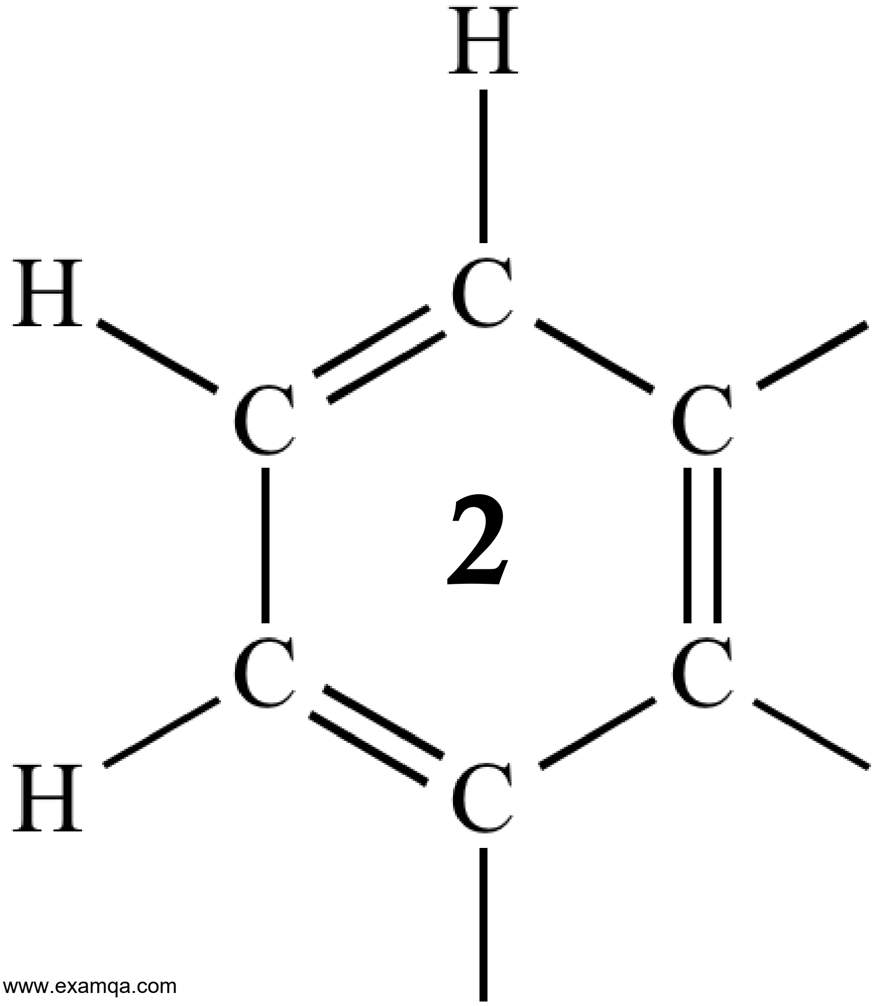
LONDON SCIENCE COLLEGE

AQA A2 CHEMISTRY

THERMODYNAMICS



1 (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)

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

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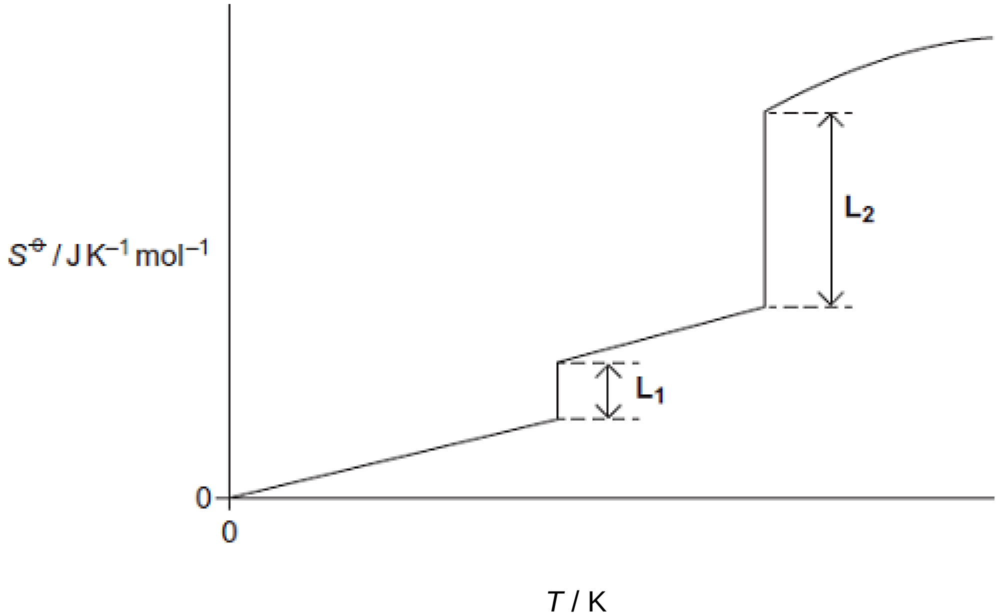
(5)
(Total 13 marks)

