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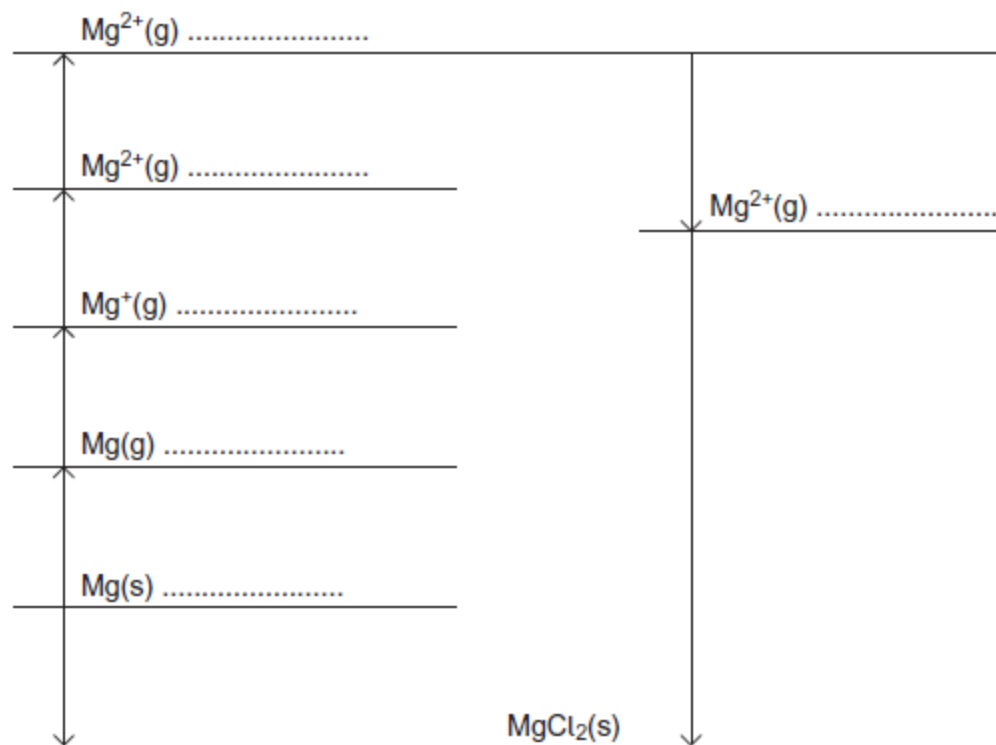
(a) Define the term **electron affinity** for chlorine.

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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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(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)

2

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



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

| Substance | $\Delta H_f^\ominus / \text{kJ mol}^{-1}$ | $S^\ominus / \text{J K}^{-1} \text{mol}^{-1}$ |
|---------------------|---|---|
| CH ₄ (g) | -75 | 186 |
| H ₂ O(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, ΔH , for the reaction of steam with methane.

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

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- (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.



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

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

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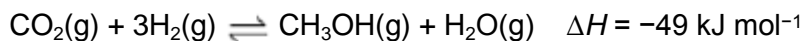
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(2)
(Total 15 marks)

3

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 ₃ OH(g) | H ₂ O(g) |
|--|---------------------|--------------------|-----------------------|---------------------|
| Entropy (S°) / J K ⁻¹ mol ⁻¹ | 214 | 131 | 238 | 189 |



- (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)

4

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

Write an equation for this reaction.

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(1)

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

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- (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)

5

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)

6

(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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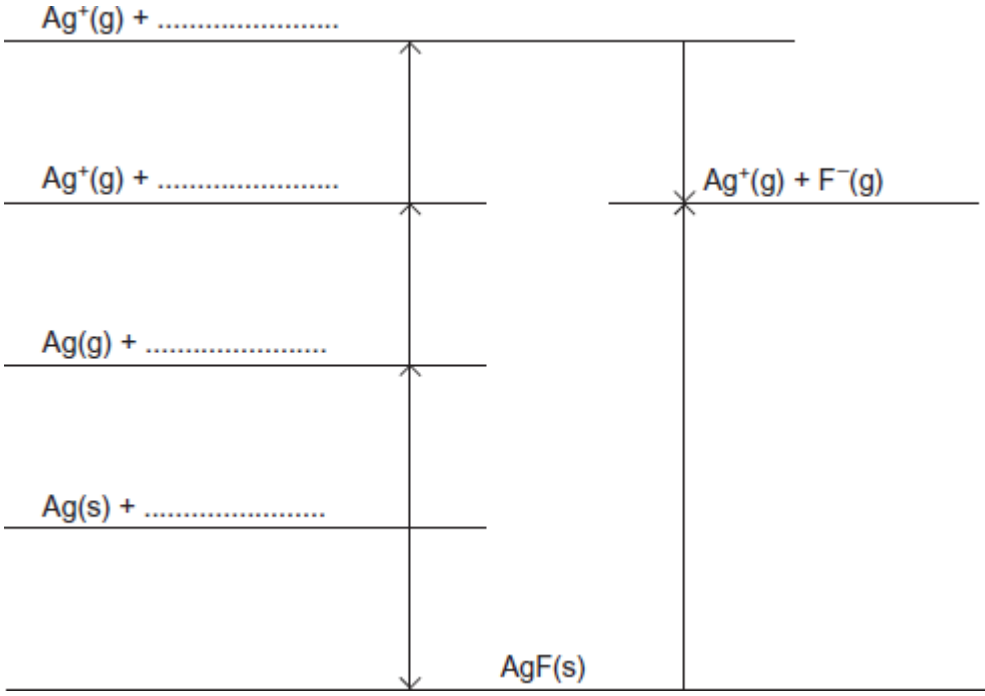
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(2)

(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 $+870 \text{ kJ mol}^{-1}$.

- (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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(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)

(2)
(Total 12 marks)

7

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

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

8

(a) Define the term *lattice enthalpy of dissociation*.

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(2)

(b) Lattice enthalpy can be calculated theoretically using a **perfect ionic model**.

Explain the meaning of the term *perfect ionic model*.

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(1)

(c) Suggest **two** properties of ions that influence the value of a lattice enthalpy calculated using a perfect ionic model.

Property 1

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Property 2

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(2)

(d) Use the data in the table to calculate a value for the lattice enthalpy of dissociation for silver chloride.

| Enthalpy change | Value / kJ mol ⁻¹ |
|---|------------------------------|
| Enthalpy of atomisation for silver | +289 |
| First ionisation energy for silver | +732 |
| Enthalpy of atomisation for chlorine | +121 |
| Electron affinity for chlorine | -364 |
| Enthalpy of formation for silver chloride | -127 |

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(3)

- (e) Predict whether the magnitude of the lattice enthalpy of dissociation that you have calculated in part (d) will be less than, equal to or greater than the value that is obtained from a perfect ionic model. Explain your answer.

Prediction compared with ionic model

Explanation

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(2)
(Total 10 marks)

9

The enthalpy of hydration for the chloride ion is -364 kJ mol^{-1} and that for the bromide ion is -335 kJ mol^{-1} .

- (a) By describing the nature of the attractive forces involved, explain why the value for the enthalpy of hydration for the chloride ion is more negative than that for the bromide ion.

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(3)

- (b) The enthalpy of hydration for the potassium ion is -322 kJ mol^{-1} . The lattice enthalpy of dissociation for potassium bromide is $+670 \text{ kJ mol}^{-1}$.

Calculate the enthalpy of solution for potassium bromide.

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(2)

- (c) The enthalpy of solution for potassium chloride is $+17.2 \text{ kJ mol}^{-1}$.

- (i) Explain why the free-energy change for the dissolving of potassium chloride in water is negative, even though the enthalpy change is positive.

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(Extra space)

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(3)

- (ii) A solution is formed when 5.00 g of potassium chloride are dissolved in 20.0 g of water. The initial temperature of the water is 298 K.

Calculate the final temperature of the solution.

In your calculation, assume that only the 20.0 g of water changes in temperature and that the specific heat capacity of water is $4.18 \text{ J K}^{-1} \text{ g}^{-1}$.

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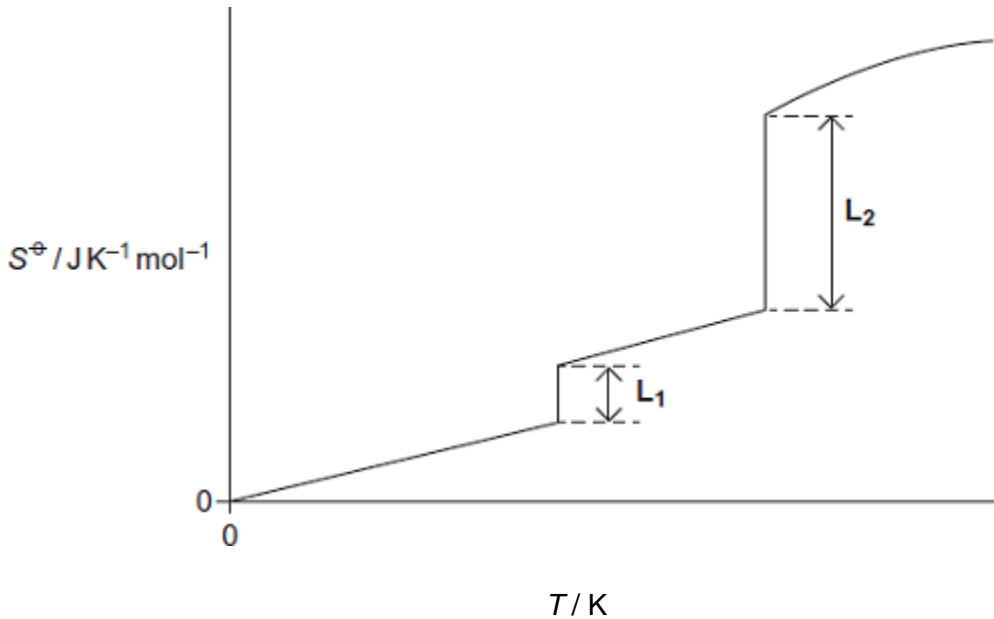
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(5)
(Total 13 marks)

10

(a) **Figure 1** shows how the entropy of a molecular substance **X** varies with temperature.

Figure 1



(i) Explain, in terms of molecules, why the entropy is zero when the temperature is zero Kelvin.

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(Extra space)
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(2)

(ii) Explain, in terms of molecules, why the first part of the graph in **Figure 1** is a line that slopes up from the origin.

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(Extra space)
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(2)

(iii) On **Figure 1**, mark on the appropriate axis the boiling point (T_b) of substance **X**.

(1)

(iv) In terms of the behaviour of molecules, explain why L_2 is longer than L_1 in **Figure 1**.

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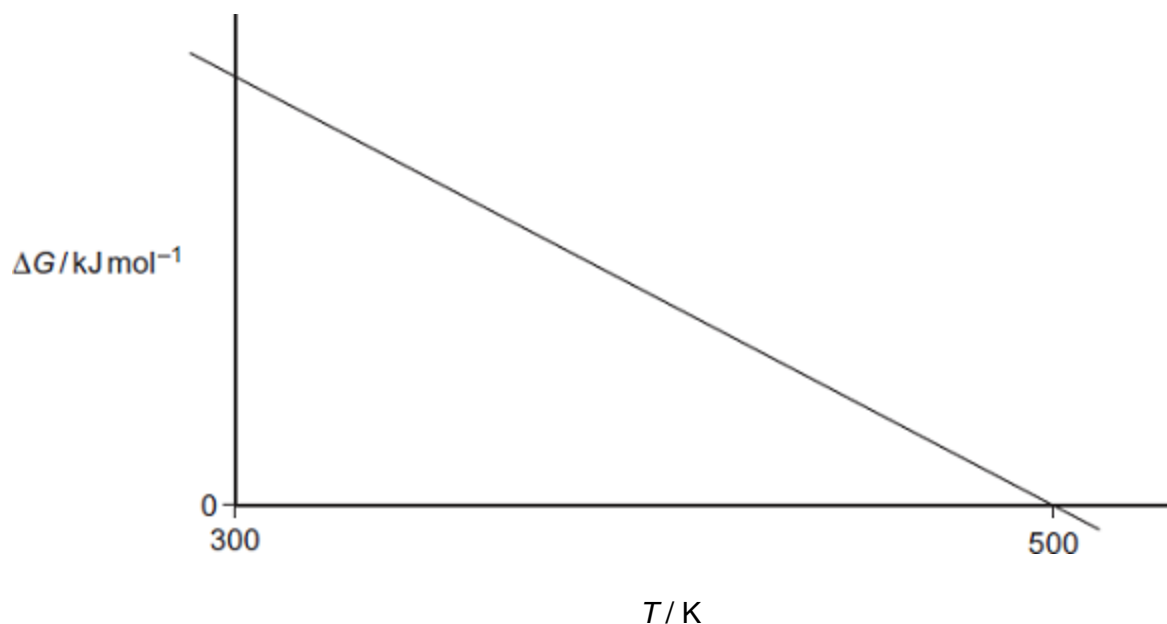
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(2)

- (b) **Figure 2** shows how the free-energy change for a particular gas-phase reaction varies with temperature.

Figure 2



- (i) Explain, with the aid of a thermodynamic equation, why this line obeys the mathematical equation for a straight line, $y = mx + c$.

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- (ii) Explain why the magnitude of ΔG decreases as T increases in this reaction.

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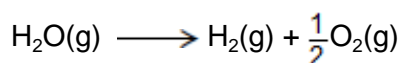
(1)

- (iii) State what you can deduce about the feasibility of this reaction at temperatures lower than 500 K.

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(1)

(c) The following reaction becomes feasible at temperatures above 5440 K.



The entropies of the species involved are shown in the following table.

| | | | |
|--|--------------------------------|------------------------|------------------------|
| | $\text{H}_2\text{O}(\text{g})$ | $\text{H}_2(\text{g})$ | $\text{O}_2(\text{g})$ |
| S / J K⁻¹ mol⁻¹ | 189 | 131 | 205 |

(i) Calculate the entropy change ΔS for this reaction.

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(1)

(ii) Calculate a value, with units, for the enthalpy change for this reaction at 5440 K.

(If you have been unable to answer part (c)(i), you may assume that the value of the entropy change is +98 J K⁻¹ mol⁻¹. This is **not** the correct value.)

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(3)

(Total 15 marks)

11

This table contains some values of lattice dissociation enthalpies.

| | | | |
|--|-----------------|-----------------|--------------|
| Compound | MgCl_2 | CaCl_2 | MgO |
| Lattice dissociation enthalpy / kJ mol⁻¹ | 2493 | 2237 | 3889 |

(a) Write an equation, including state symbols, for the reaction that has an enthalpy change equal to the lattice dissociation enthalpy of magnesium chloride.

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(1)

(b) Explain why the lattice dissociation enthalpy of magnesium chloride is greater than that of calcium chloride.

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(Extra space)
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(2)

(c) Explain why the lattice dissociation enthalpy of magnesium oxide is greater than that of magnesium chloride.

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(2)

(d) When magnesium chloride dissolves in water, the enthalpy of solution is -155 kJ mol^{-1} .
The enthalpy of hydration of chloride ions is -364 kJ mol^{-1} .

Calculate the enthalpy of hydration of magnesium ions.

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(Extra space)
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(3)

- (e) Energy is released when a magnesium ion is hydrated because magnesium ions attract water molecules.

Explain why magnesium ions attract water molecules.
You may use a labelled diagram to illustrate your answer.

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(2)

- (f) Suggest why a value for the enthalpy of solution of magnesium oxide is **not** found in any data books.

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(1)

(Total 11 marks)

12

The feasibility of a physical or a chemical change depends on the balance between the thermodynamic quantities of enthalpy change (ΔH), entropy change (ΔS) and temperature (T).

- (a) Suggest how these quantities can be used to predict whether a change is feasible.

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(2)

- (b) Explain why the evaporation of water is spontaneous even though this change is endothermic.
In your answer, refer to the change in the arrangement of water molecules and the entropy change.

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(4)

(c) This table contains some thermodynamic data for hydrogen, oxygen and water.

| | $S^\ominus / \text{J K}^{-1} \text{mol}^{-1}$ | $\Delta H_f^\ominus / \text{kJ mol}^{-1}$ |
|--------------------------------|---|---|
| $\text{H}_2(\text{g})$ | 131 | 0 |
| $\text{O}_2(\text{g})$ | 205 | 0 |
| $\text{H}_2\text{O}(\text{g})$ | 189 | -242 |
| $\text{H}_2\text{O}(\text{l})$ | 70 | |

(i) Calculate the temperature above which the reaction between hydrogen and oxygen to form gaseous water is **not** feasible.

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(4)

(ii) State what would happen to a sample of gaseous water that was heated to a temperature higher than that of your answer to part (c)(i).
Give a reason for your answer.

