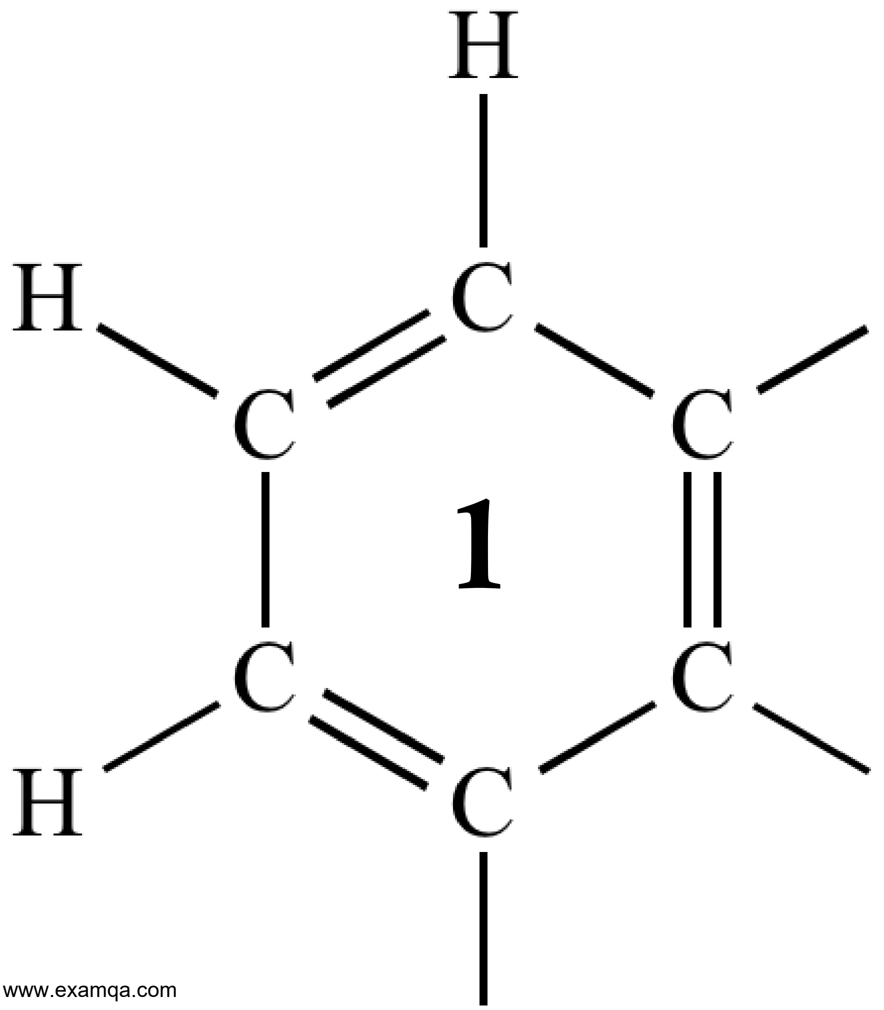
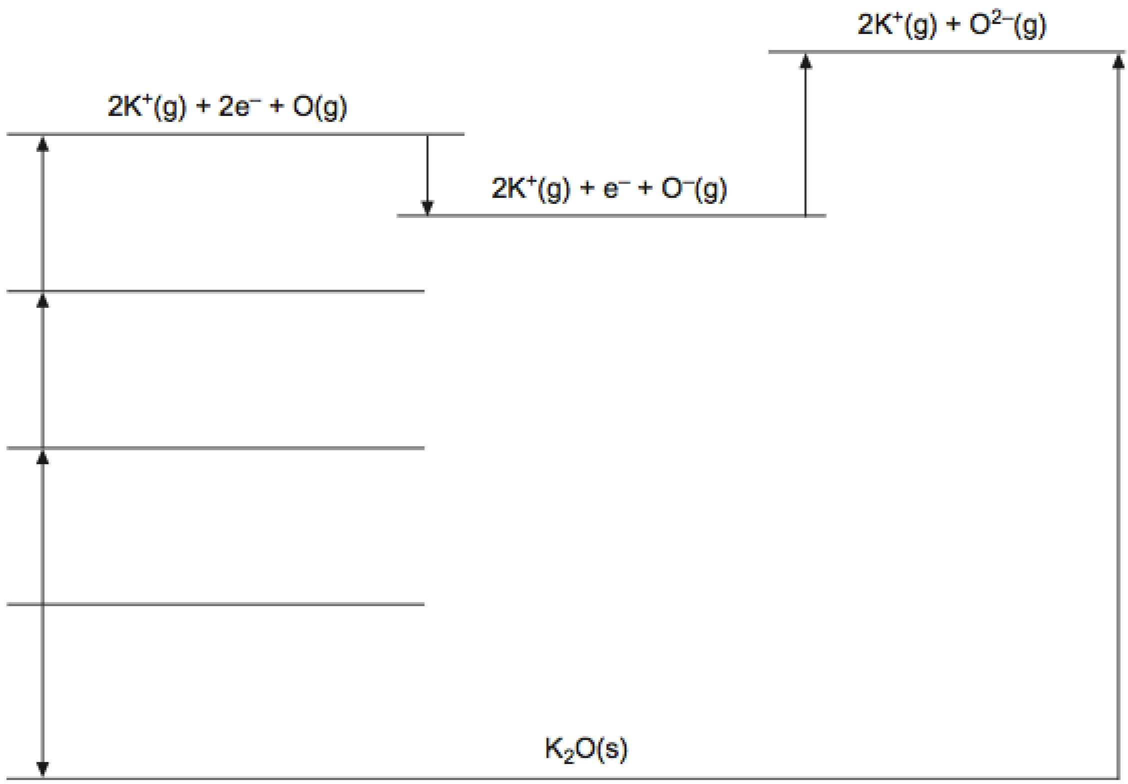
AQA A2 CHEMISTRY

