



Cambridge International AS & A Level

CANDIDATE NAME

CENTRE NUMBER

--	--	--	--	--

CANDIDATE NUMBER

--	--	--	--

CHEMISTRY

9701/42

Paper 4 A Level Structured Questions

February/March 2024

2 hours

You must answer on the question paper.

No additional materials are needed.

INSTRUCTIONS

- Answer all questions.
- Use a black or dark blue pen. You may use an HB pencil for any diagrams or graphs.
- Write your name, centre number and candidate number in the boxes at the top of the page.
- Write your answer to each question in the space provided.
- Do **not** use an erasable pen or correction fluid.
- Do **not** write on any bar codes.
- You may use a calculator.
- You should show all your working and use appropriate units.

INFORMATION

- The total mark for this paper is 100.
- The number of marks for each question or part question is shown in brackets [].
- The Periodic Table is printed in the question paper.
- Important values, constants and standards are printed in the question paper.

This document has 28 pages. Any blank pages are indicated.

9281939058



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

(a) KI forms an ionic lattice that is soluble in water.

(i) Define enthalpy change of solution, ΔH_{sol}

.....

.....

..... [1]

(ii) KI(s) has a high solubility in water although its enthalpy change of solution is endothermic.

Explain how this high solubility is possible.

.....

.....

..... [2]

(b) Table 1.1 gives some data about the halide ions, Cl^- , Br^- and I^- , and their potassium salts.

Table 1.1

halide ion	enthalpy change of hydration, $\Delta H_{\text{hyd}}/\text{kJ mol}^{-1}$	lattice energy of potassium halide, $\Delta H_{\text{latt}}/\text{kJ mol}^{-1}$
Cl^-	-364	-701
Br^-	-335	-670
I^-	-293	-629

(i) Explain the trend in the enthalpy change of hydration of the halide ions.

.....

.....

..... [2]

(ii) The ΔH_{sol} values of these potassium halides are almost constant.

Use the ΔH_{hyd} and ΔH_{latt} data in Table 1.1 to suggest why.

.....

.....

..... [1]



DO NOT WRITE IN THIS MARGIN

(iii) The enthalpy change of solution of KI(s) is +21.0 kJ mol⁻¹.

Use this information and the data in Table 1.1 to calculate the enthalpy change of hydration of the potassium ion, K⁺(g).

Substance	Standard enthalpy of formation / kJ mol ⁻¹
K ⁺ (g)	0
K ⁺ (aq)	-322
I ⁻ (g)	0
I ⁻ (aq)	-120
KI(s)	-329

ΔH_{hyd} of K⁺(g) = kJ mol⁻¹ [1]

(iv) Solid PbI₂ forms when KI(aq) is mixed with Pb²⁺(aq) ions.

The solubility product, K_{sp}, of PbI₂ is 7.1 × 10⁻⁹ mol³ dm⁻⁹ at 25 °C.

Calculate the solubility, in mol dm⁻³, of PbI₂(s).

solubility of PbI₂(s) = mol dm⁻³ [2]

(v) The ionic radius of Pb²⁺ is 0.120 nm compared to 0.133 nm for K⁺.

Suggest how the $\Delta H_{\text{latt}}^{\ominus}$ of PbI₂(s) differs from $\Delta H_{\text{latt}}^{\ominus}$ of KI(s).

Explain your answer.

.....
.....
..... [2]

DO NOT WRITE IN THIS MARGIN

(c) KI slowly oxidises in air, forming I_2 .

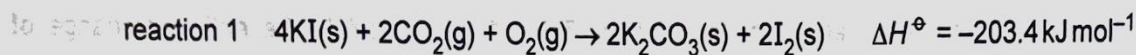


Table 1.2 shows some data relevant to this question.

Table 1.2

substance	standard entropy, $S^\ominus / \text{JK}^{-1} \text{mol}^{-1}$
$CO_2(g)$	213.6
$I_2(s)$	116.1
$K_2CO_3(s)$	155.5
$KI(s)$	106.3
$O_2(g)$	205.2

(i) Calculate the standard entropy change, ΔS^\ominus , of reaction 1.

$$\Delta S^\ominus = \dots\dots\dots \text{JK}^{-1} \text{mol}^{-1} \quad [2]$$

(ii) Use your answer to (c)(i) to show that reaction 1 is spontaneous at 298 K.

[2]

(iii) The Group 1 carbonates are much more thermally stable than the Group 2 carbonates.

State and explain the trend in the thermal stability of the Group 2 carbonates.

.....

.....

.....

.....

[2]

DO NOT WRITE IN THIS MARGIN

(d) A student electrolyses a solution of KI(aq) for 8 minutes using a direct current.

The half-equation for the reaction that occurs at the anode is given.

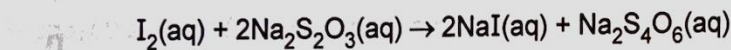


(i) Write a half-equation for the reaction that occurs at the cathode.

Include state symbols.

..... [1]

(ii) After the electrolysis, the I₂(aq) produced requires 21.35 cm³ of 0.100 mol dm⁻³ Na₂S₂O₃(aq) to react completely.



