Lattice Enthalpy

Reminder from 2.3.1 Enthalpy Changes and 1.2.1 Electron structure

Standard conditions are used when comparing energy changes. The conditions are:

Pressure 100 kPa
Temperature 298K
Concentration 1.0M for any solutions

Standard Enthalpy Change of Formation, $\Delta H^{\theta}f$ is the enthalpy change when one mole of a compound is formed from its elements in their standard states under standard conditions.

First ionisation energy is the energy needed to remove one electron form each atom, in a mole of atoms, in the gas phase.

$$X_{(g)} \longrightarrow X^{+}_{(g)} + e^{-}_{(g)}$$

Second ionisation energy is the energy needed to remove one electron from each ion, in one mole of +1 ions, in the gas phase.

$$X^{+}_{(g)} \longrightarrow X^{2+}_{(g)} + e^{-}_{(g)}$$

Lattice enthalpy gives us a measure of ionic bond strength. It is the enthalpy change when one mole of an ionic solid is formed from gaseous ions under standard conditions.

The equation is $Na^{+}_{(g)} + Cl^{-}_{(g)} \rightarrow NaCl_{(s)}$

Lattice enthalpy is always negative (exothermic). A stronger lattice has a more exothermic lattice enthalpy.

Standard enthalpy change of atomisation is the enthalpy change when one mole of gaseous atoms is formed from the element in its standard state under standard conditions.

eg $Na_{(s)} \rightarrow Na_{(g)}$ or $\frac{1}{2}Cl_{2(g)} \rightarrow Cl_{(g)}$

Electron Affinity is the enthalpy change when one electron is added to each atom in one mole of gaseous atoms

$$Cl_{(g)} + e^{-} \rightarrow Cl^{-}_{(g)}$$

The Born Haber Cycle is used to calculate lattice enthalpy

$$LE = \Delta H_f - \Delta H_{at} - \Delta H_{ie} - \Delta H_{ea}$$

NB 2+ ions have two ionisation energies (first and second)
2- ions have two electron affinities (first and second)

Examples of Born Haber Cycles

Born-Haber Cycle - NaCl

1. **Enthalpy of formation of NaCl**
   $Na(s) + \frac{1}{2}Cl_2(g) \longrightarrow NaCl(s)$

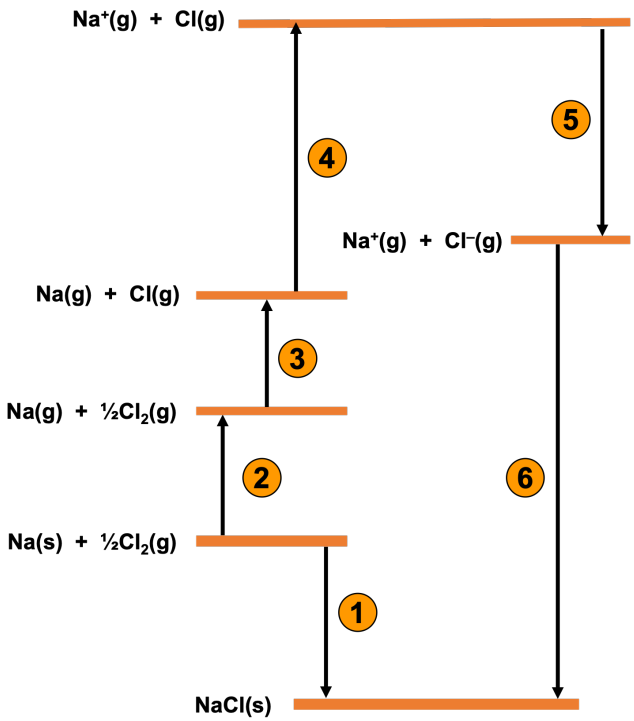
2. Enthalpy of atomisation of sodium
   $Na_{(s)} \rightarrow Na_{(g)}$

3. **Enthalpy of atomisation of chlorine**
   $\frac{1}{2}Cl_2(g) \longrightarrow Cl(g)$

4. **Ist Ionisation Energy of sodium**
   $Na(g) \longrightarrow Na^+(g) + e^-$

5. **Electron Affinity of chlorine**
   $Cl(g) + e^- \longrightarrow Cl^-(g)$

6. **Lattice Enthalpy of NaCl**
   $Na^+(g) + Cl^-(g) \longrightarrow NaCl(s)$



Lattice Enthalpy is exothermic. Oppositely charged ions are attracted to each other.