THERMODYNAMICS



1 (a) The diagram is a Born–Haber cycle for potassium oxide, K_2O. The diagram is not to scale and not fully labelled.

(i) Complete the diagram by writing the formulae, including state symbols, of the appropriate species on each of the three blank lines.



(3)

(ii) The table shows some enthalpy data.

Enthalpy change	**$\Delta H^\ominus$/kJ mol^{-1}**
Enthalpy of atomisation of potassium	+90
First ionisation enthalpy of potassium	+418
Enthalpy of atomisation of oxygen	+248
First electron affinity of oxygen	-142
Second electron affinity of oxygen	+844
Enthalpy of formation of potassium oxide	-362

Use the data in the table to calculate the enthalpy of lattice dissociation of potassium oxide, K_2O.

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(3)

(b) Explain why the enthalpy of lattice dissociation of potassium oxide is less endothermic than that of sodium oxide.

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(2)
(Total 8 marks)

2 This question is about magnesium chloride.

(a) Write the equation, including state symbols, for the process corresponding to the enthalpy of solution of magnesium chloride.

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(1)

(b) Use these data to calculate the standard enthalpy of solution of magnesium chloride.

Enthalpy of lattice dissociation of $MgCl_2$	= +2493 kJ mol^{-1}
Enthalpy of hydration of magnesium ions	= –1920 kJ mol^{-1}
Enthalpy of hydration of chloride ions	= –364 kJ mol^{-1}

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(2)

(c) Solubility is the measure of how much of a substance can be dissolved in water to make a saturated solution. A salt solution is saturated when an undissolved solid is in equilibrium with its aqueous ions.

Use your answer to part **(b)** to deduce how the solubility of $MgCl_2$ changes as the temperature is increased.
Explain your answer.

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(3)
(Total 6 marks)

3 In the Contact Process sulfur dioxide reacts with oxygen to form sulfur trioxide as shown in the equation.

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

The table shows some thermodynamic data.

	$\Delta H_f^\ominus$/kJ mol^{-1}	$S^\ominus$/J K^{-1} mol^{-1}
$SO_2(g)$	–297	248
$O_2(g)$	0	205
$SO_3(g)$	–395	256

(a) Use data from the table to calculate the standard enthalpy change for this reaction.

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(2)

(b) Use data from the table to calculate the standard entropy change for this reaction.

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(2)

(c) State what the sign of the entropy change in your answer to part **(b)** indicates about the product of this reaction relative to the reactants.

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(1)

(d) Use your answers to parts **(a)** and **(b)** to calculate a value for the free–energy change for this reaction at 50°C.

(If you were unable to calculate ΔH in part **(a)** assume a value of –250 kJ mol^{-1}.
If you were unable to calculate ΔS in part **(b)** assume a value of –250 J K^{-1} mol^{-1}.
These are not the correct values.)

