

Please write clearly in block capitals.

Centre number

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Candidate number

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Surname *StemUp Model Solution*

Forename(s)

Candidate signature

I declare this is my own work.

INTERNATIONAL A-LEVEL CHEMISTRY (9620)

Unit 3: Inorganic 2 and Physical 2

Time allowed: 1 hour 30 minutes

Materials

For this paper you must have:

- the Periodic Table/Data Sheet, provided as an insert
- a ruler with millimetre measurements
- a scientific calculator, which you are expected to use where appropriate.

Instructions

- Use black ink or black ball-point pen. Use pencil only for drawing.
- Fill in the boxes at the top of this page.
- Answer **all** questions.
- You must answer the questions in the spaces provided. Do not write outside the box around each page or on blank pages.
- All working must be shown.
- If you need extra space for your answer(s), use the lined pages at the end of this book. Write the question number against your answer(s).
- Do all rough work in this book. Cross through any work you do not want to be marked.

Information

- The marks for questions are shown in brackets.
- The maximum mark for this paper is 80.

For Examiner's Use	
Question	Mark
1	
2	
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4	
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7	
8	
TOTAL	



Answer **all** questions in the spaces provided.

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0 1

This question is about sodium fluoride.

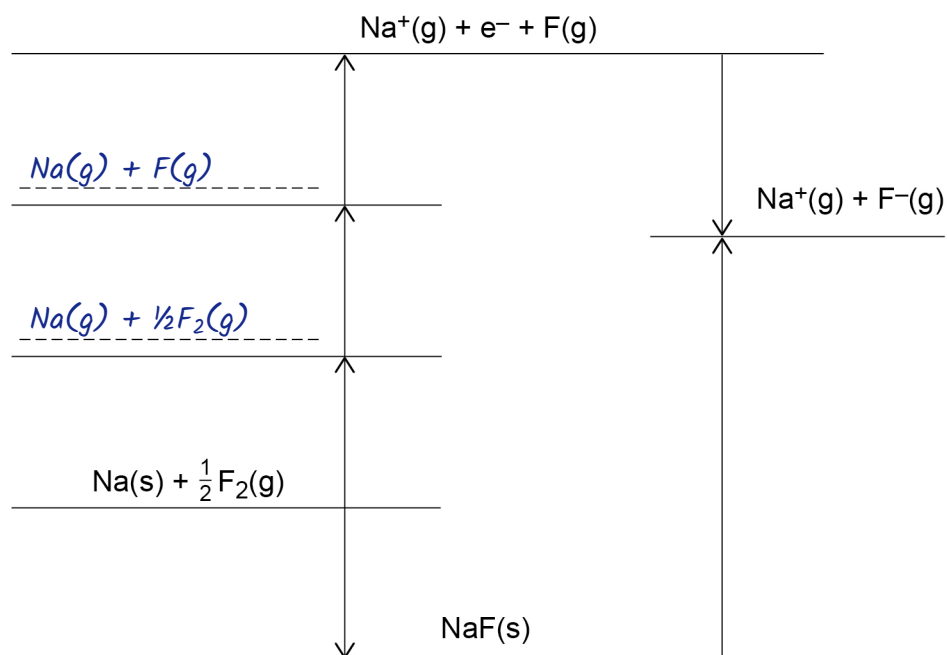
0 1 . 1

Figure 1 shows an incomplete Born–Haber cycle for the formation of sodium fluoride.

Complete **Figure 1** by writing the formulas, including state symbols, of the appropriate species on the two dotted lines.

[2 marks]

Figure 1



0 1 . 2 Table 1 shows some thermodynamic data.

Table 1

	$\Delta H^\ominus / \text{kJ mol}^{-1}$
$\text{Na(s)} \rightarrow \text{Na(g)}$	+109
$\text{Na(g)} \rightarrow \text{Na}^+(\text{g}) + \text{e}^-$	+494
$\text{F}_2(\text{g}) \rightarrow 2\text{F(g)}$	+158
$\text{F(g)} + \text{e}^- \rightarrow \text{F}^-(\text{g})$	-348
$\text{NaF(s)} \rightarrow \text{Na}^+(\text{g}) + \text{F}^-(\text{g})$	+902

Use **Figure 1** and the values given in **Table 1** to calculate a value for the enthalpy of formation of sodium fluoride.

