

Cambridge International AS & A Level

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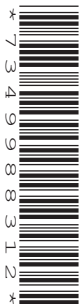
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CHEMISTRY

9701/42

Paper 4 A Level Structured Questions

February/March 2023

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 (a) The most common zinc mineral contains zinc(II) sulfide, ZnS.

- (i) Complete the electrons in boxes diagram in Fig. 1.1 to show the electronic configuration of a zinc(II) ion.

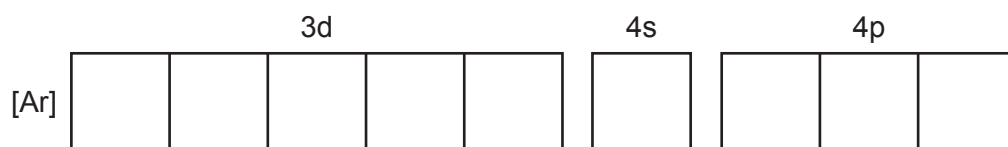


Fig. 1.1

[1]

- (ii) Complete Fig. 1.2 to show the Born–Haber diagram for the ionic solid ZnS.

Include state symbols of relevant species.

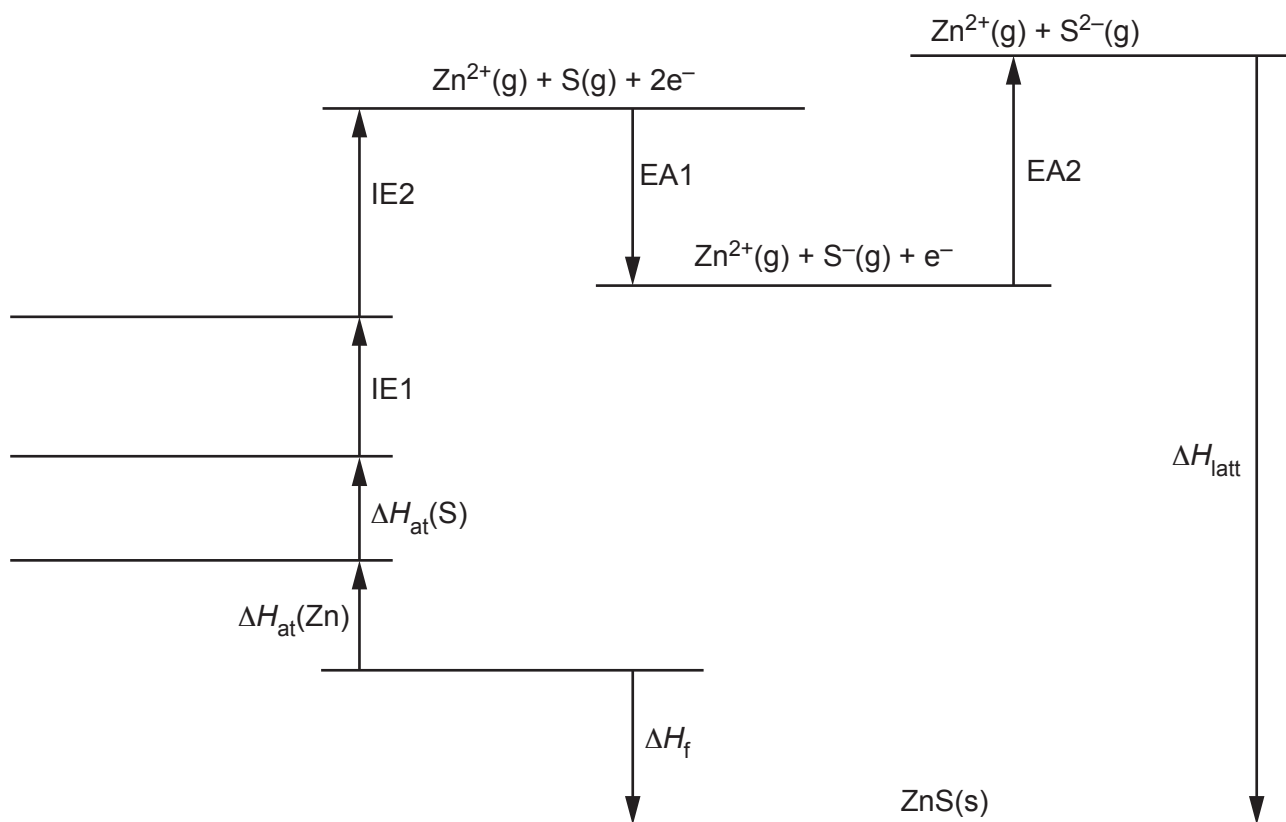


Fig. 1.2

[3]

- (iii) Describe the trend in the first electron affinity of the Group 16 elements S to Te.

