



# Cambridge International AS & A Level

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**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.

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,  $\Delta H_{\text{sol}}$ .

.....  
 .....  
 ..... [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,  $\text{Cl}^-$ ,  $\text{Br}^-$  and  $\text{I}^-$ , 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, $\Delta H_{\text{latt}}/\text{kJ mol}^{-1}$
$\text{Cl}^-$	-364	-701
$\text{Br}^-$	-335	-670
$\text{I}^-$	-293	-629

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

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

(ii) The  $\Delta H_{\text{sol}}$  values of these potassium halides are almost constant.

Use the  $\Delta H_{\text{hyd}}$  and  $\Delta H_{\text{latt}}$  data in Table 1.1 to suggest why.

.....  
 .....  
 ..... [1]

- (iii) The enthalpy change of solution of KI(s) is  $+21.0 \text{ kJ mol}^{-1}$ .

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

$$\Delta H_{\text{hyd}} \text{ of } \text{K}^+(\text{g}) = \dots\dots\dots \text{ kJ mol}^{-1} \quad [1]$$

- (iv) Solid  $\text{PbI}_2$  forms when KI(aq) is mixed with  $\text{Pb}^{2+}(\text{aq})$  ions.

The solubility product,  $K_{\text{sp}}$ , of  $\text{PbI}_2$  is  $7.1 \times 10^{-9} \text{ mol}^3 \text{ dm}^{-9}$  at  $25^\circ\text{C}$ .

Calculate the solubility, in  $\text{mol dm}^{-3}$ , of  $\text{PbI}_2(\text{s})$ .

$$\text{solubility of } \text{PbI}_2(\text{s}) = \dots\dots\dots \text{ mol dm}^{-3} \quad [2]$$

- (v) The ionic radius of  $\text{Pb}^{2+}$  is  $0.120 \text{ nm}$  compared to  $0.133 \text{ nm}$  for  $\text{K}^+$ .

Suggest how the  $\Delta H_{\text{latt}}^\ominus$  of  $\text{PbI}_2(\text{s})$  differs from  $\Delta H_{\text{latt}}^\ominus$  of KI(s).

Explain your answer.

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

(c) KI slowly oxidises in air, forming I<sub>2</sub>.



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 <sub>2</sub> (g)	213.6
I <sub>2</sub> (s)	116.1
K <sub>2</sub> CO <sub>3</sub> (s)	155.5
KI(s)	106.3
O <sub>2</sub> (g)	205.2

(i) Calculate the standard entropy change,  $\Delta S^\ominus$ , 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.

.....

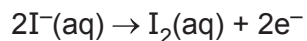
.....

.....

..... [2]

(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.

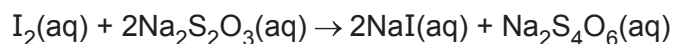


(i) Write a half-equation for the reaction that occurs at the cathode.

Include state symbols.

..... [1]

(ii) After the electrolysis, the  $\text{I}_2(\text{aq})$  produced requires  $21.35\text{ cm}^3$  of  $0.100\text{ mol dm}^{-3}$   $\text{Na}_2\text{S}_2\text{O}_3(\text{aq})$  to react completely.



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

current = .....A [3]

(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.