CALCULATING THE LATTICE ENTHALPY

Apply Hess's Law

6 = -5 -4 -3 -2 +1

The minus shows you are going in the opposite direction to the definition

= - (-364) - (+500) - (+121) - (+108) + (-411)
= - 776 kJ mol^{-1}

NOTE:

Exothermic: arrow down

Endothermic: arrow up

Born-Haber Cycle - $MgCl_2$

1. **Enthalpy of formation of $MgCl_2$**
   $Mg(s) + Cl_2(g) \longrightarrow MgCl_2(s)$

2. Enthalpy of atomisation of magnesium
   $Mg_{(s)} \rightarrow Mg_{(g)}$

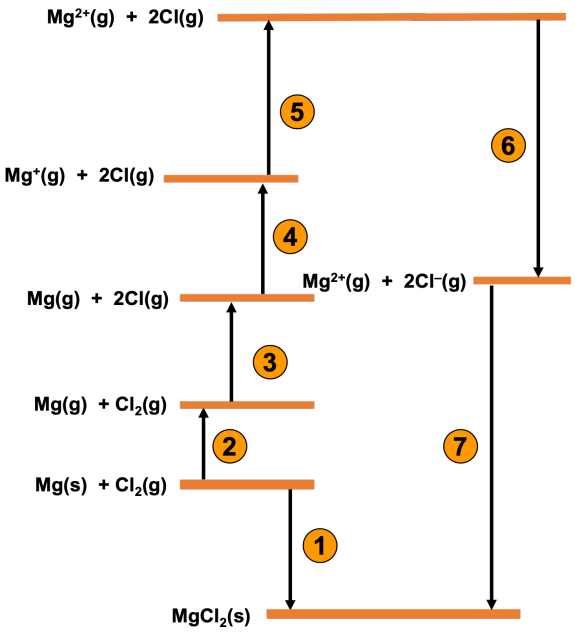
3. **Enthalpy of atomisation of chlorine** x2
   $\frac{1}{2}Cl_2(g) \longrightarrow Cl(g)$

4. **Ist Ionisation Energy of magnesium**
   $Mg(g) \longrightarrow Mg^+(g) + e^-$

5. **2nd Ionisation Energy of magnesium**
   $Mg^+(g) \longrightarrow Mg^{2+}(g) + e^-$

6. **Electron Affinity of chlorine** x2
   $Cl(g) + e^- \longrightarrow Cl^-(g)$

7. **Lattice Enthalpy of $MgCl_2$**
   $Mg^{2+}(g) + 2Cl^-(g) \longrightarrow MgCl_2(s)$



The **Standard Enthalpy of Hydration** is the enthalpy change when 1 mole of gaseous ions become hydrated (surrounded by water molecules), measured under standard conditions.

E.g. for sodium ions

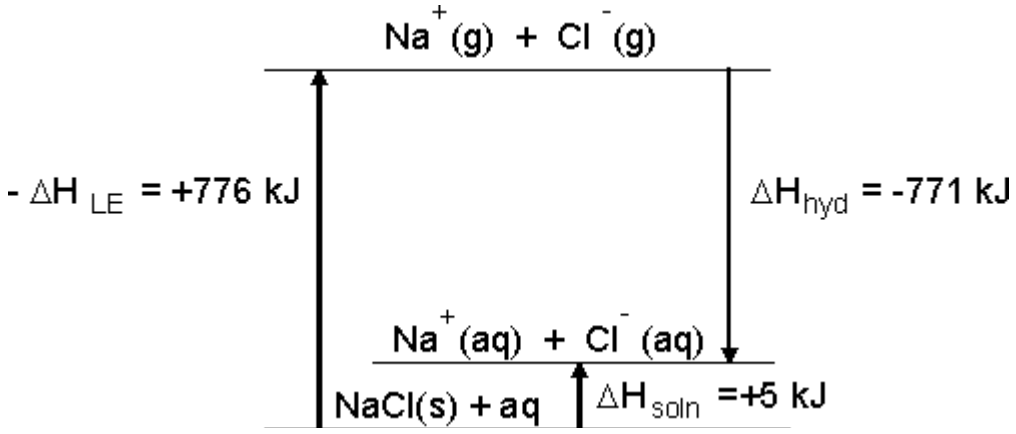
$Na^+_{(g)} + aq \rightarrow Na^+_{(aq)}$

The **Standard Enthalpy of Solution** is the enthalpy change which takes place when one mole of a solute is completely dissolved in a solvent to form a solution of concentration 1 mol dm^{-3}, measured under standard conditions.

E.g. Standard Enthalpy of Solution of sodium chloride:

$NaCl_{(s)} + (aq) \rightarrow Na^+_{(aq)} + Cl^-_{(aq)}$

Relationship between lattice energy, Standard Enthalpy of Solution and Standard Enthalpy of Hydration



$$\Delta H_{solution} = -\Delta H_{Lattice\ Enthalpy} + (\Delta H_{hydration\ (anion)} + \Delta H_{hydration\ (cation)})$$

Factors affecting Lattice enthalpy:

Stronger lattices (with more exothermic lattice enthalpies) occur with

1) **Smaller ions with smaller ionic radius** which can pack more closely together giving stronger attractive forces

2) **Ions with a double charge (2+ or 2-)** have much stronger attractive forces than single charges

As the ionic charge increases and ionic radius decreases, the enthalpy change of hydration becomes more exothermic because:

Increasing the ionic charge and decreasing the ionic radius both INCREASE the charge density of the cation.
As the cation's charge density increases, this leads to a stronger attraction for the water molecules.