Explain your answer.

.....

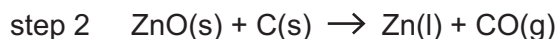
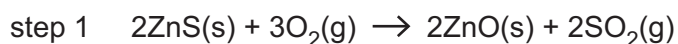
 [2]

- (iv) Explain why the lattice energy, ΔH_{latt} , of ZnO is more exothermic than that of ZnS.

.....

 [2]

- (b) Zinc metal can be obtained in a two-step process as shown.



The reactions are carried out at 800 °C.

- (i) Predict the sign of the entropy change, $\Delta S^\ominus$, of the reaction in **step 1**.

Explain your answer.

.....
 [1]

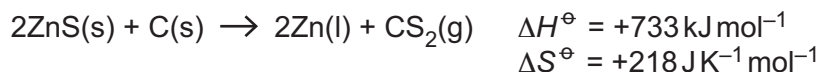
- (ii) Use the data in Table 1.1 to calculate $\Delta S^\ominus$ of the reaction shown in **step 2**.

Table 1.1

chemical	ZnO(s)	C(s)	Zn(l)	CO(g)
$S^\ominus / \text{JK}^{-1}\text{mol}^{-1}$	43.7	5.7	50.8	197.7

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

- (iii) An equation for the direct reduction of ZnS by carbon is shown.



This reaction is **not** feasible at 800 °C.

Calculate $\Delta G^\ominus$ for this reaction at 800 °C.

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

- (c) $\text{Zn(NO}_3)_2$ undergoes thermal decomposition when heated. The reaction is similar to the thermal decomposition of Group 2 nitrates.

- (i) Construct an equation for the thermal decomposition of $\text{Zn(NO}_3)_2$.

..... [1]

- (ii) The radii of some Group 2 cations and Zn^{2+} are shown in Table 1.2.

Table 1.2

cation	Mg^{2+}	Ca^{2+}	Sr^{2+}	Ba^{2+}	Zn^{2+}
radius/pm	65	99	113	135	74

State and explain the trend in thermal stability of the Group 2 nitrates down the group.

.....

 [2]

- (iii) Use Table 1.2 to suggest which Group 2 nitrates are **less** thermally stable than zinc nitrate.

..... [1]

[Total: 16]

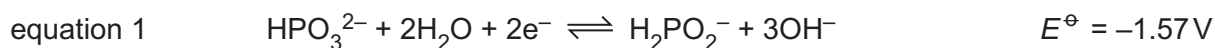
2 Hypophosphorous acid is an inorganic acid.

The conjugate base of hypophosphorous acid is H_2PO_2^- .

(a) Give the formula of hypophosphorous acid.

..... [1]

(b) H_2PO_2^- is a strong reducing agent. It can be used to reduce metal cations without the need for electrolysis.



(i) In an experiment, an alkaline $\text{HPO}_3^{2-}/\text{H}_2\text{PO}_2^-$ half-cell is constructed with $[\text{H}_2\text{PO}_2^-] = 0.050\text{ mol dm}^{-3}$.

All other ions are at their standard concentration.

Predict how the value of E of this half-cell differs from its $E^\ominus$ value.

Explain your answer.

.....

 [2]

(ii) The Cr^{3+}/Cr half-cell has a standard electrode potential of -0.74V .

An electrochemical cell consists of an alkaline $\text{HPO}_3^{2-}/\text{H}_2\text{PO}_2^-$ half-cell and a Cr^{3+}/Cr half-cell.

Calculate the standard cell potential, $E_{\text{cell}}^\ominus$.

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

- (iii) Complete the diagram in Fig. 2.1 to show how the standard electrode potential of the Cr^{3+}/Cr half-cell can be measured relative to that of the standard hydrogen electrode.

Identify the chemicals, conditions and relevant pieces of apparatus.

