

Edexcel Chemistry A-level

Topic 13: Energetics II

Detailed Notes

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Topic 13A: Lattice Energy

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

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

Lattice **dissociation** enthalpy is an **endothermic process** and 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.

Lattice **formation** enthalpy is an **exothermic process** and is defined as:

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

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

Atomisation enthalpy 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 ($\Delta_{\text{ea}}H$)

Enthalpy of electron affinity is defined as:

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

Born-Haber Cycles

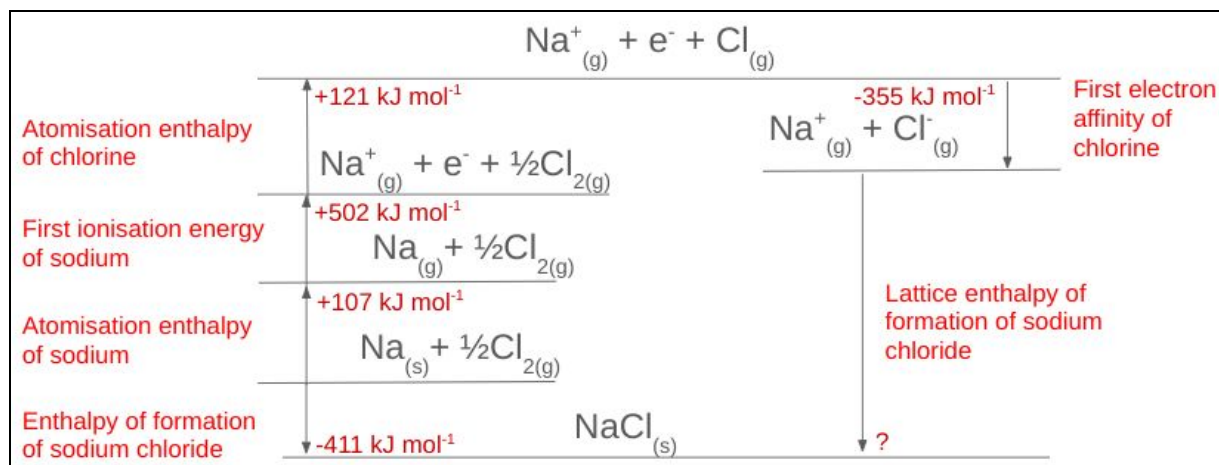
Born-Haber cycles are similar to the cycles used with Hess's Law. They allow **enthalpy changes** to be determined which cannot be measured directly.

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 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 ($\Delta_f H$) is calculated by following anticlockwise around the cycle: $\Delta_f H = [-(-355) - (121) - (502) - 107 + (-411)] = -786 \text{ kJ mol}^{-1}$

This cycle, derived from **empirical** data, will produce a different value for lattice enthalpy compared with the theoretical value predicted using **electrostatic theory**. This 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

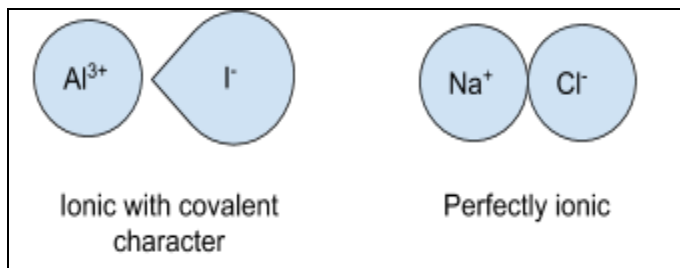
Hydration enthalpy is heavily influenced by the **size and charge** of the molecules being dissolved. Therefore, it is often assumed that the ions are '**perfectly ionic**'.

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 ions when two joined 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 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.

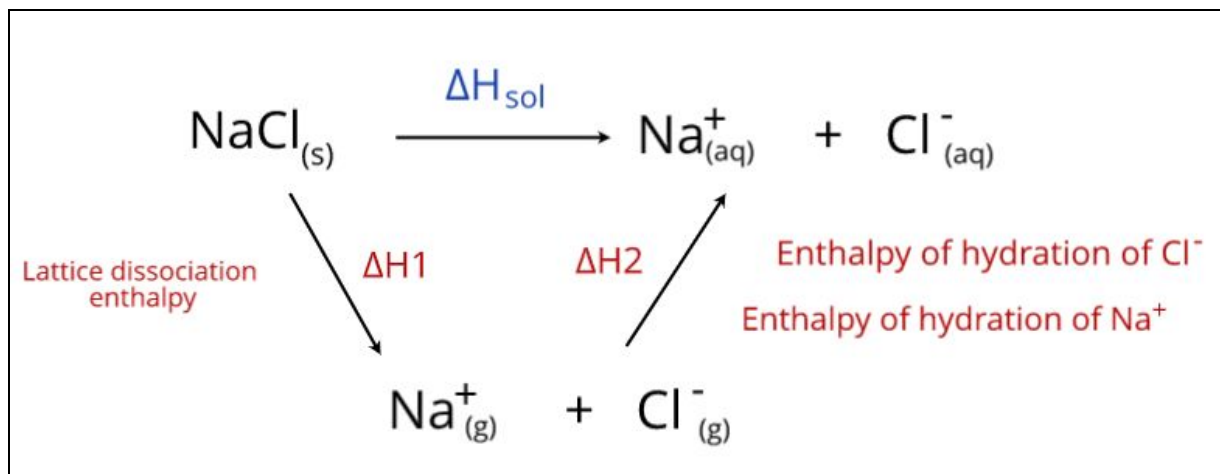
Enthalpy of **hydration** is defined as:

