AQA A-LEVEL CHEMISTRY · 7405

CHEMISTRY



EXAM QUESTION PACK

3.1.8 THERMODYNAMICS

SCORE	PERCENTAGE
/581	%

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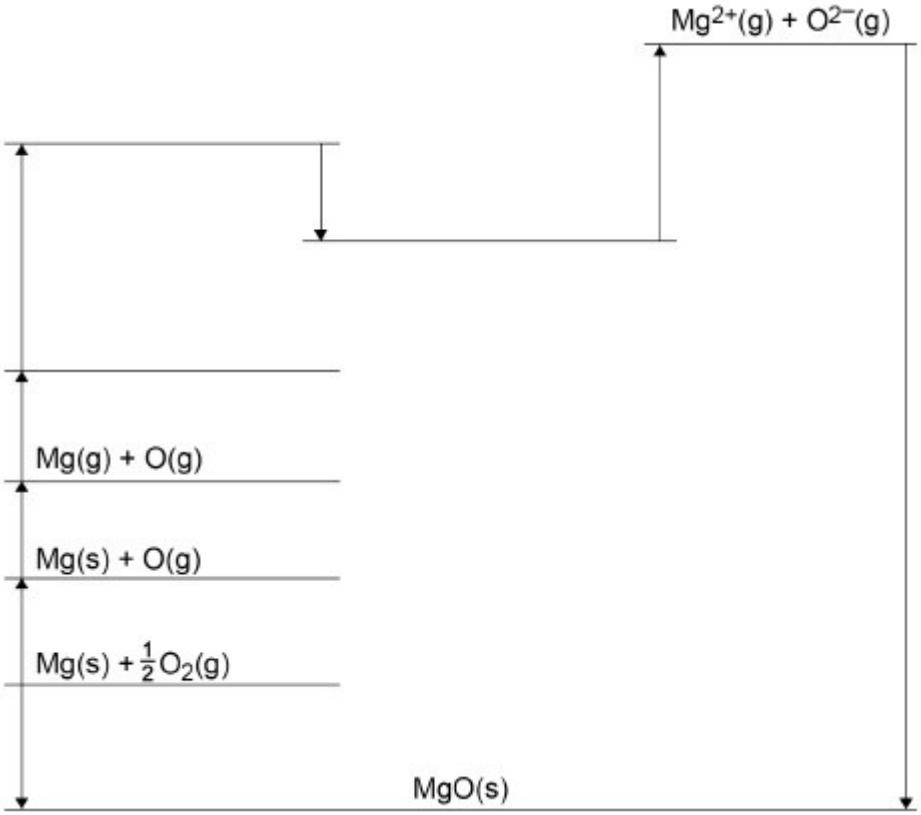
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Q1.

This question is about lattice enthalpies.

(a) The diagram shows a Born–Haber cycle for the formation of magnesium oxide.

Complete the diagram by writing the missing symbols on the appropriate energy levels.



(3)

(b) The table contains some thermodynamic data.

	Enthalpy change / kJ mol^{-1}
Enthalpy of formation for magnesium oxide	–602
Enthalpy of atomisation for magnesium	+150
First ionisation energy for magnesium	+736
Second ionisation energy for magnesium	+1450
Bond dissociation enthalpy for oxygen	+496
First electron affinity for oxygen	–142
Second electron affinity for oxygen	+844

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Calculate a value for the enthalpy of lattice formation for magnesium oxide.

Enthalpy of lattice formation _____ kJ mol^{-1}

(3)

(Total 6 marks)

Q2.

Which equation represents the process that occurs when the standard enthalpy of atomisation of iodine is measured?

A $\frac{1}{2} I_2(s) \rightarrow I(g)$ ○

B $I_2(s) \rightarrow 2I(g)$ ○

C $\frac{1}{2} I_2(g) \rightarrow I(g)$ ○

D $I_2(g) \rightarrow 2I(g)$ ○

(Total 1 mark)

Q3.

Lattice enthalpy values can be obtained from Born–Haber cycles and by calculations based on a perfect ionic model.

Which compound shows the greatest percentage difference between these two values?

A CsF ○

B CsI ○

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C LiF ⬭

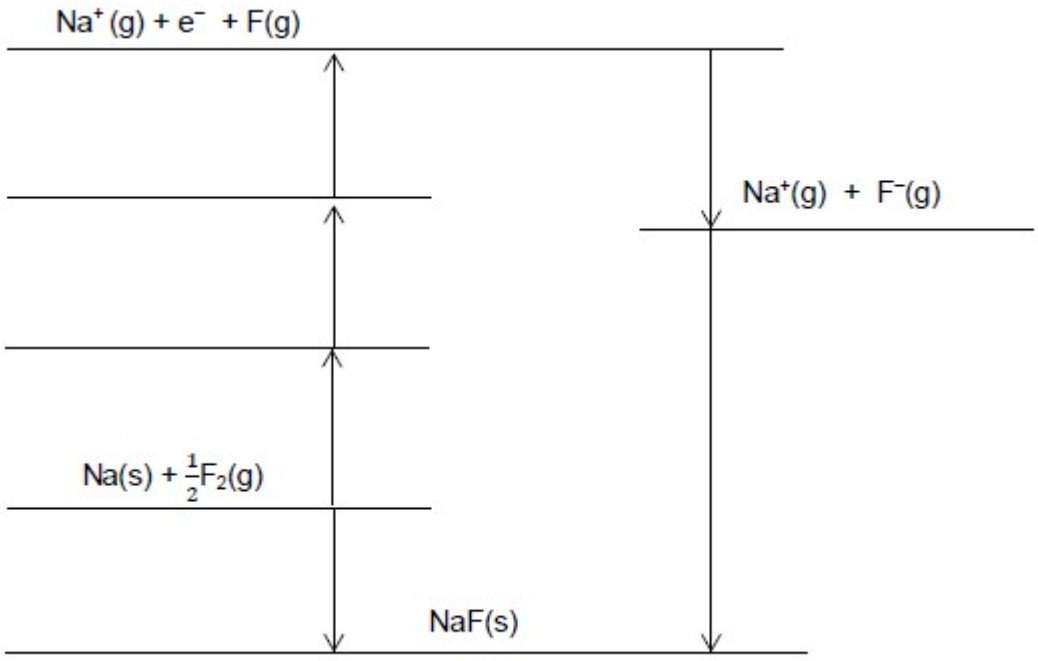
D LiI ⬭

(Total 1 mark)

Q4.

This question is about sodium fluoride.

(a) Complete the Born–Haber cycle for sodium fluoride by adding the missing species on the lines.



(2)

(b) Use the data in the table and your completed Born–Haber cycle from part **(a)** to calculate the enthalpy of lattice formation of sodium fluoride.

	$\Delta H^\ominus$ / kJ mol^{-1}
$Na(s) \longrightarrow Na(g)$	+109
$Na(g) \longrightarrow Na^+(g) + e^-$	+494
$F_2(g) \longrightarrow 2F(g)$	+158
$F(g) + e^- \longrightarrow F^-(g)$	−348
$Na(s) + \frac{1}{2}F_2(g) \longrightarrow NaF(s)$	−569

Enthalpy of lattice formation _____ kJ mol^{-1}

(2)

(c) Suggest how the enthalpy of lattice formation of NaCl compares with that of NaF

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Justify your answer.

How enthalpies of formation compare _____

_____

Justification _____

_____

_____

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_____

(3)

(d) Calculate the volume, in cm^3, of fluorine gas at 298 K and 100 kPa required to produce 1.00 g of sodium fluoride by reaction with an excess of sodium.

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

Volume _____ cm^3

(4)

(Total 11 marks)

Q5.

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

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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)

Q6.

This question is about silver iodide.

(a) Define the term enthalpy of lattice formation.

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_____

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_____

(2)

(b) Some enthalpy change data are shown in the table.

	Enthalpy change / kJ mol^{-1}
$AgI(s) \longrightarrow Ag^+(aq) + I^-(aq)$	+112
$Ag^+(g) \longrightarrow Ag^+(aq)$	−464
$I^-(g) \longrightarrow I^-(aq)$	−293

Use the data in the table to calculate the enthalpy of lattice formation of silver iodide.

Enthalpy of lattice formation = _____ kJ mol^{-1}

(2)

(c) A calculation of the enthalpy of lattice formation of silver iodide based on a perfect ionic model gives a smaller numerical value than the value calculated in part (b)

Explain this difference.

_____

_____

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(2)

(d) Identify a reagent that could be used to indicate the presence of iodide ions in an aqueous solution and describe the observation made.