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(3)

(e) Use your answer to part **(d)** to explain whether the reaction is feasible at 50°C.

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(1)

(f) Vanadium(V) oxide acts as a heterogeneous catalyst in the Contact Process.

(i) State what is meant by the term heterogeneous.

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(1)

(ii) Write **two** equations that show how this catalyst is involved in the Contact Process.

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(2)

(iii) Suggest why the vanadium(V) oxide is used in small pellet form rather than as large lumps.

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(1)

(iv) State why the reactants should be purified before they come into contact with the vanadium(V) oxide.

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(1)

(Total 14 marks)

4 The table below 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.

Substance	CO_2(g)	H_2(g)	CH_3OH(g)	H_2O(g)
Entropy ($S^\ominus$) / J K^{-1} mol^{-1}	214	131	238	189

$$CO_2(g) + 3H_2(g) \rightleftharpoons CH_3OH(g) + H_2O(g) \quad \Delta H = -49 \text{ kJ mol}^{-1}$$

(a) Use this enthalpy change and data from the table to calculate a value for the free-energy change of the reaction at 250 °C.
Give units with your answer.

Free-energy change = ... Units = ...

(4)

(b) Calculate a value for the temperature when the reaction becomes feasible.

Temperature = ... K

(2)

(c) 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.

Diagram

Explanation ....

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(4)
(Total 10 marks)

5 (a) A co-ordinate bond is formed when a transition metal ion reacts with a ligand.

Explain how this co-ordinate bond is formed.

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(2)

(b) 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.

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(4)

(c) When the complex ion $[Cu(NH_3)_4(H_2O)_2]^{2+}$ reacts with 1,2-diaminoethane, the ammonia molecules but not the water molecules are replaced.

Write an equation for this reaction.

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(1)

(d) Suggest why the enthalpy change for the reaction in part **(c)** is approximately zero.

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(2)

(e) Explain why the reaction in part **(c)** occurs despite having an enthalpy change that is approximately zero.

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(2)
(Total 11 marks)

6 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.

(a) Describe the steps you would take to determine an accurate minimum temperature that is **not** influenced by heat from the surroundings.

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(4)

(b) 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.

Enthalpy of solution = ... kJ mol^{-1}

(4)

(c) The enthalpy of solution of calcium chloride is −82.9 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.

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

(2)

(d) Explain why your answer to part **(c)** is different from the lattice enthalpy of dissociation for magnesium chloride.

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(2)
(Total 12 marks)

7 (a) Define the term **electron affinity** for chlorine.

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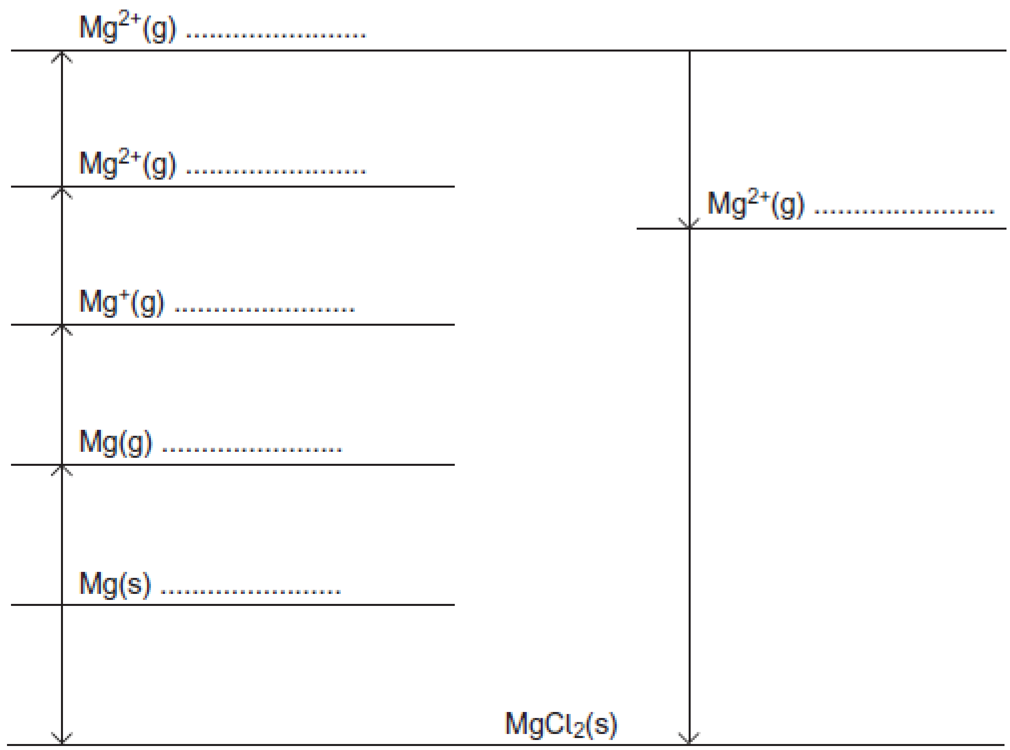
(2)

