

## Cambridge International AS & A Level

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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.

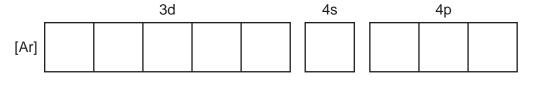


Fig. 1.1

[1]

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

Include state symbols of relevant species.

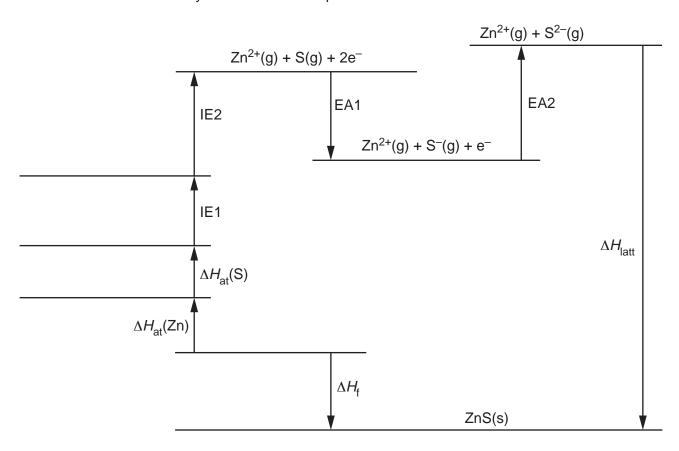


Fig. 1.2

[3]

| (iii)                            | Describe          | e the trend in the firs         | st electron affinity                  | of the Group 16 elen          | nents S to Te.    |       |
|----------------------------------|-------------------|---------------------------------|---------------------------------------|-------------------------------|-------------------|-------|
|                                  | Explain           | your answer.                    |                                       |                               |                   |       |
|                                  |                   |                                 |                                       |                               |                   |       |
| (iv)                             | Explain           | why the lattice ener            | gy, $\Delta H_{\text{latt}}$ , of ZnO | is more exothermic tl         | nan that of ZnS.  |       |
|                                  |                   |                                 |                                       |                               |                   |       |
| <b>(b)</b> Zind                  | c metal ca        | an be obtained in a t           | wo-step process                       | as shown.                     |                   |       |
| step                             | o 1 2Zr           | $nS(s) + 3O_2(g) \rightarrow 2$ | 2ZnO(s) + 2SO <sub>2</sub> (g         | <b>a</b> )                    |                   |       |
| step                             | 2 Zn(             | $D(s) + C(s) \rightarrow Zn(I)$ | ) + CO(g)                             |                               |                   |       |
| The                              | reaction          | s are carried out at 8          | 300°C.                                |                               |                   |       |
| (i)                              | Predict t         | the sign of the entro           | py change, ∆S <sup>o</sup> ,          | of the reaction in <b>ste</b> | p 1.              |       |
|                                  | Explain           | your answer.                    |                                       |                               |                   |       |
|                                  |                   |                                 |                                       |                               |                   | . [1] |
| (ii)                             | Use the           | data in Table 1.1 to            |                                       | the reaction shown in         | n <b>step 2</b> . |       |
|                                  |                   |                                 | Table 1.1                             |                               |                   |       |
| chemical                         |                   | ZnO(s)                          | C(s)                                  | Zn(I)                         | CO(g)             |       |
| S <sup>e</sup> /JK <sup>-1</sup> | mol <sup>-1</sup> | 43.7                            | 5.7                                   | 50.8                          | 197.7             |       |
| S <sup>e</sup> /JK <sup>-1</sup> | mol <sup>-1</sup> | 43.7                            | 5.7                                   | 50.8                          | 197.7             |       |

| $\Delta S^{\Theta} = \dots JK^{-}$ | <sup>1</sup> mol <sup>-1</sup> | [1] |
|------------------------------------|--------------------------------|-----|
|------------------------------------|--------------------------------|-----|

4

| (iii) An equation for the direct reduction of ZnS by carbo | on is sh | nown |
|--|----------|------|
|--|----------|------|

$$2 ZnS(s) + C(s) \rightarrow 2 Zn(l) + CS_2(g) \qquad \Delta H^{\oplus} = +733 \, kJ \, mol^{-1} \\ \Delta S^{\oplus} = +218 \, J \, K^{-1} \, mol^{-1}$$

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

Calculate  $\Delta G^{\Theta}$  for this reaction at 800 °C.

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

- (c) Zn(NO<sub>3</sub>)<sub>2</sub> 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  ${\rm Zn(NO_3)_2}$ .

(ii) The radii of some Group 2 cations and Zn<sup>2+</sup> are shown in Table 1.2.

