OCR A Chemistry A-Level

Module 5 - Physical Chemistry & Transition Elements

Enthalpy and Entropy

Notes and Example Calculations

Answers given at the end of the booklet

Born-Haber cycles

Lattice Enthalpy

The enthalpy change when 1 mole of an ionic crystal lattice is formed from its isolated gaseous ions.

$$Na^+ (g) + Cl^- (g) \rightarrow NaCl (s)$$

This enthalpy change cannot be measured directly so a Born-Haber cycle is used to determine its value. These cycles use a range of different enthalpy changes to determine the lattice enthalpy for a substance. These include:

Enthalpy of Formation

The enthalpy change when 1 mole of a substance is formed from its constituent elements.

(1st) Ionisation Energy

The energy required to remove one electron from the outermost shell of an atom in the a mole of atoms in the gaseous state

Enthalpy of Atomisation

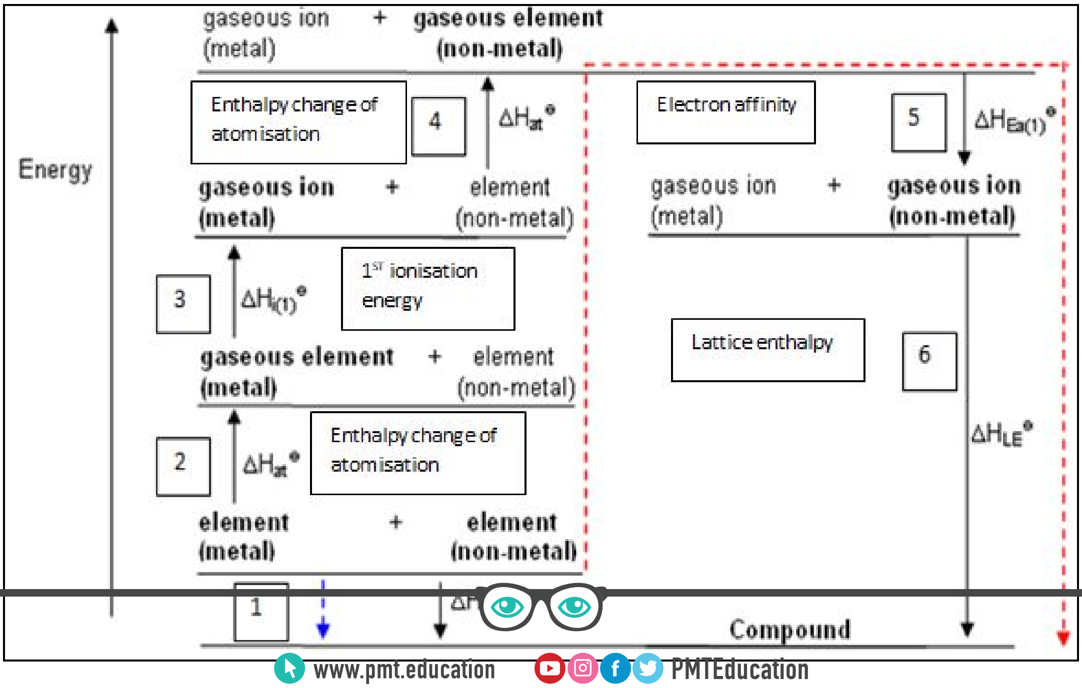
The enthalpy change when one mole of gaseous atoms is formed from an element.

Electron affinity

The enthalpy change when one moles of gaseous atoms acquires one mole of electrons to form one mole of gaseous negative ions.

This is the basic template of the Born- Haber cycle to work out lattice enthalpy is:

⇒ Step 1 (ΔH_f) = (Step 2) + (Step 3) + (Step 4) + (Step 5) + (Step 6)

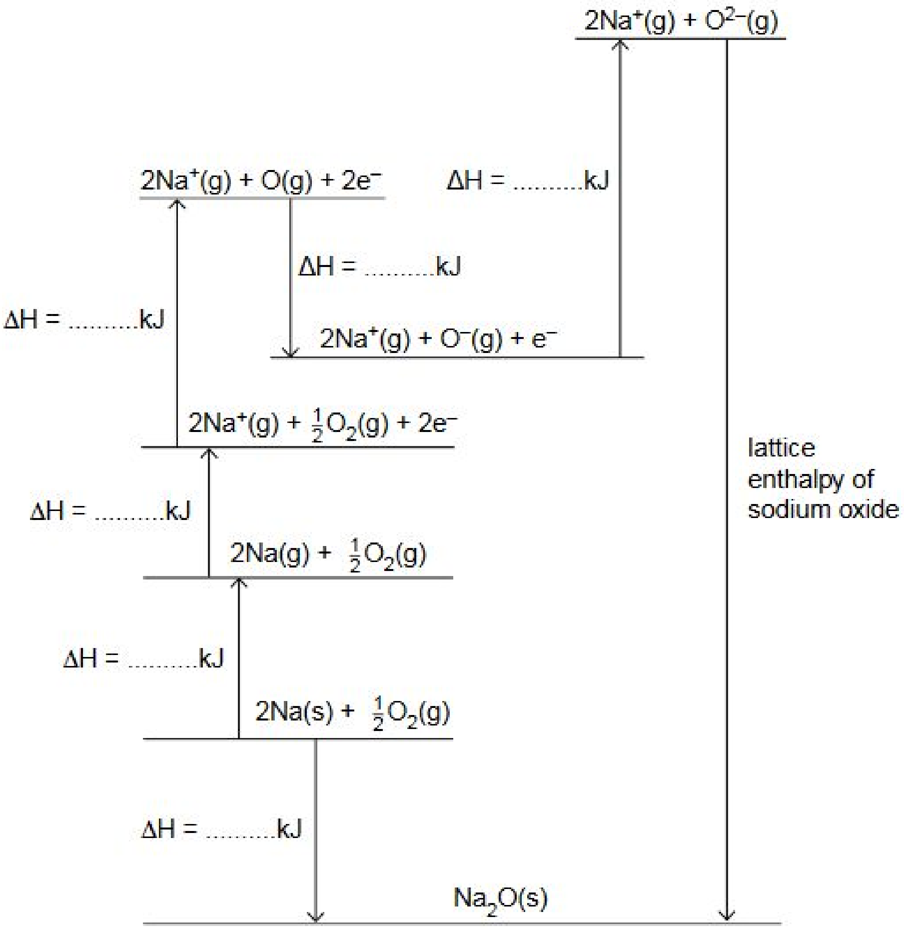


Example 1:

The table below shows the enthalpy changes needed to construct a Born-Haber cycle for sodium oxide, Na_2O.