[2 marks]

$$\Delta H_f = \Delta H_a(\text{Na}) + \text{IE}(\text{Na}) + \frac{1}{2}E(\text{F-F}) + \text{EA}(\text{F}) - \Delta H_L$$

$$\Delta H_f = +109 + 494 + \frac{1}{2}(158) + (-348) - 902$$

$$\Delta H_f = -568 \text{ kJ mol}^{-1}$$

Enthalpy of formation -568 kJ mol⁻¹

0 1 . 3 State why the theoretical enthalpy of lattice dissociation for sodium fluoride in a data book is less endothermic than the experimental value calculated using a Born-Haber cycle.

[1 mark]

The theoretical value assumes a perfect ionic model (spherical point charges), but the ions are polarised so NaF has some covalent character.

Turn over ►



0 1 . 4

How does the value for the enthalpy of lattice dissociation for sodium chloride compare with the value for the enthalpy of lattice dissociation for sodium fluoride?

[1 mark]

Tick (✓) **one** box.

The value for sodium chloride is more endothermic.

☐

The values for sodium chloride and for sodium fluoride are the same.

☐

The value for sodium chloride is less endothermic.

☒

0 1 . 5

An equation for the process that happens when sodium fluoride dissolves in water is shown.

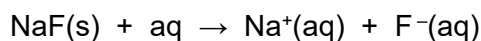


Table 2 shows some thermodynamic data.

Table 2

	Enthalpy change / kJ mol^{-1}
Enthalpy of lattice dissociation for NaF(s)	+902
Enthalpy of hydration for $\text{Na}^+(\text{g})$	−406
Enthalpy of hydration for $\text{F}^-(\text{g})$	−506

Use the data in **Table 2** to calculate the enthalpy of solution for sodium fluoride.

[2 marks]

$$\Delta H_{\text{soln}} = \Delta H_{\text{L}}(\text{dissociation}) + \Delta H_{\text{hyd}}(\text{Na}^+) + \Delta H_{\text{hyd}}(\text{F}^-)$$

$$\Delta H_{\text{soln}} = +902 + (-406) + (-506)$$

$$\Delta H_{\text{soln}} = -10 \text{ kJ mol}^{-1}$$

Enthalpy of solution −10 kJ mol^{-1}



Turn over for the next question

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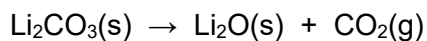
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0 2

Lithium carbonate decomposes as shown.



The Gibbs free-energy change, ΔG , varies with temperature as shown

$$\Delta G = \Delta H - T\Delta S$$

Table 3 shows how the value for ΔG for the decomposition of lithium carbonate varies with temperature.

Table 3

T / K	$\Delta G / \text{kJ mol}^{-1}$
300	177
600	128
900	80
1200	31
1500	-18

0 2 . 1

Use the data in **Table 3** and the grid on page 7 to plot a graph of ΔG (y-axis) against temperature.

[2 marks]

0 2 . 2

Use the gradient of your graph to deduce the entropy change (ΔS) for this reaction.

State the units.

[3 marks]

$$\text{gradient} = (-2 - 161) \div (1400 - 400) = -0.163 \text{ kJ K}^{-1} \text{ mol}^{-1}$$