Calculate the average current used in 8 minutes during the electrolysis.

current = A [3]

DO NOT WRITE IN THIS MARGIN

DO NOT WRITE IN THIS MARGIN

DO NOT WRITE IN THIS MARGIN

DO NOT WRITE IN THIS MARGIN

DO NOT WRITE IN THIS MARGIN



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

One example of this is shown in the synthetic route in Fig. 1.1.

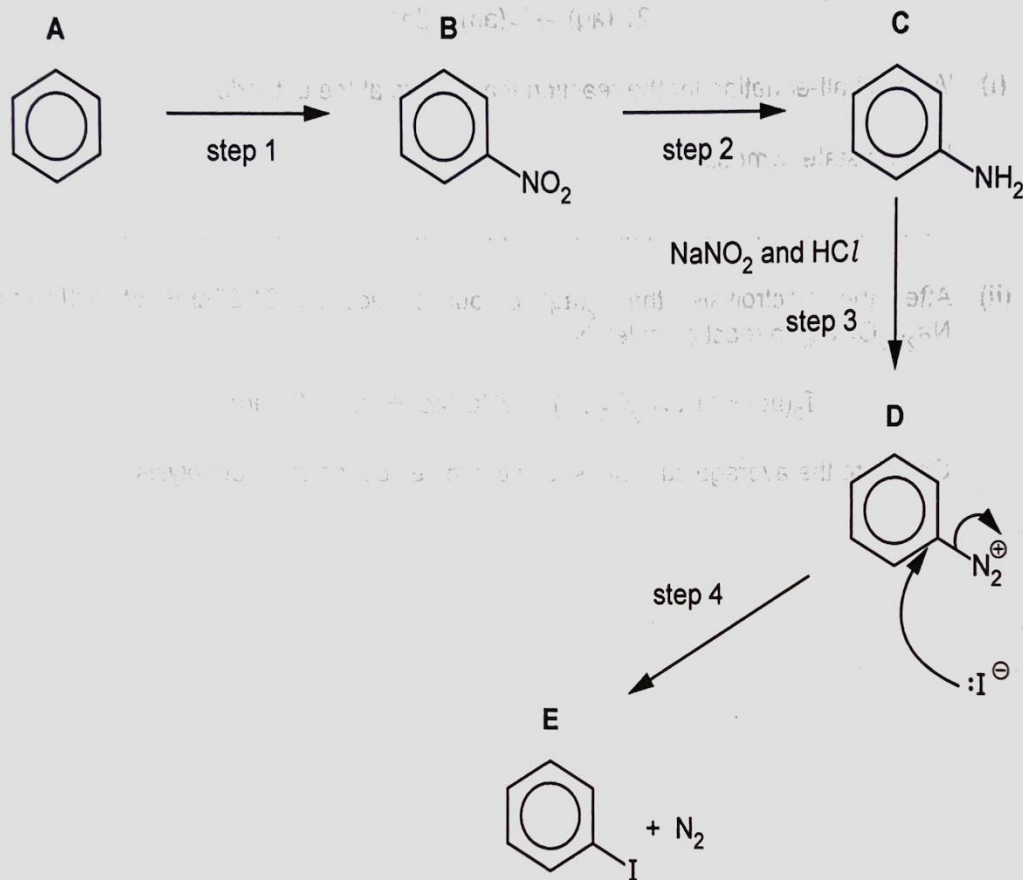


Fig. 1.1

(i) Identify the reagents required for steps 1 and 2.

step 1

step 2

[2]





DO NOT WRITE IN THIS MARGIN

(ii) Step 3 occurs in two stages.

stage I NaNO_2 and HCl undergo an acid-base reaction to produce HNO_2 .

stage II HNO_2 reacts with $\text{C}_6\text{H}_5\text{NH}_2$ to produce D , $\text{C}_6\text{H}_5\text{N}_2^+$.

Complete the equations for stage I and for stage II.

stage I $\text{NaNO}_2 + \text{HCl} \rightarrow \dots\dots\dots$

stage II $\dots\dots\dots$

[2]

(iii) The I^- from KI reacts with D in step 4. The mechanism is shown in Fig. 1.1.

Suggest the name for this mechanism.

$\dots\dots\dots$

[1]

[Total: 26]





2 Water is an amphoteric compound that also acts as a good solvent of polar and ionic compounds.

(a) Equation 1 shows water acting as a Brønsted–Lowry acid.



(i) Identify the two conjugate acid–base pairs in equation 1.

acid I conjugate base of acid I

acid II conjugate base of acid II

[1]

(ii) Water also behaves as a Brønsted–Lowry acid when it dissolves CH₃NH₂.

Explain the ability of CH₃NH₂ to act as a base.

[95 15107]

..... [1]

(iii) Write an equation to show water acting as a base with CH₃COOH.

..... [1]

(b) The ionic product of water, K_w , measures the extent to which water dissociates.

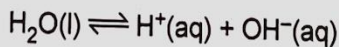


Fig. 2.1 shows how K_w varies with temperature.