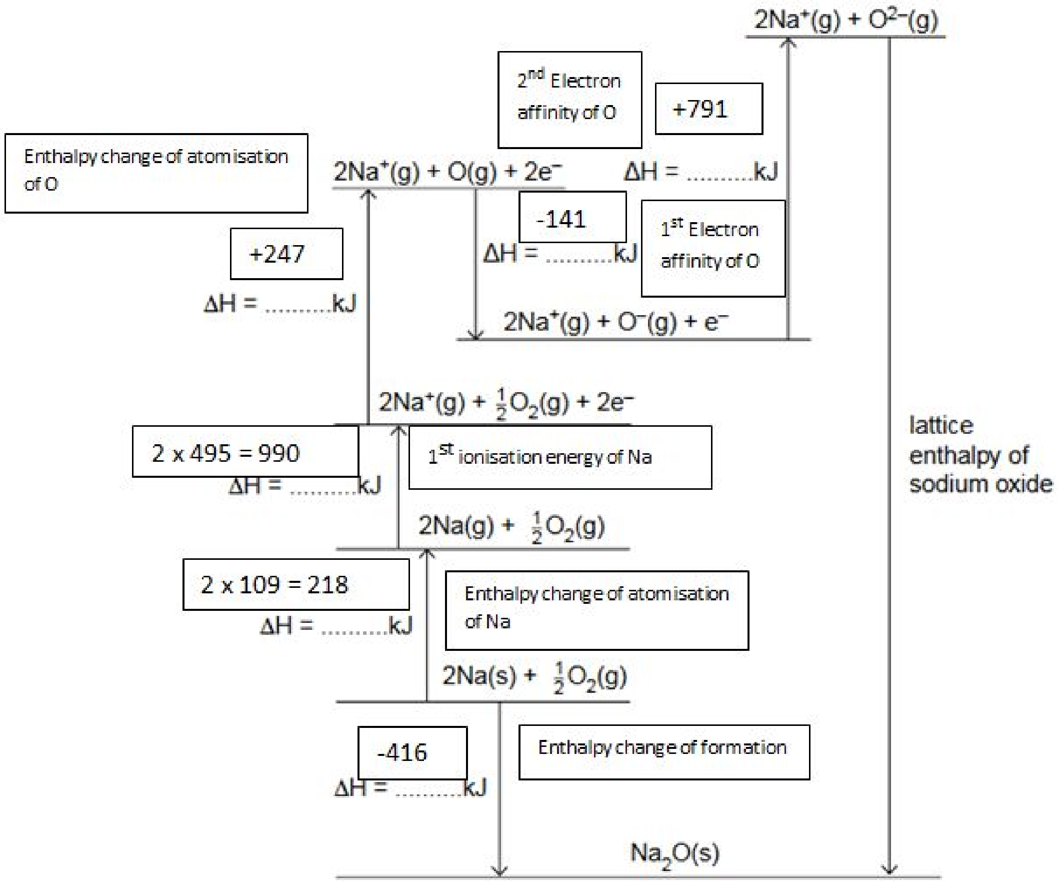
process	enthalpy change / kJ mol^{-1}
first ionisation energy of sodium	+495
first electron affinity of oxygen	–141
second electron affinity of oxygen	+791
enthalpy change of formation for sodium oxide	–416
enthalpy change of atomisation for sodium	+109
enthalpy change of atomisation for oxygen	+247

(a) Use the table of enthalpy changes to complete the Born-Haber cycle by putting in the correct numerical values on the appropriate dotted line.



[4]

Step 1: Follow the reactions to work out which enthalpy change occurs at each stage.



(b) Use the Born-Haber cycle to calculate the lattice enthalpy of sodium oxide.

Step 1: Set up equation.

ΔH_f (Step 1) = (Step 2) + (Step 3) + (Step 4) + (Step 5) + (Step 6)

$\Rightarrow -416 = 218 + 990 + 247 + (-141) + 791 + x$

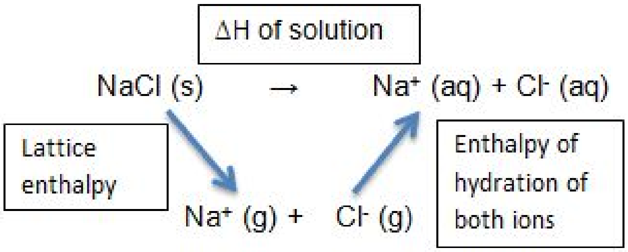
Step 2: Rearrange equation to work out x.

$\Rightarrow -416 = 2105 + x$

$x = \Delta_{LE}H =$ **$\underline{-2521 \text{ kJ mol}^{-1}}$**

Enthalpy of Solution

The enthalpy change when one mole of a solid dissolves in water under standard conditions.



The enthalpy change of solution can be calculated using:

Lattice enthalpy + enthalpy of hydration of positive ion and negative ion = enthalpy change of solution

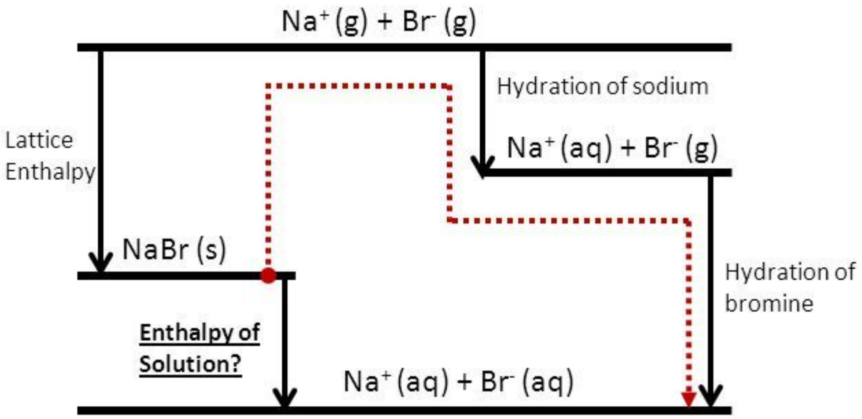
Example 1:

[This is an example using a Born-Haber cycle.]

Use the cycle below to calculate the enthalpy change of solution of sodium bromide.

