Edexcel IAL Chemistry A-level

Topic 12: Entropy and Energetics

Detailed notes

Topic 12A: Entropy

Entropy, ∆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, **∆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**.

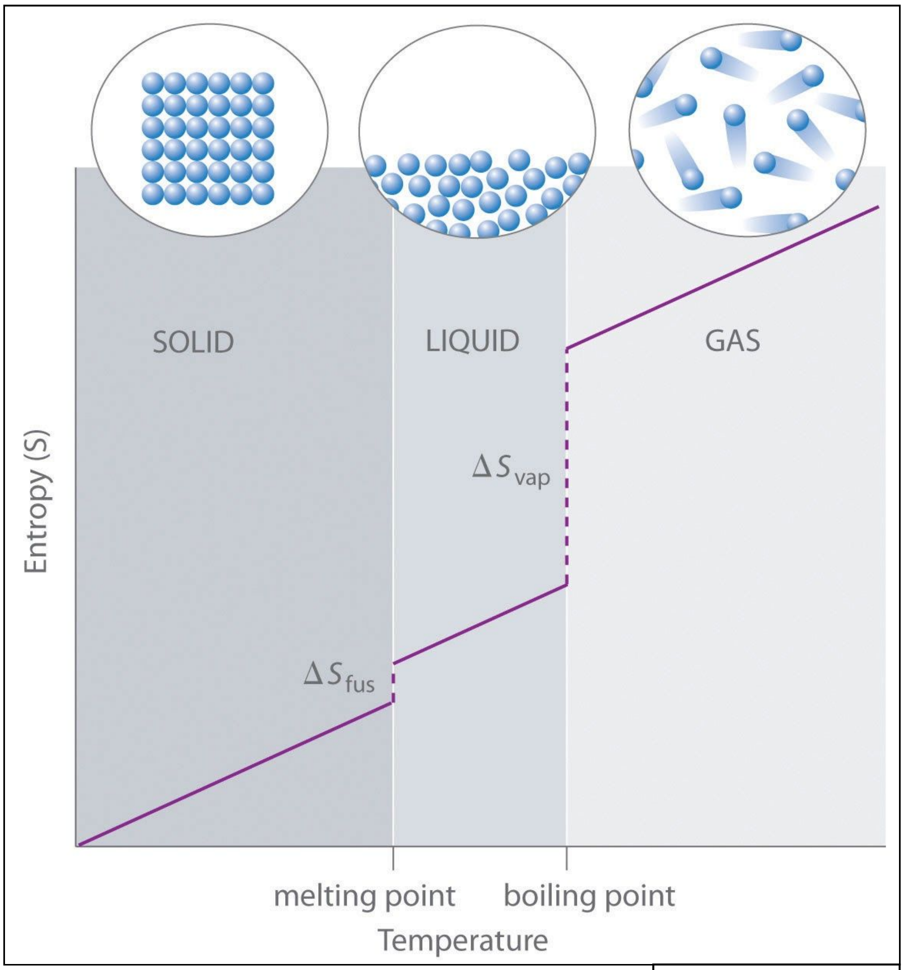


Image courtesy of Lumen Learning

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** 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 **$JK^{-1}mol^{-1}$**:

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

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

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

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**:

$$\boxed{\Delta S_{system} = \Sigma\Delta S_{products} - \Sigma\Delta S_{reactants}}$$

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 (ΔG)

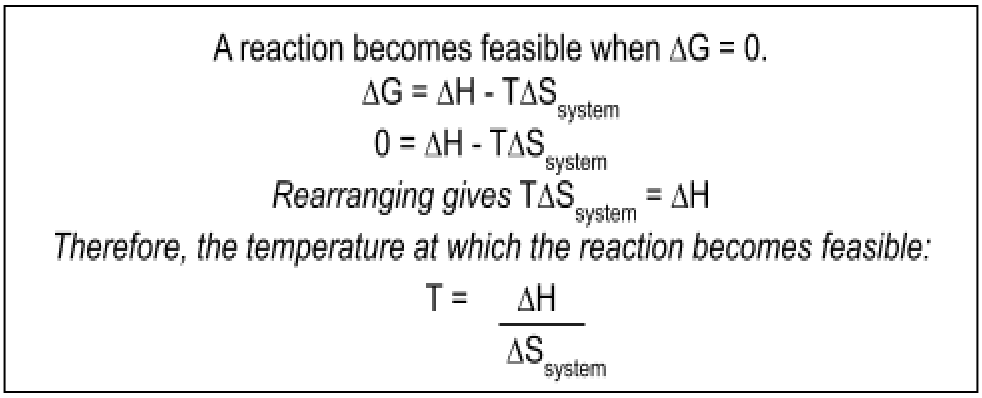
Gibbs free-energy quantifies the balance between entropy and enthalpy in a system, acting as an **indicator of reaction feasibility**. It also allows ΔS to be found without needing to measure the effects on the surroundings:

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

Free-energy is measured in **kJ mol^{-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 (y axis) against T (x axis).

ΔG is **nonpositive for all spontaneous reactions**. The minimum temperature at which a reaction is spontaneous 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 reaction becomes feasible when $\Delta G = 0$.

