

# Edexcel IAL Chemistry A-level

## Topic 12: Entropy and Energetics

### Detailed notes

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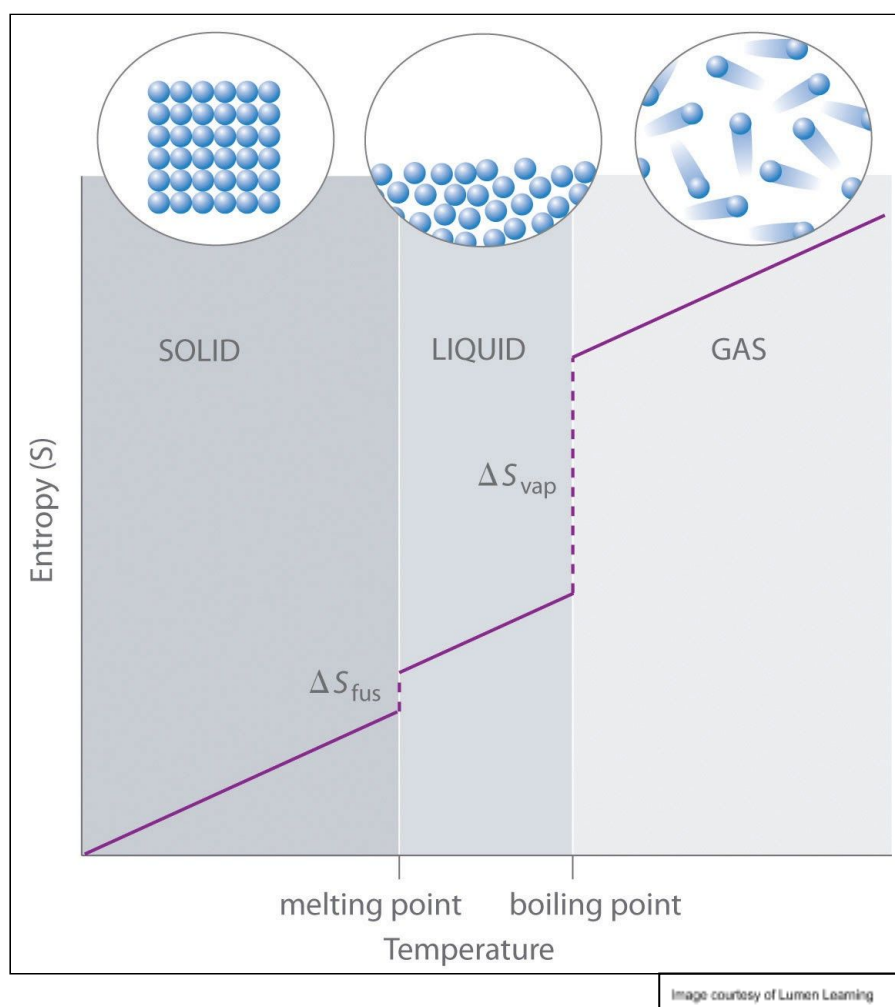
## Topic 12A: Entropy

### Entropy, $\Delta S$

Some **endothermic reactions** are able to occur **spontaneously** at room temperature. This shows how enthalpy is not the only driver of chemical reactions. **Entropy** is also key.

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

Since entropy of a substance increases with temperature, **gases** have the **greatest entropy** compared to solids and liquids. A **perfect crystal** at **absolute zero** (zero Kelvin) would have an entropy of zero, because there would be no movement, and therefore **no disorder**.



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** than reactants. In this case there is an **increase in disorder**.

When a **lattice** is **dissolved** in solution there is an increase in entropy. This is because the ions that make up the lattice are **dissociated** and can **move** in the solution, as opposed to being held in their position by strong bonds. This freedom of movement causes an **increase in disorder**.

The overall entropy change for a reaction can be calculated as follows. It is measured in **JK<sup>-1</sup>mol<sup>-1</sup>**:

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

The entropy of the surroundings is dependant on **enthalpy change** and **temperature**:

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

The entropy change for a reaction within a system can be calculated by finding the difference between the standard entropies of the **products** and the **reactants**:

$$\Delta S_{\text{system}} = \sum \Delta S_{\text{products}} - \sum \Delta S_{\text{reactants}}$$

If the entropy change for a reaction is **positive**, the products are **more disordered** than the reactants.

If the entropy change for a reaction is **negative**, the products are **less disordered** than the reactants.

The **natural direction of change** is towards a more disorderly state overall, which is a **positive change** in entropy. An example of this is the natural and spontaneous spreading of gas throughout a room, or the expansion of the universe.