ΔH lattice (L) = -733
ΔH hydration sodium = -406
ΔH hydration bromine = -335

-(-733) + (-406) + (-335)
= **<u>-8 kJmol^{-1}</u>**



Example 2:

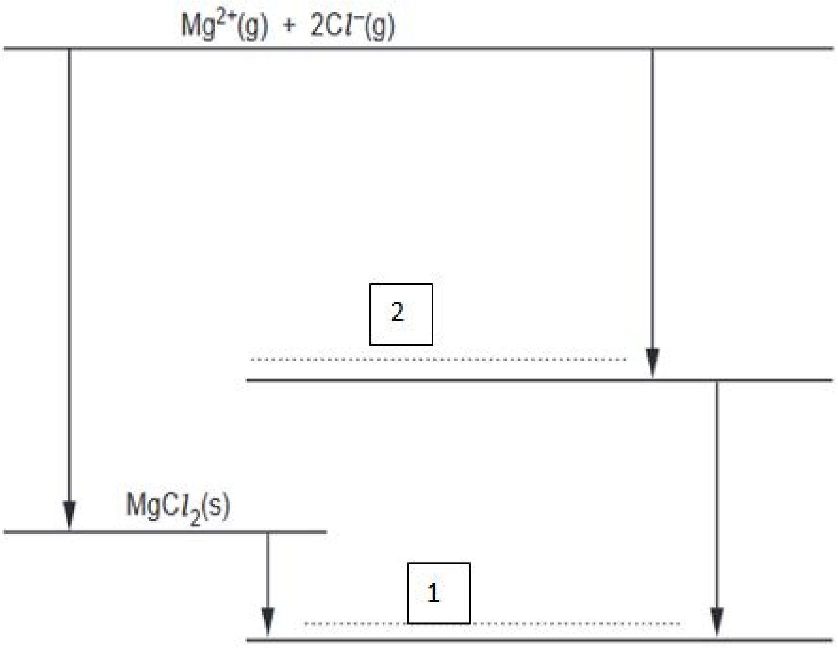
Born–Haber cycles provide a model that chemists use to determine unknown enthalpy changes from known enthalpy changes. In this question, you will use a Born–Haber cycle to determine an enthalpy change of hydration.

(b) The table below shows the enthalpy changes that are needed to determine the enthalpy change of hydration of magnesium ions.

enthalpy change	**energy/kJ mol^{-1}**
lattice enthalpy of magnesium chloride	–2493
enthalpy change of solution of magnesium chloride	–154
enthalpy change of hydration of chloride ions	–363

(ii) In this part, you will use the Born–Haber cycle to determine the enthalpy change of hydration of magnesium ions.

On the two dotted lines, add the species present, including state symbols.



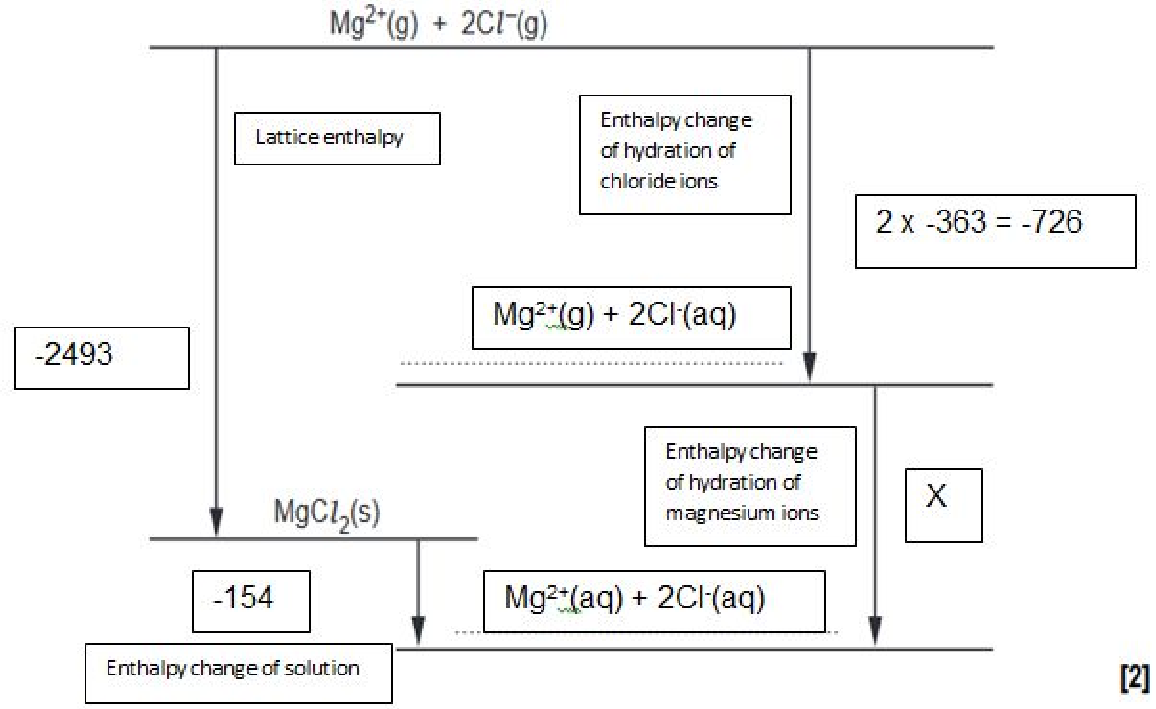
[2]

Step 1: The arrow from $MgCl_2$ (s) shows the enthalpy change of solution this is the enthalpy change where a solid dissolves in water thus producing aqueous ions.

Step 2: The label is for the enthalpy change of hydration for one of the gaseous ions into aqueous ions.

⇒ $Mg^{2+}(g) + 2Cl^-(aq)$

(iii) Calculate the enthalpy change of hydration of magnesium ions.



[2]

Step 1: Set up the equation for the cycle.

-154 = 2493 -726 + *x*

Step 2: Rearrange for *x*.

x = -2647 + 726

X = **-1921 kJmol^{-1}**

Worked Exam Style Questions

Question 1

Lattice enthalpies can be calculated indirectly using Born–Haber cycles.

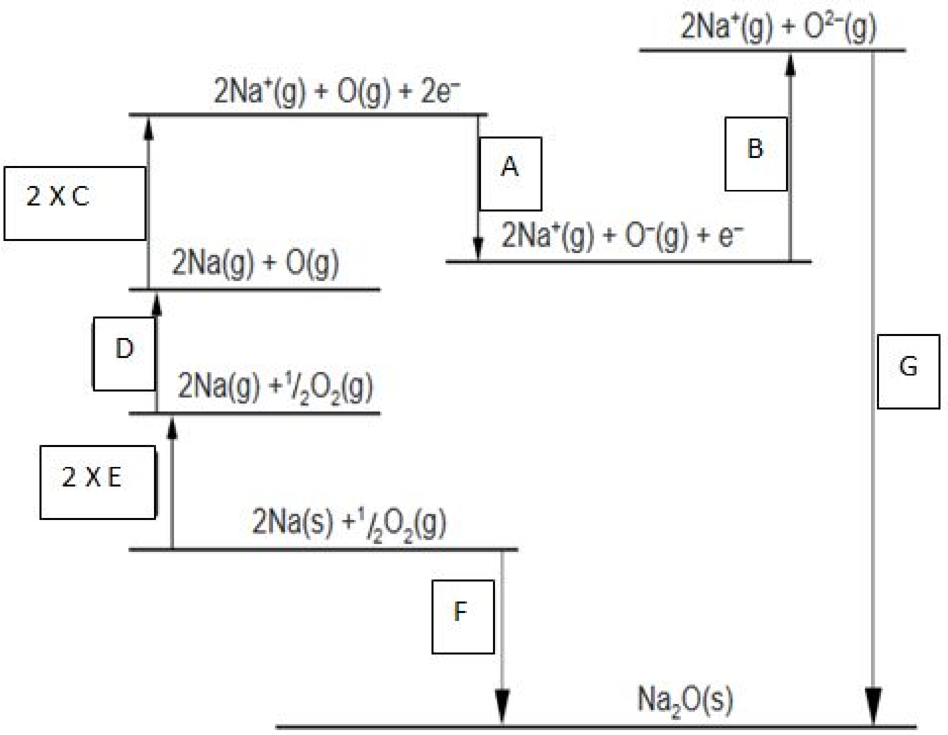
Table 2.1 shows enthalpy changes needed to calculate the lattice enthalpy of sodium oxide, Na_2O.

