Q1.

(a) Write an equation for the process that has an enthalpy change equal to the electron affinity of chlorine.

[1 mark]

....

(b) In terms of electrostatic forces, suggest why the electron affinity of fluorine has a negative value.

[2 marks]

....

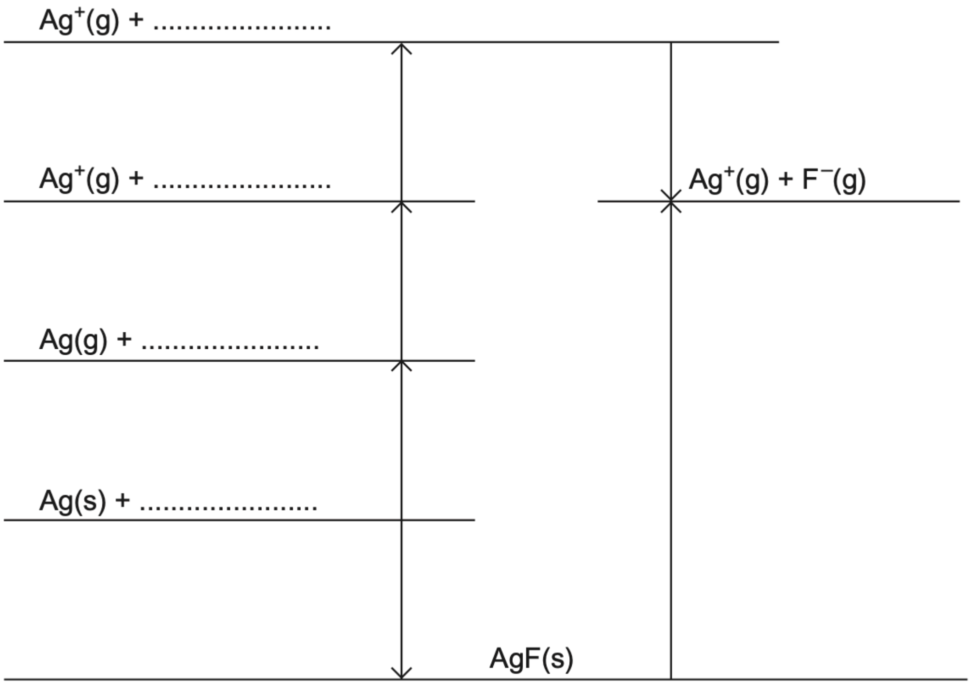
....

....

....

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

[3 marks]



(c) (ii) Use the cycle in Question **1 (c) (i)** and the data in **Table 1** to calculate a value, in kJ mol^{-1}, for the bond enthalpy of the fluorine–fluorine bond.

[2 marks]

Table 1

Enthalpy change	**Value / kJ mol^{-1}**
Enthalpy of atomisation for silver	+289
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

....

....

....

....

....

(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}.

(d) (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–Haber cycle.

[2 marks]

....

....

....

....

....

[Extra space] ....

....

(d) (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.

[2 marks]

....

....

....

....

....

[Extra space] ....

....