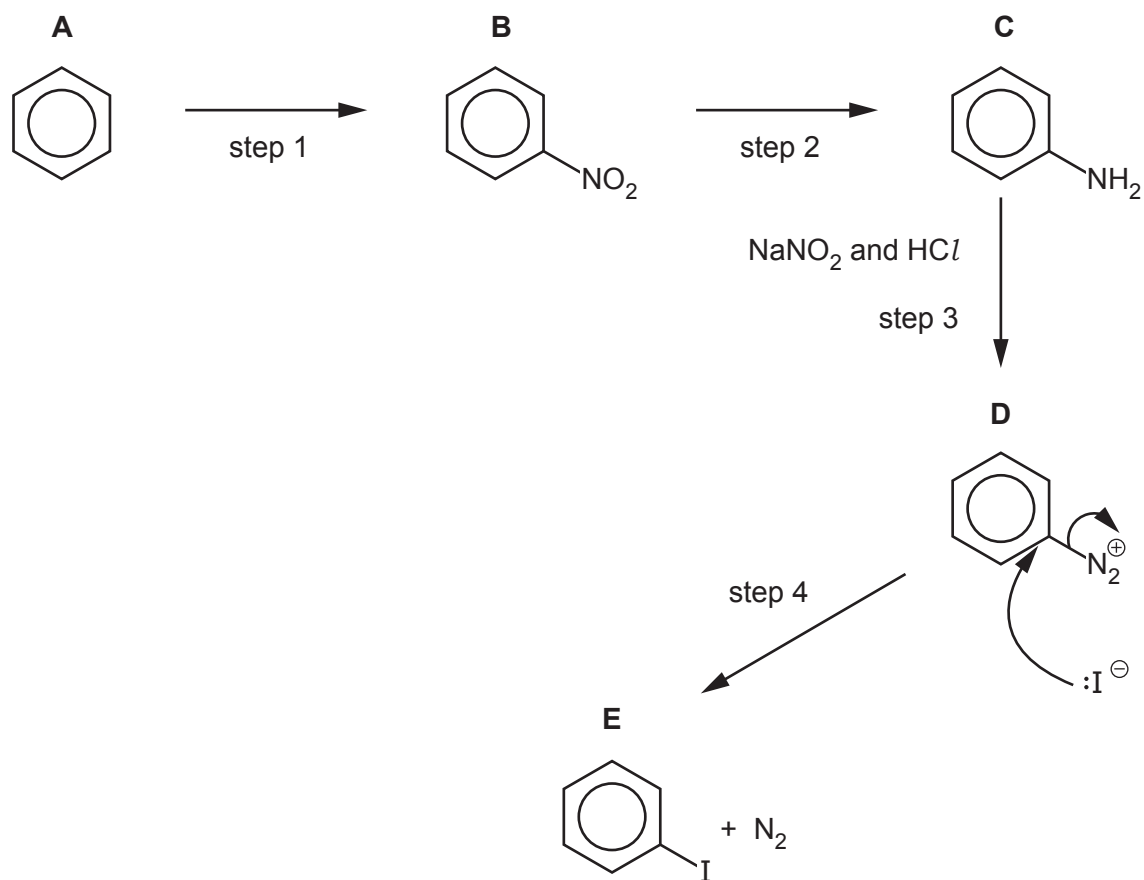


Fig. 1.1

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

step 1 .....

step 2 .....

[2]

(ii) Step 3 occurs in two stages.

stage I  $\text{NaNO}_2$  and  $\text{HCl}$  undergo an acid–base reaction to produce  $\text{HNO}_2$ .

stage II  $\text{HNO}_2$  reacts with **C**,  $\text{C}_6\text{H}_5\text{NH}_2$ , 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  $\text{I}^-$  from  $\text{KI}$  reacts with **D** in step 4. The mechanism is shown in Fig. 1.1.

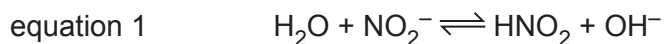
Suggest the name for this mechanism.

$\dots\dots\dots$  [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  $\text{CH}_3\text{NH}_2$ .

Explain the ability of  $\text{CH}_3\text{NH}_2$  to act as a base.

..... [1]

(iii) Write an equation to show water acting as a base with  $\text{CH}_3\text{COOH}$ .

..... [1]

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

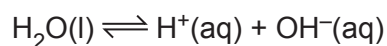


Fig. 2.1 shows how  $K_w$  varies with temperature.