letter	**enthalpy change**	**energy /kJ mol^{-1}**
A	1st electron affinity of oxygen	–141
B	2nd electron affinity of oxygen	+790
C	1st ionisation energy of sodium	+496
D	atomisation of oxygen	+249
E	atomisation of sodium	+108
F	formation of sodium oxide	–414
G	lattice enthalpy of sodium oxide	

Table 2.1

The Born–Haber cycle below links the lattice enthalpy of sodium oxide with its enthalpy change of formation.

(i) On the Born–Haber cycle, write the correct letter from **Table 2.1** in each box.



[3]

Calculate the lattice enthalpy of sodium oxide.

Step 1: Set up the cycle equation.

ΔH_f (Step 1) = (Step 2) + (Step 3) + (Step 4) + (Step 5) + (Step 6)

$\Rightarrow -414 = (2 \times 108) + 249 + (2 \times 496) + (-141) + 790 + x$

Step 2: Rearrange equation to work out x.

$x = -414 - 2106$

$x =$ **<u>-2520 kJmol^{-1}</u>**

Question 2

Energy changes take place when water dissolves compounds and when water changes its physical state.

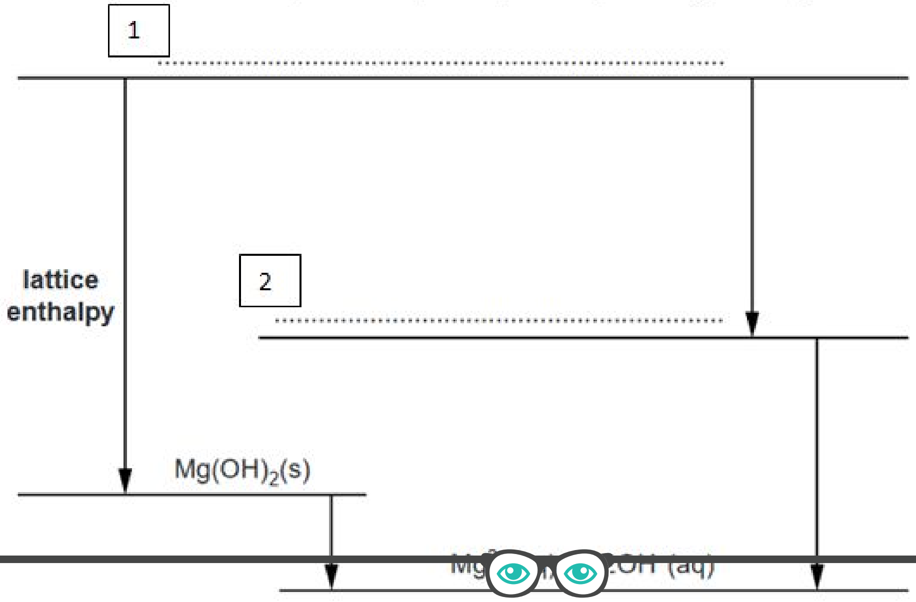
(a) You are provided with the following information.

Ion	**$\Delta H_{hydration}$ /kJ mol^{-1}**
Na^+	–405
Mg^{2+}	–1926
OH^-	–460

The enthalpy change of solution of $Mg(OH)_2$ is –152 kJ mol^{-1}.

A Born–Haber cycle can be drawn to link the lattice enthalpy and enthalpy change of solution of $Mg(OH)_2$ with hydration enthalpies.

On the two dotted lines, add the species present, including state symbols.

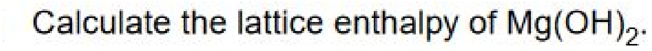


[2]

Step 1: Follow the reactions to determine the species present.

1. Mg^{2+} (g) + $2OH^{-}$ (g)

2. Mg^{2+} (g) + $2OH^{-}$ (aq)



Calculate the lattice enthalpy of $Mg(OH)_2$.

Step 1: Set up the equation.

lattice enthalpy + enthalpy of solution = enthalpy of hydration.

-152 + x = -1926 + (2 x -460)

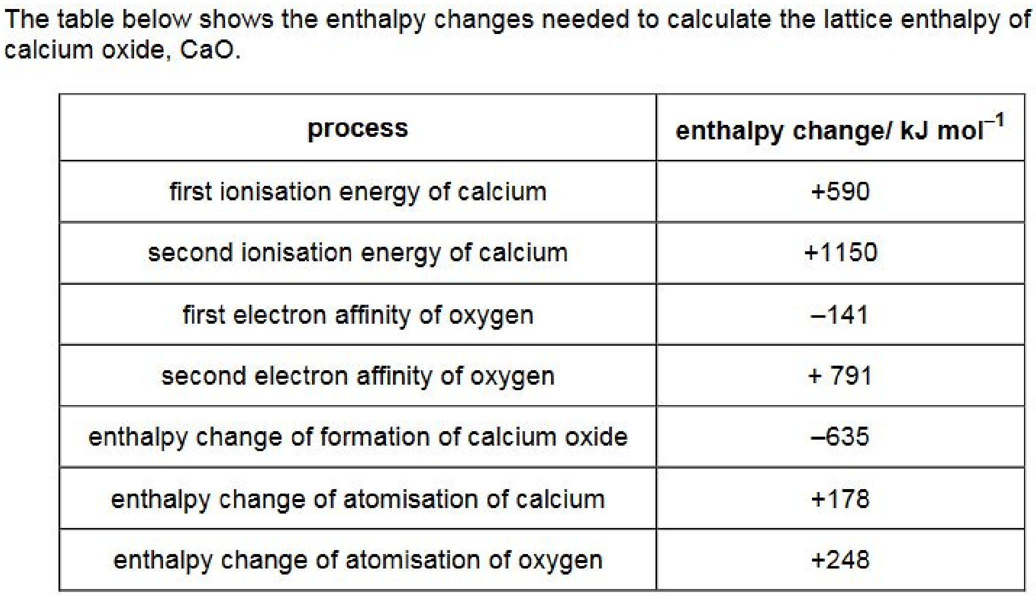
Step 2: Rearrange equation to work out x.

