FACTFILE:
GCE CHEMISTRY

4.1 LATTICE ENTHALPY

Rewarding Learning

Learning Outcomes

Students should be able to:

4.1.1 define and understand the term lattice enthalpy;

4.1.2 construct Born-Haber cycles and carry out associated calculations, such as the halides and oxides of Groups I and II; and

4.1.3 define and understand the enthalpy changes associated with the dissolving of ionic compounds in water, and carry out associated calculations

Born-Haber cycles

A Born-Haber cycle is an energy cycle based on Hess's law. To draw a Born-Haber cycle you must recall and understand the definitions for the following.

1. **Enthalpy of atomisation ($\Delta_a H^\ominus$)is the enthalpy change when one mole of gaseous atoms is formed from the element in its standard state.**

eg $Na(s) \rightarrow Na(g)$
$\frac{1}{2}Cl_2(g) \rightarrow Cl(g)$

2. **Bond enthalpy/ Bond dissociation enthalpy is the energy needed to break a one mole of a specific bond**

eg $Cl_2(g) \rightarrow 2Cl(g)$

Bond dissociation is twice the enthalpy of atomisation for diatomic elements.

3. **First ionisation energy–this is the energy required to convert one mole of gaseous atoms into gaseous ions with a single positive charge.**

eg $Na(g) \rightarrow Na^+(g) + e^-$

4. **First electron affinity – this is the enthalpy change when one mole of gaseous atoms is converted into gasesous ions with a single negative charge.**

eg $Cl(g) + e^- \rightarrow Cl^-(g)$

Note that $2Cl(g) + 2e^- \rightarrow 2Cl^-(g)$ is 2 x electron affinity of chlorine

For the formation of ions X^{2-} the second electron affinity values must be considered.

Second electron affinity – this is the enthalpy change when one mole of gaseous ions with a single negative charge is converted into gasesous ions with a 2 - charge.

These values are positive since an electron is being gained by a species that is already negatively charged $O^-(g) + e^- \rightarrow O^{2-}(g)$

5. **Lattice enthalpy – the enthalpy change when one mole of an ionic compound is converted to gaseous ions** (endothermic)

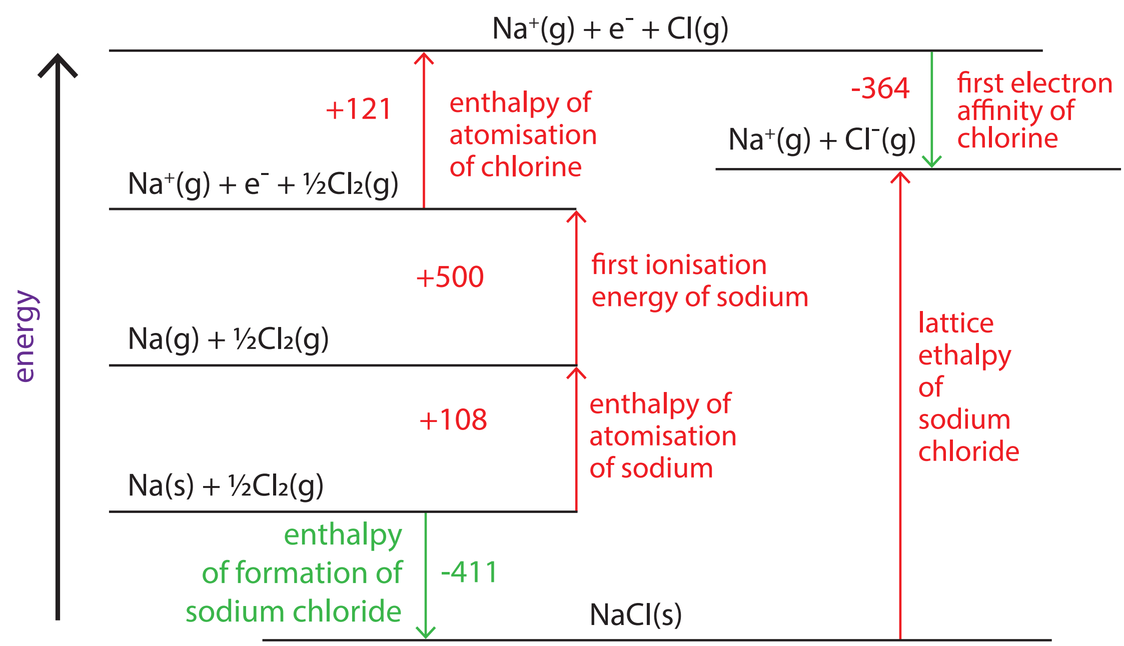
eg. $NaCl(s) \rightarrow Na^+(g) + Cl^-(g)$