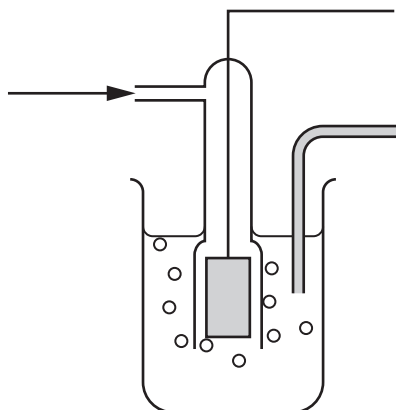


Fig. 2.1

[3]

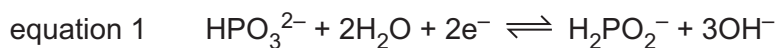
- (iv) Label Fig. 2.1 to show:

- which is the positive electrode
- the direction of electron flow in the external circuit.

[1]

- (v) H_2PO_2^- reduces Ni^{2+} to Ni in alkaline conditions.

Use equation 1 to construct the ionic equation for this reaction.



..... [1]

(c) $\text{H}_2\text{PO}_2^-(\text{aq})$ reacts with $\text{OH}^-(\text{aq})$.

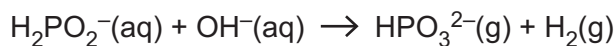


Table 2.1 shows the results of a series of experiments used to investigate the rate of this reaction.

Table 2.1

experiment	$[\text{H}_2\text{PO}_2^-(\text{aq})]$ / mol dm^{-3}	$[\text{OH}^-(\text{aq})]$ / mol dm^{-3}	volume of H_2 produced in 60 s / cm^3
1	0.40	2.00	6.4
2	0.80	2.00	12.8
3	1.20	1.00	4.8

(i) The volume of H_2 was measured under room conditions.

Use the molar volume of gas, V_m , and the data from experiment 1 to calculate the rate of reaction in $\text{mol dm}^{-3} \text{s}^{-1}$.

rate of reaction = $\text{mol dm}^{-3} \text{s}^{-1}$ [1]

(ii) The rate equation was found to be:

$$\text{rate} = k [\text{H}_2\text{PO}_2^-(\text{aq})] [\text{OH}^-(\text{aq})]^2$$

Show that the data in Table 2.1 is consistent with the rate equation.

.....

 [2]

(iii) State the units of the rate constant, k , for the reaction.

..... [1]

- (iv) The experiment is repeated using a large excess of $\text{OH}^-(\text{aq})$.

Under these conditions, the rate equation is:

$$\text{rate} = k_1 [\text{H}_2\text{PO}_2^-(\text{aq})]$$

$$k_1 = 8.25 \times 10^{-5} \text{ s}^{-1}$$

Calculate the value of the half-life, $t_{\frac{1}{2}}$, of the reaction.

$$t_{\frac{1}{2}} = \dots\dots\dots \text{ s [1]}$$

- (v) Describe how an increase in temperature affects the value of the rate constant, k_1 .

.....
 [1]

- (d) A student suggests that the reaction between $\text{H}_2\text{PO}_2^-(\text{aq})$ and $\text{OH}^-(\text{aq})$ might happen more quickly in the presence of a heterogeneous catalyst.

Describe the mode of action of a heterogeneous catalyst.

.....

 [2]

[Total: 17]

3 Vanadium is a transition element in Period 4 of the Periodic Table.

(a) Define transition element.

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

(b) Vanadium shows typical chemical properties of transition elements, including variable oxidation states.

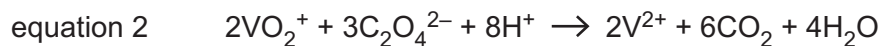
(i) State **two** other typical chemical properties of transition elements.

1
2 [1]

(ii) Explain why transition elements have variable oxidation states.

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

- (c) VO_2^+ can be reduced to V^{2+} by $\text{C}_2\text{O}_4^{2-}$ in acidic conditions.



- (i) In a titration, 25.00 cm^3 of $0.0300\text{ mol dm}^{-3}$ $\text{VO}_2^+(\text{aq})$ is added to 10 cm^3 of dilute sulfuric acid.

A solution of $0.0400\text{ mol dm}^{-3}$ $\text{C}_2\text{O}_4^{2-}(\text{aq})$ is then added from a burette until the end-point is reached.

The titration is repeated and concordant results obtained, as shown in Table 3.1.

Table 3.1

	1	2
volume of $\text{C}_2\text{O}_4^{2-}(\text{aq})$ added / cm^3	28.15	28.10

Show that these results are consistent with the stoichiometry of equation 2.