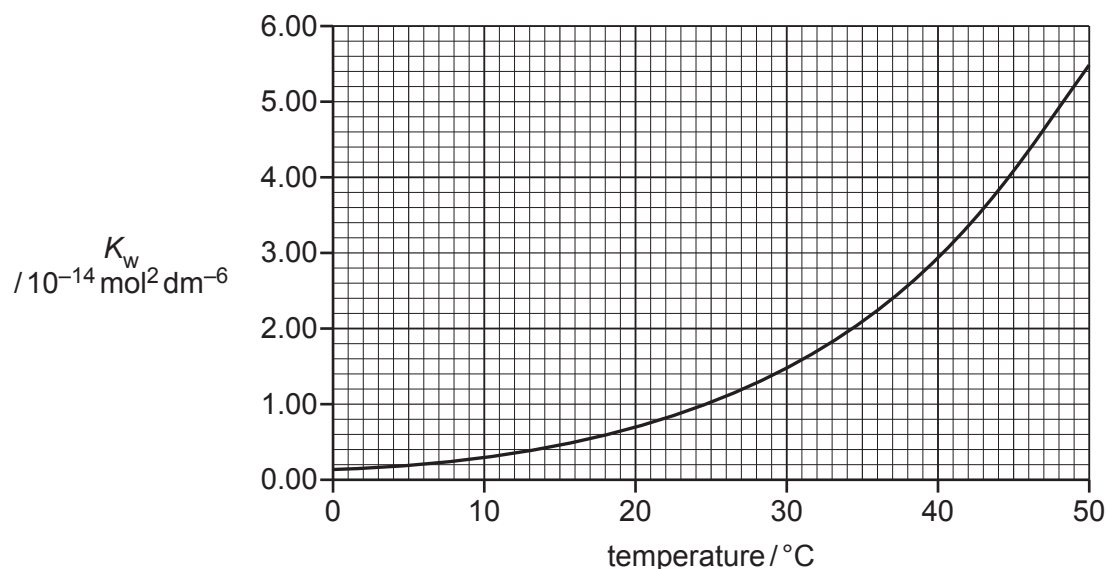


Fig. 2.1

(i) Write an expression for  $K_w$ .

..... [1]



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

Explain your answer.

.....  
.....  
..... [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]

- (c) The three physical states of H<sub>2</sub>O have different standard entropies,  $S^\ominus$ , associated with them. Table 2.1 shows these  $S^\ominus$  values.

Table 2.1

state of H <sub>2</sub> O	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 H<sub>2</sub>O(s) and H<sub>2</sub>O(l).

.....  
 ..... [1]

- (ii) Explain why the increase in  $S^\ominus$  is **much** greater when H<sub>2</sub>O boils than when it melts.

.....  
 ..... [1]

- (iii) The energy changes for H<sub>2</sub>O(s) → H<sub>2</sub>O(l) are shown.

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

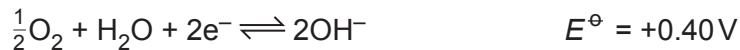
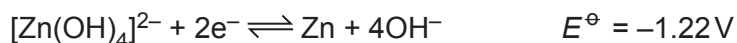
$$\Delta H = +6.03 \text{ kJ mol}^{-1}$$

Use these data to show that the melting point of H<sub>2</sub>O(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,  $E_{\text{cell}}^\ominus$ , of the zinc–air battery.

$$E_{\text{cell}}^\ominus = \dots\dots\dots\text{V} \quad [1]$$

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

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

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

Calculate the electrode potential,  $E$ , at pH 11.

$$E = \dots\dots\dots\text{V} \quad [2]$$

[Total: 13]

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 Fe<sup>3+</sup>.

Fe [Ar].....  
 Fe<sup>3+</sup> [Ar]..... [1]

(b) An aqueous solution of Fe(NO<sub>3</sub>)<sub>3</sub> contains the complex [Fe(H<sub>2</sub>O)<sub>6</sub>]<sup>3+</sup>.

When solutions of KSCN(aq) and [Fe(H<sub>2</sub>O)<sub>6</sub>]<sup>3+</sup>(aq) are mixed, a colour change is observed. The red complex [Fe(H<sub>2</sub>O)<sub>5</sub>SCN]<sup>2+</sup> forms.

(i) Define complex.

.....  
 ..... [1]

(ii) State the coordination number of Fe in [Fe(H<sub>2</sub>O)<sub>6</sub>]<sup>3+</sup>.

..... [1]

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

Suggest the H—O—H bond angle in [Fe(H<sub>2</sub>O)<sub>6</sub>]<sup>3+</sup>.