Reagent _____

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Observation _____

_____

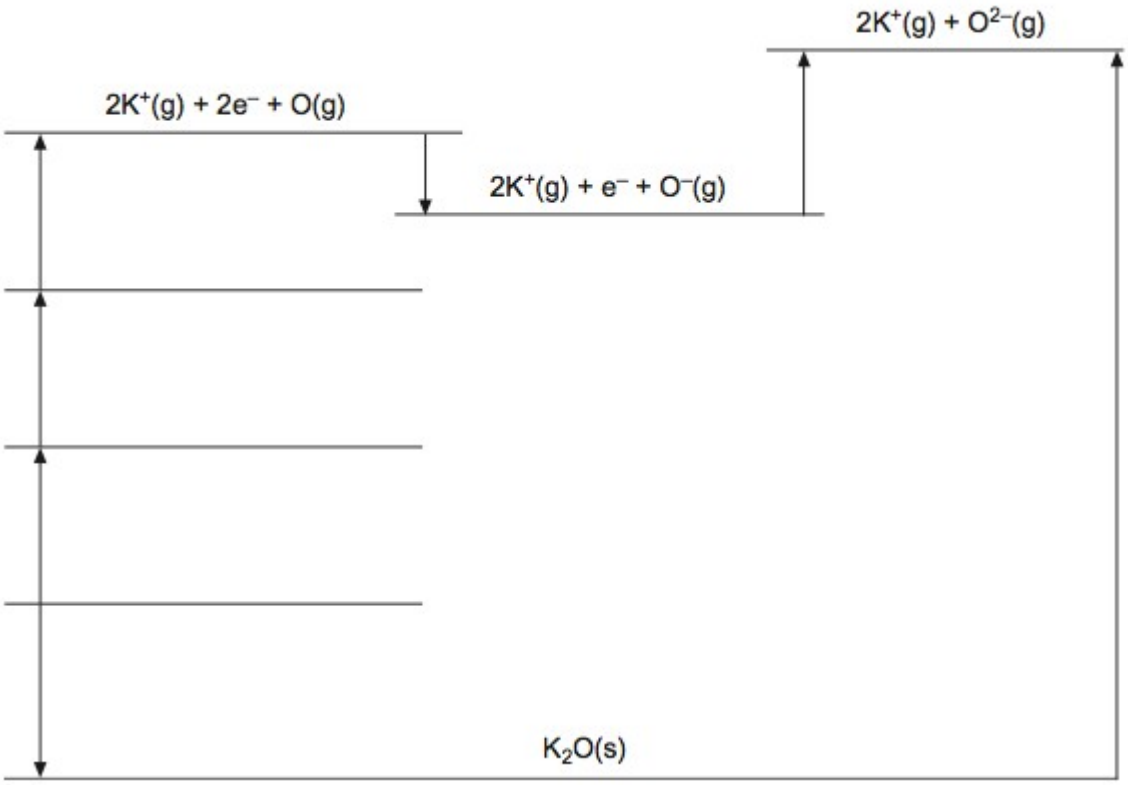
(2)

(Total 8 marks)

Q7.

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

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



(3)

(ii) The table shows some enthalpy data.

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

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oxide	

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

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(3)

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

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(2)

(Total 8 marks)

Q8.

This question is about magnesium chloride.

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

_____

(1)

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

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

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(2)

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

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

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(3)
(Total 6 marks)

Q9.

(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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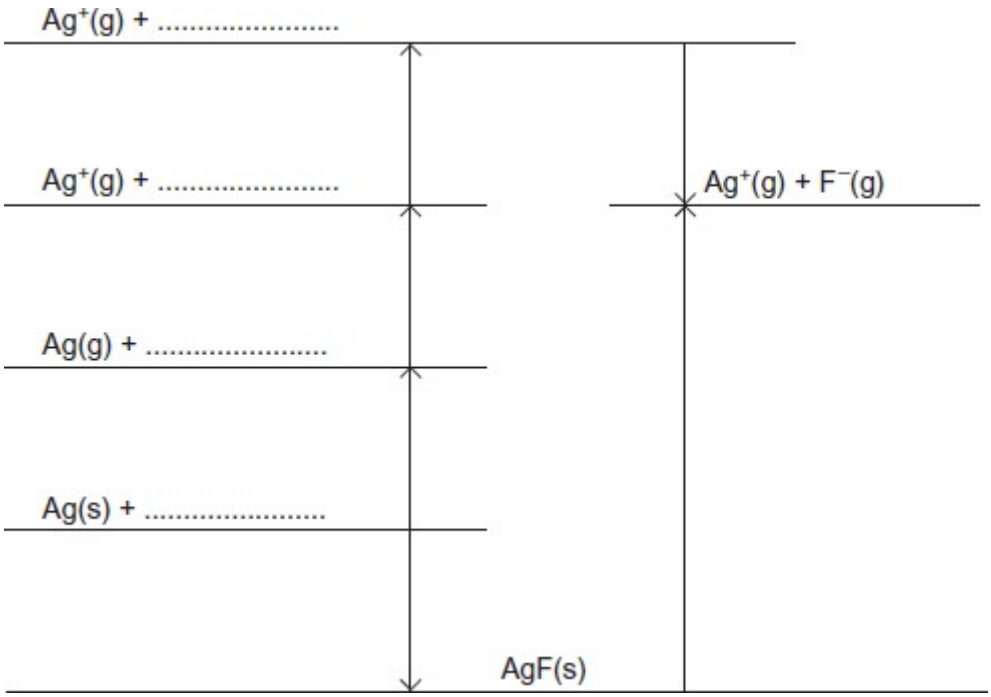
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(2)

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

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(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

(2)

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

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

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

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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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(2)

(Total 12 marks)

Q10.

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

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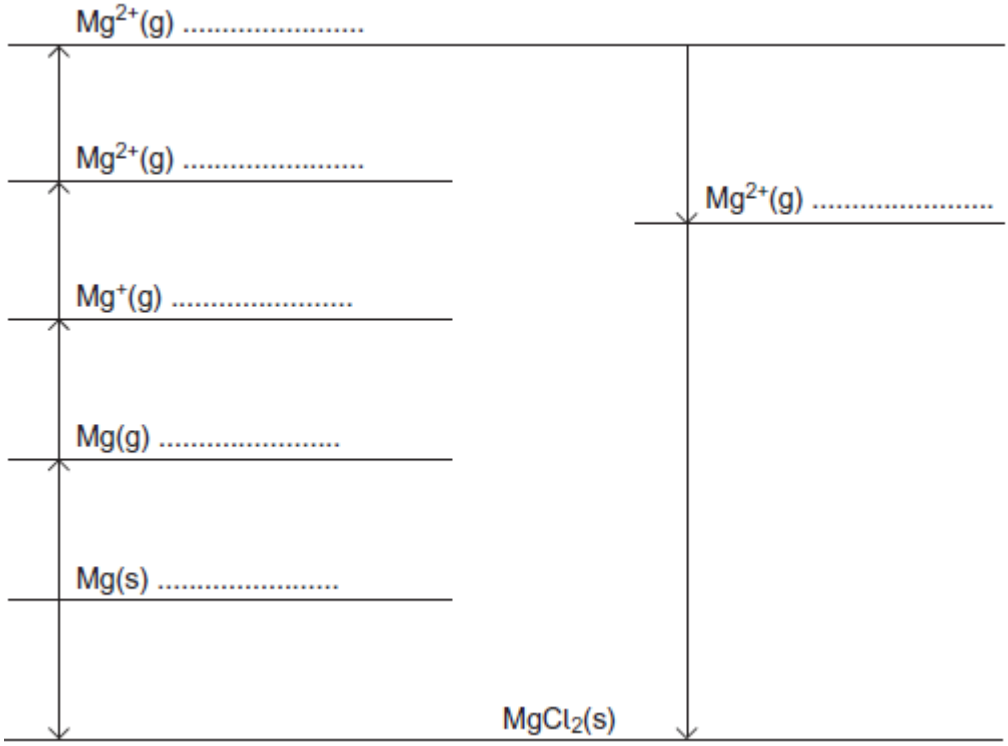
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(2)

(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.

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(6)

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

Table 1

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

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

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(3)

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

Table 2

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

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

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(2)

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

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(2)

(Total 15 marks)

Q11.

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

	Δ*H* / kJ mol^{-1}	**Δ*S* / J K^{-1} mol^{-1}**
$AgCl(s) \longrightarrow Ag^{+}(g) + Cl^{-}(g)$	+905	
$AgCl(s) \longrightarrow Ag^{+}(aq) + Cl^{-}(aq)$	+77	+33

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$AgF(s) \longrightarrow Ag^+(aq) + F^-(aq)$	–15	to be calculated
$Ag^+(g) \longrightarrow Ag^+(aq)$	–464	

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

(2)

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

(2)

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

(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 _____

(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.

(3)

(Total 13 marks)

Q12.

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

(2)

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

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

(1)

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

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Property 1 _____

_____

Property 2 _____

_____

(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)

Q13.

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 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 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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(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 J K^{-1} g^{-1}.

(5)

(Total 13 marks)

Q14.

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 $X^-(g)$ / kJ mol^{-1}	–506	–364

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(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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(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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(3)

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

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(1)

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

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(2)

(Total 12 marks)

Q15.

