = +1.36V$**

$I_2 + 2e \rightleftharpoons 2I^-$ **$E^\theta = +0.54V$**

$2KI + Cl_2 \rightarrow 2KCl + I_2$

$E^\theta_{cell} = (+1.36) - (+0.54) = +0.82V$

Since $E^\theta_{cell} > 0$, Cl_2 oxidises I^- to form I_2. OR

Since **$E^\theta(Cl_2/Cl^-)$ is more positive $E^\theta(I_2/I^-)$**, Cl_2 will be reduced and I^- will be oxidised.

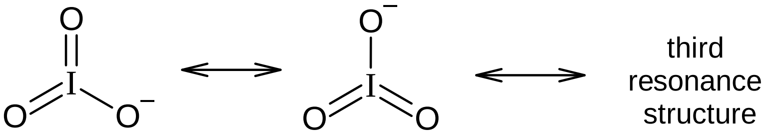
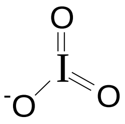
The solution turns from pale yellow to **brown**.

No reaction when KC*l*(aq) is added to I_2(aq) because **$E^\theta(Cl_2/Cl^-)$ is more positive $E^\theta(I_2/I^-)$**, I_2 cannot oxidise Cl^-. Solution **remains brown**.

(b) Potassium iodide is a common additive used to “iodise” salt, so as to prevent iodine deficiency in humans. However, when the iodised salts are exposed to air, oxidation of iodide ion occurs to cause a loss in iodine content. The equation for this reaction is as shown.

$$4KI(s) + 2CO_2(g) + O_2(g) \rightarrow 2K_2CO_3(s) + 2I_2(s)$$

[TURN OVER

		(i)	Suggest the appearance of an aged sample of iodised salt after exposure to moist air for some time.	**[1]**
			The aged sample salt appears **brown or black** due to formation of I_2. **[1]** **Reject purple.**	
		(ii)	Potassium carbonate decomposes on strong heating in a similar manner to calcium carbonate. Suggest why very high temperatures are needed for the thermal decomposition of potassium carbonate.	**[2]**
			Charge density and hence, polarising power **of K^+ is low** due to its small charge and large cationic radius. Hence, the **electron cloud of CO_3^{2-} is distorted/polarised to a small extent**, resulting in **C-O to be weakened to a small extent**, requiring **a lot of energy** to overcome it.	
		(iii)	To prevent the loss of iodine by oxidation, potassium iodate, KIO_3, is used to iodise some salts. IO_3^- is resonance stabilised. Fig. 5.2 shows the resonance structures of IO_3^-.  **Fig. 5.2** Draw the third resonance structure of IO_3^-. Hence, explain why IO_3^- is resonance stabilised.	**[2]**
			 **[1]** The lone pair of electrons on O^- and the pi electrons are delocalised, leading to the **delocalisation of negative charge over the 3 O atoms / over O-I-O**. **[1]**	

(c) KI is used as a source of I^- in organic synthesis.

An example of this is shown in Fig. 5.3.