(b) Complete this Born−Haber cycle for magnesium chloride by giving the missing species on the dotted lines. Include state symbols where appropriate.

The energy levels are **not** drawn to scale.



(6)

(c) **Table 1** contains some enthalpy data.

Table 1

	Enthalpy change / kJ mol^{-1}
Enthalpy of atomisation of magnesium	+150
Enthalpy of atomisation of chlorine	+121
First ionisation energy of magnesium	+736
Second ionisation energy of magnesium	+1450
Enthalpy of formation of magnesium chloride	−642
Lattice enthalpy of formation of magnesium chloride	−2493

Use your Born−Haber cycle from part (b) and data from **Table 1** to calculate a value for the electron affinity of chlorine.

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(3)

(d) **Table 2** contains some more enthalpy data.

Table 2

	Enthalpy change / kJ mol^{-1}
Enthalpy of hydration of Mg^{2+} ions	−1920
Enthalpy of hydration of Na^{+} ions	−406
Enthalpy of hydration of Cl^{-} ions	−364

(i) Explain why there is a difference between the hydration enthalpies of the magnesium and sodium ions.

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(2)

(ii) Use data from **Table 1** and **Table 2** to calculate a value for the enthalpy change when one mole of magnesium chloride dissolves in water.

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(2)

(Total 15 marks)

8 Hydrogen can be manufactured from the reaction of steam with methane.

$$CH_4(g) + H_2O(g) \longrightarrow CO(g) + 3H_2(g)$$

(a) The table contains some enthalpy of formation and entropy data.

Substance	**$\Delta H^\ominus_f$ / kJ mol^{-1}**	**$S^\ominus$ / J K^{-1} mol^{-1}**
$CH_4(g)$	−75	186
$H_2O(g)$	−242	189
$CO(g)$	−111	198
$H_2(g)$	0	131
$CO_2(g)$	−394	214

(i) Use data from the table to calculate the enthalpy change, Δ*H*, for the reaction of steam with methane.

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(3)

(ii) Use data from the table to calculate the entropy change, Δ*S*, for the reaction of steam with methane.

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(2)

(b) Use your values of ΔH and ΔS from parts (a)(i) and (a)(ii) to calculate the temperature above which this reaction is feasible.

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(4)

(c) The temperature used for this manufacture of hydrogen is usually about 1300 K.

Suggest **one** reason, other than changing the position of equilibrium, why this temperature is used rather than the value that you calculated in part (b).

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(1)

(d) Hydrogen can also be obtained by reaction of carbon monoxide with steam.

$CO(g) + H_2O(g) \longrightarrow CO_2(g) + H_2(g)$ $\Delta H = -41\ kJ\ mol^{-1}$, $\Delta S = -42\ J\ K^{-1}\ mol^{-1}$

(i) Explain, using a calculation, why this reaction should **not** occur at 1300 K.

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(3)

(ii) Explain how the conditions for the reaction could be changed to allow this reaction to take place.

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(2)
(Total 15 marks)

9 (a) Write an equation for the process that has an enthalpy change equal to the electron affinity of chlorine.

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(1)

(b) In terms of electrostatic forces, suggest why the electron affinity of fluorine has a negative value.

