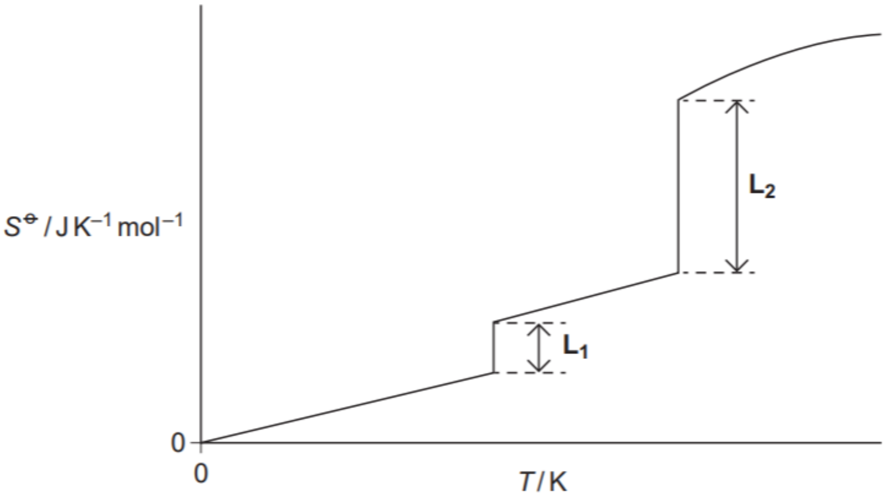
CHAPTER 17 THERMODYNAMICS

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

Figure 1



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

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(2 marks)

(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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(2 marks)

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

(1 mark)

(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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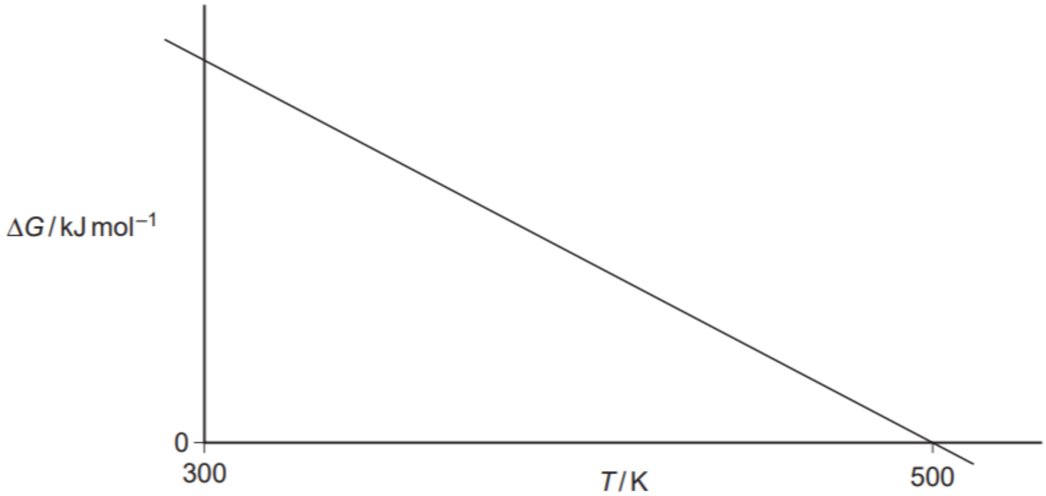
(2 marks)

(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 marks)

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

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(1 mark)

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

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(1 mark)

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

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

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 mark)

(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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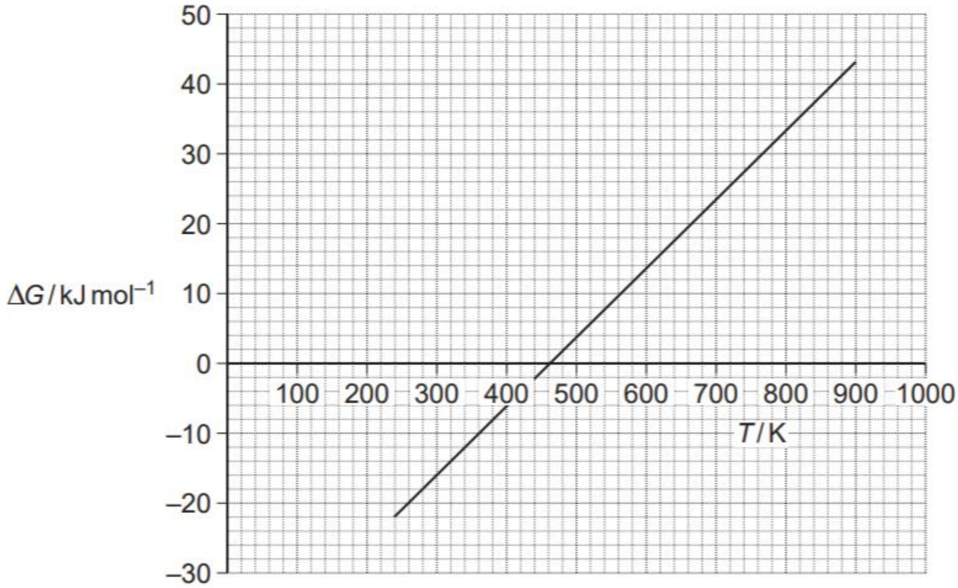
(3 marks)

2 The following equation shows the formation of ammonia.

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

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 mark)

(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 marks)

(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 marks)

(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 mark)

3 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 marks)

(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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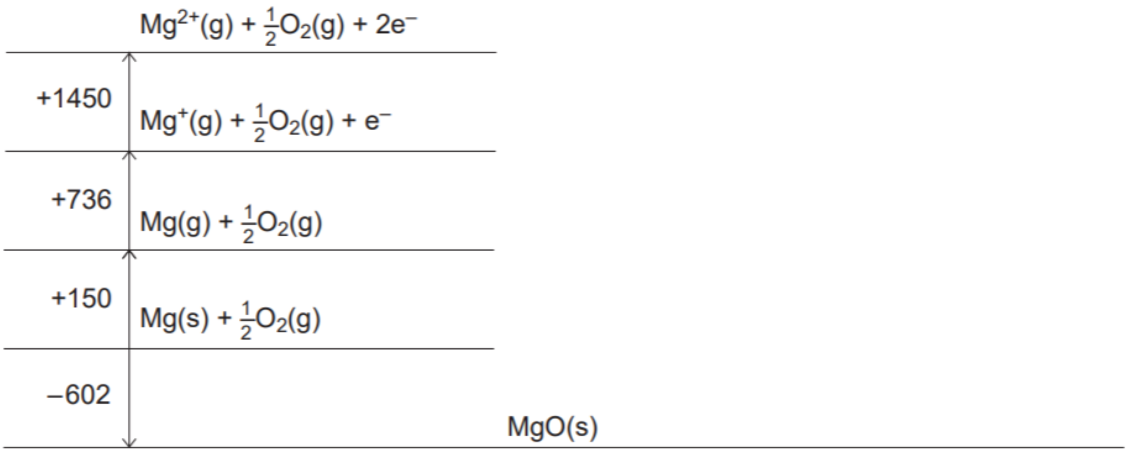
(1 mark)

(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 marks)

(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 marks)

(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 mark)

(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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(3 marks)

(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 marks)