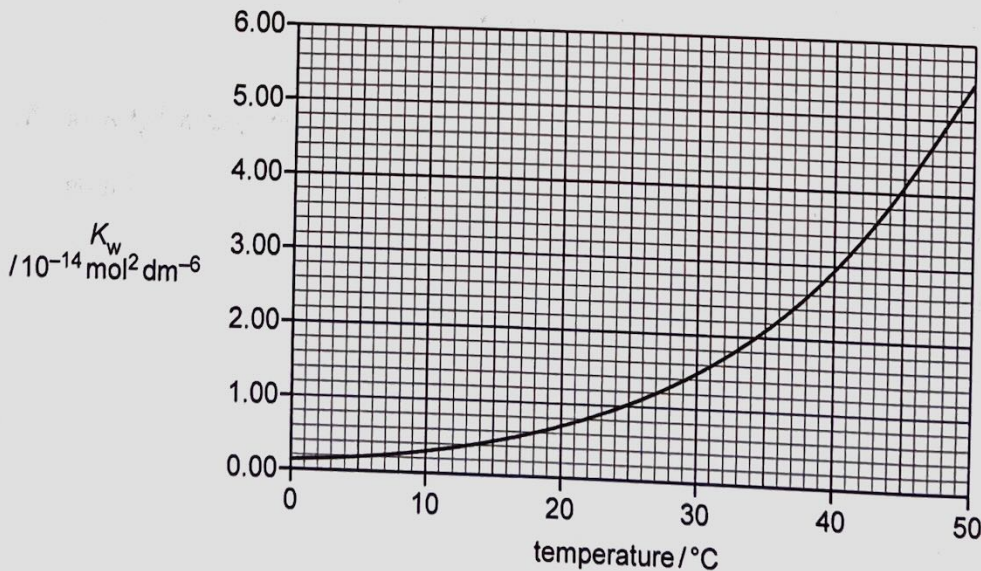


Fig. 2.1

(i) Write an expression for K_w .

..... [1]



DO NOT WRITE IN THIS MARGIN



(ii) Use information from Fig. 2.1 to deduce whether the dissociation of water is an exothermic or an endothermic process.

Explain your answer.

state of H ₂ O	standard enthalpy of formation / kJ mol ⁻¹
gas	+138
liquid	+70
solid	+48

[1]

(iii) An aqueous solution has pH = 7.00 at 30 °C.

Use information from Fig. 2.1 to explain why this solution can be considered to be alkaline at 30 °C.

.....

.....

.....

[2]

DO NOT WRITE IN THIS MARGIN



- (c) The three physical states of H_2O have different standard entropies, S^\ominus , associated with them. Table 2.1 shows these S^\ominus values.

Table 2.1

state of H_2O	standard entropy, $S^\ominus/\text{JK}^{-1}\text{mol}^{-1}$
solid	+48.0
liquid	+70.1
gas	+188.7

- (i) Explain the difference in the S^\ominus values of $\text{H}_2\text{O}(\text{s})$ and $\text{H}_2\text{O}(\text{l})$.

.....
 [1]

- (ii) Explain why the increase in S^\ominus is **much** greater when H_2O boils than when it melts.

.....
 [1]

- (iii) The energy changes for $\text{H}_2\text{O}(\text{s}) \rightarrow \text{H}_2\text{O}(\text{l})$ are shown.

$$\Delta G = 0.00 \text{ kJ mol}^{-1}$$

$$\Delta H = +6.03 \text{ kJ mol}^{-1}$$

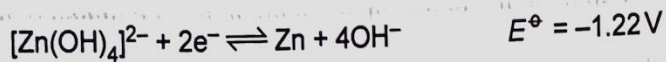
Use these data to show that the melting point of $\text{H}_2\text{O}(\text{s})$ is 0°C .

[1]



(d) Metal-air batteries are electrochemical cells that generate electrical energy from the reaction of metal anodes with air.

The standard electrode potentials for the zinc-air battery are shown.



(i) Calculate the standard cell potential, E^\ominus_{cell} , of the zinc-air battery.

$E^\ominus_{cell} = \dots\dots\dots V$ [1]

(ii) The zinc-air battery usually operates at pH 11 and 298 K. The overall cell potential is dependent on $[OH^-]$.

The Nernst equation shows how the electrode potential at the cathode changes with $[OH^-]$.

$E = 0.40 - \left(\frac{0.059}{z}\right) \log([OH^-]^2)$

Calculate the electrode potential, E , at pH 11.

$E = \dots\dots\dots V$ [2]

[Total: 13]

DO NOT WRITE IN THIS MARGIN



3 Iron is a transition metal in Group 8 of the Periodic Table.

(a) (i) Explain why iron has variable oxidation states.

.....
.....
.....

[1]

(ii) Complete the shorthand electronic configurations of Fe and Fe³⁺.

Fe [Ar].....

Fe³⁺ [Ar].....

[1]

(b) An aqueous solution of Fe(NO₃)₃ contains the complex [Fe(H₂O)₆]³⁺.