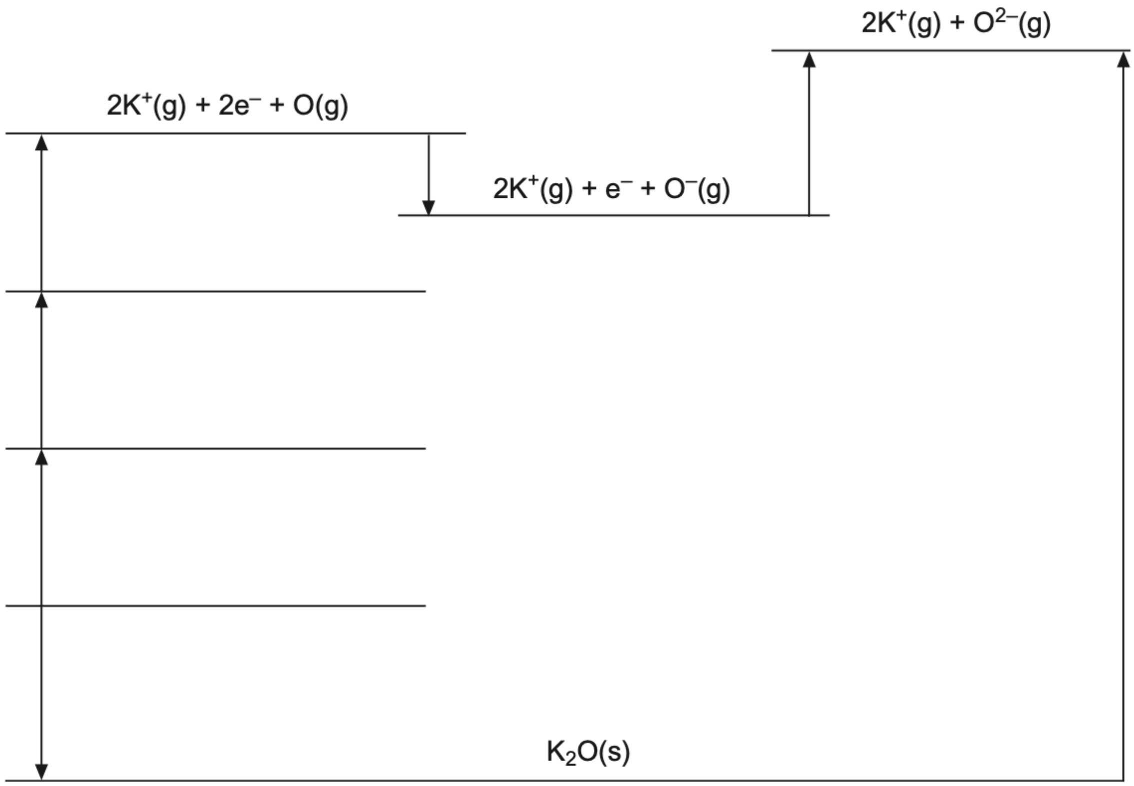
Q2.

(a) **Figure 1** is a Born–Haber cycle for potassium oxide, K_2O. **Figure 1** is not to scale and not fully labelled.

(a) (i) Complete **Figure 1** by writing the formulae, including state symbols, of the appropriate species on each of the three blank lines.

[3 marks]

Figure 1



(a) (ii) **Table 1** shows some enthalpy data.

Table 1

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 oxide	–362

Use the data in **Table 1** to calculate the enthalpy of lattice dissociation of potassium oxide, K_2O

[3 marks]

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

[2 marks]

Q3.

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 mark]

(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}

[2 marks]

(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.

[3 marks]

Q4.

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

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

(a) **Table 4** contains some enthalpy of formation and entropy data.

Table 4

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

(a) (i) Use data from **Table 4** to calculate the enthalpy change, ΔH, for the reaction of steam with methane.

[3 marks]

....

....

....

....

....

....

....

(a) (ii) Use data from **Table 4** to calculate the entropy change, ΔS, for the reaction of steam with methane.

[2 marks]

....

....

....

....

....

(b) Use your values of ΔH and ΔS from Questions **3 (a) (i)** and **3 (a) (ii)** to calculate the temperature above which this reaction is feasible.

[4 marks]

....

....

....

....

....

....

....

....

(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 temperature is used rather than the value that you calculated in Question **3 (b)**.

[1 mark]

....

....

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

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

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

[3 marks]

....

....

....

....

....

....

....

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

[2 marks]

....

....

....

