

A-level Chemistry (7405/1)

Paper 1: Inorganic and Physical Chemistry

Specimen 2015 v0.5

Session

2 hours

Materials

For this paper you must have:

- the Data Booklet, provided as an insert
- a ruler
- a calculator.

Instructions

- Answer **all** questions.
- Show **all** your working.

Information

- The maximum mark for this paper is 105.

Please write clearly, in block capitals, to allow character computer recognition.

Centre number

Candidate number

Surname STEMUP MODEL SOLUTION

Forename(s)

Candidate signature _____

Answer **all** questions.

- 0 1** . **1** Explain how the electron pair repulsion theory can be used to deduce the shape of, and the bond angle in, PF_3

[6 marks]

Phosphorus is in Group 5 so it has 5 electrons in its outer shell.

Each of the 3 fluorine atoms shares one electron with P, so there are a total of 8 electrons in the outer shell of P.

These form 3 bonding pairs and 1 non-bonding (lone) pair of electrons around P.

Electron pair repulsion theory: electron pairs repel each other and arrange themselves to be as far apart as possible, so 4 pairs give a tetrahedral arrangement.

A lone pair repels more strongly than a bonding pair (lone pair to bond pair repulsion > bond pair to bond pair repulsion).

Therefore the shape of PF_3 is trigonal pyramidal and the bond angle is reduced from 109.5° to about 107° .

0 1 . 2 State the full electron configuration of a cobalt(II) ion.

[1 mark]

$1s^2 2s^2 2p^6 3s^2 3p^6 3d^7$

0 1 . 3 Suggest **one** reason why electron pair repulsion theory **cannot** be used to predict the shape of the $[\text{CoCl}_4]^{2-}$ ion.

[1 mark]

There are too many electrons in the d sub-shell (d orbitals), so the d
electrons do not behave as simple bonding or lone pairs.

0 1 . 4 Predict the shape of, and the bond angle in, the complex rhodium ion $[\text{RhCl}_4]^{2-}$

[2 marks]

Shape Tetrahedral

Bond angle 109.5°

Turn over for the next question

- 0 2 . 1** Explain why the atomic radii of the elements decrease across Period 3 from sodium to chlorine.

[2 marks]

Across the period the number of protons increases, so the nuclear charge increases (shielding stays about the same).

Therefore the attraction between the nucleus and the outer electrons increases, pulling them closer.

- 0 2 . 2** Explain why the melting point of sulfur (S_8) is greater than that of phosphorus (P_4).

[2 marks]

S_8 molecules are bigger than P_4 molecules (larger surface area and larger M_r).

Therefore the van der Waals (London / dispersion) forces between molecules are stronger in sulfur, so more energy is needed to overcome them.

- 0 2 . 3** Explain why sodium oxide forms an alkaline solution when it reacts with water.

[2 marks]

Sodium oxide is ionic and contains O^{2-} ions.

These O^{2-} ions react with water forming OH^- ions:



- 0 2 . 4** Write an ionic equation for the reaction of phosphorus(V) oxide with an excess of sodium hydroxide solution.

[1 mark]



Turn over for the next question

- 3 Fuel cells are an increasingly important energy source for vehicles. Standard electrode potentials are used in understanding some familiar chemical reactions including those in fuel cells.

Table 1 contains some standard electrode potential data.

Table 1

Electrode half-equation	$E^\ominus / \text{V}$
$\text{F}_2 + 2\text{e}^- \longrightarrow 2\text{F}^-$	+2.87
$\text{Cl}_2 + 2\text{e}^- \longrightarrow 2\text{Cl}^-$	+1.36
$\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \longrightarrow 2\text{H}_2\text{O}$	+1.23
$\text{Br}_2 + 2\text{e}^- \longrightarrow 2\text{Br}^-$	+1.07
$\text{I}_2 + 2\text{e}^- \longrightarrow 2\text{I}^-$	+0.54
$\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \longrightarrow 4\text{OH}^-$	+0.40
$\text{SO}_4^{2-} + 4\text{H}^+ + 2\text{e}^- \longrightarrow \text{SO}_2 + 2\text{H}_2\text{O}$	+0.17
$2\text{H}^+ + 2\text{e}^- \longrightarrow \text{H}_2$	0.00
$4\text{H}_2\text{O} + 4\text{e}^- \longrightarrow 4\text{OH}^- + 2\text{H}_2$	-0.83

- 0 3 . 1 A salt bridge was used in a cell to measure electrode potential.