[2]

- (ii) An excess of $\text{C}_2\text{O}_4^{2-}$ reacts with VO_2^+ to form a mixture of two octahedral complex ions. The complex ions are stereoisomers of each other.

Each complex ion contains a V^{2+} cation and three $\text{C}_2\text{O}_4^{2-}$ ions.

Complete the diagram to show the three-dimensional structure of **one** of the complex ions.

Include the charge of the complex ion.

Use $\text{O} \text{---} \text{O}$ to represent a $\text{C}_2\text{O}_4^{2-}$ ion.



(d) $V^{2+}(aq)$ can be oxidised by $H_2O_2(aq)$.

Table 3.2 gives some relevant data.

Table 3.2

	half-equation	$E^\ominus / V$
1	$H_2O_2(aq) + 2H^+(aq) + 2e^- \rightleftharpoons 2H_2O(l)$	+1.77
2	$VO_2^+(aq) + 2H^+(aq) + e^- \rightleftharpoons VO^{2+}(aq) + H_2O(l)$	+1.00
3	$VO^{2+}(aq) + 2H^+(aq) + e^- \rightleftharpoons V^{3+}(aq) + H_2O(l)$	+0.34
4	$V^{3+}(aq) + e^- \rightleftharpoons V^{2+}(aq)$	-0.26

- (i) Identify the vanadium species that forms when an excess of $H_2O_2(aq)$ reacts with $V^{2+}(aq)$ under standard conditions.

Explain your answer with reference to the data in Table 3.2.

.....

 [1]

- (ii) Concentrated acidified H_2O_2 can react with V^{2+} to form red VO_2^{3+} ions.

VO_2^{3+} contains vanadium combined with the peroxide anion, O_2^{2-} .

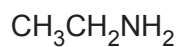
Deduce the oxidation state of vanadium in VO_2^{3+} .

..... [1]

[Total: 9]

- 4 Ethylamine and phenylamine are primary amines.

ethylamine



phenylamine

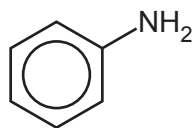


Fig. 4.1

These two compounds are synthesised by different methods.

- (a) Several methods can be used to form ethylamine.

- (i) Ethylamine forms when ethanamide, CH_3CONH_2 , is reduced by LiAlH_4 .

Write an equation for this reaction. Use [H] to represent one atom of hydrogen from the reducing agent.

..... [1]

- (ii) Ethylamine is a product of the reaction of bromoethane with ammonia.

Name the mechanism of this reaction and state the conditions used.

mechanism

conditions

[2]

- (iii) The reaction in (a)(ii) also forms secondary and tertiary amines.

Suggest the identity of a secondary or tertiary amine formed by the reaction in (a)(ii).

..... [1]

(b) Ethylamine is a weak base.

State the relative basicities of ammonia, ethylamine and phenylamine.

Explain your answer.

..... < <
least basic most basic

.....

.....

.....

.....

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.....

.....

..... [4]

(c) Pure phenylamine, $\text{C}_6\text{H}_5\text{NH}_2$, can be prepared from benzene in two steps.

Draw the structure of the intermediate compound.

Suggest reagents and conditions for each step.

.....

.....

.....

.....

..... [3]

(d) Fig. 4.2 shows some reactions of phenylamine.