X = -2846 + 152

⇒ X = **-2694 kJ mol^{-1}**

Try these questions…

1.

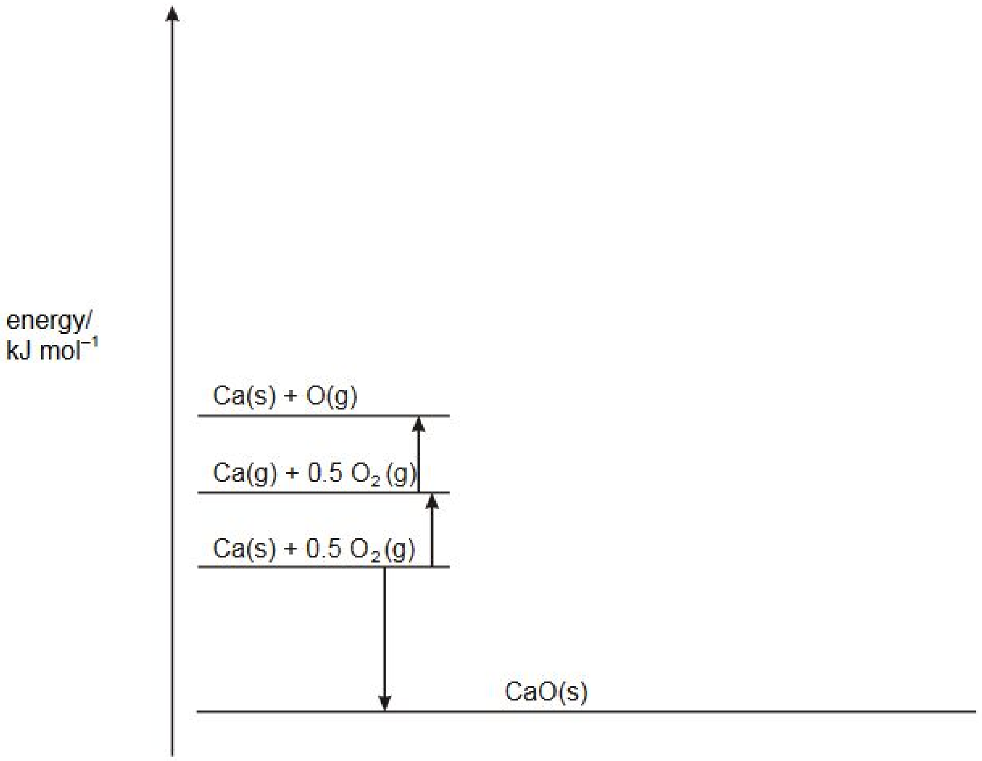


The table below shows the enthalpy changes needed to calculate the lattice enthalpy of calcium oxide, CaO.

process	enthalpy change/ kJ mol^{-1}
first ionisation energy of calcium	+590
second ionisation energy of calcium	+1150
first electron affinity of oxygen	–141
second electron affinity of oxygen	+ 791
enthalpy change of formation of calcium oxide	–635
enthalpy change of atomisation of calcium	+178
enthalpy change of atomisation of oxygen	+248

Complete the Born–Haber cycle for calcium oxide below.

Use the data in the table to calculate the lattice enthalpy of calcium oxide.



lattice enthalpy = ... kJ mol^{-1}

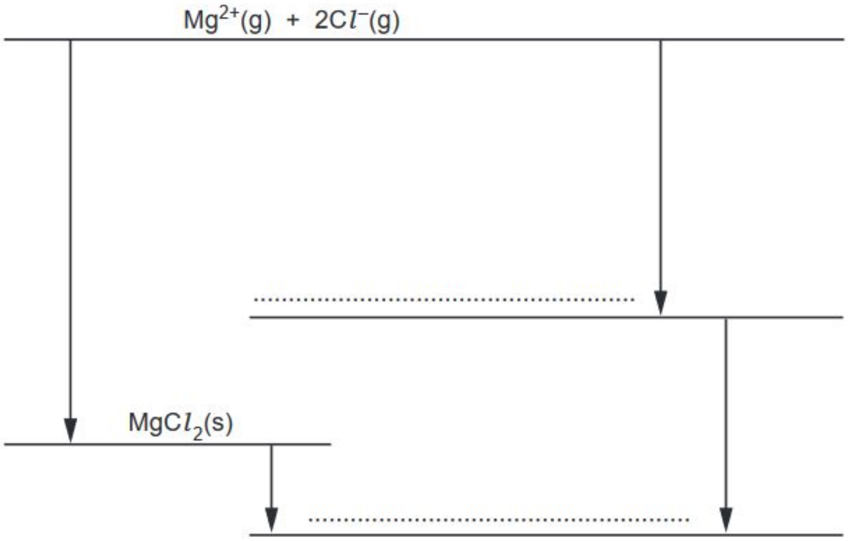
5 marks

2.

enthalpy change	energy/kJ mol^{-1}
lattice enthalpy of magnesium chloride	–2493
enthalpy change of solution of magnesium chloride	–154
enthalpy change of hydration of chloride ions	–363

In this part, you will use the Born–Haber cycle to determine the enthalpy change of hydration of magnesium ions.

On the two dotted lines, add the species present, including state symbols.



[2]

2 marks

Calculate the enthalpy change of hydration of magnesium ions.

Entropy

Entropy refers to the different number of ways a system can be arranged and the level of ‘disorder’ these arrangements have. High entropy suggests that the system can be arranged in many different, disordered ways whereas low entropy suggests can’t be rearranged in many ways and are very ordered.

Therefore gases have high entropy because the particles are free to move. Solids have low entropy because particles are in fixed position.

The entropy of a system can change during a chemical reaction depending on what is produced for example if more gas molecules are produced then the entropy of that system increases (becomes more positive).

Entropy change, ΔS, can be calculated by:

$$\boxed{\Delta S^{\theta}_{\text{reaction}} = \Sigma S^{\theta}_{\text{products}} - \Sigma S^{\theta}_{\text{reactants}}}$$

Example 1:

$$BaCl_2(s) \rightarrow Ba(s) + Cl_2(g)$$

	$BaCl_2(s)$	$Ba(s)$	$Cl_2(g)$
$S^{\ominus}$ / $J\,K^{-1}\,mol^{-1}$	124	63	223

Calculate the entropy change of this reaction.

Step 1: Calculate the total entropy of the reactants.

⇒ The only reactant in this case is $BaCl_2$.

