ST ANDREW'S JUNIOR COLLEGE

JC2 PRELIMINARY EXAMINATIONS

HIGHER 2

CANDIDATE NAME	
CLASS	**2 3 S**

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]**

(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.

Table 1.1

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

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

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(b) (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]**

(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]**

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[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 / ^{o}C
beryllium	1287
magnesium	650

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

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

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

(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.

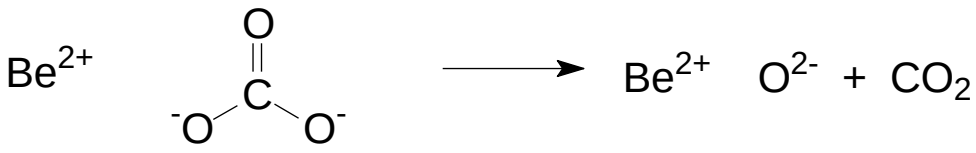

Fig 2.1

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(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 ºC.

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

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

(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.

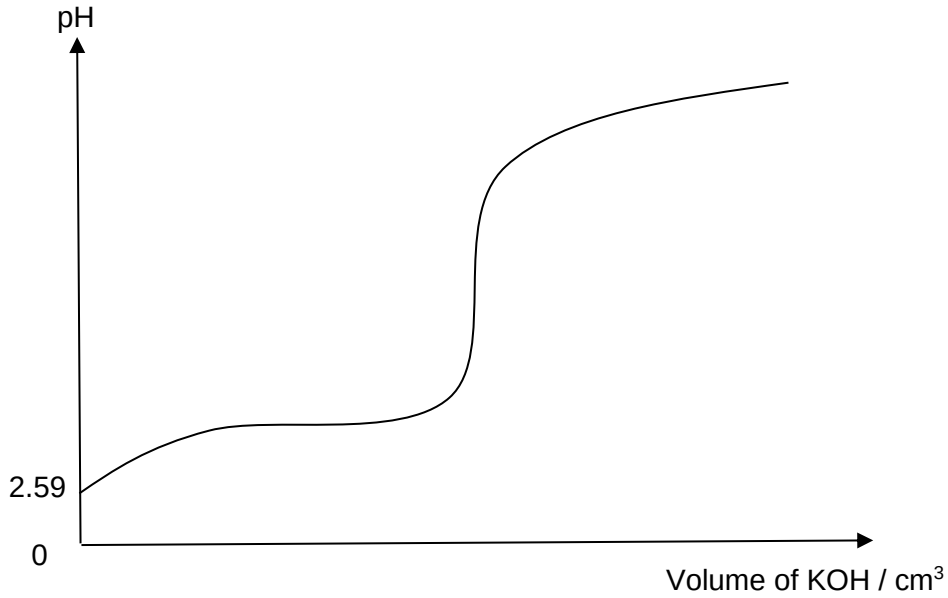
Table 2.2

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]**

(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]**

(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]**

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

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

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(c) (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]**

(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]**

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[Total: 21]

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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.

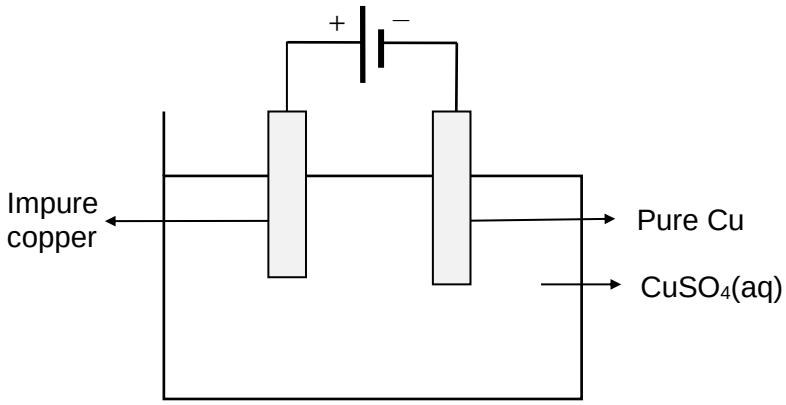

Fig. 3.1

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]**

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(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]**

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

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

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

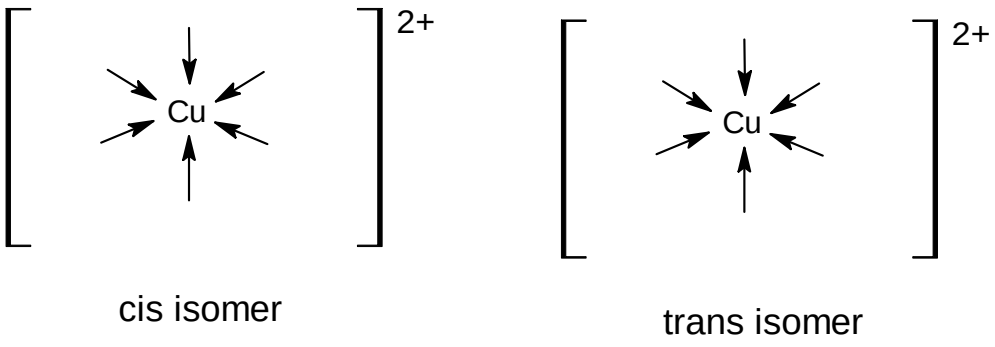
Reaction 1 $[Cu(H_2O)_6]^{2+} + 2en \rightleftharpoons [Cu(en)_2(H_2O)_2]^{2+} + 4H_2O$