When solutions of KSCN(aq) and [Fe(H₂O)₆]³⁺(aq) are mixed, a colour change is observed. The red complex [Fe(H₂O)₅SCN]²⁺ forms.

(i) Define complex.

.....
.....

[1]

(ii) State the coordination number of Fe in [Fe(H₂O)₆]³⁺.

.....

[1]

(iii) The H—O—H bond angle in water is 104.5°.

Suggest the H—O—H bond angle in [Fe(H₂O)₆]³⁺.

Explain your answer.

.....
.....
.....

[1]



DO NOT WRITE IN THIS MARGIN



(iv) Explain why iron complexes are coloured.

.....
.....
.....
.....
..... [3]

(v) Aqueous solutions of complexes $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ and $[\text{Fe}(\text{H}_2\text{O})_5\text{SCN}]^{2+}$ are different colours.

Explain why these complexes are different colours.

.....
.....
..... [2]

.....
.....
.....

.....
.....

(c) Table 3.1 gives values for the stability constants, K_{stab} , of different complexes of iron.

Table 3.1

complex	stability constant, K_{stab}
$[\text{Fe}(\text{H}_2\text{O})_5(\text{H}_2\text{PO}_4)]^{2+}$	5.90×10^1
$[\text{Fe}(\text{H}_2\text{O})_5\text{SCN}]^{2+}$	1.30×10^2

(i) $[\text{Fe}(\text{H}_2\text{O})_5(\text{H}_2\text{PO}_4)]^{2+}$ can form when H_3PO_4 reacts with $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$.

Write an equation for this reaction.

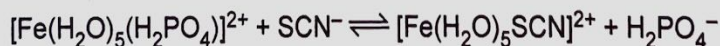
..... [1]

(ii) Write an expression for K_{stab} of $[\text{Fe}(\text{H}_2\text{O})_5\text{SCN}]^{2+}$ and give its units.

$$K_{\text{stab}} =$$

units = [2]

(iii) Use the stability constant data in Table 3.1 to calculate the value of the equilibrium constant, K_c , for the following equilibrium.



value of K_c = [1]

[Total: 14]



4 Ruthenium and osmium are transition metals below iron in Group 8 of the Periodic Table. (d)

(a) Two different complex ions, X and Y, can form when anhydrous RuCl_3 reacts with water under certain conditions.

X and Y have octahedral geometry.

Aqueous samples of X and Y react separately with an excess of $\text{AgNO}_3(\text{aq})$. Different amounts of AgCl are precipitated:

- 1 mole of complex ion X produces 2 moles of AgCl
- 1 mole of complex ion Y produces 1 mole of AgCl

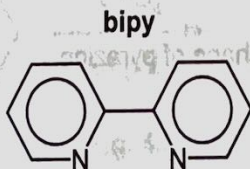
(i) Complete Table 4.1 to suggest formulae for X and Y.

Table 4.1

	X	Y
formula of complex		


[2]

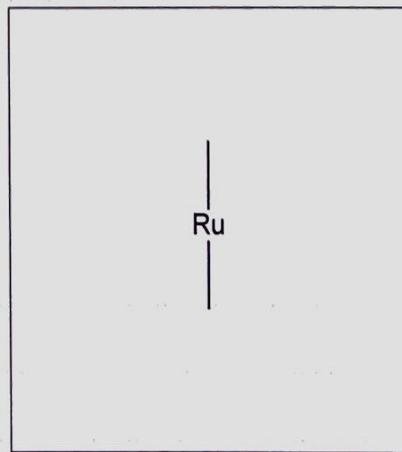
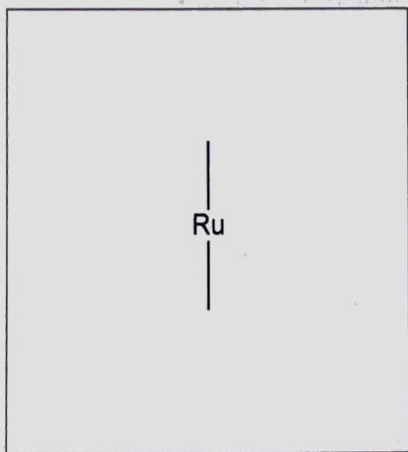
(ii) Both complexes react with an excess of bipyridine, bipy, to form a mixture of two stereoisomers of $[\text{Ru}(\text{bipy})_3]^{3+}$.



Bipyridine is a bidentate ligand.

Draw three-dimensional diagrams of the two stereoisomers of $[\text{Ru}(\text{bipy})_3]^{3+}$.

Use N  N to represent the bipy ligand in your structures.



[2]



(b) Fig. 4.1 shows another ruthenium complex.

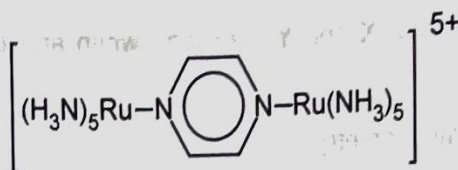
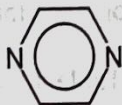


Fig. 4.1

This complex contains the neutral ligand pyrazine.

pyrazine



(i) Suggest how pyrazine is able to bond to two separate ruthenium ions.

