Chemical energetics (A Level)

Lattice energy and Born–Haber cycles, electron affinity, enthalpies of solution and hydration, entropy, and Gibbs free energy and the feasibility of reactions.

23.1 Lattice energy and Born-Haber cycles

- **Enthalpy change of atomisation**, $\Delta H_{at}^{\ominus}$: the enthalpy change when **one mole of gaseous atoms** is formed from the element in its standard state. ΔH_{at} of Cl_2 is half the bond energy of Cl–Cl.
- **Lattice energy**, $\Delta H_{latt}^{\ominus}$: the enthalpy change when **one mole of a solid ionic compound is formed from its gaseous ions** (this definition gives a negative, exothermic value). The reverse (breaking up the lattice) is the same number with the opposite sign.
- **First electron affinity**, EA_1: the enthalpy change when one mole of electrons is added to one mole of gaseous atoms to form one mole of gaseous 1− ions, $X(g) + e^- \rightarrow X^-(g)$. It is exothermic for most non-metals. The **second** electron affinity (for $O^-(g) + e^- \rightarrow O^{2-}(g)$) is **endothermic** because the electron is added to an ion that already has a negative charge.

Electron affinity trends

Electron affinity depends on nuclear charge, atomic radius, shielding and electron repulsion. In **Group 17**, first electron affinity generally becomes **less exothermic from chlorine downwards** as the added electron is further from the nucleus and more shielded. Fluorine is an important exception: its first electron affinity is **less negative than chlorine's**, because adding an electron to its compact $2p$ sub-shell creates substantial repulsion. **Group 16** shows an analogous exception: oxygen's first electron affinity is less exothermic than sulfur's because its compact $2p$ sub-shell creates greater repulsion; from sulfur downwards values generally become less exothermic. Compare attraction and repulsion rather than applying a perfectly smooth trend.

Born–Haber cycle

A Born–Haber cycle applies Hess's law to the formation of an ionic solid. For $NaCl$:

$$\Delta H_f = \Delta H_{at}(Na) + IE_1(Na) + \Delta H_{at}(Cl) + EA_1(Cl) + \Delta H_{latt}$$

The cycle goes: elements in standard states → gaseous atoms (atomisation of each element) → gaseous ions (ionisation energies of the metal, electron affinities of the non-metal) → solid lattice (lattice energy), with the direct formation at the bottom. For $MgCl_2$ include **both** ionisation energies of Mg and $2\Delta H_{at}(Cl)$ and $2EA_1(Cl)$. Cycles are limited to +1 and +2 cations and −1 and −2 anions.

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Find the lattice energy of NaCl from: ΔH_f −411, ΔH_{at}(Na) +107, IE_1(Na) +496, ΔH_{at}(Cl) +122, EA_1 (Cl) −349 kJ mol^{-1}.

$\Delta H_{latt} = -411 - (107 + 496 + 122 - 349) = -411 - 376 = -787$ kJ mol^{-1}.

What affects the magnitude of lattice energy

The lattice energy is **more exothermic** with **higher ionic charges** and **smaller ionic radii**, because the electrostatic attraction between ions is greater. MgO (Mg^{2+}, O^{2-}) has a much more exothermic lattice energy than $NaCl$.

Drawing a complete Born–Haber route

Start with the balanced formation equation for **one mole of ionic solid**, including each element in its standard state. Then take the elements through gaseous atoms to gaseous ions before forming the lattice. Every intermediate state must contain the same total numbers of atoms as the formation equation. This prevents missing factors of two when a diatomic element or a 2+ ion is involved.

For MgO the route requires Mg atomisation, half an O_2 bond dissociation, both magnesium ionisation energies and both oxygen electron affinities. The second electron affinity is positive because the incoming electron is repelled by an already negative ion. A strongly exothermic lattice formation can still make the overall solid formation exothermic despite this unfavourable step.

Worked example — a 2+ cation: for illustrative $MgCl_2$ data, take $\Delta H_f = -642$, Mg atomisation +148, $IE_1 + IE_2 = +2189$, chlorine atomisation +121 per mole atoms, and chlorine electron affinity −349 kJ mol^{-1}. The non-lattice total is $148 + 2189 + 2(121) + 2(-349) = 1881$ kJ mol^{-1}. Therefore $\Delta H_{latt} = -642 - 1881 = \mathbf{-2523}$ kJ mol^{-1}. Both chlorine terms appear twice; the magnesium ionisation term already includes two electron removals.

When a value is missing, write the complete cycle equation before rearranging it. A negative lattice-formation enthalpy is not a mistake. Some sources instead define a positive lattice-**dissociation** enthalpy: read the stated definition and reverse the sign when necessary. Mixing the two conventions is a common source of an apparently plausible but incorrect answer.