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

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

(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 $H_2N\overset{\frown}{\quad}NH_2$ to represent en. **[2]**



cis isomer

trans isomer

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(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]**

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

The half-equations for the cell are as given.

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

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

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

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

(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]**

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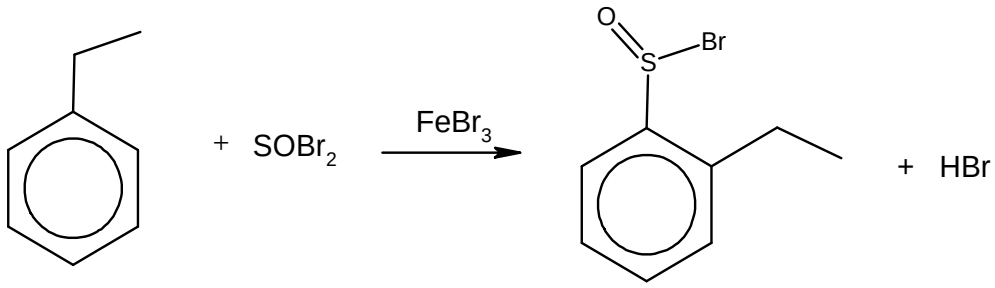
[Total: 20]

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]**

(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]**

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(a) **(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]**

(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]**

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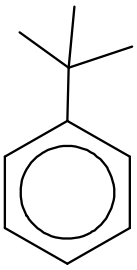
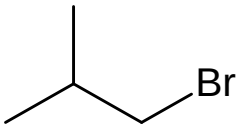
(b) t-Butylbenzene is a colourless liquid widely used as a solvent for organic synthesis.



t-butylbenzene

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



Compound **X**

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

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(b) (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]**

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[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.

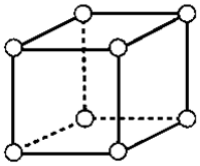

Fig. 5.1

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]

(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]**

(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]**

(a) (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),
- KCl(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]**

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(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.

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

(i) Suggest the appearance of an aged sample of iodised salt after exposure to moist air for some time. **[1]**

(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]**

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(b) **(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^-.

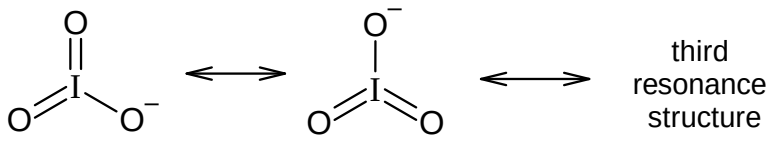

Fig. 5.2

Draw the third resonance structure of IO_3^-. Hence, explain why IO_3^- is resonance stabilised.

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

An example of this is shown in Fig. 5.3.