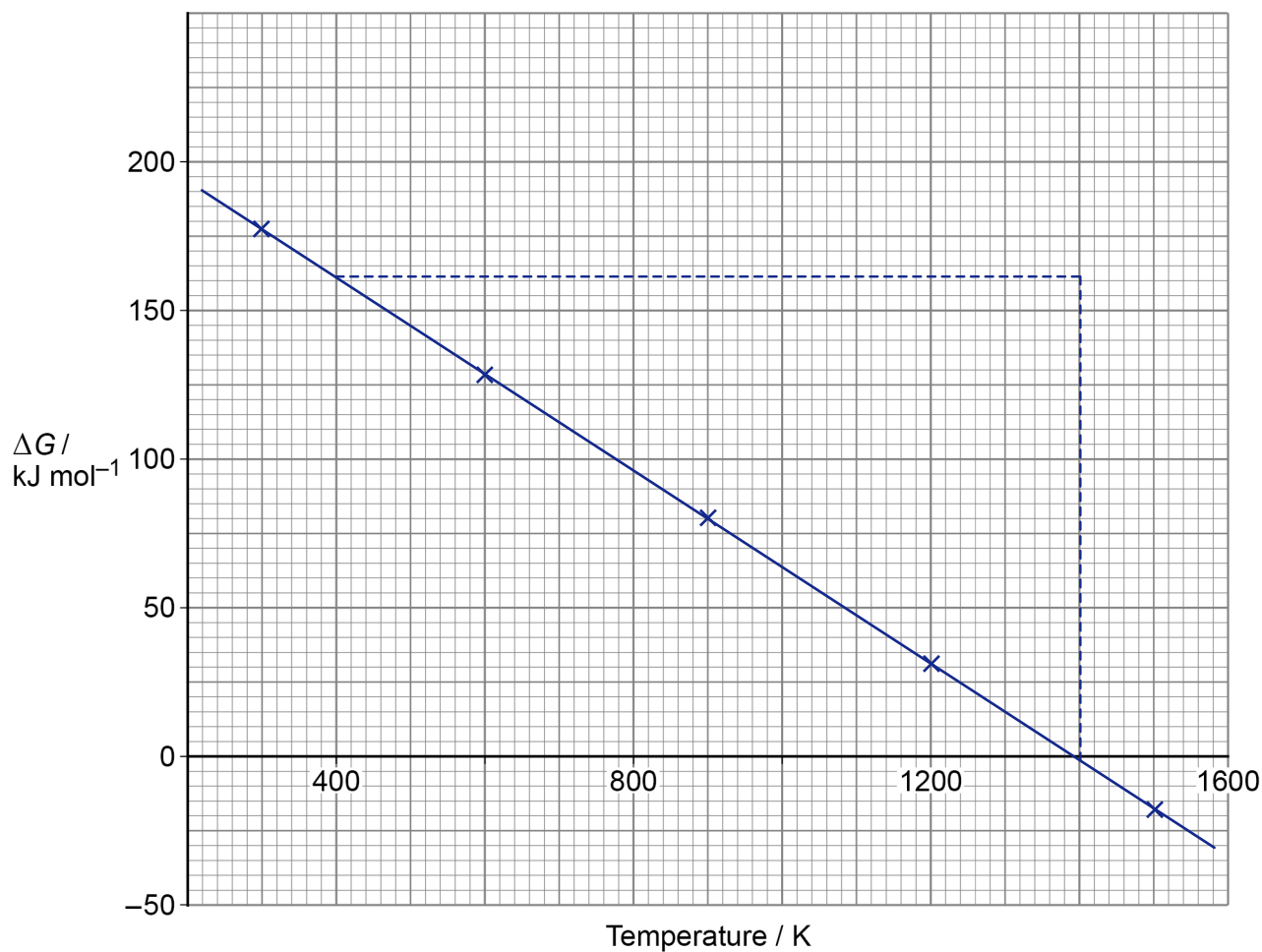
$$\Delta G = \Delta H - T\Delta S, \text{ so gradient} = -\Delta S$$

$$\Delta S = -(-0.163) = +0.163 \text{ kJ K}^{-1} \text{ mol}^{-1}$$

$$\Delta S \quad +0.163$$

$$\text{Units} \quad \text{kJ K}^{-1} \text{ mol}^{-1}$$





0 2 . 3

Use your graph to deduce the temperature, in K, at which the reaction becomes feasible.

[1 mark]

Feasible when $\Delta G \leq 0$, where the line crosses the T axis

1390

K

6

Turn over for the next question

Turn over ►



0 3

This question is about the elements in Period 3 and their compounds.

0 3 . 1

Give **two** observations made when sodium reacts with oxygen.

Write an equation for this reaction.

[3 marks]

Observation 1 a bright yellow (orange) flame

Observation 2 a white solid (powder) is formed

Equation

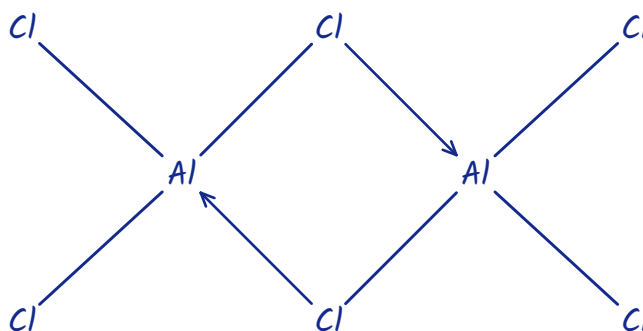


0 3 . 2

Draw the structure of the compound ($M_r = 267.0$) formed when aluminium reacts with chlorine.

