RIVER VALLEY HIGH SCHOOL
JC 2 PRELIMINARY EXAMINATION

CANDIDATE NAME								
CLASS	2	4	J					
CENTRE NUMBER	S					INDEX NUMBER		

H2 CHEMISTRY 9729/03

Paper 3 Free Response

23 September 2025

2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your Centre number, index number, class and name on all the work that you hand in.
Write in dark blue or black pen.
You may use an HB pencil for any diagrams or graphs.
Do not use staples, paper clips, glue or correction fluid.
DO **NOT** WRITE IN ANY BARCODES.

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** the questions.

Section B
Answer **one** question. **Circle** the question number of the question you attempted.

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

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

For Examiner's Use								
Question Number	**1**	**2**	**3**	**4**	**5**	**units**	**s.f.**	**Total**
Marks	/21	/18	/21	/20	/20			/80

This document consists of **31** printed pages and **1** blank page.

Section A

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

1 Benzene undergoes many different types of reactions to form its derivatives. One such example is the Gattermann–Koch reaction.

(a) The chlorides of the elements, sodium to phosphorus, dissolve or react with water.

Describe the reactions when excess water is added to separate samples of $MgCl_2$ and PCl_5.

Write equations for all reactions that occur and suggest the pH of the resulting solutions. [4]

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(b) Describe and explain the variation in thermal stability of HCl, HBr and HI. [3]

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(c) Explain why benzene undergoes substitution reactions rather than addition reactions. [1]

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(d) In the Gattermann–Koch reaction, benzene is used to produce benzaldehyde. An example is provided below in Fig. 1.1.

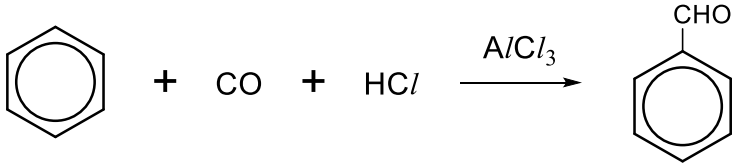

Fig. 1.1

The mechanism of this reaction occurs in 2 steps.

Step 1: Generation of electrophile, HCO^+

Step 2: Reaction of benzene with electrophile, HCO^+, to obtain benzaldehyde

(i) Define the term *electrophile*. [1]

(ii) In Step 1, CO reacts with HC*l* in the presence of A*l*C*l*$_3$ to form HCO^+.

$$HCl + CO \rightarrow HCO^+ + Cl^-$$

$$AlCl_3 + Cl^- \rightarrow [AlCl_4]^-$$

State the roles of CO and A*l*C*l*$_3$ respectively in Step 1. [2]

(iii) Name and draw the mechanism in Step 2. Use the displayed formula of HCO^+, and show relevant curly arrows, charges and the structure of the intermediate. [3]

(iv) The synthesis of compound **Z** shown in Fig. 1.2 involves the Gattermann-Koch reaction.

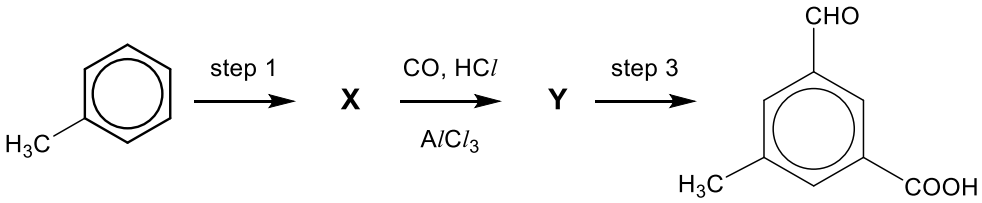

Fig. 1.2

State the reagents and conditions required of Step 1 and Step 3 in Fig. 1.2. Draw the structures of **X** and **Y**. [4]

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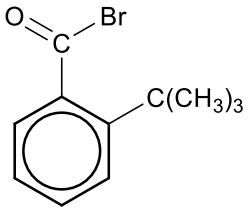
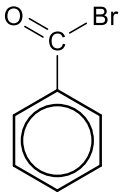
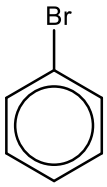
(e) Three organobromine compounds, **A**, **B** and **C** are shown below.