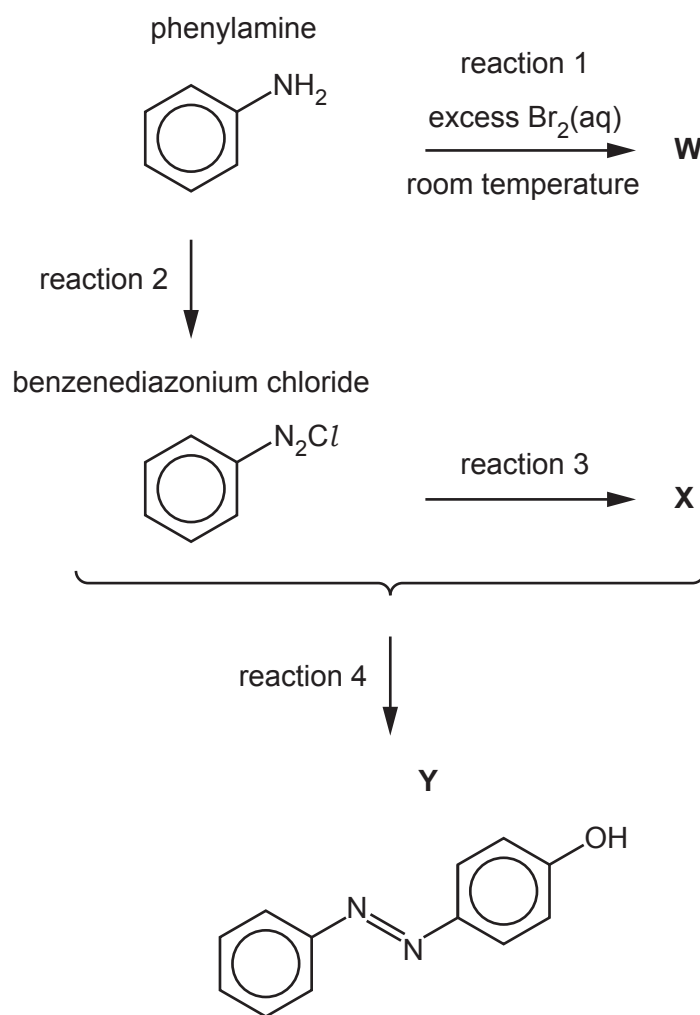


Fig. 4.2

- (i) Draw the structure of **W**, the organic product of reaction 1.

[1]

- (ii) State the reagents used in reaction 2.

..... [1]

Benzenediazonium chloride, $\text{C}_6\text{H}_5\text{N}_2\text{Cl}$, and **X** react together in reaction 4 to form **Y**, an azo compound.

- (iii) Name **X**, the organic product of reaction 3.

..... [1]

- (iv) State the necessary conditions for reaction 4 to occur.

..... [1]

- (v) Suggest a use for **Y**.

..... [1]

(e) Methylamine, CH_3NH_2 , is another primary amine. CH_3NH_2 can act as a monodentate ligand.

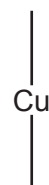
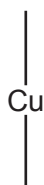
(i) Define monodentate ligand.

.....

 [2]

(ii) $\text{Cu}^{2+}(\text{aq})$ reacts with CH_3NH_2 to form $[\text{Cu}(\text{CH}_3\text{NH}_2)_2(\text{H}_2\text{O})_4]^{2+}$.

Draw three-dimensional diagrams to show the two geometrical isomers of $[\text{Cu}(\text{CH}_3\text{NH}_2)_2(\text{H}_2\text{O})_4]^{2+}$.

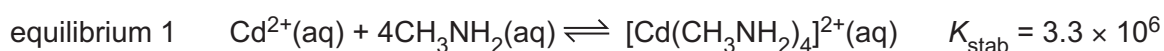


[2]

(iii) State the coordination number of copper in $[\text{Cu}(\text{CH}_3\text{NH}_2)_2(\text{H}_2\text{O})_4]^{2+}$.

..... [1]

(f) $\text{Cd}^{2+}(\text{aq})$ ions form tetrahedral complexes with CH_3NH_2 , OH^- and Cl^- ions, as shown in equilibria 1, 2 and 3.



(i) Give the units of K_{stab} for equilibrium 1.

..... [1]

(ii) Write an expression for K_{stab} for equilibrium 3.

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

- (iii) A solution of $\text{Cl}^-(\text{aq})$ is added to $\text{Cd}^{2+}(\text{aq})$ and allowed to reach equilibrium. The equilibrium concentrations are given.

$$[\text{Cd}^{2+}(\text{aq})] = 0.043 \text{ mol dm}^{-3}$$

$$[\text{Cl}^-(\text{aq})] = 0.072 \text{ mol dm}^{-3}$$

Use your expression in (f)(ii) to calculate the concentration of $\text{CdCl}_4^{2-}(\text{aq})$ in the equilibrium mixture.

$$[\text{CdCl}_4^{2-}(\text{aq})] = \dots\dots\dots \text{ mol dm}^{-3} \quad [1]$$

- (iv) When $\text{CH}_3\text{NH}_2(\text{aq})$ is added to $\text{Cd}^{2+}(\text{aq})$, a mixture of $[\text{Cd}(\text{CH}_3\text{NH}_2)_4]^{2+}(\text{aq})$ and $[\text{Cd}(\text{OH})_4]^{2-}(\text{aq})$ forms.