Table 1.2

| cation    | Mg <sup>2+</sup> | Ca <sup>2+</sup> | Sr <sup>2+</sup> | Ba <sup>2+</sup> | Zn <sup>2+</sup> |
|-----------|------------------|------------------|------------------|------------------|------------------|
| radius/pm | 65               | 99               | 113              | 135              | 74               |

| State and explain the trend in thermal stability of the Group 2 nitrates down the group.           |         |
|--|---------|
|  |         |
|  | <br>[2] |
| Use Table 1.2 to suggest which Group 2 nitrates are <b>less</b> thermally stable the zinc nitrate. |         |
|  | [1]     |

[Total: 16]

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(iii)

2

| Нур | oph   | osphorous aci  | id is an inorganic acid.   |   |                                |
|-----|-------|--|--|---|--------------------------------|
| The | e con | jugate base of   | f hypophosphorous acid i   | s H <sub>2</sub> PO <sub>2</sub> <sup>-</sup> .                           |                                |
| (a) | Giv   | e the formula  | of hypophosphorous acid  |   |                                |
|     |       |  |  |   | [1]                            |
| (b) |       | PO <sub>2</sub> <sup>-</sup> is a stror<br>electrolysis. | ng reducing agent. It can  | be used to reduce metal cations   | without the need               |
|     | equ   | ation 1  | HPO <sub>3</sub> <sup>2-</sup> + 2H <sub>2</sub> O + 2e <sup>-</sup>               | $\implies$ H <sub>2</sub> PO <sub>2</sub> <sup>-</sup> + 3OH <sup>-</sup> | $E^{\oplus} = -1.57  \text{V}$ |
|     | (i)   | In an experim $[H_2PO_2^{-1}] = 0$                       | ment, an alkaline HPO <sub>3</sub> <sup>2-</sup> /<br>0.050 mol dm <sup>-3</sup> . | 'H <sub>2</sub> PO <sub>2</sub> <sup>-</sup> half-cell is constructed wi  | th                             |
|     |       | All other ions   | s are at their standard cor  | centration.   |                                |
|     |       | Predict how  | the value of <i>E</i> of this half-  | cell differs from its $E^{\Theta}$ value.                                 |                                |
|     |       | Explain your   | answer.  |   |                                |
|     |       |  |  |   |                                |
|     |       |  |  |   |                                |
|     |       |  |  |   |                                |
|     |       |  |  |   | [2]                            |
|     | (ii)  | The Cr <sup>3+</sup> /Cr                                 | half-cell has a standard e   | lectrode potential of -0.74 V.  |                                |
|     |       | An electroch half-cell.                                  | nemical cell consists of a   | n alkaline HPO <sub>3</sub> 2-/H <sub>2</sub> PO <sub>2</sub> - half-ce   | ell and a Cr <sup>3+</sup> /Cr |
|     |       | Calculate the  | e standard cell potential, I   | cell·   |                                |
|     |       |  |  |   |                                |
|     |       |  |  | E <sub>cell</sub> =   | V [1]                          |

(iii) Complete the diagram in Fig. 2.1 to show how the standard electrode potential of the Cr³+/Cr half-cell can be measured relative to that of the standard hydrogen electrode.

Identify the chemicals, conditions and relevant pieces of apparatus.

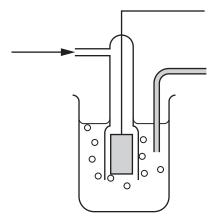


Fig. 2.1

[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.

equation 1 
$$HPO_3^{2-} + 2H_2O + 2e^- \rightleftharpoons H_2PO_2^- + 3OH^-$$

.....[1]

(c)  $H_2PO_2^-(aq)$  reacts with  $OH^-(aq)$ .

$$\mathrm{H_2PO_2^{-1}(aq)} + \mathrm{OH^{-}(aq)} \, \longrightarrow \, \mathrm{HPO_3^{\,2-}(g)} + \mathrm{H_2(g)}$$

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

Table 2.1

| experiment | [H <sub>2</sub> PO <sub>2</sub> <sup>-</sup> (aq)]<br>/moldm <sup>-3</sup> | [OH <sup>-</sup> (aq)]<br>/moldm <sup>-3</sup> | volume of H <sub>2</sub><br>produced in 60 s<br>/cm <sup>3</sup> |
|------------|--|--|--|
| 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<sub>2</sub> was measured under room conditions.

