BORN HABER CYCLES

The Born Haber cycles is an adaption of Hess's law to calculate lattice enthalpy from other data
The lattice enthalpy cannot be determined directly. We calculate it indirectly by making use of changes for which data are available and link them together in an enthalpy cycle the Born Haber cycle

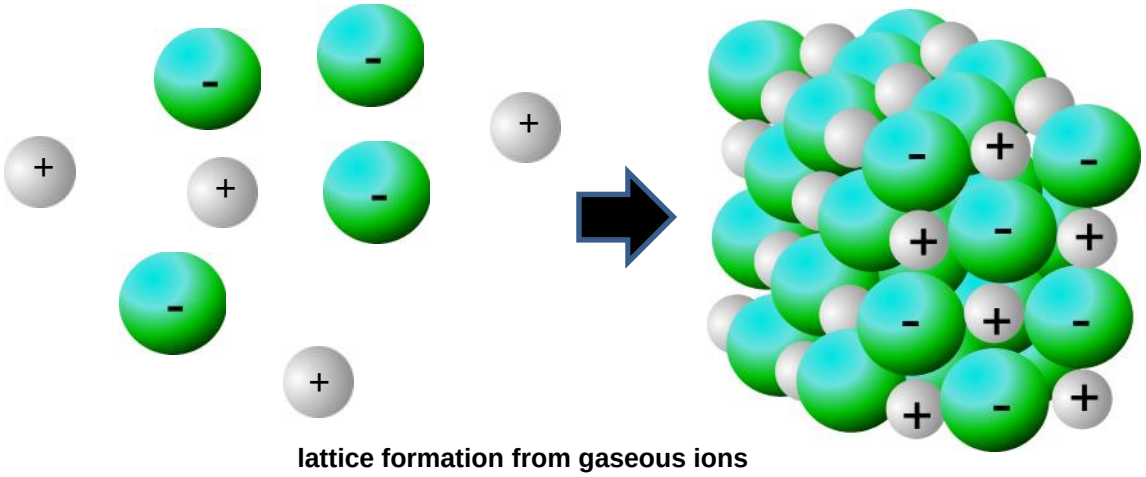
Generally Lattice Enthalpy refers to the enthalpy change when a lattice is made from gaseous ions. Some exam boards refer to the opposite process at times. Hence the two definitions below

Enthalpy of lattice formation
The Enthalpy of lattice formation is the standard enthalpy change when **1 mole** of an ionic crystal lattice is formed from its constituent **ions in gaseous form**.

$Na^+ (g) + Cl^- (g) \rightarrow NaCl (s)$ $[\Delta_{Latt} H = -787 \text{ kJ mol}^{-1}]$

Enthalpy of lattice dissociation
The Enthalpy of lattice dissociation is the standard enthalpy change when 1 mole of an ionic crystal lattice form is separated into its constituent ions in gaseous form.

$NaCl (s) \rightarrow Na^+ (g) + Cl^- (g)$ $[\Delta_{Latt} H = +787 \text{ kJ mol}^{-1}]$



lattice formation from gaseous ions

This process cannot be measured experimentally directly. The following data can be used to work out the lattice enthalpy

Enthalpy change of formation
The standard enthalpy change of formation of a compound is the energy transferred when **1 mole of the compound** is formed from **its elements** under **standard conditions (298K and 100kpa), all reactants and products being in their standard states**

$Na (s) + \frac{1}{2}Cl_2 (g) \rightarrow NaCl (s)$ $[\Delta_f H = -411.2 \text{ kJ mol}^{-1}]$

Enthalpy of atomisation
The enthalpy of atomisation of an element is the enthalpy change when 1 mole of gaseous atoms is formed from the element in its standard state

$Na (s) \rightarrow Na(g)$ $[\Delta_{at} H = +148 \text{ kJ mol}^{-1}]$
$\frac{1}{2} O_2 (g) \rightarrow O (g)$ $[\Delta_{at} H = +249 \text{ kJ mol}^{-1}]$