Explain your answer.

.....  
 .....  
 ..... [1]

(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,  $K_{\text{stab}}$ , of different complexes of iron.

**Table 3.1**

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

(i)  $[\text{Fe}(\text{H}_2\text{O})_5(\text{H}_2\text{PO}_4)]^{2+}$  can form when  $\text{H}_3\text{PO}_4$  reacts with  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ .

Write an equation for this reaction.

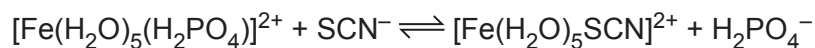
..... [1]

(ii) Write an expression for  $K_{\text{stab}}$  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.

(a) Two different complex ions, **X** and **Y**, can form when anhydrous  $\text{RuCl}_3$  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  $\text{AgCl}$  are precipitated:

- 1 mole of complex ion **X** produces 2 moles of  $\text{AgCl}$
- 1 mole of complex ion **Y** produces 1 mole of  $\text{AgCl}$ .

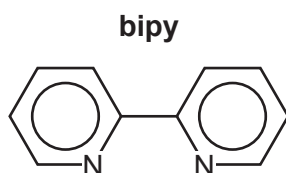
(i) Complete Table 4.1 to suggest formulae for **X** and **Y**.

Table 4.1

	<b>X</b>	<b>Y</b>
formula of complex		

[2]

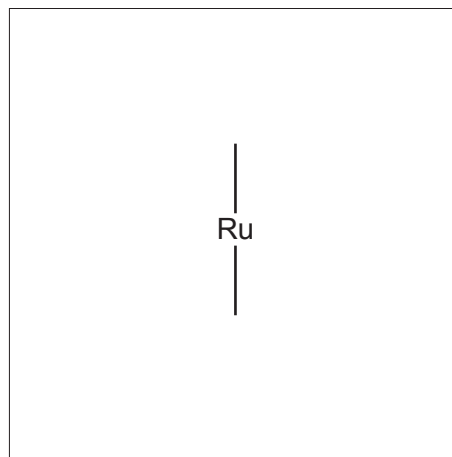
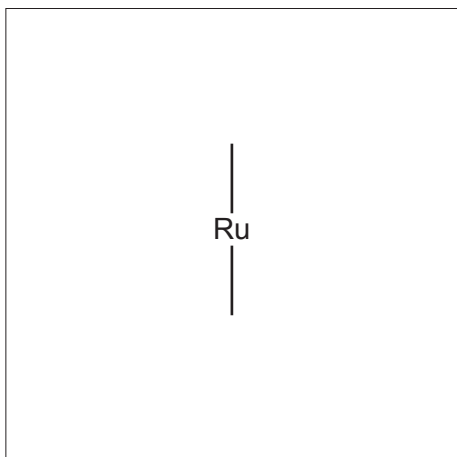
(ii) Both complexes react with an excess of bipyridine, bipy, to form a mixture of two stereoisomers of  $[\text{Ru}(\text{bipy})_3]^{3+}$ .



Bipyridine is a bidentate ligand.

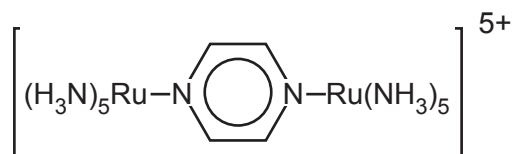
Draw three-dimensional diagrams of the two stereoisomers of  $[\text{Ru}(\text{bipy})_3]^{3+}$ .

Use  $\text{N} \text{---} \text{N}$  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  $\pi$  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.

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

(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,  $\text{OsO}_4$ , reacts with alkenes in a similar manner to cold dilute acidified  $\text{MnO}_4^-$ .