		
A	**B**	**C**

Arrange **A**, **B** and **C** in order of decreasing ease of hydrolysis.

Explain your answer. [3]

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2 An organic compound, $C_4H_6O_2$, known as **MMA**, is the precursor to a thermoplastic known as PMMA.

- On treatment with hot acidic $KMnO_4$(aq), **MMA** produces only 1 organic product, **F**, with a loss of 1 C atom.
- The same compound **F** is also produced as one of the products when **G**, $C_6H_8O_2$, a sweet-smelling compound, is treated with hot acidic $KMnO_4$(aq).
- On warming with I_2(aq) in the presence of NaOH(aq), **F** gives a yellow ppt and a sodium salt of **H**.
- 1 mole of **H**, M_r = 90.0**,** reacts with excess Na(s) to give 22.7 dm^3 of hydrogen gas under standard temperature and pressure.

(a) Suggest structures for **MMA**, **F**, **G** and **H**. Explain the reactions. [8]

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PMMA, also known as Plexiglass, is commonly used at the vessel for electrolytic processes as it is generally resistant to many chemicals.

In the Kolbe electrolysis reaction, the electrolyte used is aqueous potassium ethanoate. At the anode, ethane and carbon dioxide gases are produced.

The overall equation is shown below.

$$2CH_3CO_2^- + 2H_2O \rightarrow C_2H_6 + 2CO_2 + H_2 + 2OH^- \qquad \Delta G = 92.64 \text{ kJ mol}^{-1}$$

(b) Deduce the two half-equations that contribute to the overall equation. [2]

(c) **(i)** The Kolbe electrolysis will only proceed at an appreciable rate when the applied potential exceeds the theoretical galvanic cell potential by 0.70 V.

Minimum voltage = |theoretical galvanic cell| + 0.70

Calculate the minimum potential that should be applied. [2]

(ii) Suggest a reason why the applied potential has to exceed the theoretical galvanic cell potential by 0.70 V for the reaction to occur at an appreciable rate. [1]

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In another reaction, electrolysis was performed on molten chromium(III) chloride, $CrCl_3$. This experiment was conducted to determine Avogadro's number, ***L***.

The mass of chromium deposited was 6.46 g when a current of 5.07 A passed through the electrolytic setup for 2.00 hour.

(d) **(i)** Calculate the amount of charge needed to deposit 6.46 g of chromium. [1]

(ii) Hence, determine ***L*** with the aid of the *Data Booklet*. [2]

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PMMA is used in the medical field together with calcium phosphate cement in bone repairs.

(e) State how the reactivity of Group 2 metals as reducing agents varies down the group and relate this variation to relevant $E^{\ominus}$ values. [2]

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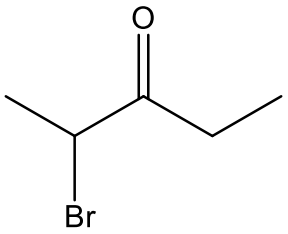
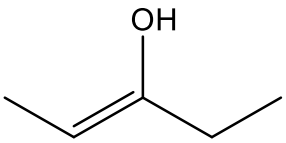
3 **(a)** Pentan−3−one reacts with bromine to undergo acid−catalysed alpha halogenation to form product **T**.



T

(i) Explain what is meant by the term *acid−catalysed* reaction. [1]

(ii) The first step of this mechanism involves the reaction of pentan−3−one with H_3O^+ to give **S**.



S

S has a stereoisomer. Suggest the structure of this stereoisomer and explain how it arises. [2]

(iii) Suggest the type of reaction for pentan−3−one reaction with bromine to give **T**. [1]

(iv) The reaction of **S** to form **T** involves an oxygen cation intermediate.

- The first step involves the formation of π bond between oxygen and carbon using a lone pair of electrons from oxygen. Simultaneously, the π electrons from C=C attack the bromine atom to form the oxygen cation intermediate.
- This intermediate is deprotonated by a bromide ion to generate **T**.