The enthalpy change for a solid metal turning to gaseous atoms can also be called the **Enthalpy of sublimation** and will numerically be the same as the enthalpy of atomisation
$Na (s) \rightarrow Na(g)$ $[\Delta_{sub} H = +148 \text{ kJ mol}^{-1}]$

Bond dissociation enthalpy (bond energy)
The bond dissociation enthalpy is the standard molar enthalpy change when one mole of a covalent bond is broken into two gaseous atoms (or free radicals)

$Cl_{2\,(g)} \rightarrow 2Cl_{(g)}$ $\Delta_{diss} H = +242 \text{ kJ mol}^{-1}$
Or
$CH_{4\,(g)} \rightarrow CH_{3\,(g)} + H_{(g)}$ $\Delta_{diss} H = +435 \text{ kJ mol}^{-1}$

For diatomic molecules the $\Delta_{diss} H$ of the molcule is the same as 2x $\Delta_{at} H$ of the element
$Cl_{2\,(g)} \rightarrow 2Cl_{(g)}$ $\Delta H_{diss} = +242 \text{ kJ mol}^{-1}$
$\frac{1}{2} Cl_{2\,(g)} \rightarrow Cl_{(g)}$ $\Delta_{at} H = +121 \text{ kJ mol}^{-1}$

First Ionisation enthalpy
The first ionisation enthalpy is the enthalpy change required to remove 1 mole of electrons from 1 mole of gaseous atoms to form 1 mole of gaseous ions with a +1 charge
$Mg (g) \rightarrow Mg^+ (g) + e^-$ $[\Delta_{IE\,1} H]$

Second Ionisation enthalpy
The second ionisation enthalpy is the enthalpy change to remove 1 mole of electrons from one mole of gaseous 1+ ions to produces one mole of gaseous 2+ ions.
$Mg^+ (g) \rightarrow Mg^{2+} (g) + e^-$ $[\Delta_{IE\,2} H]$

First Electron affinity

The first electron affinity is the enthalpy change that occurs when 1 mole of gaseous atoms gain 1 mole of electrons to form 1 mole of gaseous ions with a –1 charge

$O(g) + e^- \rightarrow O^-(g)$ $[\Delta_{ea1}H] = -141.1\ kJ\ mol^{-1}]$

The first electron affinity is exothermic for atoms that normally form negative ions because the ion is more stable than the atom and there is an attraction between the nucleus and the electron

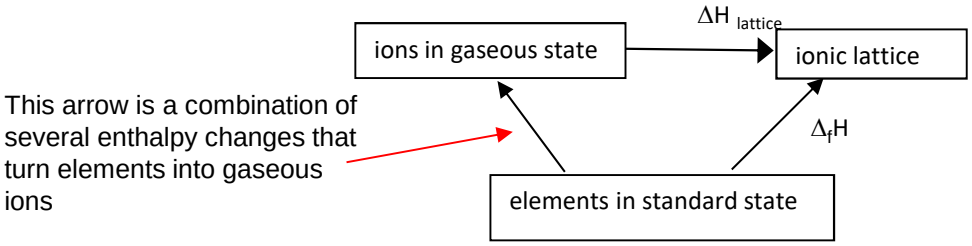
second electron affinity

The second electron affinity is the enthalpy change when one mole of gaseous 1- ions gains one electron per ion to produce gaseous 2- ions.

$O^-(g) + e^- \rightarrow O^{2-}(g)$ $[\Delta_{ea2}H = +798\ kJ\ mol^{-1}]$

The second electron affinity for oxygen is **endothermic** because it take energy to overcome the **repulsive force** between the **negative ion and the electron**