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

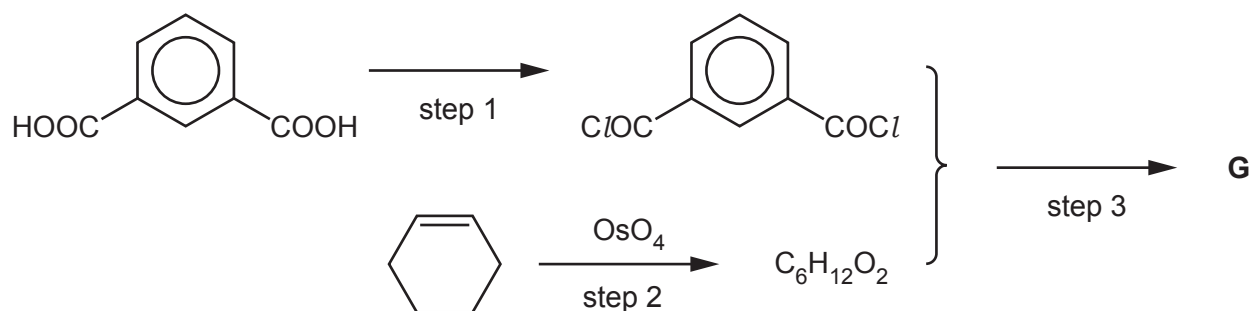


Fig. 4.2

(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.

[2]

[Total: 13]