Explain the function of the salt bridge.

[2 marks]

The ions in the ionic substance in the salt bridge move through the salt bridge,

to maintain charge balance in each half-cell and complete the circuit.

- 0 3 . 2 Use data from **Table 1** to deduce the halide ion that is the weakest reducing agent.

[1 mark]

F⁻ (fluoride ion)

- 0 3 . 3** Use data from **Table 1** to justify why sulfate ions should **not** be capable of oxidising bromide ions.

[1 mark]

$E^\ominus(\text{SO}_4^{2-}/\text{SO}_2) = +0.17 \text{ V}$ is less than $E^\ominus(\text{Br}_2/\text{Br}^-) = +1.07 \text{ V}$, so SO_4^{2-} is a weaker oxidising agent than Br_2 and cannot oxidise Br^- .

- 0 3 . 4** Use data from **Table 1** to calculate a value for the EMF of a hydrogen–oxygen fuel cell operating under alkaline conditions.

[1 mark]

$$EMF = E(\text{O}_2/\text{OH}^-) - E(\text{H}_2\text{O}/\text{H}_2) = +0.40 - (-0.83)$$

$$EMF = \underline{\quad 1.23 \quad} \text{ V}$$

- 0 3 . 5** There are two ways to use hydrogen as a fuel for cars. One way is in a fuel cell to power an electric motor, the other is as a fuel in an internal combustion engine.

Suggest the major advantage of using the fuel cell.

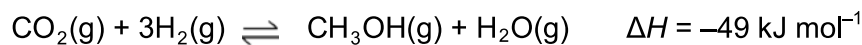
[1 mark]

A fuel cell converts more of the available energy from the hydrogen into kinetic energy of the car; an internal combustion engine wastes more energy as heat.

Turn over for the next question

- 4 Many chemical processes release waste products into the atmosphere. Scientists are developing new solid catalysts to convert more efficiently these emissions into useful products, such as fuels. One example is a catalyst to convert these emissions into methanol. The catalyst is thought to work by breaking a H–H bond.

An equation for this formation of methanol is given below.



Some mean bond enthalpies are shown in **Table 2**.

Table 2

Bond	C=O	C–H	C–O	O–H
Mean bond enthalpy / kJ mol^{-1}	743	412	360	463

- 0 4 . 1 Use the enthalpy change for the reaction and data from **Table 2** to calculate a value for the H–H bond enthalpy.

[3 marks]

$$\text{Bonds broken} = 2(\text{C}=\text{O}) + 3(\text{H}-\text{H}) = 2 \times 743 + 3(\text{H}-\text{H})$$

$$\text{Bonds formed} = 3(\text{C}-\text{H}) + (\text{C}-\text{O}) + 3(\text{O}-\text{H}) = 3 \times 412 + 360 + 3 \times 463$$

$$\Delta H = \text{broken} - \text{formed}$$

$$-49 = [2 \times 743 + 3(\text{H}-\text{H})] - [3 \times 412 + 360 + 3 \times 463]$$

$$3(\text{H}-\text{H}) = -49 - 2 \times 743 + 2985 = 1450$$

$$\text{H}-\text{H} = 1450 / 3 = 483 \text{ kJ mol}^{-1}$$

$$\text{H}-\text{H bond enthalpy} = \underline{483} \text{ kJ mol}^{-1}$$

- 0 4 . 2 A data book value for the H–H bond enthalpy is 436 kJ mol^{-1} .

Suggest **one** reason why this value is different from your answer to Question 4.1.

[1 mark]

Mean bond enthalpies are averages and are not the same as the actual
bond enthalpies in CO_2 , CH_3OH and H_2O .

- 0 4 . 3** Suggest **one** environmental advantage of manufacturing methanol fuel by this reaction.