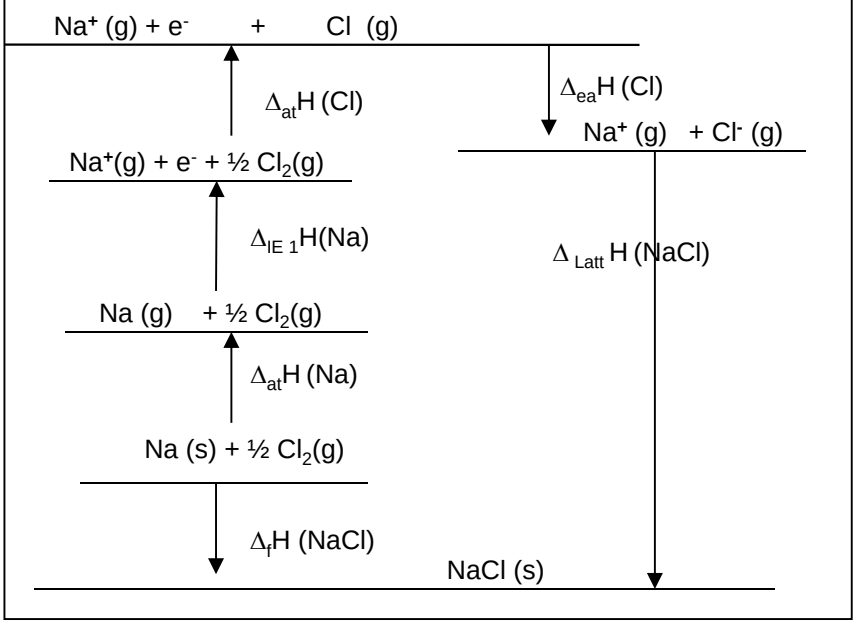
The Born Haber cycle links all these enthalpy changes in an enlarged version of a Hess's law cycle.



This arrow is a combination of several enthalpy changes that turn elements into gaseous ions

Born-Haber cycles calculate a measure of ionic bond strength based on experimental data.

Born Haber cycle: sodium Chloride



Pay attention to state symbols and direction of arrows.

Usually all pieces of data are given except the one that needs to be calculated

Careful

This Born Haber cycle has been constructed using a lattice enthalpy of formation. Sometimes questions will give the enthalpy of lattice dissociation which has the opposite sign and the arrow points in the opposite direction. This changes the calculation

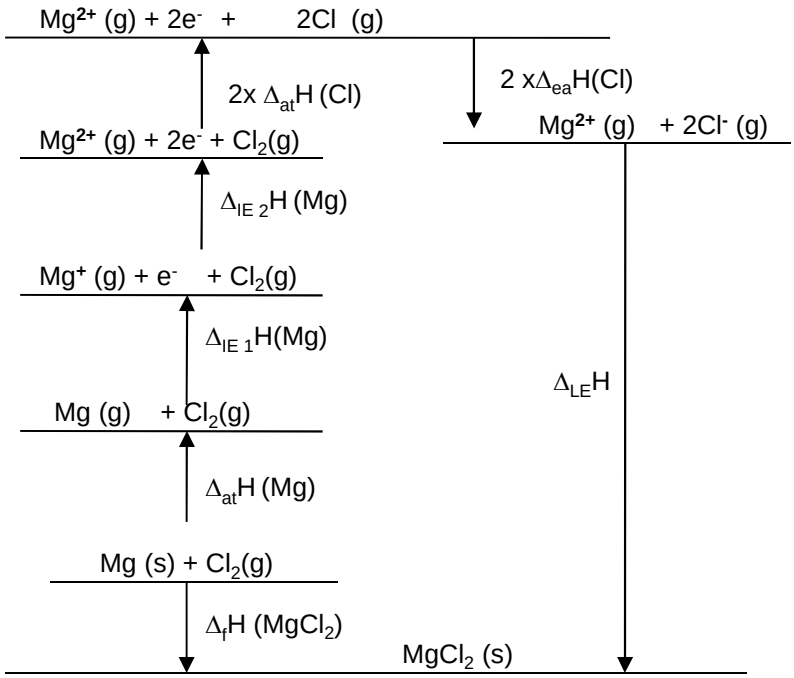
By applying Hess's law the heat of formation equals to the sum of everything else

$\Delta_fH = \Delta_{at}H\ (Na) + \Delta_{IE}H(Na) + \Delta_{at}H(Cl) + \Delta_{ea}H(Cl) + \Delta_{Latt}H$

