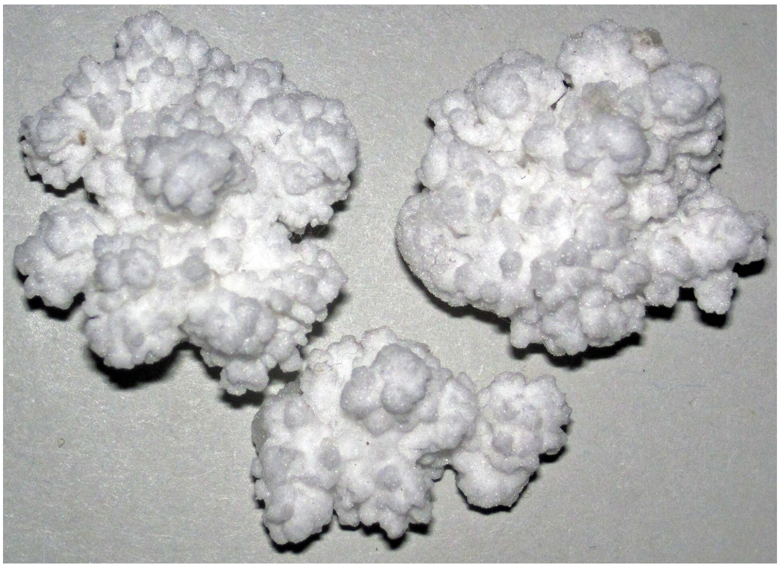
Chemical energetics

A-Level Chemistry

Lattice energy and Born–Haber cycles

These cycles use several **enthalpy changes** 焓变 (ΔH). Two new ones are:

- the **enthalpy change of atomisation** 原子化焓变, ΔH_{at} —the energy to make **one mole** of gaseous atoms from an element. It is always positive (bonds must break).
- the **lattice energy** 晶格能, ΔH_{latt} —the energy change when one mole of a solid ionic lattice forms from its gaseous ions. It is always negative (strong bonds form).



An ionic solid such as sodium chloride is a giant, regular lattice of ions —the lattice energy is released when it forms

Image: James St. John, CC BY 2.0 (commons.wikimedia.org)

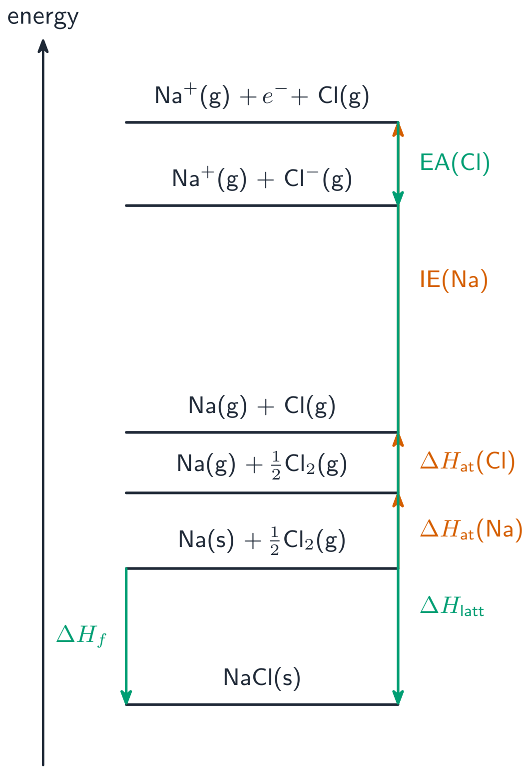
Electron affinity

The **first electron affinity** 电子亲和能 (EA) is the energy change when one mole of gaseous atoms each gain one electron to form one mole of $1-$ ions. The first EA is usually negative.

The same factors as ionisation energy apply (nuclear charge, atomic radius, shielding). Going down Group 16 or 17, the EA becomes **less** exothermic, because the atom is larger and pulls the extra electron in less strongly. (The very top element is an exception: its atom is so small that electron repulsion makes its EA less exothermic than the one below it.)

