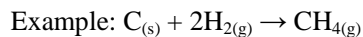


**Energetics - Higher level**

*Define and use the terms standard state and standard enthalpy change of formation ( $\Delta H_f^\ominus$ )*

The arbitrary zero point for enthalpies is elements in their standard states under standard conditions.

*The standard enthalpy change of formation: “the enthalpy change when one mole of compound is made in its standard state from its constituent elements in their standard states”.*



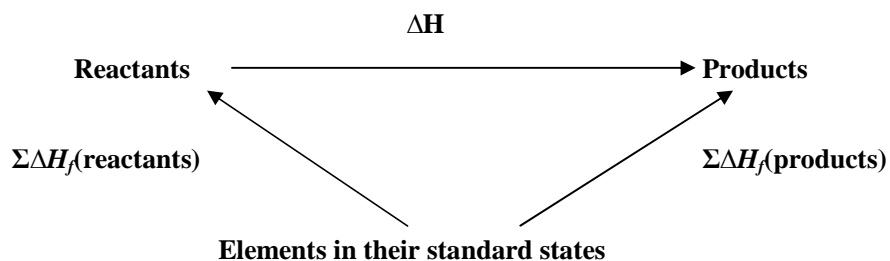
Standard state:

- 25°C (298K)
- 1 atmosphere pressure (101.3 kPa) - not to be confused with STP
- Most common allotrope e.g.  $O_2$  not  $O_3$

The enthalpy change for a reaction can be calculated as the difference between the enthalpy of formation of the products *minus* the enthalpy of formation of the reactants:

$$\Delta H = \Sigma\Delta H_f(\text{products}) - \Sigma\Delta H_f(\text{reactants})$$

**Enthalpy cycle**



Be careful with signs (+and -) as it can be confusing!

*Calculate the enthalpy change of a reaction using standard enthalpy changes.*

## IB Chemistry

### Lattice Enthalpy

Each ion exerts an electrostatic field that attracts the oppositely charged ions.

The ions are all drawn together into a giant lattice in which every positive ion is surrounded by negative ions and *vice-versa*.

Lattice enthalpy may be seen defined in two different ways, depending on the reference literature. For the IB it is defined as “the energy released when 1 mole of an ionic substance is formed from its constituent ions at infinite separation”.



The value of lattice enthalpy is negative for the formation of the lattice (an exothermic - bond forming process), and positive for the breaking up of the lattice (an endothermic - bond breaking process).

Hess' law can also be applied to the formation of ionic lattices *via* a series of steps. In the case of ionic substances this is called a ***Born-Haber cycle*** (see later).

## IB Chemistry

*Compare the effect of both the relative sizes and the charges of ions on the lattice enthalpies of different ionic compounds.*

Lattice enthalpy increases with higher ionic charge and with smaller ionic radius (due to increased force of attraction).

The bond between ions of opposite charge is strongest when the ions are small.

The lattice energies for the alkali metal halides is therefore largest for LiF and smallest for CsI, as shown in the table below.

*Lattice Energies of Alkali Metals Halides (kJ/mol)*

	<b>F<sup>-</sup></b>	<b>Cl<sup>-</sup></b>	<b>Br<sup>-</sup></b>	<b>I<sup>-</sup></b>
<b>Li<sup>+</sup></b>	<b>1036</b>	853	807	757
<b>Na<sup>+</sup></b>	923	787	747	704
<b>K<sup>+</sup></b>	821	715	682	649
<b>Rb<sup>+</sup></b>	785	689	660	630
<b>Cs<sup>+</sup></b>	740	659	631	<b>604</b>

The ionic bond should also become stronger as the charge on the ions becomes larger. The data in the table below show that the lattice energies for salts of the OH<sup>-</sup> and O<sup>2-</sup> ions increase rapidly as the charge on the ion becomes larger.

