

Chemical Energetics

A-Level Chemistry ■ Topic 23

A-Level Chemistry



What we will cover

- 1 Lattice energy & Born–Haber
- 2 Enthalpies of solution
- 3 Entropy ΔS
- 4 Gibbs free energy ΔG





Lattice energy and Born–Haber

Lattice energy is the enthalpy change when 1 mol of an ionic solid forms from gaseous ions. It is always **exothermic**. A **Born–Haber cycle** - applies Hess's law around the formation of the solid: atomisation $\rightarrow$ ionisation $\rightarrow$ electron affinity $\rightarrow$ lattice energy, closing with ΔH_f .

More negative (stronger) for a **higher ionic charge** and a **smaller ionic radius**.

The enthalpy changes a Born-Haber cycle needs

enthalpy of atomisation

forming **one mole of gaseous atoms** from the element in its standard state

electron affinity

adding one mole of electrons to one mole of gaseous atoms

first EA

exothermic; the second is **endothermic**, because you push an electron onto an ion that is already negative

the trend

the same factors as ionisation energy – nuclear charge, radius, shielding. Down Group 16 or 17 the EA becomes **less exothermic**

enthalpy of hydration

one mole of gaseous ions dissolved in water – always exothermic

enthalpy of solution

$= -\text{lattice energy} + \text{the hydration enthalpies}$

By **Hess's law** the direct formation route equals the route up and round the cycle. Build the cycle first, then read the unknown off it.

The four definitions a Born–Haber cycle needs

Atomisation

Enthalpy change of atomisation ΔH_{at} : energy to make **one mole of gaseous atoms** from an element. Always **positive** – bonds must break.

Ionisation energy

Energy to remove one mole of electrons from one mole of gaseous atoms. Positive.

First electron affinity

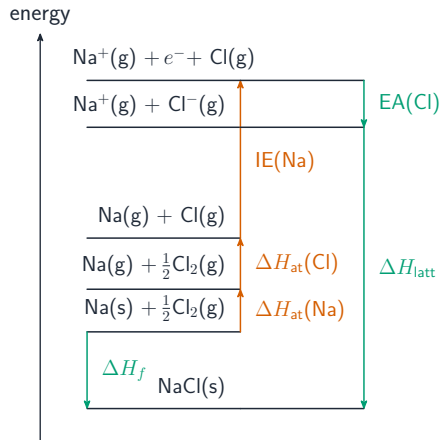
First electron affinity : the change when one mole of gaseous atoms each **gain** an electron to give 1– ions. Usually **negative**.

Lattice energy

The change when one mole of the ionic solid forms from its gaseous ions. Strongly negative – and the step the cycle usually asks you to find.

Every definition here says **one mole** and names the **state**. Marks are lost on those two words far more often than on the arithmetic.

Lattice energy and Born–Haber, in detail



A Born–Haber cycle for NaCl: going up costs energy (atomisation, ionisation); coming down releases

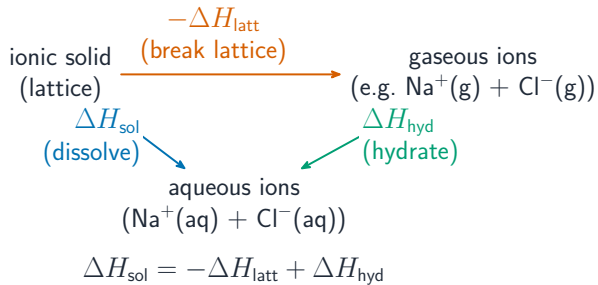
Lattice energy: worked example

NaCl from the cycle

$$\Delta H_{\text{latt}} = \Delta H_f - (\Delta H_{\text{at}} + \text{IE} + \text{EA}) = -411 - (107 + 122 + 496 - 349) = -787 \text{ kJ mol}^{-1}$$

Lattice energy is **more negative** (stronger) for a **higher ionic charge** and a **smaller ionic radius** – both strengthen the attraction.

Enthalpies of solution and hydration



To dissolve, pull the lattice apart, then **hydrate** the ions:

$$\Delta H_{\text{sol}} = -\Delta H_{\text{latt}} + \Delta H_{\text{hyd}}$$

Hydration is more exothermic for higher charge & smaller radius.

Dissolving, as a cycle of two competing steps

Enthalpy change of solution

Enthalpy change of solution ΔH_{sol} : the change when one mole of solute dissolves fully in water.

Enthalpy change of hydration

Enthalpy change of hydration ΔH_{hyd} : the change when one mole of *gaseous* ions is surrounded by water. Exothermic.

The competition

$\Delta H_{\text{sol}} = -\Delta H_{\text{latt}} + \sum \Delta H_{\text{hyd}}$: pulling the lattice apart costs, hydrating the ions pays.

Which wins

Both grow with charge density, so the sign of ΔH_{sol} is a small difference between two large numbers – which is why some salts dissolve endothermically.