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

Gibbs free-energy quantifies the balance between entropy and enthalpy in a system, acting as an **indicator of reaction feasibility**. It also allows  $\Delta S$  to be found without needing to measure the effects on the surroundings:

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



Free-energy is measured in  **$\text{kJ mol}^{-1}$**  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  $\Delta G$  (y axis) against  $T$  (x axis).

$\Delta G$  is **nonpositive for all spontaneous reactions**. The minimum temperature at which a reaction is spontaneous 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.

A reaction becomes feasible when  $\Delta G = 0$ .

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

$$0 = \Delta H - T\Delta S_{\text{system}}$$

Rearranging gives  $T\Delta S_{\text{system}} = \Delta H$

Therefore, the temperature at which the reaction becomes feasible:

$$T = \frac{\Delta H}{\Delta S_{\text{system}}}$$

Since  $\Delta G$  is dependent on both the enthalpy and the entropy, if the entropy change for a reaction is positive and large enough, a reaction with a positive  $\Delta H$  (**endothermic reaction**) could still have an overall **negative  $\Delta G$**  and occur **spontaneously**.

## Kinetics vs. Thermodynamics

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  $\Delta G$  value but require a large activation energy that is not provided by the reaction conditions. Therefore, this reaction will not occur spontaneously.

Alternatively, a reaction may be thermodynamically feasible but kinetic factors may lead it to occur at **such a slow rate** that, in practice, it does not appear to occur at all.



## Topic 12B: Lattice Energy

### Key Terms

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

Lattice enthalpies are used for **ionic substances**.

Lattice **dissociation** enthalpy is defined as:

**The enthalpy change when one mole of a solid ionic compound is completely dissociated into its gaseous constituent ions under standard conditions.**

This is an **endothermic process**.

Lattice **formation** enthalpy is defined as:

**The enthalpy change when one mole of a solid ionic compound is formed from its gaseous constituent ions under standard conditions.**

This is an **exothermic process**.

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

This is defined as:

**The energy required for the formation of one mole of gaseous atoms from an element 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 one mole of gaseous atoms to form one mole of gaseous 1- ions under standard conditions.**

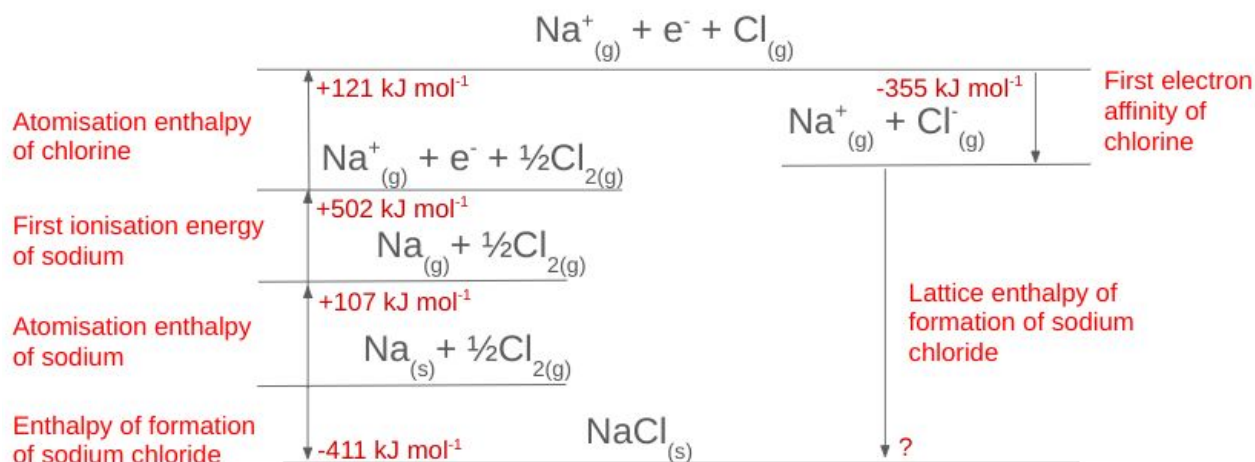
### Born-Haber Cycles

Born-Haber cycles are similar to the cycles used with Hess's Law. They allow **enthalpy changes** to be determined **indirectly**.