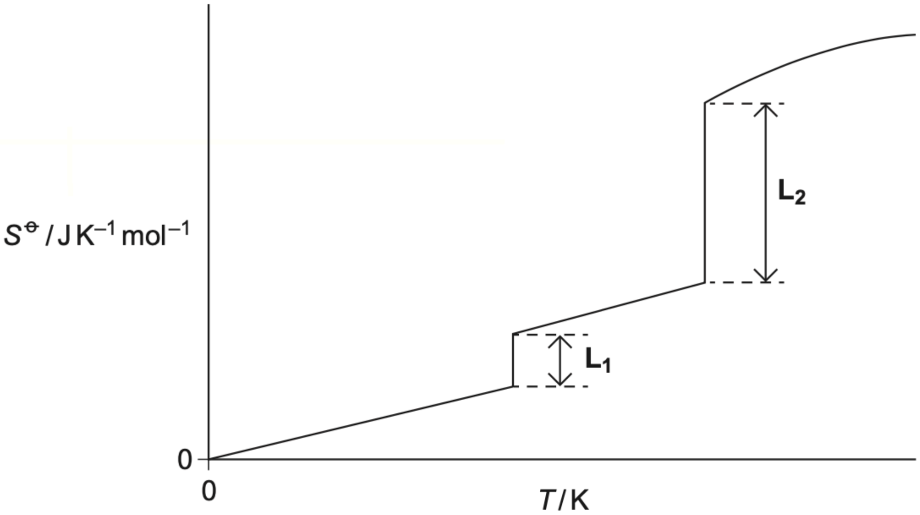
....

....

Q5.

(a) **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.

....

....

....

....

(2 marks)

(Extra space) ....

....

(a) (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 marks)

(Extra space) ....

....

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

(1 mark)

(a) (iv) In terms of the behaviour of molecules, explain why $\mathbf{L_2}$ is longer than $\mathbf{L_1}$ in **Figure 1**.

....

....

....

....

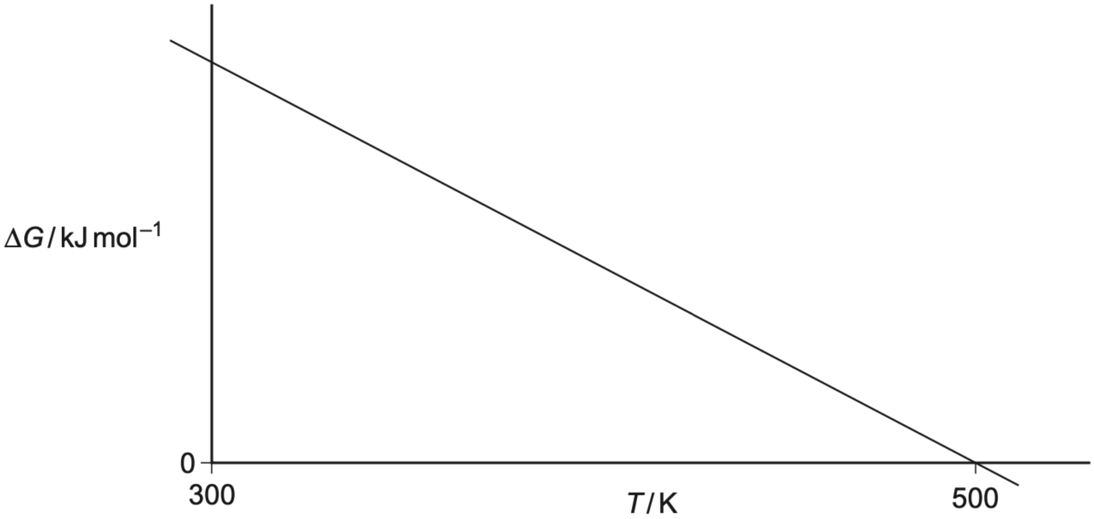
(2 marks)

(Extra space) ....

....

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

Figure 2



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

....

....

....

....

....

....

(2 marks)

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

....

....

(1 mark)

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

....

....

(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

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

....

....

(1 mark)

(c) (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.)

....

....

....

....

....

....

(3 marks)

Q1.