Suggest how the $[\text{Cd}(\text{OH})_4]^{2-}(\text{aq})$ is formed.

.....
 [1]

- (v) $\text{Cd}^{2+}(\text{aq})$ exists as a complex ion, $[\text{Cd}(\text{H}_2\text{O})_6]^{2+}(\text{aq})$.

Identify the most stable and the least stable of the complexes in Table 4.1 by placing **one** tick (✓) in each column.

Explain your answer.

Table 4.1

complex	most stable	least stable
$[\text{Cd}(\text{H}_2\text{O})_6]^{2+}(\text{aq})$		
$[\text{Cd}(\text{OH})_4]^{2-}(\text{aq})$		
$[\text{Cd}(\text{CH}_3\text{NH}_2)_4]^{2+}(\text{aq})$		
$[\text{CdCl}_4]^{2-}(\text{aq})$		

explanation

 [2]

- 5 Tulobuterol is used in some medicines.

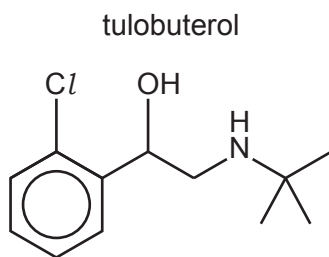


Fig. 5.1

- (a) Tulobuterol contains a benzene ring in its structure.

Describe and explain the shape of benzene.

In your answer, include:

- the bond angle between carbon atoms
- the hybridisation of the carbon atoms
- how orbital overlap forms σ and π bonds between the carbon atoms.

.....

.....

.....

..... [3]

- (b) In a synthesis of tulobuterol, the first step involves the formation of chlorobenzene. Benzene reacts with Cl_2 in the presence of an AlCl_3 catalyst.

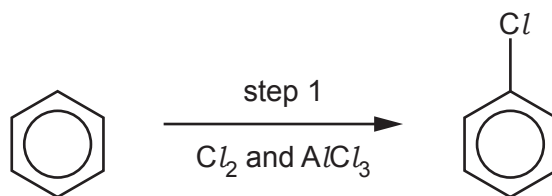


Fig. 5.2

- (i) Write an equation to show how Cl_2 reacts with AlCl_3 to generate an electrophile.

..... [1]

- (ii) Complete the mechanism in Fig. 5.3 for the reaction of benzene with the electrophile generated in (b)(i).

Include all relevant curly arrows and charges.

Draw the structure of the intermediate.

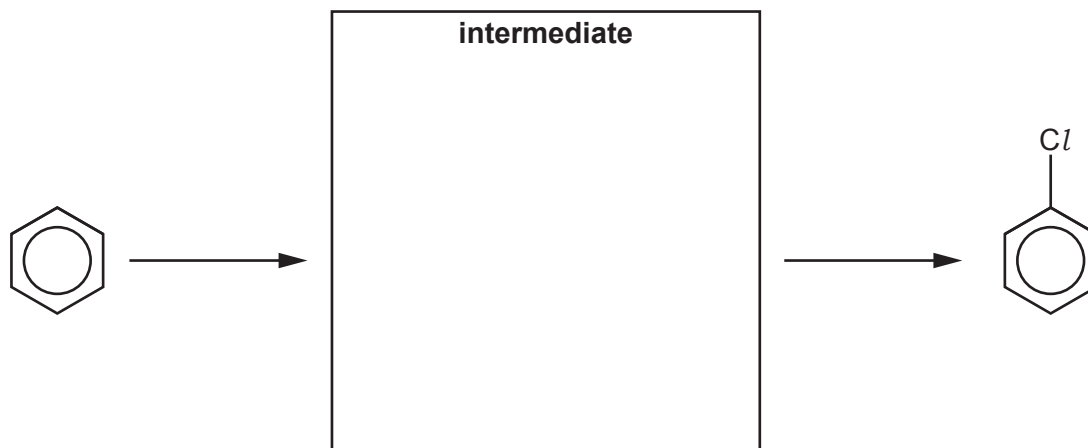


Fig. 5.3

[3]

- (c) The second step of the synthesis involves the reaction of chlorobenzene with ClCOCH_2Cl , also in the presence of an AlCl_3 catalyst, forming compound **Q**.