⇒ $\Delta S = 124\ JK^{-1}mol^{-1}$

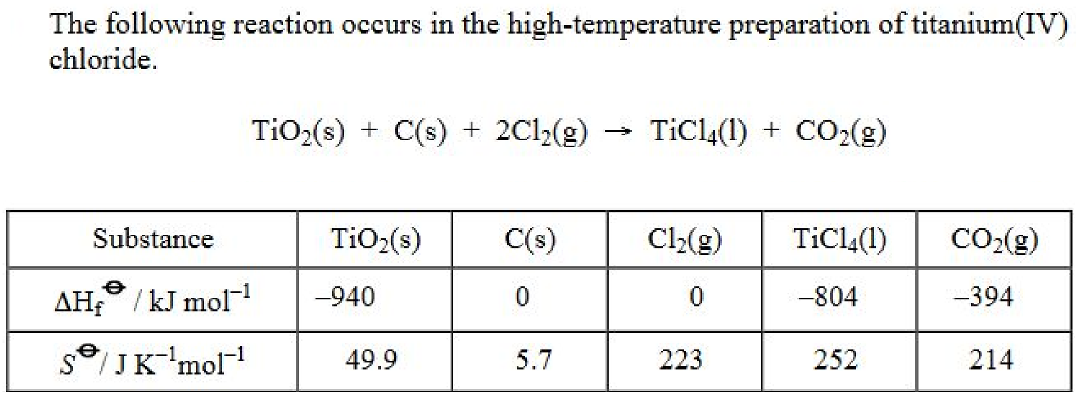
Step 2: Calculate the total entropy of the products.

⇒ $63 + 223 = 286\ JK^{-1}mol^{-1}$

Step 3: Work out the entropy change using the formula $\Delta S° = \Sigma S°(\text{products}) - \Sigma S°(\text{reactants})$.

286 - 124 = **162 $JK^{-1}mol^{-1}$**

Example 2:



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

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

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

Calculate the standard entropy change for this reaction.

Step 1: Calculate the total entropy of the reactants.

⇒ 49.9 + 5.7 + (2 x 223) = 501.6

Step 2: Calculate the total entropy of the products.

⇒ 252 + 214 = 466

Step 3: Work out the entropy change using the formula $\Delta S° = \Sigma S°(\text{products}) - \Sigma S°(\text{reactants})$.

⇒ 466 - 501.6 = **-35.6 JK^{-1}mol^{-1}**

Free Energy

A spontaneous/feasible process means that it is can take place of its own accord. Two factors that affect chemical reactions taking place:

- Enthalpy, ΔH
- Entropy, ΔS

These factors are linked to form this formula:

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

(ΔG = Gibbs free energy change) (ΔH = enthalpy change) (ΔS = entropy change)

If ΔG is a negative value, a reaction is feasible. The more negative the value the more likely the process will take place.

If ΔG is zero a reaction is in equilibrium and feasible.

If ΔG is a positive value, a reaction is not feasible.

Example 1:

Calculate the free energy change for the following reaction at 298 K and state whether the reaction is feasible or not.

$$MgCO_3\ (s) \rightarrow MgO\ (s) + CO_2\ (g)$$

$$\Delta H = +117\ kJ\ mol^{-1} \quad \Delta S = +175\ J\ K^{-}\ mol^{-1}$$

Step 1: Convert the units of one of the enthalpy changes so that they are uniform.

[Convert J for ΔS into kJ so it matches the units for ΔH]

$175 / 1000 = 0.175\ kJmol^{-1}$

Step 2: Input the values into the free energy formula ($\Delta G = \Delta H - T\Delta S$)

$\Delta G = 117 - (0.175 \times 298)$

$= \underline{\mathbf{+64.85\ kJmol^{-1}}}$

⇒ ΔG is **positive** therefore the reaction is **not feasible** at this temperature.

Example 2:

Use the following data to calculate the entropy change when one mole of ammonia is formed from its elements.

S ($JK^{-1}mol^{-1}$):

$N_2(g) = 191.6$,
$H_2(g) = 130.6$,
$NH_3(g) = 192.3$

Given that the enthalpy of formation of ammonia is $-46\ kJmol^{-1}$, determine the temperature at which this reaction becomes feasible

Step 1: Write a balanced equation of the reaction.

⇒ $0.5N_2 + 1.5H_2 \rightarrow NH_3$

Step 2: Work out the entropy change using the formula ΔS° = ΣS°(products) - ΣS°(reactants)

⇒ Total entropy of reactants = (191.6 x 0.5) + (1.5 x 130.6)
= 291.7

⇒ Total entropy of products = 192.3

⇒ 192.3 - 291.7 = -99.4 $JK^{-1}mol^{-1}$
= -0.0994 kJ mol^{-1}

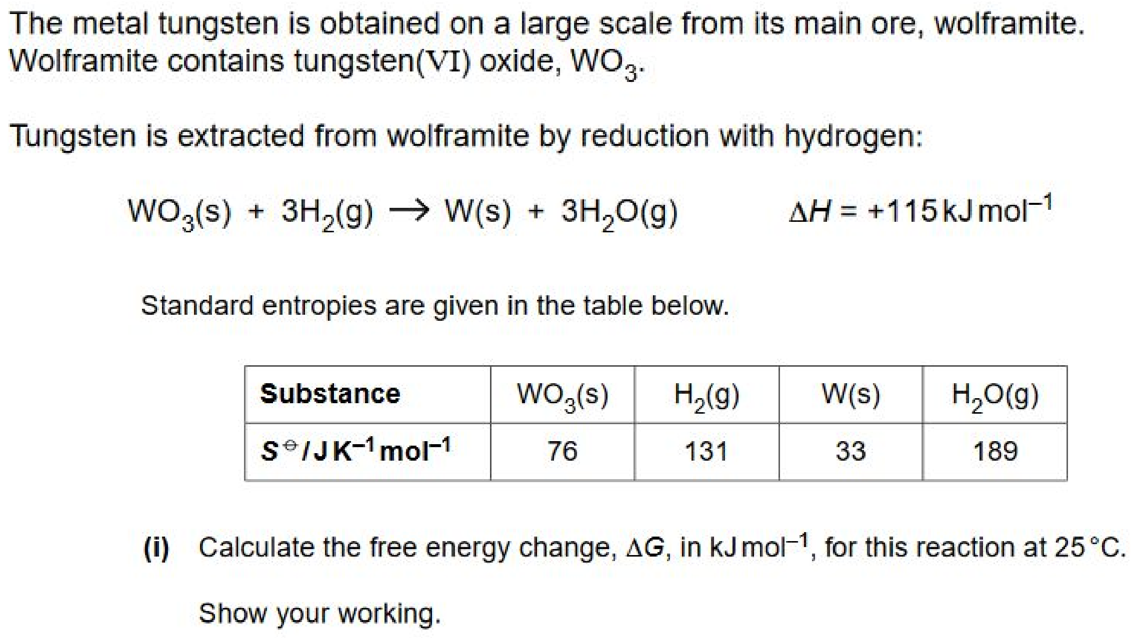
Step 3: Input the values into the free energy equation (ΔG = ΔH - TΔS)

⇒ The temperature at which any reaction becomes feasible is when ΔG = 0

-46 - (T x -0.0994) = 0
T x -0.0994 = -46
T = **<u>462.8 K</u>**

Worked Exam Style Questions

Question 1



The metal tungsten is obtained on a large scale from its main ore, wolframite. Wolframite contains tungsten(VI) oxide, WO_3.