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

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

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

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(3)

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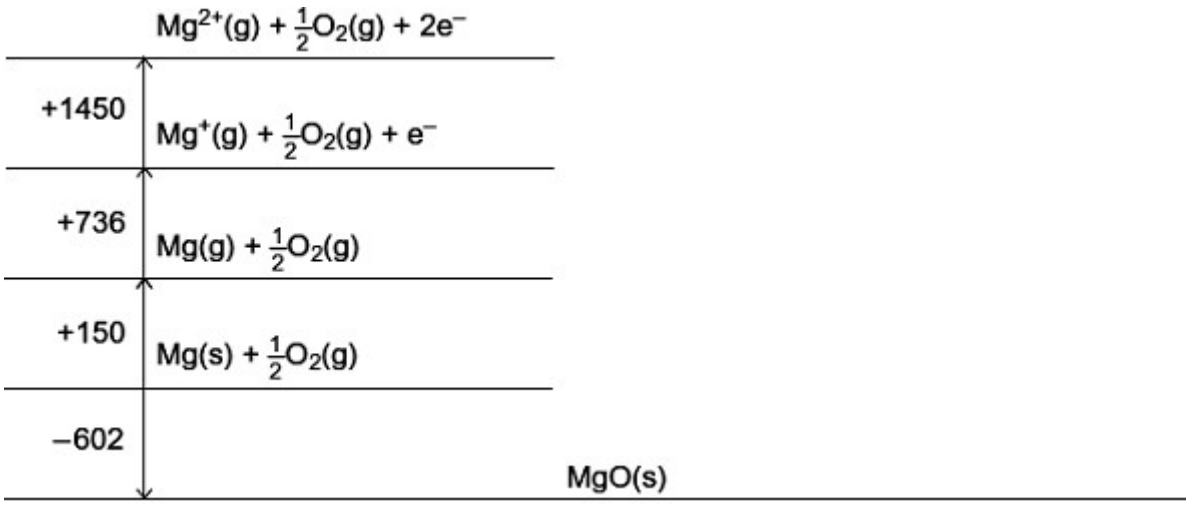
(b) In terms of the forces acting on particles, suggest **one** reason why the first electron affinity of oxygen is an exothermic process.

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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, $\Delta G_f^{\ominus} = -570$ 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 $\Delta G_f^{\ominus}$.

_____

_____

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(1)

(f) Use the value of $\Delta G_f^{\ominus}$ given in part (e) and the value of $\Delta H_f^{\ominus}$ from part (c) to calculate a value for the entropy change $\Delta S^{\ominus}$ when one mole of magnesium oxide is formed from magnesium and oxygen at 298 K. Give the units of $\Delta S^{\ominus}$.

(3)

(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).

(2)

(Total 16 marks)

Q16.

Consider the following process that represents the melting of ice.

$H_2O(s) \longrightarrow H_2O(l)$ $\Delta H^{\ominus} = +6.03$ kJ mol^{-1}, $\Delta S^{\ominus} = +22.1$ J K^{-1} mol^{-1}

(a) State the meaning of the symbol $^{\ominus}$ in $\Delta H^{\ominus}$.

(1)

(b) Use your knowledge of bonding to explain why $\Delta H^{\ominus}$ is positive for this process.

(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)

Q17.

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.

_____

(1)

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

_____

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(2)

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

(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.

(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.

(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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_____

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(1)

(Total 11 marks)

Q18.

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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_____

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(2)

(ii) enthalpy of hydration for fluoride ions

_____

_____

_____

(1)

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

_____

_____

_____

_____

(2)

(c) Consider the following data.

	$\Delta H^{\ominus}$/ 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)

Q19.

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 _____

_____

_____

Lattice dissociation enthalpy _____

_____

_____

(4)

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

	$\Delta H^{\ominus}$/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)

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(c) Consider the following lattice dissociation enthalpy (ΔH_L°) data.

	NaBr	AgBr
ΔH_L°(experimental)/kJ mol^{-1}	+733	+890
ΔH_L°(theoretical)/kJ mol^{-1}	+732	+758

The values of ΔH_L° (experimental) have been determined from Born–Haber cycles.

The values of ΔH_L° (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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_____

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(2)

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

_____

_____

(1)

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

_____

_____

(1)

(Total 11 marks)

Q20.

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

Name of enthalpy change	**ΔH° /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

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Enthalpy of formation of silver chloride	–127

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

_____

(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)

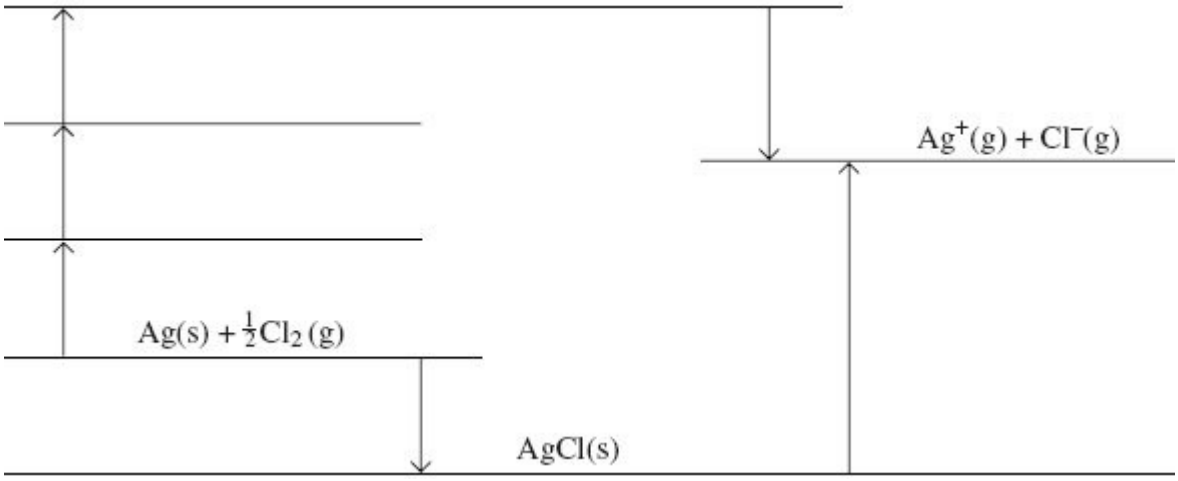
(c) Suggest why the electron affinity of chlorine is an exothermic change.

_____

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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*.

_____

_____

(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 _____

_____

_____

(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.

_____

_____

_____

(2)

(Total 15 marks)

Q21.

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	ΔH° / kJ mol^{-1}
$Ca(s) \rightarrow Ca(g)$	+193
$Ca(g) \rightarrow Ca^{+}(g) + e^{-}$	+590
$Ca^{+}(g) \rightarrow Ca^{2+}(g) + e^{-}$	+1150
$F_2(g) \rightarrow 2F(g)$	+158
$F(g) + e^{-} \rightarrow F^{-}(g)$	–348

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Table 2

Name of enthalpy change	$\Delta H^{\ominus}$ / 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.

_____

(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.

_____

(1)

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

_____

_____

_____

_____

_____

_____

(3)

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

_____

_____

_____

_____

(2)

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

$$CaCl_2(s) \rightleftharpoons Ca^{2+}(aq) + 2Cl^-(aq)$$

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

_____

_____

_____

_____

_____

_____

(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 _____

_____

_____

_____

(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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_____

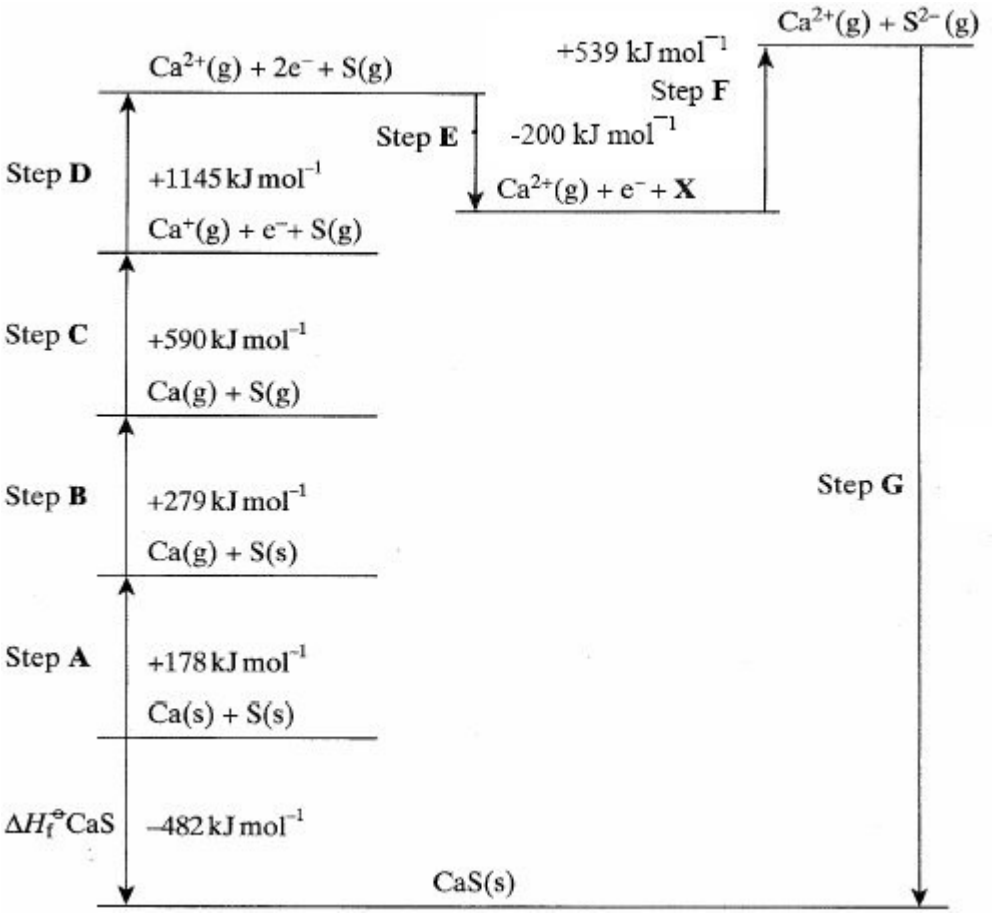
_____

(2)

(Total 17 marks)

Q22.