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

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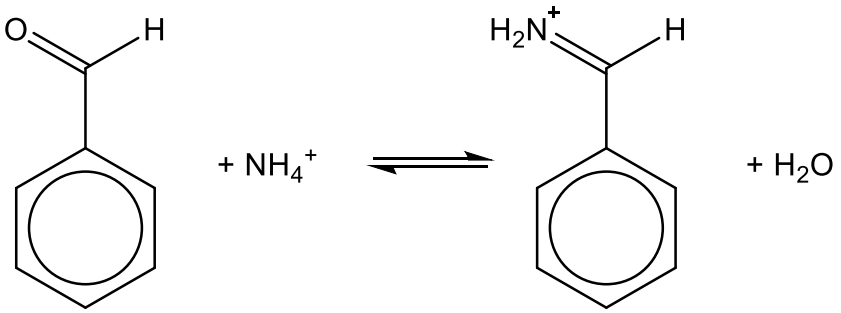
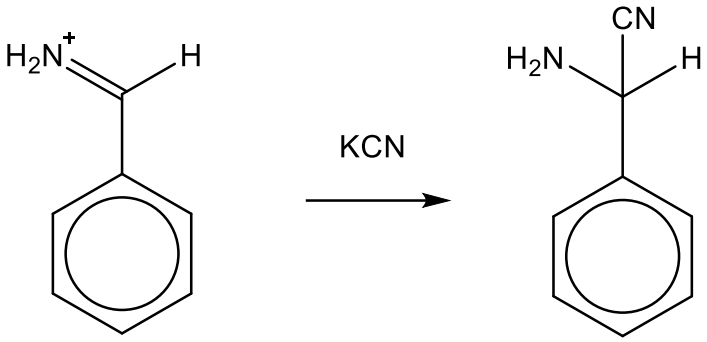
(b) Benzaldehyde undergoes Strecker synthesis to form amino acid in a 3−step mechanism. The first step is shown below.

Step 1:

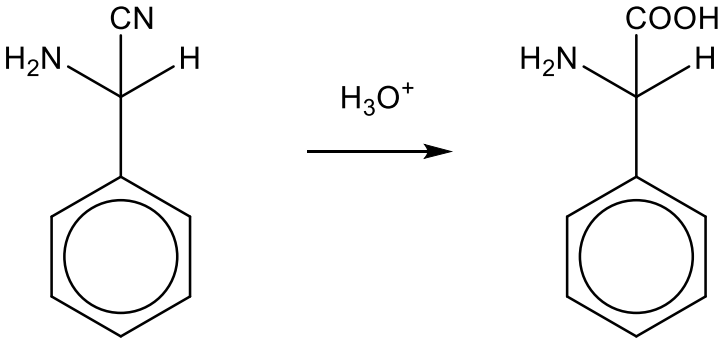


Benzylimine

Step 2:



Step 3:



phenylglycine

(i) 0.212 g of benzaldehyde and 10.7 g of ammonium chloride are dissolved in 200 cm^3 of solution. The solution is allowed to reach equilibrium and the concentration of benzylimine is found to be 8.80×10^{-3} mol dm^{-3}.

Show that the initial concentration of benzaldehyde is 0.0100 mol dm^{-3} and the initial concentration of ammonium chloride is 1.00 mol dm^{-3}. [1]

(ii) Write an expression and unit of K_c for the equilibrium in Step 1, and use the data given to calculate its value. Show your working. [3]

(iii) Suggest why the yield of benzylimine decreases when pH of the solution increases in Step 1. Explain your answer fully. [1]

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(c) The 3−step Strecker synthesis between benzaldehyde, ammonium chloride and potassium cyanide follow the reaction mechanism shown in **(b)**.