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

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 δ^- **oxygen atoms**, and **negative ions** will be attracted to the δ^+ **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.





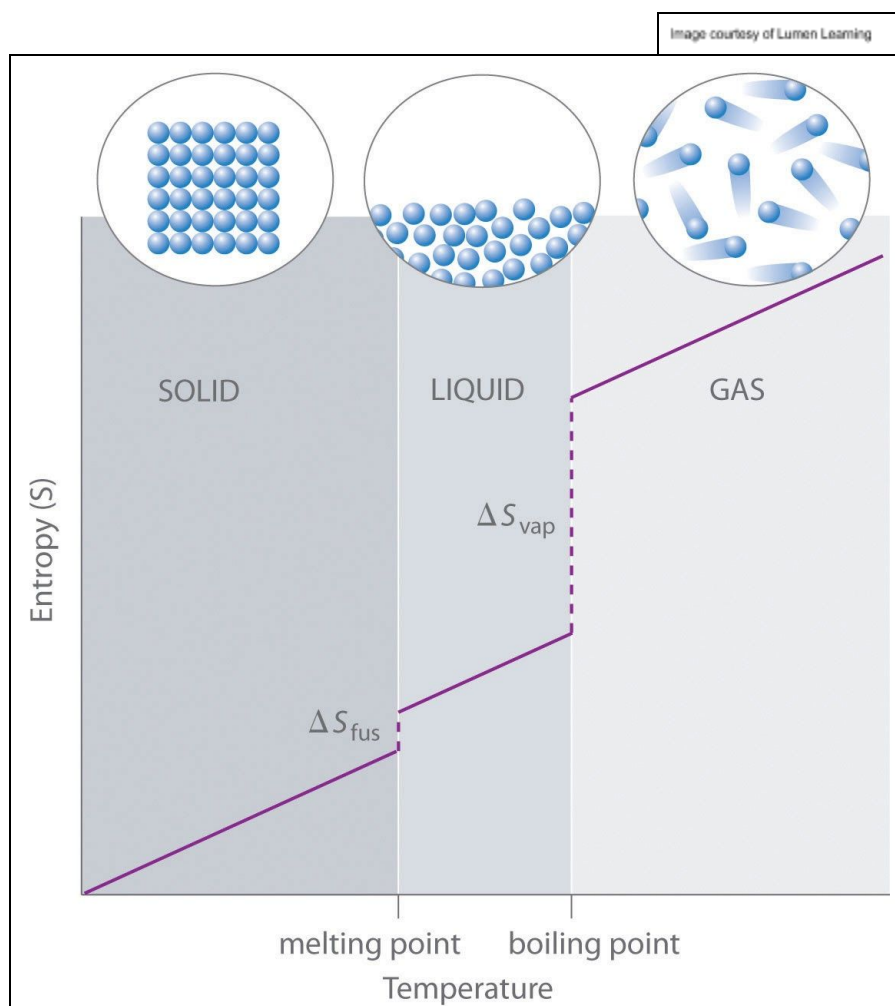
Topic 13B: Entropy

Entropy, ΔS

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, ΔS , is a **measure of this disorder**. The more disordered a substance, the greater its entropy value. **Entropy increases as temperature increases** because the particles **gain energy** and move **faster and further apart**, in other words, 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.





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 and it is measured in **$\text{JK}^{-1}\text{mol}^{-1}$** :

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

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 (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:

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

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 (y-axis) against T (x-axis).

ΔG is **less than or equal to zero 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 $\Delta G = 0$.

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

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

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

Therefore, the temperature at which the reaction becomes feasible:

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

Since 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**.

A second equation for ΔG can also be used, that relates it to the **equilibrium constant**:

$$\Delta G = -RT \ln(K)$$

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





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.