What would happen to gaseous water

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Reason

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(2)

- (d) When hydrogen is used as a fuel, more heat energy can be obtained if the gaseous water formed is condensed into liquid water.

Use entropy data from the table in part (c) to calculate the enthalpy change when one mole of gaseous water is condensed at 373 K.

Assume that the free-energy change for this condensation is zero.

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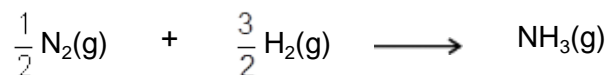
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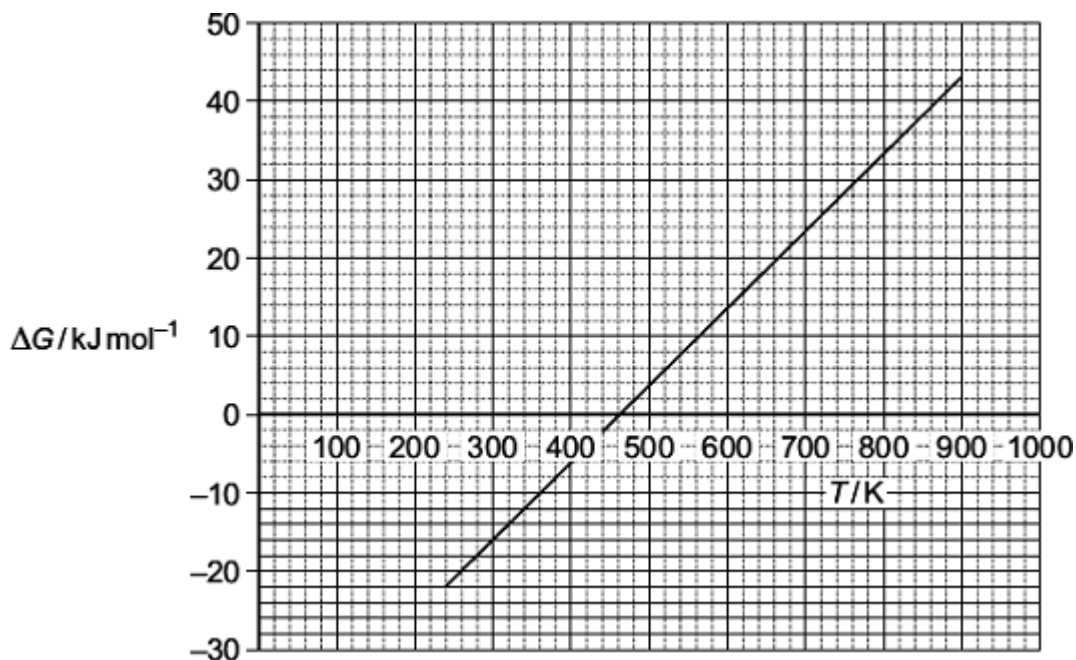
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(Total 15 marks)

13

The following equation shows the formation of ammonia.



The graph shows how the free-energy change for this reaction varies with temperature above 240 K.



- (a) Write an equation to show the relationship between ΔG , ΔH and ΔS .

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(1)

- (b) Use the graph to calculate a value for the slope (gradient) of the line. Give the units of this slope and the symbol for the thermodynamic quantity that this slope represents.

Value of the slope

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Units

Symbol

(3)

- (c) Explain the significance, for this reaction, of temperatures below the temperature value where the line crosses the temperature axis.

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(2)

- (d) The line is not drawn below a temperature of 240 K because its slope (gradient) changes at this point.

Suggest what happens to the ammonia at 240 K that causes the slope of the line to change.

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(1)

(Total 7 marks)

14

Some thermodynamic data for fluorine and chlorine are shown in the table. In the table, X represents the halogen F or Cl.

| | Fluorine | Chlorine |
|--|----------|----------|
| Electronegativity | 4.0 | 3.0 |
| Electron affinity / kJ mol^{-1} | -348 | -364 |
| Enthalpy of atomisation / kJ mol^{-1} | +79 | +121 |
| Enthalpy of hydration of $\text{X}^{-}(\text{g})$ / kJ mol^{-1} | -506 | -364 |

(a) Explain the meaning of the term *electron affinity*.

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(2)

(b) Explain why the electronegativity of fluorine is greater than the electronegativity of chlorine.

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(Extra space)

(2)

(c) Explain why the hydration enthalpy of the fluoride ion is more negative than the hydration enthalpy of the chloride ion.

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(2)

(d) The enthalpy of solution for silver fluoride in water is -20 kJ mol^{-1} .

The hydration enthalpy for silver ions is -464 kJ mol^{-1} .

(i) Use these data and data from the table to calculate a value for the lattice enthalpy of dissociation of silver fluoride.

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(ii) Suggest why the entropy change for dissolving silver fluoride in water has a positive value.

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(iii) Explain why the dissolving of silver fluoride in water is always a spontaneous process.

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(Total 12 marks)

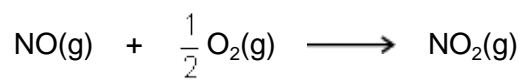
15

The oxides nitrogen monoxide (NO) and nitrogen dioxide (NO₂) both contribute to atmospheric pollution.

The table gives some data for these oxides and for oxygen.

| | S[°] / JK⁻¹ mol⁻¹ | ΔH_f[°] / kJ mol⁻¹ |
|---------------------|---|---|
| O ₂ (g) | 211 | 0 |
| NO(g) | 205 | +90 |
| NO ₂ (g) | 240 | +34 |

Nitrogen monoxide is formed in internal combustion engines. When nitrogen monoxide comes into contact with air, it reacts with oxygen to form nitrogen dioxide.



(a) Calculate the enthalpy change for this reaction.

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(2)

(b) Calculate the entropy change for this reaction.

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(2)

(c) Calculate the temperature below which this reaction is spontaneous.

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(2)

(d) Suggest **one** reason why nitrogen dioxide is **not** formed by this reaction in an internal combustion engine.

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(1)

(e) Write an equation to show how nitrogen monoxide is formed in an internal combustion engine.

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(1)

(f) Use your equation from part (e) to explain why the free-energy change for the reaction to form nitrogen monoxide stays approximately constant at different temperatures.

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(2)

(Total 10 marks)

16

This question is about magnesium oxide. Use data from the table below, where appropriate, to answer the following questions.

| | $\Delta H^\ominus / \text{kJ mol}^{-1}$ |
|--|---|
| First electron affinity of oxygen (formation of $\text{O}^-(\text{g})$ from $\text{O}(\text{g})$) | -142 |
| Second electron affinity of oxygen (formation of $\text{O}^{2-}(\text{g})$ from $\text{O}^-(\text{g})$) | +844 |
| Atomisation enthalpy of oxygen | +248 |

(a) Define the term *enthalpy of lattice dissociation*.

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(3)

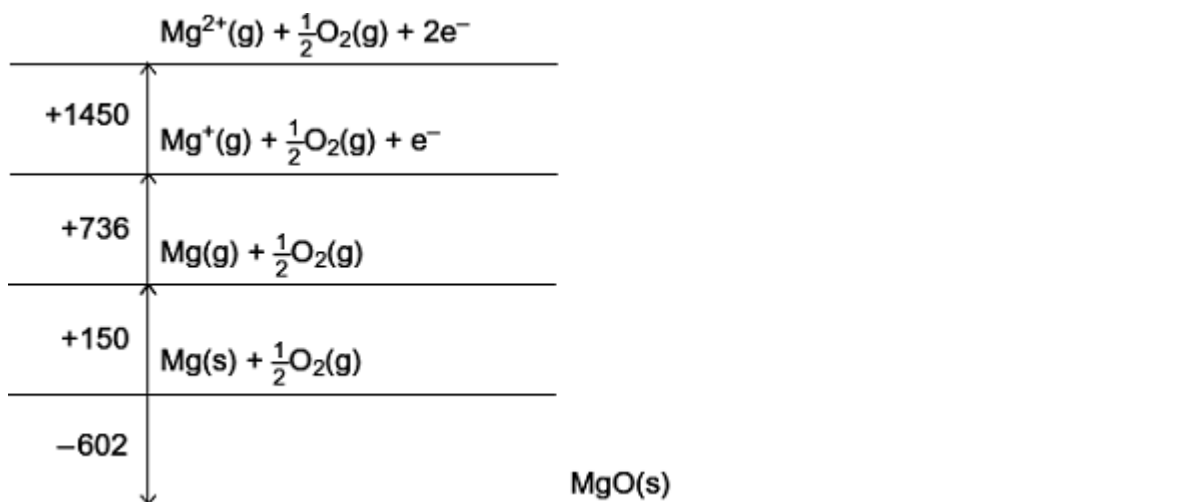
(b) In terms of the forces acting on particles, suggest **one** reason why the first electron affinity of oxygen is an exothermic process.

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(1)

- (c) Complete the Born–Haber cycle for magnesium oxide by drawing the missing energy levels, symbols and arrows.

The standard enthalpy change values are given in kJ mol^{-1} .



(4)

- (d) Use your Born–Haber cycle from part (c) to calculate a value for the enthalpy of lattice dissociation for magnesium oxide.

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(2)

- (e) The standard free-energy change for the formation of magnesium oxide from magnesium and oxygen, $\Delta G_f^\ominus = -570 \text{ kJ mol}^{-1}$.

Suggest **one** reason why a sample of magnesium appears to be stable in air at room temperature, despite this negative value for ΔG_f^\ominus .

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 (Extra space)

(1)

- (f) Use the value of ΔG_f^\ominus given in part (e) and the value of ΔH_f^\ominus from part (c) to calculate a value for the entropy change ΔS^\ominus when one mole of magnesium oxide is formed from magnesium and oxygen at 298 K. Give the units of ΔS^\ominus .

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- (g) In terms of the reactants and products and their physical states, account for the sign of the entropy change that you calculated in part (f).

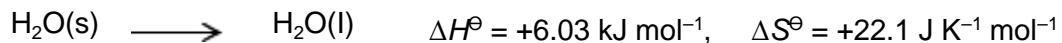
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(2)

(Total 16 marks)

17

Consider the following process that represents the melting of ice.



- (a) State the meaning of the symbol $^\ominus$ in ΔH^\ominus .

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(1)

(b) Use your knowledge of bonding to explain why ΔH^\ominus is positive for this process.

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(2)

(c) Calculate the temperature at which $\Delta G^\ominus = 0$ for this process. Show your working.

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(3)

(d) The freezing of water is an exothermic process. Give **one** reason why the temperature of a sample of water can stay at a constant value of 0 °C when it freezes.

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(1)

(e) Pure ice can look pale blue when illuminated by white light. Suggest an explanation for this observation.

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(2)

(Total 9 marks)

18

Thermodynamics can be used to investigate the changes that occur when substances such as calcium fluoride dissolve in water.

(a) Give the meaning of each of the following terms.

(i) enthalpy of lattice formation for calcium fluoride

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(2)

(ii) enthalpy of hydration for fluoride ions

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(1)

(b) Explain the interactions between water molecules and fluoride ions when the fluoride ions become hydrated.

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(2)

(c) Consider the following data.

| | $\Delta H^\ominus / \text{kJ mol}^{-1}$ |
|--|---|
| Enthalpy of lattice formation for CaF_2 | -2611 |
| Enthalpy of hydration for Ca^{2+} ions | -1650 |
| Enthalpy of hydration for F^- ions | -506 |

Use these data to calculate a value for the enthalpy of solution for CaF_2

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(2)
(Total 7 marks)

19

When potassium nitrate (KNO_3) dissolves in water the value of the enthalpy change $\Delta H = +34.9 \text{ kJ mol}^{-1}$ and the value of the entropy change $\Delta S = +117 \text{ J K}^{-1} \text{ mol}^{-1}$.

(a) Write an equation, including state symbols, for the process that occurs when potassium nitrate dissolves in water.

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(1)

(b) Suggest why the entropy change for this process is positive.

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(1)

(c) Calculate the temperature at which the free-energy change, ΔG , for this process is zero.

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(3)

- (d) (i) Deduce what happens to the value of ΔG when potassium nitrate dissolves in water at a temperature lower than your answer to part (c).

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(1)

- (ii) What does this new value of ΔG suggest about the dissolving of potassium nitrate at this lower temperature?

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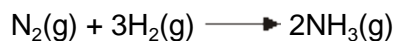
(1)

(Total 7 marks)

20

Ammonia can be manufactured by the Haber Process.

The equation for the reaction that occurs is shown below.



- (a) The table below contains some bond enthalpy data.

| | | | |
|---|----------------------------|---------------------|---------------------|
| | $\text{N} \equiv \text{N}$ | $\text{H}-\text{H}$ | $\text{N}-\text{H}$ |
| Mean bond enthalpy / kJ mol^{-1} | 944 | 436 | 388 |

- (i) Use data from the table to calculate a value for the enthalpy of formation for one mole of ammonia.

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(3)

- (ii) A more accurate value for the enthalpy of formation of ammonia is -46 kJ mol^{-1} .

Suggest why your answer to part (a) (i) is different from this value.

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(1)

- (b) The table below contains some entropy data.

| | | | |
|--|------------------------|------------------------|-------------------------|
| | $\text{H}_2(\text{g})$ | $\text{N}_2(\text{g})$ | $\text{NH}_3(\text{g})$ |
| $S^\ominus / \text{J K}^{-1} \text{ mol}^{-1}$ | 131 | 192 | 193 |

Use these data to calculate a value for the entropy change, with units, for the formation of one mole of ammonia from its elements.

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(3)

- (c) The synthesis of ammonia is usually carried out at about 800 K.

- (i) Use the ΔH value of -46 kJ mol^{-1} and your answer from part (b) to calculate a value for ΔG , with units, for the synthesis at this temperature.

(If you have been unable to obtain an answer to part (b), you may assume that the entropy change is $-112 \text{ J K}^{-1} \text{ mol}^{-1}$. This is not the correct answer.)

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(3)

- (ii) Use the value of ΔG that you have obtained to comment on the feasibility of the reaction at 800 K.

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(1)
(Total 11 marks)

21

Comparison of lattice enthalpies from Born-Haber cycles with lattice enthalpies from calculations based on a perfect ionic model are used to provide information about bonding in crystals.

- (a) Define the terms *enthalpy of atomisation* and *lattice dissociation enthalpy*.

Enthalpy of atomisation

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.....

Lattice dissociation enthalpy

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.....

(4)

- (b) Use the following data to calculate a value for the lattice dissociation enthalpy of sodium chloride.

| | $\Delta H^\ominus / \text{kJ mol}^{-1}$ |
|---|---|
| Na(s) \longrightarrow Na(g) | +109 |
| Na(g) \longrightarrow Na ⁺ (g) + e ⁻ | +494 |
| Cl ₂ (g) \longrightarrow 2Cl(g) | +242 |
| Cl(g) + e ⁻ \longrightarrow Cl ⁻ (g) | -364 |
| Na(s) + $\frac{1}{2}$ Cl ₂ (g) \longrightarrow NaCl(s) | -411 |

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(3)

(c) Consider the following lattice dissociation enthalpy (ΔH_{L}^{\ominus}) data.

| | NaBr | AgBr |
|--|------|------|
| $\Delta H_{L}^{\ominus}(\text{experimental})/\text{kJ mol}^{-1}$ | +733 | +890 |
| $\Delta H_{L}^{\ominus}(\text{theoretical})/\text{kJ mol}^{-1}$ | +732 | +758 |

The values of ΔH_{L}^{\ominus} (experimental) have been determined from Born–Haber cycles.

The values of ΔH_{L}^{\ominus} (theoretical) have been determined by calculation using a perfect ionic model.

(i) Explain the meaning of the term *perfect ionic model*.

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(2)

(ii) State what you can deduce about the bonding in NaBr from the data in the table.

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(1)

(iii) State what you can deduce about the bonding in AgBr from the data in the table.

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(1)

(Total 11 marks)

22

The balance between enthalpy change and entropy change determines the feasibility of a reaction. The table below contains enthalpy of formation and entropy data for some elements and compounds.

| | N ₂ (g) | O ₂ (g) | NO(g) | C(graphite) | C(diamond) |
|---|--------------------|--------------------|-------|-------------|------------|
| $\Delta H_f^\ominus/\text{kJ mol}^{-1}$ | 0 | 0 | +90.4 | 0 | +1.9 |
| $S^\ominus/\text{J K}^{-1} \text{mol}^{-1}$ | 192.2 | 205.3 | 211.1 | 5.7 | 2.4 |

- (a) Explain why the entropy value for the element nitrogen is much greater than the entropy value for the element carbon (graphite).

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(2)

- (b) Suggest the condition under which the element carbon (diamond) would have an entropy value of zero.

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(1)

- (c) Write the equation that shows the relationship between ΔG , ΔH and ΔS for a reaction.

.....