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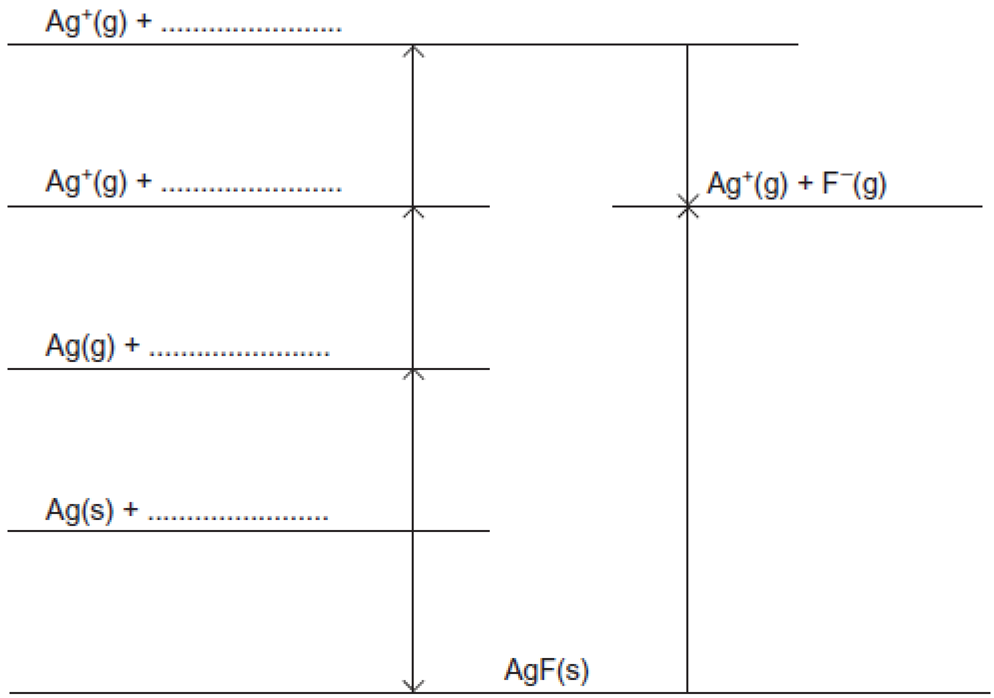
(2)

(c) (i) Complete the Born–Haber cycle for silver fluoride by adding the missing species on the dotted lines.



(3)

(ii) Use the cycle in part (i) and the data in the table to calculate a value, in kJ mol^{-1}, for the bond enthalpy of the fluorine–fluorine bond.

Enthalpy change	**Value / kJ mol^{-1}**
Enthalpy of atomisation for silver	+298
First ionisation energy for silver	+732
Electron affinity for fluorine	–348
Experimental enthalpy of lattice dissociation for silver fluoride	+955
Enthalpy of formation for silver fluoride	–203

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(2)

(d) A theoretical value for enthalpy of lattice dissociation can be calculated using a perfect ionic model.

The theoretical enthalpy of lattice dissociation for silver fluoride is +870 kJ mol^{-1}.

(i) Explain why the theoretical enthalpy of lattice dissociation for silver fluoride is different from the experimental value that can be calculated using a Born–Haber cycle.

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(Extra space) ....

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(2)

(ii) The theoretical enthalpy of lattice dissociation for silver chloride is +770 kJ mol^{-1}.

Explain why this value is less than the value for silver fluoride.

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(Extra space) ....

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(2)
(Total 12 marks)

10 The following table shows some enthalpy change and entropy change data.

	Δ*H* / kJ mol^{-1}	**Δ*S* / J K^{-1} mol^{-1}**
$AgCl(s) \longrightarrow Ag^+(g) + Cl^-(g)$	+905	
$AgCl(s) \longrightarrow Ag^+(aq) + Cl^-(aq)$	+77	+33
$AgF(s) \longrightarrow Ag^+(aq) + F^-(aq)$	–15	to be calculated
$Ag^+(g) \longrightarrow Ag^+(aq)$	–464	

(a) Define the term **enthalpy of hydration** of an ion.

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(2)

(b) Use data from the table to calculate a value for the enthalpy of hydration of the chloride ion.

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(2)

(c) Suggest why hydration of the chloride ion is an exothermic process.

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(2)

(d) Silver chloride is insoluble in water at room temperature.

Use data from the table to calculate the temperature at which the dissolving of silver chloride in water becomes feasible.
Comment on the significance of this temperature value.

Calculation of temperature ....

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Significance of temperature value ....

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(4)

(e) When silver fluoride dissolves in water at 25 °C, the free-energy change is –9 kJ mol^{-1}.

Use this information and data from the table to calculate a value, with units, for the entropy change when silver fluoride dissolves in water at 25 °C.

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(3)
(Total 13 marks)