[1 mark]

The carbon dioxide (produced when methanol is burned) is used up in this reaction, so there is no net increase in CO₂.

- 0 4 . 4** Use Le Chatelier's principle to justify why the reaction is carried out at a high pressure rather than at atmospheric pressure.

[3 marks]

There are 4 mol of gas on the left and only 2 mol of gas on the right.

At high pressure the position of equilibrium moves to the right, to the side with fewer gas moles, to lower (oppose) the pressure.

This increases the yield of methanol.

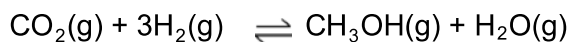
- 0 4 . 5** Suggest why the catalyst used in this process may become less efficient if the carbon dioxide and hydrogen contain impurities.

[1 mark]

Impurities (such as sulfur compounds) adsorb onto and block the active sites, so the catalyst is poisoned.

Question 4 continues on the next page

- 0 4 . 6** In a laboratory experiment to investigate the reaction shown in the equation below, 1.0 mol of carbon dioxide and 3.0 mol of hydrogen were sealed into a container. After the mixture had reached equilibrium, at a pressure of 500 kPa, the yield of methanol was 0.86 mol.



Calculate a value for K_p
 Give your answer to the appropriate number of significant figures.
 Give units with your answer.

[7 marks]



$$\text{initial: } 1.0 \quad 3.0 \quad 0 \quad 0$$

$$\text{eqm: } 0.14 \quad 0.42 \quad 0.86 \quad 0.86$$

$$(1.0 - 0.86 = 0.14; \quad 3.0 - 3 \times 0.86 = 0.42)$$

$$\text{Total moles of gas} = 0.14 + 0.42 + 0.86 + 0.86 = 2.28$$

$$\text{partial pressure} = \text{mole fraction} \times p_{\text{total}}$$

$$p(\text{CO}_2) = 0.14 / 2.28 \times 500 = 30.7 \text{ kPa}$$

$$p(\text{H}_2) = 0.42 / 2.28 \times 500 = 92.1 \text{ kPa}$$

$$p(\text{CH}_3\text{OH}) = p(\text{H}_2\text{O}) = 0.86 / 2.28 \times 500 = 188.6 \text{ kPa}$$

$$K_p = p(\text{CH}_3\text{OH}) \times p(\text{H}_2\text{O}) / [p(\text{CO}_2) \times p(\text{H}_2)^3]$$

$$= 188.6 \times 188.6 / (30.7 \times 92.1^3)$$

$$= 1.483 \times 10^{-3} = 1.5 \times 10^{-3} \text{ (2 s.f.)}$$

$$\text{units: } \text{kPa} \times \text{kPa} / (\text{kPa} \times \text{kPa}^3) = \text{kPa}^{-2}$$

$$K_p = \underline{1.5 \times 10^{-3}} \quad \text{Units} = \underline{\text{kPa}^{-2}}$$

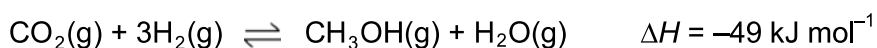
Turn over for the next question

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ANSWER IN THE SPACES PROVIDED**

- 5 **Table 3** contains some entropy data relevant to the reaction used to synthesise methanol from carbon dioxide and hydrogen. The reaction is carried out at a temperature of 250 °C.

Table 3

Substance	CO ₂ (g)	H ₂ (g)	CH ₃ OH(g)	H ₂ O(g)
Entropy (S ^o) / J K ⁻¹ mol ⁻¹	214	131	238	189



- 0 5 . 1 Use this enthalpy change and data from **Table 2** to calculate a value for the free-energy change of the reaction at 250 °C.
Give units with your answer.

[4 marks]

$$\Delta S = \Sigma S(\text{products}) - \Sigma S(\text{reactants})$$

$$= (238 + 189) - (214 + 3 \times 131) = -180 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$T = 250 + 273 = 523 \text{ K}$$

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

$$= -49 - (523 \times (-180) / 1000)$$

$$= -49 + 94.1$$

$$= +45.1 \text{ kJ mol}^{-1}$$

Free-energy change = +45.1 Units = kJ mol⁻¹

0 5 . 2 Calculate a value for the temperature when the reaction becomes feasible.