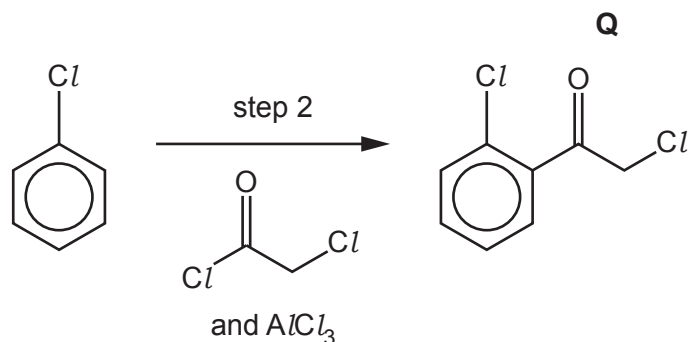


Fig. 5.4

- (i) Name the mechanism of the reaction in step 2.

..... [1]

- (ii) Draw the structure of an isomer of **Q** that forms as an organic by-product of the reaction in step 2.

[1]

- (iii) The reactants used in step 2 contain acyl chloride, alkyl chloride and aryl chloride functional groups.

State and explain the relative ease of hydrolysis of acyl chlorides, alkyl chlorides and aryl chlorides.

..... , ,
easiest to hydrolyse hardest to hydrolyse

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

(d) Tulobuterol is produced from **Q** as shown in Fig. 5.5.

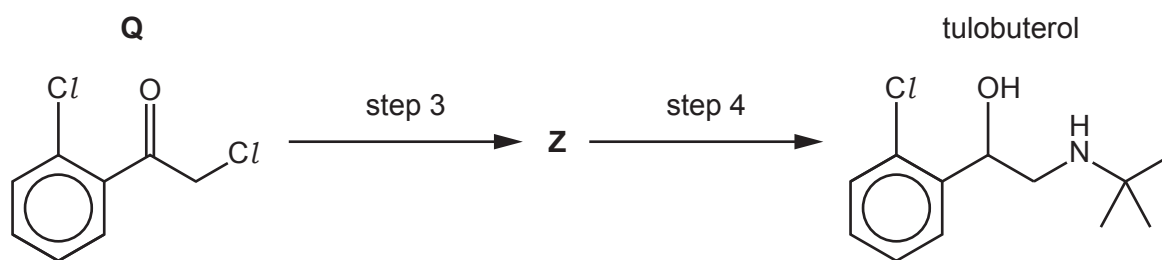


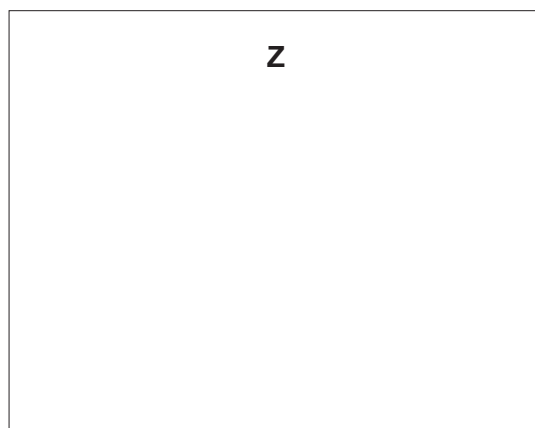
Fig. 5.5

Suggest reagents and conditions for steps 3 and 4.

Draw the structure of **Z** in the box.

step 3

step 4



[3]

(e) The synthesis produces two enantiomers of tulobuterol.

(i) Define enantiomers.

.....

 [1]

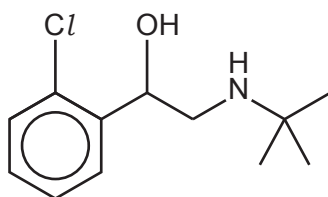
(ii) Suggest **one** disadvantage of producing two enantiomers in this synthesis.

.....
 [1]

(iii) Suggest a method of adapting the synthesis to produce a single enantiomer.

..... [1]

tulobuterol



- (f) (i) Predict the number of peaks that would be seen in the carbon-13 NMR spectrum of tulobuterol.

..... [1]

- (ii) The proton (^1H) NMR spectrum of tulobuterol dissolved in D_2O shows peaks in four different types of proton environment.

The peak for the $-\text{CH}_2\text{N}-$ environment is a doublet in the chemical shift range $\delta = 2.0\text{--}3.0$ ppm.