(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.

_____

_____

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

*Step **B*** _____

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*Step **D*** _____

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

_____

_____

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

_____

_____

_____

(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.

_____

_____

_____

_____

(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.

$$NaHCO_3(aq) + HCl(aq) \rightarrow NaCl(aq) + H_2O(l) + CO_2(g)$$

_____

_____

_____

_____

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

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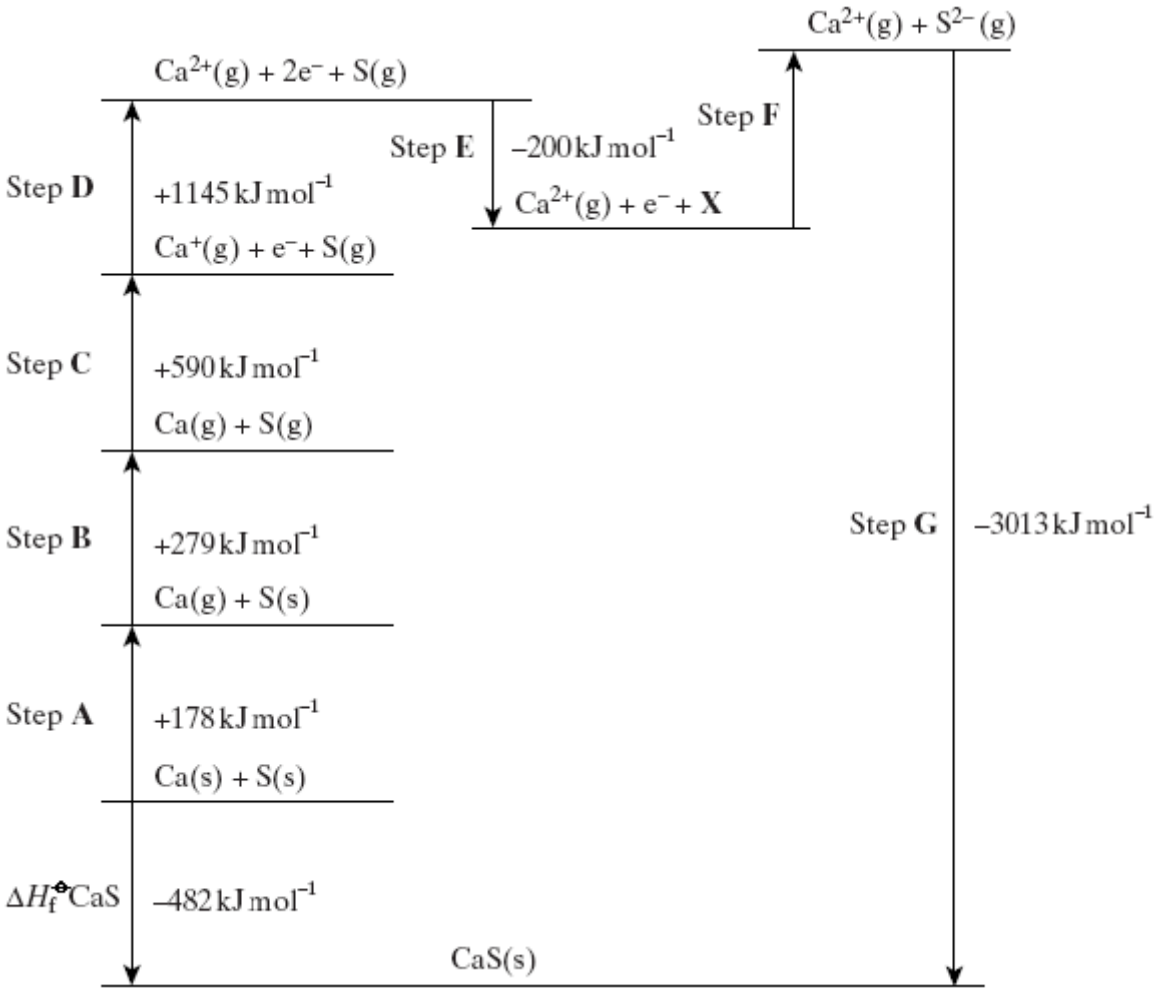
$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$

(6)

(Total 18 marks)

Q23.

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)

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(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**.

_____

_____

_____

(2)

(Total 11 marks)

Q24.

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 $[Fe(CN)_6]^{3-}$ is greater than the oxidation state of copper in $[CuCl_2]^-$

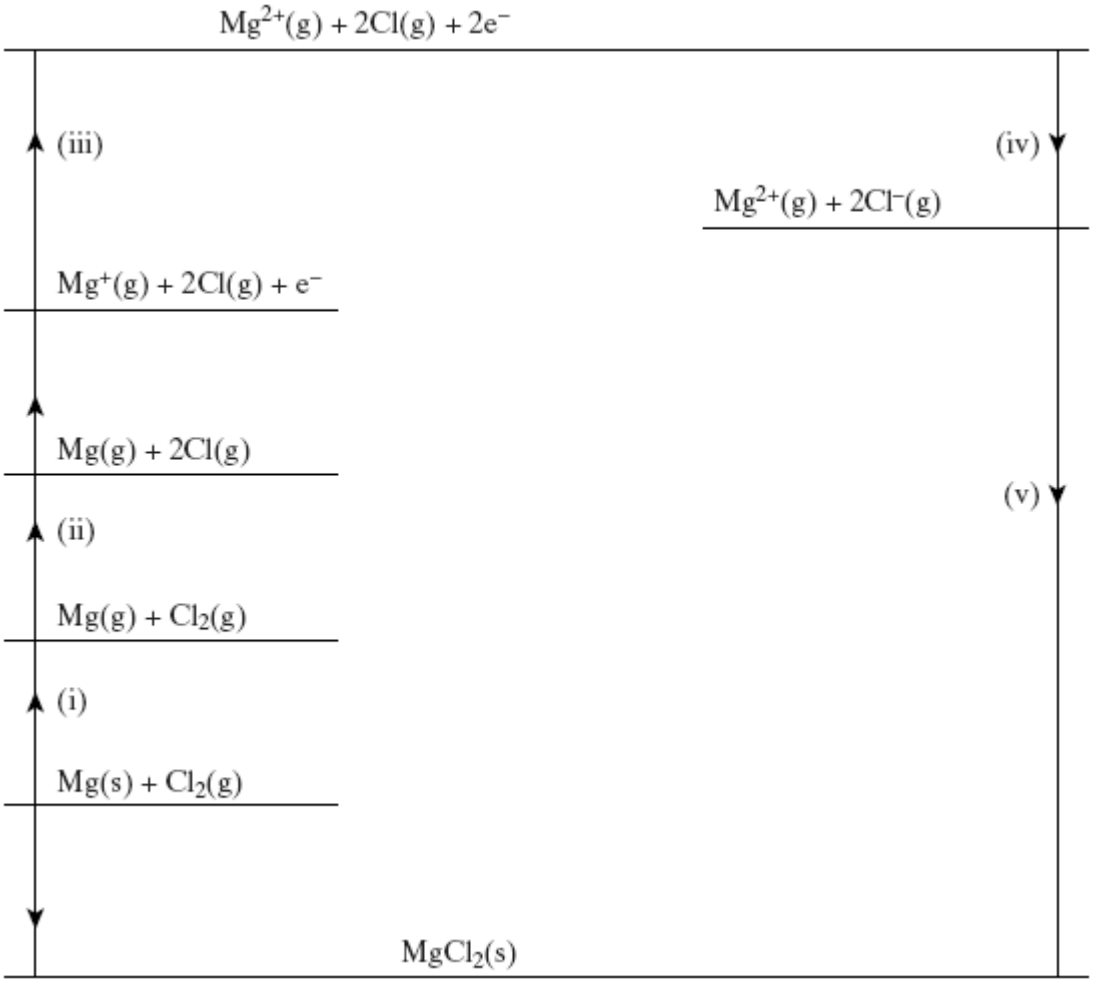
D The boiling point of C_3H_8 is lower than that of CH_3CH_2OH

(Total 1 mark)

Q25.

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

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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 $MgCl_2(s)$ and Mg(s) and use the following data to calculate a value for the enthalpy change of this reaction.

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

$\Delta H_f^{\ominus}$ $MgCl_2(s)$ = –653 kJ mol^{-1}

Equation _____

Calculation _____

_____

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_____

_____

(4)

(c) Use the data below to calculate a value for the molar enthalpy of a solution of $MgCl_2(s)$.

Lattice formation enthalpy of $MgCl_2(s)$ = –2502 kJ mol^{-1}

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

$\Delta H^{\ominus}_{hydration}$ of $Cl^-(g)$ = –364 kJ mol^{-1}

_____

_____

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_____

_____

(3)

(Total 12 marks)

Q26.

(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}

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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.

$BaCl_2(s) \rightarrow Ba(s) + Cl_2(g)$

	$BaCl_2(s)$	$Ba(s)$	$Cl_2(g)$
$S^{\ominus}$ / J K^{-1} mol^{-1}	124	63	223

_____

_____

_____

_____

_____

(4)

(Total 13 marks)

Q27.

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)

Q28.