Use the molar volume of gas,  $V_{\rm m}$ , and the data from experiment 1 to calculate the rate of reaction in mol dm<sup>-3</sup> s<sup>-1</sup>.

rate of reaction = .....  $moldm^{-3}s^{-1}$  [1]

(ii) The rate equation was found to be:

rate = 
$$k [H_2PO_2^{-}(aq)] [OH^{-}(aq)]^2$$

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 OH <sup>-</sup> (aq).   |
|-----|------|--|
|     |      | Under these conditions, the rate equation is:  |
|     |      | $rate = k_1 [H_2PO_2^-(aq)]$   |
|     |      | $k_1 = 8.25 \times 10^{-5} \mathrm{s}^{-1}$  |
|     |      | Calculate the value of the half-life, $t_{1\over 2}$ , of the reaction.  |
|     |      |  |
|     |      |  |
|     |      |  |
|     |      |  |
|     |      | $t_{\frac{1}{2}} = \dots $ s [1]   |
|     | (v)  | Describe how an increase in temperature affects the value of the rate constant, $k_1$ .  |
|     |      |  |
|     |      | [1]  |
| (d) |      | tudent suggests that the reaction between $H_2PO_2^{-}(aq)$ and $OH^{-}(aq)$ might happen more ckly in the presence of a heterogeneous catalyst. |
|     | Des  | scribe the mode of action of a heterogeneous catalyst.   |
|     |      |  |
|     |      |  |
|     |      |  |
|     |      | [2]  |
|     |      | [Total: 17]  |
|     |      | [rotali 17]  |
|     |      |  |

3

| Va  | nadiu | m is a transition element in Period 4 of the Periodic Table.                                       |
|-----|-------|--|
| (a) | Def   | ine transition element.  |
|     |       |  |
|     |       | [1]  |
| (b) |       | nadium shows typical chemical properties of transition elements, including variable dation states. |
|     | (i)   | State <b>two</b> other typical chemical properties of transition elements.                         |
|     |       | 1  |
|     |       | 2  |
|     |       | [1]  |
|     | (ii)  | Explain why transition elements have variable oxidation states.                                    |
|     |       |  |
|     |       | [4]  |

(c)  $VO_2^+$  can be reduced to  $V^{2+}$  by  $C_2O_4^{2-}$  in acidic conditions.

equation 2 
$$2VO_2^+ + 3C_2O_4^{2-} + 8H^+ \rightarrow 2V^{2+} + 6CO_2 + 4H_2O$$

(i) In a titration, 25.00 cm<sup>3</sup> of 0.0300 mol dm<sup>-3</sup> VO<sub>2</sub><sup>+</sup>(aq) is added to 10 cm<sup>3</sup> of dilute sulfuric acid.

A solution of  $0.0400\,\mathrm{mol\,dm^{-3}\,C_2O_4^{\ 2-}}$  (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 C <sub>2</sub> O <sub>4</sub> <sup>2-</sup> (aq) added/cm <sup>3</sup> | 28.15 | 28.10 |

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

[2]

(ii) An excess of  $C_2O_4^{2-}$  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  $\mathrm{C_2O_4}^{2-}$  ions.

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

Include the charge of the complex ion.

Use O O to represent a  $C_2O_4^{2-}$  ion.



[2]

(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 <sup>⊕</sup> /V |
|---|--|-------------------|
| 1 | $H_2O_2(aq) + 2H^+(aq) + 2e^- \iff 2H_2O(l)$                               | +1.77             |
| 2 | $VO_2^+(aq) + 2H^+(aq) + e^- \implies VO^{2+}(aq) + H_2O(I)$               | +1.00             |
| 3 | $VO^{2+}(aq) + 2H^{+}(aq) + e^{-} \rightleftharpoons V^{3+}(aq) + H_2O(I)$ | +0.34             |
| 4 | $V^{3+}(aq) + e^- \rightleftharpoons V^{2+}(aq)$                           | -0.26             |

| (i)  | Identify the vanadium species that forms when an excess of $\rm H_2O_2(aq)$ reacts with $\rm V^{2+}(aq)$ under standard conditions. |
|------|---|
|      | Explain your answer with reference to the data in Table 3.2.  |
|      |   |
|      |   |
|      | [1]   |
| (ii) | Concentrated acidified ${\rm H_2O_2}$ can react with ${\rm V^{2+}}$ to form red ${\rm VO_2}^{\rm 3+}$ ions.                         |
|      | $\mathrm{VO_2^{3+}}$ contains vanadium combined with the peroxide anion, $\mathrm{O_2^{2-}}$ .                                      |
|      | Deduce the oxidation state of vanadium in VO <sub>2</sub> <sup>3+</sup> .   |
|      | [1]   |
|      | [Total: 9]  |

4 Ethylamine and phenylamine are primary amines.

| ethylamine                                      | phenylamine     |
|---|-----------------|
| CH <sub>3</sub> CH <sub>2</sub> NH <sub>2</sub> | NH <sub>2</sub> |