The rate equation of this reaction is as follows.

$$\text{Rate} = k\,[C_6H_5CHO]^w\,[NH_4^+]^x\,[CN^-]^y\,[H_3O^+]^z$$

The rate of reaction can be followed by measuring the amount of benzaldehyde. Experiments were carried out by changing the initial $[H_3O^+]$ and $[C_6H_5CHO]$, but keeping the initial $[NH_4^+]$ and $[CN^-]$ constant at large excess.

experiment	initial $[H_3O^+]$/ mol dm^{-3}	initial $[C_6H_5CHO]$/ mol dm^{-3}	initial rate/ mol dm^{-3} s^{-1}
1	0.200	0.400	8.40×10^{-5}
2	0.200	0.300	6.30×10^{-5}
3	0.100	0.100	2.10×10^{-5}

(i) Determine the orders of reaction with respect to $[C_6H_5CHO]$ and $[H_3O^+]$. Explain your reasoning. [2]

(ii) Experiment 4 was carried out by measuring the amount of phenylglycine produced after various times.

Species	Initial concentation/ mol dm^{-3}
C_6H_5CHO	0.600
NH_4^+	0.0600
CN^-	0.600
H_3O^+	0.600

The following graph in Fig. 3.1 was obtained.

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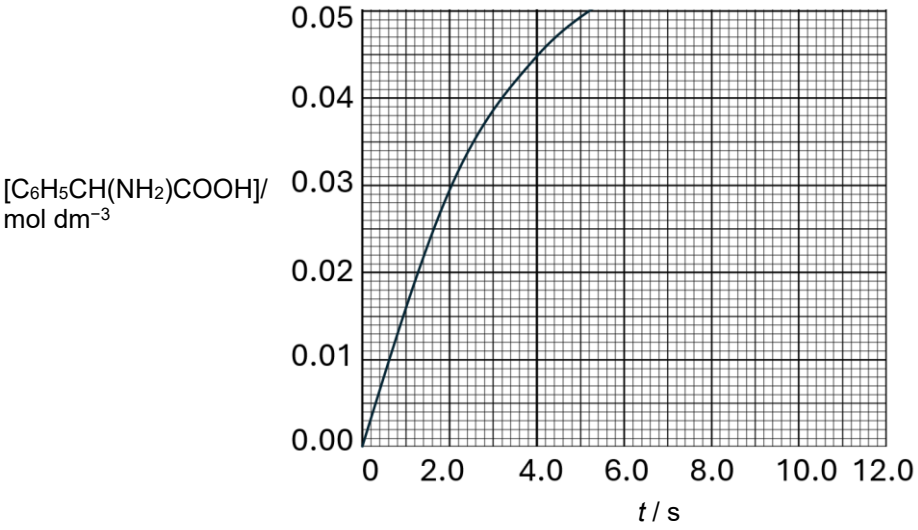
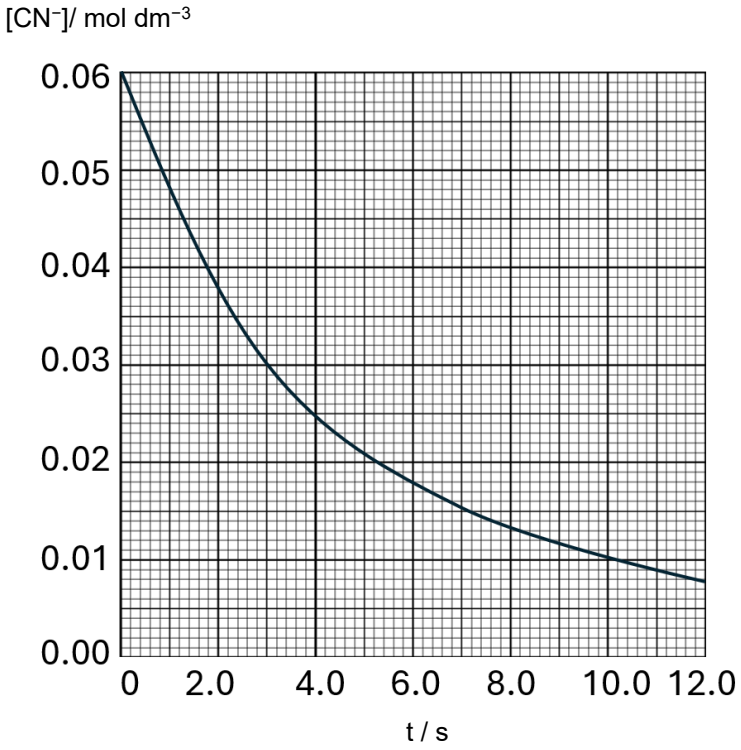


Fig. 3.1

Determine the maximum concentration of phenylglycine at the end of the reaction. Hence, show the reaction is first order with respect to $[NH_4^+]$ on Fig. 3.1. Show your working clearly. [2]

(iii) Further experiment, experiment 5, was carried out by changing initial $[CN^-]$ to 0.0600 mol dm^{-3} with all the other initial concentrations kept the same as experiment 4. The following graph was obtained.