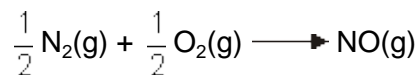
(1)

- (d) State the requirement for a reaction to be feasible.

.....

(1)

- (e) Consider the following reaction that can lead to the release of the pollutant NO into the atmosphere.



Use data from the table above to calculate the minimum temperature above which this reaction is feasible.

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(5)

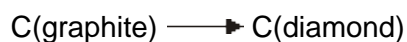
- (f) At temperatures below the value calculated in part (e), decomposition of NO into its elements should be spontaneous. However, in car exhausts this decomposition reaction does **not** take place in the absence of a catalyst. Suggest why this spontaneous decomposition does **not** take place.

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(1)

- (g) A student had an idea to earn money by carrying out the following reaction.



Use data from the table above to calculate values for ΔH^{\ominus} and ΔS^{\ominus} for this reaction. Use these values to explain why this reaction is **not** feasible under standard pressure at any temperature.

ΔH^{\ominus}

ΔS^{\ominus}

Explanation

.....

(3)
(Total 14 marks)

23

Calcium fluoride occurs naturally as the mineral fluorite, a very hard crystalline solid that is almost insoluble in water and is used as a gemstone.

Tables 1 and 2 contain thermodynamic data.

Table 1

| Process | $\Delta H^{\ominus} / \text{kJ mol}^{-1}$ |
|---|---|
| $\text{Ca}(\text{s}) \rightarrow \text{Ca}(\text{g})$ | +193 |
| $\text{Ca}(\text{g}) \rightarrow \text{Ca}^+(\text{g}) + \text{e}^-$ | +590 |
| $\text{Ca}^+(\text{g}) \rightarrow \text{Ca}^{2+}(\text{g}) + \text{e}^-$ | +1150 |
| $\text{F}_2(\text{g}) \rightarrow 2\text{F}(\text{g})$ | +158 |
| $\text{F}(\text{g}) + \text{e}^- \rightarrow \text{F}^-(\text{g})$ | -348 |

Table 2

| Name of enthalpy change | $\Delta H^\ominus / \text{kJ mol}^{-1}$ |
|---|---|
| Enthalpy of lattice dissociation for calcium fluoride | +2602 |
| Enthalpy of lattice dissociation for calcium chloride | +2237 |
| Enthalpy of hydration for F^- ions | -506 |
| Enthalpy of hydration for Cl^- ions | -364 |
| Enthalpy of hydration for Ca^{2+} ions | -1650 |

- (a) Write an equation, including state symbols, for the process that occurs when the calcium fluoride lattice dissociates and for which the enthalpy change is equal to the lattice enthalpy.

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(1)

- (b) (i) Define the term *standard enthalpy of formation*.

.....

(3)

- (ii) Write an equation, including state symbols, for the process that has an enthalpy change equal to the standard enthalpy of formation of calcium fluoride.

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(1)

- (iii) Use data from the **Tables 1 and 2** to calculate the standard enthalpy of formation for calcium fluoride.

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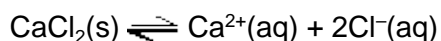
(3)

- (c) Explain why the enthalpy of lattice dissociation for calcium fluoride is greater than that for calcium chloride.

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(2)

- (d) Calcium chloride dissolves in water. After a certain amount has dissolved, a saturated solution is formed and the following equilibrium is established.



- (i) Using data from **Table 2**, calculate the enthalpy change for this reaction.

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(2)

- (ii) Predict whether raising the temperature will increase, decrease or have no effect on the amount of solid calcium chloride that can dissolve in a fixed mass of water. Explain your prediction.
(If you have been unable to obtain an answer to part (d) (i), you may assume that the enthalpy change = -60 kJ mol^{-1} . This is **not** the correct answer.)

Effect on amount of solid that can dissolve

Explanation

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(3)

- (e) Calcium fluoride crystals absorb ultra-violet light. Some of the energy gained is given out as visible light. The name of this process, fluorescence, comes from the name of the mineral, fluorite.

Use your knowledge of the equation $\Delta E = h\nu$ to suggest what happens to the electrons in fluorite when ultra-violet light is absorbed and when visible light is given out.

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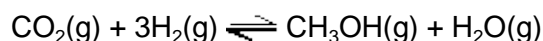
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(2)
(Total 17 marks)

24

Methanol can be regarded as a carbon-neutral fuel because it can be synthesised from carbon dioxide as shown in the equation below.



Standard enthalpy of formation and standard entropy data for the starting materials and products are shown in the following table.

| | CO ₂ (g) | H ₂ (g) | CH ₃ OH(g) | H ₂ O(g) |
|---|---------------------|--------------------|-----------------------|---------------------|
| $\Delta H_f^\ominus / \text{kJ mol}^{-1}$ | -394 | 0 | -201 | -242 |
| $S^\ominus / \text{J K}^{-1} \text{mol}^{-1}$ | 214 | 131 | 238 | 189 |

- (a) Calculate the standard enthalpy change for this reaction.

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(3)

- (d) Write an equation for the complete combustion of methanol. Use your equation to explain why the combustion reaction in the gas phase is feasible at all temperatures.

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(4)

- (e) Give **one** reason why methanol, synthesised from carbon dioxide and hydrogen, may **not** be a carbon-neutral fuel.

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(1)

(Total 17 marks)

25

The table below gives some values of standard enthalpy changes. Use these values to answer the questions.

| Name of enthalpy change | $\Delta H^\ominus / \text{kJ mol}^{-1}$ |
|--|---|
| Enthalpy of atomisation of chlorine | +121 |
| Electron affinity of chlorine | -364 |
| Enthalpy of atomisation of silver | +289 |
| First ionisation enthalpy of silver | +732 |
| Enthalpy of formation of silver chloride | -127 |

- (a) Calculate the bond enthalpy of a Cl–Cl bond.

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(1)

(b) Explain why the bond enthalpy of a Cl–Cl bond is greater than that of a Br–Br bond.

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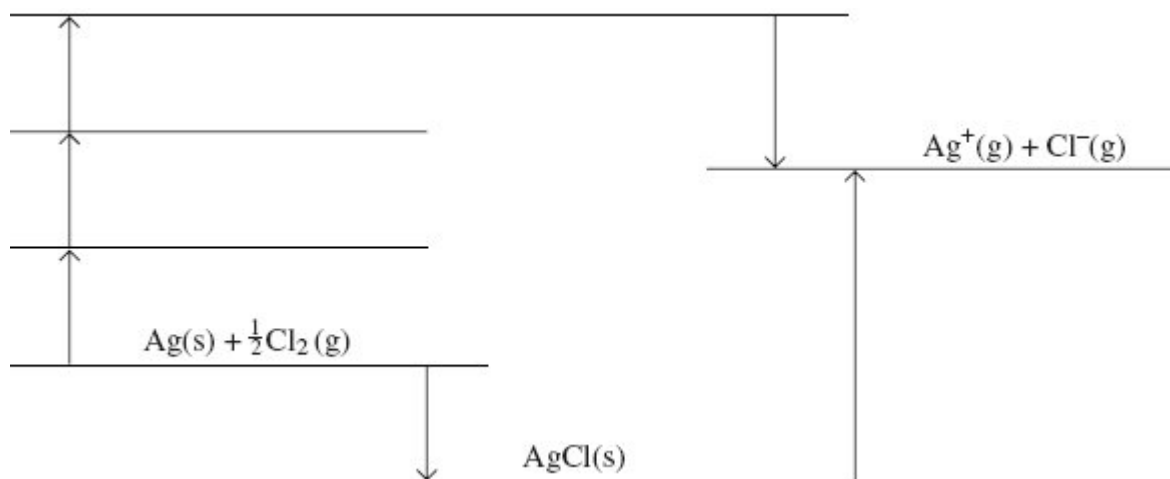
(2)

(c) Suggest why the electron affinity of chlorine is an exothermic change.

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(1)

(d) The diagram below is an incomplete Born–Haber cycle for the formation of silver chloride. The diagram is not to scale.



(i) Complete the diagram by writing the appropriate chemical symbols, with state symbols, on each of the three blank lines.

(3)

(ii) Calculate a value for the enthalpy of lattice dissociation for silver chloride.

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(2)

(e) The enthalpy of lattice dissociation for silver chloride can also be calculated theoretically assuming a perfect ionic model.

(i) Explain the meaning of the term *perfect ionic model*.

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(1)

(ii) State whether you would expect the value of the theoretical enthalpy of lattice dissociation for silver chloride to be greater than, equal to or less than that for silver bromide. Explain your answer.

Theoretical lattice enthalpy for silver chloride

Explanation

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(3)

(iii) Suggest why your answer to part (d) (ii) is greater than the theoretical value for the enthalpy of lattice dissociation for silver chloride.

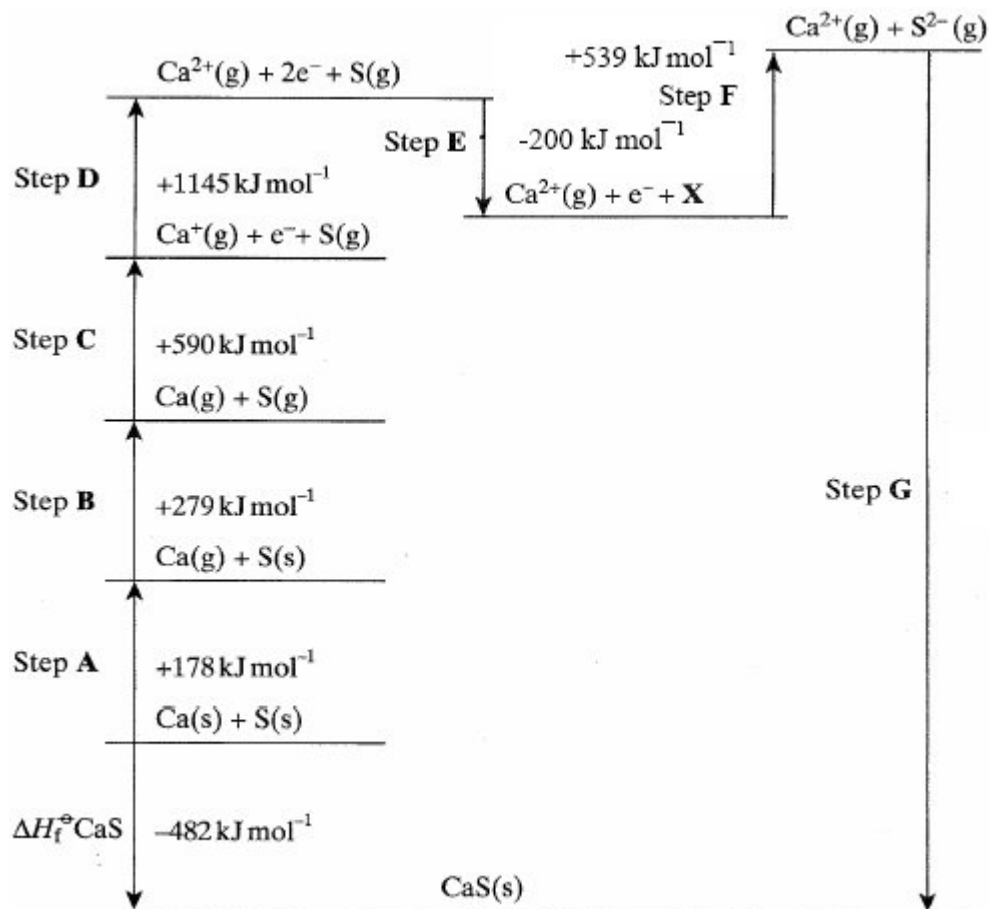
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(2)

(Total 15 marks)

26

(a) A Born–Haber cycle for the formation of calcium sulphide is shown below. The cycle includes enthalpy changes for all steps except step **G**. (The cycle is not drawn to scale.)



(i) Give the full electronic configuration of the ion S^{2-}

.....

(ii) Suggest why step **F** is an endothermic process.

.....

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(iii) Name the enthalpy changes in steps **B** and **D**.

Step **B**

Step **D**

(iv) Explain why the enthalpy change for step **D** is larger than that for step **C**.

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- (v) Use the data shown in the cycle to calculate a value for the enthalpy change for step **G**.

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(9)

- (b) Using a Born–Haber cycle, a value of -905 kJ mol^{-1} was determined for the lattice enthalpy of silver chloride. A value for the lattice enthalpy of silver chloride using the ionic model was -833 kJ mol^{-1} .

Explain what a scientist would be able to deduce from a comparison of these values.

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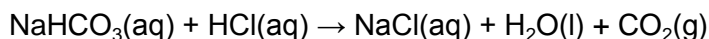
(3)

- (c) Some endothermic reactions occur spontaneously at room temperature. Some exothermic reactions do not occur if the reactants are heated together to a very high temperature.

In order to explain the following observations, another factor, the entropy change, ΔS , must be considered. The equation which relates ΔS to ΔH is given below.

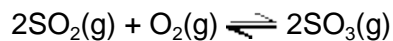
$$\Delta G = \Delta H - T\Delta S$$

- (i) Explain why the following reaction occurs at room temperature even though the reaction is endothermic.



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- (ii) Explain why the following reaction does not occur at very high temperatures even though the reaction is exothermic.



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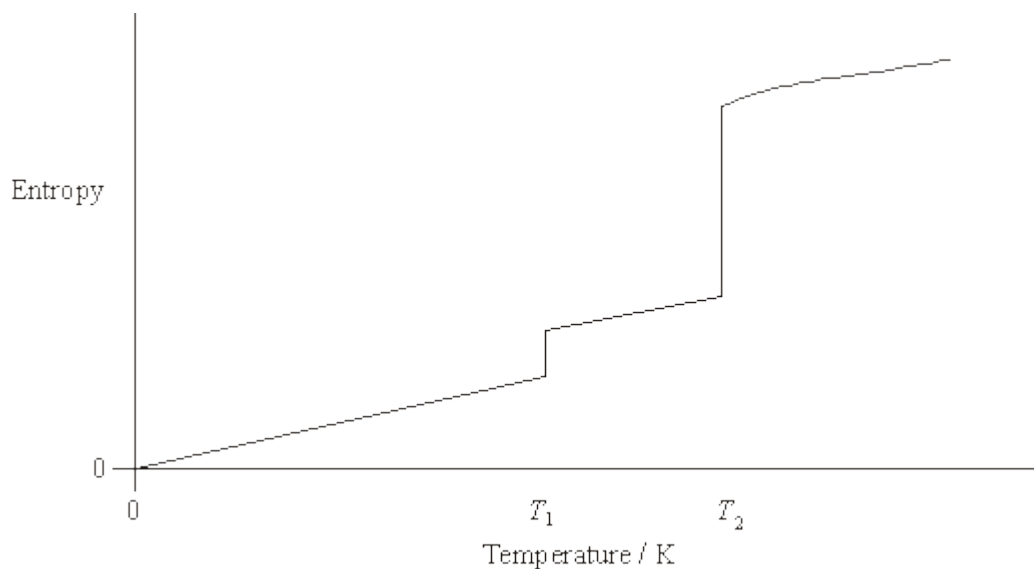
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(6)
(Total 18 marks)

27

The sketch graph below shows how the entropy of a sample of water varies with temperature.



- (a) Suggest why the entropy of water is zero at 0 K.

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(1)

- (b) What change of state occurs at temperature T_1 ?

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(1)

(c) Explain why the entropy change, ΔS , at temperature T_2 is much larger than that at temperature T_1 .

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.....
.....

(2)

(d) It requires 3.49 kJ of heat energy to convert 1.53 g of liquid water into steam at 373 K and 100 kPa.

(i) Use these data to calculate the enthalpy change, ΔH , when 1.00 mol of liquid water forms 1.00 mol of steam at 373 K and 100 kPa.

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(ii) Write an expression showing the relationship between free-energy change, ΔG , enthalpy change, ΔH , and entropy change, ΔS .

.....

(iii) For the conversion of liquid water into steam at 373 K and 100 kPa, $\Delta G = 0 \text{ kJ mol}^{-1}$

Calculate the value of ΔS for the conversion of one mole of water into steam under these conditions. State the units.

(If you have been unable to complete part (d)(i) you should assume that $\Delta H = 45.0 \text{ kJ mol}^{-1}$. This is not the correct answer.)

Calculation

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.....

Units

(6)
(Total 10 marks)

28

Which one of the equations below represents a reaction that is feasible at all temperatures?

- A $P(s) \rightarrow Q(s) + R(g)$ endothermic
B $2L(g) + M(g) \rightarrow 2N(g)$ exothermic
C $S(g) \rightarrow 2T(g)$ exothermic
D $A(g) + B(g) \rightarrow C(g)$ endothermic

(Total 1 mark)

29

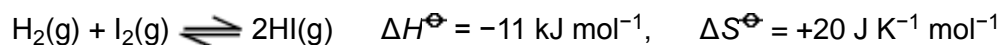
Which one of the following reactions in aqueous solution has the most positive change in entropy?