Which one of the following has the most covalent character?

A MgF_2

B $MgBr_2$

C AlF_3

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D $AlBr_3$

(Total 1 mark)

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Q1.

The equation for the reaction between ammonia and oxygen is shown.

$$4NH_3(g) + 5O_2(g) \rightleftharpoons 4NO(g) + 6H_2O(g) \qquad \Delta H = -905 \text{ kJ mol}^{-1}$$

Some standard entropies are given in the table.

Gas	S° **/ J K^{-1} mol^{-1}**
$NH_3(g)$	193
$O_2(g)$	205
$NO(g)$	211
$H_2O(g)$	189

(a) Calculate the entropy change for the reaction between ammonia and oxygen.

Entropy change _____ J K^{-1} mol^{-1}

(2)

(b) Calculate a value for the Gibbs free-energy change (ΔG), in kJ mol^{-1}, for the reaction between ammonia and oxygen at 600 °C

(If you were unable to obtain an answer to part (a), you should assume that the entropy change is 211 J K^{-1} mol^{-1}. This is not the correct answer.)

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ΔG _____ kJ mol^{-1}

(2)

(c) The reaction between ammonia and oxygen was carried out at a higher temperature.

Explain how this change affects the value of ΔG for the reaction.

_____

_____

_____

_____

_____

(2)

(d) Platinum acts as a heterogeneous catalyst in the reaction between ammonia and oxygen. It provides an alternative reaction route with a lower activation energy.

Describe the stages of this alternative route.

_____

_____

_____

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(3)

(e) Deduce the change in oxidation state of nitrogen, when NH_3 is oxidised to NO

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_____

(1)

(f) When ammonia reacts with oxygen, nitrous oxide (N_2O) can be produced instead of NO

Give an equation for this reaction.

_____

(1)

(Total 11 marks)

Q2.

Titanium(IV) chloride can be made from titanium(IV) oxide as shown in the equation.

$$TiO_2(s) + 2C(s) + 2Cl_2(g) \rightarrow 2CO(g) + TiCl_4(l) \qquad \Delta H^{\ominus} = -60.0\,kJ\,mol^{-1}$$

Some entropy data are shown in the table.

Substance	$TiO_2(s)$	$C(s)$	$Cl_2(g)$	$CO(g)$	$TiCl_4(l)$
$S^{\ominus}$ / J K^{-1} mol^{-1}	50.2	5.70	223	198	253

Use the equation and the data in the table to calculate the Gibbs free-energy change for this reaction at 989 °C

Give your answer to the appropriate number of significant figures.

Use your answer to explain whether this reaction is feasible.

Gibbs free-energy change _____ kJ mol^{-1}

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Explanation _____

_____

(Total 6 marks)

Q3.

Anhydrous magnesium chloride, $MgCl_2$, can absorb water to form the hydrated salt $MgCl_2.4H_2O$

$$MgCl_2(s) + 4H_2O(l) \rightarrow MgCl_2.4H_2O(s)$$

(a) Suggest **one** reason why the enthalpy change for this reaction cannot be determined directly by calorimetry.

_____

_____

(1)

(b) Some enthalpies of solution are shown in Table 1.

Table 1

Salt	Enthalpy of solution / kJ mol^{-1}
$MgCl_2(s)$	−155
$MgCl_2.4H_2O(s)$	−39

Calculate the enthalpy change for the absorption of water by $MgCl_2(s)$ to form $MgCl_2.4H_2O(s)$.

Enthalpy change _____ kJ mol^{-1}

(2)

(c) Describe how you would carry out an experiment to determine the enthalpy of solution of anhydrous magnesium chloride.

You should use about 0.8 g of anhydrous magnesium chloride.

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Explain how your results could be used to calculate the enthalpy of solution.

_____

_____

_____

_____

_____

_____

_____

_____

(6)

(d) Anhydrous magnesium chloride can be formed by direct reaction between its elements.

$$Mg(s) + Cl_2(g) \longrightarrow MgCl_2(s)$$

The free-energy change, ΔG, for this reaction varies with temperature as shown in **Table 2**.

Table 2

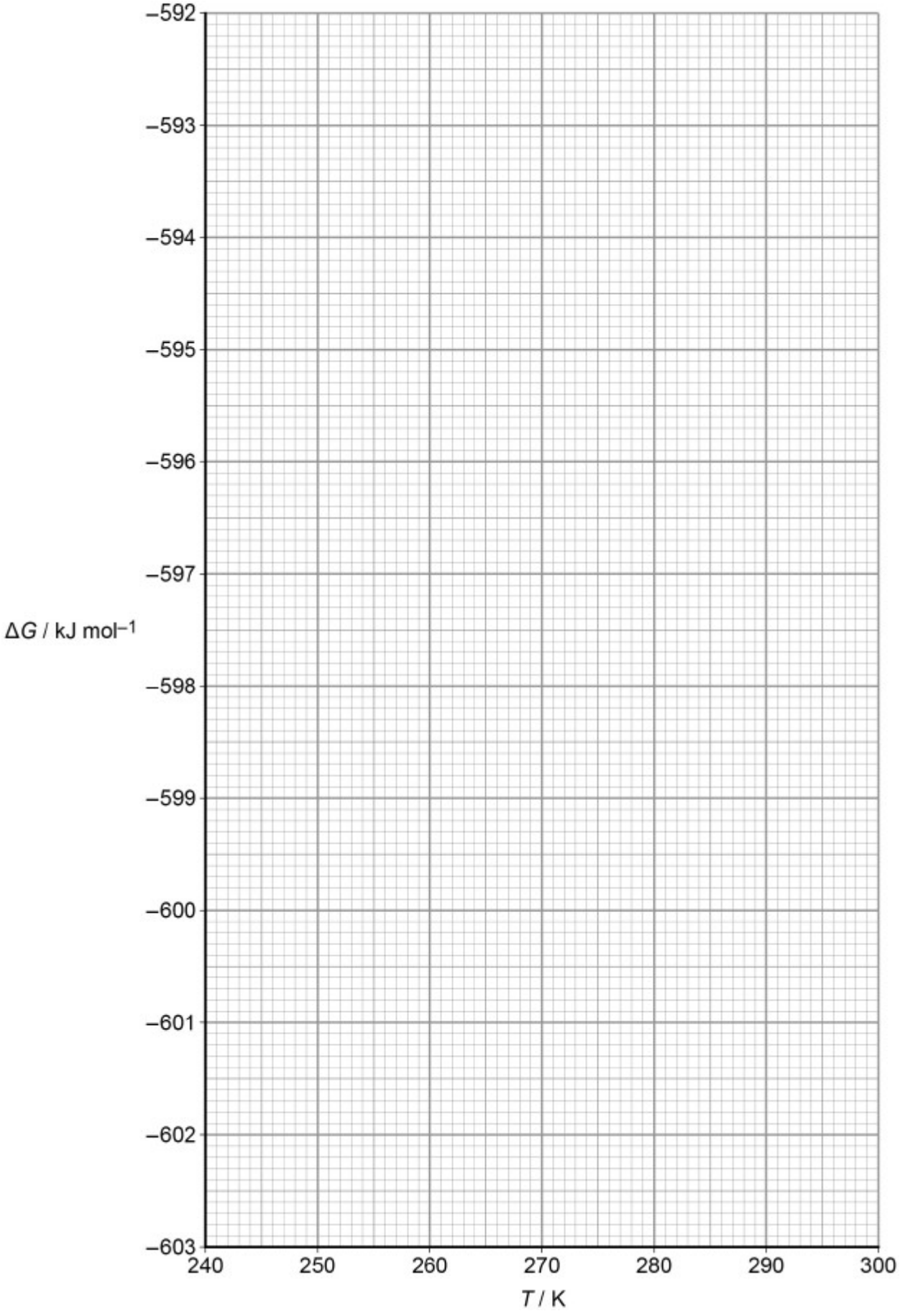
T / K	**ΔG / kJ mol^{-1}**
298	−592.5
288	−594.2
273	−596.7
260	−598.8
240	−602.2

Use these data to plot a graph of free-energy change against temperature on the grid below.

Calculate the gradient of the line on your graph and hence calculate the entropy change, ΔS, in J K^{-1} mol^{-1}, for the formation of anhydrous magnesium chloride from its elements.

Show your working.

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ΔS _____ $JK^{-1}mol^{-1}$

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(5)
(Total 14 marks)

Q4.

A reaction is exothermic and has a negative entropy change.

Which statement is correct?

A	The reaction is always feasible	⬭
B	The reaction is feasible above a certain temperature	⬭
C	The reaction is feasible below a certain temperature	⬭
D	The reaction is never feasible	⬭

(Total 1 mark)

Q5.

Hydrogen can be manufactured by the reaction of methane with steam. An equilibrium is established as shown by the equation.

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

(a) Use Le Chatelier's principle to predict the effect on the equilibrium yield of hydrogen if the overall pressure is increased.
Explain your answer.

Effect on yield _____

Explanation _____

_____

_____

_____

(3)

(b) Explain why the equilibrium yield of hydrogen is unchanged if a catalyst is used in the reaction.

_____

_____

_____

_____

_____

(2)

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(c) The table shows the standard enthalpy of formation and the standard entropy for each substance in this equilibrium reaction.