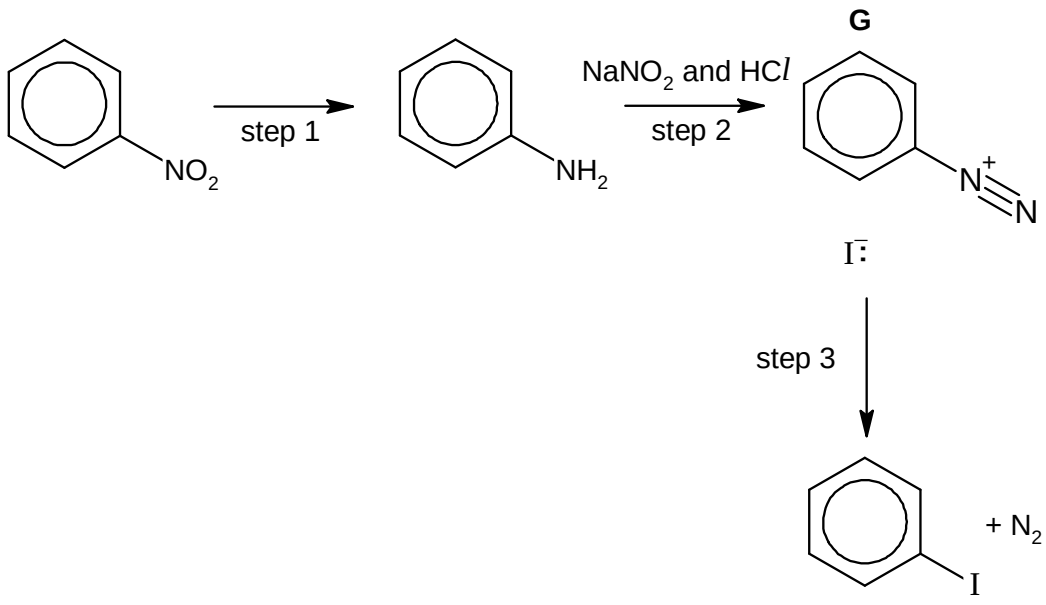

Fig. 5.3

(c) **(i)** For step 1, state the reagents and conditions, as well as the type of reaction. **[1]**

(ii) Step 2 occurs in two stages.

Stage I: $NaNO_2$ and HC*l* 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]**

(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]**

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Step 3 does not happen via S_N1 mechanism because the resulting carbocation shown in Fig. 5.4 is not stable.

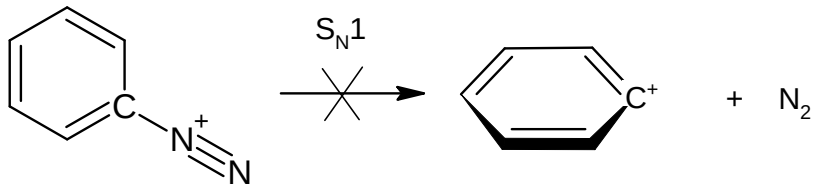

Fig. 5.4

(c) **(iv)** Suggest the type of hybridisation of the positively charged carbon. **[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]**

(vi) With reference to **(c)(v)**, suggest whether the hybrid or unhybridised orbital is empty. **[1]**

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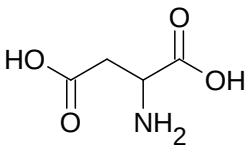
6 Glycine, H_2NCH_2COOH, is the simplest amino acid that exists.

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

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

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

Table 6.1

compound	melting point/^oC
glycine	233
aspartic acid	270

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

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

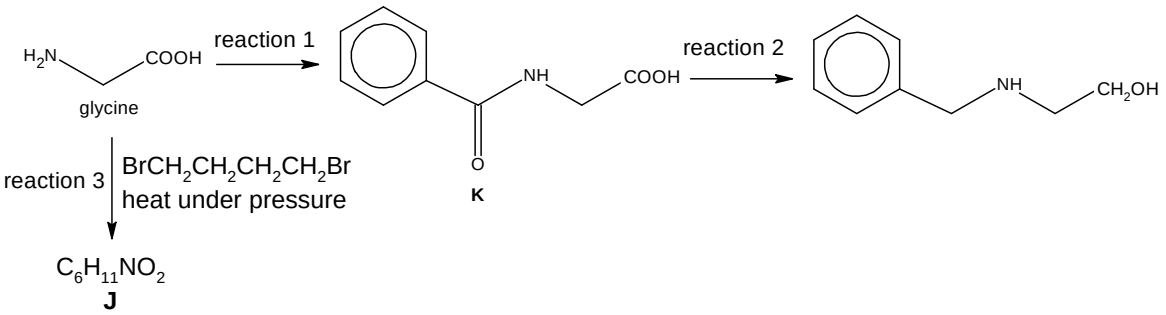

Fig. 6.1

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

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

(iv)

Table 6.2

compound	pK_a
chloroethanoic acid	2.9
3-chloropropanoic acid	4.0

Suggest a reason why the pK_a of 3-chloropropanoic acid is higher than the pK_a of chloroethanoic acid. **[2]**

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(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]**

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.

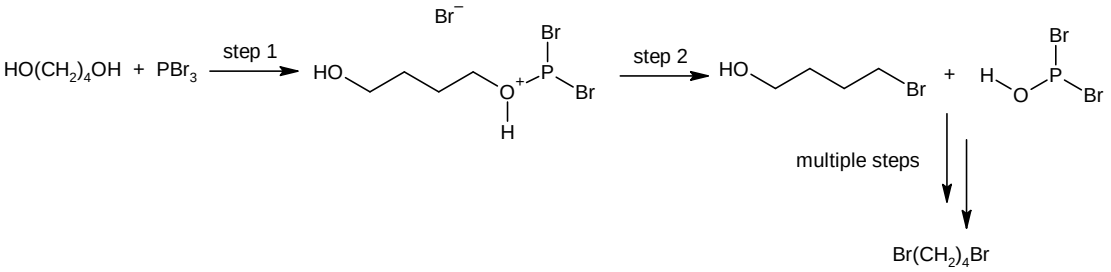

Fig. 6.2

(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]**

(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]**

(c) (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]**

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Additional Answer Space

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