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:



In this example, lattice enthalpy of formation ( $\Delta_{\text{le}}H$ ) is calculated by following anticlockwise around the cycle:

$$\Delta_{\text{le}}H = [ -(-355) - (121) - (502) - 107 + (-411) ] = -786 \text{ kJ mol}^{-1}$$

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

### Perfect Ionic Model

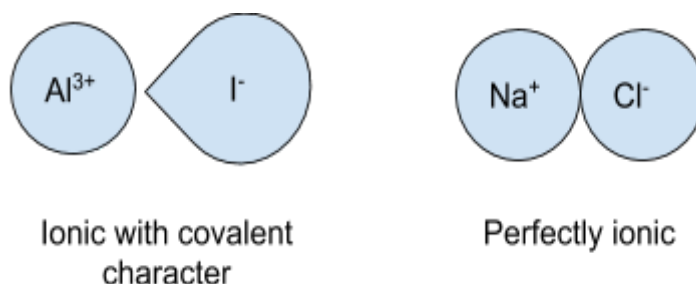
Hydration enthalpy is heavily influenced by the **size and charge** of the molecules being dissolved. Therefore it is often assumed that the ions are '**perfectly ionic**'.

The **perfect ionic model** assumes that:

- All the ions are **perfectly spherical**.
- **Charge** is distributed **evenly** throughout the ion.
- The ions display **no covalent character**.

Covalent character occurs in compounds when two bonded ions have **varying sizes or charges**, meaning the distribution of charge is **not even**. This **polarisation** of anions by cations creates **covalent character**.

Example:



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

Enthalpies of solution and hydration can be used as another means 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 solute is dissolved in water to infinite dilution so that the ions no longer interact under standard conditions.**

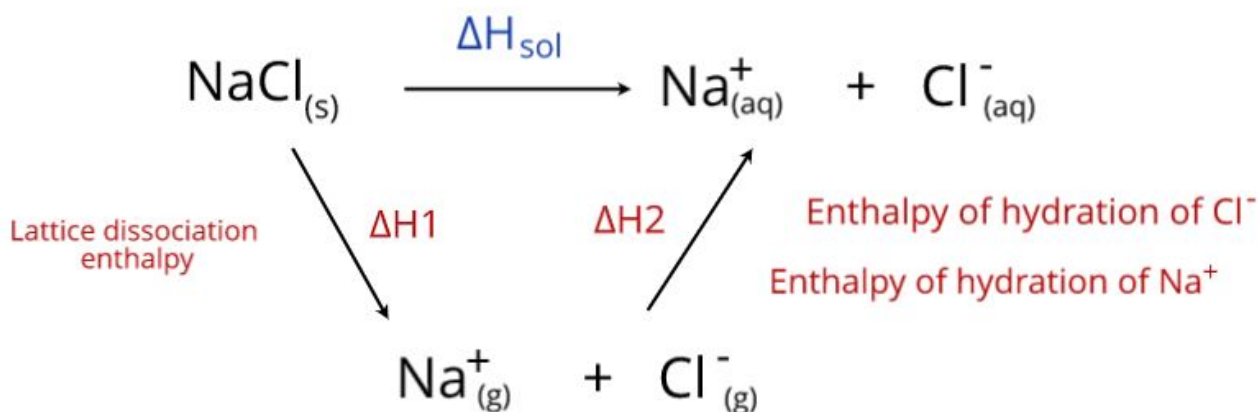
**Enthalpy of hydration** is defined as:

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

Enthalpy of hydration is nearly always **negative** as water molecules have  **$\delta^+$  regions** that naturally **attract** negative ions.

The enthalpy of solution and the enthalpy of hydration are combined in the following way to form an **energy cycle**.

*Example: Calculating the lattice dissociation enthalpy of sodium chloride*



$$\Delta H1 = \Delta H_{\text{sol}} - \Delta H2$$



## Factors affecting Enthalpy of Hydration and Lattice Enthalpy

Enthalpy of hydration is a measure of the attraction between ions (that were in a lattice) and water molecules in solution. **Positive ions** will be attracted to the  $\delta^-$  - **oxygen atoms**, and **negative ions** will be attracted to the  $\delta^+$  - **hydrogen atoms**.

Attractions are stronger with **smaller ions** and ions with a **greater charge**. This explains why hydration enthalpies **decrease** as you move **down a group** and why  $\text{Na}^+$  ions have a lower enthalpy of hydration than  $\text{Mg}^{2+}$  ions.

Lattice dissociation enthalpy also **increases** with **decreasing ionic radius** and **increasing charge**, again because the ions form **stronger attractions** and so the energy required for dissociation is greater.

Entropy, along with enthalpy changes of solution, can be used to **predict the solubility** of ionic compounds. Generally, the **less exothermic** (more endothermic) the enthalpy of solution, the **less soluble** the ionic compound is.