- A $[Cu(H_2O)_6]^{2+} + 4NH_3 \rightarrow [Cu(NH_3)_4(H_2O)_2]^{2+} + 4H_2O$
B $[Cu(H_2O)_6]^{2+} + 4Cl^- \rightarrow [CuCl_4]^{2-} + 6H_2O$
C $[Cu(H_2O)_6]^{2+} + EDTA^{4-} \rightarrow [Cu(EDTA)]^{2-} + 6H_2O$
D $[Cu(H_2O)_6]^{2+} + 2H_2NCH_2CH_2NH_2 \rightarrow [Cu(H_2NCH_2CH_2NH_2)_2(H_2O)_2]^{2+} + 4H_2O$

(Total 1 mark)

30

Refer to the following reaction



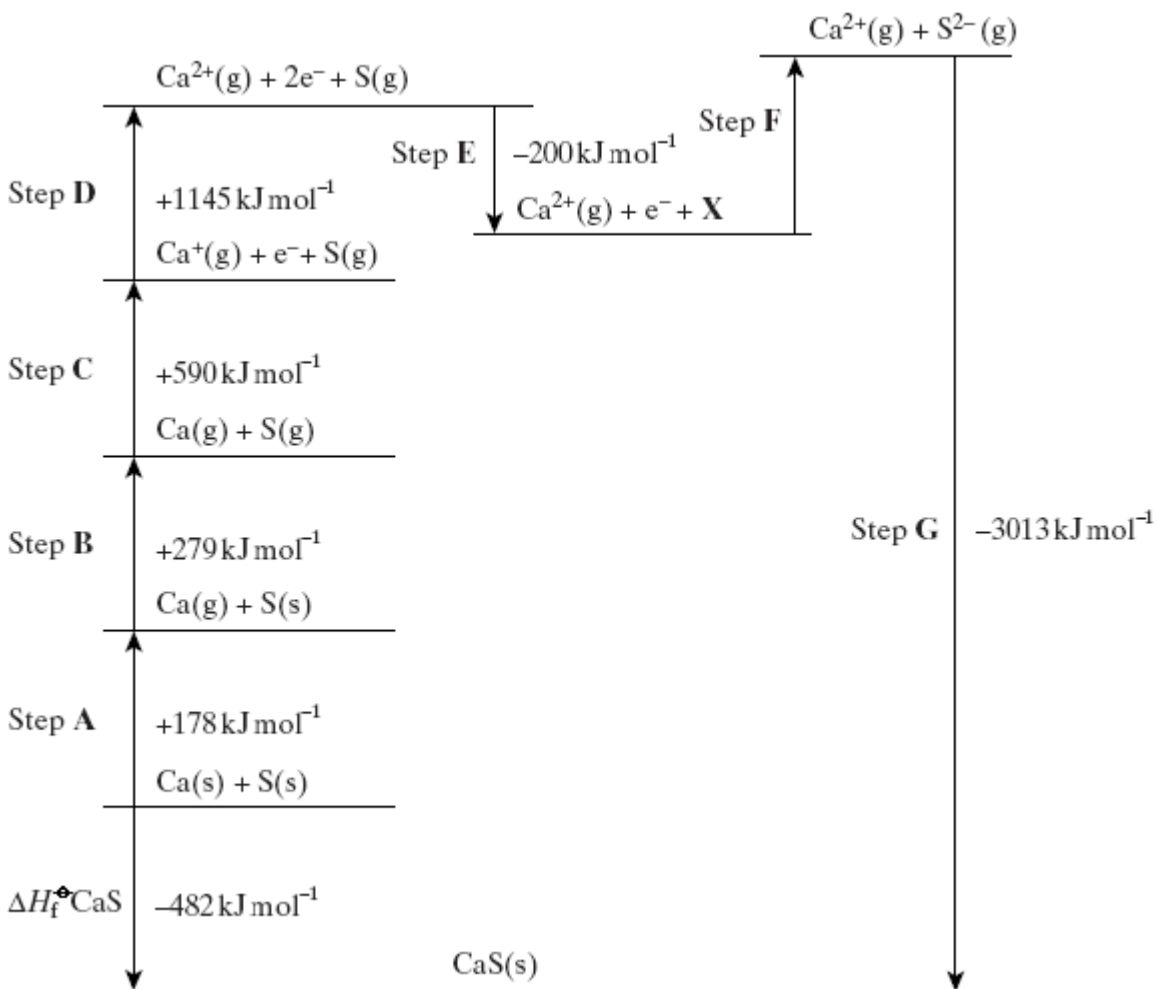
Which one of the following statements is correct?

- A This is a redox reaction.
B The reaction is **not** feasible below 298 K
C At equilibrium, the yield of hydrogen iodide is changed by increasing the pressure.
D At equilibrium, the yield of hydrogen iodide increases as the temperature is increased.

(Total 1 mark)

31

A Born–Haber cycle for the formation of calcium sulphide is shown below. The cycle includes enthalpy changes for all Steps except Step F. (The cycle is not drawn to scale.)



- (a) Give the full electronic arrangement of the ion S^{2-}

.....

(1)

- (b) Identify the species **X** formed in Step E.

.....

(1)

- (c) Suggest why Step F is an endothermic process.

.....

.....

(2)

(d) Name the enthalpy change for each of the following steps.

(i) Step **B**

(ii) Step **D**

(iii) Step **F**

(3)

(e) Explain why the enthalpy change for Step **D** is larger than that for Step **C**.

.....

.....

(2)

(f) Use the data shown in the cycle to calculate a value for the enthalpy change for Step **F**.

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.....

(2)

(Total 11 marks)

32

This question is about the reaction given below.



Enthalpy data for the reacting species are given in the table below.

| Substance | CO(g) | H ₂ O(g) | CO ₂ (g) | H ₂ (g) |
|---|-------|---------------------|---------------------|--------------------|
| $\Delta H_f^\ominus / \text{kJ mol}^{-1}$ | -110 | -242 | -394 | 0 |

Which one of the following statements is **not** correct?

- A The value of K_p changes when the temperature changes.
- B The activation energy decreases when the temperature is increased.
- C The entropy change is more positive when the water is liquid rather than gaseous.
- D The enthalpy change is more positive when the water is liquid rather than gaseous.

(Total 1 mark)

33

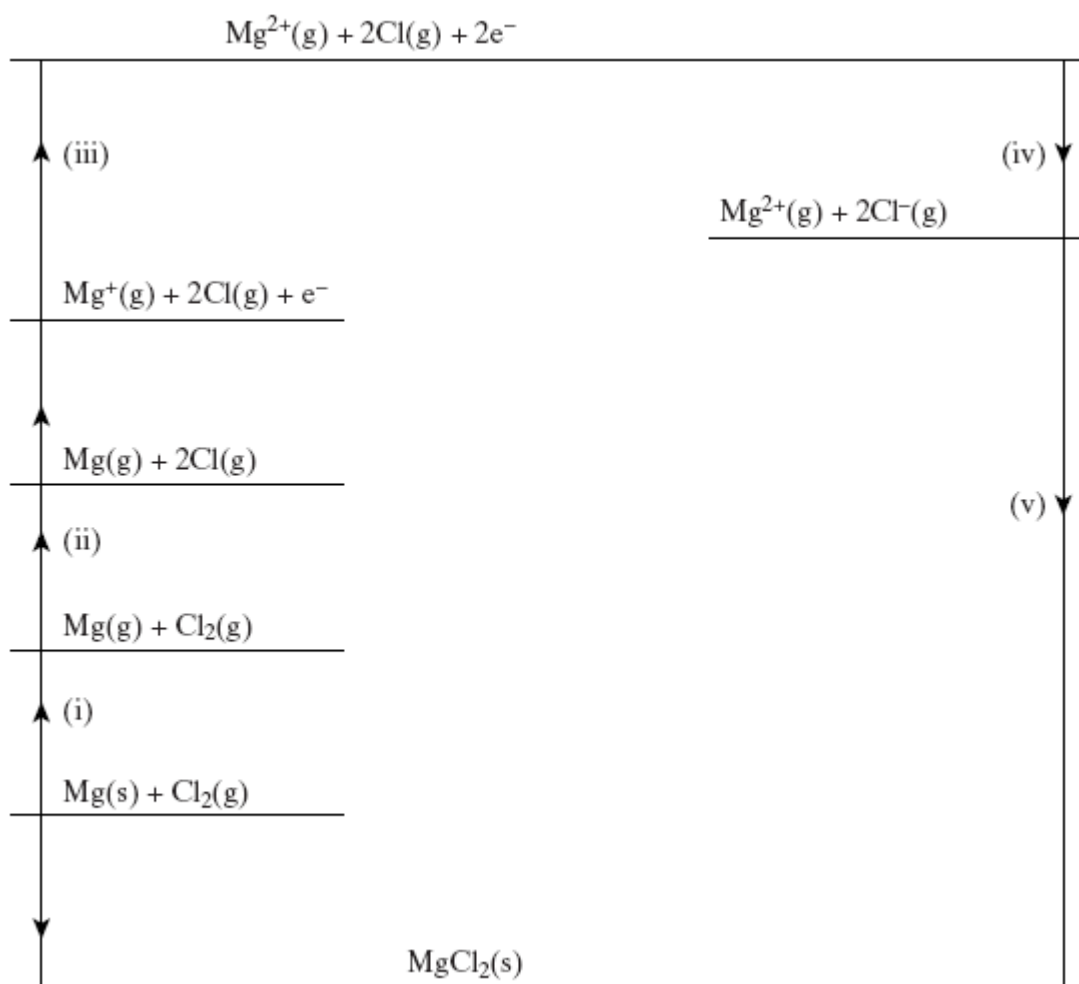
Which one of the following statements is **not** correct?

- A The first ionisation energy of iron is greater than its second ionisation energy.
- B The magnitude of the lattice enthalpy of magnesium oxide is greater than that of barium oxide.
- C The oxidation state of iron in $[\text{Fe}(\text{CN})_6]^{3-}$ is greater than the oxidation state of copper in $[\text{CuCl}_2]^-$
- D The boiling point of C_3H_8 is lower than that of $\text{CH}_3\text{CH}_2\text{OH}$

(Total 1 mark)

34

(a) A Born–Haber cycle for the formation of magnesium(II) chloride is shown below.



Taking care to note the direction of the indicated enthalpy change and the number of moles of species involved, give each of the enthalpy changes (i) to (v) above.

Enthalpy change (i)

Enthalpy change (ii)

Enthalpy change (iii)

Enthalpy change (iv)

Enthalpy change (v)

(5)

- (b) Write an equation for the decomposition of MgCl(s) into $\text{MgCl}_2\text{(s)}$ and Mg(s) and use the following data to calculate a value for the enthalpy change of this reaction.

$$\Delta H_f^\ominus \text{MgCl(s)} = -113 \text{ kJ mol}^{-1}$$

$$\Delta H_f^\ominus \text{MgCl}_2\text{(s)} = -653 \text{ kJ mol}^{-1}$$

Equation

Calculation

.....

(4)

- (c) Use the data below to calculate a value for the molar enthalpy of a solution of $\text{MgCl}_2\text{(s)}$.

$$\text{Lattice formation enthalpy of MgCl}_2\text{(s)} = -2502 \text{ kJ mol}^{-1}$$

$$\Delta H_{\text{hydration}}^\ominus \text{ of Mg}^{2+}\text{(g)} = -1920 \text{ kJ mol}^{-1}$$

$$\Delta H_{\text{hydration}}^\ominus \text{ of Cl}^-\text{(g)} = -364 \text{ kJ mol}^{-1}$$

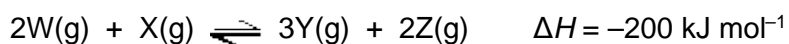
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(3)

(Total 12 marks)

35

- (a) The gaseous reactants **W** and **X** were sealed in a flask and the mixture left until the following equilibrium had been established.



Write an expression for the equilibrium constant, K_p , for this reaction.

State one change in the conditions which would both increase the rate of reaction and decrease the value of K_p . Explain your answers.

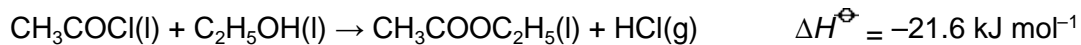
(7)

(b) Ethyl ethanoate can be prepared by the reactions shown below.

Reaction 1



Reaction 2



- (i) Give one advantage and one disadvantage of preparing ethyl ethanoate by **Reaction 1** rather than by **Reaction 2**.
- (ii) Use the information given above and the data below to calculate values for the standard entropy change, ΔS^\ominus , and the standard free-energy change, ΔG^\ominus , for **Reaction 2** at 298 K.

| | | | | |
|---|------------------------------------|---|--|------------------------|
| | $\text{CH}_3\text{COCl}(\text{l})$ | $\text{C}_2\text{H}_5\text{OH}(\text{l})$ | $\text{CH}_3\text{COOC}_2\text{H}_5(\text{l})$ | $\text{HCl}(\text{g})$ |
| $S^\ominus/\text{JK}^{-1}\text{mol}^{-1}$ | 201 | 161 | 259 | 187 |

(8)
(Total 15 marks)

36

Chlorine is formed in a reversible reaction as shown by the equation



- (a) Use the data below to calculate the standard enthalpy change, ΔH^\ominus , and the standard entropy change, ΔS^\ominus , for this reaction.

| Substance | HCl(g) | O ₂ (g) | Cl ₂ (g) | H ₂ O(g) |
|---|--------|--------------------|---------------------|---------------------|
| $\Delta H_f^\ominus / \text{kJ mol}^{-1}$ | -92 | 0 | 0 | -242 |
| $S^\ominus / \text{J K}^{-1} \text{mol}^{-1}$ | 187 | 205 | 223 | 189 |

Standard enthalpy change, ΔH^\ominus

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.....

Standard entropy change, ΔS^\ominus

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(6)

- (b) The data below apply to a different gas phase reversible reaction.

Standard enthalpy change, $\Delta H^\ominus = +208 \text{ kJ mol}^{-1}$

Standard entropy change, $\Delta S^\ominus = +253 \text{ J K}^{-1} \text{mol}^{-1}$

- (i) Deduce the effect of an increase in temperature on the position of the equilibrium in this reaction. Use Le Chatelier's principle to explain your answer.

Effect

Explanation

(ii) Calculate the minimum temperature at which this reaction is feasible.

.....

.....

.....

.....

(7)
(Total 13 marks)

37

(a) (i) Draw a fully-labelled Born–Haber cycle for the formation of solid barium chloride, BaCl_2 , from its elements. Include state symbols for all species involved.

- (ii) Use your Born–Haber cycle and the standard enthalpy data given below to calculate a value for the electron affinity of chlorine.

| | |
|---|----------------------------|
| Enthalpy of atomisation of barium | +180 kJ mol ⁻¹ |
| Enthalpy of atomisation of chlorine | +122 kJ mol ⁻¹ |
| Enthalpy of formation of barium chloride | -859 kJ mol ⁻¹ |
| First ionisation enthalpy of barium | +503 kJ mol ⁻¹ |
| Second ionisation enthalpy of barium | +965 kJ mol ⁻¹ |
| Lattice formation enthalpy of barium chloride | -2056 kJ mol ⁻¹ |

.....

.....

.....

.....

(9)

- (b) Use data from part (a)(ii) and the entropy data given below to calculate the lowest temperature at which the following reaction becomes feasible.



| | BaCl ₂ (s) | Ba(s) | Cl ₂ (g) |
|---|-----------------------|-------|---------------------|
| $S^\ominus / \text{J K}^{-1} \text{mol}^{-1}$ | 124 | 63 | 223 |

.....

.....

.....

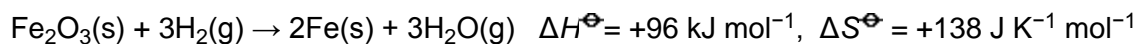
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(4)
(Total 13 marks)

38

Using the information below, answer this question.



| | $\text{Fe}_2\text{O}_3(\text{s})$ | $\text{H}_2(\text{g})$ | $\text{Fe}(\text{s})$ |
|---|-----------------------------------|------------------------|-----------------------|
| $\Delta H_f^\ominus / \text{kJ mol}^{-1}$ | -822.0 | 0 | 0 |
| $\Delta S^\ominus / \text{J K}^{-1} \text{ mol}^{-1}$ | 90.0 | 131.0 | 27.0 |

The standard entropy value for steam is

- A +332 J K⁻¹ mol⁻¹
- B +189 J K⁻¹ mol⁻¹
- C +145 J K⁻¹ mol⁻¹
- D +85 J K⁻¹ mol⁻¹

(Total 1 mark)

39

In which one of the following reactions is there a decrease in entropy?

