Edexcel Chemistry A-Level

Topic 13: Energetics II

Detailed Notes

Topic 13A: Lattice Energy

Lattice Enthalpy ($\Delta_{le}H$)

Lattice enthalpies are used for **ionic substances**. Lattice **dissociation** enthalpy is defined as:

The energy required to break apart an ionic lattice into its constituent ions in a gaseous state under standard conditions.

Lattice **formation** enthalpy is defined as:

The energy required to form an ionic lattice from its constituent ions in a gaseous state under standard conditions.

Atomisation Enthalpy ($\Delta_{at}H$)

This is defined as:

The energy required for the formation of a mole of gaseous atoms under standard conditions.

Enthalpy of Electron Affinity ($\Delta_{ea}H$)

This is defined as:

The enthalpy change when one mole of electrons is added to a mole of gaseous atoms under standard conditions.

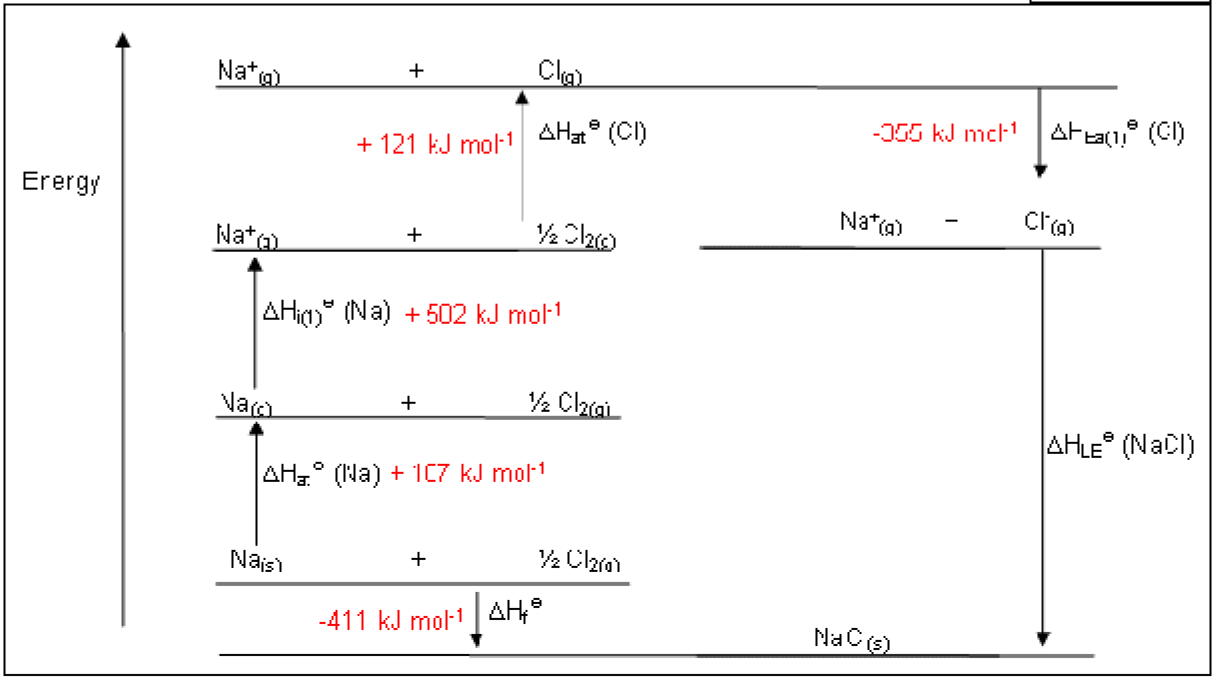
Born-Haber Cycles

Born-Haber cycles are similar to the cycles used with Hess's Law. They allow **enthalpy changes** to be determined which cannot be measured directly.

The different enthalpy changes can be **combined** to produce a **Born-Haber cycle**. In a similar way to Hess's Law, the arrows represent a reaction and are therefore treated like vectors. If the cycle **counters the direction** of the arrow, the sign of the enthalpy change represented by that arrow is **reversed**.

Example:

Image courtesy of Quora



In this example, $\Delta_{le}H$ is calculated by following around the cycle:

$$\Delta H = - - 411 + 107 + 502 + 121 - 355$$
$$= 786\ kJmol^{-1}$$

This cycle, derived from **empirical** data, will produce a different value for lattice enthalpy compared with the theoretical value predicted using **electrostatic theory**. This theory assumes a **'perfect ionic model'** meaning experimentally derived lattice enthalpies can be used as indicators of the degree of covalent bonding in a molecule.