[2 marks]

When $\Delta G = 0$, $\Delta H = T\Delta S$, so $T = \Delta H / \Delta S$

$T = -49 \times 1000 / -180 = 272 \text{ K}$

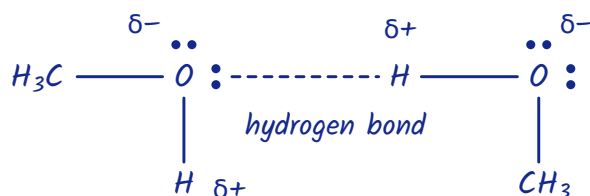
Temperature = 272 K

0 5 . 3 Gaseous methanol from this reaction is liquefied by cooling before storage.

Draw a diagram showing the interaction between two molecules of methanol.
Explain why methanol is easy to liquefy.

[4 marks]

Diagram



($\delta+$ H attracted to a lone pair on O of the other molecule)

Explanation Hydrogen bonding between methanol

molecules is a strong enough force to hold the molecules together in a
liquid, so methanol is easy to liquefy.

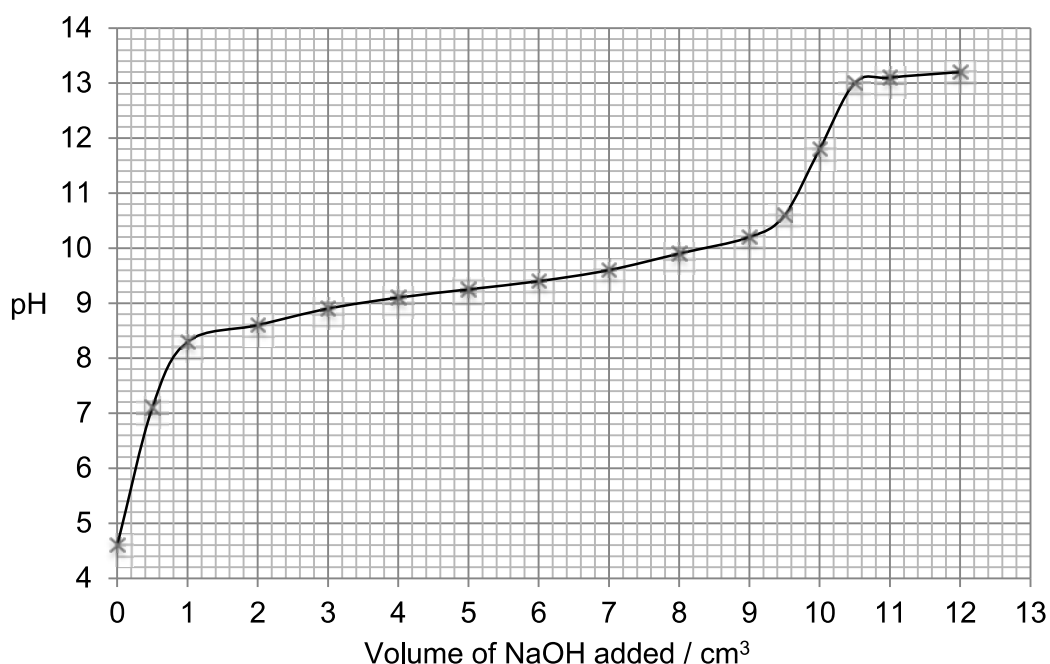
6

Ammonium chloride, when dissolved in water, can act as a weak acid as shown by the following equation.



Figure 1 shows a graph of data obtained by a student when a solution of sodium hydroxide was added to a solution of ammonium chloride. The pH of the reaction mixture was measured initially and after each addition of the sodium hydroxide solution.

Figure 1



0 6 . 1 Suggest a suitable piece of apparatus that could be used to measure out the sodium hydroxide solution.

Explain why this apparatus is more suitable than a pipette for this purpose.

[2 marks]

Apparatus Burette

Explanation it can deliver variable volumes

(a pipette only delivers one fixed volume), so NaOH can be added in
small portions.

