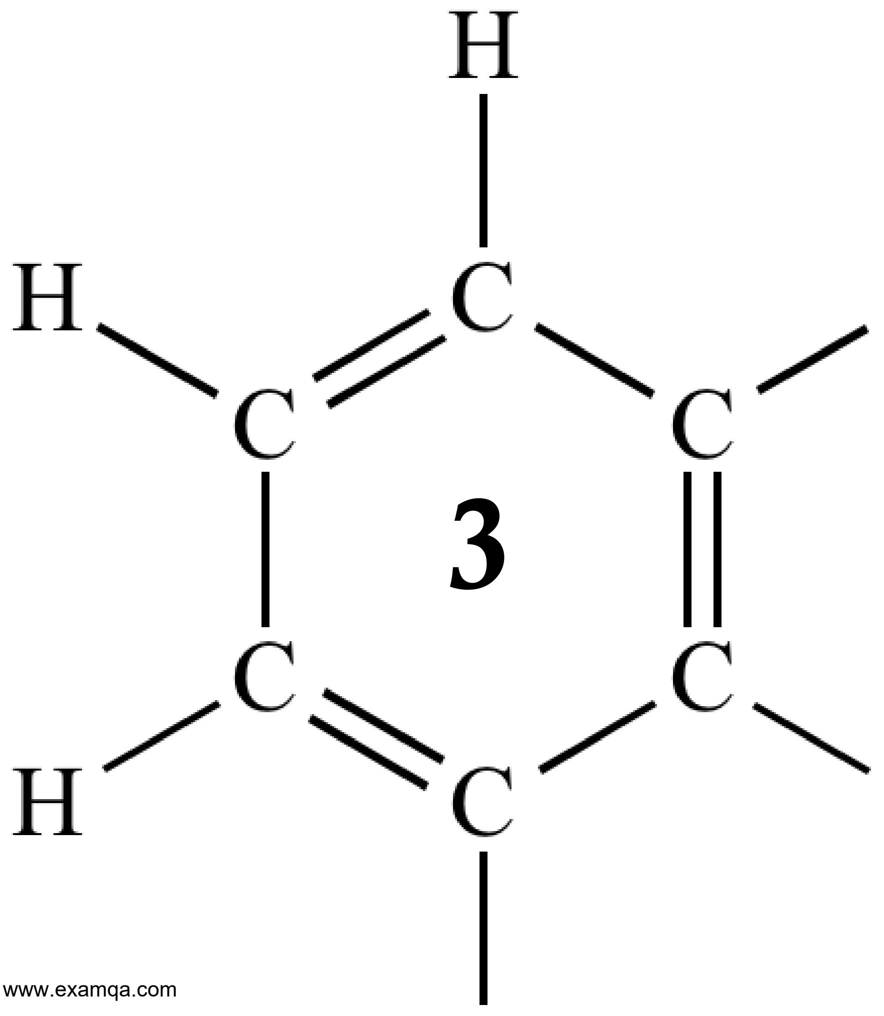
LONDON SCIENCE COLLEGE

AQA A2 CHEMISTRY

THERMODYNAMICS



1 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

....

....

....

....

(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

....

....

....

....

(2)
(Total 7 marks)

2 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.

....

....

....

....

....

....

(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?

....

....

(1)

(Total 7 marks)

3 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.

	$N \equiv N$	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.

....

....

....

....

....

....

(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.

....

....

....

....

....

(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.)

....

....

....

....

....

....

(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)

4 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

....

....

....

....

....

....

....

....

(3)

(c) Consider the following lattice dissociation enthalpy ($\Delta H_L^{\ominus}$) data.

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

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

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

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

....

....

....

....

(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)

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

	N_2(g)	O_2(g)	NO(g)	C(graphite)	C(diamond)
$\Delta H_f^{\ominus}$/kJ mol^{-1}	0	0	+90.4	0	+1.9
$S^{\ominus}$/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)

(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.