Rearrange to give $\Delta_{Latt}H = \Delta_fH - (\Delta_{at}H\ (Na) + \Delta_{IE}H(Na) + \Delta_{at}H\ (Cl)\ \Delta_{ea}H(Cl))$

$\Delta_{Latt}H = -411 - (+107 + 496 + 122 + -349) = -787\ kJmol^{-1}$

Born Haber cycle: magnesium Chloride



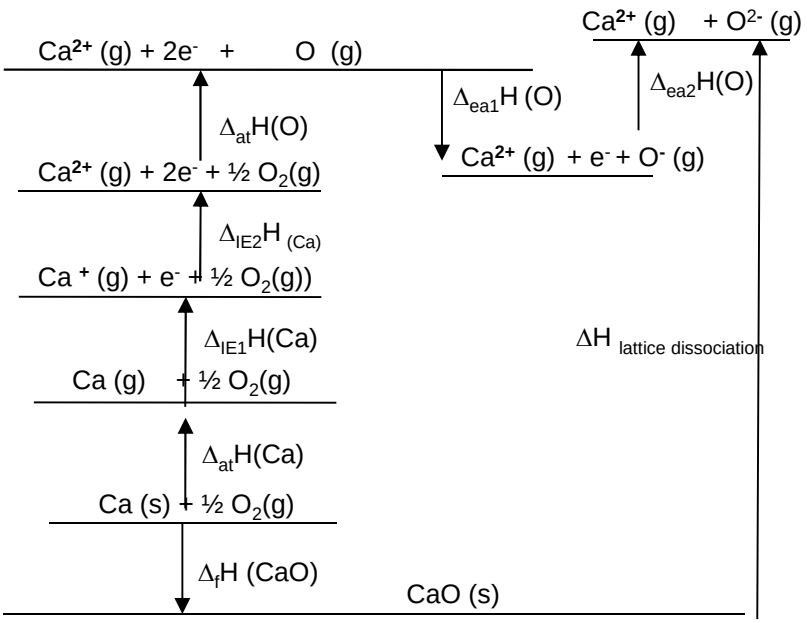
The data for the Δ_{at} H (Cl) could also be given as the bond energy for E(Cl-Cl) bond.

Remember :

E(Cl-Cl) = 2 x Δ_{at} H (Cl)

Note in this example the first and second ionisation energies of magnesium are needed as Mg is a +2 ion

Born Haber cycle: calcium oxide



Notice the second electron affinity for oxygen is **endothermic** because it take energy to overcome the **repulsive force** between the **negative ion and the electron**

In this case the cycle has been constructed using
$\Delta H_{\text{lattice dissociation}}$
The calculation therefore is:

$[\Delta_f H\ (CaO) + \Delta H_{\text{lattice dissociation}}\ ] = [\Delta_{at} HCa + \Delta_{IE\ 1} H\ (Ca) + \Delta_{IE\ 2} H\ (Ca) + \Delta_{at} H\ (O) + \Delta H_{ea1}\ (O) + \Delta H_{ea2}\ (O)\ ]$

Trends in Lattice Enthalpies

The strength of a enthalpy of lattice formation depends on the following factors

1. **The sizes of the ions:**

   The larger the ions, the less negative the enthalpies of lattice formation (i.e. a weaker lattice). As the ions are larger the charges become further apart and so have a weaker attractive force between them.

2. **The charges on the ion:**

   The bigger the charge of the ion, the greater the attraction between the ions so the stronger the lattice enthalpy (more negative values).

The lattice enthalpies become less negative down any group.
e.g. LiCl, NaCl, KCl, RbCl

e.g group 1 halides (eg NaF KI) have lattice enthalpies of around –700 to -1000

group 2 halides (eg $MgCl_2$) have lattice enthalpies of around –2000 to –3500

group 2 oxides eg MgO have lattice enthalpies of around –3000 to –4500 $kJmol^{-1}$

Perfect Ionic Model

Theoretical lattice enthalpies assumes a **perfect ionic model** where the **ions are 100% ionic** and **spherical** and the **attractions are purely electrostatic**.