This is an endothermic reaction since energy is needed to overcome the attractive forces between the ions and separate them.

6. Standard Enthalpy of formation($\Delta_f H^{\ominus}$) is the enthalpy change when one mole of a compound is formed from its elements under standard conditions.

Lattice energy cannot be found by experiment and so is calculated using a Born Haber cycle using other quantities which can be found experimentally.

A Born-Haber cycle for sodium chloride, with each energy value (in kJ mol^{-1}) inserted, is shown;



The endothermic reactions absorb energy and the arrows point upwards on the energy axis. The exothermic reactions release energy and point downwards on the energy axis.

This cycle can be used to calculate the lattice enthalpy. Go from the bottom of the lattice enthalpy cycle to the top the other way round the cycle.

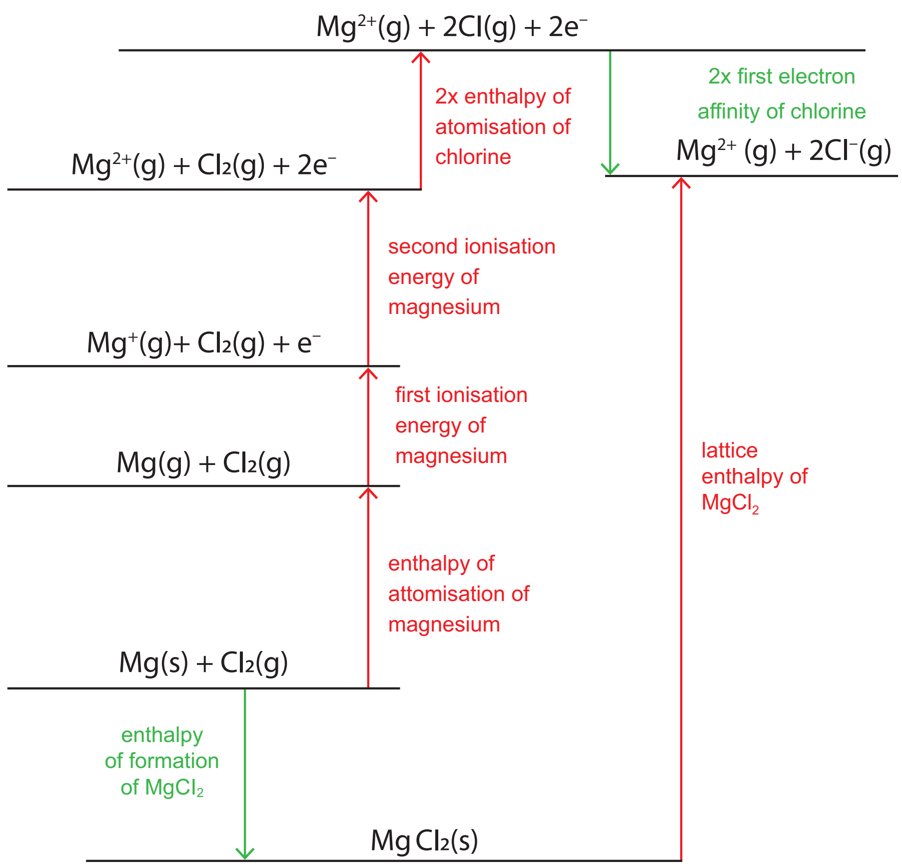
+411 + 108 +500 +121 -364 = lattice enthalpy
+776 kJ mol^{-1} = lattice enthalpy

Example Born-Haber cycle for a Group 2 halide

Draw a Born-Haber for magnesium chloride and use the enthalpy values in the table below to calculate the value for the first electron affinity of chlorine.