Tungsten is extracted from wolframite by reduction with hydrogen:

$$WO_3(s) + 3H_2(g) \rightarrow W(s) + 3H_2O(g) \qquad \Delta H = +115\,kJ\,mol^{-1}$$

Standard entropies are given in the table below.

Substance	$WO_3(s)$	$H_2(g)$	W(s)	$H_2O(g)$
$S^{\ominus}$ / $J\,K^{-1}\,mol^{-1}$	76	131	33	189

(i) Calculate the free energy change, ΔG, in $kJ\,mol^{-1}$, for this reaction at 25 °C.

Show your working.

Step 1: Work out the entropy change using the formula: $\Delta S^\circ = \Sigma S^\circ(\text{products}) - \Sigma S^\circ(\text{reactants})$

Total entropy for reactants = 76 + (3 x 131)
= 469
Total entropy for products = 33 + (3 x 189)
= 600

600 - 469 = +131 $JK^{-1}mol^{-1}$
= **<u>0.131 $kJK^{-1}mol^{-1}$</u>**

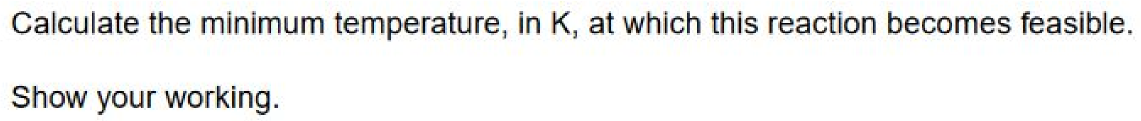
Step 2: Convert 25 °C to Kelvin.

[0 °C = 273 K]

⇒ 25 + 273 = 298 K

Step 3: Input value into the free energy formula: $\Delta G = \Delta H - T\Delta S$

ΔG = +115 - (298 x 0.131)
= **<u>76 $kJmol^{-1}$</u>**



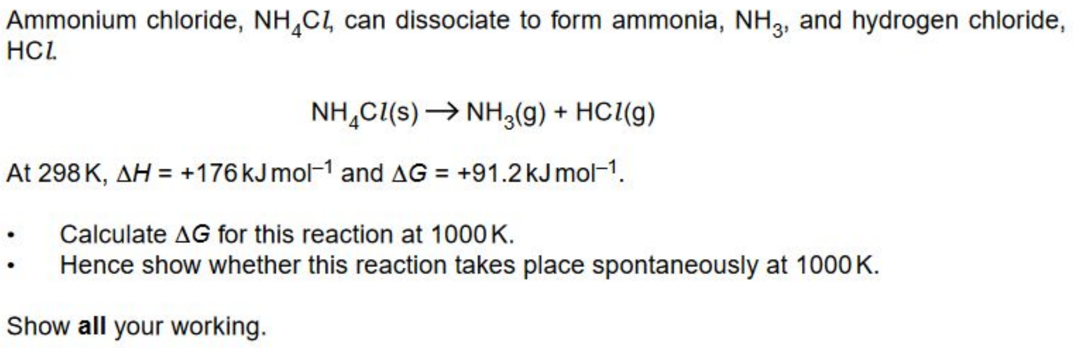
Calculate the minimum temperature, in K, at which this reaction becomes feasible.

Show your working.

Step 1: Equal ΔG to zero to work out the minimum temperature.

+115 - (T x 0.131) = 0
T x 0.131 = 115
T = **<u>878 K</u>**

Question 2



Ammonium chloride, NH_4Cl, can dissociate to form ammonia, NH_3, and hydrogen chloride, HCl.

$$NH_4Cl(s) \longrightarrow NH_3(g) + HCl(g)$$

At 298 K, $\Delta H = +176\,kJ\,mol^{-1}$ and $\Delta G = +91.2\,kJ\,mol^{-1}$.

- Calculate ΔG for this reaction at 1000 K.
- Hence show whether this reaction takes place spontaneously at 1000 K.

Show **all** your working.

Step 1: Rearrange the free energy formula so that ΔS is the subject.

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

$$\Delta S = \frac{\Delta H - \Delta G}{T}$$

Step 2: Work out the entropy change.

$$\Delta S = \frac{176 - 91.2}{298}$$

$= \underline{\mathbf{0.2846\ kJK^{-1}mol^{-1}}}$

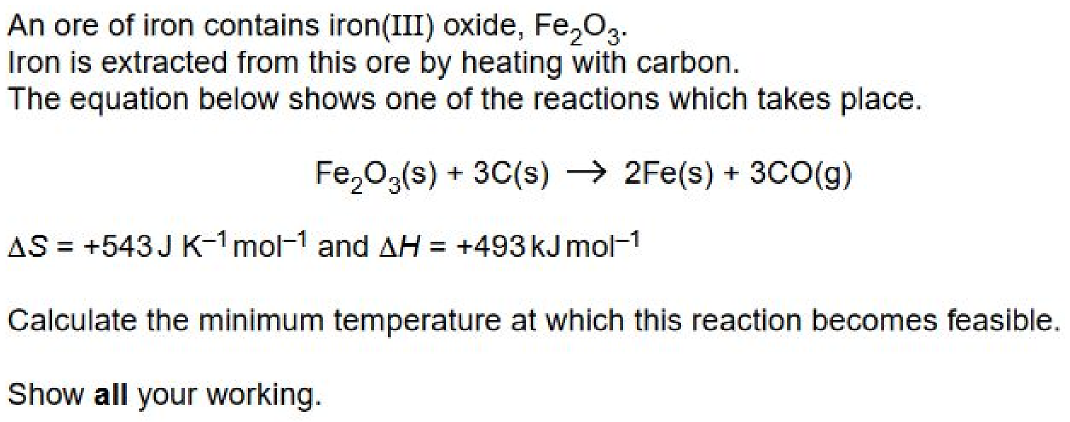
Step 3: Input the values into the free energy formula.

$$\begin{aligned}\Delta G &= \Delta H - T\Delta S \\ &= 176 - (1000 \times 0.2846) \\ &= \underline{\mathbf{-108.6\ kJmol^{-1}}}\end{aligned}$$

This reaction is **feasible** as ΔG is **negative.**

Try these questions…

3.