....

....

....

....

....

....

....

....

(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.

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

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

$\Delta H^{\ominus}$ ....

$\Delta S^{\ominus}$ ....

Explanation ....

....

(3)
(Total 14 marks)

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

Tables 1 and **2** contain thermodynamic data.

Table 1

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

Table 2

Name of enthalpy change	ΔH° / 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)

(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.

....

....

....

....

(2)
(Total 17 marks)

7 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.

....

....

....

....

....

....

....

(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)

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

....

....

....

(1)
(Total 17 marks)

8 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
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.

....

....

....

....

(2)

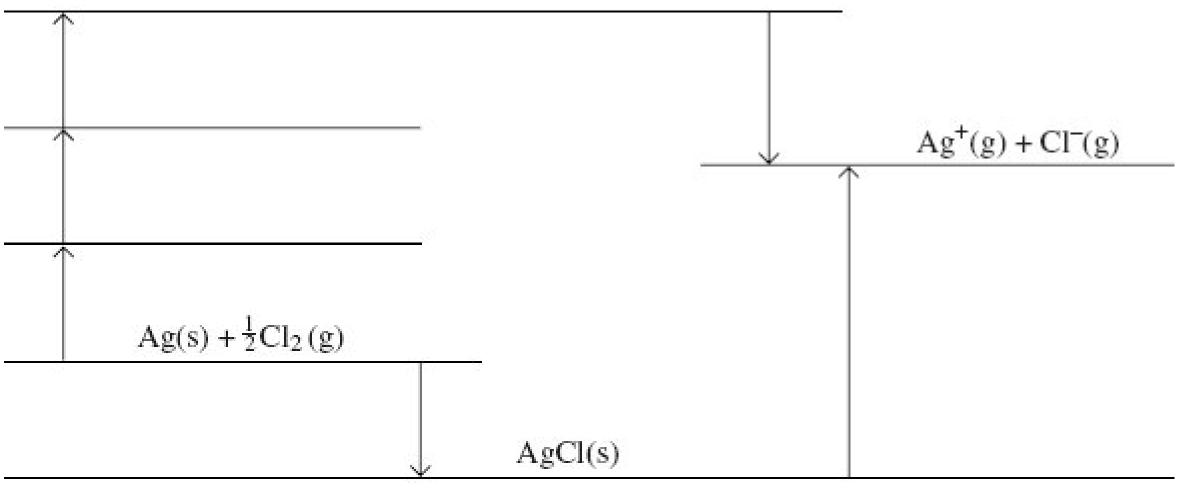
(c) Suggest why the electron affinity of chlorine is an exothermic change.

....

....

(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.

....

....

....

....

(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.

....