With reference to **(c)(ii)**, explain why $t_{1/2}$ is not constant although the reaction is first order with respect to $[CN^-]$. [1]

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(iv) In experiment 4, the rate equation could be rearranged as

$$\text{rate} = k' [NH_4^+]$$

Express k' in terms of k and initial concentrations.

You may find the information given and your answers in **(c)(i)** – **(iii)** useful. [1]

(v) Hence, with reference to **(c)(ii)**, calculate a value for the rate constant k. Include units in your answer. [2]

(vi) With reference to the reaction mechanism in **(b)** and the overall rate equation, identify the rate determining step of Strecker synthesis. Explain your answer fully. [2]

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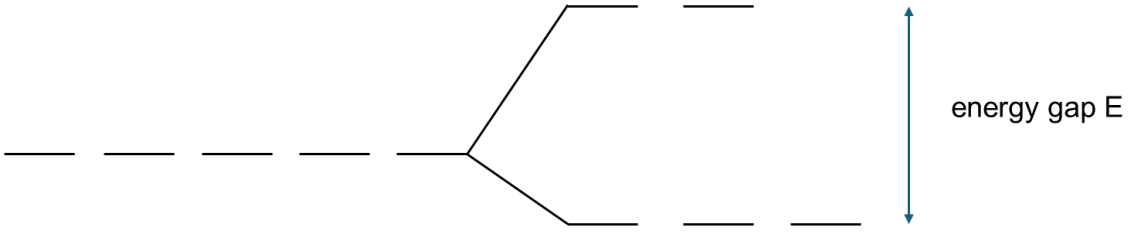
Section B

Answer **one** question from this section.

4 (a) The iron atoms in haemoglobin are in the oxidation state +2 and are in an octahedral environment. Each iron atom is surrounded by five nitrogen-containing ligands, and one oxygen-containing ligand, which is H_2O in deoxyhaemoglobin and O_2 in oxyhaemoglobin.

The following diagram shows how the d-orbitals are split in an octahedral environment.



(i) Use this diagram to outline the origin of the red colour of haemoglobin. [2]

When the H_2O ligand in haemoglobin is changed to an O_2 ligand, the Fe^{2+} ion changes its electronic configuration from a 'high spin' state to a 'low spin' state.

In a 'high spin' state, the electrons occupy all the d-orbitals singly, before starting to pair up in the lower energy d-orbitals.

In a 'low spin' state, the lower energy d-orbitals are filled first, by pairing up if necessary, before the higher energy d-orbitals are used.

(ii) Suggest why electrons usually prefer to occupy orbitals singly, rather than in pairs. [1]

(iii) Using this explanation, together with the information given above concerning the spin states of deoxyhaemoglobin and oxyhaemoglobin, state and explain which of the two haemoglobins will contain the larger energy gap, ΔE, between its d-orbitals. [2]

(iv) Draw a suitable diagram to show the electron distribution in the 3d subshell of a Fe^{2+} ion in oxyhaemoglobin in the ***excited*** state, where an electron from a lower energy d-orbital has been promoted to a higher energy d-orbital by absorbing light of a certain wavelength. [1]

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(b) The standard reduction potentials of two complex ions of iron(III) are shown below.

ion	equation	$E^{\ominus}$
$[Fe(H_2O)_6]^{3+}$	$[Fe(H_2O)_6]^{3+} + e^- \rightleftharpoons [Fe(H_2O)_6]^{2+}$	+0.77 V
$[Fe(CN)_6]^{3-}$	$[Fe(CN)_6]^{3-} + e^- \rightleftharpoons [Fe(CN)_6]^{4-}$	+0.36 V

(i) Explain why transition metal ions form complexes. [1]

(ii) Explain why standard reduction potential of $[Fe(CN)_6]^{3-}$ is lower than that of $[Fe(H_2O)_6]^{3+}$. [1]

(iii) Outline one simple experiment that could be performed to demonstrate that $[Fe(CN)_6]^{3-}$ is a weaker oxidising agent than $[Fe(H_2O)_6]^{3+}$. Include the observations made. [2]

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(c) The numerical value of the solubility products of some iron-containing salts at 298 K are given below.