Question	Marking Guidance		Comments
1(a)	$Cl(g) + e^- \rightarrow Cl^-(g)$	1	State symbols essential Allow e with no charge This and all subsequent equations must be balanced
1(b)	There is an attraction between the nucleus / protons and (the added) electron(s) Energy is released (when the electron is gained)	1 1	Allow product more stable / product has lower energy Allow reaction exothermic / heat released Allow reference to chlorine rather than fluorine Wrong process eg ionisation, boiling CE = 0
1(c)(i)	Top line: $+ e^- + F(g)$ Second line from top : $+ e^- + \frac{1}{2}F_2(g)$ Bottom two lines: $+ \frac{1}{2}F_2(g)$	1 1 1	Penalise missing / wrong state symbols one mark only Penalise Fl or Cl one mark only Mark independently Allow e with no charge Penalise each lack of an electron in M1 and M2 each time

Q1.

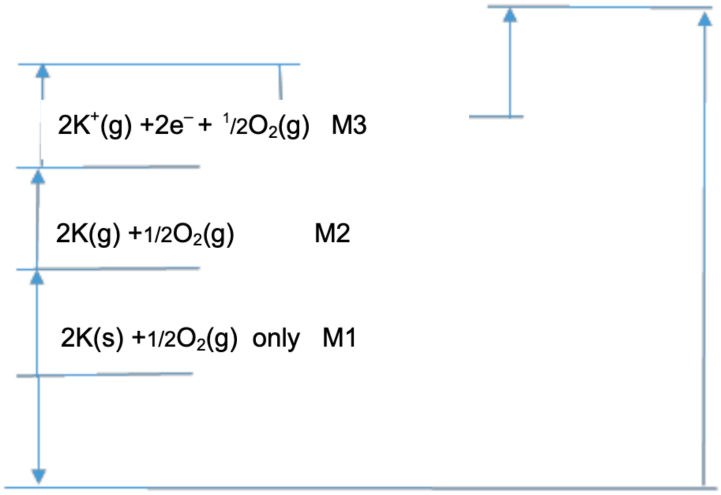
1(c)(ii)	$\frac{1}{2}$E(F–F) + 732 + 289 + +203 = 348 + 955		
	$\frac{1}{2}$E(F–F) = 79	1	
	E(F–F) = 158 (kJ mol^{-1})	1	Award one mark (M2) if M1 wrong but answer = M1 × 2 Ignore no units, penalise wrong units but allow kJ mol^{-} Any negative answer, CE = 0

1(d)(i)	Experimental lattice enthalpy value allows for / includes covalent interaction / non–spherical ions / distorted ions / polarisation OR AgF has covalent character	1	Allow discussion of AgCl instead of AgF CE = 0 for mention of molecules, atoms, macromolecular, mean bond enthalpy, intermolecular forces (imf), electronegativity
	Theoretical lattice enthalpy value assumes only ionic interaction / point charges / no covalent / perfect spheres / perfectly ionic OR AgF is not perfectly ionic	1	

Q1.

1(d)(ii)	Chlor<u>ide</u> <u>ion</u> larger (than fluor<u>ide</u> ion) / fluor<u>ide</u> <u>ion</u> smaller (than chlor<u>ide</u> ion)	1	Penalise chlorine ion once only Allow Cl^- and F^- instead of names of ions Allow chloride ion has smaller charge density / smaller charge to size ratio but penalise mass to charge ratio
	<u>Attraction</u> between Ag^+ and Cl^- weaker / <u>attraction</u> between Ag^+ and F^- stronger	1	For M2 Cl^- and F^- can be implied from an answer to M1 Mark M1 and M2 independently provided no contradiction CE = 0 for mention of chlorine not chloride ion, molecules, atoms, macromolecular, mean bond enthalpy, intermolecular forces (imf), electronegativity

Q2.

Question	Marking guidance	Mark	Comments
2ai	 $2K^+(g) + 2e^- + {}^1/{}_2O_2(g)$ M3 $2K(g) + 1/2O_2(g)$ M2 $2K(s) + 1/2O_2(g)$ only M1	1 1 1	Mark each line independently, but follow one route only. Must have state symbols, but ignore s.s. on electrons. Penalise lack of state symbols each time. Alternative answers $2K(g) + O(g)$ M3 $2K(g) + 1/2O_2(g)$ M2 $2K(s) + 1/2O_2(g)$ only M1 or $2K(g) + O(g)$ M3 $2K(s) + O(g)$ M2 $2K(s) + 1/2O_2(g)$ only M1

Q2.