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

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(Extra space) ....

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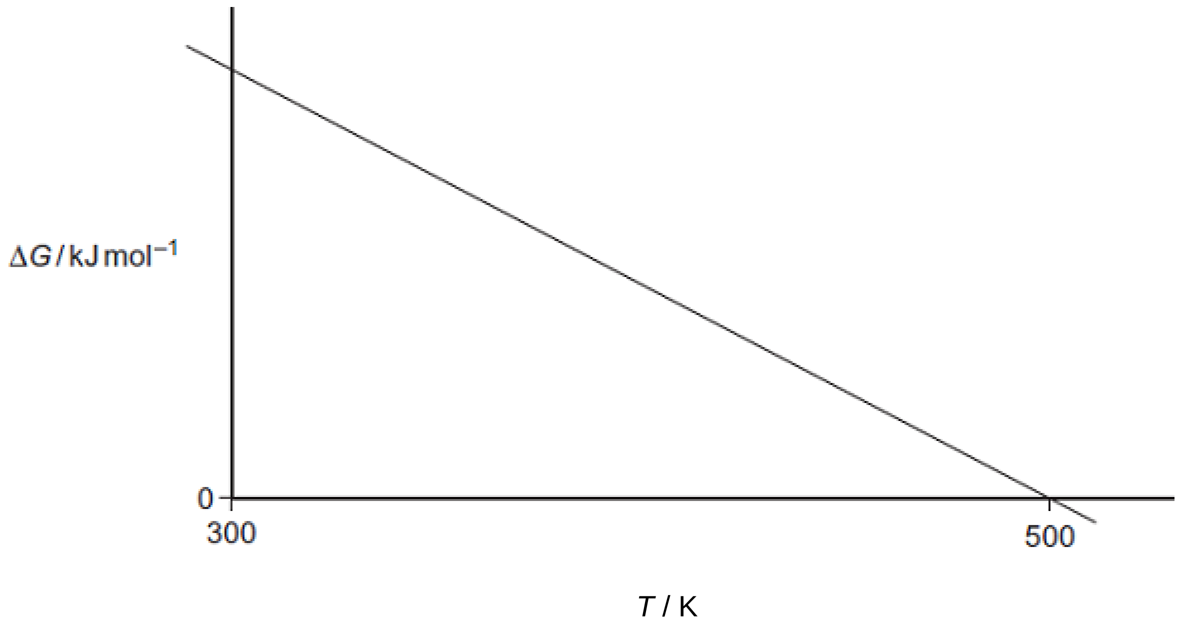
(2)

(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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(2)

(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.

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

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.

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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)

4 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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(Extra space) ....

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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)

5 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.

	$S^{\ominus}$ / 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.

