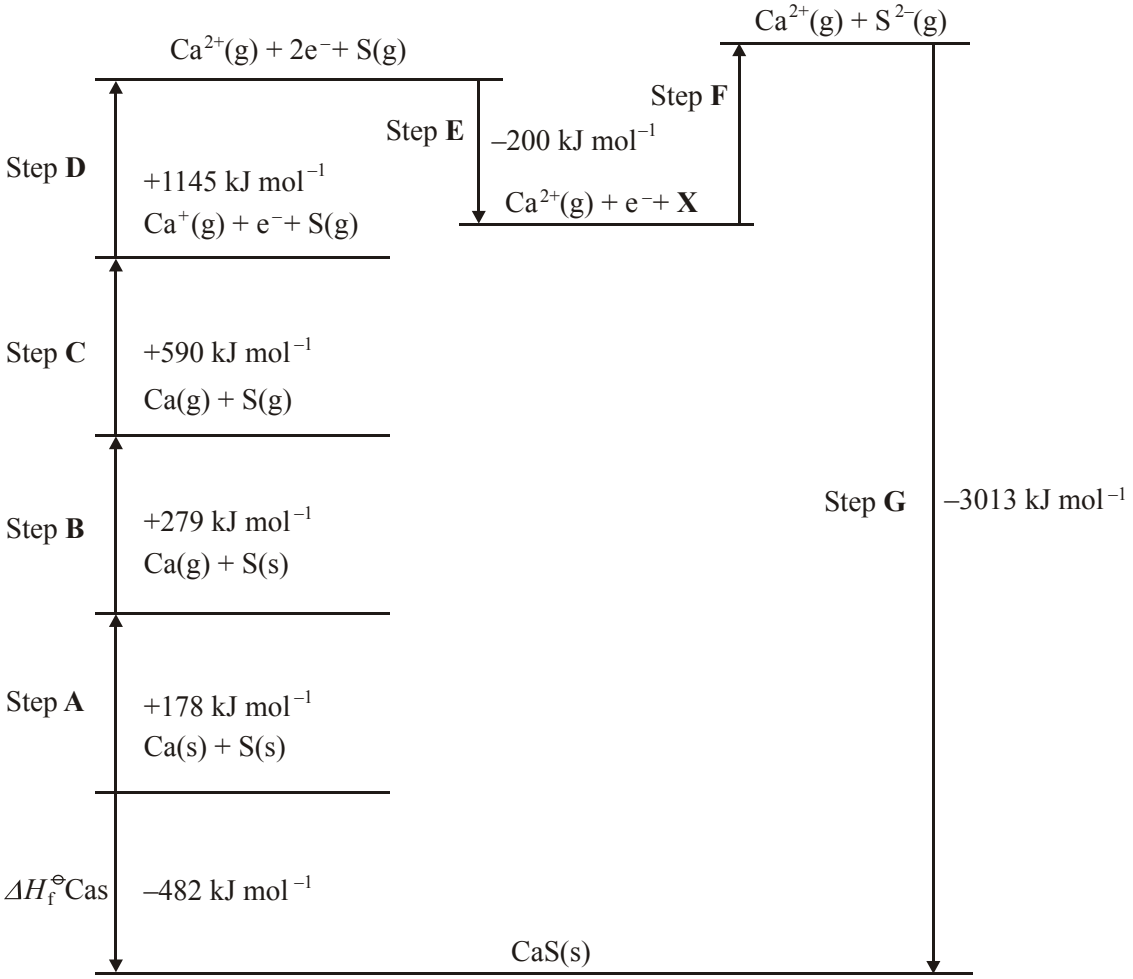
Enthalpy and Entropy

1. 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-}

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(1)

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

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(1)

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

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(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**.