An ore of iron contains iron(III) oxide, Fe_2O_3.
Iron is extracted from this ore by heating with carbon.
The equation below shows one of the reactions which takes place.

$$Fe_2O_3(s) + 3C(s) \rightarrow 2Fe(s) + 3CO(g)$$

$\Delta S = +543\ J\ K^{-1}\ mol^{-1}$ and $\Delta H = +493\ kJ\ mol^{-1}$

Calculate the minimum temperature at which this reaction becomes feasible.

Show **all** your working.

3 marks

4.

Calcium oxide, CaO, is used to make cement. Calcium oxide is manufactured by the thermal decomposition of calcium carbonate.

$$CaCO_3(s) \rightarrow CaO(s) + CO_2(g) \qquad \Delta H = +178\,kJ\,mol^{-1}$$

Standard entropies of $CaCO_3(s)$, $CaO(s)$ and $CO_2(g)$ are given in the table below.

substance	$CaCO_3(s)$	$CaO(s)$	$CO_2(g)$
S / J $K^{-1}mol^{-1}$	89	40	214

- Using the information in the table, show that the entropy change, ΔS, for the decomposition of calcium carbonate is 0.165 kJ K^{-1} mol^{-1}.
- Show that calcium carbonate is stable at room temperature (25 °C).
- Calculate the minimum temperature needed to decompose calcium carbonate.

Show all your working.

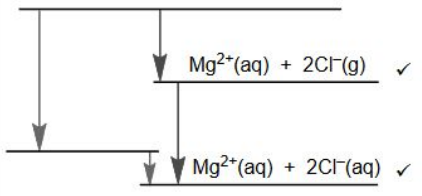
[7 marks]

Answers

1.

completes Born-Haber cycle showing 1st IE↑ 2nd IE↑ 1st EA ↓ 2nd
EA↑
and LE↓**(1)(1)(1)** (lose 1 mark for each error/omission)
LE = –**(1)**3451 kJ mol^{-1} **(1)** 5

2.

	2	Correct species **AND** state symbols required for both marks Mark each marking point independently **ALLOW** response on upper line: $Mg^{2+}(g)$ + $2Cl^-(aq)$ (ie Cl^- hydrated before Mg^{2+}) **ALLOW** $MgCl_2(aq)$

Question			Answer	Mark	Guidance
1	(b)	(iii)	**FIRST, CHECK THE ANSWER ON ANSWER LINE** **IF answer = –1921 (kJ mol^{-1}) award 2 marks** -- (–2493) + (–154) = (2 x –363) + $\Delta H_{hyd}(Mg^{2+})$ ✓ $\Delta H_{hyd}(Mg^{2+})$ = (–2493) + (–154) – (2 x –363) = –1921 (kJ mol^{-1}) ✓	2	**IF** there is an alternative answer, check to see if there is any **ECF** credit possible using working below. **See list below for marking of answers from common errors** -- **ALLOW** for **1 mark**: –2284 use of Cl^- rather than 2 x Cl^- (+)1921 signs all reversed **OR** lack of 2 for 363 –1613 sign wrong for 154 (+)3065 sign wrong for 2493 –3373 sign wrong for 2 x 363

3.

(For feasibility,) $\Delta G < 0$ **OR** $\Delta G = 0$ **OR** $0 < \Delta H - T\Delta S$ **OR** $0 = \Delta H - T\Delta S$ **OR** $0 = 493 - T \times 543/1000$ ✓ $T = \frac{\Delta H}{\Delta S} = 493 \times 1000/543$ ✓ = 908 K ✓ Units of temperature are **required**	3	**ALLOW** total entropy statement: ΔS(total) = 0 **OR** ΔS(total) >0 **ALLOW** $0 = 493 - T \times 543$ ✓ *i.e. This mark focuses on ΔG **OR** $\Delta H - T\Delta S$ being = 0 and **NOT** on conversion of ΔS value into kJ K^{-1} mol^{-1}* **Mark temperature given on answer line** **ALLOW** 3 SF up to calculator value 907.9189687 correctly rounded, e.g. 907.9, 907.92 **ALLOW** temperature in °C: i.e. **ALLOW** by subtraction of 273: 635, 634.9, 634.91 °C **ALLOW** by subtraction of 273.15: 635, 634.8, 634.77 °C up to calculator value correctly rounded **ALLOW** C for °C; °K for K IF ΔS has not been converted to kJ, **DO NOT ALLOW** 2nd mark **BUT** … **ALLOW** calculated answer = 493/543 = 0.91 K (calculator: 0.907918968) ***ALLOW 2 marks only for absence of one of the statements required for 1st marking point***

4.

$\Delta S = \Sigma S(\text{products}) - \Sigma S(\text{reactants})$ $= 40 + 214 - 89 = 165\ (\text{J K}^{-1}\ \text{mol}^{-1})$ $= 0.165\ (\text{kJ K}^{-1}\ \text{mol}^{-1})$ ✓	1	**ANNOTATE WITH TICKS AND CROSSES, etc** *Mark is for the working line:* 40 + 214 – 89 = 165
At 25 °C, $\Delta G = +178 - 298 \times 0.165$ ✓ = (+)129 ✓ units: kJ mol^{-1} ✓ **OR** (+)129,000 ✓ units: J mol^{-1} ✓ As $\Delta G > 0$, reaction is **not** feasible **OR** as $\Delta G > 0$, $CaCO_3$ is stable ✓ ---	4	**UNITS** have a separate mark **ALLOW** 129 to calculator value of 128.83 **DO NOT ALLOW** 128 (incorrect rounding) **IF** 25 °C used rather than 298 K, credit by ECF, calculated ΔG = 174 to calculator value of 173.875 ***ENTROPY APPROACH***---------------------- **ALLOW** At 25 °C, $\Delta S_{\text{total}} = 0.165 - \frac{178}{298}$ ✓ = –0.432 ✓ $\text{kJ K}^{-1}\ \text{mol}^{-1}$ ✓ **OR** –432 ✓ $\text{J K}^{-1}\ \text{mol}^{-1}$ ✓ As $\Delta S < 0$, reaction is **not** feasible ✓
Minimum temperature for feasibility when $0 = \Delta H - T\Delta S$ **OR** $\Delta H = T\Delta S$ **OR** $T = \frac{\Delta H}{\Delta S}$ ✓ $= \frac{178}{0.165} = 1079$ K **OR** 806 °C ✓ The units **must** be with the stated temperature	2	***ENTROPY APPROACH***-- Minimum temperature for feasibility when $0 = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}}$ **OR** $\Delta S_{\text{system}} = \frac{\Delta H}{T}$ **ALLOW** 1080 K up to calculator value of 1078.787879, correctly rounded, eg 1078.79 is correct value to 6SF **DO NOT ALLOW** 1078 (incorrect rounding) **IF** 1079 K is given and additional temperature in °C is incorrect, **IGNORE** °C temperature (and vice versa)