- A $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}(\text{aq}) + 3\text{C}_2\text{O}_4^{2-}(\text{aq}) \rightarrow [\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}(\text{aq}) + 6\text{H}_2\text{O}(\text{l})$
- B $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}(\text{aq}) + \text{EDTA}^{4-}(\text{aq}) \rightarrow [\text{Cu}(\text{EDTA})]^{2-}(\text{aq}) + 6\text{H}_2\text{O}(\text{l})$
- C $[\text{CoCl}_4]^{2-}(\text{aq}) + 6\text{H}_2\text{O}(\text{l}) \rightarrow [\text{Co}(\text{H}_2\text{O})_6]^{2+}(\text{aq}) + 4\text{Cl}^-(\text{aq})$
- D $\text{Na}_2\text{CO}_3(\text{s}) + 2\text{H}^+(\text{aq}) \rightarrow 2\text{Na}^+(\text{aq}) + \text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{l})$

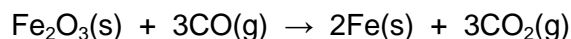
(Total 1 mark)

40

Use the data in the table below to answer the questions which follow.

| Substance | $\text{Fe}_2\text{O}_3(\text{s})$ | $\text{Fe}(\text{s})$ | $\text{C}(\text{s})$ | $\text{CO}(\text{g})$ | $\text{CO}_2(\text{g})$ |
|--|-----------------------------------|-----------------------|----------------------|-----------------------|-------------------------|
| $\Delta H_f^\ominus / \text{kJ mol}^{-1}$ | -824.2 | 0 | 0 | -110.5 | -393.5 |
| $S^\ominus / \text{J K}^{-1} \text{ mol}^{-1}$ | 87.4 | 27.3 | 5.7 | 197.6 | 213.6 |

(a) The following equation shows one of the reactions which can occur in the extraction of iron.



- (i) Calculate the standard enthalpy change and the standard entropy change for this reaction.

Standard enthalpy change

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

Standard entropy change

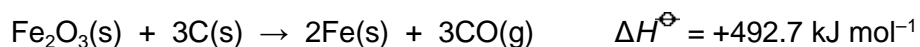
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.....
.....
.....

- (ii) Explain why this reaction is feasible at all temperatures.

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

(9)

- (b) The reaction shown by the following equation can also occur in the extraction of iron.



The standard entropy change, ΔS^\ominus , for this reaction is $+542.6 \text{ J K}^{-1} \text{ mol}^{-1}$

Use this information to calculate the temperature at which this reaction becomes feasible.

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

(3)

- (c) Calculate the temperature at which the standard free-energy change, ΔG^\ominus has the same value for the reactions in parts (a) and (b).

.....

.....

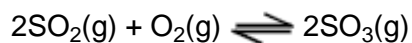
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(3)
(Total 15 marks)

41

This question relates to the equilibrium gas-phase synthesis of sulphur trioxide:



Thermodynamic data for the components of this equilibrium are:

| Substance | $\Delta H_f^\ominus / \text{kJ mol}^{-1}$ | $S^\ominus / \text{J K}^{-1} \text{mol}^{-1}$ |
|-------------------------|---|---|
| $\text{SO}_3(\text{g})$ | -396 | +257 |
| $\text{SO}_2(\text{g})$ | -297 | +248 |
| $\text{O}_2(\text{g})$ | 0 | +204 |

This equilibrium, at a temperature of 585 K and a total pressure of 540 kPa, occurs in a vessel of volume 1.80 dm^3 . At equilibrium, the vessel contains 0.0500 mol of $\text{SO}_2(\text{g})$, 0.0800 mol of $\text{O}_2(\text{g})$ and 0.0700 mol of $\text{SO}_3(\text{g})$.

The standard entropy change for this reaction is

- A $-222 \text{ J K}^{-1} \text{mol}^{-1}$
- B $-195 \text{ J K}^{-1} \text{mol}^{-1}$
- C $-186 \text{ J K}^{-1} \text{mol}^{-1}$
- D $+198 \text{ J K}^{-1} \text{mol}^{-1}$

(Total 1 mark)

42 Which one of the following best explains why the lattice enthalpy of magnesium chloride is much larger than that of lithium chloride?

- A Magnesium has a greater electronegativity than lithium.
- B Magnesium ions have a greater polarising power than lithium ions.
- C Magnesium ions have a greater ionic radius than lithium ions.
- D Magnesium ions have a greater charge than lithium ions.

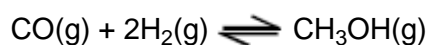
(Total 1 mark)

43 Which one of the following has the most covalent character?

- A MgF_2
- B MgBr_2
- C AlF_3
- D AlBr_3

(Total 1 mark)

44 The following information concerns the equilibrium gas-phase synthesis of methanol.



At equilibrium, when the temperature is 68 °C, the total pressure is 1.70 MPa.

The number of moles of CO, H₂ and CH₃OH present are 0.160, 0.320 and 0.180, respectively.

Thermodynamic data are given below.

| Substance | $\Delta H_f^\ominus / \text{kJ mol}^{-1}$ | $S^\ominus / \text{J K}^{-1} \text{mol}^{-1}$ |
|-----------------------|---|---|
| CO(g) | -110 | 198 |
| H ₂ (g) | 0 | 131 |
| CH ₃ OH(g) | -201 | 240 |

The standard entropy change for this reaction is

- A $-220 \text{ J K}^{-1} \text{mol}^{-1}$
- B $+220 \text{ J K}^{-1} \text{mol}^{-1}$
- C $-89 \text{ J K}^{-1} \text{mol}^{-1}$
- D $+89 \text{ J K}^{-1} \text{mol}^{-1}$

(Total 1 mark)

45 The compound lithium tetrahydridoaluminate(III), LiAlH_4 , is a useful reducing agent. It behaves in a similar fashion to NaBH_4 . Carbonyl compounds and carboxylic acids are reduced to alcohols. However, LiAlH_4 also reduces water in a violent reaction so that it must be used in an organic solvent.

Which one of the following concerning the violent reaction between LiAlH_4 and water is **false**?

- A A gas is produced.
- B The activation energy for the reaction is relatively high.
- C The reaction has a negative free-energy change.
- D Aqueous lithium ions are formed.

(Total 1 mark)

46 Which one of the following has the most covalent character?

- A MgF_2
- B MgBr_2
- C AlF_3
- D AlBr_3

(Total 1 mark)

Mark schemes

1

- (a) The enthalpy change / heat energy change / ΔH for the formation of one mole of (chloride) ions from (chlorine) atoms

Allow enthalpy change for $Cl + e^- \rightarrow Cl^-$

Do not allow energy change

ionisation energy description is $CE=0$

Allow enthalpy change for the addition of 1 mol of electrons to Chlorine atoms

penalise Cl_2 and chlorine molecules $CE = 0$

allow chlorine ions

1

Atoms and ions in the gaseous state

Or state symbols in equation

Cannot score M2 unless M1 scored

except allow M2 if energy change rather than enthalpy change

ignore standard conditions

1

- (b) $Mg^{2+}(g) + 2e^- + 2Cl(g)$ (1)
(M5)

| | |
|---|-------------------------------------|
| $Mg^{2+}(g) + 2e^- + Cl_2(g)$ (1) (M4) | |
| | $Mg^{2+}(g) + 2Cl^-(g)$ (1) (M6) |
| $Mg^+(g) + e^- + Cl_2(g)$ (1) (M3) | |
| $Mg(g) + Cl_2(g)$ (1) (M2) | |
| $Mg(s) + Cl_2(g)$ (1) (M1) | |
| | $MgCl_2(s)$ |

Allow e for electrons (i.e. no charge)

State symbols essential

If no electrons allow M5 but not M3,M4

If incorrect 1 / 2 Cl_2 used allow M3 and M4 for correct electrons (scores 2 / 6)

6

- (c) $-\Delta H_f(\text{MgCl}_2) + \Delta H_a(\text{Mg}) + 1^{\text{st}} \text{IE}(\text{Mg}) + 2^{\text{nd}} \text{IE}(\text{Mg}) + 2\Delta H_a(\text{Cl}) = -2\text{EA}(\text{Cl}) - \text{LE}(\text{MgCl}_2)$
Allow Enthalpy of Formation = sum of other enthalpy changes (incl lattice formation)

1

$$-2\text{EA}(\text{Cl}) = 642 + 150 + 736 + 1450 + 242 - 2493 = 727$$

1

$$\text{EA}(\text{Cl}) = -364 \text{ (kJ mol}^{-1}\text{)}$$

Allow -363 to -364

Allow M1 and M2 for -727

Allow 1 (1 out of 3) for +364 or +363 but award 2 if due to arithmetic error after correct M2

Also allow 1 for -303

Units not essential but penalise incorrect units

Look for a transcription error and mark as AE-1

1

- (d) (i) Magnesium (ion) is smaller **and** more charged (than the sodium ion)
OR

magnesium (ion) has higher charge to size ratio / charge density

Do not allow wrong charge on ion if given

Do not allow similar size for M1

Do not allow mass / charge ratio

1

(magnesium ion) attracts water more strongly

Mark independently

Mention of intermolecular forces, (magnesium) atoms or atomic radius CE = 0

1

- (ii) Enthalpy change = $-\text{LE}(\text{MgCl}_2) + \Sigma(\Delta H_{\text{hyd}}\text{ions})$

$$= 2493 + (-1920 + 2 \times -364)$$

1

$$= -155 \text{ (kJ mol}^{-1}\text{)}$$

Units not essential but penalise incorrect units

1

[15]

2

- (a) (i) $\Delta H = \Sigma(\text{enthalpies formation products}) - \Sigma(\text{enthalpies formation reactants})$
Or correct cycle with enthalpy changes labelled

1

$$= -111 - (-75 - 242)$$

1

$$= (+)206 \text{ (kJ mol}^{-1}\text{)}$$

-206 scores 1 only

Units not essential if ans in kJ mol⁻¹ but penalise incorrect units

1

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

$$= 198 + 3 \times 131 - (186 + 189)$$

1

$$= (+) 216 \text{ (J K}^{-1} \text{ mol}^{-1}\text{)}$$

OR

$$0.216 \text{ kJ K}^{-1} \text{ mol}^{-1}$$

Units not essential but penalise incorrect units

1

- (b) When $\Delta G = 0$ OR $\Delta H = T\Delta S$

1

$$T = \Delta H / \Delta S$$

M2 also scores M1

1

$$= 206 \times 1000 / 216$$

Allow error carried forward from (a)(i) and (a)(ii)

Ignore unexplained change of sign from - to +

1

$$= 954 \text{ K}$$

Allow 953 - 955, Units of K essential, must be +ve

If values from (a)(i) and (a)(ii) lead to negative value in M3 allow M1 to M3 but do not allow negative temperature for M4

If negative value changed to positive for M4, allow M4

1

- (c) To speed up the rate of reaction OR wtte

Allow so that more molecules have energy greater than the activation energy

IF T in (b) > 1300 allow answers such as;

to reduce energy cost

to slow down reaction

do NOT allow to increase rate

1

- (d) (i) **Method 1**
 $\Delta G = \Delta H - T\Delta S$
 $\Delta G = -41 - (1300 \times -42 / 1000)$ (M1)
If 42 and not 42 / 1000 used can score M3 only
but allow $\Delta G = -41 \times 1000 - (1300 \times -42)$ (M1)

1

$$= +13.6 \text{ kJ mol}^{-1}$$

$$= 13600 \text{ J mol}^{-1}$$
 (M2)
Units essential

1

ΔG must be negative for the reaction to be feasible.

OR ΔG is positive so reaction is not feasible

1

Method 2

For reaction to be feasible ΔG must be negative or zero

1

$$T \text{ when } \Delta G = 0 = \Delta H / \Delta S = 976 \text{ K}$$

1

ΔS is -ve so ΔG must be +ve at temperatures above 976K / at 1300 K

1

- (ii) If the temperature is lowered

(Ignore reference to catalyst and / or pressure)

Alternative mark scheme (if T is calculated)

Allow T reduced to 976 K or lower M1

1

ΔG will become (more) negative because

the $-T\Delta S$ term will be less positive / $T\Delta S > \Delta H$

At this temperature (the reaction becomes feasible because) $\Delta G <$

$= 0$ M2

1

[15]

3

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

1

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

1

$$= -49 - \frac{523 \times (-180)}{1000}$$

1

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

Units essential

1

(b) When $\Delta G = 0$, $\Delta H = T\Delta S$ therefore $T = \Delta H / \Delta S$

1

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

Mark consequentially to ΔS in part (a)

1

(c) Diagram marks

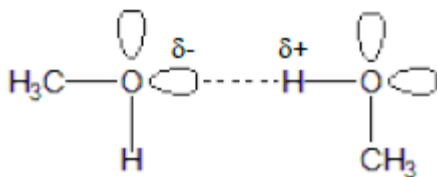


Diagram of a molecule showing O–H bond and two lone pairs on each oxygen

1

Labels on diagram showing $\delta+$ and $\delta-$ charges

Allow explanation of position of $\delta+$ and $\delta-$ charges on H and O

1

Diagram showing $\delta+$ hydrogen on one molecule attracted to lone pair on a second molecule

1

Explanation mark

Hydrogen bonding (the name mentioned) is a strong enough force (to hold methanol molecules together in a liquid)

1

[10]

4

(a) An electron pair on the ligand

1

Is donated from the ligand to the central metal ion

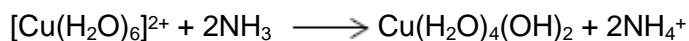
1

(b) Blue precipitate

1

Dissolves to give a dark blue solution

1



1



1

(c) $[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+} + 2\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2 \longrightarrow [\text{Cu}(\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2)_2(\text{H}_2\text{O})_2]^{2+} + 4\text{NH}_3$

1

(d) Cu–N bonds formed have similar enthalpy / energy to Cu–N bonds broken 1

And the same number of bonds broken and made 1

(e) 3 particles form 5 particles / disorder increases because more particles are formed / entropy change is positive 1

Therefore, the free-energy change is negative

M2 can only be awarded if M1 is correct

1
[11]

5 (a) Start a clock when KCl is added to water 1

Record the temperature every subsequent minute for about 5 minutes

Allow record the temperature at regular time intervals until some time after all the solid has dissolved for M2

1

Plot a graph of temperature vs time 1

Extrapolate back to time of mixing = 0 and determine the temperature 1

(b) Heat taken in = $m \times c \times \Delta T = 50 \times 4.18 \times 5.4 = 1128.6 \text{ J}$
Max 2 if 14.6 °C used as ΔT 1

Moles of KCl = $5.00 / 74.6 = 0.0670$ 1

Enthalpy change per mole = $+1128.6 / 0.0670 = 16\,839 \text{ J mol}^{-1}$ 1

= +16.8 (kJ mol⁻¹)
Answer must be given to this precision 1

(c) $\Delta H_{\text{solution}} = \Delta H_{\text{lattice}} + \Delta H(\text{hydration of calcium ions}) + 2 \times \Delta H(\text{hydration of chloride ions})$

$\Delta H_{\text{lattice}} = \Delta H_{\text{solution}} - \Delta H(\text{hydration of calcium ions}) - 2 \times \Delta H(\text{hydration of chloride ions})$ 1

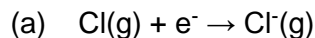
$\Delta H_{\text{lattice}} = -82 - 9 - (-1650 + 2 \times -364) = +2295 \text{ (kJ mol}^{-1}\text{)}$ 1

(d) Magnesium ion is smaller than the calcium ion 1

Therefore, it attracts the chloride ion more strongly / stronger ionic bonding

1
[12]

6



State symbols essential

Allow e with no charge

This and all subsequent equations must be balanced

1

(b) There is an attraction between the nucleus / protons and (the added) electron(s)

1

Energy is released (when the electron is gained)

Allow product more stable / product has lower energy

Allow reaction exothermic / heat released

Allow reference to chlorine rather than fluorine

Wrong process eg ionisation, boiling CE = 0

1

(c) (i) Top line: $+\text{e}^- + \text{F(g)}$

Penalise missing / wrong state symbols one mark only

Penalise F1 or Cl one mark only

1

Second line from top : $+\text{e}^- + \frac{1}{2}\text{F}_2\text{(g)}$

Mark independently

Allow e with no charge

1

Bottom two lines: $+\frac{1}{2}\text{F}_2\text{(g)}$

Penalise each lack of an electron in M1 and M2 each time

1

(ii) $\frac{1}{2}\text{E(F-F)} + 732 + 289 + +203 = 348 + 955$

$$\frac{1}{2}\text{E(F-F)} = 79$$

1

$$\text{E(F-F)} = 158 \text{ (kJ mol}^{-1}\text{)}$$

Award one mark (M2) if M1 wrong but answer = M1 × 2

Ignore no units, penalise wrong units but allow kJ mol⁻¹

Any negative answer, CE = 0

1

- (d) (i) Experimental lattice enthalpy value allows for / includes covalent interaction / non-spherical ions / distorted ions / polarisation

