15.2 – Born-Haber Cycles

15.2.1 - Define and apply the terms *lattice enthalpy* and *electron affinity*

Lattice Enthalpy – The energy required to completely separate one mole of a solid ionic compound into its gaseous ions.

Electron Affinity – The energy change that occurs when mole of electrons is accepted by one mole of atoms in the gaseous state to form one mole of negative ions.

15.2.2 - Explain how the relative sizes and the charges of ions affect the lattice enthalpies of different ionic compounds

An ionic lattice with a higher enthalpy is considered *more stable*, because it is harder to break apart. It would have a higher melting and boiling point.

$$Lattice\ Enthalpy \propto \frac{charge\ on\ cation \times charge\ on\ anion}{sum\ of\ ionic\ radii}$$

Lattice Enthalpies [kJ mol^{-1}]		Ionic Radii [10^{-12}m]	
NaCl	+771	Na^+	98
KCl	+701	K^+	133
		Cl^-	181
NaF	+902	Na^+	98
NaBr	+733	F^-	133
NaI	+684	Br^-	196
		I^-	219
MgF_2	+2957	Mg^{2+}	65
NaF	+902	Na^+	98
		F^-	133

The size and charge of the ions affect the force of attraction within the lattice, which affects the enthalpy. The size of this attraction occurs according to Coulomb's Law:

$$F = k\frac{q_1 q_2}{r^2}$$

Here, q_1 and q_2 represent the charges on the two ions, and r is the sum of their radii, which is the distance between them.

When the **charge increases** on either one of the ions, or the **distance between them decreases**, then the force of attraction is larger.

NaCl - KCl

- Here, the cations are different, but the anions are the same.
- Same charge on the metal ions
- K^+ has a greater ionic radius than Na^+ due to its higher number of shells
- KCl has a lower lattice enthalpy because there are weaker attractive forces, mainly because of the size of the ions.

NaF - NaBr - NaI

- All have the same cations, however the anions are different
- The anions have the same charge
- The anions are different sizes, with I as the largest.
- Lattice enthalpy: NaI < NaBr < NaF
- Based on the size of the ions

MgF_2 - NaF

- Mg ion has the higher charge
- Magnesium is a smaller ion
- MgF_2 has the greatest force of attraction because of both of these factors.

So, in a nutshell:

- Larger charge = Larger enthalpy
- Smaller radius = Larger enthalpy

15.2.3 - Construct a Born-Haber cycle for group 1 and 2 oxides and chlorides, and use it to calculate an enthalpy change