	$CH_4(g)$	$H_2O(g)$	$CO(g)$	$H_2(g)$
$\Delta_f H^\theta$ / kJ mol^{-1}	−75	−242	−111	0
Sθ / J K^{-1} mol^{-1}	186	189	198	131

Use data from the table to calculate the standard enthalpy change for this equilibrium reaction.

Standard enthalpy change _____ kJ mol^{-1}

(2)

Use your answer from part **(c)** and the entropy data from the table above to calculate the minimum temperature, in °C, needed for this reaction to be feasible. Give your answer to the appropriate number of significant figures.

(If you did not complete part **(c)** you should assume a value of 120 kJ mol^{-1} for the standard enthalpy change. This is **not** the correct value).

Minimum temperature _____ °C

(5)

(Total 12 marks)

Q6.

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

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

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

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

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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 _____

_____

_____

(4)

(Total 10 marks)

Q7.

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

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

The table shows some thermodynamic data.

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

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$SO_3(g)$	–395	256

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

(2)

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

(2)

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

(1)

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

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

(3)

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

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_____

(1)

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

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

_____

(1)

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

_____

_____

_____

(2)

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

_____

_____

(1)

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

_____

_____

(1)

(Total 14 marks)

Q8.

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

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

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

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

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

(3)

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

(2)

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

(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

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temperature is used rather than the value that you calculated in part (b).

_____

_____

(1)

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

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

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

_____

_____

_____

_____

_____

_____

_____

(3)

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

_____

_____

_____

_____

_____

(2)

(Total 15 marks)

Q9.

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

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

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

(2)

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

(2)

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

(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 _____

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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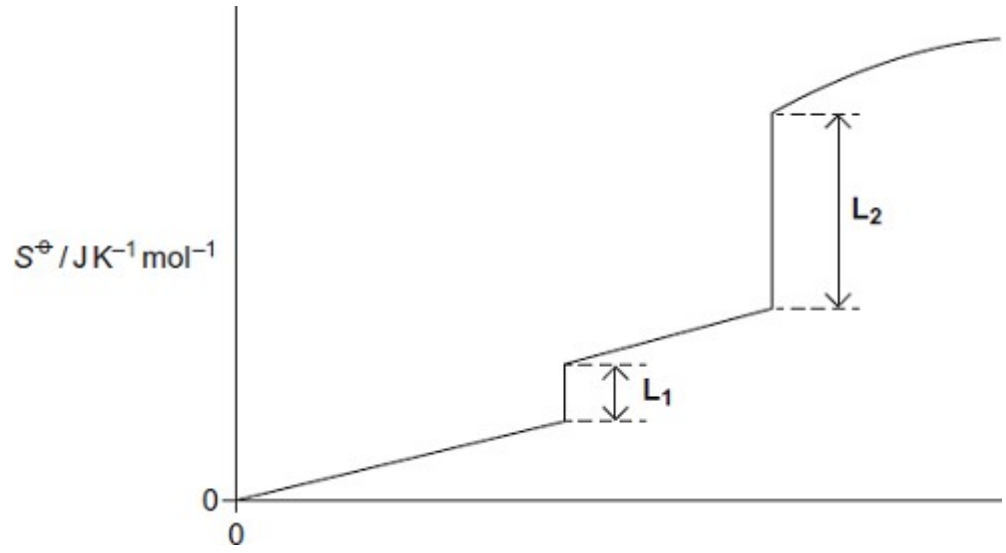
(3)

(Total 13 marks)

Q10.

(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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_____

_____

_____

(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.

_____

_____

_____

_____

(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 $\mathbf{L_2}$ is longer than $\mathbf{L_1}$ in **Figure 1**.

_____

_____

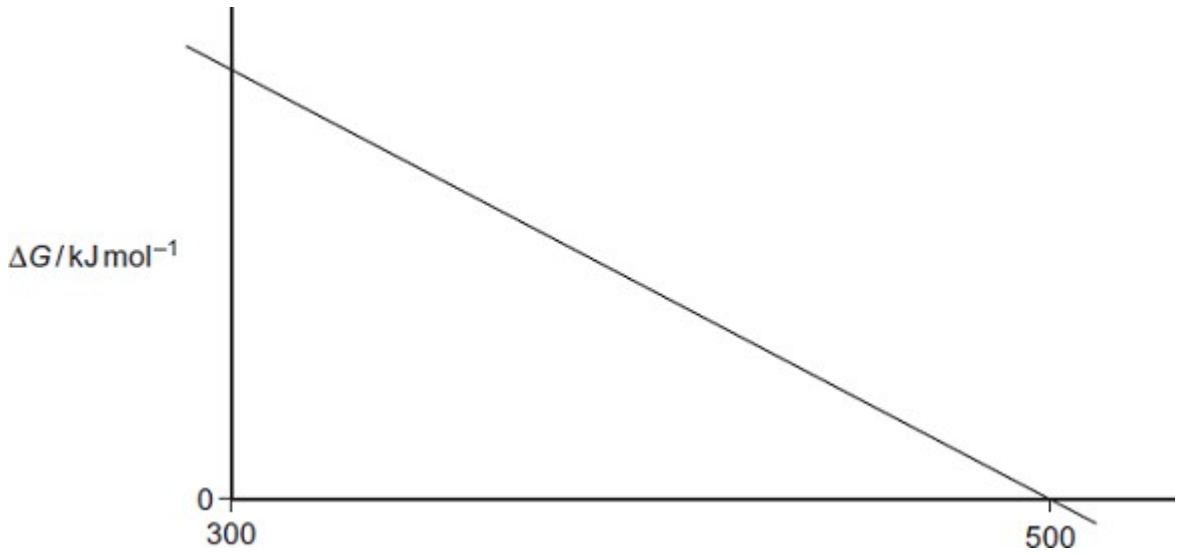
_____

_____

(2)

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

Figure 2



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T / K

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

(2)

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

(1)

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

(1)

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

$$H_2O(g) \longrightarrow H_2(g) + \frac{1}{2}O_2(g)$$

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

	$H_2O(g)$	$H_2(g)$	$O_2(g)$
S / J K^{-1} mol^{-1}	189	131	205

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

(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)

Q11.

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)

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

	$S^{\ominus}$ / J K^{-1} mol^{-1}	$\Delta H_f^{\ominus}$/ kJ mol^{-1}
$H_2(g)$	131	0
$O_2(g)$	205	0
$H_2O(g)$	189	−242
$H_2O(l)$	70	

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

_____

_____

_____

_____

_____

_____

_____

_____

(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 _____

_____

Reason _____

_____

_____

(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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(3)

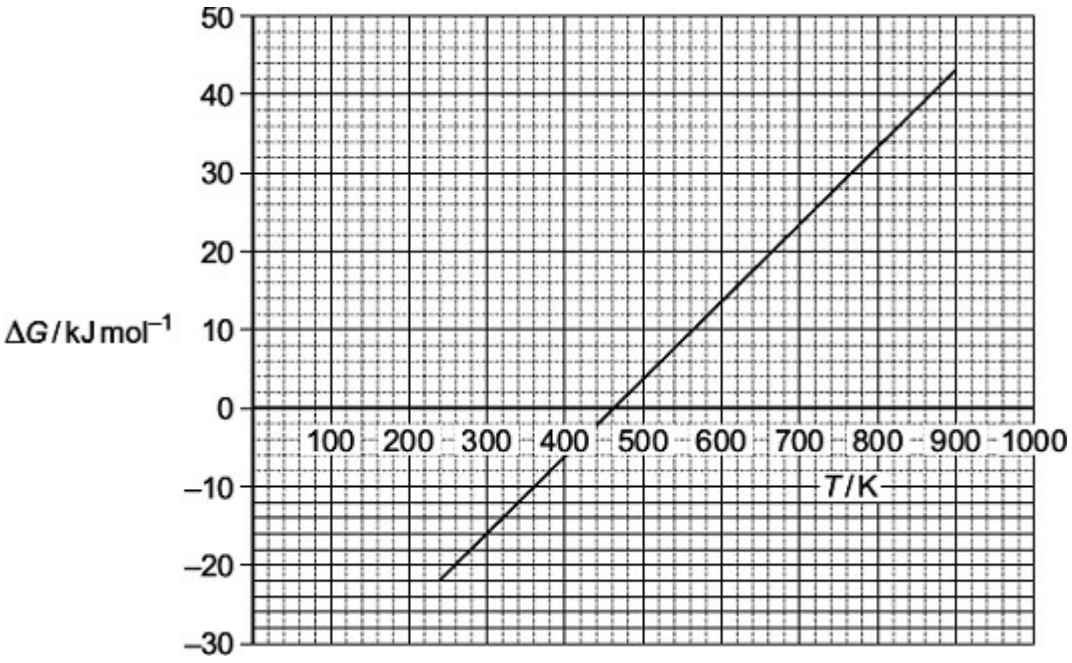
(Total 15 marks)

Q12.

The following equation shows the formation of ammonia.

$$\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \longrightarrow NH_3(g)$$

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.

_____

(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.

_____

_____

(1)

(Total 7 marks)

Q13.

The oxides nitrogen monoxide (NO) and nitrogen dioxide (NO_2) both contribute to atmospheric pollution.

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

	$S^{\ominus}$ / JK^{-1} mol^{-1}	$\Delta H_f^{\ominus}$ / 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.

$$NO(g) + \frac{1}{2}O_2(g) \longrightarrow NO_2(g)$$

(a) Calculate the enthalpy change for this reaction.