2aii	(2 x 90) + 248 + (2 x 418) – 142 + 844 = – 362 + Lattice enthalpy of dissociation enthalpy of lattice dissociation = (+) 2328 (kJmol^{-1})	3	M1 for (2 x 90) and (2 x 418) M2 for a correct expression (either in numbers or with words/formulae) M3 for answer 2328 kJmol^{-1} scores 3 marks. Allow answers given to 3sf. Answer of 1820, scores zero marks as two errors in calculation. Answers of 2238, 1910, 2204 max = 1 mark only since one chemical error in calculation (incorrect/missing factor of 2) Allow 1 mark for answer of -2328 (kJmol^{-1}) Penalise incorrect units by one mark.

Q2.

2b	K^+ (ion)/K ion is bigger (than Na^+ ion)	1	K^+ has lower charge density / Na^+ has higher charge density. Ignore K atom is bigger
	(Electrostatic) attraction between (oppositely charged) ions is weaker	1	If attraction is between incorrect ions, then lose M2 *Attraction between molecules/atoms or mention of intermolecular forces CE=0/2* Allow converse for Na_2O if explicit

Q3.

Question	Marking guidance	Mark	Comments
3a	$MgCl_2(s) \rightarrow Mg^{2+}(aq) + 2Cl^-(aq)$	1	State symbols essential Do not allow this equation with H_2O on the LHS Ignore + aq on the LHS Allow H_2O written over the arrow / allow equation written as an equilibrium, Allow correct equations to form $[Mg(H_2O)_6]^{2+}$ ions.
3b	$\Delta H_{soln}\ MgCl_2 = LE + (\Delta H_{hyd}Mg^{2+}) + 2(\Delta H_{hyd}Cl^-)$ $\Delta H_{soln}\ MgCl_2 = 2493 - 1920 + (2 \times -364)$	1	M1 for expression in words or with correct numbers
	$= -155\ (kJ\ mol^{-1})$	1	Ignore units, but penalise incorrect units
3c	M1: Solubility decreases (as temp increases)	1	If M1 is incorrect then CE=0/3
	M2: the enthalpy of solution is exothermic / reaction is exothermic / backwards reaction is endothermic	1	If answer to 3b is a +ve value, allow:
	M3: (According to Le Chatelier) the equilibrium moves to absorb heat/reduce temperature/oppose the increase in temperature (in the endothermic direction)	1	M1: Solubility increases (as temp increases) M2: Enthalpy of solution is endothermic etc. M3: (According to Le Chatelier) the equilibrium moves to absorb heat/reduce the temperature/oppose the increase in temperature (in the endothermic direction)

Q4.

Question	Marking Guidance	Mark	Comments
(a)(i)	ΔH = Σ(enthalpies formation products) – Σ(enthalpies formation reactants)	1	Or correct cycle with enthalpy changes labelled
	= –111 –(–75 – 242)	1	
	= (+)206 (kJ mol^{-1})	1	–206 scores 1 only Units not essential if ans in kJ mol^{-1} but penalise incorrect units
(a)(ii)	ΔS = Σ(entropies of products) – Σ(entropies reactants)		
	= 198 + 3 × 131 – (186 + 189)	1	
	= (+) 216 (J K^{-1} mol^{-1}) OR 0.216 kJ K^{-1} mol^{-1}	1	Units not essential but penalise incorrect units

Q4.