Enthalpy change	Value in kJ mol^{-1}
Standard enthalpy of formation of magnesium chloride	-642
Standard enthalpy of atomisation of magnesium	+150
First ionisation energy of magnesium	+736
Second ionisation energy of magnesium	+1450
Standard atomisation energy of chlorine	+121
Lattice enthalpy of magnesium chloride	+2492

Remember when drawing the cycle for a Group II halide that the standard atomisation energy multiplied by two as there are two chlorine atoms required. The first electron affinity is also multiplied by two, for two chloride ions.



The first electron affinity may be calculated using the cycle. You must take into account the direction of the arrows, if the direction is reversed then the negative of the values must be taken

lattice enthalpy of $MgCl_2$ = - (enthalpy of formation of $MgCl_2$) + (enthalpy of atomisation of Mg) + (first ionisation energy of Mg) + (second ionisation energy of Mg) + 2 x (enthalpy of atomisation of Cl) + 2 x (first electron affinity of Cl)

+ 2492 = - (-642) + (+150) + (+736) + (+1450) + 2(+121) + 2 x first electron affinity

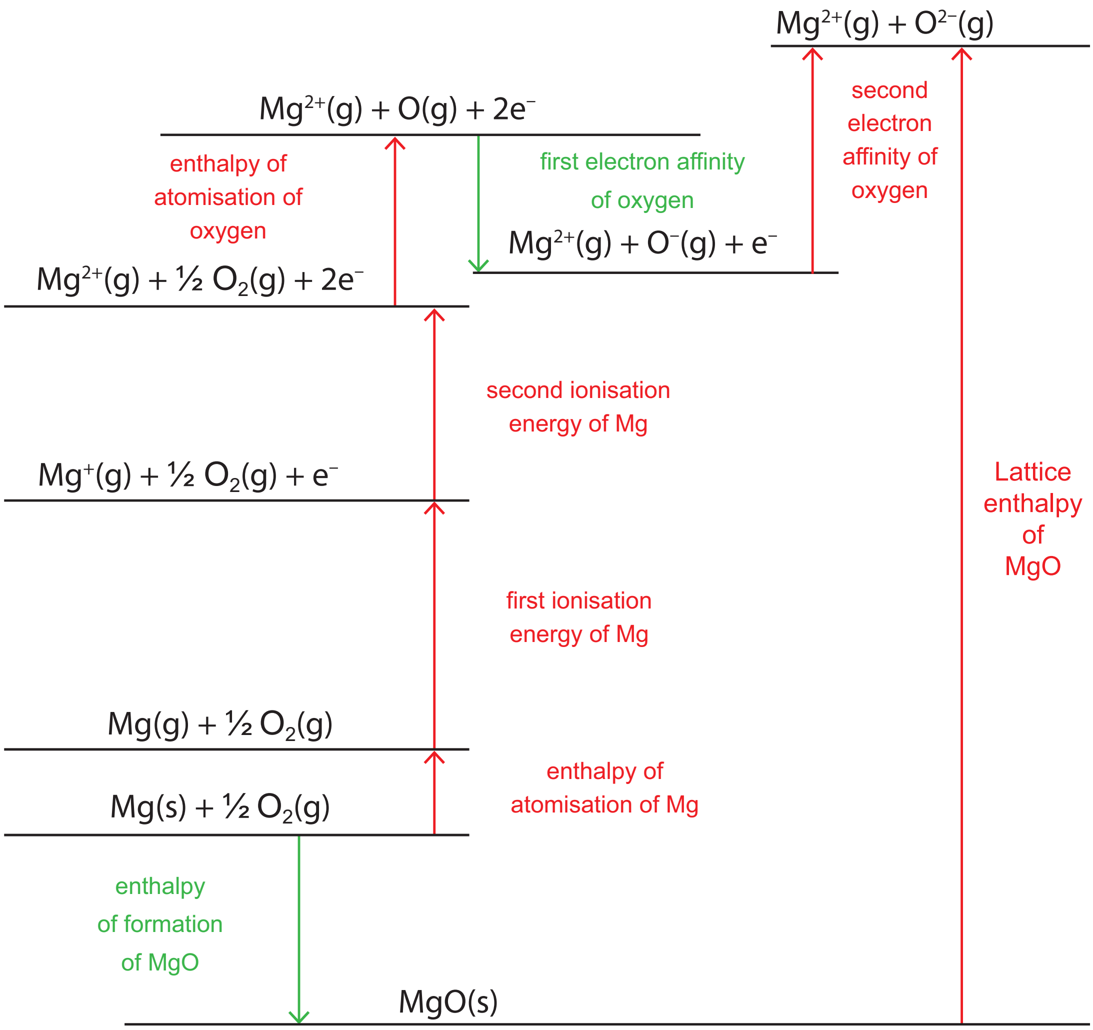
2 x first electron affinity = 2492 - 642 - 150 - 736 - 1450 - 242 = -728