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<sub>3</sub>CONH<sub>2</sub>, is reduced by LiA*l*H<sub>4</sub>.
    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, C <sub>6</sub> H <sub>5</sub> NH <sub>2</sub> , can be prepared from benzene in two steps. |  |  |  |  |  |  |  |
|     | Draw the structure of the intermediate compound.   |  |  |  |  |  |  |  |
|     | Suggest reagents and conditions for each step.   |  |  |  |  |  |  |  |
|     |  |  |  |  |  |  |  |  |
|     |  |  |  |  |  |  |  |  |
|     |  |  |  |  |  |  |  |  |
|     |  |  |  |  |  |  |  |  |
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|     |  |  |  |  |  |  |  |  |
|     |  |  |  |  |  |  |  |  |
|     |  |  |  |  |  |  |  |  |
|     | [3]  |  |  |  |  |  |  |  |

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

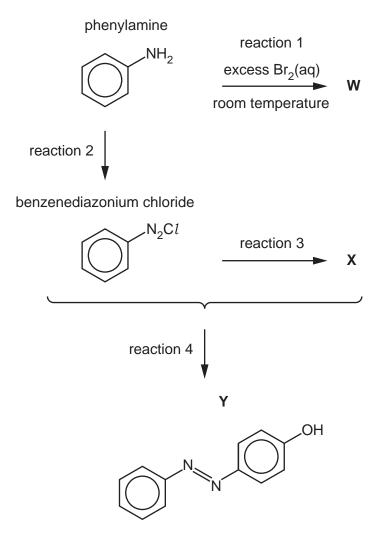


Fig. 4.2

| /i\ | Draw the structure of W  | the organic r    | araduat of  | roootion 1 |   |
|-----|--------------------------|------------------|-------------|------------|---|
| (') | Diaw the structure of wy | , tile organic p | Ji Oddel Oi | reaction i | ٠ |

|       |  | [1] |
|-------|--|-----|
| (ii)  | State the reagents used in reaction 2.   |     |
|       |  | [1] |
|       | nzenediazonium chloride, $\rm C_6H_5N_2C\it{l}$ , and <b>X</b> react together in reaction 4 to form <b>Y</b> , an an anapound. | ZO  |
| (iii) | Name <b>X</b> , 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 <sub>3</sub> NH <sub>2</sub> , is another primary amine. CH <sub>3</sub> NH <sub>2</sub> can act as a monodentate ligand |                                |  |                                  |  |  |  |  |  |
|-----|--|--------------------------------|--|----------------------------------|--|--|--|--|--|
|     | (i)  | Define mo                      | nodentate ligand.  |                                  |  |  |  |  |  |
|     |  |                                |  |                                  |  |  |  |  |  |
|     |  |                                |  |                                  |  |  |  |  |  |
|     |  |                                |  | [2                               |  |  |  |  |  |
|     | (ii)   | Cu <sup>2+</sup> (aq) r        | eacts with $CH_3NH_2$ to form $[Cu(CH_3NH_2)_2(H_2O)_4]^{2+}$ .  |                                  |  |  |  |  |  |
|     |  |                                | ee-dimensional diagrams to show the two geometry, $\left(\mathrm{H_2O}\right)_4\right]^{2+}$ .                       | ometrical isomers o              |  |  |  |  |  |
|     |  |                                |  |                                  |  |  |  |  |  |
|     |  |                                |  |                                  |  |  |  |  |  |
|     |  | (                              | <br>Qu Qu  |                                  |  |  |  |  |  |
|     |  |                                |  |                                  |  |  |  |  |  |
|     |  |                                |  |                                  |  |  |  |  |  |
|     |  |                                |  |                                  |  |  |  |  |  |
|     |  |                                |  | [2]                              |  |  |  |  |  |
|     | (iii)  | State the o                    | oordination number of copper in [Cu(CH <sub>3</sub> NH <sub>2</sub> ) <sub>2</sub> (H <sub>2</sub> O) <sub>4</sub> ] | 2+.                              |  |  |  |  |  |
|     |  |                                |  | [1]                              |  |  |  |  |  |
| f)  |  | ²+(aq) ions<br>illibria 1, 2 a | form tetrahedral complexes with $\mathrm{CH_3NH_2}$ , $\mathrm{OH^-}$ and $\mathrm{nd}$ 3.                           | C <i>l</i> ⁻ ions, as shown ir   |  |  |  |  |  |
|     | equ  | ilibrium 1                     | $Cd^{2+}(aq) + 4CH_3NH_2(aq) \Longrightarrow [Cd(CH_3NH_2)_4]^{2+}(aq)$  | $K_{\rm stab} = 3.3 \times 10^6$ |  |  |  |  |  |
|     | equ  | ilibrium 2                     | $Cd^{2+}(aq) + 4OH^{-}(aq) \Longrightarrow Cd(OH)_4^{2-}(aq)$  | $K_{\rm stab} = 5.0 \times 10^8$ |  |  |  |  |  |
|     | equ  | ilibrium 3                     | $Cd^{2+}(aq) + 4Cl^{-}(aq) \Longrightarrow CdCl_4^{2-}(aq)$  | $K_{\rm stab} = 6.3 \times 10^2$ |  |  |  |  |  |
|     | (i)  | Give the u                     | nits of $K_{ m stab}$ for equilibrium 1.   |                                  |  |  |  |  |  |
|     |  |                                |  | [1]                              |  |  |  |  |  |
|     | (ii)   | Write an e                     | expression for $K_{ m stab}$ for equilibrium 3.  |                                  |  |  |  |  |  |
|     |  | K <sub>stab</sub> =            | =  |                                  |  |  |  |  |  |
|     |  | Stab                           |  |                                  |  |  |  |  |  |

