

Chemical energetics (A Level)

A-Level Chemistry 9701 · Topic 23 revision notes

Everything from the 4 lessons of this topic on a few pages: the key idea of each lesson, the diagram to remember, the points to learn and the traps examiners set. Read it, cover it, test yourself.

1. Lattice energy and Born-Haber cycles

3. Entropy change

2. Enthalpies of solution and hydration

4. Gibbs free energy change

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1 Lattice energy and Born-Haber cycles

Syllabus 23.1

The **lattice energy** is the enthalpy change when 1 mol of an ionic compound is formed from its **gaseous ions** under standard conditions, e.g. $\text{Na}^+(\text{g}) + \text{Cl}^-(\text{g}) \rightarrow \text{NaCl}(\text{s})$; it is always **exothermic**. A **Born-Haber cycle** is a Hess cycle linking it to measurable steps: **enthalpy change of atomisation** of each element, **ionisation energies** of the metal, **electron affinities** of the non-metal and the **enthalpy change of formation**. For NaCl: $LE = -411 - (+107 + 496 + 122 - 349) = -787 \text{ kJ mol}^{-1}$. Lattice energy becomes more exothermic when the ions have **higher charge** and **smaller radius**, because the electrostatic attraction between them is stronger.

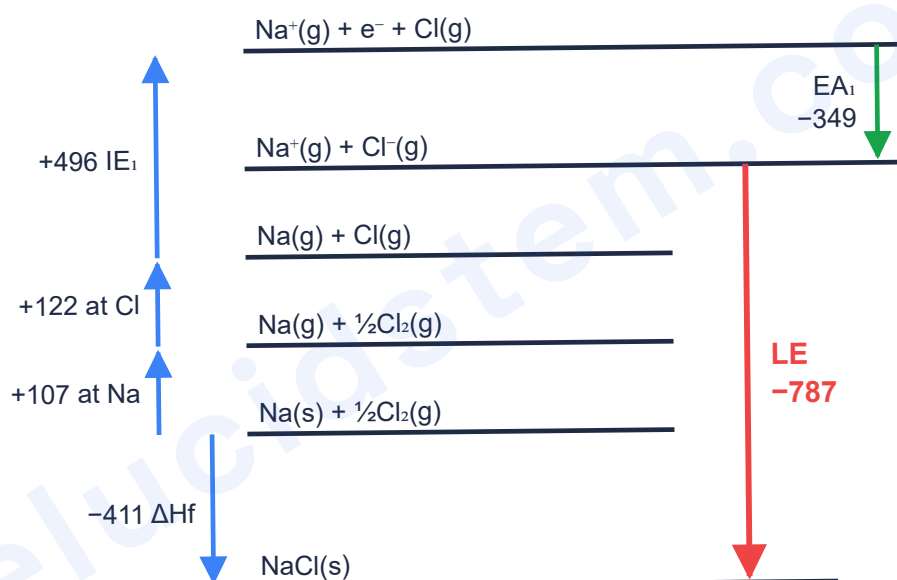


Fig. 1: Born-Haber cycle for sodium chloride (values in kJ mol^{-1} , not to scale)

Gaseous ions in, solid lattice out.

- ✓ **LE:** gaseous ions $\rightarrow$ 1 mol solid, always negative.
- ✓ **Atomisation of X_2 :** half the bond energy, per mole of atoms.
- ✓ **2+ ions:** $IE_1 + IE_2$; **2- ions:** $EA_1 + EA_2$ (EA_2 positive).
- ✓ **$LE = \Delta H_f - (\text{sum of the other steps})$.**

Watch out!

Lattice energy goes **from gaseous ions to the solid**, so it is **negative**; do not reverse it. Use $\frac{1}{2}$ the bond energy for the atomisation of Cl or O, and remember MgO needs **both** $IE_1 + IE_2$ and $EA_1 + EA_2$, with EA_2 **positive**. For $MgCl_2$, the chlorine steps are doubled.

