

# AQA Chemistry A-level

## 3.1.8: Thermodynamics Detailed Notes

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### 3.1.8.1 - 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.

#### Lattice Enthalpies ( $\Delta_{\text{l}}H$ )

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 ( $\Delta_{\text{at}}H$ )

This is defined as:

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

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

This is defined as:

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



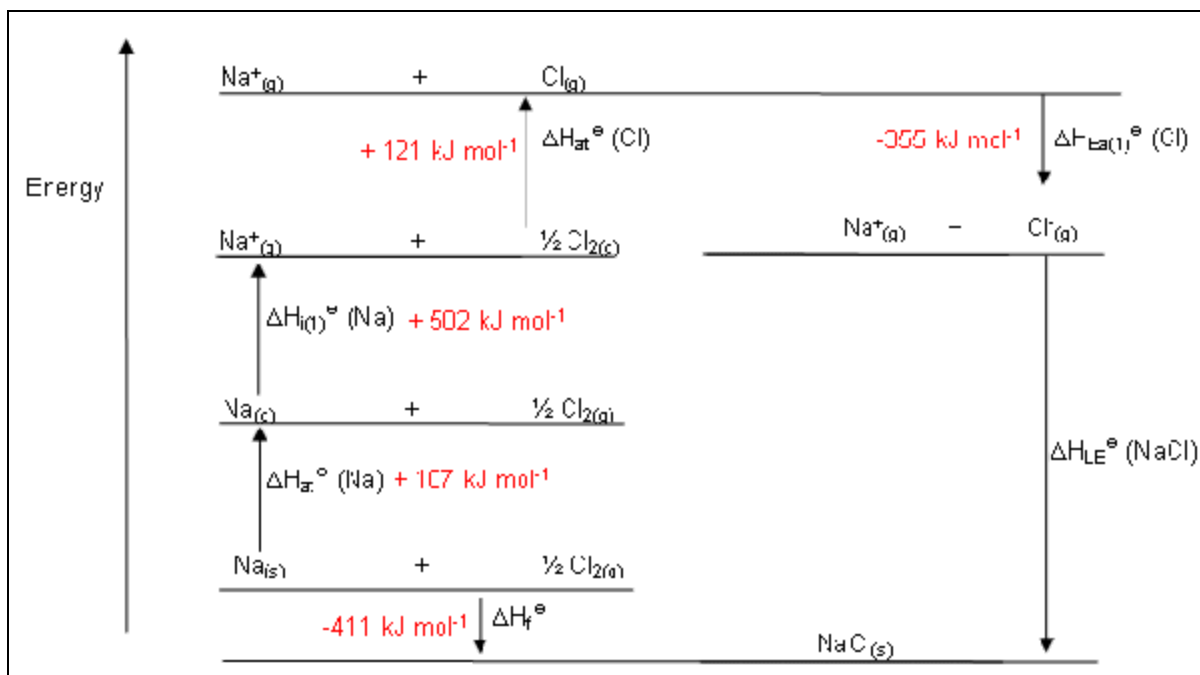


## Born-Haber Cycles

These 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**.

Image courtesy of Quora

Example:



*In this example,  $\Delta_f H$  of formation is calculated by following around the cycle, starting at the beginning of the arrow working round to the head of the arrow:*

$$\begin{aligned}\Delta H &= -355 - 121 - 502 - 107 - 411 \\ &= -786 \text{ kJ mol}^{-1}\end{aligned}$$

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

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:

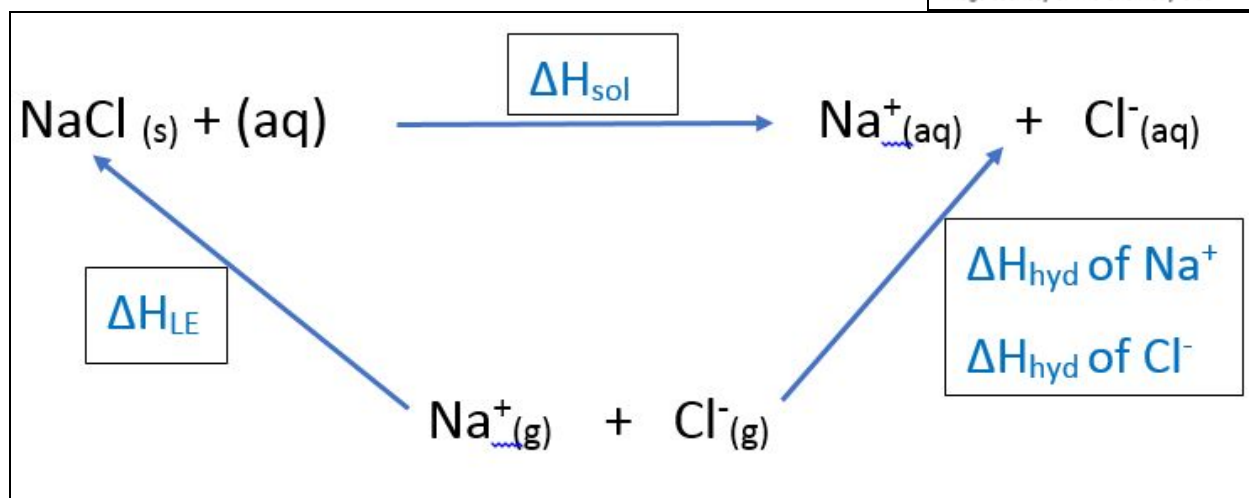
**The enthalpy change when one mole of gaseous ions is dissolved in water to form one mole of aqueous ions under standard conditions.**

It is nearly always negative as water has a  $\delta^+$  region that naturally attracts -ve ions.