.....

.....

[1]

(ii) Pyrazine is an aromatic compound. The bonding and structure of pyrazine is similar to that of benzene.

Describe and explain the shape of pyrazine.

In your answer, include:

- the hybridisation of the nitrogen and carbon atoms
- how orbital overlap forms π bonds between the atoms in the ring.

.....

.....

.....

[2]



(iii) Predict the number of peaks seen in the carbon-13 NMR spectrum of pyrazine.

Explain your answer.



(iv) The overall charge of the ruthenium complex in Fig. 4.1 is 5+.

Deduce the possible oxidation states of the two ruthenium ions in the complex.

..... [1]

(c) Osmium tetroxide, OsO_4 , reacts with alkenes in a similar manner to cold dilute acidified MnO_4^- .

Fig. 4.2 shows a proposed synthesis of a condensation polymer G.

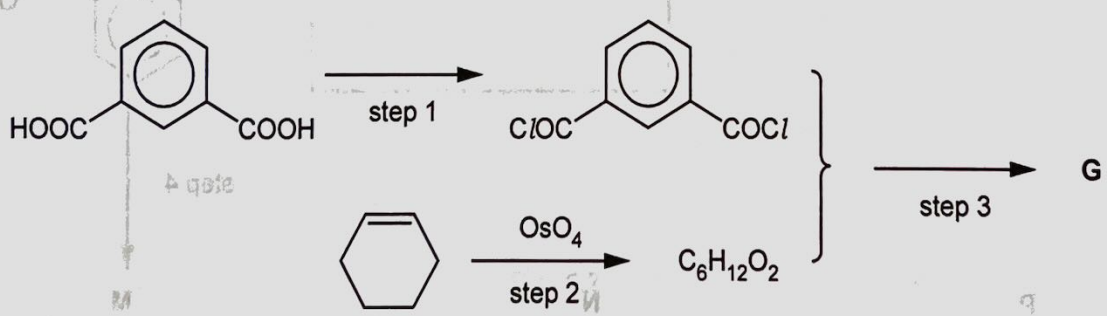


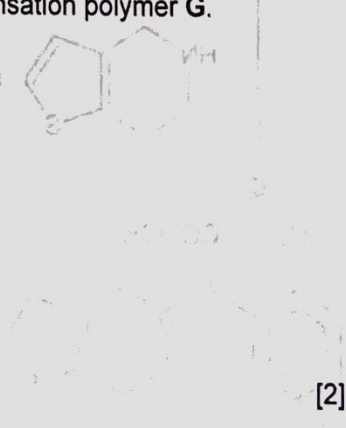
Fig. 4.2

(i) Suggest a reagent for step 1.

..... [1]

(ii) Draw the structure of exactly one repeat unit of the condensation polymer G.

The ester linkage should be shown fully displayed.



[Total: 13]

- 5 Compound Q can be synthesised from chlorobenzene in seven steps, using the route shown in Fig. 5.1.