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(2)

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

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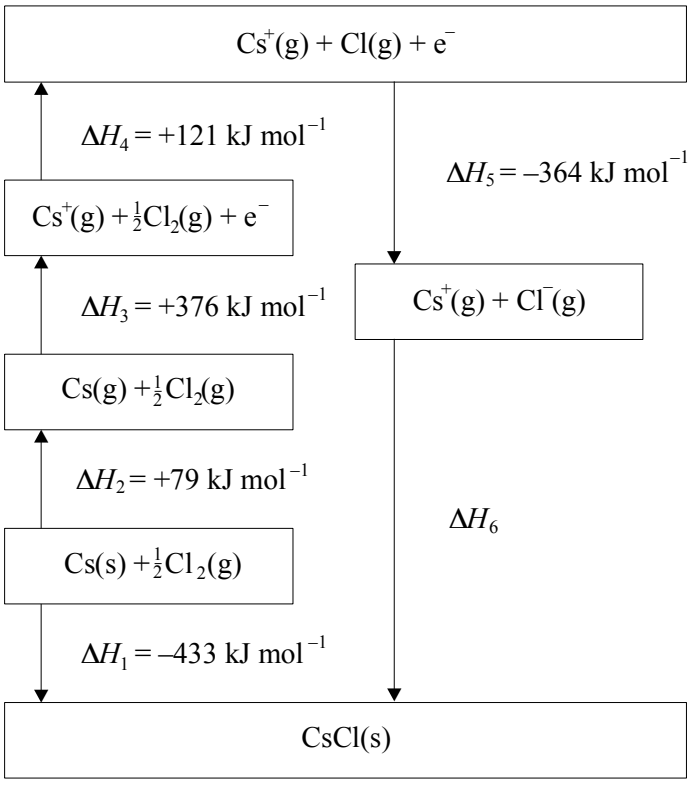
(2)

(Total 11 marks)

2. The energy level diagram (Born-Haber cycle) for caesium chloride is shown below.



(a) Give the names of the enthalpy changes represented by ΔH_1, ΔH_2 and ΔH_5.

ΔH_1 .....

ΔH_2 .....

ΔH_5 .....

(3)

(b) Calculate the value of the lattice energy ΔH_6.

(2)

(c) Explain why the enthalpy change represented by ΔH_3 has a lower magnitude for caesium than for sodium.

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(3)
(Total 8 marks)

3. **Figure 1** shows the energy level diagram (Born-Haber cycle) for the formation of rubidium iodide from its elements.