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2 Enthalpies of solution and hydration

Syllabus 23.2

The **enthalpy change of hydration** is the enthalpy change when 1 mol of gaseous ions dissolves in water, e.g. $\text{Na}^+(\text{g}) \rightarrow \text{Na}^+(\text{aq})$; it is always **exothermic** because water dipoles are attracted to the ion. The **enthalpy change of solution** is the enthalpy change when 1 mol of an ionic solid dissolves in enough water to give an infinitely dilute solution, e.g. $\text{NaCl}(\text{s}) \rightarrow \text{Na}^+(\text{aq}) + \text{Cl}^-(\text{aq})$. A Hess cycle through the gaseous ions gives **$LE + \Delta H_{\text{sol}} = \Sigma \Delta H_{\text{hyd}}$** , so for NaCl $\Delta H_{\text{sol}} = (-406 - 377) - (-787) = +4 \text{ kJ mol}^{-1}$. Hydration is more exothermic for ions of **higher charge and smaller radius** (higher charge density).

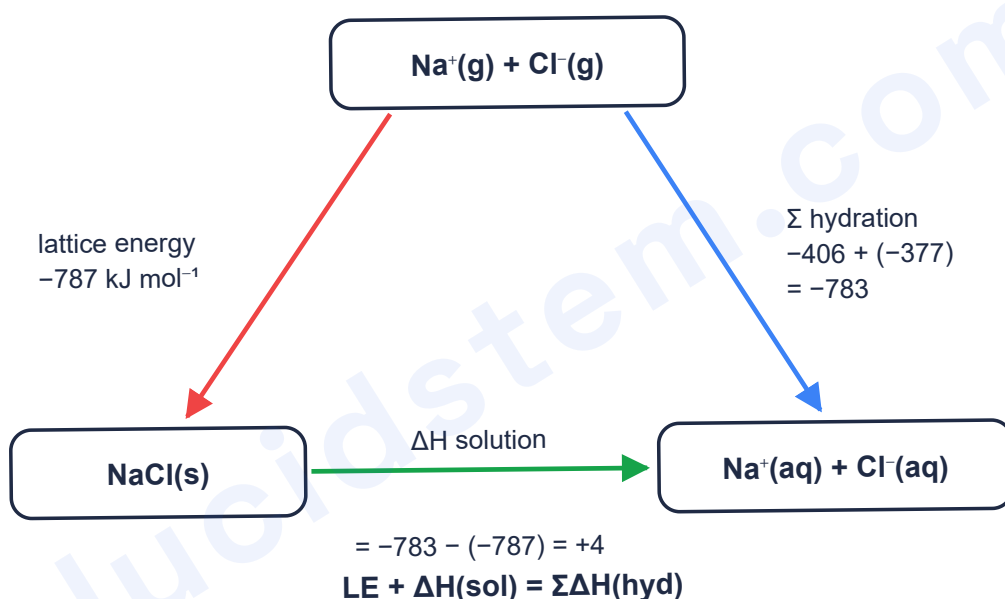


Fig. 1: energy cycle for dissolving sodium chloride (values in kJ mol⁻¹)

Lattice out, hydration in.

- ✓ **Hydration:** gaseous ion → aqueous ion, always negative.
- ✓ **Solution:** solid → aqueous ions, small, either sign.
- ✓ **$\Delta H_{\text{sol}} = \Sigma \Delta H_{\text{hyd}} - LE$** , counting every ion.
- ✓ **High charge density** (small, highly charged): more exothermic hydration.

Watch out!

Hydration starts from **gaseous** ions, not the solid. In the cycle, the solid goes to gaseous ions by the **reverse** of lattice energy, so $\Delta H_{\text{sol}} = \Sigma \Delta H_{\text{hyd}} - LE$; adding LE instead gives a hugely negative answer. Multiply each hydration enthalpy by the **number of ions** in the formula.

3 Entropy change

Syllabus 23.3

Entropy, S , is a measure of the **dispersal of energy** in a system: the more ways the particles and their energy can be arranged, the greater the entropy. Its units are **$\text{J K}^{-1} \text{mol}^{-1}$** , not kJ. Entropy increases from **solid to liquid to gas** (ice 48, water 70, steam 189), when temperature rises, when a solid dissolves, and when a reaction produces **more moles of gas**. A positive ΔS means energy becomes more dispersed. The standard entropy change of a reaction is **$\Delta S^\circ = \sum S^\circ(\text{products}) - \sum S^\circ(\text{reactants})$** , using the stoichiometric coefficients; for $\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2$ it is $40 + 214 - 93 = \textbf{+161 J K}^{-1} \text{mol}^{-1}$.

S of water rises as energy spreads out



entropy increases: solid < liquid < gas (units $\text{J K}^{-1} \text{mol}^{-1}$)

Fig. 1: standard entropies of water in its three states

Products minus reactants, in joules.