|       |   | 17  |   |  |  |  |  |
|-------|---|---|---|--|--|--|--|
| (iii) | A solution of Cl <sup>-</sup> (equilibrium concent  |   | allowed to reach equilibrium. The           |  |  |  |  |
|       |   | $[Cd^{2+}(aq)] = 0.043 \text{mol dm}^{-3}$<br>$[Cl^{-}(aq)] = 0.072 \text{mol dm}^{-3}$ |   |  |  |  |  |
|       | Use your express equilibrium mixture  |   | concentration of $CdCl_4^{2-}(aq)$ in the   |  |  |  |  |
|       |   |   |   |  |  |  |  |
|       |   |   |   |  |  |  |  |
|       |   | $[CdCl_4^{2-}(aq)] =$   | mol dm <sup>-3</sup> [1                     |  |  |  |  |
| (iv)  | When $\mathrm{CH_3NH_2(aq)}$ is added to $\mathrm{Cd^{2+}(aq)}$ , a mixture of $[\mathrm{Cd}(\mathrm{CH_3NH_2})_4]^{2+}(aq)$ and $[\mathrm{Cd}(\mathrm{OH})_4]^{2-}(aq)$ forms. |   |   |  |  |  |  |
|       | Suggest how the $[Cd(OH)_4]^{2-}$ (aq) is formed.   |   |   |  |  |  |  |
|       |   |   |   |  |  |  |  |
|       |   |   | [1  |  |  |  |  |
| (v)   | Cd <sup>2+</sup> (aq) exists as   | a complex ion, [Cd(H <sub>2</sub> O) <sub>6</sub> ] <sup>2+</sup> (aq)                  |   |  |  |  |  |
|       | Identify the most statick (✓) in each cold  |   | complexes in Table 4.1 by placing <b>on</b> |  |  |  |  |
|       | Explain your answe  | er.   |   |  |  |  |  |
|       |   | Table 4.1   |   |  |  |  |  |
|       | complex   | most stable   | least stable                                |  |  |  |  |
| [C    | d(H <sub>2</sub> O) <sub>6</sub> ] <sup>2+</sup> (aq)   |   |   |  |  |  |  |
| [C    | d(OH) <sub>4</sub> ] <sup>2-</sup> (aq)   |   |   |  |  |  |  |
| [Cd(  | CH <sub>2</sub> NH <sub>2</sub> ),1 <sup>2+</sup> (ag)  |   |   |  |  |  |  |

| complex   | most stable | least stable |
|---|-------------|--------------|
| [Cd(H <sub>2</sub> O) <sub>6</sub> ] <sup>2+</sup> (aq)                 |             |              |
| [Cd(OH) <sub>4</sub> ] <sup>2-</sup> (aq)                               |             |              |
| [Cd(CH <sub>3</sub> NH <sub>2</sub> ) <sub>4</sub> ] <sup>2+</sup> (aq) |             |              |
| $[CdCl_4]^{2-}(aq)$   |             |              |

| explanation | <br> | <br>    |
|-------------|------|---------|
| •           |      |         |
|             |      |         |
|             | <br> | <br>    |
|             |      |         |
|             |      | <br>[2] |
|             | <br> | <br>    |

[Total: 27]

5 Tulobuterol is used in some medicines.

tulobuterol

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  $\sigma$  and  $\pi$  bonds between the carbon atoms.

| <br> | <br> |     |
|------|------|-----|
|      |      |     |
| <br> | <br> |     |
|      |      | เรา |