- 0 6 . 2** Use information from the curve in **Figure 1** to explain why the end point of this reaction would be difficult to judge accurately using an indicator.

[2 marks]

The change in pH is gradual, not rapid, at the end point (no steep vertical section).

So an indicator would change colour over a range of volumes of sodium hydroxide, not sharply with one drop.

- 0 6 . 3** The pH at the end point of this reaction is 11.8

Use this pH value and the ionic product of water, $K_w = 1.0 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$, to calculate the concentration of hydroxide ions at the end point of the reaction.

[3 marks]

$$[H^+] = 10^{-pH} = 10^{-11.8} = 1.58 \times 10^{-12} \text{ mol dm}^{-3}$$

$$K_w = [H^+][OH^-] \text{ so } [OH^-] = K_w / [H^+]$$

$$[OH^-] = 1.0 \times 10^{-14} / 1.58 \times 10^{-12}$$

$$= 6.33 \times 10^{-3} \text{ mol dm}^{-3}$$

$$\text{Concentration} = \underline{6.33 \times 10^{-3}} \text{ mol dm}^{-3}$$

Question 6 continues on the next page

0 6 . 4 The expression for the acid dissociation constant for aqueous ammonium ions is

$$K_a = \frac{[NH_3][H^+]}{[NH_4^+]}$$

The initial concentration of the ammonium chloride solution was 2.00 mol dm^{-3} .

Use the pH of this solution, before any sodium hydroxide had been added, to calculate a value for K_a

[3 marks]

Initial pH (from graph) = 4.6; at this point $[NH_3] = [H^+]$

so $K_a = [H^+]^2 / [NH_4^+]$

$[H^+] = 10^{-4.6} = 2.51 \times 10^{-5} \text{ mol dm}^{-3}$

$K_a = (2.51 \times 10^{-5})^2 / 2.00 = 3.15 \times 10^{-10} \text{ mol dm}^{-3}$

$K_a = \underline{3.15 \times 10^{-10}} \text{ mol dm}^{-3}$

0 6 . 5 A solution contains equal concentrations of ammonia and ammonium ions.

Use your value of K_a from Question **6.4** to calculate the pH of this solution. Explain your working.

(If you were unable to calculate a value for K_a you may assume that it has the value $4.75 \times 10^{-9} \text{ mol dm}^{-3}$. This is **not** the correct value.)

[2 marks]

When $[NH_3] = [NH_4^+]$, they cancel in the K_a expression,

so $K_a = [H^+]$ and $pH = -\log K_a$

$pH = -\log_{10}(3.15 \times 10^{-10}) = 9.50$

pH= 9.50

Turn over for the next question

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7

Table 4 shows some successive ionisation energy data for atoms of three different elements **X**, **Y** and **Z**.

Elements **X**, **Y** and **Z** are Ca, Sc and V but not in that order.

Table 4

	First	Second	Third	Fourth	Fifth	Sixth
X	648	1370	2870	4600	6280	12 400
Y	590	1150	4940	6480	8120	10 496
Z	632	1240	2390	7110	8870	10 720

For questions **7.1** and **7.2**, only **one** answer per question is allowed.

For each answer, completely fill in the circle alongside the appropriate answer.

CORRECT METHOD



WRONG METHODS



If you want to change your answer you must cross out your original answer as shown.



If you wish to return to an answer previously crossed out, ring the answer you now wish to select as shown.



0 7 . 1

Which element is calcium?

[1 mark]

X



Y



Z



0 7 . 2

Which element is vanadium?

[1 mark]

X



Y



Z



0 7 . 3 Justify your choice of vanadium in Question 7.2

[1 mark]

There is a big jump in ionisation energy after removal of the fifth electron, so X has 5 outer electrons ($4s^2 3d^3$), like V.

0 7 . 4 An acidified solution of NH_4VO_3 reacts with zinc.

Explain how observations from this reaction show that vanadium exists in at least two different oxidation states.

[2 marks]

Different colours of solution are observed as the reaction proceeds (yellow, then blue, green and finally violet).

Each colour is due to vanadium in a different oxidation state (+5, +4, +3, +2).