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

Example:

Image courtesy of The Chemistry Club



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

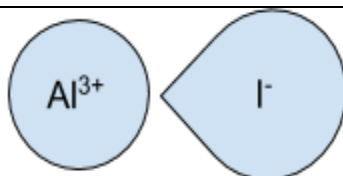
### Perfect Ionic Model

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**'.

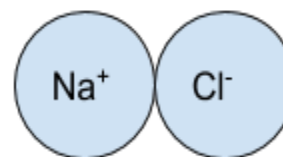
The perfect ionic model assumes that:

- 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**.



Ionic with covalent character



Perfectly ionic



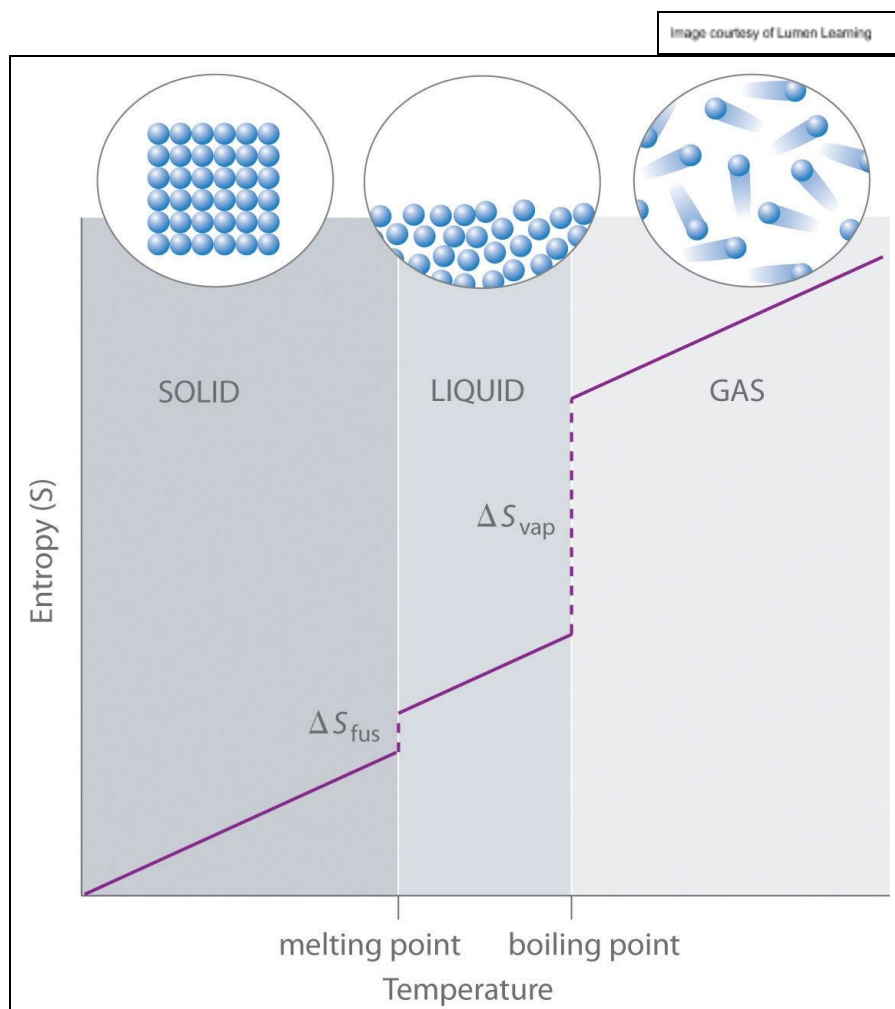


### 3.1.8.2 - Gibbs Free-Energy and Entropy

#### Entropy ( $\Delta S$ )

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

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



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.





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

$$\Delta S_{\text{total}} = \Delta S_{\text{products}} - \Delta S_{\text{reactants}}$$

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

### Gibbs Free-Energy ( $\Delta G$ )

This quantity allows  $\Delta S$  to be found without needing to measure the effects on the surroundings. It uses the **reaction temperature, enthalpy ( $\Delta H$ ) and entropy ( $\Delta S$ )** changes to determine a value for  $\Delta G$ :

$$\Delta G = \Delta H - T\Delta S$$

Free-energy is measured in  $\text{kJmol}^{-1}$  so it is important that  $\Delta H$  and  $\Delta S$  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  $\Delta G$  against  $\Delta S$ .

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

Image courtesy of SlidePlayer

$\Delta H$	$\Delta S$	As temp. increases...	Feasible?
positive	positive	makes $T\Delta S > \Delta H$	yes, above a certain temp.
negative	positive	makes $\Delta G$ more negative	always
positive	negative	no effect: $\Delta G$ always positive	never
negative	negative	unlikely to make $T\Delta S > \Delta H$	usually