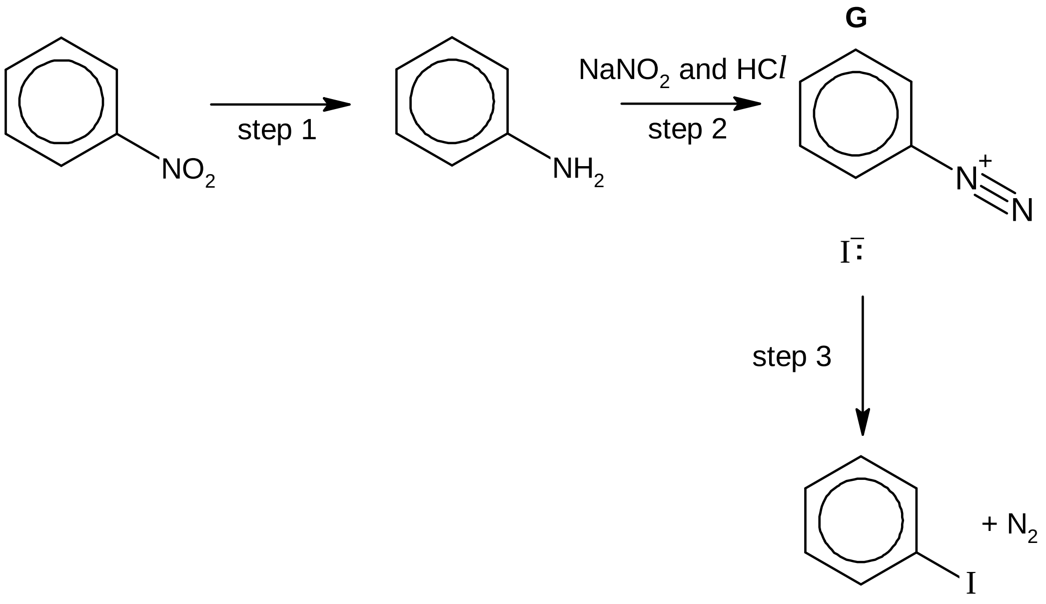
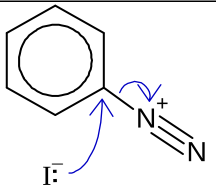
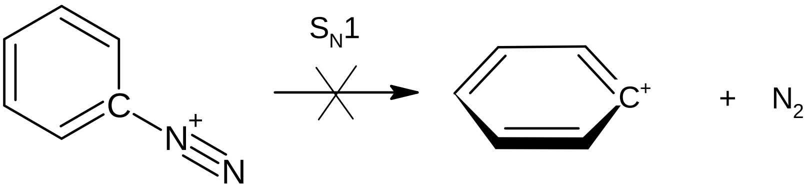
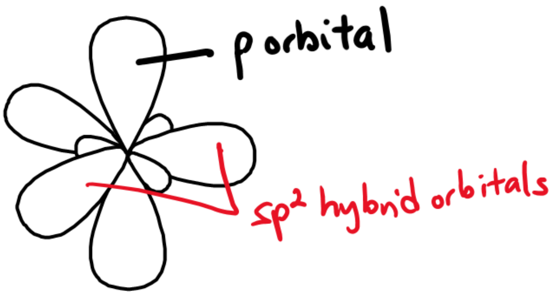


Fig. 5.3

(i)	For step 1, state the reagents and conditions, as well as the type of reaction.	**[1]**
	Reduction **Sn in conc HCl, heat** followed by **NaOH(aq)** **[1]**	
(ii)	Step 2 occurs in two stages. Stage I: $NaNO_2$ and HCl react to form HNO_2 and a salt. Stage II: HNO_2 reacts with phenylamine, $C_6H_5NH_2$ and H^+ to produce compound **G**, $C_6H_5N_2^+$ and water. Write the equations for stage I and for stage II.	**[2]**
	$NaNO_2 + HCl \rightarrow HNO_2 + NaCl$ **[1]** $HNO_2 + C_6H_5NH_2 + H^+ \rightarrow C_6H_5N_2^+ + 2H_2O$ **[1]**	
(iii)	I^- from KI reacts with **G** in step 3 via the S_N2 mechanism. Complete the mechanism for step 3 by adding curly arrows on Fig. 5.3.	**[1]**

			 [1]	
		Step 3 does not happen via S_N1 mechanism because the resulting carbocation shown in Fig. 5.4 is not stable.  **Fig. 5.4**		
		(iv)	Suggest the type of hybridisation of the positively charged carbon.	**[1]**
			sp^2 [1]	
		(v)	With reference to the carbocation in Fig. 5.4, draw a labelled diagram to show how the valence hybrid and unhybridised orbitals are arranged around the positively charged carbon atom.	**[1]**
			 [1] **Ecf from (c)(iv)**	
		(vi)	With reference to **(c)(v)**, suggest whether the hybrid or unhybridised orbital is empty.	**[1]**
			sp^2 **hybrid orbital** [1]	
			[Total: 20]	

6 Glycine, H_2NCH_2COOH, is the simplest amino acid that exists.

(a) Glycine exists as a zwitterion at pH 6.2.