Question 7 continues on the next page

- 07 . 5** The vanadium in 50.0 cm^3 of a $0.800 \text{ mol dm}^{-3}$ solution of NH_4VO_3 reacts with 506 cm^3 of sulfur(IV) oxide gas measured at 20.0°C and 98.0 kPa .

Use this information to calculate the oxidation state of the vanadium in the solution after the reduction reaction with sulfur(IV) oxide.

Explain your working.

The gas constant $R = 8.31 \text{ J K}^{-1} \text{ mol}^{-1}$.

[6 marks]

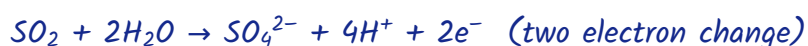
Stage 1: moles

$$n(\text{V}) = 50.0 \times 0.800 / 1000 = 4.00 \times 10^{-2} \text{ mol}$$

$$\begin{aligned} n(\text{SO}_2) &= pV / RT = (98\,000 \times 506 \times 10^{-6}) / (8.31 \times 293) \\ &= 2.04 \times 10^{-2} \text{ mol} \end{aligned}$$

Stage 2: electrons added to NH_4VO_3

SO_2 acts as a reducing agent and is oxidised to sulfate(VI):



$$\text{moles of electrons released} = 2.04 \times 10^{-2} \times 2 = 4.08 \times 10^{-2}$$

Stage 3: conclusion

In NH_4VO_3 vanadium is in oxidation state +5

$4.00 \times 10^{-2} \text{ mol V}$ gains $4.08 \times 10^{-2} \text{ mol electrons}$, so

$$\text{1 mol V gains } 4.08 \times 10^{-2} / 4.00 \times 10^{-2} = 1 \text{ mol electrons}$$

(to the nearest integer), so new oxidation state = $5 - 1 = +4$

Oxidation state = +4

Turn over for the next question

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ANSWER IN THE SPACES PROVIDED**

0 8 . 1 A co-ordinate bond is formed when a transition metal ion reacts with a ligand.

Explain how this co-ordinate bond is formed.

[2 marks]

A lone pair of electrons on the ligand

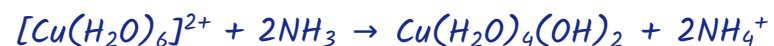
is donated from the ligand to the central metal ion, forming a dative covalent bond.

0 8 . 2 Describe what you would observe when dilute aqueous ammonia is added dropwise, to excess, to an aqueous solution containing copper(II) ions. Write equations for the reactions that occur.

[4 marks]

A pale blue precipitate forms at first,

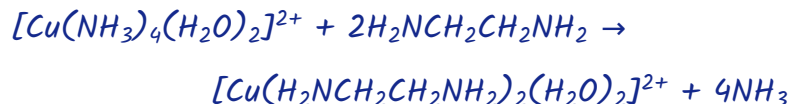
which dissolves in excess ammonia to give a dark (deep) blue solution.



- 0 8 . 3** When the complex ion $[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}$ reacts with 1,2-diaminoethane, the ammonia molecules but not the water molecules are replaced.

Write an equation for this reaction.

[1 mark]



- 0 8 . 4** Suggest why the enthalpy change for the reaction in Question 8.3 is approximately zero.

[2 marks]

The Cu-N bonds formed have similar enthalpy (energy) to the Cu-N bonds broken,

and the same number of bonds are broken and made (4 Cu-N each).

- 0 8 . 5** Explain why the reaction in Question 8.3 occurs despite having an enthalpy change that is approximately zero.

[2 marks]

3 particles form 5 particles, so disorder increases and the entropy change is positive.

Therefore $\Delta G = \Delta H - T\Delta S$ is negative, so the reaction is feasible.

Turn over for the next question

- 9 A 5.00 g sample of potassium chloride was added to 50.0 g of water initially at 20.0 °C. The mixture was stirred and as the potassium chloride dissolved, the temperature of the solution decreased.

- 0 9 . 1 Describe the steps you would take to determine an accurate minimum temperature that is **not** influenced by heat from the surroundings.

[4 marks]

Start a clock when the KCl is added to the water (record the water temperature for a few minutes before mixing).

Record the temperature every minute for about 5 minutes after mixing, stirring.