- ✓ **Solid < liquid < gas** for entropy.
- ✓ **More moles of gas:** ΔS positive.
- ✓ **$\Delta S^\circ = \sum S^\circ(\text{products}) - \sum S^\circ(\text{reactants})$** , times coefficients.
- ✓ **Units:** $\text{J K}^{-1} \text{mol}^{-1}$; elements are not zero.

Watch out!

Entropy values are in $\text{J K}^{-1} \text{mol}^{-1}$, not kJ. Elements do **not** have zero entropy, so O_2 , H_2 and N_2 must be included. Multiply by the **coefficients**, and always do **products minus reactants**. The state symbol matters: $\text{H}_2\text{O}(\text{l})$ is 70 but $\text{H}_2\text{O}(\text{g})$ is 189.

4 Gibbs free energy change

Syllabus 23.4

The **Gibbs free energy change** combines enthalpy and entropy: $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$, with T in kelvin. ΔH is in kJ mol^{-1} but ΔS is in $\text{J K}^{-1} \text{mol}^{-1}$, so **divide ΔS by 1000** first. A reaction is **feasible when $\Delta G \leq 0$** . When ΔH and ΔS have the same sign, temperature decides: the switch-over happens where $\Delta G = 0$, at **$T = \Delta H / \Delta S$** . For $\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2$ ($\Delta H +178 \text{ kJ mol}^{-1}$, $\Delta S +161 \text{ J K}^{-1} \text{mol}^{-1}$), $T = 178 / 0.161 = 1106 \text{ K}$. A feasible reaction may still be very slow if its **activation energy** is high.

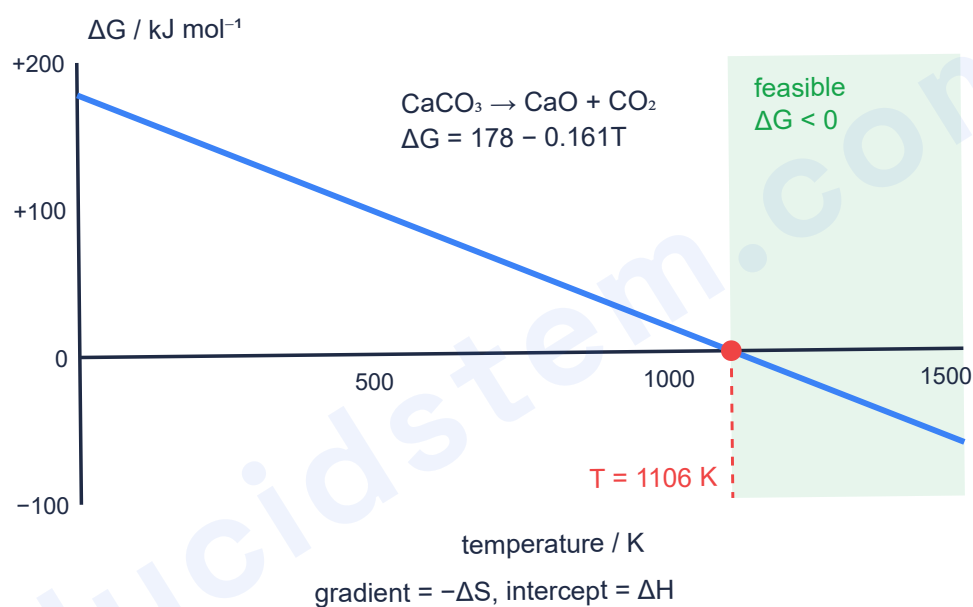


Fig. 1: ΔG against temperature for the decomposition of calcium carbonate

Convert, substitute, read the sign.

- ✓ $\Delta G = \Delta H - T\Delta S$, T in K.
- ✓ $\Delta S \div 1000$ to get $\text{kJ K}^{-1} \text{mol}^{-1}$.
- ✓ **Feasible** when $\Delta G \leq 0$.
- ✓ **Switch temperature:** $T = \Delta H / \Delta S$; say above or below.

Watch out!

The classic slip is forgetting to **divide ΔS by 1000**: $178 - 298 \times 161$ gives a nonsense $-47\,800 \text{ kJ mol}^{-1}$. Temperature must be in **kelvin**. $\Delta G \leq 0$ means **feasible**, not fast. When ΔH and ΔS have **the same sign**, always state whether the reaction is feasible **above** or **below** the calculated temperature.

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