_____

_____

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(2)

(b) Calculate the entropy change for this reaction.

(2)

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

(2)

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

(1)

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

(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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_____

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(2)

(Total 10 marks)

Q14.

Consider the following process that represents the melting of ice.

$H_2O(s) \longrightarrow H_2O(l)$ $\quad \Delta H^{\ominus} = +6.03 \text{ kJ mol}^{-1}, \quad \Delta S^{\ominus} = +22.1 \text{ J K}^{-1} \text{ mol}^{-1}$

(a) State the meaning of the symbol $^{\ominus}$ in $\Delta H^{\ominus}$.

_____

_____

(1)

(b) Use your knowledge of bonding to explain why $\Delta H^{\ominus}$ is positive for this process.

_____

_____

_____

(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.

_____

_____

_____

(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)

Q15.

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

	$\Delta H^{\ominus}$ / kJ mol^{-1}
First electron affinity of oxygen (formation of O^-(g) from O(g))	–142
Second electron affinity of oxygen (formation of O^{2-}(g) from O^-(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.

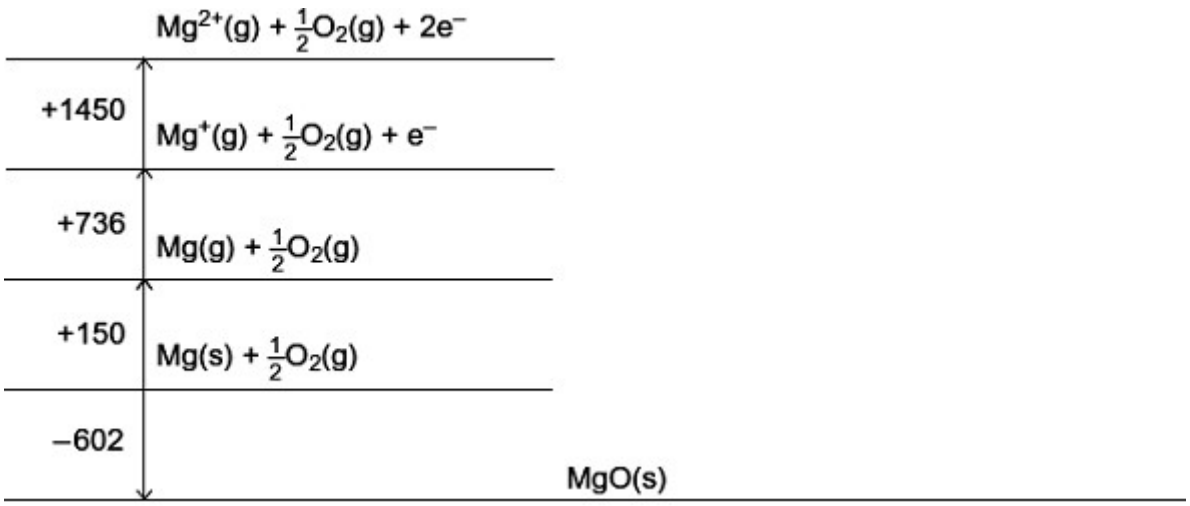
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(1)

(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}.

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(4)

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

(2)

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

(1)

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

(3)

(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)

Q16.

When potassium nitrate (KNO_3) dissolves in water the value of the enthalpy change ΔH = +34.9 kJ mol^{-1} and the value of the entropy change ΔS = +117 J K^{-1} mol^{-1}.

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

_____

(1)

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

_____

_____

(1)

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

_____

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_____

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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).

_____

_____

(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)

Q17.

Ammonia can be manufactured by the Haber Process.

The equation for the reaction that occurs is shown below.

$$N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$$

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

	N ≡ N	H–H	N–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.

_____

_____

(1)

(b) The table below contains some entropy data.

	$H_2(g)$	$N_2(g)$	$NH_3(g)$
$S\ominus$ / J K^{-1} 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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_____

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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 J K^{-1} 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.

_____

(1)

(Total 11 marks)

Q18.

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)
ΔH_f^o/kJ mol^{-1}	0	0	+90.4	0	+1.9
S^o/J K^{-1} 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).

_____

_____

_____

(2)

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

_____

(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.

$$\frac{1}{2}N_2(g) + \frac{1}{2}O_2(g) \longrightarrow NO(g)$$

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.

_____

_____

(1)

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

$$C(\text{graphite}) \longrightarrow C(\text{diamond})$$

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

ΔH° _____

ΔS° _____

Explanation _____

_____

(3)

(Total 14 marks)

Q19.

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

$$CO_2(g) + 3H_2(g) \rightleftharpoons CH_3OH(g) + H_2O(g)$$

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

	$CO_2(g)$	$H_2(g)$	$CH_3OH(g)$	$H_2O(g)$
$\Delta H_f^{\ominus}$ / kJ mol^{-1}	–394	0	–201	–242
$S^{\ominus}$ / J K^{-1} mol^{-1}	214	131	238	189

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

_____

_____

_____

_____

_____

_____

(3)

(b) Calculate the standard entropy change for this reaction.

_____

_____

_____

_____

_____

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(3)

(c) Use your answers to parts (a) and (b) to explain why this reaction is **not** feasible at high temperatures.

Calculate the temperature at which the reaction becomes feasible.

Suggest why the industrial process is carried out at a higher temperature than you have calculated.

(If you have been unable to calculate values for ΔH and ΔS you may assume that they are –61 kJ mol^{-1} and –205 J K^{-1} mol^{-1} respectively. These are **not** the correct values.)

(6)

(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.

(4)

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

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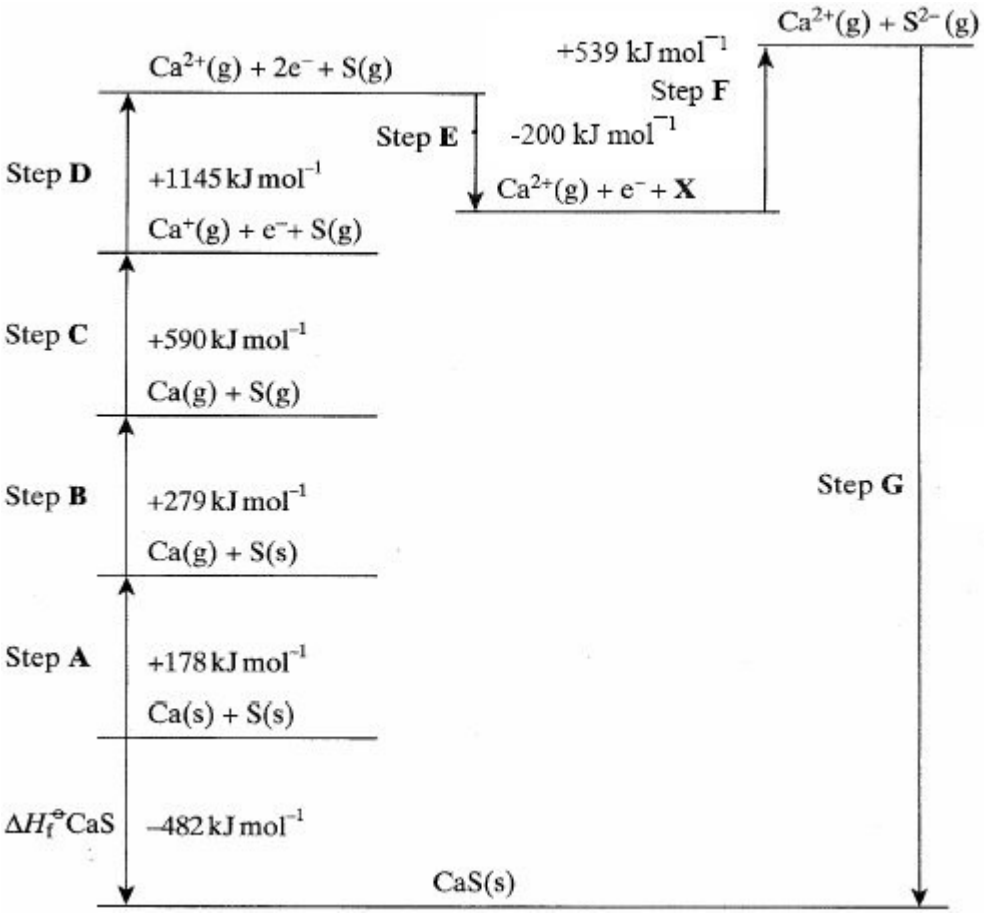
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(1)

(Total 17 marks)

Q20.

(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.

_____

_____

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

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*Step **B*** _____

*Step **D*** _____

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

_____

_____

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

_____

_____

_____

(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.

_____

_____

_____

_____

(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.

$$NaHCO_3(aq) + HCl(aq) \rightarrow NaCl(aq) + H_2O(l) + CO_2(g)$$

_____

_____

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(ii) Explain why the following reaction does not occur at very high temperatures

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even though the reaction is exothermic.