Theoretical Lattice Energies

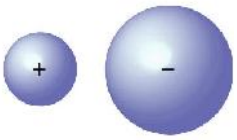
It is possible to calculate lattice energies theoretically by assuming that a lattice is an array of charged spheres in contact. The spheres are separate entities, each with its charge distributed uniformly around it. The principles of electrostatics predict the lattice energy using this model.
The model calculates lattice energies for substances with 100% ionic character. By comparing lattice energies calculated theoretically with those obtained experimentally (i.e. from a Born-Haber cycle) we have measure of how ionic an "ionic substance" is.

Differences between theoretical and Born Haber (experimental) lattice enthalpies

The Born Haber lattice enthalpy is the real experimental value.
When a compound shows covalent character, the theoretical and the born Haber lattice enthalpies differ. The more the covalent character the bigger the difference between the values.

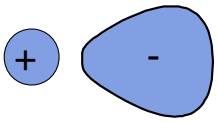
When the negative ion becomes distorted and more covalent we say it becomes polarised. The metal cation that causes the polarisation is called more polarising if it polarises the negative ion.

100% ionic



When 100 % ionic the ions are spherical.
The theoretical and the born Haber lattice enthalpies will be the same

Ionic with covalent character



The charge cloud is distorted .The theoretical and the experimental Born Haber lattice enthalpies will differ

There is a tendency towards covalent character in ionic substances when
- the positive ion is small
- the positive ion has multiple charges
- the negative ion is large
- the negative ion has multiple negative charges.

When a compound has some covalent character- it tends towards giant covalent so the lattice is stronger than if it was 100% ionic. Therefore the born haber value would be larger than the theoretical value.

Why does Calcium chloride have the formula $CaCl_2$ and not CaCl or $CaCl_3$?

It is useful to draw out the born haber cycles for each potential case.

We need to calculate an enthalpy of formation for each case.

The one with the **most exothermic enthalpy of formation** will be the one that forms as it will be the most thermodynamically stable

Theoretical lattice enthalpies have been calculated for each case

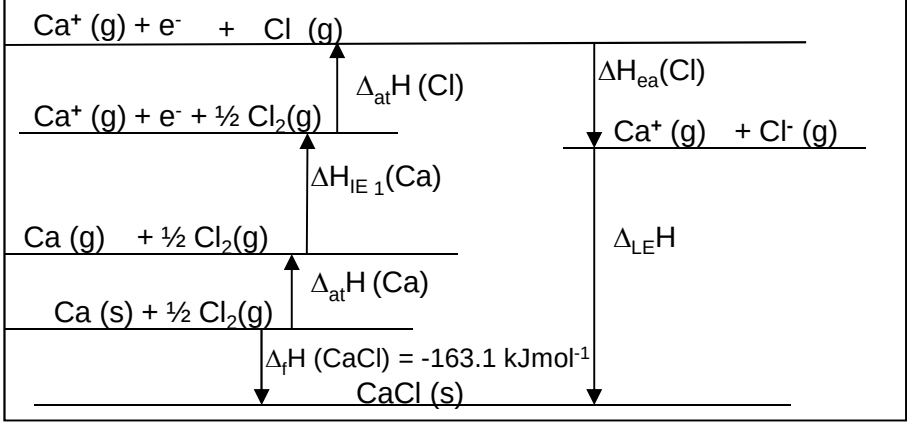
Theoretical lattice enthalpies
ΔH_{latt} CaCl = -719 kJ mol^{-1}
ΔH_{latt} $CaCl_2$ = -2218 kJ mol^{-1}
ΔH_{latt} $CaCl_3$ = -4650 kJ mol^{-1}

These get larger as the positive charge on the calcium ion becomes bigger.