Show each covalent bond as a line (—) and each co-ordinate bond as an arrow (→).

[2 marks]



0 3 . 3

Write an equation for the reaction of phosphorus(V) oxide with water.

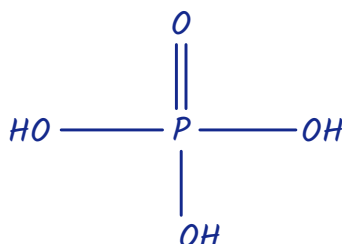
Draw the structure of the phosphorus-containing compound formed.

[2 marks]

Equation

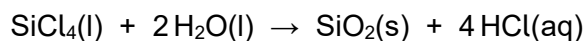


Structure



0 3 . 4

A 0.750 g sample of silicon tetrachloride reacts with an excess of water to form an acidic solution.

Calculate the volume, in cm^3 , of $0.500 \text{ mol dm}^{-3}$ aqueous sodium hydroxide needed to neutralise the acidic solution formed.**[3 marks]**

$$M_r(SiCl_4) = 28.1 + 4(35.5) = 170.1$$

$$n(SiCl_4) = 0.750 \div 170.1 = 4.41 \times 10^{-3} \text{ mol}$$

$$n(HCl) = n(NaOH) = 4 \times 4.41 \times 10^{-3} = 0.0176 \text{ mol}$$

$$\text{volume} = 0.0176 \div 0.500 = 0.0353 \text{ dm}^3$$

$$\text{volume} = 0.0353 \times 1000 = 35.3 \text{ cm}^3$$

Volume 35.3 cm^3

Turn over ►



0 3 . 5

Table 4 shows the melting points of silicon dioxide and silicon tetrachloride.

Table 4

	Melting point / K
Silicon dioxide	1986
Silicon tetrachloride	204

Explain, in terms of structure and bonding, why the melting points of silicon dioxide and silicon tetrachloride are different.

[4 marks]

Silicon dioxide has a giant covalent (macromolecular) structure, in which every atom is held by many strong covalent bonds.

A lot of energy is needed to break these strong covalent bonds, so its melting point is very high.

Silicon tetrachloride has a simple covalent molecular structure.

Only weak van der Waals' forces act between the SiCl_4 molecules, which need little energy to overcome, so its melting point is low.



Turn over for the next question

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0 4

This question is about hydrated ammonium iron(II) sulfate, $(\text{NH}_4)_2\text{SO}_4 \cdot \text{FeSO}_4 \cdot x\text{H}_2\text{O}$ where x is a whole number.

0 4 . 1

A student determines the number of moles of water of crystallisation in hydrated ammonium iron(II) sulfate. The value of x can be calculated using the results from a titration of an acidified solution of ammonium iron(II) sulfate with potassium manganate(VII).

Method

- Dissolve 6.615 g of hydrated ammonium iron(II) sulfate in sulfuric acid and make the solution up to 250 cm^3
- Transfer a 25.0 cm^3 portion of this solution to a conical flask.
- Add $0.0150 \text{ mol dm}^{-3}$ potassium manganate(VII) solution from a burette until the mixture in the conical flask just becomes pink.
- Repeat the titration until concordant results are obtained.

The student calculates the mean titre of the potassium manganate(VII) solution to be 22.50 cm^3

Use the data to calculate the value of x in hydrated ammonium iron(II) sulfate.

M_r of $(\text{NH}_4)_2\text{SO}_4 \cdot \text{FeSO}_4 = 284.0$

[5 marks]



$$n(\text{MnO}_4^-) = 22.50 \times 0.0150 \div 1000 = 3.375 \times 10^{-4} \text{ mol}$$

$$n(\text{Fe}^{2+}) \text{ in } 25.0 \text{ cm}^3 = 5 \times 3.375 \times 10^{-4} = 1.6875 \times 10^{-3} \text{ mol}$$

$$n(\text{Fe}^{2+}) \text{ in } 250 \text{ cm}^3 = 10 \times 1.6875 \times 10^{-3} = 1.6875 \times 10^{-2} \text{ mol}$$

$$M_r \text{ of hydrated salt} = 6.615 \div (1.6875 \times 10^{-2}) = 392.0$$

$$18.0x = 392.0 - 284.0 = 108.0$$

$$x = 108.0 \div 18.0 = 6$$

Value of x 6



0 4 . 2

State why the mixture in the conical flask becomes pink when the end point of the titration is reached.