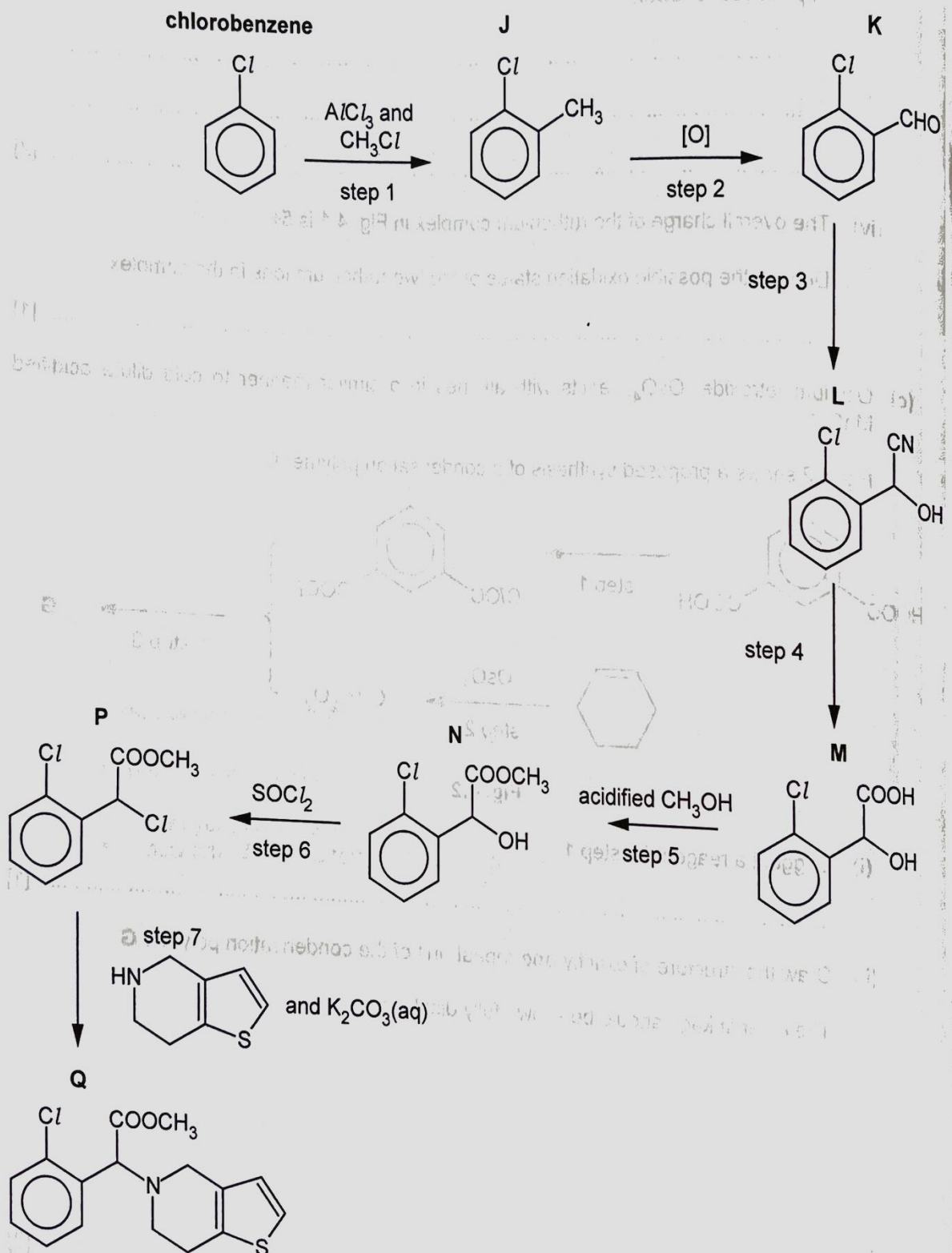


Fig. 5.1

(a) (i) Write an equation for the formation of the electrophile for step 1.
 [1]

(ii) Complete the mechanism in Fig. 5.2 for step 1, the alkylation of chlorobenzene.
 Include all relevant curly arrows and charges.
 Draw the structure of the intermediate.

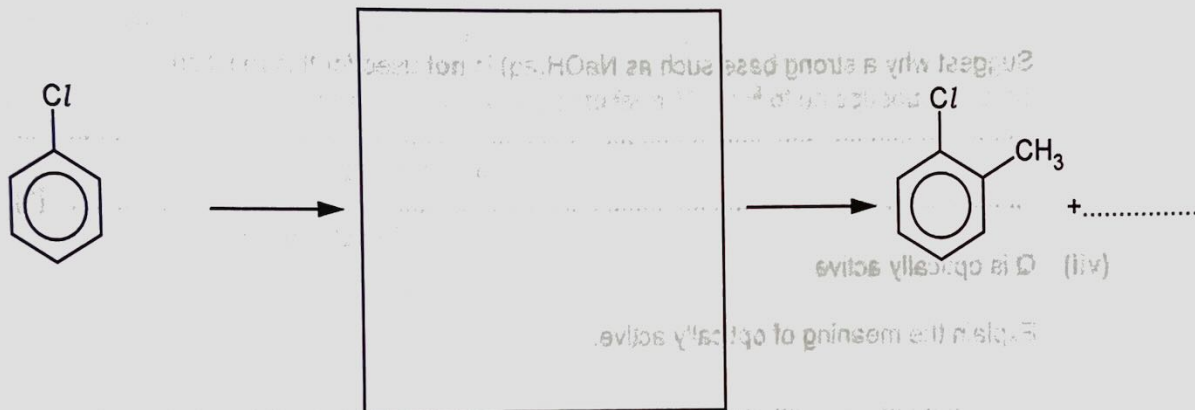


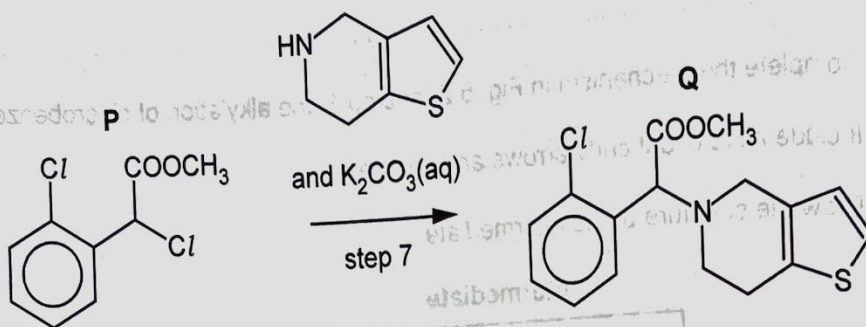
Fig. 5.2 [3]

(iii) Step 2 is an oxidation reaction.
 Construct an equation for the reaction in step 2.
 Use [O] to represent an atom of oxygen from an oxidising agent.
 [1]

(iv) Suggest reagents for the conversion of K to M in steps 3 and 4.
 step 3
 step 4 [2]

(v) Identify the type of reaction that occurs in step 5.
 [1]

(vi) Step 7 takes place when **P** is heated with a weak base such as $K_2CO_3(aq)$.