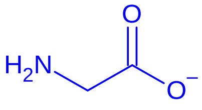
(i) State what is meant by the term *zwitterion*. **[1]**

A zwitterion is a **neutral** compound that has **both positive and negative charges. [1]**

OR

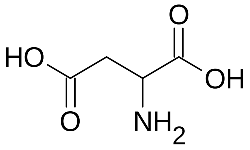
A zwitterion is a compound/species that has **equal number of positive and negative charges. [1]**

(ii) Draw the structure of the predominant species of glycine at pH 12.0. **[1]**



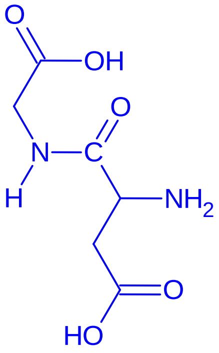
[1]

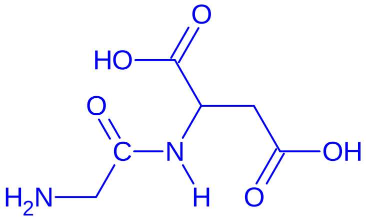
(iii) A molecule of glycine can react with a molecule of aspartic acid to form two dipeptides.



aspartic acid

Draw the structures of these dipeptides. The peptide bond formed in each dipeptide should be shown displayed. **[2]**





(iv) The melting points of glycine and aspartic acid are shown in Table 6.1.

[TURN OVER

Table 6.1

compound	melting point/°C
glycine	233
aspartic acid	270

Explain, in terms of structure and bonding, the similarity in melting points of glycine and aspartic acid. **[1]**

Both amino acids exist as **giant ionic lattices** with **ionic bonds of similar strength between the zwitterions**. Hence, similar amount of energy is required to break the ionic bonds and the melting points are thus similar. **[1]**

(b) Fig. 6.1. shows two syntheses starting with glycine.

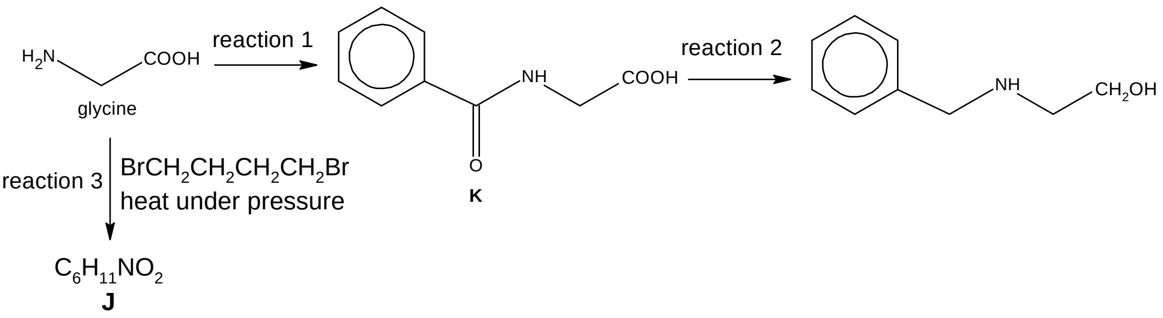


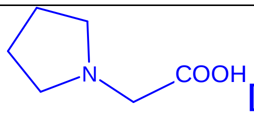
Fig. 6.1

(i) For reactions 1 and 2, state the type of reaction and the reagents and conditions needed. **[2]**

Step 1: **condensation**, **C_6H_5COCl** (penalise when (aq) is given) **[1]**

Step 2: **reduction**, **$LiAlH_4$ in dry ether** **[1]**

(ii) Draw the structure of compound **J**. **[1]**



[1]

(iii) A student proposed the reaction of benzamide, $C_6H_5CONH_2$, with chloroethanoic acid to form compound **K**.
Explain why this synthesis cannot work. **[1]**

In benzamide, the **lone pair of electrons on N is delocalised over N-C-O** and into the benzene ring. Hence, the lone pair of electrons on N is **not available** / **benzamide cannot be a nucleophile** to attack the C of C-C*l*. **[1]**

(iv)

Table 6.2

compound	p*K*$_a$
chloroethanoic acid	2.9
3-chloropropanoic acid	4.0

Suggest a reason why the p*K*$_a$ of 3-chloropropanoic acid is higher than the p*K*$_a$ of chloroethanoic acid. **[2]**

In 3-chloropropanoate, the **electron-withdrawing or electronegative C*l* is further away from the negative charge on O**. Hence, the **negative charge on O is less dispersed**. As **3-chloropropanoate is less stable**, **less H$^+$ is produced from 3-chloropropanoic acid** and **3-chloropropanoic acid is less acidic**.