[1 mark]

All the Fe^{2+} ions have reacted, so the MnO_4^- ions (KMnO_4) are now in excess and their pink colour remains.

0 4 . 3

One reagent can be used to show that a solution of ammonium iron(II) sulfate contains both NH_4^+ ions and Fe^{2+} ions.

Identify this reagent.

Give the observation(s) that would be made with this reagent that shows the presence of each cation.

[3 marks]

Reagent sodium hydroxide solution, NaOH(aq)

Observation to show the presence of NH_4^+ ions pungent gas given off on warming, turns damp red litmus at the mouth of the tube blue

Observation to show the presence of Fe^{2+} ions a green precipitate forms

9

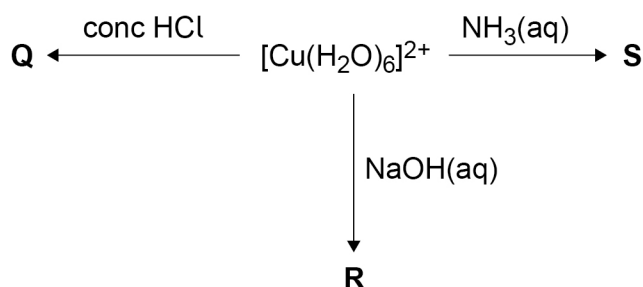
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0 5

Some reactions involving aqueous copper(II) complex ions are shown.



0 5 . 1

State the meaning of the term complex ion.

[1 mark]

A central metal ion surrounded by ligands that are bonded to it by co-ordinate bonds.

0 5 . 2

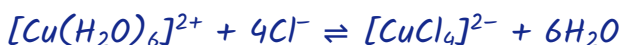
Aqueous copper(II) ions react with an excess of concentrated hydrochloric acid to form a solution containing complex ion **Q**.

Write an equation for the reaction.

Give a reason why there is a colour change in this reaction.

[2 marks]

Equation



Reason *There is a change of ligand (H_2O replaced by Cl^-) and a change in co-ordination number (6 to 4), so the d orbital energy gap changes.*



0 5 . 3

Aqueous copper(II) ions react with aqueous sodium hydroxide to form complex **R**.

State what would be observed.

Write an equation for the reaction.

[2 marks]

Observation a pale blue precipitate forms

Equation



0 5 . 4

Aqueous copper(II) ions react with an excess of aqueous ammonia to form a solution containing complex ion **S**.

State what would be observed when aqueous ammonia is added dropwise, until in excess, to a solution containing aqueous copper(II) ions.

Write an equation for the overall reaction.

[3 marks]

Observations With a few drops of ammonia a pale blue precipitate forms.

In excess ammonia the precipitate dissolves to give a deep blue solution.

Equation



8

Turn over for the next question

Turn over ►



0 6

This question is about transition metal complex ions.

0 6 . 1

An octahedral complex absorbs light with a wavelength (λ) of 535 nm because of d–d electron transitions.

The energy difference (ΔE) between the ground state and the excited state of the d electrons is

$$\Delta E = \frac{hc}{\lambda}$$

Planck constant, $h = 6.63 \times 10^{-34} \text{ J s}$

Speed of light, $c = 3.00 \times 10^8 \text{ m s}^{-1}$

Calculate the energy difference, in J, between the d orbitals.

Assume that the light is absorbed only in d–d electron transitions.

[2 marks]

$$\Delta E = hc \div \lambda = (6.63 \times 10^{-34} \times 3.00 \times 10^8) \div (535 \times 10^{-9})$$

$$\Delta E = 3.72 \times 10^{-19} \text{ J}$$

Energy difference 3.72×10^{-19} J

0 6 . 2

State **two** changes that could be made to a transition metal ion in solution that would influence the ability of the transition metal ion to change from a higher to a lower oxidation state.