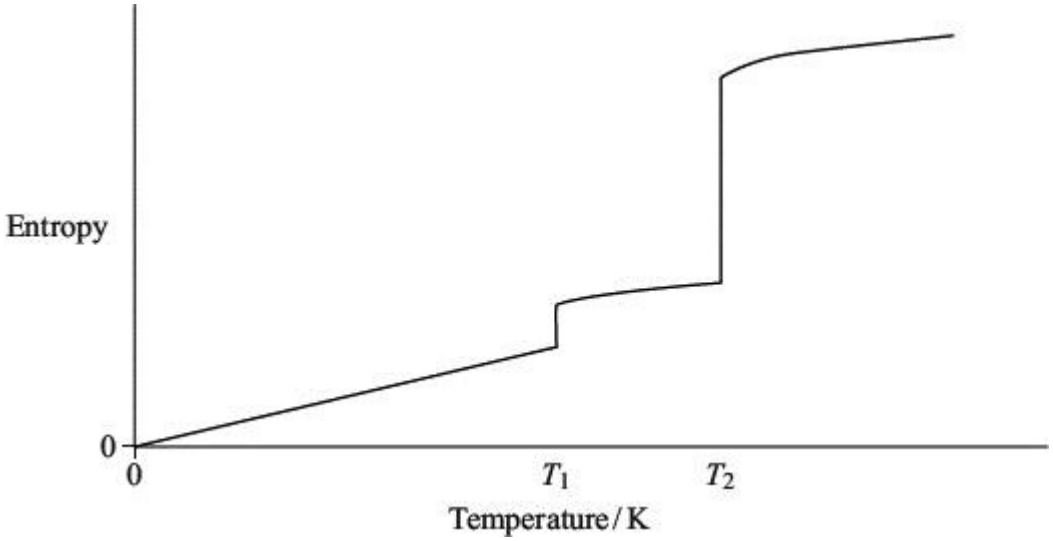
$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

(6)

(Total 18 marks)

Q21.

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.

(1)

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

(1)

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

(2)

(d) It requires 3.49 kJ of heat energy to convert 1.53 g of liquid water into steam at

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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.

_____

_____

_____

_____

(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, $\Delta G = 0$ 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 $\Delta H = 45.0$ kJ mol^{-1}. This is not the correct answer.)

Calculation _____

_____

_____

Units _____

(6)

(Total 10 marks)

Q22.

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)

Q23.

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

A $[Cu(H_2O)_6]^{2+} + 4NH_3 \rightarrow [Cu(NH_3)_4(H_2O)_2]^{2+} + 4H_2O$

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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)

Q24.

This question is about the reaction given below.

$$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$$

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

Substance	CO(g)	$H_2O(g)$	$CO_2(g)$	$H_2(g)$
$\Delta H_f^{\ominus}$ / 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)

Q25.

Refer to the following reaction

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g) \qquad \Delta H^{\ominus} = -11 \text{ kJ mol}^{-1}, \qquad \Delta S^{\ominus} = +20 \text{ J K}^{-1} \text{ mol}^{-1}$$

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)

Q26.

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

$$2W(g) + X(g) \rightleftharpoons 3Y(g) + 2Z(g) \qquad \Delta H = -200 \text{ kJ mol}^{-1}$$

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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

$CH_3COOH(l) + C_2H_5OH(l) \rightleftharpoons CH_3COOC_2H_5(l) + H_2O(l)$ $\Delta H^{\ominus} = -2.0$ kJ mol^{-1}

Reaction 2

$CH_3COCl(l) + C_2H_5OH(l) \rightarrow CH_3COOC_2H_5(l) + HCl(g)$ $\Delta H^{\ominus} = -21.6$ kJ mol^{-1}

(i) Give one advantage and one disadvantage of preparing ethyl ethanoate by **Reaction 1** rather than by **Reaction 2**.

(2)

(ii) Use the information given above and the data below to calculate values for the standard entropy change, $\Delta S^{\ominus}$, and the standard free-energy change, $\Delta G^{\ominus}$, for **Reaction 2** at 298 K.

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	$CH_3COCl(l)$	$C_2H_5OH(l)$	$CH_3COOC_2H_5(l)$	$HCl(g)$
$S^{\ominus}$/JK^{1}mol^1	201	161	259	187

(6)

(Total 15 marks)

Q27.

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

$$4HCl(g) + O_2(g) \rightleftharpoons 2Cl_2(g) + 2H_2O(g)$$

(a) Use the data below to calculate the standard enthalpy change, $\Delta H^{\ominus}$, and the standard entropy change, $\Delta S^{\ominus}$, for this reaction.

Substance	$HCl(g)$	$O_2(g)$	$Cl_2(g)$	$H_2O(g)$
$\Delta H_f^{\ominus}$/kJ mol^{-1}	–92	0	0	–242
$S^{\ominus}$/ J K^{-1} mol^{-1}	187	205	223	189

Standard enthalpy change, $\Delta H^{\ominus}$ _____

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Standard entropy change, $\Delta S^{\ominus}$ _____

_____

_____

_____

_____

(6)

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

Standard enthalpy change, $\Delta H^{\ominus}$ = +208 kJ mol^{-1}
Standard entropy change, $\Delta S^{\ominus}$ = +253 J K^{-1} 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)

Q28.

(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.

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(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.

$BaCl_2(s) \rightarrow Ba(s) + Cl_2(g)$

	$BaCl_2(s)$	Ba(s)	$Cl_2(g)$
$S^{\ominus}$ / J K^{-1} mol^{-1}	124	63	223

_____

_____

_____

_____

_____

(4)

(Total 13 marks)

Q29.

Using the information below, answer this question.

$Fe_2O_3(s) + 3H_2(g) \rightarrow 2Fe(s) + 3H_2O(g)$ $\Delta H^{\ominus} = +96$ kJ mol^{-1}, $\Delta S^{\ominus} = +138$ J K^{-1} mol^{-1}

	$Fe_2O_3(s)$	**$H_2(g)$**	**Fe(s)**
$\Delta H_f^{\ominus}$ / kJ mol^{-1}	−822.0	0	0
$\Delta S^{\ominus}$ / J K^{-1} mol^{-1}	90.0	131.0	27.0

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The standard entropy value for steam is

A +332 J $K^{1ف}$ mol^{-1}

B +189 J $K^{1ف}$ mol^{-1}

C +145 J $K^{1ف}$ mol^{-1}

D +85 J $K^{1ف}$ mol^{-1}

(Total 1 mark)

Q30.

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

A $[Fe(H_2O)_6]^{3+}(aq) + 3C_2O_4^{2-}(aq) \rightarrow [Fe(C_2O_4)_3]^{3-}(aq) + 6H_2O(l)$

B $[Cu(H_2O)_6]^{2+}(aq) + EDTA^{4-}(aq) \rightarrow [Cu(EDTA)]^{2-}(aq) + 6H_2O(l)$

C $[CoCl_4]^{2-}(aq) + 6H_2O(l) \rightarrow [Co(H_2O)_6]^{2+}(aq) + 4Cl^-(aq)$

D $Na_2CO_3(s) + 2H^+(aq) \rightarrow 2Na^+(aq) + CO_2(g) + H_2O(l)$

(Total 1 mark)

Q31.

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

Substance	$Fe_2O_3(s)$	Fe(s)	C(s)	CO(g)	$CO_2(g)$
$\Delta H_f^{\ominus}$ / kJ mol^{-1}	–824.2	0	0	–110.5	–393.5
$S^{\ominus}$ / J K^{-1} 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.

$$Fe_2O_3(s) + 3CO(g) \rightarrow 2Fe(s) + 3CO_2(g)$$

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

Standard enthalpy change _____

_____

_____

_____

_____

_____

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Standard entropy change _____

_____

_____

_____

_____

(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.

$Fe_2O_3(s) + 3C(s) \rightarrow 2Fe(s) + 3CO(g)$ $\Delta H^{\ominus} = +492.7$ kJ mol^{-1}

The standard entropy change, $\Delta S^{\ominus}$, for this reaction is +542.6 J K^{-1} 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, $\Delta G^{\ominus}$ has the same value for the reactions in parts (a) and (b).

_____

_____

_____

_____

(3)

(Total 15 marks)

Q32.

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

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

Thermodynamic data for the components of this equilibrium are:

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Substance	$\Delta H_f^{\ominus}$ / kJ mol^{-1}	$S^{\ominus}$ / J K^{-1} mol^{-1}
$SO_3(g)$	−396	+257
$SO_2(g)$	–297	+248
$O_2(g)$	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 $SO_2(g)$, 0.0800 mol of $O_2(g)$ and 0.0700 mol of $SO_3(g)$.

The standard entropy change for this reaction is

A −222 J K^{-1} mol^{-1}

B −195 J K^{-1} mol^{-1}

C −186 J K^{-1} mol^{-1}

D +198 J K^{-1} mol^{-1}

(Total 1 mark)

Q33.

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

$$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$$

At equilibrium, when the temperature is 68 °C, the total pressure is 1.70 MPa.
The number of moles of CO, H_2 and CH_3OH present are 0.160, 0.320 and 0.180, respectively.

Thermodynamic data are given below.

Substance	$\Delta H_f^{\ominus}$ / kJ mol^{-1}	$S^{\ominus}$ / J K^{-1} mol^{-1}
CO(g)	−110	198
$H_2(g)$	0	131
$CH_3OH(g)$	−201	240

The standard entropy change for this reaction is

A −220 J K^{-1} mol^{-1}

B +220 J K^{-1} mol^{-1}

C −89 J K^{-1} mol^{-1}

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D +89 J K^{-1} mol^{-1}

(Total 1 mark)

Q34.

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)

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