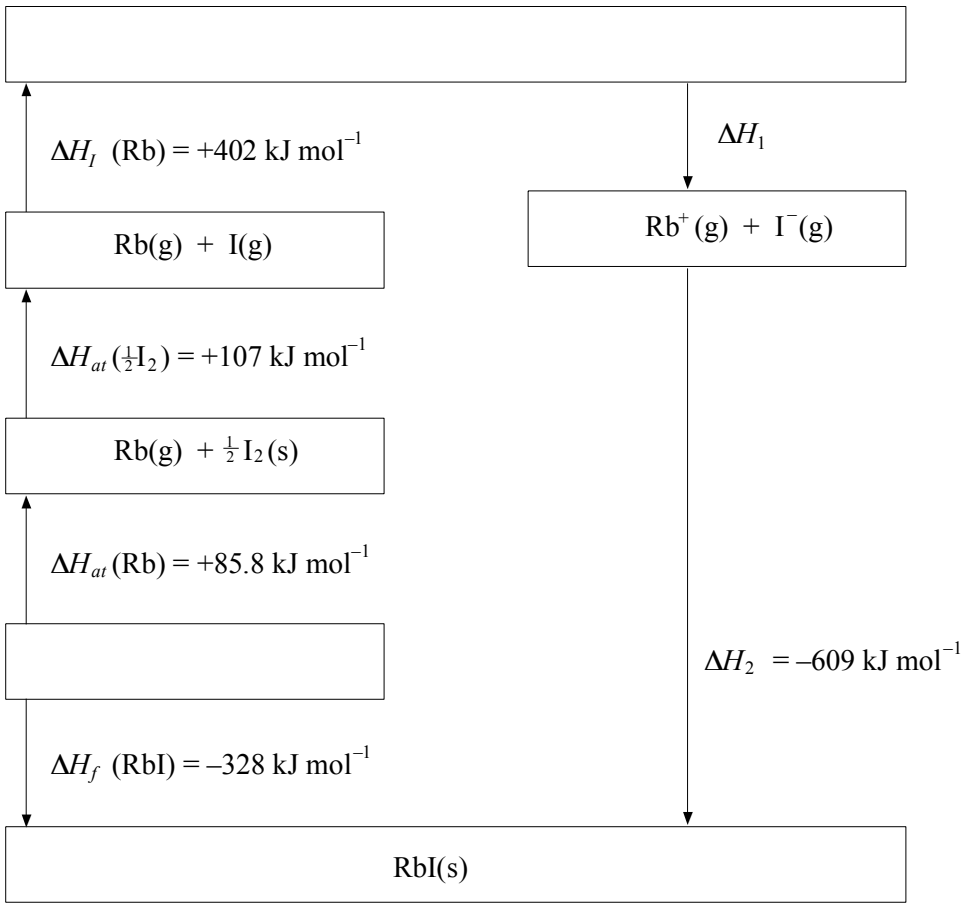


Figure 1

(i) Complete the diagram giving the identities of the missing species

(2)

(ii) Give the names of the enthalpy changes represented by ΔH_1 and ΔH_2.

ΔH_1 .....

ΔH_2 .....

(2)

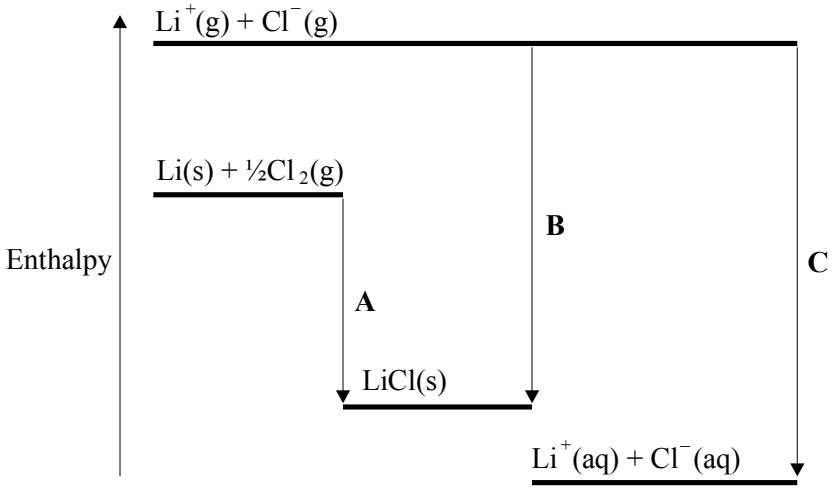
(iii) Calculate the value of the enthalpy change represented by ΔH_1.

(2)
(Total 6 marks)

4. The following data relate to lithium chloride.

Standard molar enthalpy change of solution is –37.0 kJ mol^{-1}.

Lattice enthalpy is –846 kJ mol^{-1}.



(i) Give the name of each of the changes **A** and **B**.

A.....

B.....

(2)

(ii) Calculate the value of the enthalpy change represented by **C** and suggest the name(s) of the enthalpy change(s).