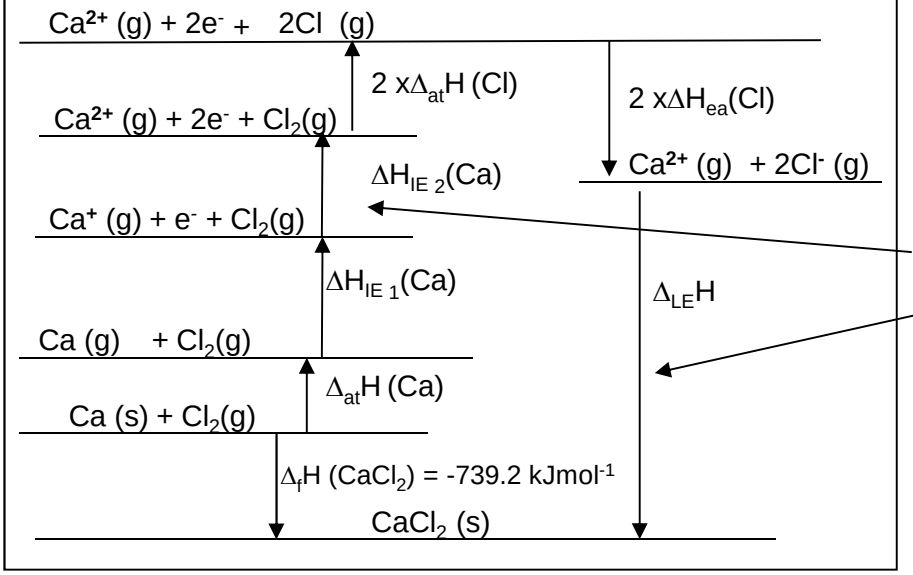
The enthalpy of formation is largely a balance of the ionisation energy and lattice enthalpy.

ΔH_f (CaCl) is -163.1 kJ mol^{-1}. This is exothermic.

Born Haber Cycle for CaCl



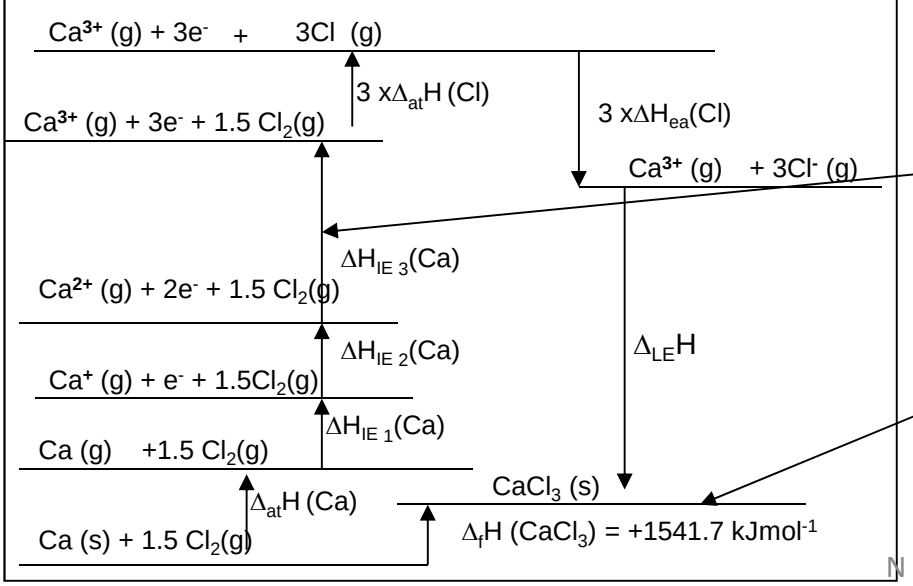
Born Haber Cycle for $CaCl_2$



The increased ionisation enthalpy to form Ca^{2+} is more than compensated for by the stronger lattice enthalpy of formation

The enthalpy of formation is therefore more exothermic. This is the most stable form

Born Haber Cycle for $CaCl_3$



The big increase in ionisation enthalpy to remove the 3rd electron is not compensated for by the stronger lattice enthalpy of formation

The enthalpy of formation is therefore endothermic. This is the least stable form

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