Explaining lattice trends and electron affinity exceptions

For comparable lattices, greater ionic charge and shorter ion separation strengthen electrostatic attraction. Comparing MgO with NaCl changes both ion charges, whereas comparing NaF with NaI primarily changes anion radius. State which factor is being compared instead of relying on “more stable”. The electrostatic

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model treats ions as spherical charges; substantial polarisation can give bonding some covalent character and make a simple model less exact.

For electron affinity trends, distinguish **more negative** from numerically larger. A value of −350 kJ mol^{-1} is more exothermic than −300. Fluorine's compact 2p sub-shell creates greater repulsion for an added electron than chlorine's larger 3p sub-shell, so the simple down-group trend has an important exception. Similar competition between nuclear attraction and electron repulsion explains why a trend must be justified rather than assumed perfectly regular.

> **TRY IT**
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> Why is the second electron affinity of oxygen endothermic even though the oxygen nucleus attracts electrons?

Answer: The electron is added to $O^-(g)$, not a neutral atom. Work is required to overcome repulsion between the incoming electron and the negatively charged ion. The equation is $O^-(g) + e^- \rightarrow O^{2-}(g)$.

23.2 Enthalpies of solution and hydration

- **Enthalpy change of hydration**, $\Delta H^{\ominus}_{hyd}$: the enthalpy change when **one mole of gaseous ions** dissolves in water to form one mole of aqueous ions. Always exothermic.
- **Enthalpy change of solution**, $\Delta H^{\ominus}_{sol}$: the enthalpy change when **one mole of an ionic solid dissolves** in enough water that no further change occurs on adding more.

The energy cycle (with the lattice energy defined as forming the lattice from gaseous ions):

$$\Delta H_{sol} = -\Delta H_{latt} + \Delta H_{hyd}(\text{cation}) + \Delta H_{hyd}(\text{anion})$$

First break the lattice (endothermic, so the sign of the lattice energy is reversed), then hydrate the ions (exothermic). For $MgCl_2$ use $2\Delta H_{hyd}(Cl^-)$. If the hydration releases more energy than is needed to break the lattice, the dissolving is exothermic.

> **TRY IT**
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> $\Delta H_{latt}(NaCl) = -787$, $\Delta H_{hyd}(Na^+) = -406$, $\Delta H_{hyd}(Cl^-) = -364$ kJ mol^{-1}. Find ΔH_{sol}.

$\Delta H_{sol} = +787 - 406 - 364 = +17$ kJ mol^{-1} (slightly endothermic).

Hydration enthalpy is more exothermic for ions with a **higher charge** and a **smaller radius**: a greater charge density attracts water molecules more strongly. So Mg^{2+} is more exothermic than Na^+, and F^- than Cl^-.

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Applying the solution cycle consistently

Hydration involves ion–dipole attractions: oxygen ends of water point towards cations, while hydrogen ends orient towards anions. A high charge density strengthens these interactions and usually makes hydration more exothermic. Dissolution must also overcome the original lattice attractions. Consequently, strongly hydrated ions do not automatically imply a very soluble salt: the competing lattice contribution matters too.

Worked example: an illustrative MX_2 solid has lattice-formation enthalpy −2400 kJ mol^{-1}, cation hydration −1500 and anion hydration −420 kJ mol^{-1}. Then $\Delta H_{sol} = +2400 - 1500 - 2(420) = +60$ kJ mol^{-1}. Dissolution is endothermic by this calculation. Whether it is thermodynamically favourable also depends on entropy; a positive solution enthalpy does not prove that nothing dissolves.

If solution and lattice enthalpies are supplied, the same cycle can determine a missing hydration value. Include the number of **moles of each ion per formula unit**. State aqueous and gaseous species in definitions; hydrating one mole of gaseous ions is different from dissolving one mole of an ionic solid.

> **TRY IT**
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> For a 1 : 1 salt, lattice formation is −800 kJ mol^{-1} and hydration totals −825 kJ mol^{-1}. Find the solution enthalpy.

Answer: Reverse lattice formation to obtain +800, then add hydration: $+800 - 825 = \mathbf{-25}$ kJ mol^{-1}. The solution warms if this heat release is transferred to it under the experimental conditions.

23.3 Entropy change, ΔS

Entropy, S, is a measure of the number of possible arrangements of the particles and their energy in a given system, so of **disorder**. Its unit is J K^{-1} mol^{-1}, and the standard entropy $S^{\ominus}$ of any substance above 0 K is positive.