**(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.

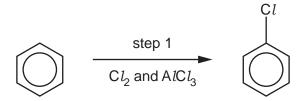


Fig. 5.2

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

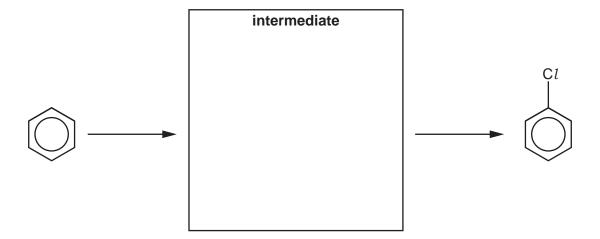


Fig. 5.3

[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**.

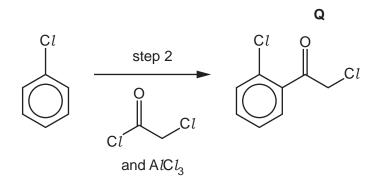


Fig. 5.4

| (i)   | Name the mechanism of the reaction in step 2.  |
|-------|--|
| (ii)  | Draw the structure of an isomer of <b>Q</b> 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.

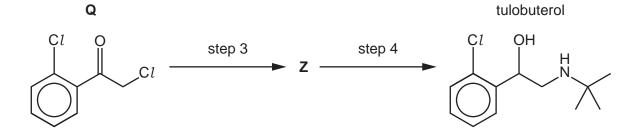


Fig. 5.5

Suggest reagents and conditions for steps 3 and 4.

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

| step 3 | <br> | <br> | <br> | <br> | <br> | <br> |
|--------|------|------|------|------|------|------|
| step 4 | <br> | <br> | <br> | <br> | <br> | <br> |

Z

[3]

**(e)** The synthesis produces two enantiomers of tulobuterol.

| (i)  | Define enantiomers.   |       |
|------|---|-------|
|      |   |       |
|      |   |       |
|      |   | . [1] |
| (ii) | Suggest <b>one</b> disadvantage of producing two enantiomers in this synthesis. |       |
|      |   |       |
|      |   | F4 1  |

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

[Turn over

tulobuterol

| (f) | (i)  | Predict the number of peaks that would be seen in the carbon-13 NMR spectrum of tulobuterol.  |
|-----|------|---|
|     |      | [1]   |
|     | (ii) | The proton ( <sup>1</sup> H) NMR spectrum of tulobuterol dissolved in D <sub>2</sub> O shows peaks in four different types of proton environment. |
|     |      | The peak for the — $CH_2N$ — environment is a doublet in the chemical shift range $\delta = 2.0-3.0  \text{ppm}$ .                                |

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 <sup>1</sup>H 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                             | -CH <sub>3</sub> , -CH <sub>2</sub> -, >CH-                                   | 0.9–1.7                    |
| alkyl next to C=O                  | CH <sub>3</sub> -C=O, -CH <sub>2</sub> -C=O,<br>>CH-C=O                       | 2.2–3.0                    |
| alkyl next to aromatic ring        | CH <sub>3</sub> -Ar, -CH <sub>2</sub> -Ar,<br>>CH-Ar                          | 2.3–3.0                    |
| alkyl next to electronegative atom | $\begin{array}{c} \mathrm{CH_3-O,-CH_2-O,} \\ \mathrm{-CH_2-C} l \end{array}$ | 3.2–4.0                    |
| attached to alkene                 | =C <b>H</b> R   | 4.5–6.0                    |
| attached to aromatic ring          | <b>H</b> –Ar  | 6.0–9.0                    |
| aldehyde                           | <b>H</b> COR  | 9.3–10.5                   |
| alcohol                            | ROH   | 0.5–6.0                    |
| phenol                             | Ar–O <b>H</b>   | 4.5–7.0                    |
| carboxylic acid                    | RCOOH   | 9.0–13.0                   |
| alkyl amine                        | R-N <b>H</b> -  | 1.0-5.0                    |
| aryl amine                         | Ar-N <b>H</b> <sub>2</sub>  | 3.0-6.0                    |
| amide                              | RCON <b>H</b> R   | 5.0-12.0                   |

[Total: 22]

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.

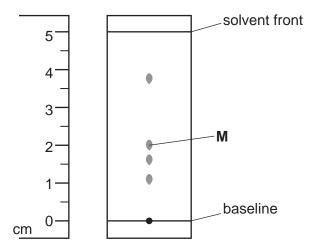


Fig. 6.1

| (a) | (i) | Suggest a compound that could be used as the stationary phase in this experiment. |     |
|-----|-----|---|-----|
|     |     |   | [1] |

(ii) Table 6.1 shows the  $R_{\rm f}$  values for different metal cations when separated by TLC using water as a solvent.