OR AgF has covalent character

Allow discussion of AgCl instead of AgF

CE = 0 for mention of molecules, atoms, macromolecular, mean bond enthalpy, intermolecular forces (imf), electronegativity

1

Theoretical lattice enthalpy value assumes only ionic interaction / point charges / no covalent / perfect spheres / perfectly ionic

OR AgF is not perfectly ionic

1

- (ii) Chloride ion larger (than fluoride ion) / fluoride ion smaller (than chloride ion)

Penalise chlorine ion once only

Allow Cl⁻ and F⁻ instead of names of ions

Allow chloride ion has smaller charge density / smaller charge to size ratio but penalise mass to charge ratio

1

Attraction between Ag⁺ and Cl⁻ weaker / attraction between Ag⁺ and F⁻ stronger

For M2 Cl⁻ and F⁻ can be implied from an answer to M1

Mark M1 and M2 independently provided no contradiction

CE = 0 for mention of chlorine not chloride ion, molecules, atoms, macromolecular, mean bond enthalpy, intermolecular forces (imf), electronegativity

1

[12]

7

- (a) Enthalpy change / ΔH when 1 mol of a gaseous ion

Enthalpy change for $X^{+/-}(g) \rightarrow X^{+/-}(aq)$ scores M1 and M2

1

forms aqueous ions

Allow heat energy change instead of enthalpy change

Allow 1 mol applied to aqueous or gaseous ions

If substance / atoms in M1 CE = 0

If wrong process (eg boiling) CE = 0

1

- (b) $\Delta H(\text{solution}) = \Delta H(\text{lattice}) + \sum(\Delta H_{\text{hydration}})$

OR $+77 = +905 - 464 + \Delta H(\text{hydration, Cl}^-)$

OR $\Delta H(\text{hydration, Cl}^-) = +77 - 905 + 464$

Allow any one of these three for M1 even if one is incorrect

1

$$= -364 \text{ (kJ mol}^{-1}\text{)}$$

Allow no units, penalise incorrect units, allow kJ mol⁻¹

Allow lower case j for J (Joules)

+364 does not score M2 but look back for correct M1

1

(c) Water is polar / water has H δ^+

1

(Chloride ion) attracts (the H in) water molecules

(note chloride ion can be implied from the question stem)

Idea that there is a force of attraction between the chloride ion and water

Do not allow H bonds / dipole–dipole / vdW / intermolecular but ignore loose mention of bonding

Do not allow just chlorine or chlorine atoms / ion

Mark independently

1

(d) $\Delta G = \Delta H - T\Delta S$

Look for this equation in part (d) and / or (e); equation can be stated or implied by correct use. Record the mark in part (d)

1

$$(\Delta G = 0 \text{ so}) T = \Delta H / \Delta S$$

1

$$T = 77 \times 1000 / 33 = 2333 \text{ K (allow range 2300 to 2333.3)}$$

Units essential, allow lower case k for K (Kelvin)

Correct answer with units scores M1, M2 and M3

2.3 (K) scores M1 and M2 but not M3

1

Above the boiling point of water (therefore too high to be sensible) / water would evaporate

Can only score this mark if M3 >373 K

1

(e) $\Delta S = (\Delta H - \Delta G) / T$ OR $\Delta S = (\Delta G - \Delta H) / -T$

1

$$= ((-15 + 9) \times 1000) / 298 \text{ OR } (-15 + 9) / 298$$

1

$= -20 \text{ J K}^{-1} \text{ mol}^{-1}$ OR $-0.020 \text{ kJ K}^{-1} \text{ mol}^{-1}$

(allow -20 to -20.2) (allow -0.020 to -0.0202)

Answer with units must be linked to correct M2

For M3, units must be correct

Correct answer with appropriate units scores M1, M2 and M3 and possibly M1 in part (d) if not already given

Correct answer without units scores M1 and M2 and possibly M1 in part (d) if not already given

Answer of -240 / -0.24 means temperature of 25 used instead of 298 so scores M1 only

If ans = $+20$ / $+0.020$ assume AE and look back to see if M1 and possibly M2 are scored

1

[13]

8

- (a) Enthalpy change (to separate) 1 mol of an (ionic) substance into its ions

If ionisation or hydration / solution, CE = 0

If atoms / molecules / elements mentioned, CE = 0

Allow heat energy change but not energy change alone.

If forms 1 mol ions, lose M1

1

Forms ions in the gaseous state

If lattice formation not dissociation, allow M2 only.

Ignore conditions.

Allow enthalpy change for

$\text{MX(s)} \rightarrow \text{M}^+(\text{g}) + \text{X}^-(\text{g})$ (or similar) for M1 and M2

1

- (b) Any **one** of:

- Ions are point charges
- Ions are perfect spheres
- Only electrostatic attraction / bonds (between ions)
- No covalent interaction / character
- Only ionic bonding / no polarisation of ions

If atoms / molecules mentioned, CE = 0

1 max

- (c) (Ionic) radius / distance between ions / size

Allow in any order.

Do not allow charge / mass or mass / charge.

1

(Ionic) charge / charge density

Do not allow 'atomic radius'.

1

(d) $\Delta H_L = \Delta H_a(\text{chlorine}) + \Delta H_a(\text{Ag}) + \text{I.E.}(\text{Ag}) + \text{EA}(\text{Cl}) - \Delta H_f^\ominus$

Or cycle

If AgCl_2 , $\text{CE}=0 / 3$

1

$$= 121 + 289 + 732 - 364 + 127$$

1

$$= (+) 905 \text{ (kJ mol}^{-1}\text{)}$$

Allow 1 for -905

Allow 1 for (+)844.5 (use of 121 / 2)

Ignore units even if incorrect.

1

(e) M1 Greater

Do not penalise AgCl_2

1

M2 (Born-Haber cycle method allows for additional) covalent interaction

Allow AgCl has covalent character.

Only score M2 if M1 is correct

OR

M1 Equal

M2 AgCl is perfectly ionic / no covalent character

1

[10]

9

(a) Chloride (ions) are smaller (than bromide ions)

Must state or imply ions.

Allow chloride has greater charge density (than bromide).

Penalise chlorine ions once only (max 2 / 3).

1

So the force of attraction between chloride ions and water is stronger

This can be implied from M1 and M3 but do not allow intermolecular forces.

1

Chloride ions attract the δ^+ on H of water / electron deficient H on water

Allow attraction between ions and polar / dipole water.

*Penalise H^+ (ions) and mention of hydrogen bonding for **M3***

Ignore any reference to electronegativity.

Note: If water not mentioned can score M1 only.

1

(b) $\Delta H_{\text{solution}} = \Delta H_{\text{L}} + \Delta H_{\text{hyd}} \text{ K}^+ \text{ ions} + \Delta H_{\text{hyd}} \text{ Br}^- \text{ ions} / = 670 - 322 - 335$

Allow $\Delta H_{\text{solution}} = \Delta H_{\text{L}} + \Sigma \Delta H_{\text{hyd}}$

1

= (+)13 (kJ mol⁻¹)

Ignore units even if incorrect.

+13 scores M1 and M2

-13 scores 0

-16 scores M2 only (transcription error).

1

(c) (i) The entropy change is positive / entropy increases

ΔS is negative loses M1 and M3

1

Because 1 mol (solid) → 2 mol (aqueous ions) / no of particles increases

Allow the aqueous ions are more disordered (than the solid).

Mention of atoms / molecules loses M2

1

Therefore $T\Delta S > \Delta H$

1

(ii) Amount of KCl = $5/M_r = 5/74.6 = 0.067(0)$ mol

If moles of KCl not worked out can score M3, M4 only (answer to M4 likely to be 205.7 K)

1

Heat absorbed = $17.2 \times 0.0670 = 1.153$ kJ

Process mark for M1 × 17.2

1

Heat absorbed = mass × sp ht × ΔT

$(1.153 \times 1000) = 20 \times 4.18 \times \Delta T$

If calculation uses 25 g not 20, lose M3 only (M4 = 11.04, M5 = 287)

1

$\Delta T = 1.153 \times 1000 / (20 \times 4.18) = 13.8$ K

If 1000 not used, can only score M1, M2, M3

M4 is for a correct ΔT

Note that 311.8 K scores 4 (M1, M2, M3, M4).

1

$T = 298 - 13.8 = 284(.2)$ K

If final temperature is negative, M5 = 0

Allow no units for final temp, penalise wrong units.

1

[13]

10

- (a) (i) (At 0 K) particles are stationary / not moving / not vibrating

Allow have zero energy.

Ignore atoms / ions.

1

No disorder / perfect order / maximum order

Mark independently.

1

- (ii) As T increases, particles start to move / vibrate

Ignore atoms / ions.

Allow have more energy.

If change in state, $CE = 0$

1

Disorder / randomness increases / order decreases

1

- (iii) Mark on temperature axis vertically below second 'step'

Must be marked as a line, an 'x', T_b or 'boiling point' on the temperature axis.

1

- (iv) L_2 corresponds to boiling / evaporating / condensing / $l \rightarrow g$ / $g \rightarrow l$

And L_1 corresponds to melting / freezing / $s \rightarrow l$ / $l \rightarrow s$

There must be a clear link between L_1 , L_2 and the change in state.

1

Bigger change in disorder for L_2 / boiling compared with L_1 / melting

M2 answer must be in terms of changes in state and not absolute states eg must refer to change from liquid to gas not just gas.

Ignore reference to atoms even if incorrect.

1

- (b) (i) $\Delta G = \Delta H - T\Delta S$

1

$\Delta H = c$ and $(-)\Delta S = m$ / ΔH and ΔS are constants (approx)

Allow ΔH is the intercept, and $(-)\Delta S$ is the slope / gradient.

Can only score M2 if M1 is correct.

1

- (ii) Because the entropy change / ΔS is positive / $T\Delta S$ gets bigger

Allow $-T\Delta S$ gets more negative

1

- (iii) Not feasible / unfeasible / not spontaneous

1

(c) (i) $+ 44.5 \text{ J K}^{-1} \text{ mol}^{-1}$

*Allow answer without units but if units given they must be correct
(including mol^{-1})*

1

(c) (ii) At 5440 $\Delta H = T\Delta S$

$= 5440 \times 44.5 = 242\,080$

1

(OR using given value $= 5440 \times 98 = 533\,120$)

Mark is for answer to (c)(i) $\times 5440$

1

$\Delta H = 242 \text{ kJ mol}^{-1}$

(OR using given value $\Delta H = 533 \text{ kJ mol}^{-1}$)

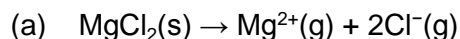
Mark is for correct answer to M2 with correct units (J mol^{-1} or kJ mol^{-1}) linked to answer.

If answer consequentially correct based on (c)(i) except for incorrect sign (eg -242), max 1 / 3 provided units are correct.

1

[15]

11



1

(b) The magnesium ion is smaller / has a smaller radius / greater charge density (than the calcium ion)

If not ionic or if molecules / IMF / metallic / covalent / bond pair / electronegativity mentioned, CE = 0

1

Attraction between ions / to the chloride ion stronger

Allow ionic bonds stronger

Do not allow any reference to polarisation or covalent character

Mark independently

1

(c) The oxide ion has a greater charge / charge density than the chloride ion

If not ionic or if molecules / IMF / metallic / covalent / bond pair mentioned, CE = 0

Allow oxide ion smaller than chloride ion

1

So it attracts the magnesium ion more strongly

Allow ionic bonds stronger

Mark independently

1

(d) $\Delta H_{\text{solution}} = \Delta H_{\text{L}} + \Sigma \Delta H_{\text{hyd}} \text{Mg}^{2+} \text{ ions} + \Sigma \Delta H_{\text{hyd}} \text{Cl}^{-} \text{ ions}$

Allow correct cycle

1

$$-155 = 2493 + \Delta H_{\text{hyd}} \text{Mg}^{2+} \text{ ions} - 2 \times 364$$

$$\Delta H_{\text{hyd}} \text{Mg}^{2+} \text{ ions} = -155 - 2493 + 728$$

1

$$= -1920 \text{ (kJ mol}^{-1}\text{)}$$

Ignore units

Allow max 1 for +1920

Answer of + or -1610, CE = 0

Answer of -2284, CE = 0

1

(e) Water is polar / O on water has a delta negative charge

Allow O (not water) has lone pairs (can score on diagram)

1

Mg²⁺ ion / +ve ion / + charge attracts (negative) O on a water molecule

Allow Mg²⁺ attracts lone pair(s)

M2 must be stated in words (QoL)

Ignore mention of co-ordinate bonds

CE = 0 if O²⁻ or water ionic or H bonding

1

(f) Magnesium oxide reacts with water / forms Mg(OH)₂

Allow MgO does not dissolve in water / sparingly soluble / insoluble

1

[11]

12

(a) $\Delta G = \Delta H - T\Delta S$

Or expression $\Delta H - T\Delta S$ must be evaluated

1

If ΔG / expression ≤ 0 reaction is feasible

Or any explanation that this expression ≤ 0

Do not allow just $\Delta G = 0$

1

(b) The molecules become more disordered / random when water changes from a liquid to a gas / evaporates

For M1 must refer to change in state AND increase in disorder

1

Therefore the entropy change is positive / Entropy increases

Only score M2 if M1 awarded

1

$$T\Delta S > \Delta H$$

Allow M3 for T is large / high (provided M2 is scored)

1

$$\Delta G < 0$$

Mark M3, M4 independently

1

(c) (i) Condition is $T = \Delta H / \Delta S$

1

$$\Delta S = 189 - 205 / 2 - 131 = -44.5;$$

1

$$\Delta H = -242 \text{ therefore } T = (-242 \times 1000) / -44.5$$

1

$$= 5438 \text{ K (allow 5400 - 5500 K)}$$

Units essential (so 5438 alone scores 3 out of 4)

2719 K allow score of 2

5.4 (K) scores 2 for M1 and M2 only

1646 (K) scores 1 for M1 only

1

(ii) It would decompose into hydrogen and oxygen / its elements

Can score this mark if mentioned in M2

1

Because ΔG for this reaction would be ≤ 0

Allow the reverse reaction / decomposition is feasible

Only score M2 if M1 awarded

1

(d) $\Delta H = T\Delta S$

Allow correct substituted values instead of symbols

1

$$\Delta S = 70 - 189 = -119 \text{ JK}^{-1} \text{ mol}^{-1}$$

1

$$\Delta H = (-119 \times 373) / 1000 = -44.4 \text{ kJ (mol}^{-1}\text{)} \text{ (allow -44 to -45)}$$

Allow -44000 to -45000 J (mol⁻¹)

Answer must have correct units of kJ or J

1

[15]

13

(a) $\Delta G = \Delta H - T\Delta S$

Ignore e

1

(b) 0.098 or 98

Allow 0.097 to 0.099/97 to 99

Allow 0.1 only if 0.098 shown in working

1

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

$\text{J K}^{-1} \text{mol}^{-1}$

Allow in any order

Unless slope is approx. 100(90-110) accept only $\text{kJ K}^{-1} \text{mol}^{-1}$. If no slope value given, allow either units

1

$-\Delta S/\Delta S$

1

- (c) ΔG becomes negative

Mark independently unless ΔG +ve then $CE = 0$

1

So reaction becomes spontaneous/feasible

Or reaction can occur below this temperature

Or reaction is not feasible above this temperature

1

- (d) Ammonia liquefies (so entropy data wrong/different)

Allow any mention of change in state or implied change in state even if incorrect

eg freezing/boiling

1

[7]

14

- (a) Enthalpy change/heat energy change when one mole of gaseous atoms

Allow explanation with an equation that includes state symbols

1

Form (one mole of) gaseous negative ions (with a single charge)

If ionisation/ionisation energy implied, $CE=0$ for both marks

Ignore conditions

1

- (b) Fluorine (atom) is smaller than chlorine/shielding is less/ outer electrons closer to nucleus

Fluorine molecules/ions/charge density $CE=0$ for both marks

1

(Bond pair of) electrons attracted more strongly to the nucleus/protons

1

- (c) Fluoride (ions) smaller (than chloride) / have larger charge density

Any reference to electronegativity $CE=0$

1

So (negative charge) attracts (δ^+ hydrogen on) water more strongly

Allow H on water, do not allow O on water

Allow F^- hydrogen bonds to water, chloride ion does not

Mark independently

1

(d) (i) $\Delta H(\text{solution}) = LE + \Sigma(\text{hydration enthalpies})$ / correct cycle

AgF₂ or other wrong formula CE = 0

Ignore state symbols in cycle

1

$$LE = -20 - (-464 + -506)$$

1

$$= (+) 950 \text{ kJ mol}^{-1}$$

Ignore no units, penalise M3 for wrong units

-950 scores max 1 mark out of 3

990 loses M3 but M1 and M2 may be correct

808 is transfer error (AE) scores 2 marks

848 max 1 if M1 correct

1456 CE=0 (results from AgF₂)

1

(ii) There is an increase in the number of particles / more disorder / less order

Allow incorrect formulae and numbers provided number increases

Do not penalise reference to atoms/molecules

Ignore incorrect reference to liquid rather than solution

1

(iii) Entropy change is positive/entropy increases and enthalpy change negative/exothermic

1

So ΔG is (always) negative

1

[12]

15

(a) $\Delta H = \Sigma(\Delta H_f \text{ products}) - \Sigma(\Delta H_f \text{ reactants})$

Allow correct cycle

1

$$/= +34 - +90$$

$$= -56 \text{ kJ mol}^{-1}$$

Ignore no units, penalise incorrect units

1

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

1

$$\Delta H = 240 - (205 + 211/2)$$

$$= -70.5 \text{ J K}^{-1} \text{ mol}^{-1} / -0.0705 \text{ kJ K}^{-1} \text{ mol}^{-1}$$

Ignore no units, penalise incorrect units

Allow -70 to -71/-0.070 to -0.071

1

(c) $T = \Delta H/\Delta S$ / $T = (\text{Ans to part(a)} \times 1000)/\text{ans to part(b)}$

Mark consequentially on answers to parts (a) and (b)

1

$$\Delta H = -56 / (-70.5 \div 1000)$$

$$= 794 \text{ K (789 to 800 K)}$$

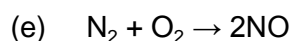
Must have correct units

Ignore signs; allow + or – and –ve temps

1

(d) Temperatures exceed this value

1



Allow multiples

1

(f) there is no change in the number of moles (of gases)

Can only score these marks if the equation in (e) has equal number of moles on each side

Numbers, if stated must match equation

1

So entropy/disorder stays (approximately) constant / entropy/disorder change is very small / $\Delta S=0$ / $T\Delta S=0$

1

[10]

16

(a) Enthalpy change when 1 mol of an (ionic) compound/lattice (under standard conditions)

Allow heat energy change

1

Is dissociated/broken/separated into its (component) ions

1

The ions being in the gaseous state (at infinite separation)

Mark independently. Ignore any conditions.