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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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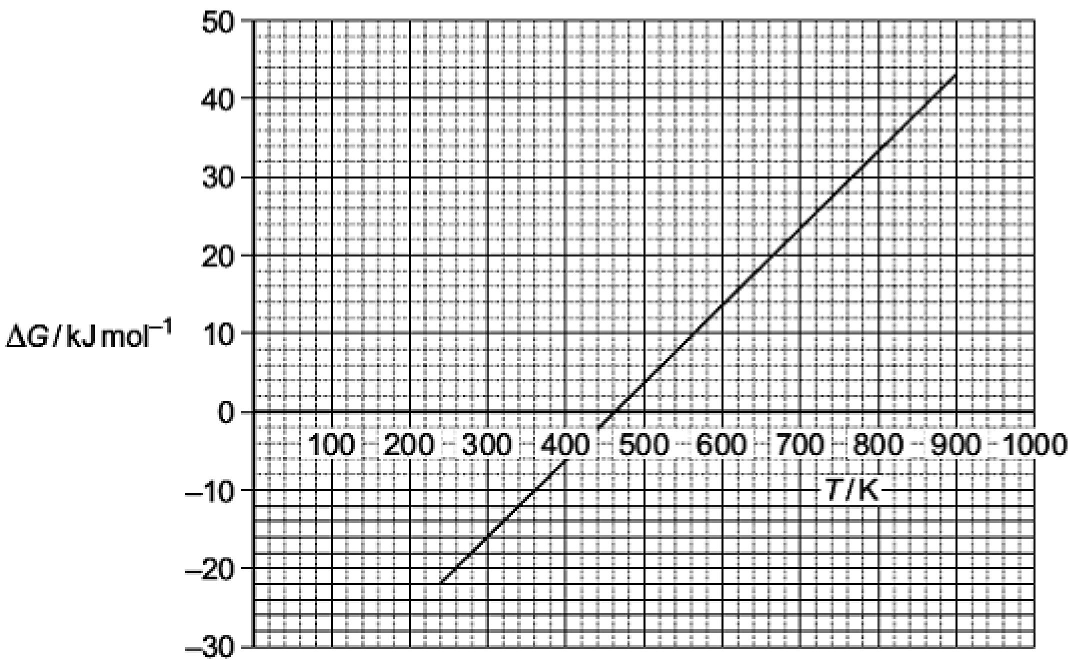
(3)
(Total 15 marks)

6 The following equation shows the formation of ammonia.

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

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.

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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)

7 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

(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) ....

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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)

8 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.

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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)

9 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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(Extra space) ....

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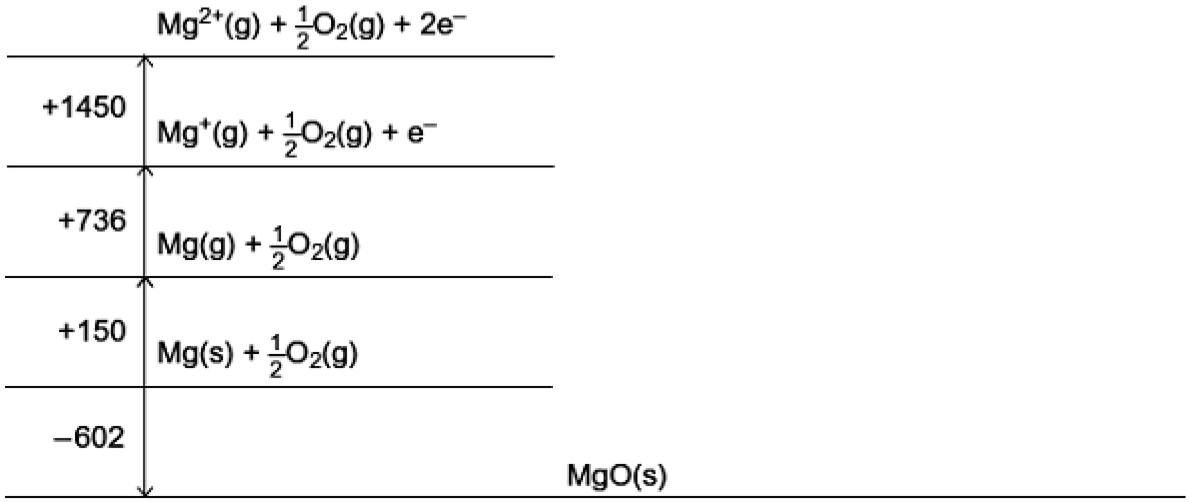
(1)

(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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(Extra space) ....

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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 $\Delta S^\ominus$.

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(Extra space) ....

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(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)

10 Consider the following process that represents the melting of ice.

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

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

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(1)

(b) Use your knowledge of bonding to explain why $\Delta H^{\ominus}$ 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)