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

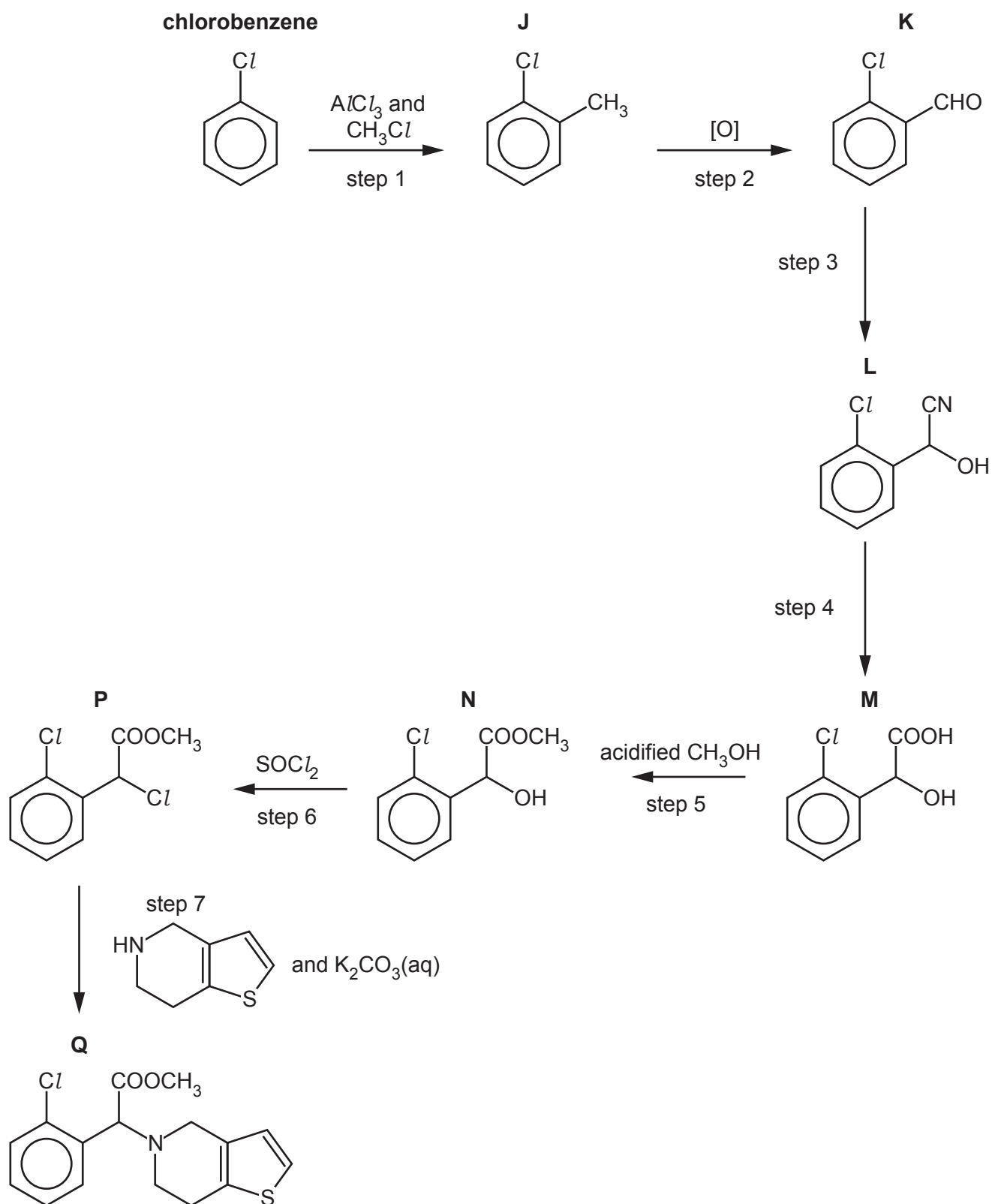


Fig. 5.1

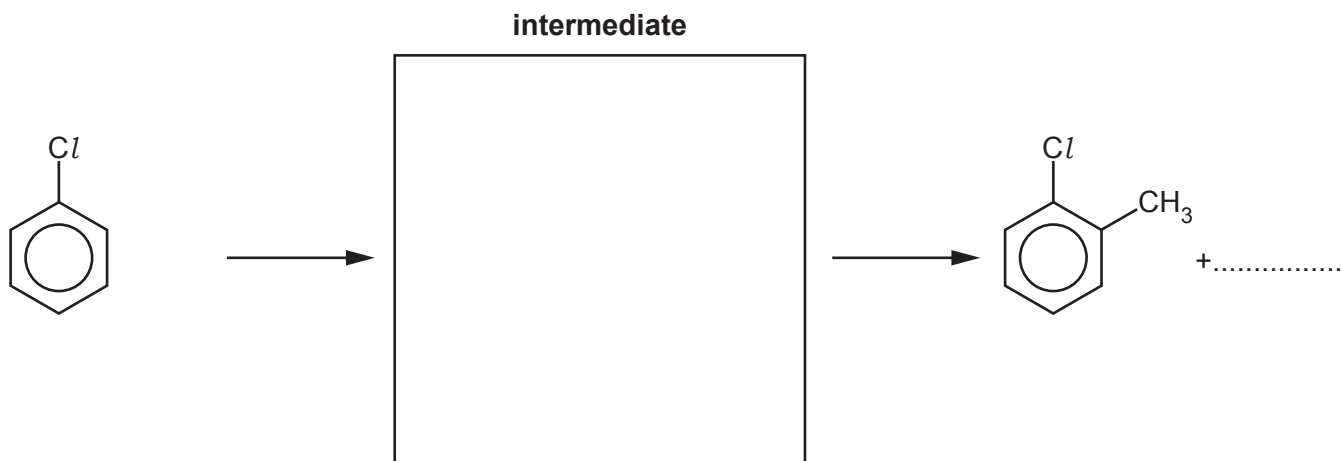
- (a) (i) Write an equation for the formation of the electrophile for step 1.

..... [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**

- (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 .....

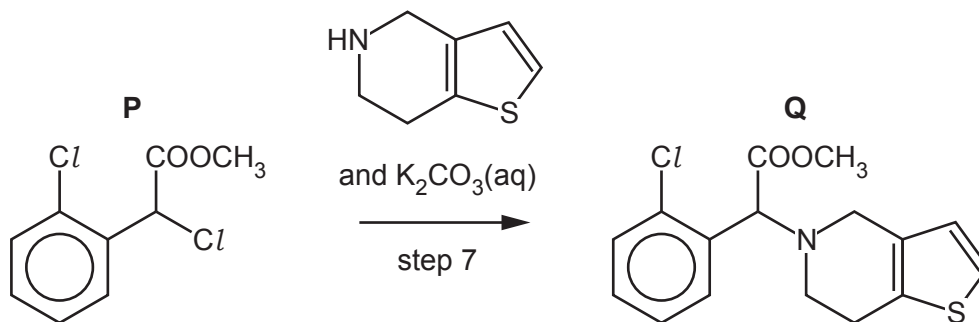
step 4 .....