Give details for each of the other **three** peaks in the proton NMR spectrum of tulobuterol, to include:

- chemical shift
- environment of the proton
- splitting pattern
- number of ^1H atoms responsible.

Table 5.1 gives information about typical chemical shift values.

.....

.....

.....

.....

.....

.....

..... [3]

Table 5.1

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 , $-\text{CH}_2-\text{O}$, $-\text{CH}_2-\text{Cl}$	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

[Total: 22]

- 6 A student uses thin-layer chromatography (TLC) to analyse a mixture containing different metal cations. The student repeats the experiment using different solvents.

Fig. 6.1 shows the chromatogram obtained by the student using water as a solvent.

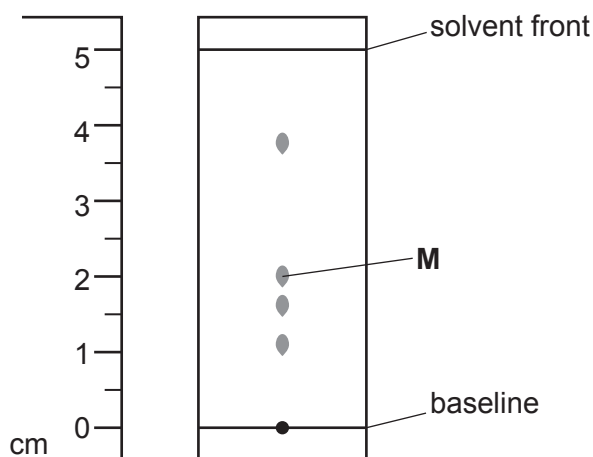


Fig. 6.1

- (a) (i) Suggest a compound that could be used as the stationary phase in this experiment.

..... [1]

- (ii) Table 6.1 shows the R_f values for different metal cations when separated by TLC using water as a solvent.

Table 6.1

cation	R_f value (water)
$\text{Cd}^{2+}(\text{aq})$	0.40
$\text{Co}^{2+}(\text{aq})$	0.77
$\text{Cu}^{2+}(\text{aq})$	0.32
$\text{Fe}^{3+}(\text{aq})$	0.12
$\text{Hg}^{2+}(\text{aq})$	0.23
$\text{Ni}^{2+}(\text{aq})$	0.75

Suggest the identity of the cation that causes the spot at **M** in Fig. 6.1.

Explain your answer.

.....
 [1]

- (b) The student repeats the experiment using butan-1-ol as a solvent.

The metal cations do **not** travel as far up the TLC plate in this experiment.

Suggest why the metal cations do not move as far up the TLC plate with butan-1-ol as a solvent.

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

- (c) The student sprays the TLC plate in Fig. 6.1 with KSCN(aq).

The colour of some of the spots changes, as some of the metal cations undergo a ligand exchange reaction.

Identify the ligands involved in the ligand exchange reaction.

..... exchanges with [1]

- (d) In a third experiment, the pH of the mixture of metal ions is kept constant using a buffer solution.

The student prepares the buffer solution by mixing 20.0 cm^3 of 0.150 mol dm^{-3} KOH(aq) and 50.0 cm^3 of 0.100 mol dm^{-3} $\text{C}_8\text{H}_5\text{O}_4\text{K(aq)}$.

$\text{C}_8\text{H}_5\text{O}_4\text{K}$ is a weak carboxylic acid that has $\text{p}K_{\text{a}} = 5.40$.

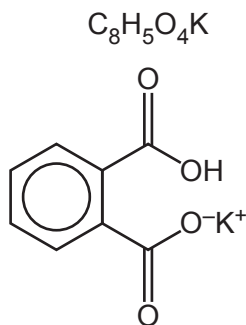


Fig. 6.2

- (i) Complete the equation for the reaction of $\text{C}_8\text{H}_5\text{O}_4\text{K(aq)}$ with KOH(aq) .

$\text{C}_8\text{H}_5\text{O}_4\text{K} + \dots\dots\dots$ [1]

- (ii) Calculate the pH of the buffer solution. Show all your working.

pH = [4]

[Total: 9]

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	$c = 4.18 \text{ kJ kg}^{-1} \text{ K}^{-1}$ ($4.18 \text{ J g}^{-1} \text{ K}^{-1}$)

The Periodic Table of Elements

Group																						
1	2													13	14	15	16	17	18			
														1 H hydrogen 1.0								2 He helium 4.0