(c) Phosphorus tribromide, PBr_3, is commonly used in the laboratory to convert alcohols into bromoalkanes. In the first step of this reaction, it involves the alcohol attacking phosphorus in phosphorus tribromide with its lone pair of electrons on oxygen atom, resulting in the formation of Br^- leaving group.

(i) Phenol does not react with PBr_3.
Suggest why there is no reaction between these two compounds. **[1]**

Phenol is a poor nucleophile as the **lone pair of electrons on O will delocalise into benzene ring**. **[1]**

The reagent used in reaction 3 of Fig. 6.1 can be produced from the reaction of butane-1,4-diol with PBr_3.
The mechanism for the reaction between butane-1,4-diol and PBr_3 is shown in Fig. 6.2.

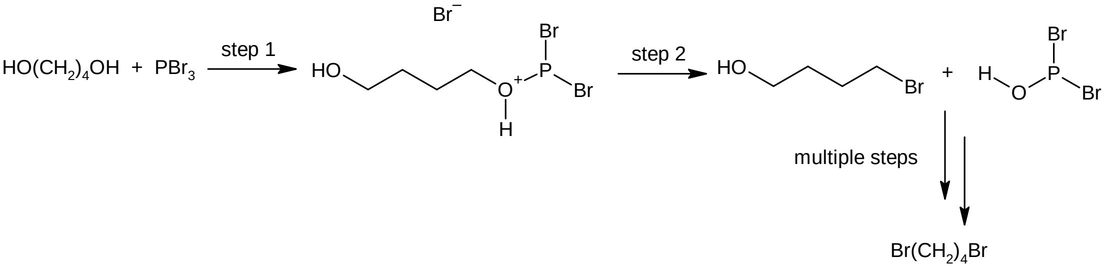
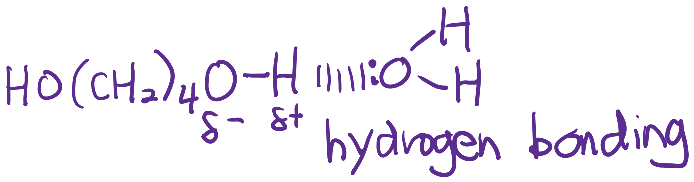


Fig. 6.2

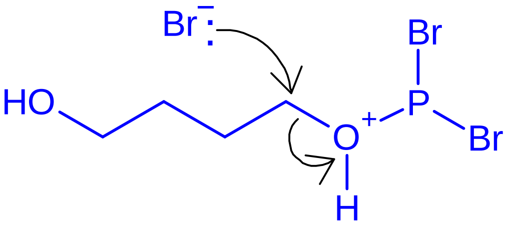
(ii) Draw a labelled diagram to show the significant force of attraction between butane-1,4-diol and a water molecule. Include the name of the attraction in your diagram. **[2]**



[1]

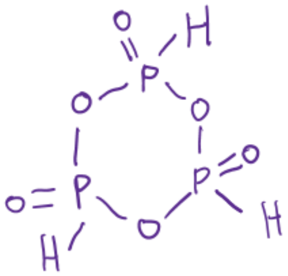
Hydrogen bonding **[1]**

(iii) Complete the mechanism for step 2 on Fig. 6.2 by adding a lone pair and curly arrows. **[2]**



(iv) The reaction in Fig 6.2 must be done in anhydrous conditions. Otherwise, PBr$_3$ will react readily with water to give H_3PO_3 and HBr. When this happens, H_3PO_3 is collected and used as a substrate for yeast to metabolise. During the metabolism, condensation takes place to form a compound with molecular formula, $H_3P_3O_6$.

Suggest a structure for this compound. **[1]**

			 [1]	
		(v)	Describe and explain the trend in the thermal stability of the hydrogen halides HC*l*, HBr and HI. Include an equation for the thermal decomposition of hydrogen halides, HX, in your answer.	**[3]**
			$2HX \rightarrow X_2 + H_2$ HC*l* **does not decompose**. HBr **decomposes slightly** to give **reddish brown gas**. HI **decomposes readily** to give **purple fumes**. **Thermal stability decreases from HC*l* to HBr and to HI**. **Atomic radius / size of halogen atom increases from C*l* to Br and to I**. Hence, the **extent of effective orbital overlap between valence orbital of halogen and 1s of H becomes poorer** down the group. The **strength of H-X thus decreases from HC*l* to HBr and to HI**.	
			[Total: 20]	

END OF PAPER