Draw the triangle: solid $\rightarrow$ gaseous ions $\rightarrow$ aqueous ions, against solid $\rightarrow$ aqueous ions directly. Hess's law does the rest.



Entropy ΔS

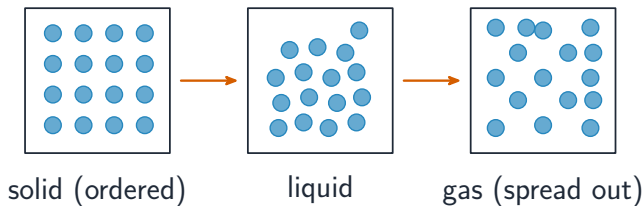
Entropy measures the number of arrangements (“disorder”).

■ solid $\rightarrow$ liquid $\rightarrow$ gas, dissolving: $\Delta S > 0$

■ more gas molecules: $\Delta S > 0$

$$\Delta S^{\ominus} = \sum S^{\ominus}_{\text{products}} - \sum S^{\ominus}_{\text{reactants}}.$$

entropy increases: $\Delta S > 0$



Calculating entropy change, and feasibility

from standard entropies

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

the units

$\text{J K}^{-1}\text{mol}^{-1}$ – joules, while ΔH is in kilojoules

the sign

predict it first from the change in moles of gas

Gibbs free energy

$$\Delta G = \Delta H - T\Delta S, \text{ with } T \text{ in kelvin}$$

feasible

when $\Delta G \leq 0$

the feasibility temperature

set $\Delta G = 0$: $T = \frac{\Delta H}{\Delta S}$ – the temperature at which it becomes possible

Convert ΔS from joules to kilojoules before substituting. That factor of 1000 is the single commonest error in this whole topic.

Gibbs free energy ΔG

	ΔS positive	ΔS negative
ΔH neg.	feasible at all temperatures	feasible only at low temperature
ΔH pos.	feasible only at high temperature	never feasible

$\Delta G = \Delta H - T\Delta S$; **feasible when $\Delta G \leq 0$**

Gibbs free energy :

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

A reaction is **feasible** when $\Delta G \leq 0$. Whether it is can depend on temperature.

ΔG : worked example

$$\Delta H = +120 \text{ kJ mol}^{-1}, \Delta S = +0.200 \text{ kJ K}^{-1}\text{mol}^{-1}$$

$$\text{at } 298 \text{ K: } \Delta G = 120 - 298 \times 0.200 = +60 \text{ kJ mol}^{-1} \text{ (not yet feasible)}$$

$$\text{Set } \Delta G = 0: T = \frac{\Delta H}{\Delta S} = \frac{120}{0.200} = 600 \text{ K} - \text{feasible above } 600 \text{ K.}$$

Enthalpies of solution and hydration, continued



An instant cold pack feels cold because its salt dissolves endothermically (a positive ΔH_{sol}), driven by the rise in entropy

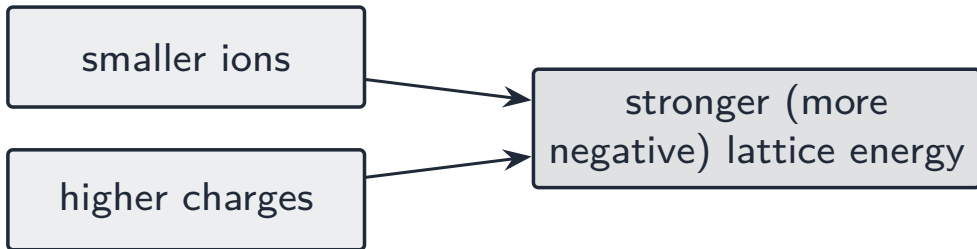
Electron affinity



energy released (usually)

A gaseous atom gains an electron, usually releasing energy

What controls the size of a lattice energy



Smaller ions and higher charges give a stronger lattice energy

Exam tips

- In a **Born-Haber cycle** get each step's direction and sign right (atomisation, ionisation +; electron affinity, lattice formation –) and apply Hess's law around it.
- **Lattice energy** is more exothermic for **smaller, more highly charged ions** (higher charge density).
- Predict the **sign of ΔS** from the state changes (more gas moles = more disorder).
- Use $\Delta G = \Delta H - T\Delta S$; feasible when $\Delta G \leq 0$ – convert ΔS from $\text{J K}^{-1} \text{mol}^{-1}$ ($\div 1000$).



Topic 23 – key takeaways

1

Born–Haber

Hess cycle to find lattice energy

2

Lattice

stronger for high charge, small radius

3

Entropy

$\Delta S > 0$ for more disorder/gas

4

Gibbs

feasible when $\Delta G = \Delta H - T\Delta S \leq 0$

Check yourself

- 1 Is lattice energy positive or negative?
- 2 What makes a lattice energy stronger?
- 3 Sign of ΔS when a gas forms?
- 4 A reaction is feasible when ΔG is what?



Answers 1. negative 2. higher charge & smaller radius 3. positive 4. negative (or zero)