(b)	When $\Delta G = 0$ OR $\Delta H = T\Delta S$	1	
	$T = \Delta H/\Delta S$	1	M2 also scores M1
	= 206 × 1000/216	1	Allow error carried forward from (a)(i) and (a)(ii) Ignore unexplained change of sign from – to +
	= 954 K	1	Allow 953 – 955, Units of K essential, must be +ve If values from (a)(i) and (a)(ii) lead to negative value in M3 allow M1 to M3 but do not allow negative temperature for M4 If negative value changed to positive for M4, allow M4
(c)	To speed up the rate of reaction OR wtte	1	Allow so that more molecules have energy greater than the activation energy IF T in 3(b) > 1300 allow answers such as; to reduce energy cost to slow down reaction do NOT allow to increase rate

Q4.

(d)(i)	**Method 1** $\Delta G = \Delta H - T\Delta S$		
	ΔG = –41 – (1300 × –42/1000) (M1)	1	If 42 and not 42/1000 used can score M3 only but allow ΔG = –41 x 1000 – (1300 × –42) (M1)
	= +13.6 kJ mol^{-1}	1	=13600 J mol^{-1} (M2) Units essential
	ΔG must be negative for the reaction to be feasible. OR ΔG is positive so reaction is not feasible	1	
	Method 2 For reaction to be feasible ΔG must be negative or zero	1	
	T when $\Delta G = 0 = \Delta H / \Delta S$ = 976K	1	
	ΔS is -ve so ΔG must be +ve at temperatures above 976K / at 1300 K	1	
(d)(ii)	If the temperature is lowered (Ignore reference to catalyst and/or pressure)	1	Alternative mark scheme (if T is calculated) Allow T reduced to 976 K or lower M1
	ΔG will become (more) negative because the $-T\Delta S$ term will be less positive/ $T\Delta S > \Delta H$	1	At this temperature (the reaction becomes feasible because) ΔG <= 0 M2

Q5.

Question	Marking Guidance	Mark	Comments
(a)(i)	(At 0 K) particles are stationary / not moving / not vibrating No disorder / perfect order / maximum order	1 1	Allow have zero energy. Ignore atoms / ions. Mark independently.
(a)(ii)	As *T* increases, particles start to move / vibrate Disorder / randomness increases / order decreases	1 1	Ignore atoms / ions. Allow have more energy. If change in state, CE = 0
(a)(iii)	Mark on temperature axis vertically below second 'step'	1	Must be marked as a line, an 'x' , T_b or 'boiling point' on the temperature axis.
(a)(iv)	L_2 corresponds to boiling / evaporating / condensing / l → g / g → l And L_1 corresponds to melting / freezing / s → l / l → s Bigger change in disorder for L_2 / boiling compared with L_1 / melting	1 1	There must be a clear link between L_1, L_2 and the change in state. M2 answer must be in terms of changes in state and not absolute states eg must refer to change from liquid to gas not just gas. Ignore reference to atoms even if incorrect.

Q5.

(b)(i)	$\Delta G = \Delta H - T\Delta S$ $\Delta H = c$ and $(-)\Delta S = m$ / ΔH and ΔS are constants (approx)	1 1	Allow ΔH is the intercept, and $(-)\Delta S$ is the slope / gradient. Can only score M2 if M1 is correct.
(b)(ii)	Because the entropy change / ΔS is positive / $T\Delta S$ gets bigger	1	Allow $-T\Delta S$ gets more negative.
(b)(iii)	Not feasible / unfeasible / not spontaneous	1	
(c)(i)	+ 44.5 J K^{-1} mol^{-1}	1	Allow answer without units but if units given they must be correct (including mol^{-1})
(c)(ii)	At 5440 $\Delta H = T\Delta S$ = 5440 × 44.5 = 242 080 (***OR*** using given value = 5440 × 98 = 533 120) $\Delta H =$ 242 kJ mol^{-1} (***OR*** using given value $\Delta H =$ 533 kJ mol^{-1})	1 1 1	Mark is for answer to (c)(i) × 5440 Mark is for correct answer to M2 with correct units (J mol^{-1} or kJ mol^{-1}) linked to answer. If answer consequentially correct based on (c)(i) except for incorrect sign (eg -242), max 1/3 provided units are correct.