[2 marks]

1 change the pH of the solution

2 change the ligand(s) bonded to the metal ion



0 6 . 3

Ethane-1,2-diamine ($\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$) can act as a bidentate ligand. When an excess of ethane-1,2-diamine is added to a solution containing $[\text{Co}(\text{NH}_3)_6]^{2+}$ ions, all the ammonia ligands are replaced.

Write an equation for this reaction.

Explain the chelate effect in terms of the entropy change and the enthalpy change in this reaction.

[5 marks]

Equation



Explanation

Three bidentate ethane-1,2-diamine molecules replace six monodentate

NH_3 ligands, so the number of particles increases from 4 to 7.

This increases the disorder, so the entropy change ΔS is positive.

The same number (six) and type of Co–N co-ordinate bonds are broken and formed, so the enthalpy change ΔH is approximately zero.

Therefore $\Delta G = \Delta H - T\Delta S$ is negative, so the reaction is feasible and the chelate complex is more stable.

Question 6 continues on the next page

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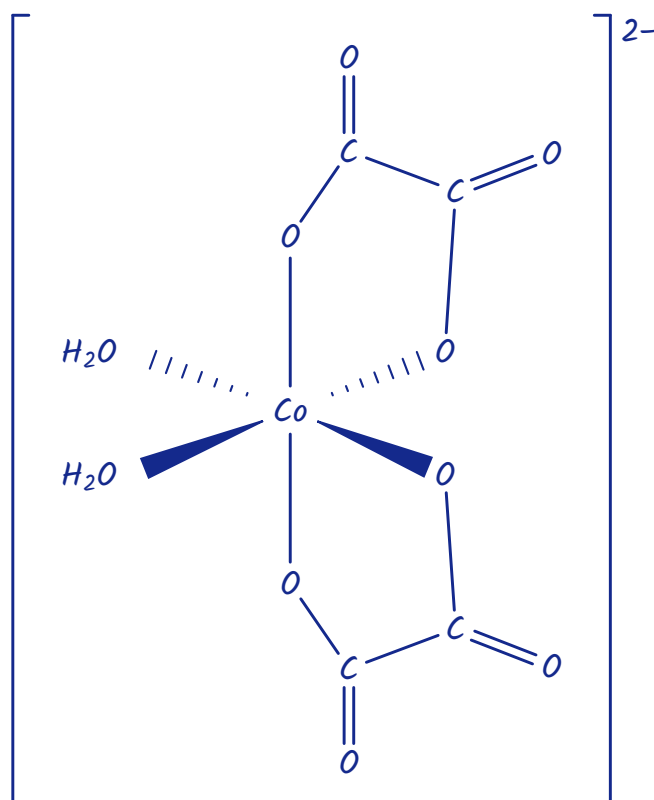


0 6 . 4

The complex ion $[\text{Co}(\text{H}_2\text{O})_2(\text{C}_2\text{O}_4)_2]^{2-}$ exists in three isomeric forms. It exhibits both *cis-trans* and optical isomerism.

Draw the structure of **one** of the optical isomers.

[1 mark]



10



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0 7

This question is about electrochemical cells.

Table 5 shows some standard electrode potential data.

Table 5

Electrode half-equation	$E^\ominus / \text{V}$
$2\text{BrO}_3^-(\text{aq}) + 12\text{H}^+(\text{aq}) + 10\text{e}^- \rightarrow \text{Br}_2(\text{aq}) + 6\text{H}_2\text{O}(\text{l})$	+1.52
$\text{Br}_2(\text{aq}) + 2\text{e}^- \rightarrow 2\text{Br}^-(\text{aq})$	+1.07
$\text{Fe}^{3+}(\text{aq}) + \text{e}^- \rightarrow \text{Fe}^{2+}(\text{aq})$	+0.77
$\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Cu}(\text{s})$	+0.34
$\text{Fe}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Fe}(\text{s})$	-0.44

0 7 . 1

Identify the species in **Table 5** that can oxidise iron to iron(II) ions with no further reaction.

Deduce an overall equation for this reaction.