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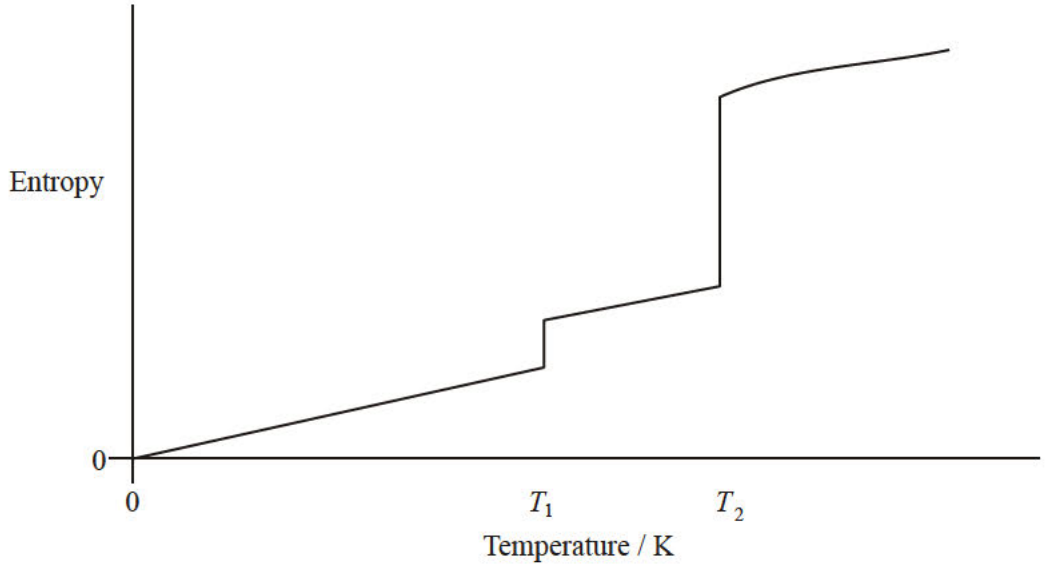
(3)
(Total 5 marks)

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



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

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(1)

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

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(1)

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

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(2)

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

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

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

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(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 .....

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Units .....

(6)
(Total 10 marks)

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

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

Enthalpy of atomisation of barium	+180 kJ mol^{-1}
Enthalpy of atomisation of chlorine	+122 kJ mol^{-1}
Enthalpy of formation of barium chloride	–859 kJ mol^{-1}
First ionisation enthalpy of barium	+503 kJ mol^{-1}
Second ionisation enthalpy of barium	+965 kJ mol^{-1}
Lattice formation enthalpy of barium chloride	–2056 kJ mol^{-1}

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(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

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(4)
(Total 13 marks)

7. (a) The following reaction occurs in the high-temperature preparation of titanium(IV) chloride.

$$TiO_2(s) + C(s) + 2Cl_2(g) \rightarrow TiCl_4(l) + CO_2(g)$$

(i) Use the data given below to calculate the standard enthalpy change and the standard entropy change for this reaction.

Substance	$TiO_2(s)$	$C(s)$	$Cl_2(g)$	$TiCl_4(l)$	$CO_2(g)$
$\Delta H_f^{\ominus}$ / kJ mol^{-1}	–940	0	0	–804	–394
$S^{\ominus}$/ J $K^{-1}mol^{-1}$	49.9	5.7	223	252	214

Standard enthalpy change .....

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Standard entropy change .....

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(ii) Calculate the temperature at which this reaction ceases to be feasible.

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(9)
(Total 9 marks)

8. 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 .....

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

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(9)

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

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

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.

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(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).

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(3)
(Total 15 marks)

9. Hydrogen used in the manufacture of ammonia is produced by the reaction between methane and steam shown in the following equation.

$$CH_4(g) + 2H_2O(g) \rightleftharpoons CO_2(g) + 4H_2(g)$$

Use the data given below to answer the questions which follow.

	$CH_4(g)$	$H_2O(g)$	$CO_2(g)$	$H_2(g)$
ΔH_f /kJ mol^{-1}	–74.8	–241.8	–393.5	0
S /J K^{-1} mol^{-1}	186.2	188.7	213.6	130.6

(a) Calculate the standard enthalpy change, $\Delta H^{\ominus}$, for this reaction.

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(3)

(b) (i) Explain, in terms of disorder, why entropy increases in this reaction.

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

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(5)

(c) (i) Calculate the temperature at which the free-energy change, ΔG, for the above reaction is zero. (Assume that ΔH and ΔS do not vary with temperature.)

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(ii) What is the significance of this temperature?

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(5)
(Total 13 marks)

10. Methanol can be synthesised from carbon monoxide and hydrogen according to the equation

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

Use the thermodynamic data below to answer the questions that follow.

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

(a) Determine the standard enthalpy change and the standard entropy change for the synthesis of methanol from carbon monoxide and hydrogen.