1

- (b) There is an attractive force between the nucleus of an O atom and an external electron.
Allow any statement that implies attraction between the nucleus and an electron 1
- (c) $Mg^{2+}(g) + O(g) + 2e^{-}$
Ignore lack of state symbols
Penalise incorrect state symbols 1
- $Mg^{2+}(g) + O^{-}(g) + e^{-}$ 1
- $Mg^{2+}(g) + O^{2-}(g)$ 1
- First new level for Mg^{2+} and O above last on L
If levels are not correct allow if steps are in correct order with arrows in the correct direction and correct ΔH values 1
- Next level for Mg^{2+} and O^{-} below that
- Next level for Mg^{2+} and O^{2-} above that and also above that for Mg^{2+} and O
Allow +124
Allow M4 with incorrect number of electrons
- (d) LE $MgO = 602 + 150 + 736 + 1450 + 248 - 142 + 844$
Note use of 124 instead of 248 CE=0 1
- $= +3888 \text{ kJ mol}^{-1}$
Allow 1 for -3888
Allow no units
Penalise wrong units 1
- (e) Forms a protective layer/barrier of MgO / MgO prevents oxygen attacking Mg
Allow activation energy is (very) high
Allow reaction (very) slow 1
- (f) $\Delta G = \Delta H - T\Delta S$

$$\Delta S = \frac{(\Delta H - \Delta G)}{T}$$
 1
- $\Delta S = (-602 - (-570)) \times 1000 / 298$ 1

$$= -107 \text{ J K}^{-1} \text{ mol}^{-1} / -0.107 \text{ kJ K}^{-1} \text{ mol}^{-1}$$

If units not correct or missing, lose mark

Allow -107 to -108

+107 with correct units scores max 1/3

1

- (g) 1 mol of solid and 0.5 mol of gas reactants form 1 mol solid products

Decrease in number of moles (of gas/species)

Allow gas converted into solid

Numbers of moles/species, if given, must be correct

1

System becomes more ordered

Allow consequential provided ΔS is -ve in 1(f)

If ΔS is +ve in 1(f) can only score M1

1

[16]

17

- (a) Standard pressure (100 kPa) (and a stated temperature)

Allow standard conditions. Do not allow standard states

Allow any temperature

Allow 1 bar but not 1atm

Apply list principle if extra wrong conditions given

Penalise reference to concentrations

1

- (b) Hydrogen bonds between water molecules

1

Energy must be supplied in order to break (or loosen) them

Allow M2 if intermolecular forces mentioned

Otherwise cannot score M2

CE = 0/2 if covalent or ionic bonds broken

1

- (c) $T = \Delta H / \Delta S$

1

$$= (6.03 \times 1000) / 22.1$$

1

= 273 K

Allow 272 to 273; units K must be given

Allow 0°C if units given

0.273 (with or without units) scores 1/3 only

Must score M2 in order to score M3

Negative temperature can score M1 only

1

(d) The heat given out escapes

1

(e) (Red end of white) light (in visible spectrum) absorbed by ice

Allow complementary colour to blue absorbed

1

Blue light / observed light is reflected / transmitted / left

Penalise emission of blue light

1

[9]

18

(a) (i) (Enthalpy change for formation of) 1 mol (of CaF_2) from its ions

allow heat energy change

do not allow energy or wrong formula for CaF_2

penalise 1 mol of ions

CE=0 if atoms or elements or molecules mentioned

ignore conditions

1

ions in the gaseous state

ions can be mentioned in M1 to score in M2

allow fluorine ions

$\text{Ca}^{2+}(\text{g}) + 2\text{F}^{-}(\text{g}) \rightarrow \text{CaF}_2$ scores M1 and M2

1

(ii) (enthalpy change when) 1 mol of gaseous (fluoride) ions (is converted) into aqueous ions / an aqueous solution

allow $\text{F}^{-}(\text{g}) \rightarrow \text{F}^{-}(\text{aq})$ (ignore + aq)

do not penalise energy instead of enthalpy

allow fluorine ions

do not allow F^{-} ions surrounded by water

1

(b) water is polar / H on water is $\delta+$ / is electron deficient / is unshielded

1

penalise H^+ on water 1 mark

(F^- ions) attract water / $\delta+$ on H / hydrogen

allow H on water forms H-bonds with F^-

allow fluorine ions

penalise co-ordinate bonds for M2

penalise attraction to O for M2

1

(c) $\Delta H = -(-2611) - 1650 + 2x - 506$

ignore cycles

M1 is for numbers and signs correct in expression

1

$= -51 \text{ (kJ mol}^{-1}\text{)}$

correct answer scores 2

ignore units even if incorrect

1

[7]

19

(a) $\text{KNO}_3(\text{s}) \rightarrow \text{K}^+(\text{aq}) + \text{NO}_3^-(\text{aq})$

do not allow equations with H_2O

allow aq and the word 'water' in equation

1

(b) increase in disorder because solid \rightarrow solution / increase in number of particles / 1 mol (solid) gives 2 mol (ions/particles) / particles are more mobile

allow random or chaos instead of disorder

penalise if molecules/atoms stated instead of ions

allow any reference to increase in number of particles even if number of particles wrong

1

(c) $\Delta G = \Delta H - T\Delta S / T = \Delta H/\Delta S$ 1

$T = \Delta H/\Delta S = (34.9 \times 1000)/117$
also scores M1 1

$= 298 \text{ K}$
correct answer scores 3, units essential
0.298 scores M1 only 1

(d) (i) positive / increases / $\Delta G > 0$
Allow more positive 1

(ii) if ans to (d) (i) positive, dissolving is no longer spontaneous / no longer feasible / potassium nitrate does not dissolve / less soluble

if ans to (d) (i) negative, dissolving is spontaneous / feasible / potassium nitrate dissolves / more soluble
If no mention of change to ΔG in (d)(i),
Mark = 0 for (d)(ii) 1

[7]

20

(a) (i) $\Delta H = \Sigma \text{ bonds broken} - \Sigma \text{ bonds formed}$ 1

$= 944/2 + 3/2 \times 436 - 3 \times 388$ 1

$= -38 \text{ (kJ mol}^{-1}\text{)}$
ignore units even if incorrect
correct answer scores 3
-76 scores 2/3
+38 scores 1/3 1

(ii) mean / average bond enthalpies are from a range of compounds
or
mean / average bond enthalpies differ from those in a single compound / ammonia 1

(b) $\Delta S = \Sigma S \text{ products} - \Sigma S \text{ reactants}$ 1

$= 193 - (192/2 + 131 \times 3/2)$ 1

$= -99.5 \text{ J K}^{-1} \text{ mol}^{-1}$

units essential for M3

correct answer with units scores 3

-199 J K⁻¹ mol⁻¹ & -99.5 score 2/3

-199 and + 99.5 J K⁻¹ mol⁻¹ score 1/3

1

(c) (i) $\Delta G = \Delta H - T\Delta S = -46 + 800 \times 99.5/1000$
mark is for putting in numbers with 1000
if factor of 1000 used incorrectly CE = 0

1

$= 33.6 \text{ or } 33600$

allow 33 to 34 (or 33000 to 34000)

1

kJ mol^{-1} with J mol^{-1}

correct units for answer essential

if answer to part (b) is wrong or if -112 used, mark consequentially
e.g.

• *-199 gives 113 to 114 kJ mol⁻¹ (scores 3/3)*

• *-112 gives 43 to 44 kJ mol⁻¹ (scores 3/3)*

1

(ii) If answer to (c) (i) is positive: not feasible / not spontaneous

If answer to (c) (i) is negative: feasible / spontaneous

if no answer to (c) (i) award zero marks

1

[11]

21

- (a) Enthalpy change for the formation of 1 mol of gaseous atoms
allow heat energy change for enthalpy change 1

From the element (in its standard state)
ignore reference to conditions 1

Enthalpy change to separate 1 mol of an ionic lattice/solid/compound
enthalpy change not required but penalise energy 1

Into (its component) gaseous ions
mark all points independently 1

- (b) $\Delta H_L = -\Delta H_f + \Delta H_a + \text{I.E.} + 1/2E(\text{Cl-Cl}) + \text{EA}$
Or correct Born-Haber cycle drawn out 1

$$= +411 + 109 + 494 + 121 - 364$$
 1

$$= +771 \text{ (kJ mol}^{-1}\text{)}$$

-771 scores 2/3
+892 scores 1/3
-51 scores 1/3
-892 scores zero
+51 scores zero ignore units 1

- (c) (i) Ions are perfect spheres (or point charges) 1

Only electrostatic attraction/no covalent interaction
mention of molecules/intermolecular forces/covalent bonds
CE = 0
allow ionic bonding only
If mention of atoms CE = 0 for M2 1

- (ii) Ionic
Allow no covalent character/bonding 1

- (iii) Ionic with additional covalent bonding
Or has covalent character/partially covalent
Allow mention of polarisation of ions or description of polarisation

1

[11]

22

- (a) Because it is a gas compared with solid carbon
Mark independently

1

Nitrogen is more disordered/random/chaotic/free to move

1

- (b) 0 K/-273 C/absolute zero

1

- (c) $\Delta G = \Delta H - T\Delta S$

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

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

$\Delta S = (\Delta H - \Delta G)/T$

Ignore e in ΔG^\ominus

1

- (d) ΔG is less than or equal to zero ($\Delta G \leq 0$)

Allow ΔG is less than zero ($\Delta G < 0$)

Allow ΔG is equal to zero ($\Delta G = 0$)

Allow ΔG is negative

1

- (e) When $\Delta G = 0$ $T = \frac{\Delta H}{\Delta S}$

1

$\Delta H = +90.4$

Allow $\Delta H = +90$

1

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

1

$\Delta S = 211.1 - 205.3/2 - 192.2/2 = \underline{12.35}$

1

$T = (90.4 \times 1000)/12.35 = 7320 \text{ K}/7319.8 \text{ K}$

Allow 7230 to 7350 K (Note 7.32 K scores 4 marks)

Units of temperature essential to score the mark

1

- (f) Activation energy is high
Allow chemical explanation of activation energy
Allow needs route with lower activation energy
Allow catalyst lowers activation energy 1
- (g) $\Delta H = 1.9 \text{ (kJ mol}^{-1}\text{)}$ 1
- $\Delta S = 2.4 - 5.7 = -3.3 \text{ (J K}^{-1} \text{ mol}^{-1}\text{)}$
for M1 and M2 allow no units, penalise wrong units 1
- ΔG is always positive
This mark can only be scored if ΔH is +ve and ΔS is -ve 1

[14]

23

- (a) $\text{CaF}_2(\text{s}) \rightarrow \text{Ca}^{2+}(\text{g}) + 2\text{F}^{-}(\text{g})$ 1
- (b) (i) Enthalpy change for formation of 1 mol of substance
Allow heat energy change, NOT energy 1
- From its elements 1
- Reactants and products/all substances in their standard states
Or normal states at 298 K, 1 bar (100 kPa) 1
- (ii) $\text{Ca}(\text{s}) + \text{F}_2(\text{g}) \rightarrow \text{CaF}_2(\text{s})$ 1
- (iii) $\Delta H_f(\text{CaF}_2) = \Delta H_a(\text{Ca}) + 1\text{st IE}(\text{Ca}) + 2^{\text{nd}} \text{IE}(\text{Ca}) + \text{BE}(\text{F}_2) + 2 \times \text{EA}(\text{F}) - \Delta H_L(\text{CaF}_2)$
Or labelled diagram 1
- $= 193 + 590 + 1150 + 158 + (2 \times -348) - 2602$ 1
- $= -1207 \text{ kJ mol}^{-1}$
- Correct answer scores 3*
-842 scores 2 (transfer error)
-859 scores 1 only (using one E.A.)
Units not required, wrong units lose 1 mark 1

(c) Electrostatic attraction stronger/ionic bonding stronger/attraction between ions stronger/more energy to separate ions
Molecular attraction/atoms/intermolecular forces CE=0 1

Because fluoride (ion) smaller than chloride
Do not allow F or fluorine 1

(d) (i) $\Delta H = \Delta H_L + \Sigma\Delta H_{\text{hyd}} = 2237 - 1650 + (2 \times -364)$
Can be on cycle/diagram 1

$= -141 \text{ kJ mol}^{-1}$
Correct answer scores 2
Units not required, wrong units lose 1 mark 1

(ii) Decreases
If ans to (d)(i) positive allow increases 1

Reaction exothermic/ ΔH -ve
If (d)(i) +ve allow endothermic/ ΔH + ve 1

(Equilibrium) shifts to left/backwards
(as temperature rises)/equilibrium
opposes the change
If (d) (i) +ve allow shifts to right/forwards/equilibrium opposes the change
If no answer to (d) (i) assume -ve ΔH used
If effect deduced incorrectly from any ΔH CE = 0 for these 3 marks 1

(e) u.v. absorbed: electrons/they move to higher energy
(levels)/electrons excited 1

visible light given out: electrons/they fall back down/move to lower energy (levels)
Must refer to absorbing u.v. NOT visible light or this must be implied. 1

[17]

24

(a) $\Delta H = \Sigma\Delta H_f(\text{products}) - \Sigma\Delta H_f(\text{reactants})$

1

$$= -201 - 242 - (-394)$$

1

$$= -49 \text{ kJ mol}^{-1}$$

+49 kJ mol⁻¹ = 1 mark

units not required, wrong units lose 1 mark

1

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

1

$$= 238 + 189 - (214 + 3 \times 131)$$

1

$$= -180 \text{ J K}^{-1} \text{ mol}^{-1}$$

+180 = 1 mark

units not required, wrong units lose 1 mark

1

(c) $\Delta G = \Delta H - T\Delta S$

If use G not ΔG penalise M1 but not M2 and M3

1

(ΔS is negative so) at high temp $-T\Delta S$ (is positive and) greater than ΔH/large

Do not award M2 or M3 if positive ΔS value used

1

So $\Delta G > 0$

Independent mark unless positive ΔS value used

1

(Limiting condition $\Delta G = 0$ so) $T = \Delta H/\Delta S$

1

$$= 272 \text{ K}$$

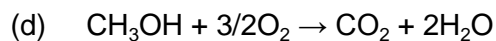
Allow 297-298 if used given values.

Do not award M5 if T -ve or if M4 should give T -ve

1

Reaction is too slow at this temperature/to speed up the reaction

1



Allow multiples.

Ignore state symbols.

Do not allow equation for wrong compound but mark on provided number of moles increases or stays the same.