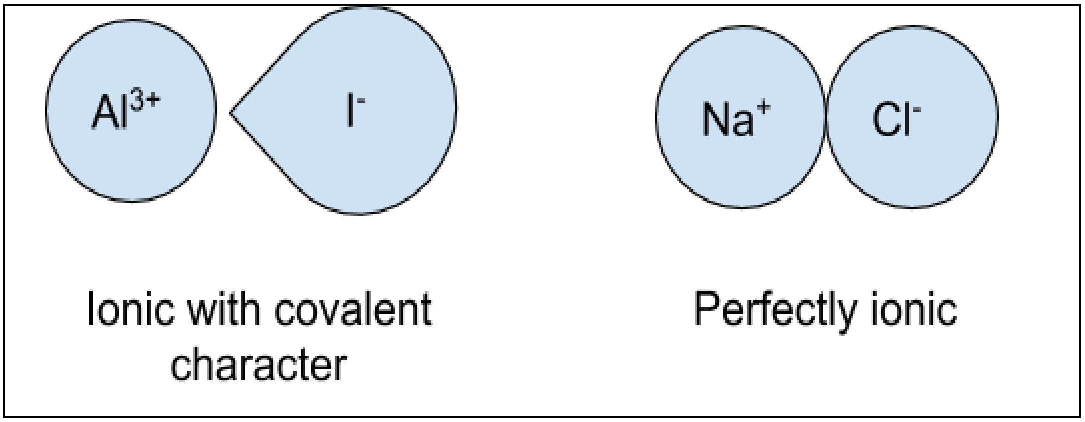
Perfect Ionic Model

Hydration enthalpy is heavily influenced by the **size and charge** of the molecules being dissolved. Therefore it is often assumed that the ions are **'perfectly ionic'**.

The perfect ionic model assumes that:

- All the ions are **perfectly spherical**.
- The ions display **no covalent character**.

Covalent character occurs in ions when two joined ions have **varying sizes or charges** meaning the distribution of charge is **not even**.
Example:



Enthalpies of Solution ($\Delta_{sol}H$) and Hydration ($\Delta_{hyd}H$)

These can be used as another way of measuring lattice enthalpies **indirectly**. They are combined using a similar idea to Hess's Law.

Enthalpy of **solution** is defined as:

The enthalpy change when one mole of ionic solid is dissolved in water to infinite dilution so that the ions no longer interact under standard conditions.

Enthalpy of **hydration** is defined as:

The enthalpy change when one mole of gaseous ions is dissolved in water to form one mole of aqueous ions under standard conditions.

It is nearly always negative as water has a $\partial+$ region that naturally attracts negative ions.

They are combined in the following way to form an energy cycle.
Example:

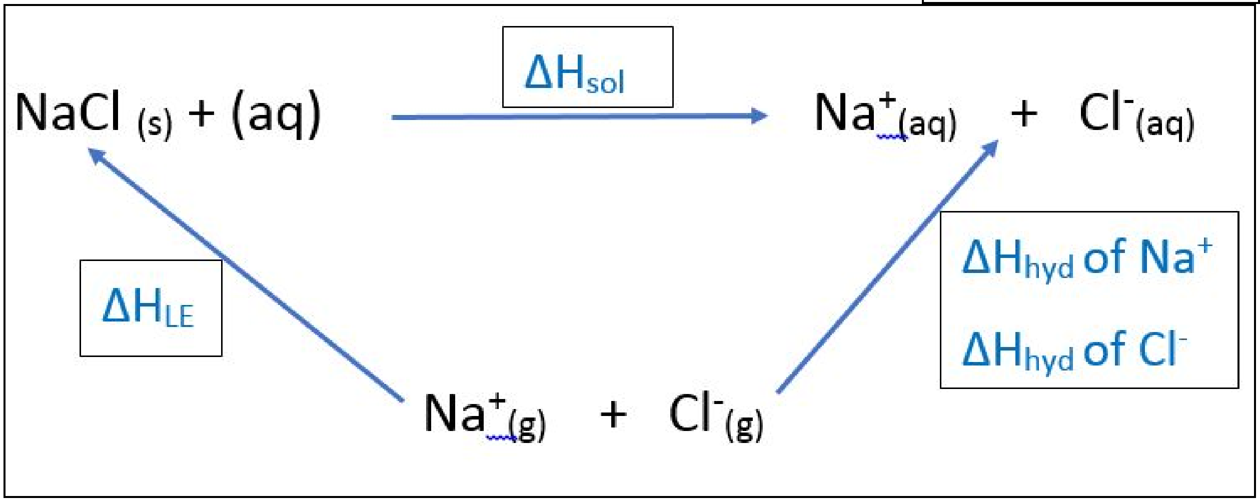


Image courtesy of The Chemistry Club

$$\Delta_{le}H = (\sum\Delta_{hyd}H) - \Delta_{sol}H$$

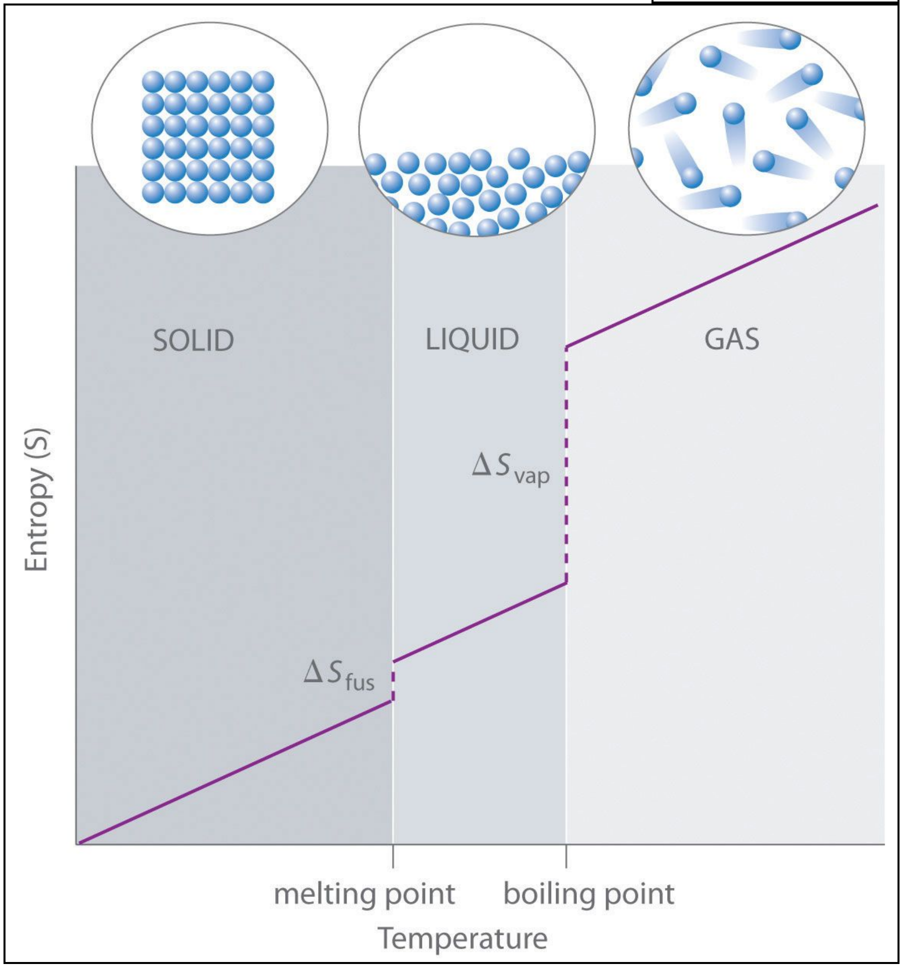
Topic 13B: Entropy

Some endothermic reactions are able to occur spontaneously at room temperature. This shows how enthalpy is no the only driver of chemical reactions. Entropy is also key.

In chemistry, things tend towards a state of **disorder**. Entropy is a **measure of this disorder**, ΔS. The more disordered a substance, the greater its entropy value. **Entropy increases as temperature increases** because the particles **gain energy** and move **further apart**, ie. they become less ordered.

Gases have the **greatest entropy** compared to solids and liquids.

Image courtesy of Lumen Learning



When a substance melts or evaporates, there is a **sudden increase** in entropy. The entropy change of vaporisation is much greater than that of fusion as a **gas is much more disordered** than a liquid or a solid.

Another case where there is a sudden increase in entropy is in a reaction when there are **more moles of product** compared to reactants. In this case there is an **increase in disorder**.

The overall entropy change for a reaction can be calculated and it is measured in **$JK^{-1}mol^{-1}$**:

$$\boxed{\Delta S_{total} = \Delta S_{system} + \Delta S_{surroundings}}$$

Entropy of the surroundings is dependant on enthalpy and temperature:

$$\boxed{\Delta S_{surroundings} = \frac{-\Delta H}{T}}$$

Since all things tend towards a state of disorder, all **spontaneous** reactions have a **positive entropy value**, ie. disorder increases.

Gibbs Free-Energy (ΔG)

This value quantifies the balance between entropy and enthalpy in a system, acting as an **indicator of reaction feasibility**. It also allows ΔS to be found without needing to measure the effects on the surroundings:

$$\boxed{\Delta G = \Delta H - T\Delta S_{system}}$$

Free-energy is measured in **$kJmol^{-1}$** so it is important that ΔH and ΔS are used in the same, **standard units**.

This equation also takes the form **'y = mx + c'** meaning it can be represented graphically as a straight line graph of ΔG against ΔS.

ΔG is **negative for all spontaneous reactions**. This becomes true at a certain, specific temperature which can be found by putting **ΔG equal to zero**. Changing the temperature or the type of reaction occurring will **change the feasibility** of the reaction happening.

A second equation for ΔG (**standard** free energy change) can also be used, that relates it to the **equilibrium constant**:

$$\boxed{\Delta G = -RT \ln(K)}$$

This shows that reactions are feasible (ΔG is negative) when the reaction has a **large value** for the equilibrium constant.

Although a reaction may be thermodynamically feasible, it still may not be able to occur due to **kinetic factors**. An example of this is **activation energy**. A reaction may have a negative ΔG value but requires a large activation energy that is not provided by the reaction conditions, therefore will not occur spontaneously.