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

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

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

Therefore, the temperature at which the reaction becomes feasible:

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

Since ΔG 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 ΔH (**endothermic reaction**) could still have an overall **negative ΔG** 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 ΔG 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 ($\Delta_{le}H$)

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 ($\Delta_{at}H$)

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 ($\Delta_{ea}H$)

This is defined as:

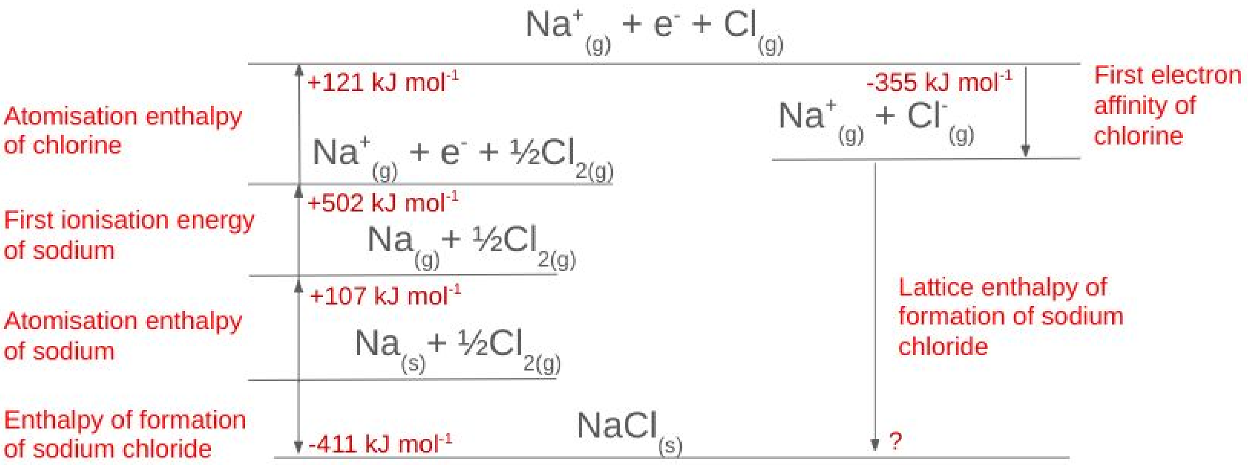
The enthalpy change when one mole of electrons is added to one mole of gaseous atoms to form one mole of gaseous 1- ions under standard conditions.

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 ($\Delta_{le}H$) is calculated by following anticlockwise around the cycle:

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

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

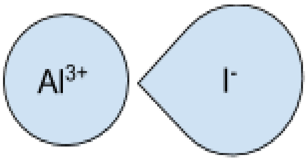
Hydration enthalpy is heavily influenced by the **size and charge** of the molecules being dissolved. Therefore it is often assumed that the ions are **'perfectly ionic'**.

The **perfect ionic model** assumes that:

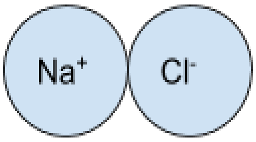
- All the ions are **perfectly spherical**.
- **Charge** is distributed **evenly** throughout the ion.
- The ions display **no covalent character**.

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:



Ionic with covalent character



Perfectly ionic

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

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.

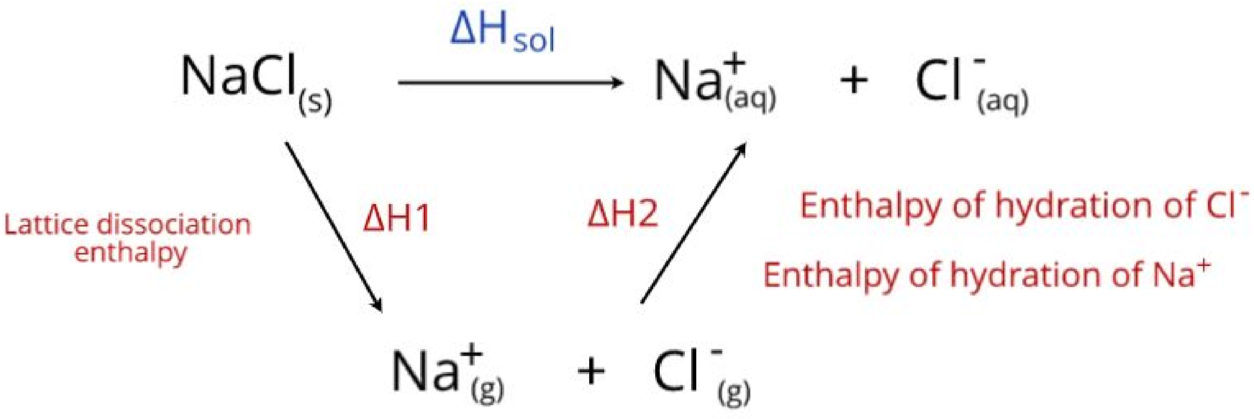
Enthalpy of hydration is defined as:

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 **∂+ 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



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

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 Na^+ ions have a lower enthalpy of hydration than 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.