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

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

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(4)

(b) Explain what is meant by the term feasible reaction and determine the temperature at which the methanol synthesis reaction is no longer feasible.

Feasible reaction.....

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Temperature.....

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(3)
(Total 7 marks)

11. Sulphur dioxide reacts with oxygen to form sulphur trioxide according to the equation

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

Data for this reaction are shown in the table below.

	$\Delta H_f^{\ominus}$/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

(a) Determine the standard enthalpy, the standard entropy and standard free energy changes at 298 K for this reaction.

ΔH_{298} .....

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ΔS_{298} .....

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ΔG_{298} .....

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(7)

(b) The reaction is said to be feasible. In terms of free energy change, explain the meaning of the term *feasible*. Calculate the temperature at which the reaction between sulphur dioxide and oxygen ceases to be feasible.

Feasible reaction.....

Temperature.....

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(3)
(Total 10 marks)

12. Sulphuric acid is manufactured by the Contact Process. One stage of the process is the oxidation of sulphur dioxide according to the equation:

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) \qquad \Delta H = -196 \text{ kJ mol}^{-1}$$

Typical operating conditions are a temperature of about 450 °C**,** close to atmospheric pressure and the presence of a catalyst. The use of a converter containing four catalyst beds results in a 99.5% conversion.

The value of the entropy change, ΔS, for the reaction between sulphur dioxide and oxygen –188 J mol^{-1} K^{-1}.

(i) Explain why there is a decrease in entropy of the system.

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(2)

(ii) Use the equation

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

to calculate the value of ΔG for the reaction between sulphur dioxide and oxygen at 25 °C. Explain the significance of the sign of the value obtained.

Calculation

Explanation .....

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(4)
(Total 6 marks)

13. (a) (i) Construct a Born-Haber cycle for the formation of calcium chloride, $CaCl_2$, from its elements. Name each step in the cycle and mark on the cycle each species involved together with its state symbol.

(ii) When calcium reacts with chlorine under normal laboratory conditions $CaC1_2$ is formed not CaCl. Identify the stages in the Born-Haber cycle for the formation of CaCl which differ from those in the cycle for the formation of $CaC1_2$

(11)

(b) (i) Use the data given below to calculate the standard enthalpy of solution of $CaCl_2$.

Lattice dissociation enthalpy of $CaCl_2$ = +2255 kJ mol^{-1}
Hydration enthalpy of calcium ions = –1650 kJ mol^{-1}
Hydration enthalpy of chloride ions = –384 kJ mol^{-1}

(ii) Using your answer to part (b)(i), deduce how the solubility of $CaCl_2$ changes as temperature is increased. Explain your answer.

(6)
(Total 17 marks)

14. Construct a Born-Haber cycle for the formation of the hypothetical crystalline solid magnesium(I) chloride, MgCl(s).

The table below shows values of standard enthalpies for some processes involving magnesium and chlorine. Use these values to calculate the standard enthalpy of formation of the hypothetical MgCl(s).

Use your answer to calculate the standard enthalpy change for the reaction

$$2MgCl(s) \rightleftharpoons MgCl_2(s) + Mg(s)$$

given that the standard enthalpy of formation of $MgCl_2(s)$, $\Delta H_f^{\ominus}$, is –653 kJ mol^{-1}

Explain why the standard entropy change in this reaction is likely to be negligibly small. Comment on the stability of MgCl(s) relative to that of $MgCl_2(s)$.

			$\Delta H^{\ominus}$ kJ mol^{-1}
$Mg^+(g) + Cl^-(g)$	→	MgCl(s)	–753
$Cl(g) + e^-$	→	$Cl^-(g)$	-364
$\frac{1}{2} Cl_2(g)$	→	Cl(g)	+121
Mg(s)	→	Mg(g)	+146
Mg(s)	→	$Mg^+(g) + e^-$	+736

(Total 10 marks)

15. (a) State what is meant by the term *enthalpy change*.

(2)

(b) Construct a fully-labelled Born-Haber cycle for the formation of MgO and use the data given below to calculate a value for the enthalpy of lattice formation of this oxide.