Table 6.1

| cation                | R <sub>f</sub> value (water) |
|-----------------------|------------------------------|
| Cd <sup>2+</sup> (aq) | 0.40                         |
| Co <sup>2+</sup> (aq) | 0.77                         |
| Cu <sup>2+</sup> (aq) | 0.32                         |
| Fe <sup>3+</sup> (aq) | 0.12                         |
| Hg <sup>2+</sup> (aq) | 0.23                         |
| Ni <sup>2+</sup> (aq) | 0.75                         |

Suggest the identity of the cation that causes the spot at  ${\bf M}$  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 <b>not</b> 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 $^{-3}$  C $_8$ H $_5$ O $_4$ K(aq).

 $C_8H_5O_4K$  is a weak carboxylic acid that has  $pK_a = 5.40$ .

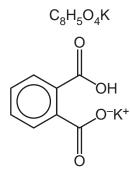


Fig. 6.2

(i) Complete the equation for the reaction of  $C_8H_5O_4K(aq)$  with KOH(aq).

$$C_8H_5O_4K + \dots$$
 [1]

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

[Total: 9]

27

## Important values, constants and standards

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

The Periodic Table of Elements

|       | 18 | 2 | He | helium<br>4.0   | 10            | Ne           | neon                         | 18                                      | Ar | argon<br>39.9      | 36 | 궃      | krypton<br>83.8   | 54               | Xe       | xenon<br>131.3     | 98                 | R           | radon             | 118               | Ö         | ganes son         |                 |   |                  |     |   |                    |
|-------|----|---|----|-----------------|---------------|--------------|------------------------------|---|----|--------------------|----|--------|-------------------|------------------|----------|--------------------|--------------------|-------------|-------------------|-------------------|-----------|-------------------|-----------------|---|------------------|-----|---|--------------------|
|       | 17 |   |    |                 |               |              |                              | +                                       |    | chlorine<br>35.5   |    |        |                   |                  |          |                    |                    |             |                   |                   | <u>R</u>  | eu                |                 |   |                  |     |   |                    |
|       | 16 |   |    |                 | 8             | 0            | oxygen<br>16.0               | 16                                      | S  | sulfur<br>32.1     | 34 | Se     | selenium<br>79.0  | 52               | <u>e</u> | tellurium<br>127.6 | 84                 | Ъо          | polonium          | 116               |           | livermorium —     |                 |   |                  |     |   |                    |
|       | 15 |   |    |                 | 7             | z            | nitrogen<br>14.0             | 15                                      | ۵  | phosphorus<br>31.0 | 33 | As     | arsenic<br>74.9   | 51               | Sp       | antimony<br>121.8  | 83                 | Ξ           | bismuth<br>209.0  | 115               | Mc        | E                 |                 |   |                  |     |   |                    |
|       | 14 |   |    |                 | 9             | ပ            | carbon<br>12.0               | 14                                      | S  | silicon<br>28.1    | 32 | Ge     | germanium<br>72.6 | 20               | S        | tin<br>118.7       | 82                 | Ъ           | lead<br>207.2     | 114               | F1        | flerovium<br>—    |                 |   |                  |     |   |                    |
|       | 13 |   |    |                 | 2             | Ω            | boron<br>10.8                | 13                                      | Αl | aluminium<br>27.0  | 31 | Ga     | gallium<br>69.7   | 49               | In       | indium<br>114.8    | 81                 | 11          | thallium<br>204.4 | 113               | Z         | nihonium<br>—     |                 |   |                  |     |   |                    |
|       |    |   |    |                 |               |              |                              |   |    | 12                 | 30 | Zu     | zinc<br>65.4      | 48               | b        | cadmium<br>112.4   | 80                 | Нg          | mercury<br>200.6  | 112               | S         | copernicium<br>—  |                 |   |                  |     |   |                    |
|       |    |   |    |                 |               |              |                              |   |    | 7                  | 59 | n<br>O | copper<br>63.5    | 47               | Ag       | silver<br>107.9    | 62                 | Au          | gold<br>197.0     | 111               | Rg        | roentgenium<br>-  |                 |   |                  |     |   |                    |
| dn    |    |   |    |                 |               |              |                              |   |    | 10                 | 28 | Z      | nickel<br>58.7    | 46               | Pd       | palladium<br>106.4 | 78                 | ₫           | platinum<br>195.1 | 110               | Ds        | darmstadtium<br>- |                 |   |                  |     |   |                    |
| Group |    |   |    |                 |               |              |                              |   |    | 6                  | 27 | ပိ     | cobalt<br>58.9    | 45               | Rh       | rhodium<br>102.9   | 77                 | ľ           | iridium<br>192.2  | 109               | Ŭ         | meitnerium<br>—   |                 |   |                  |     |   |                    |
|       |    | 1 | I  | hydrogen<br>1.0 |               |              |                              |   |    | œ                  | 26 | Fe     | iron<br>55.8      | 44               | Ru       | ruthenium<br>101.1 | 9/                 | SO          | osmium<br>190.2   | 108               | Hs        | hassium<br>-      |                 |   |                  |     |   |                    |
|       |    |   |    |                 |               |              |                              |   |    | 7                  | 25 | M      | manganese<br>54.9 | 43               | ပ        | technetium<br>-    | 75                 | Re          | rhenium<br>186.2  | 107               | Bh        | bohrium<br>—      |                 |   |                  |     |   |                    |
|       |    |   |    |                 |               |              | pol                          | SS                                      |    |                    | 9  | 24     | ပ်                | chromium<br>52.0 | 42       | Mo                 | molybdenum<br>95.9 | 74          | ≯                 | tungsten<br>183.8 | 106       | Sg                | seaborgium<br>- |   |                  |     |   |                    |
|       |    |   |    | Key             | atomic number | atomic symbo | name<br>relative atomic mass |   |    | 2                  | 23 | >      | vanadium<br>50.9  | 14               | q        | niobium<br>92.9    | 73                 | ā           | tantalum<br>180.9 | 105               | Op        | dubnium<br>-      |                 |   |                  |     |   |                    |
|       |    |   |    |                 |               |              |                              |   |    |                    |    | atc    | <u>a</u>          |                  |          | 4                  | 22                 | F           | titanium<br>47.9  | 40                | Zr        | zirconium<br>91.2 | 72              | 士 | hafnium<br>178.5 | 104 | ¥ | rutherfordium<br>— |
|       |    |   |    |                 |               |              |                              |   |    | ဇ                  | 21 | Sc     | scandium<br>45.0  | 39               | >        | yttrium<br>88.9    | 57–71              | lanthanoids |                   | 89–103            | actinoids |                   |                 |   |                  |     |   |                    |
|       | 2  |   |    |                 | 4             | Be           | beryllium<br>9.0             | 12                                      | Mg | magnesium<br>24.3  | 20 | Ca     | calcium<br>40.1   | 38               | ഗ്       | strontium<br>87.6  | 56                 | Ва          | barium<br>137.3   | 88                | Ra        | radium<br>-       |                 |   |                  |     |   |                    |
|       | _  |   |    |                 | 3             | :-           | lithium<br>6.9               | = ===================================== | Na | sodium<br>23.0     | 19 | メ      | potassium<br>39.1 | 37               | Rb       | rubidium<br>85.5   | 55                 | Cs          | caesium<br>132.9  | 87                | Ļ         | francium<br>-     |                 |   |                  |     |   |                    |