Table 4.1

salt	value of solubility product
iron(II) sulfide, FeS	6.00×10^{-18}
iron(II) hydroxide, $Fe(OH)_2$	4.87×10^{-17}
iron(II) phosphate, $Fe_3(PO_4)_2$	1.07×10^{-29}

(i) Using Table 4.1, calculate the solubility of iron(II) phosphate. [1]

(ii) Solid iron(II) nitrate was added slowly to a solution containing 0.150 mol dm^{-3} of sodium sulfide and 0.200 mol dm^{-3} of sodium hydroxide.

Calculate the concentration of sulfide ions remaining in the solution when iron(II) hydroxide starts to precipitate. [2]

(iii) A beaker of Fe^{2+} ions and Al^{3+} ions have been found in the lab.

Suggest how the separation of the two aqueous ions can be effectively carried out.

Use equilibria concepts to explain your observations and include relevant equations in your answer. [2]

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(d) The melting points of some Period 3 elements are shown below.

Element	Na	Mg	A*l*	Si	P	S	C*l*
Melting point/ K	371	923	933	1687	317	388	172

(i) With reference to the data above, describe and explain the difference in melting points of the elements above. [3]

(ii) An oxide of Period 3 element, **Y**, dissolves in concentrated base but is insoluble in water and acid.

Identify element **Y**. Write an equation to describe the behaviour of its oxide with base. [2]

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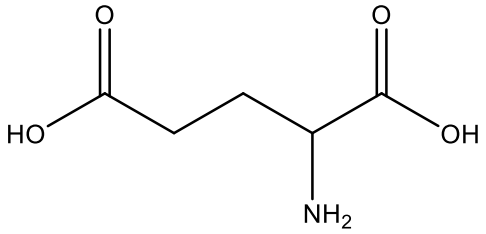
5 Glutamic acid is a naturally occurring amino acid with the following structure:



There are three pK_a values associated with glutamic acid: 2.19, 4.25 and 9.67.

(a) State which carboxylic group has the lower pK_a value. Explain your reasoning. [2]

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(b) At pH 4.0, glutamic acid is able to act as a buffer.

Write an equation to show how glutamic acid behaves as a buffer when a small amount of $H_3O^+(aq)$ is added. [1]

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(c) A 10.0 cm^3 sample of the fully protonated form of 0.200 mol dm^{-3} glutamic acid is titrated against 0.100 mol dm^{-3} NaOH. The titration curve is shown in Fig. 5.1.

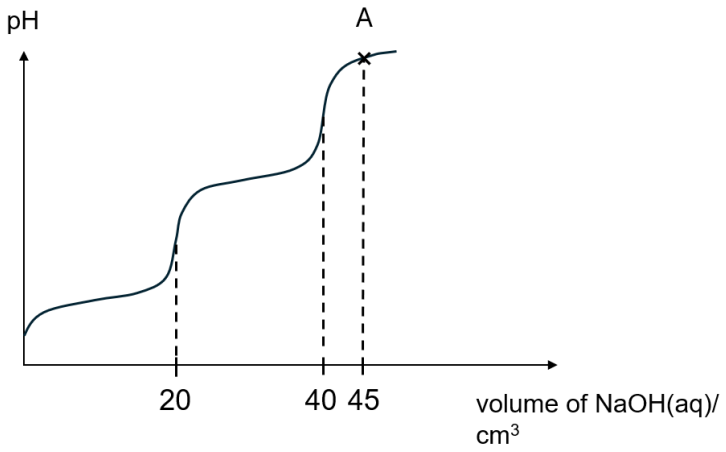

Fig. 5.1

(i) Identify the species present when 40.00 cm^3 of NaOH was added. Hence, calculate the pH of the solution at point **A**. [3]