*Lattice Energies of Salts of the OH<sup>-</sup> and O<sup>2-</sup> Ions (kJ/mol)*

	<b>OH<sup>-</sup></b>	<b>O<sup>2-</sup></b>
<b>Na<sup>+</sup></b>	900	2481
<b>Mg<sup>2+</sup></b>	3006	3791
<b>Al<sup>3+</sup></b>	5627	<b>15916</b>

**Construct a Born-Haber cycle and use it to calculate an enthalpy change.**

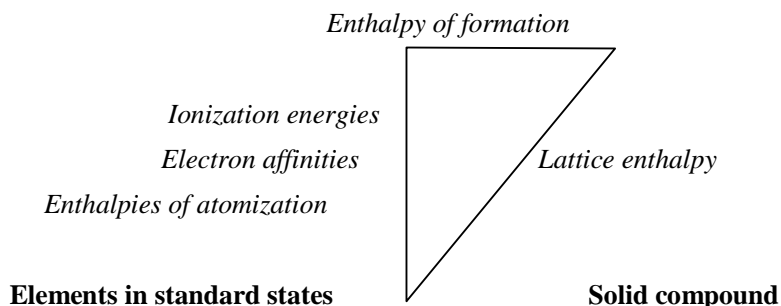
[http://www-users.york.ac.uk/~srms500/siti.org.uk/generated/enthalpy\\_change\\_2.doc.htm](http://www-users.york.ac.uk/~srms500/siti.org.uk/generated/enthalpy_change_2.doc.htm)

[http://en.wikipedia.org/wiki/Born-Haber\\_cycle](http://en.wikipedia.org/wiki/Born-Haber_cycle)

The **Born-Haber Cycle** is an approach to analyzing reaction energies. It was named after and developed by the two German scientists Max Born and Fritz Haber.

“A *mathematical* description of the *relationship* between the *electron affinity*, *heats of atomisation*, *ionisation energy* and *lattice energy* of *ionic compounds*”.

**Diagrammatic representation of the Born-Haber cycle**



The Born-Haber cycle involves the formation of an ionic compound from the reaction of a metal (often a Group I or Group II element) with a non-metal.

Born-Haber cycles are used primarily as a means of calculating lattice enthalpies, which cannot be measured directly.

*The lattice enthalpy is the enthalpy change involved in formation of the ionic compound from gaseous ions. (note: some chemists define it as the energy to break the ionic compound into gaseous ions).*

A **Born-Haber cycle** calculates the lattice enthalpy by comparing the standard enthalpy change of formation of the ionic compound (from the elements) to the enthalpy required to make gaseous ions from the elements (note: this is an application of Hess's Law).

To make gaseous ions from elements it is necessary to atomise the elements (turn each into gaseous atoms) and then to ionise the atoms.

The energy involved in removing electrons to make a cation is called the **ionization energy**.

The enthalpy of adding electrons to an atom to make it an anion is called the **electron affinity**.

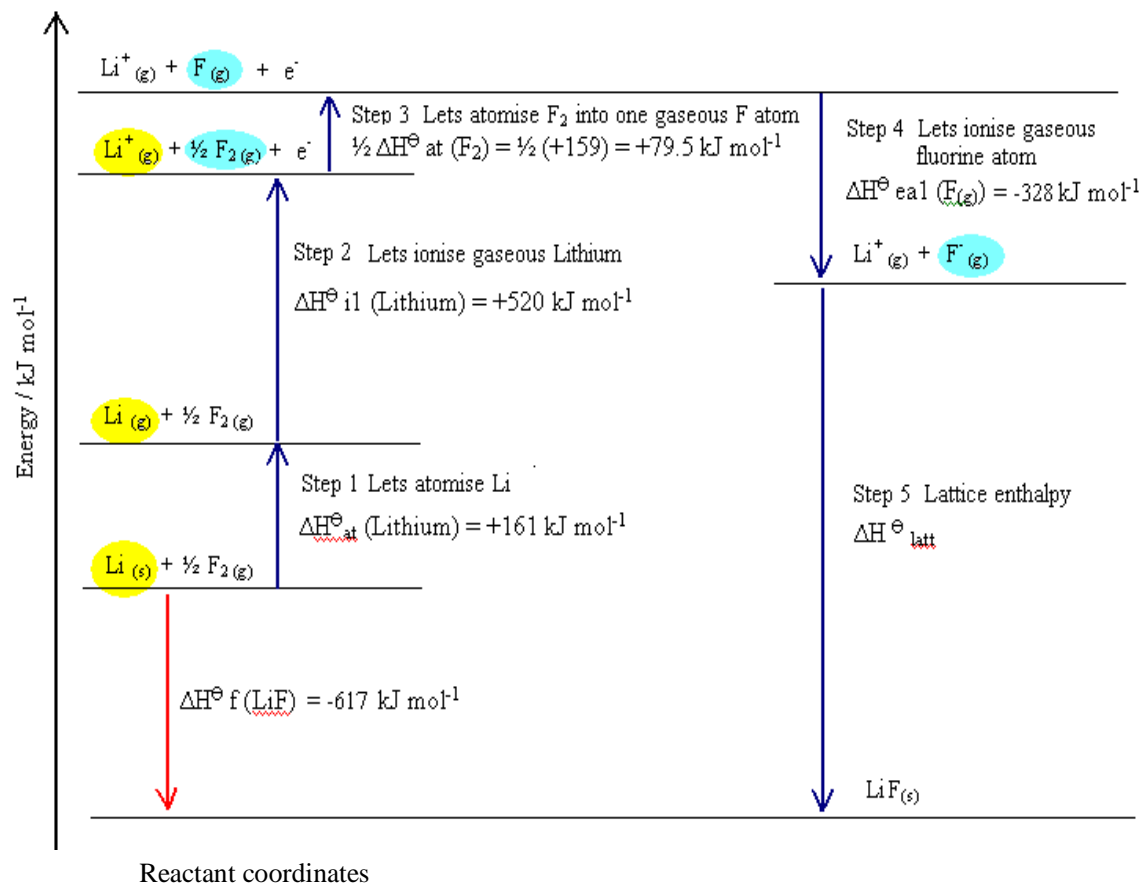
### Example: The Born-Haber cycle for the standard enthalpy change of formation of lithium fluoride.