| 71 | P  | lutetium<br>175.0     | 103 | ۲         | lawrencium   | I     |  |
|----|----|-----------------------|-----|-----------|--------------|-------|--|
| 70 | ΥÞ | ytterbium<br>173.1    | 102 | 2         | nobelium     | ı     |  |
| 69 | T  | thulium<br>168.9      | 101 | Md        | mendelevium  | I     |  |
| 89 | ш  | erbium<br>167.3       | 100 | Fm        | fermium      | ı     |  |
| 29 | 웃  | holmium<br>164.9      | 66  | Es        | einsteinium  | 1     |  |
| 99 | ò  | dysprosium<br>162.5   | 86  | ŭ         | californium  | ı     |  |
| 65 | Д  | terbium<br>158.9      | 26  | Ř         | berkelium    | ı     |  |
| 64 | Вd | gadolinium<br>157.3   | 96  | Cm        | curium       | ı     |  |
| 63 | En | europium<br>152.0     | 92  | Am        | americium    | ı     |  |
| 62 | Sm | samarium<br>150.4     | 94  | Pu        | plutonium    | ı     |  |
| 61 | Pm | promethium<br>—       | 93  | Δ         | neptunium    | ı     |  |
| 09 | PZ | neodymium<br>144.4    | 92  | $\supset$ | uranium      | 238.0 |  |
| 59 | Ā  | praseodymium<br>140.9 | 91  | Ра        | protactinium | 231.0 |  |
| 58 | Ce | cerium<br>140.1       | 06  | ┖         | thorium      | 232.0 |  |
| 22 | Га | lanthanum<br>138.9    | 68  | Ac        | actinium     | ı     |  |

lanthanoids

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