Process	**$\Delta H^{\ominus}$/kJ mol^{-1}**
$Mg(s) + \frac{1}{2} O_2(g) \rightarrow MgO(s)$	–602
$Mg(s) \rightarrow Mg(g)$	+148
$Mg(g) \rightarrow Mg^+(g) + e^-$	+738
$Mg+(g) \rightarrow Mg^{2+}(g) + e^-$	+1451
$O_2(g) \rightarrow 2O(g)$	+498
$O(g) + e^- \rightarrow O^-(g)$	–141
$O^-(g) + e^- \rightarrow O^{2-}(g)$	+798

(8)

(c) By consideration of the entropy changes in the reaction and the data given below, explain why the following reaction is never feasible.

$$MgCl_2(s) + \tfrac{1}{2}\ Cl_2(g) \rightarrow MgCl_3(s)$$

Compound	**$\Delta H_f^{\ominus}$ / kJ mol^{-1}**
$MgCl_2(s)$	–653
$MgCl_3(s)$	+3904

(5)
(Total 15 marks)

16. Ethyl ethanoate can be prepared by the reactions shown below.

Reaction 1

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

Reaction 2

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

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.

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

(6)
(Total 6 marks)

17. The equations for two industrial equilibrium reactions are given below.

Reaction 1 $CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g)$

Reaction 2 $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

(a) Use the information in the table below to calculate the temperatures at which the free-energy change for each reaction is equal to zero.

	$CH_4(g)$	$H_2O(g)$	$CO(g)$	$H_2(g)$	$N_2(g)$	$NH_2(g)$
ΔH_f /kJ mol $^{-1}$	–74.8	–241.8	–110.5	0	0	–46.1
S /J K^{-1} mol^{-1}	186.2	188.7	197.6	130.6	191.6	192.3

(10)

(b) In industry, **Reaction 1** and **Reaction 2** are carried out at high temperatures. State how, using temperatures higher than those calculated in part (a), the yields of products are altered in **Reaction 1** and in **Reaction 2**. In each case, explain why a high temperature is used in practice.

(5)
(Total 15 marks)

18. (a) The reaction given below does not occur at room temperature.

$$CO_2(g) + C(s) \rightarrow 2CO(g)$$

Use the data given below to calculate the lowest temperature at which this reaction becomes feasible.

	C(s)	CO(g)	$CO_2(g)$
$\Delta H_f^{\ominus}$/kJ mol^{-1}	0	–110.5	–393.5
$S^{\ominus}$/J K^{-1} mol^{-1}	5.7	197.6	213.6

(8)

(b) When an electrical heating coil was used to supply 3675 J of energy to a sample of water which was boiling at 373 K, 1.50 g water were vaporised. Use this information to calculate the entropy change for the process

$$H_2O(l) \rightarrow H_2O(g)$$

(3)
(Total 11 marks)

19. Iron (II) oxide can be reduced to iron both by carbon, which is oxidised to carbon monoxide, and by carbon monoxide, which is oxidised to carbon dioxide, as shown in the equations below.

$$FeO(s) + C(s) \rightarrow Fe(s) + CO(g)$$

$$FeO(s) + CO(g) \rightarrow Fe(s) + CO_2(g)$$

(a) Use the data given below to deduce the free energy change, $\Delta G^{\ominus}$, measured at 450 K, for **each** of these reduction processes.

(Assume that the enthalpy change and the entropy change in each of these reactions remain the same if the temperature is raised from 298 K to 450 K.)

	FeO(s)	Fe(s)	C(s)	CO(g)	$CO_2(g)$
$\Delta H_f^{\ominus}$/kJ mol^{-1}	–271.9	0	0	–110.5	-393.5
$S^{\ominus}$/J K^{-1} mol^{-1}	58.5	27.3	5.7	197.6	213.6

(10)

(b) Deduce how an increase in temperature will affect the feasibility of each of the processes in which iron(II) oxide is reduced to iron.

(5)
(Total 15 marks)