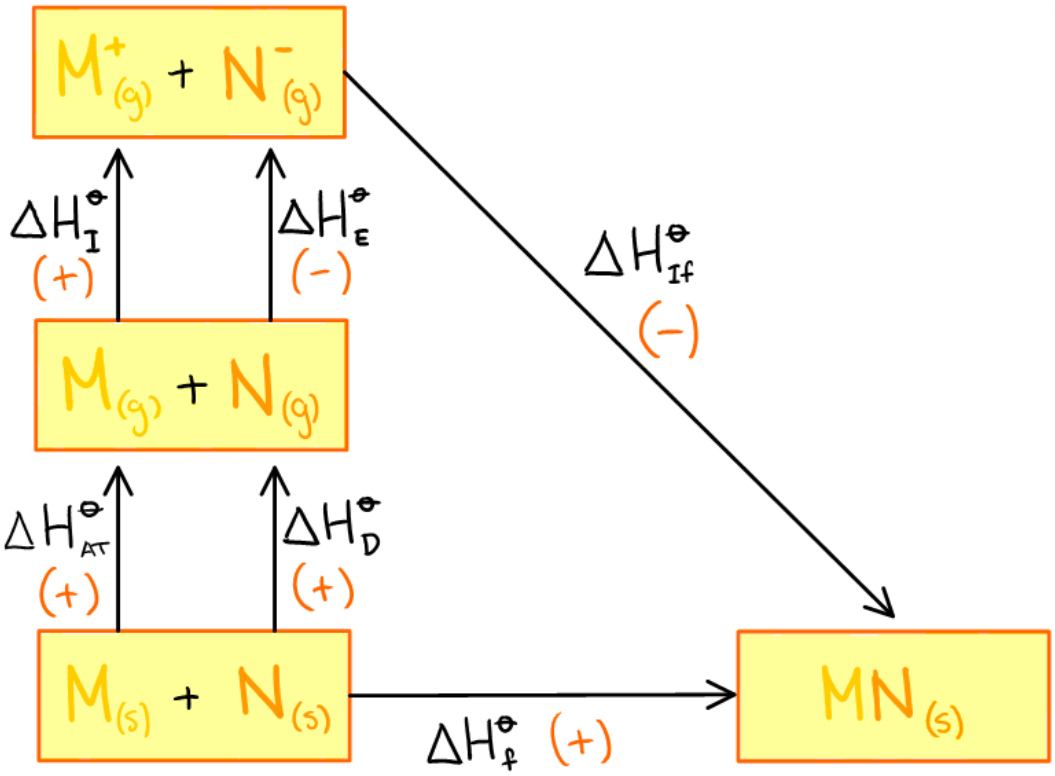
When metals and non-metals combine to form ionic lattices, there are a number of other processes which also take place. This is called the **Born-Haber process**, and can be compared to Hess's Law.

1. The **atomisation** of the solid metal $\{\Delta H^{\ominus}_{at}\}$ which is where the metal goes into the gaseous state. This is an *endothermic process*.
2. **Ionisation** of the gaseous metal $\{\Delta H^{\ominus}_{I}\}$ which is where the metal loses electrons to form a cation. This is an *endothermic process*.
3. The **dissociation**/ atomisation of the molecular non-metal into atoms $\{\Delta H^{\ominus}_{D}\}$, which is where the non-metal goes into the gaseous state and is broken into individual atoms. This is an *endothermic process*.
4. **Addition** of electrons to the non-metal atoms, or electron affinity $\{\Delta H^{\ominus}_{E}\}$ where the non-metal atoms gain electrons to form anions. This is an *exothermic process*.
5. The **reaction** between the gaseous ions to form the solid ionic lattice $\{\Delta H^{\ominus}_{lf}\}$. This is an *exothermic process*.

The more negative the standard enthalpy change of formation of the ionic compound, the more stable it is.

The enthalpy of formation for step five is of the same magnitude (but opposite sign) to the lattice enthalpy of the compound.

The Born-Haber cycle can be applied to find an enthalpy that cannot be measured.



15.2.4 - Discuss the difference between theoretical and experimental lattice enthalpy values of ionic compounds in terms of their covalent character

Born-Haber Cycles allow us to find the lattice enthalpies from experimental results. However, to find the theoretical enthalpy values, we use **Coulomb's law**.

Compound	Lattice Enthalpy (kJ mol^{-1})		
	Experimental	Theoretical	% Discrepancy
NaF	902	891	1.2
NaCl	771	766	0.6
NaBr	733	732	0.1
NaI	684	686	0.3
AgF	955	870	8.9
AgCl	905	770	14.9
AgBr	890	758	14.8
AgI	876	736	16.0

In some cases, we are led to believe that the ionic model is *an accurate representation* of the compound because the theoretical and experimental lattice enthalpies are close.

Sodium halides have proven to be very close to these theoretical values, so we assume that our current model for their ionic model is very accurate.

However, the *silver halides* do not have similar experimental and theoretical lattice enthalpies, so we still need to refine the current model to suit what actually happens within the lattice.

The experimental lattice enthalpy tends to be *larger* than the theoretical one. This is due to the effect of distorting the electron cloud, which results in a higher electron density between the ions, causing an almost polar bond.