[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.

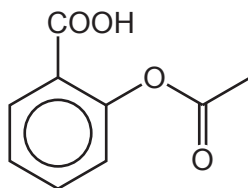
.....  
 .....  
 ..... [1]

(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  $100\text{ cm}^3$  of an aqueous solution.

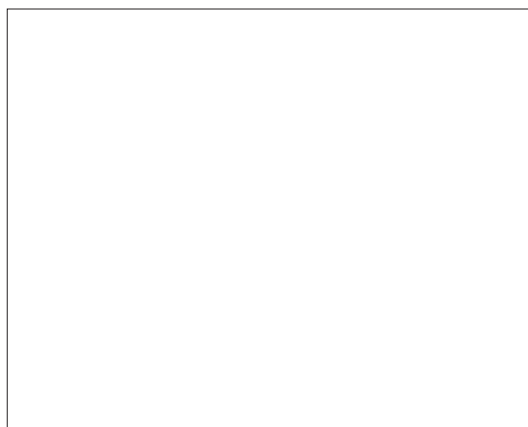
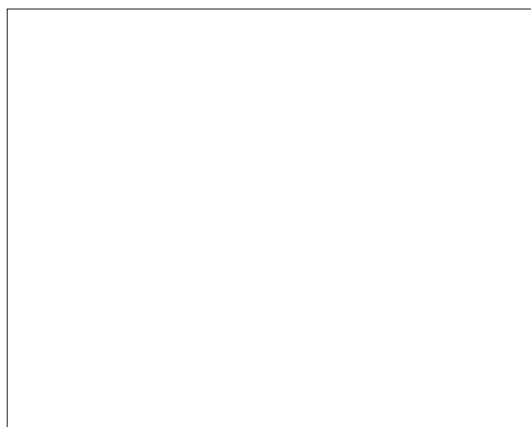
Calculate the pH of this solution.

[ $M_r$ : 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]

6 Amino acids are molecules that contain  $\text{—NH}_2$  and  $\text{—COOH}$  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.

.....  
 ..... [1]

(ii) Draw the structure of glycine at pH4.

[1]