First electron affinity = -728/2 = -364 kJ mol^{-1}

Example Born-Haber cycle for a Group 2 oxide

Draw a Born-Haber for magnesium oxide and use the enthalpy values in the table below to calculate the value for the lattice enthalpy of magnesium oxide.

Enthalpy change	Value in kJ mol^{-1}
Standard enthalpy of formation of magnesium oxide	-602
Standard enthalpy of atomisation of magnesium	+150
First ionisation energy of magnesium	+736
Second ionisation energy of magnesium	+1450
Standard atomisation energy of oxygen	+248
First electron affinity of oxygen	-142
Second electron affinity of oxygen	+844



This cycle is slightly different as it includes the second electron affinity of oxygen, which is endothermic.

Lattice enthalpy = -(enthalpy of formation of MgO) + (enthalpy of atomisation of Mg)+ (first ionisation ionisation energy of Mg) + (second ionisation energy of Mg) + (enthalpy of atomisation of oxygen)+ (first electron affinity of oxygen) + (second electron affinity of oxygen)
Lattice enthalpy = - (-602) + (+150) + (+736) + (1450) + (+248) + (-142) + (+844)
Lattice enthalpy = +3888 kJ mol^{-1}

Dissolving ionic compounds in water

When an ionic compound dissolves in water two processes occur

1. Energy has to be taken in to break up the lattice and separate the positive and negative ions. This is the lattice enthalpy

2. The ions become surrounded by solvent and bonds form - energy is released when these ions form bonds with water molecules. This is called the hydration enthalpy

The balance of the break-up of the ionic lattice and the bonds forming with water determines the enthalpy of solution.

Enthalpy of hydration – the enthalpy change when one mole of gaseous ions is converted to one mole of aqueous ions. (this is called the solvation energy if the solvent is not water)

$Na^+(g) \rightarrow Na^+(aq)$
$Cl^-(g) \rightarrow Cl^-(aq)$

Enthalpy of solution is the enthalpy change when one mole of a solute dissolves in water.

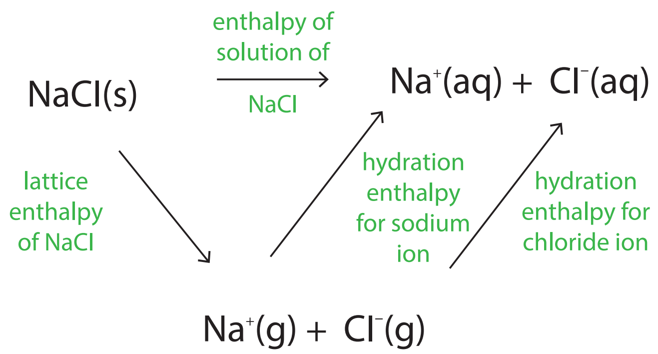
$NaCl(s) \rightarrow Na^+(aq) + Cl^-(aq)$