The Born-Haber cycle consists of several steps of measurable enthalpy values e.g. enthalpy of ionisation, enthalpy of atomization and electron affinity, from which the lattice enthalpy  $\Delta H^\ominus_{latt}$  can be calculated.

#### Lithium Fluoride

Find the lattice enthalpy  $\Delta H^\ominus_{latt}$  of Lithium Fluoride ( $\text{LiF}_{(s)}$ )

#### Step 1- Draw the Born-Haber cycle for LiF



Note: The atomisation of lithium and fluorine and ionization of lithium are endothermic.

Electron affinity (mole of gaseous atoms/anions gaining electrons) is exothermic.

#### Procedure

Deal with the enthalpies associated to Lithium first (left of diagram), then Fluorine.

The appropriate enthalpy values should be given in the question paper, otherwise they can be found in the **chemistry data book**. Note that the bottom left arrow represents a direct route for the formation of LiF lattice.

The other arrows represent the multi-steps formation of LiF lattice which includes one step for lattice enthalpy.

'at' = atomisation, 'i1' = first ionisation, 'ea1' = first electron affinity. 'latt' = lattice and 'f' = formation

#### Step 2 - Calculate the lattice enthalpy for LiF

$\Delta H^\ominus_{latt}$ (Step 5)	= $\Delta H^\ominus_f - (\text{Step 1} + \text{Step 2} + \text{Step 3} + \text{Step 4})$
	= $-617 - \{ 161 + 520 + 79.5 + (-328) \}$
	= $-1049.5 \text{ kJ mol}^{-1}$

## IB Chemistry

### Exercise

Find the lattice enthalpy for sodium chloride  $\text{NaCl}_{(s)}$ . The appropriate enthalpies are as follows:

$\Delta H^{\circ} f(\text{NaCl})$	= - 411 kJ mol <sup>-1</sup>
$\Delta H^{\circ} \text{at}(\text{Na}_{(s)})$	= +107 kJ mol <sup>-1</sup>
$\Delta H^{\circ} \text{at}(\text{Cl}_{2(g)})$	= +242 kJ mol <sup>-1</sup>
$\Delta H^{\circ} \text{il}(\text{Na}_{(g)})$	= +496 kJ mol <sup>-1</sup>
$\Delta H^{\circ} \text{ea1}(\text{Cl}_{(g)})$	= - 348 kJ mol <sup>-1</sup>

Step 1 - Construct a Born-Haber cycle.

Step 2 - Calculate the lattice enthalpy for NaCl

## IB Chemistry

### *Analyse theoretical and experimental lattice enthalpy values.*

A significant degree of covalent character in some ionic compounds is associated with an increase in lattice enthalpy and decreased solubility.

#### **Theoretical Value**

Using the laws of electrostatics, the known sizes of the ions, the charges on the ions and *assuming a perfect ionic lattice*, theoretical values for the lattice enthalpy can be calculated.