(ii) Calculate the volume of NaOH that must be added to the solution in **(c)(i)** to increase its pH to 9.67. [1]

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(d) The table below gives the melting points of glutamic acid and octanoic acid ($C_8H_{16}O_2$).

compound	M_r	melting point/ °C
glutamic acid	147	200
octanoic acid	144	16

Explain, in terms of structure and bonding, the difference in melting points. [3]

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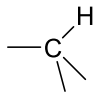
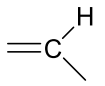
(e) (i) Alkenes do not undergo free radical substitution but alkanes do.

The table below contains information about bond dissociation energies of C−H bonds.

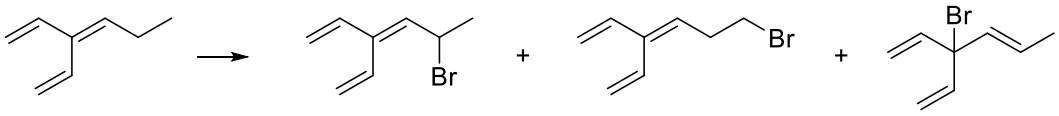
bonds	intermediate formed in the first step of propagation	energy/ kJ mol^{-1}
		410
		451

The electronegativity of carbon is proportional to the s-character in the hybridised orbital. In addition, you may assume that the hybridisation states remain unchanged during the reaction.

Using this information, explain the difference in reactivity by reference to bond energies.

Hence, deduce the stability of the intermediates formed in the first step of propagation. Explain your answer. [2]

Three possible monobromoalkanes that can be formed from the reaction of compound **V** with bromine in the presence of ultra-violet light are shown below.



V **W** **X** **Y**

(ii) Explain why the reaction only starts when it is exposed to ultra-violet light. [1]

(iii) Describe the mechanism of the propagation steps for the reaction of **V** with bromine in the presence of ultra-violet light to form **W**. [1]

(iv) When bromination is carried out and the products are analysed, it is found that **Y** is formed as the major product. It is proposed that the intermediate can rearrange from one radical to another.

Draw three curly arrows on Fig. 5.2 to show the formation of the free radical intermediate used in the first propagation step to form **Y**.

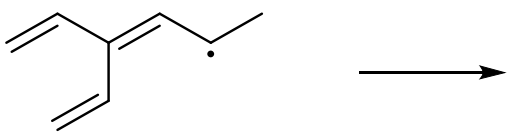


Fig. 5.2 [1]

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(v) Suggest a reason to explain why **Y** is formed the most. [1]

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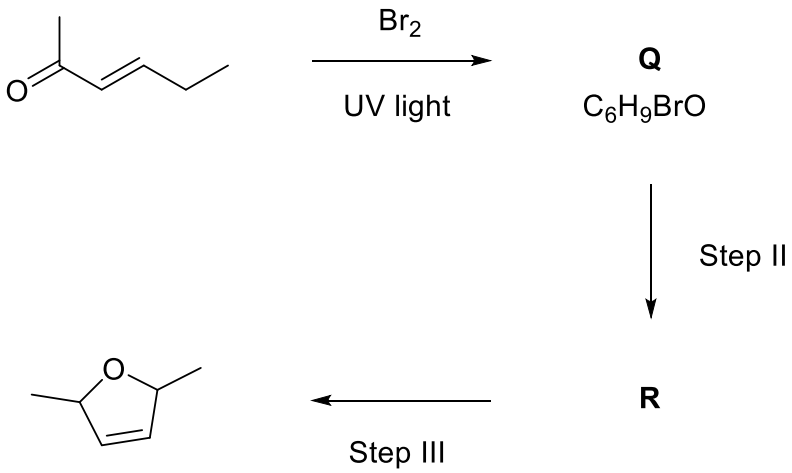
(f) Alkoxides react with halogenoalkane to give an ether, as shown below.

$$RO^- + R'X \rightarrow ROR' + X^-$$

Using this information, state the reagents and conditions required for Step II and Step III and draw the structures of the organic compounds, **Q** and **R**.



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Additional answer space

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

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