Enthalpy of solution = lattice enthalpy + enthalpy of hydration

Example: Calculate the enthalpy of solution of sodium chloride

Enthalpy change	Value in kJ mol^{-1}
Lattice enthalpy of sodium chloride	+776
Hydration enthalpy of Na^+	-407
Hydration enthalpy of Cl^-	-364

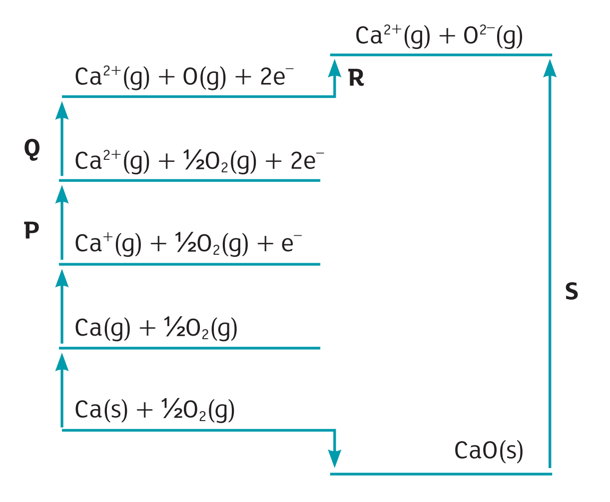
A typical enthalpy cycle for sodium chloride is shown



Enthalpy of solution of NaCl = + (+776) + (-407) + (-364) = +5 kJ mol^{-1}

Revision Questions

1 The Born-Haber cycle for calcium oxide is shown below:



Which one of the following is a correct statement about the cycle?

A	The electron affinity of oxygen is **Q**
B	The second ionisation enthalpy of calcium is **P**
D	The enthalpy of formation of calcium oxide is **S**
D	The bond dissociation enthalpy of oxygen is **R**

2 All of the chlorides form solutions when added to water. Sodium chloride dissolves in water by an overall endothermic process. It is explained by the following:

The NaCl(s) separates into its gaseous ions.

$NaCl(s) \rightarrow Na^+(g) + Cl^-(g)$ $\Delta H_1 = +776k$

The gaseous ions dissolve to form aqueous ions.

$Na^+(g) + Cl^-(g) + aq \rightarrow Na^+(aq) + Cl^-(aq)$ $\Delta H_2 = -771kJ$

(i) What is the name for the enthalpy value ΔH_1?

.... [1]

(ii) What is the name for the enthalpy value ΔH_2?

.... [1]

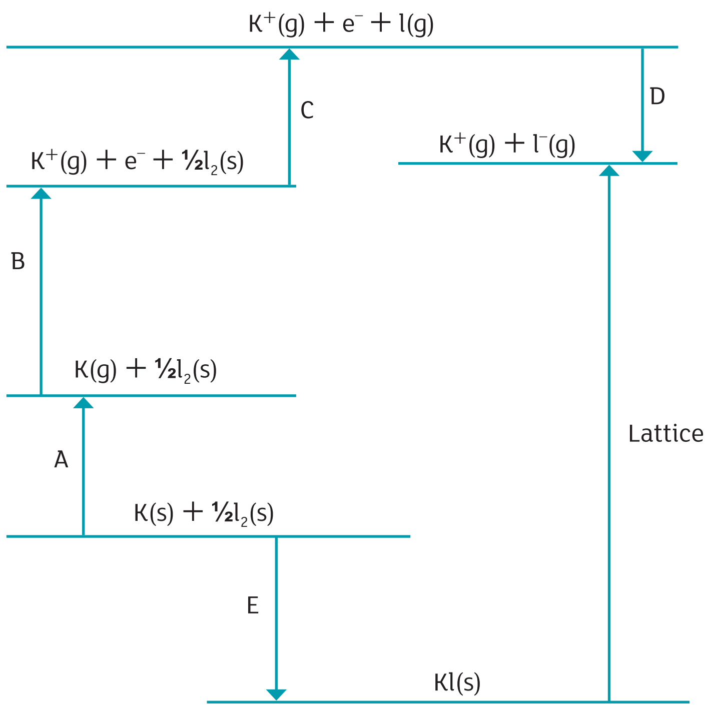
(iii) ΔH_3 is the enthalpy of solution. Draw a labelled diagram to show the relationship between ΔH_1, ΔH_2, ΔH_3.