#### **Experimental Value**

A Born-Haber cycle is used to calculate the result.

If there is a good agreement between the theoretical and experimental lattice enthalpies, then the substance is perfectly ionic (the ions are spherical and electrons are completely transferred.) If there is less agreement, then the ion has some slight covalent character creeping in due to **polarization**\*

*\*Where a positive ion distorts the electron cloud around a neighboring negative ion.*

For example:  $\text{Al}^{3+}$  has a high charge density (3+) and is very small. This gives it a high polarising power:

- If the cation is small and highly charged, it has a large polarising power.
- If the anion is large and has a relatively low charge, then it is said to have a large polarisability.

If the above is the case, and the anion is being polarised by the cation, there will be a degree of covalent character to the bond.

So the bonding in  $\text{AlCl}_3$  is virtually covalent.

Small highly charged cation + large easily polarised anion = covalent character.

There are some ionic compounds that do not exist at all. Aluminium carbonate is one such example.

- The aluminium 3+ cation is so small and highly polarising that it completely distorts the large  $\text{CO}_3^{2-}$  ion into self-decomposition.
- Instead of  $\text{Al}_2(\text{CO}_3)_3$  being formed, carbon dioxide is driven off, leaving aluminium oxide.
- Other examples include the silver halides.

## IB Chemistry

### Spontaneity of a reaction - Gibbs Free Energy

*Calculate the standard entropy change for a reaction ( $\Delta S^\ominus$ ) using values of absolute entropies.*

The standard entropy change for a reaction can be calculated from absolute entropies using the formula:

$$\Delta S = \Sigma S(\text{Products}) - \Sigma S(\text{Reactants})$$

- Reactions which release heat (and so increase stability) tend to occur.
- Reactions which increase entropy ( $\Delta S$  is positive) also tend to occur, but neither can be used to accurately predict spontaneity alone.

How can we predict whether a reaction will occur under particular conditions?



## IB Chemistry

*Calculate  $\Delta G^\theta$  for a reaction using the equation  $\Delta G^\theta = \Delta H^\theta - T\Delta S^\theta$  or by using values of the standard free energy change of formation.*

The Gibbs free energy ( $\Delta G$ ) is defined as a measure of the total entropy of the universe.

The total entropy of the universe *must* increase in order for any process to occur spontaneously.

When heat is released in a reaction (exothermic change) this energy heats up the universe and effectively increases its entropy (a greater number of possible energy states that the particles in the universe can adopt), consequently exothermic reactions are favourable.

If the entropy of a reaction mixture increases then this is also favourable as the total entropy of the universe also increases.

*Reminder: Entropy increases will be observed when any one or more of the following occur:*

- *A reaction breaks up a larger molecule into smaller molecular fragments*
- *A reaction occurs in which there is an increase in the moles of gas in the product.*
- *A process where a solid changes to a liquid or gas or a liquid changes to a gas*

The Gibbs free energy change, enthalpy, temperature and entropy are related in the expression:

$$\text{Gibbs free energy change } (\Delta G) = \Delta H - T\Delta S$$

If the Gibbs free energy change is negative (convention) then the total entropy of the universe increases and the reaction is spontaneous.

**When  $\Delta G$  is negative, the reaction is spontaneous, when it's positive, the reaction is not.**

## IB Chemistry

### Gibbs free energy calculations – alternative method

Enthalpy changes can be calculated indirectly by summing the enthalpy values of related equations using Hess's law.

Entropy changes can also be calculated in the same way from a knowledge of Gibbs free energy values in related equations.

### Spontaneity of reaction

Determined by the relationship:

$$\Delta G = \Delta H - T(\text{kelvin}) \times \Delta S$$

Enthalpy change	Entropy change	Gibbs free energy	Spontaneity
positive	positive	depends on T, may be + or -	yes, if the temperature is high enough
negative	positive	always negative	always spontaneous
negative	negative	depends on T, may be + or -	yes, if the temperature is low enough
positive	negative	always positive	never spontaneous

### Exercise

Find the lattice enthalpy for sodium chloride NaCl<sub>(s)</sub>.

$\Delta H^{\circ}_{\text{latt}}$ (Step 5)	= $\Delta H^{\circ}_{\text{f}}$ - (Step 1 + Step 2 + Step 3 + Step 4)
	= -411 - { 107 + 496 + 121 + (-348) }
	= -787 kJ Mol <sup>-1</sup>