Plot a graph of temperature against time.

Extrapolate the cooling-curve line back to the time of mixing and determine the minimum temperature there.

- 0 9 . 2 The temperature of the water decreased to 14.6 °C.

Calculate a value, in kJ mol⁻¹, for the enthalpy of solution of potassium chloride.

You should assume that only the 50.0 g of water changes in temperature and that the specific heat capacity of water is 4.18 J K⁻¹ g⁻¹.

Give your answer to the appropriate number of significant figures.

[4 marks]

$$\Delta T = 20.0 - 14.6 = 5.4 \text{ K}$$

$$\text{heat taken in, } q = m \times c \times \Delta T = 50.0 \times 4.18 \times 5.4 = 1128.6 \text{ J}$$

$$\text{moles of KCl} = 5.00 / 74.6 = 0.0670 \text{ mol}$$

$$\Delta H = +1128.6 / 0.0670 = +16\,839 \text{ J mol}^{-1}$$

$$= +16.8 \text{ kJ mol}^{-1} \text{ (endothermic, 3 s.f.)}$$

$$\text{Enthalpy of solution} = \underline{\quad +16.8 \quad} \text{ kJ mol}^{-1}$$

- 0 9 . 3 The enthalpy of solution of calcium chloride is $-82.9 \text{ kJ mol}^{-1}$.
The enthalpies of hydration for calcium ions and chloride ions are -1650 and -364 kJ mol^{-1} , respectively.

Use these values to calculate a value for the lattice enthalpy of dissociation of calcium chloride.

[2 marks]

$$\Delta H_{\text{solution}} = \Delta H_{\text{lattice}} + \Delta H_{\text{hyd}}(\text{Ca}^{2+}) + 2 \times \Delta H_{\text{hyd}}(\text{Cl}^-)$$

$$\Delta H_{\text{lattice}} = \Delta H_{\text{solution}} - \Delta H_{\text{hyd}}(\text{Ca}^{2+}) - 2 \times \Delta H_{\text{hyd}}(\text{Cl}^-)$$

$$= -82.9 - (-1650 + 2 \times -364)$$

$$= +2295 \text{ kJ mol}^{-1}$$

Lattice enthalpy of dissociation = +2295 kJ mol^{-1}

- 0 9 . 4 Explain why your answer to Question 9.3 is different from the lattice enthalpy of dissociation for magnesium chloride.

[2 marks]

The magnesium ion is smaller than the calcium ion (same charge, so
higher charge density).

Therefore it attracts the chloride ions more strongly, giving stronger ionic
bonding and a larger lattice dissociation enthalpy.

10

Table 5 shows observations of changes from some test-tube reactions of aqueous solutions of compounds **Q**, **R** and **S** with five different aqueous reagents. The initial colours of the solutions are not given.

Table 5

	$\text{BaCl}_2 + \text{HCl}$	$\text{AgNO}_3 + \text{HNO}_3$	NaOH	Na_2CO_3	HCl (conc)
Q	no change observed	pale cream precipitate	white precipitate	white precipitate	no change observed
R	no change observed	white precipitate	white precipitate, dissolves in excess of NaOH	white precipitate, bubbles of a gas	no change observed
S	white precipitate	no change observed	brown precipitate	brown precipitate, bubbles of a gas	yellow solution

1 0 . 1 Identify each of compounds **Q**, **R** and **S**.
You are **not** required to explain your answers.

[6 marks]

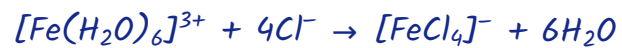
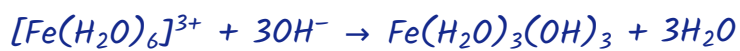
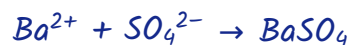
Identity of **Q** calcium bromide (or magnesium bromide), CaBr_2

Identity of **R** aluminium chloride, AlCl_3

Identity of **S** iron(III) sulfate, $\text{Fe}_2(\text{SO}_4)_3$

1 0 . **2** Write ionic equations for each of the positive observations with **S**.

[4 marks]



END OF QUESTIONS

There are no questions printed on this page

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