[3]

(iv) Calculate the value of ΔH_3.

.... [1]

3 A Born-Haber cycle for potassium iodide is shown below. The lattice enthalpy is labelled. Other enthalpy changes are shown by the letters A to E.



a) For the following questions state which letter (A to E) represents the enthalpy changes:

Standard enthalpy of formation of potassium iodide

.... [1]

First electron affinity of iodine

.... [1]

First ionisation energy of potassium

.... [1]

Enthalpy of atomisation of potassium

.... [1]

b) Calculate the lattice enthalpy of potassium iodide.

	kJ mol^{-1}
A	+89.5
B	+420.0
C	+106.6
D	-295.4
E	-327.6

....

....

.... kJ mol^{-1}[2]

c) Potassium chloride has a lattice enthalpy of +710kJ mol^{-1} and that for potassium bromide is +679kJ mol^{-1}. State **three** other enthalpy changes in a Born-Haber cycle for these compounds which would be different.

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.... [3]

d) Potassium chloride is very soluble in water.

(i) Write an equation, including state symbols, to represent potassium chloride dissolving in water.

.... [2]

(ii) The enthalpy change of hydration for the potassium ion is -305 kJ mol^{-1} and value for the chloride ion is -384kJ mol^{-1}. Using the lattice enthalpy value stated in **(c)** for potassium chloride, calculate the enthalpy change when one mole of potassium chloride is dissolved in water.

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.... [2]

(iii) Which one of the following equations represents the lattice enthalpy of sodium chloride?.

A $NaCl(aq) \rightarrow Na(g) + Cl(g)$

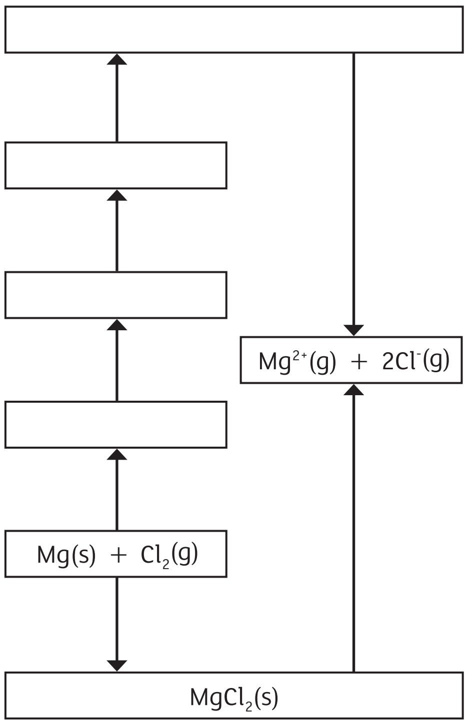
B $NaCl(aq) \rightarrow Na^+(g) + Cl^-(g)$

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

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

4 Magnesium chloride is a water-soluble ionic compound formed from magnesium and chlorine.

a) (i) Complete the Born-Haber cycle for magnesium chloride.



[4]

(ii) Using the data given below, calculate the first electron affinity of chlorine.

	kJmol^{-1}
Standard enthalpy of formation for magnesium chloride	-642
Lattice enthalpy for magnesium chloride	+2493
Atomisation enthalpy of chlorine	+121
First ionisation enthalpy of magnesium	+736
Second ionisation enthalpy of magnesium	+1450
Atomisation enthalpy of magnesium	+150

....

....

....

.... [2]

b) Give the electron structure of:

magnesium ions .... [1]

chloride ions .... [1]

c) Magnesium chloride dissolves in water and has an enthalpy of solution of $-155kJmol^{-1}$.
Define the term **enthalpy of solution**.

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.... [2]