Suggest why a strong base such as $NaOH(aq)$ is **not** used for this reaction.



[1]

(vii) **Q** is optically active.

Explain the meaning of optically active.

[1]

(viii) Give **two** reasons why it might be desirable to synthesise a single optical isomer of **Q** for use as a drug.

1

2

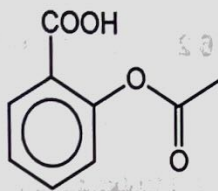
[2]





(b) Q is commonly used in conjunction with aspirin:

aspirin



Aspirin is a weak Brønsted–Lowry acid.

(i) The pK_a of aspirin is 3.49.

75 mg of aspirin dissolves in water to form 100 cm³ of an aqueous solution.

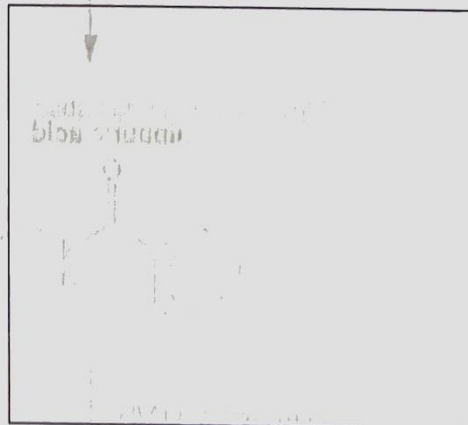
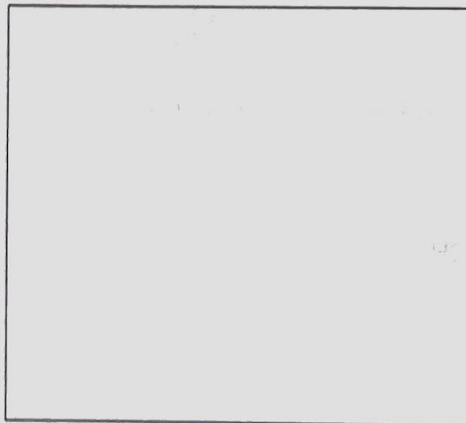
Calculate the pH of this solution.

[M_r : aspirin, 180.0]

pH = [3]

(ii) Aspirin undergoes acid hydrolysis in the stomach.

Give the structures of the organic products of this acid hydrolysis.



[2]

[Total: 17]

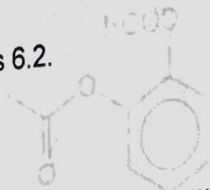
DO NOT WRITE IN THIS MARGIN

6 Amino acids are molecules that contain —NH_2 and —COOH functional groups.

Glycine, $\text{H}_2\text{NCH}_2\text{COOH}$, is the simplest stable amino acid.

(a) The isoelectric point of glycine is 6.2.

(i) Define isoelectric point.



(ii) Draw the structure of glycine at pH4.