If no equation or equation that gives a decrease in the number of moles,

CE = 0

1

2.5 mol give 3 mol (gases)

Allow statement 'increase in number of moles/molecules'

If numerical values given, they must match the equation in M1

Ignore the effect of incorrect state symbols on the number of moles of particles unless used correctly

1

Therefore ΔS is positive/entropy increases

If correct deduction from wrong equation is $\Delta S = 0$ or ΔS very small must say H -ve

1

(combustion exothermic so ΔH -ve so $\Delta H - T\Delta S$) and hence ΔG always negative (less than zero)

1

Allow G instead of ΔG

Can score 3 out of 4 marks if equation wrong but leads to increase or no change in number of moles

M4 dependent on M3

Note, if equation wrong AND there is an incorrect deduction about the change in number of moles, CE = 0

(e) $\text{CO}_2/\text{CO}/\text{CH}_4$ may be produced during H_2 manufacture/building the plant/transport /operating the plant

1

[17]

25

(a) 242

Units not essential

1

(b) Bond is shorter or bonding pair closer to nucleus
Allow Cl is a smaller atom
Allow fewer electron shells
do not allow smaller molecules 1

So attraction (between nucleus and) (to) bond pair is stronger
Allow shared pair (or bonding electrons) held more tightly
Mention of Cl⁻ loses M2 1

(c) Net attraction between the chlorine nucleus and the extra electron
Allow Cl⁻ ion more stable than Cl 1

(d) (i) step 1 $\text{Ag(s)} \rightarrow \text{Ag(g)}$ only change 1

step 2 $\text{Ag(s)} \rightarrow \text{Ag}^+(\text{g}) + \text{e}^-$ only change 1

step 3 $\frac{1}{2}\text{Cl}_2(\text{g}) \rightarrow \text{Cl(g)}$ only change
This step can be first, second or third 1

(ii) $127 + 289 + 732 + 121 - 364$ 1

 $= 905 \text{ kJ mol}^{-1}$
-905 scores 1 mark only 1

(e) (i) Ions can be regarded as point charges (or perfect spheres)
Allow no polarisation
OR *only bonding is ionic*
OR *no covalent character* 1

(ii) Greater
Electronegativity argument or mention of intermolecular,
CE = 0 1

Chloride ions are smaller than bromide
Mark independently but see above 1

They are attracted more strongly to the silver ions
Mark independently 1

(iii) AgCl has covalent character
Ignore reference to molecules 1

Forces in the lattice are stronger than pure ionic attractions
Allow stronger bonding OR additional/extra bonding 1

[15]

26

(a) (i) $1s^2 2s^2 2p^6 3s^2 3p^6$ 1

(ii) The negative S^- ion 1

repels the added electron 1

(iii) Step B is the atomisation enthalpy of sulphur 1

Step D is the second ionisation enthalpy of calcium 1

(iv) Electrons nearer to the nucleus 1

Electrons removed from a positive species or
more strongly attracted 1

(v) $+178 +279 +590 +1145 -200 + 539 + G + 482 = 0$ 1

$G + 3013 = 0$ hence $G = -3013$ 1

(b) The model used assumes the ions are spherical and in a lattice 1

The calculated value is smaller than the cycle value or
stronger attraction 1

Indicating some covalent character or ions are polarised 1

- (c) (i) For a reaction to occur $\Delta G < 0$ 1
- ΔS is positive and large as a gas is evolved 1
- $T\Delta S$ is larger than ΔH and ΔG is negative 1
- (ii) ΔS is negative 1
- Four moles gaseous reactant forming or more moles of gaseous product 1
- At high temperature $T\Delta S$ is larger than ΔH and ΔG is positive 1

[18]

27

- (a) Particles are in maximum state of order 1
(or perfect order or completely ordered or perfect crystal or minimum disorder or no disorder)
(entropy is zero at 0 k by definition)
- (b) (Ice) melts 1
(or freezes or changes from solid to liquid or from liquid to solid)
- (c) Increase in disorder 1
 Bigger (at T_2) 1
Second mark only given if first mark has been awarded
- (d) (i) Moles of water = $1.53/18$ (= 0.085) 1
- Heat change per mole = $3.49/0.085 = 41.1$ (kJ mol^{-1})
(allow 41 to 41.1, two sig. figs.)
(penalise -41 (negative value), also penalise wrong units but allow kJ only) 1

(ii) $\Delta G = \Delta H - T\Delta S$ 1

(iii) $\Delta H = T\Delta S$ or $\Delta S = \Delta H/T$
(penalise if contradiction) 1

$\Delta S = 41.1/373 = 0.110 \text{ kJ K}^{-1} (\text{mol}^{-1})$ (or $110 \text{ (J K}^{-1} (\text{mol}^{-1}))$)
(allow 2 sig. figs.)
(if use value given of 45, answer is 0.12 (or 120 to 121))
(if ΔH is negative in (d) (i), allow negative answer)
(if ΔH is negative in (d) (i), allow positive answer)
(if ΔH is positive in (d) (i), penalise negative answer) 1

Correct units as above (mol^{-1} not essential) 1

[10]

C
28 [1]

C
29 [1]

A
30 [1]

31 (a) $1s^2 2s^2 2p^6 3s^2 3p^6$ 1

(b) $S^-(g)$ 1

(c) The negative S^- ion 1

repels the electron being added 1

(d) (i) Enthalpy of atomisation of sulphur 1

(ii) Second ionisation enthalpy of calcium 1

(iii) Second electron affinity of sulphur 1

- (e) Electron more strongly attracted 1
- nearer to the nucleus or attracted by Ca^+ ion 1
- (f) Correct cycle
- e.g. $+ 178 + 279 + 590 + 1145 - 200 + E - 3013 + 482 = 0$ 1
- $= 539$ 1
- Allow one mark for $- 539$

[11]

B
32 [1]

A
33 [1]

- 34** (a) (i) ΔH atomisation/sublimation of magnesium 1
- (ii) Bond/dissociation enthalpy of Cl-Cl 1
- OR $2 \times H$ atomisation of chlorine
- (iii) Second ionisation enthalpy of magnesium 1
- (iv) $2 \times$ electron affinity of chlorine 1
- (v) Lattice formation enthalpy of MgCl_2 1

(b) Equation $2\text{MgCl(s)} \rightarrow \text{MgCl}_2\text{(s)} + \text{Mg(s)}$
State symbols not required but penalise if incorrect 1

Calculation $\Delta H_{\text{reaction}} = \Sigma\Delta H_f \text{ products} - \Sigma\Delta H_f \text{ reactants}$ 1

$= -653 - (2 \times -133)$ 1

$= -427 \text{ (kJmol}^{-1}\text{)}$

Allow +427 to score (1) mark

Other answers; award (1) for a correct ΔH reaction expression 1

(c) $\Delta H_{\text{soln MgCl}_2} = -\Delta H_{\text{Lat.form.}} + \Delta H_{\text{hyd.Mg}^{2+}} + 2\Delta H_{\text{hyd.Cl}^-}$ 1

or cycle

$= 2502 - 1920 - (2 \times 364)$ 1

$= -146 \text{ (kJmol}^{-1}\text{)}$

Allow +146 to score (1) mark

Other answers; award (1) for a correct $\Delta H_{\text{soln MgCl}_2}$ expression/cycle 1

[12]

35

- (a) M1 $K_p = (p_Y)^3 \cdot (p_Z)^2 / (p_W)^2 \cdot (p_X)$ NB [] wrong 1
- M2 temperature 1
- M3 increase 1
- M4 particles have more energy or greater velocity/speed 1
- M5 more collisions with $E > E_a$ or more successful collisions 1
- M6 Reaction exothermic or converse 1
- M7 Equilibrium moves in the left 1

Marks for other answers

Increase in pressure or concentration allow M1, M5, M6 Max 3

Addition of a catalyst; allow M1, M5, M6 Max 3

Decrease in temperature; allow M1, M2, M6 Max 3

Two or more changes made; allow M1, M6 Max 2

- (b) (i) Advantage; reaction goes to completion, not reversible or faster 1

Disadvantage; reaction vigorous/dangerous

(exothermic must be qualified)

or HCl(g) evolved/toxic

or CH₃COCl expensive

NB Allow converse answers

Do not allow reactions with other reagents e.g. water or ease of separation

1

(ii) $\Delta S = \Sigma S \text{ products} - \Sigma S \text{ reactants}$ 1

$$\Delta S = (259 + 187) - (201 + 161)$$
1

$$\Delta S = 84 \text{ (JK}^{-1} \text{ mol}^{-1}) \quad (\text{Ignore units})$$

Allow - 84 to score (1) mark

1

$$\Delta G = \Delta H - T\Delta S$$
1

$$= -21.6 - 298 \times 84/1000$$

$$= -46.6 \text{ kJ mol}^{-1} \text{ or } -46\,600 \text{ J mol}^{-1}$$
1

Allow (2) for - 46.6 without units

(Mark ΔG consequentially to incorrect ΔS)

(e.g. $\Delta S = -84$ gives $\Delta G = +3.4 \text{ kJ mol}^{-1}$)

1

[15]

36

(a) *Standard enthalpy change, ΔH^{\ominus} : $\Delta H_R = \Sigma \Delta H_{f \text{ products}} - \Sigma \Delta H_{f \text{ reactants}}$ (1)*
or cycle

$$\Delta H_R = (0 + [2 \times -242]) - (4 \times -92) \text{ (1)}$$

$$= -484 + 368$$

$$= -116 \text{ (kJ mol}^{-1}\text{)}$$

Allow max 1 for +116

Standard entropy change, ΔS^{\ominus} : $\Delta S = \Sigma \Delta H_{f \text{ products}} - \Sigma \Delta H_{f \text{ reactants}}$

$$\Delta S = ([2 \times 223] + [2 \times 189]) - (205 + [4 \times 187]) \text{ (1)}$$

$$= 824 - 953$$

$$= -129 \text{ (J K}^{-1} \text{ mol}^{-1}\text{)}$$

allow max one for +129

6

- (b) (i) *Effect:* Equilibrium displaced to right / to products **(1)**
Explanation: Reaction is endothermic **(1)**
 Constraint reduced **(1)**
mark separately

- (ii) Feasible when $\Delta G \leq 0$ **(1)**

$$\Delta G = \Delta H - T\Delta S \text{ (1)}$$

$$T = \Delta H / \Delta S = 208 \times 1000 \text{ (1)} / 253$$

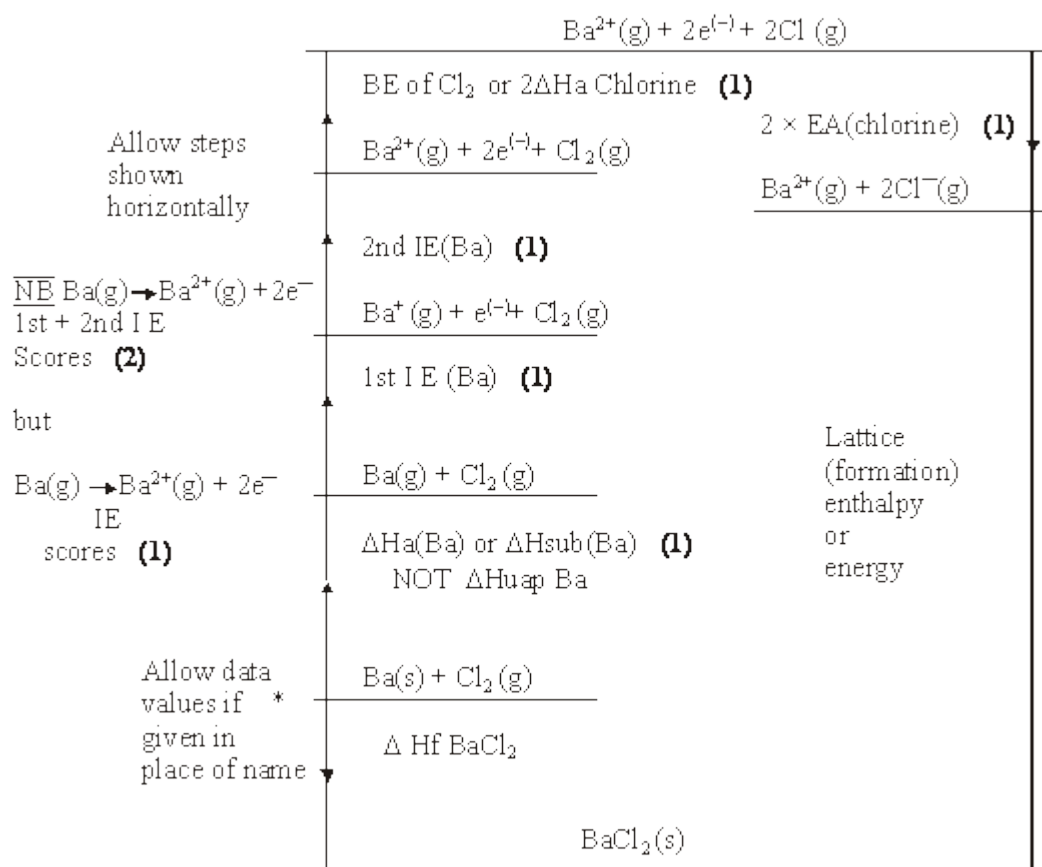
$$= 822 \text{ K (1)}$$

7

[13]

37

- (a) (i)



ONLY consider species involved in the step marked

(ii) Cycling clockwise about (*)

CE if step missing

$$\Delta H_a \text{Ba} + 1^{\text{st}} \text{IEBa} + 2^{\text{nd}} \text{IE Ba} + 2\Delta H_a \text{Cl} + 2\text{EACl} + \text{LE} - \Delta H_f \text{BaCl}_2 = 0 \text{ (1)}$$

$$+180 + 503 + 965 + 2 \times 122 + 2\text{EA} - 2056 + 859 = 0 \text{ (1)}$$

$$\text{EA} = -695/2 = - (347 \text{ to } 348) \text{ (1)}$$

Ignore units

Calculation -1 for each error

Mark conseq.

Notes: -695 scores (2)

+(347 to 348) scores (2)

-(286 to 287) scores (2)

+(286 to 287) scores (1)

-573 scores (1)

+573 scores (0)

9

(b) $\Delta S = \Sigma S \text{ products} - \Sigma S \text{ reactants}$
 $= (63 + 223) - 124 = 162 \text{ (1)}$

$$\Delta G = \Delta H - T\Delta S \quad \text{or} \quad \Delta H = T\Delta S \quad \text{or} \quad T = \Delta H/\Delta S \text{ (1)}$$

or used correctly

$$\Delta H = 859 \times 10^3 \text{ (1)} = T \times 162$$

$$T = (5\,300 \text{ to } 5304) \text{ K (1)}$$

Penalise if units °C

-1 for each error + mark conseq.

4

[13]

B
38

[1]

C
39

[1]

40

- (a) (i) *Standard enthalpy change:*
 $\Delta H_R = \Sigma\Delta H_f(\text{products}) - \Sigma\Delta H_f(\text{reactants})$ **(1)**

or cycle

$$\Delta H_R = ([2 \times 0] + [3 \times -393.5]) - (-824.2 + [3 \times -110.5])$$
 (1)
 $= -24.8 \text{ (kJ mol}^{-1}\text{)}$ **(1)**

Allow + 24.8 max one

Standard entropy change: $\Delta S = \Sigma S(\text{products}) - \Sigma S(\text{reactants})$ **(1)**

$$\Delta S = ([2 \times 27.3] + [3 \times 213.6]) - (87.4 + [3 \times 197.6])$$
 (1)
 $= (54.6 + 640.8) - (87.4 + 592.8)$ **(1)**
 $= 15.2 \text{ (JK}^{-1}\text{mol}^{-1}\text{)}$ **(1)**

Allow -15.2 max one

- (ii) $\Delta G = \Delta H - T\Delta S$ **(1)**
 ΔH negative and $-T\Delta S$ is negative **(or ΔS positive or or correct calc) (1)**
 Hence ΔG is always negative
(or feasible when $\Delta G \leq 0$) (1)

9

- (b) $\Delta G = 0 = \Delta H - T\Delta S$ Hence $\Delta H = T\Delta S$ **(1)**
 $T = \Delta H / \Delta S = 492.7 \times 1000 / 542.6$ **(1)**
 $= 908 \text{ K}$ **(1)**

penalise missing 1000 by one mark

3

- (c) $\Delta G(b) = \Delta G(a)$
 $(492.7 \times 10^3 - T \times 542.6) = (-24.8 \times 10^3 - T \times 15.2)$ **(1)**
 $517.5 \times 10^3 = 527.4 T$ **(1)**
 $T = 981.2 \text{ K}$ **(1)**

Allow 980 - 982

Penalise missing 1000 by one mark

3

[15]**41****[1]****42****[1]****43****[1]**

A
44

[1]

B
45

[1]

D
46

[1]