[2 marks]

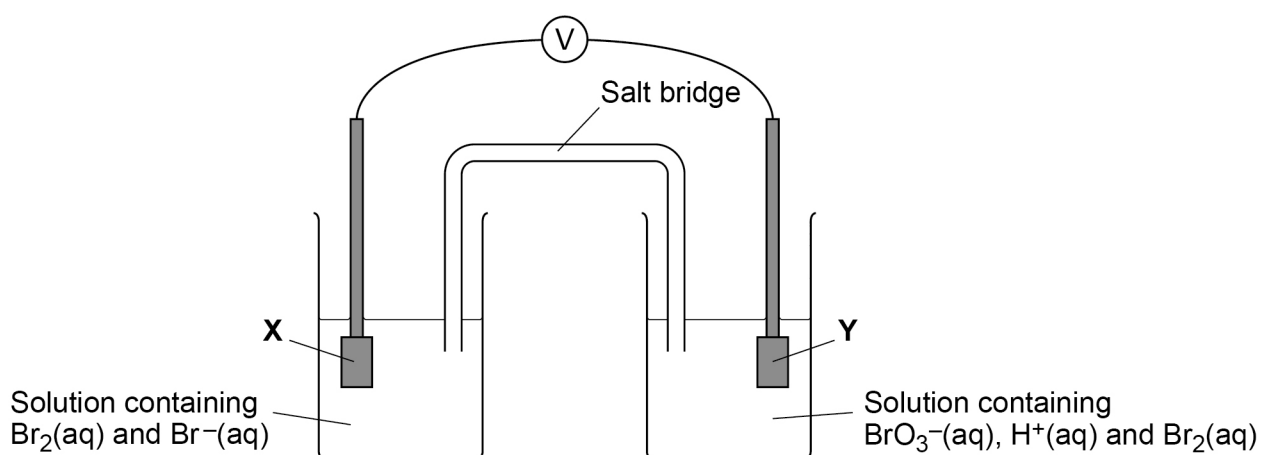
Species $\text{Cu}^{2+}(\text{aq})$

Equation



Figure 2 shows an electrochemical cell.

Figure 2



0 7 . 2 Use data from **Table 5** to calculate the EMF of the cell in **Figure 2**.

Deduce the overall redox equation for the reaction.

[3 marks]

EMF $EMF = 1.52 - 1.07 = +0.45 \text{ V}$

Equation



0 7 . 3 State why a salt bridge is needed.

Identify a salt to use in the salt bridge for this electrochemical cell.

[2 marks]

Why salt bridge is needed *To complete the circuit by allowing ions to flow between the two half-cells.*

Identity of salt *potassium nitrate, KNO₃*

0 7 . 4 Identify a material used for electrodes **X** and **Y** in **Figure 2**.

Give a reason for using this material.

[2 marks]

Material *platinum*

Reason *It is inert, so it does not react with any of the species in either half-cell (and it conducts electricity).*

0 7 . 5 What is the effect on the EMF of the cell if the surface area of both electrodes is doubled?

[1 mark]

Tick (✓) **one** box.

EMF is increased by a factor of 4

☐

EMF is increased by a factor of 2

☐

EMF is unchanged.

☒

10

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0	8
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This question is about pH.

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Define the term pH.

[1 mark]

$$pH = -\log_{10}[H^+]$$

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A 20.0 cm³ sample of 0.115 mol dm⁻³ hydrochloric acid is diluted with deionised water to form 145 cm³ of solution.

Calculate the pH of the solution formed.

Give your answer to 2 decimal places.

[3 marks]

$$n(HCl) = 0.115 \times 20.0 \div 1000 = 2.30 \times 10^{-3} \text{ mol}$$

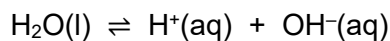
$$[H^+] = 2.30 \times 10^{-3} \div (145 \div 1000) = 0.0159 \text{ mol dm}^{-3}$$

$$pH = -\log(0.0159) = 1.80$$

pH 1.80



0 8 . 3 Water dissociates as shown.



At 45 °C, the ionic product of water (K_w) has a value of $4.02 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$

Calculate the pH of water at 45 °C

Give your answer to 2 decimal places.

[2 marks]

$$\text{In pure water } [\text{H}^+] = [\text{OH}^-], \text{ so } K_w = [\text{H}^+]^2$$

$$[\text{H}^+] = \sqrt{(4.02 \times 10^{-14})} = 2.00 \times 10^{-7} \text{ mol dm}^{-3}$$

$$\text{pH} = -\log(2.00 \times 10^{-7}) = 6.70$$

pH 6.70

0 8 . 4 Calculate the pH of $0.175 \text{ mol dm}^{-3}$ aqueous butanoic acid ($\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$) at 25 °C

For butanoic acid at 25 °C, the acid dissociation constant, $K_a = 1.51 \times 10^{-5} \text{ mol dm}^{-3}$

Give your answer to 2 decimal places.