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

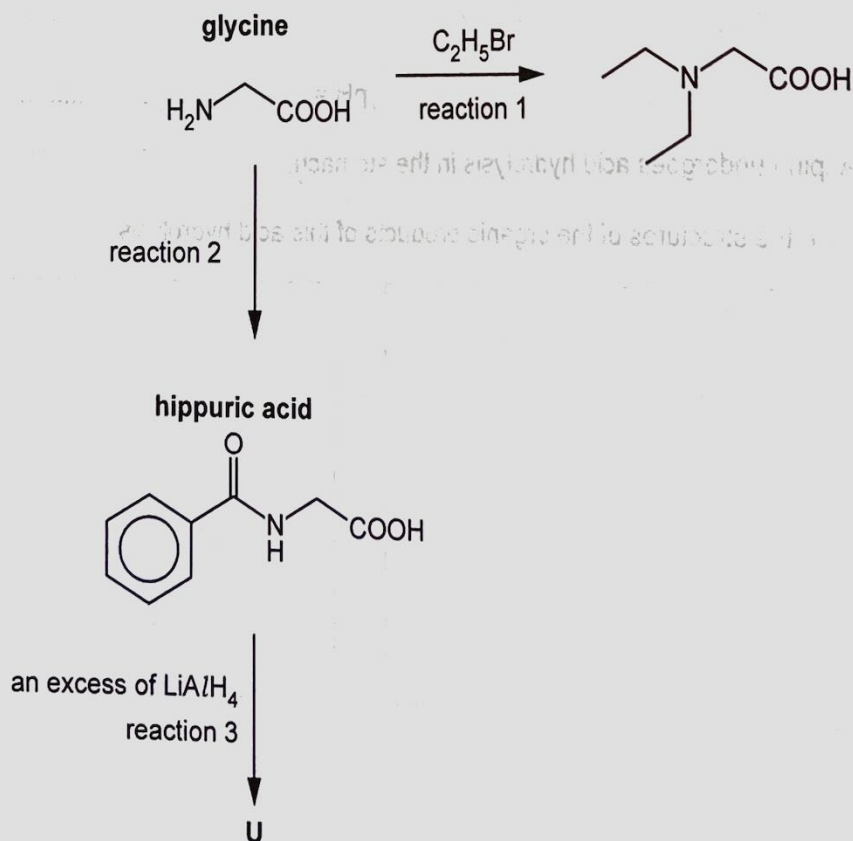


Fig. 6.1

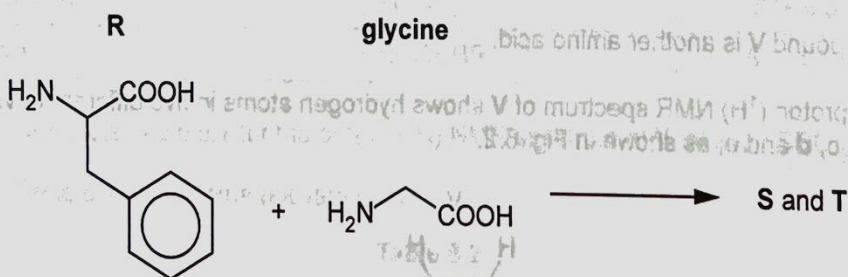




- (i) State the essential conditions for reaction 1. [1]
- (ii) Identify the reagent used in reaction 2. [1]
- (iii) Draw the structure of the organic product U that forms when hippuric acid reacts with an excess of LiAlH_4 in reaction 3. [2]

- (iv) A molecule of phenylalanine, R, can react with a molecule of glycine to form two dipeptides, S and T.

S and T are structural isomers.



Draw the structures of these dipeptides. The peptide bond formed should be shown fully displayed.

S

T

[2]

DO NOT WRITE IN THIS MARGIN

DO NOT WRITE IN THIS MARGIN

DO NOT WRITE IN THIS MARGIN

DO NOT WRITE IN THIS MARGIN

DO NOT WRITE IN THIS MARGIN



(c) A student proposes a synthesis of hippuric acid by the reaction of benzamide, $C_6H_5CONH_2$, and chloroethanoic acid, $ClCH_2COOH$.

The reaction does **not** work well because benzamide is a very weak base.

(i) Explain why amides are weaker bases than amines.

.....

 [2]

(ii) The pK_a of chloroethanoic acid is 2.86 whereas the pK_a of ethanoic acid is 4.76.

Explain the difference between these two pK_a values.

.....

 [2]

(d) Compound **V** is another amino acid.

The proton (1H) NMR spectrum of **V** shows hydrogen atoms in five different environments, **a**, **b**, **c**, **d** and **e**, as shown in Fig. 6.2.

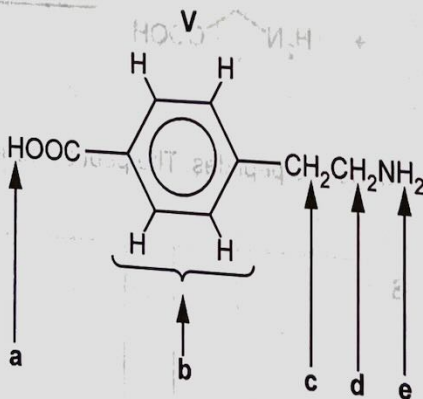


Fig. 6.2



Table 6.1

environment of proton	example	chemical shift range, δ /ppm
alkane	$-\text{CH}_3$, $-\text{CH}_2-$, $>\text{CH}-$	0.9–1.7
alkyl next to $\text{C}=\text{O}$	$\text{CH}_3-\text{C}=\text{O}$, $-\text{CH}_2-\text{C}=\text{O}$, $>\text{CH}-\text{C}=\text{O}$	2.2–3.0
alkyl next to aromatic ring	CH_3-Ar , $-\text{CH}_2-\text{Ar}$, $>\text{CH}-\text{Ar}$	2.3–3.0
alkyl next to electronegative atom	CH_3-O , $-\text{CH}_2-\text{O}$, $-\text{CH}_2-\text{Cl}$, $-\text{CH}_2-\text{N}$	3.2–4.0
attached to alkene	$=\text{CHR}$	4.5–6.0
attached to aromatic ring	$\text{H}-\text{Ar}$	6.0–9.0
aldehyde	HCOR	9.3–10.5
alcohol	ROH	0.5–6.0
phenol	$\text{Ar}-\text{OH}$	4.5–7.0
carboxylic acid	RCOOH	9.0–13.0
alkyl amine	$\text{R}-\text{NH}-$	1.0–5.0
aryl amine	$\text{Ar}-\text{NH}_2$	3.0–6.0
amide	RCONHR	5.0–12.0

(i) Complete Table 6.2 for the proton (^1H) NMR spectrum of **V** taken in CDCl_3 .

Table 6.1 gives some relevant data.

Table 6.2

proton	a	b	c	d	e
chemical shift range, δ /ppm					
name of splitting pattern		multiplet			

[4]

(ii) Complete Table 6.3 by placing a tick (\checkmark) to indicate any protons whose peaks are still present in the proton (^1H) NMR spectrum of **V** taken in D_2O .

Table 6.3

proton	a	b	c	d	e
present in D_2O					

[1]

[Total: 17]