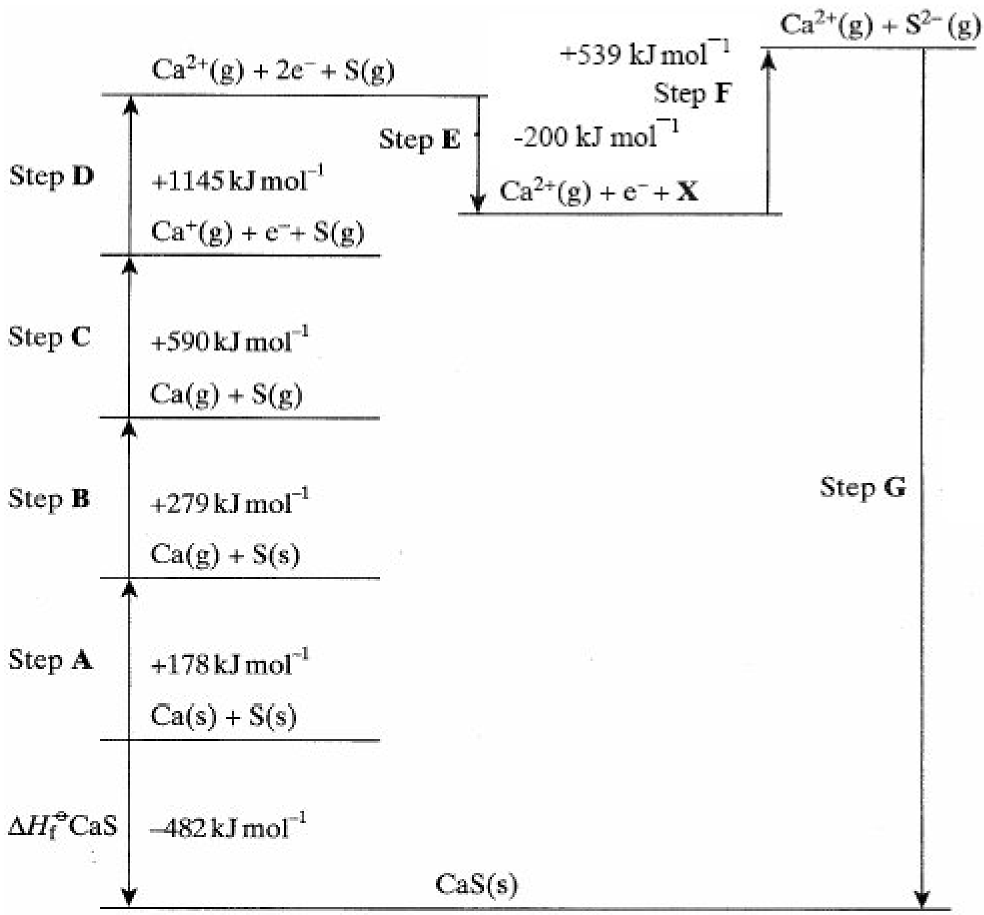
....

....

(2)

(Total 15 marks)

9 (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*** ....

*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.

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

....

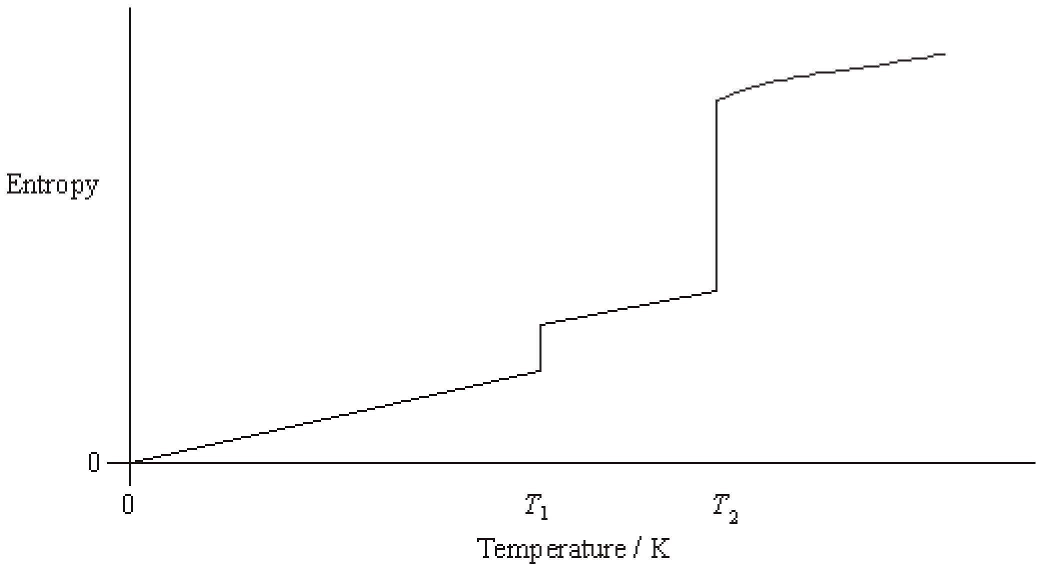
....

....

....

(6)
(Total 18 marks)

10 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 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)