Predict the sign of ΔS:

- **Change of state:** melting, boiling and sublimation generally increase entropy; their reverses decrease it. Dissolving often increases dispersal, but the overall entropy change also depends on solvent ordering around ions, so it is not invariably positive. Gases generally have far more entropy than liquids, and liquids more than solids of the same substance.
- **Temperature increase** raises entropy (more energy states are accessible).
- **A reaction** with an **increase in the number of gas molecules** has a positive ΔS; a decrease gives a negative ΔS. For example $N_2 + 3H_2 \rightarrow 2NH_3$ has a negative ΔS.

$$\Delta S^{\ominus} = \sum S^{\ominus}(\text{products}) - \sum S^{\ominus}(\text{reactants})$$

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Calculating entropy with coefficients

Standard molar entropies are not defined as zero for elements in their standard states. That zero convention applies to **formation enthalpy**, not entropy. Multiply each entropy by its equation coefficient, total each side separately, and subtract reactants from products. The unit of molar entropy is J K^{-1} mol^{-1}.

Worked example: for an illustrative $A(g) + 2B(g) \rightarrow C(g)$ reaction, standard entropies are 190, 130 and 200 J K^{-1} mol^{-1} respectively. $\Delta S^{\ominus} = 200 - [190 + 2(130)] = -250$ J K^{-1} mol^{-1}. The negative result agrees with a decrease from three gaseous moles to one, though actual data are needed for a reliable magnitude.

A temperature increase allows more energy arrangements for a substance. A change in state increases or decreases available particle and energy arrangements. “Disorder” is a useful shorthand, but refer to dispersal and available arrangements when a memorised slogan does not explain the observation.

23.4 Gibbs free energy change, ΔG

$$\Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus}$$

Use consistent units: ΔH in kJ mol^{-1}, ΔS in J K^{-1} mol^{-1} (divide by 1000), and T in kelvin.

- A reaction is **feasible (spontaneous)** if ΔG is **negative**.
- A positive ΔH with a positive ΔS is feasible only **above** the temperature where $\Delta G = 0$, so $T = \Delta H/\Delta S$.
- Negative ΔH and positive ΔS: always feasible. Positive ΔH and negative ΔS: never feasible.

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$CaCO_3 \rightarrow CaO + CO_2$: $\Delta H = +178$ kJ mol^{-1}, $\Delta S = +161$ J K^{-1} mol^{-1}. At what temperature does it become feasible?

$T = 178\,000/161 = 1106$ K (about 833 °C).

A negative ΔG shows a reaction is feasible, but says nothing about its rate. A feasible reaction can be very slow because of a high activation energy.

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Feasibility across a temperature range

ΔH	ΔS	**Consequence for $\Delta G = \Delta H - T\Delta S$**
Negative	Positive	Negative at all positive temperatures within the model
Positive	Negative	Positive at all positive temperatures within the model
Positive	Positive	Favourable above a threshold temperature
Negative	Negative	Favourable below a threshold temperature

Worked example: $\Delta H^{\ominus} = -80.0$ kJ mol^{-1} and $\Delta S^{\ominus} = -200$ J K^{-1} mol^{-1}. At 298 K, $\Delta G^{\ominus} = -80.0 - 298(-0.200) = -20.4$ kJ mol^{-1}. Setting $\Delta G^{\ominus} = 0$ gives $T = (-80.0)/(-0.200) = 400$ K. It is favourable **below** 400 K, not above. Check the signs rather than memorising "high temperature makes reactions feasible".

These threshold calculations assume enthalpy and entropy are approximately constant over the range. They concern the stated conditions; $\Delta G^{\ominus}$ describes standard-state behaviour and should not be treated as a complete prediction of every non-standard mixture. A thermodynamic driving force does not remove an activation-energy barrier.

> **TRY IT**
>
> A reaction has $\Delta H = +40.0$ kJ mol^{-1} and $\Delta S = +100$ J K^{-1} mol^{-1}. Find ΔG at 300 K and the threshold temperature.

Answer: $\Delta G = 40.0 - 300(0.100) = +10.0$ kJ mol^{-1}. The threshold is 400 K; it becomes favourable above that temperature under the constant-data approximation.

Chapter check: show complete cycles, distinguish lattice formation from dissociation, and convert entropy to kJ K^{-1} mol^{-1} before combining it with kJ enthalpies. For another connection between free energy and driving force, see **electrochemistry**.

References and further reading

Scope follows section 23 of the **Cambridge 9701 syllabus for 2025–2027**. **Chemguide's Cambridge topic index** links to alternative explanations. The worked exercises and added diagrams are original teaching examples; numerical examples are illustrative unless a specific source is identified.

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