[3 marks]

$$K_a = [\text{H}^+]^2 \div [\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}]$$

$$[\text{H}^+] = \sqrt{(K_a \times [\text{HA}])} = \sqrt{(1.51 \times 10^{-5} \times 0.175)}$$

$$[\text{H}^+] = 1.63 \times 10^{-3} \text{ mol dm}^{-3}$$

$$\text{pH} = -\log(1.63 \times 10^{-3}) = 2.79$$

pH 2.79

Turn over ►



0 8 . 5

Aqueous sodium hydroxide is added to 25.0 cm³ of aqueous butanoic acid (CH₃CH₂CH₂COOH) in a titration.

Figure 3 shows how the pH of the solution changes.

Figure 3

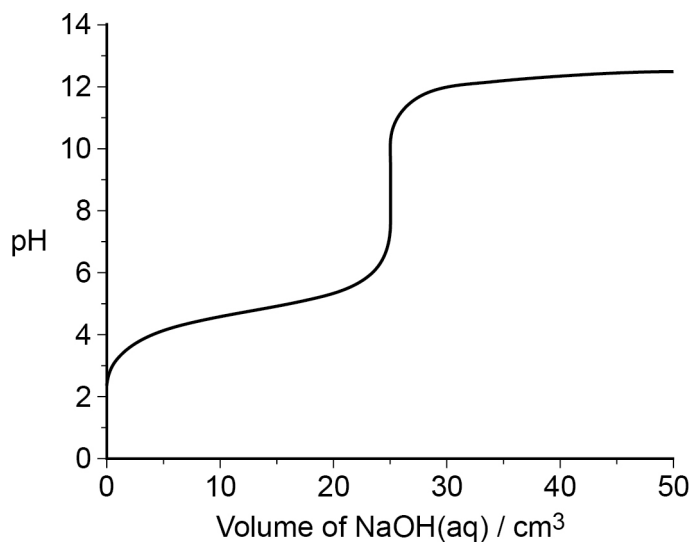


Table 6 shows the pH ranges of some indicators.

Table 6

Indicator	pH range
Thymol blue	1.2–2.8
Methyl orange	3.1–4.4
Thymolphthalein	9.3–10.5
Indigo carmine	11.6–14.0

Use **Table 6** to identify the most suitable indicator for this titration.

[1 mark]

thymolphthalein



0 8 . 6

Butanoic acid ($\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$) and sodium butanoate ($\text{CH}_3\text{CH}_2\text{CH}_2\text{COONa}$) are mixed at 25°C to form a buffer solution with $\text{pH} = 4.50$

Calculate the mass, in grams, of sodium butanoate that should be added to 50.0 cm^3 of 0.175 mol dm^{-3} aqueous butanoic acid to prepare this buffer solution.

For butanoic acid at 25°C , the acid dissociation constant, $K_a = 1.51 \times 10^{-5}\text{ mol dm}^{-3}$

[5 marks]

$$[\text{H}^+] = 10^{-4.50} = 3.16 \times 10^{-5}\text{ mol dm}^{-3}$$

$$K_a = [\text{H}^+][\text{CH}_3\text{CH}_2\text{CH}_2\text{COO}^-] \div [\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}]$$

$$[\text{CH}_3\text{CH}_2\text{CH}_2\text{COO}^-] = K_a[\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}] \div [\text{H}^+]$$

$$= 1.51 \times 10^{-5} \times 0.175 \div (3.16 \times 10^{-5}) = 0.0836\text{ mol dm}^{-3}$$

$$n(\text{sodium butanoate}) = 0.0836 \times 50.0 \div 1000 = 4.18 \times 10^{-3}\text{ mol}$$

$$M_r(\text{CH}_3\text{CH}_2\text{CH}_2\text{COONa}) = 4(12.0) + 7(1.0) + 2(16.0) + 23.0 = 110.0$$

$$\text{mass} = 4.18 \times 10^{-3} \times 110.0 = 0.460\text{ g}$$

Mass of sodium butanoate 0.460 g

15

END OF QUESTIONS



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