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

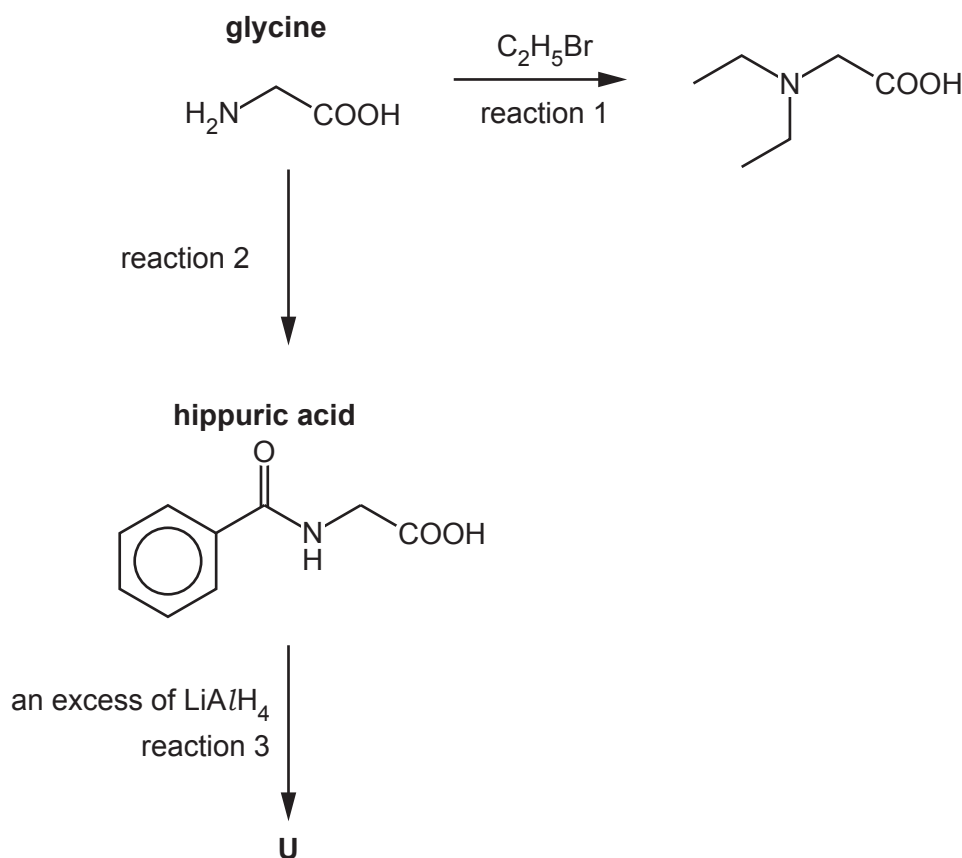


Fig. 6.1



- (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.

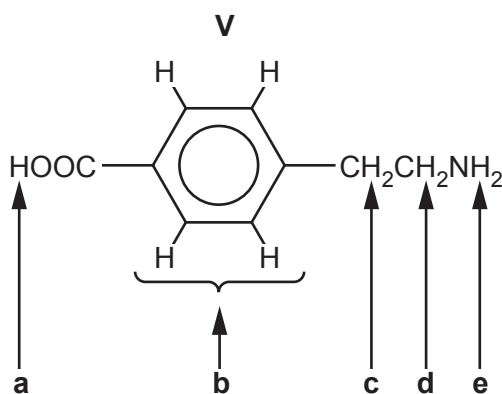


Fig. 6.2



Table 6.1

environment of proton	example	chemical shift range, $\delta$ /ppm
alkane	$-\text{CH}_3$ , $-\text{CH}_2-$ , $>\text{CH}-$	0.9–1.7
alkyl next to C=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	$\text{CH}_3-\text{Ar}$ , $-\text{CH}_2-\text{Ar}$ , $>\text{CH}-\text{Ar}$	2.3–3.0
alkyl next to electronegative atom	$\text{CH}_3-\text{O}$ , $-\text{CH}_2-\text{O}$ , $-\text{CH}_2-\text{Cl}$ , $-\text{CH}_2-\text{N}$	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	$\text{HCOR}$	9.3–10.5
alcohol	$\text{ROH}$	0.5–6.0
phenol	$\text{Ar}-\text{OH}$	4.5–7.0
carboxylic acid	$\text{RCOOH}$	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	$\text{RCONHR}$	5.0–12.0

(i) Complete Table 6.2 for the proton ( $^1\text{H}$ ) NMR spectrum of **V** taken in  $\text{CDCl}_3$ .

Table 6.1 gives some relevant data.

Table 6.2

proton	a	b	c	d	e
chemical shift range, $\delta$ /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 ( $^1\text{H}$ ) NMR spectrum of **V** taken in  $\text{D}_2\text{O}$ .

Table 6.3

proton	a	b	c	d	e
present in $\text{D}_2\text{O}$					

[1]

[Total: 17]



**Important values, constants and standards**

molar gas constant	$R = 8.31 \text{ J K}^{-1} \text{ mol}^{-1}$
Faraday constant	$F = 9.65 \times 10^4 \text{ C mol}^{-1}$
Avogadro constant	$L = 6.022 \times 10^{23} \text{ mol}^{-1}$
electronic charge	$e = -1.60 \times 10^{-19} \text{ C}$
molar volume of gas	$V_m = 22.4 \text{ dm}^3 \text{ mol}^{-1}$ at s.t.p. (101 kPa and 273 K) $V_m = 24.0 \text{ dm}^3 \text{ mol}^{-1}$ at room conditions
ionic product of water	$K_w = 1.00 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$ (at 298 K (25 °C))
specific heat capacity of water	$c = 4.18 \text{ kJ kg}^{-1} \text{ K}^{-1}$ ( $4.18 \text{ J g}^{-1} \text{ K}^{-1}$ )