Born–Haber cycles

A **Born–Haber cycle** 玻恩哈伯循环 is an energy cycle that links the enthalpy change of formation of an ionic solid with its atomisation, ionisation energy, electron affinity and lattice energy. Using Hess's law, you go round the cycle to find any one unknown step. (You only need +1 and +2 cations and −1 and −2 anions.)



A Born–Haber cycle for NaCl: going up costs energy (atomisation, ionisation); coming down releases it (electron affinity, and the large lattice energy)

What controls the size of a lattice energy

The lattice energy is more negative (stronger) when:

- the **ionic charge** is higher (e.g. Mg^{2+} beats Na^+).
- the **ionic radius** is smaller.

Both make the attraction between the ions stronger.

Enthalpies of solution and hydration

- the **enthalpy change of hydration** 水合焓变, ΔH_{hyd} —the energy change when one mole of gaseous ions is surrounded by water to form aqueous ions. It is exothermic.
- the **enthalpy change of solution** 溶解焓变, ΔH_{sol} —the energy change when one mole of solute dissolves fully in water.

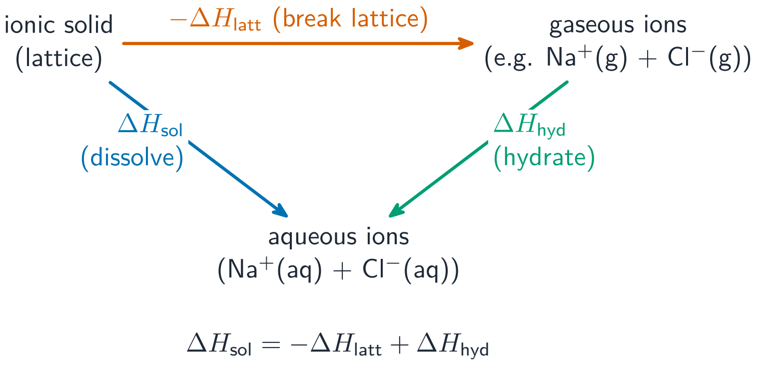
An instant cold pack feels cold because its salt dissolves endothermically (a positive ΔH_{sol}), driven by the rise in entropy

Image: photo: Qurren (talk) Taken with Canon PowerShot G9 X, CC BY-SA 4.0 (commons.wikimedia.org)

An energy cycle links the three:

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

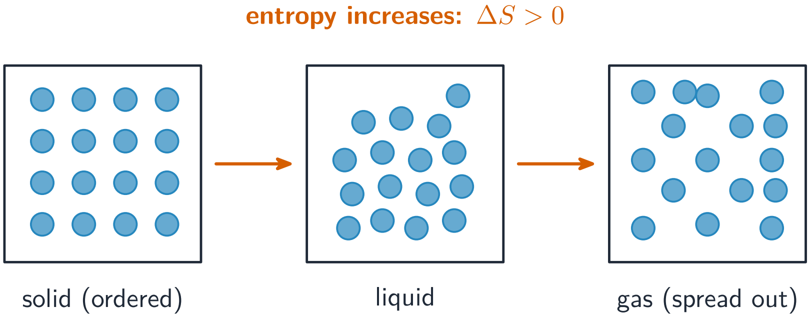
(To dissolve, you first pull the lattice apart, then hydrate the ions.) Like lattice energy, ΔH_{hyd} is more exothermic for ions with a higher charge and a smaller radius.



Dissolving energy cycle: pull the lattice apart (reverse lattice energy), then hydrate the gaseous ions, so $\Delta H_{sol} = -\Delta H_{latt} + \Delta H_{hyd}$

Entropy change, ΔS

Entropy 熵 (S) measures the number of ways the particles and their energy can be arranged in a system. More ways means more ”disorder”.



Entropy rises from solid to liquid to gas as the particles spread into more arrangements, so ΔS is positive

The **entropy change** 熵变 (ΔS) is **positive** when disorder increases, and **negative** when it falls:

Change	**Sign of ΔS**
solid → liquid → gas (melting, boiling), or dissolving	positive
a rise in temperature	positive
a reaction that makes **more** gas molecules	positive
a reaction that makes **fewer** gas molecules	negative

You can calculate it from standard entropies:

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

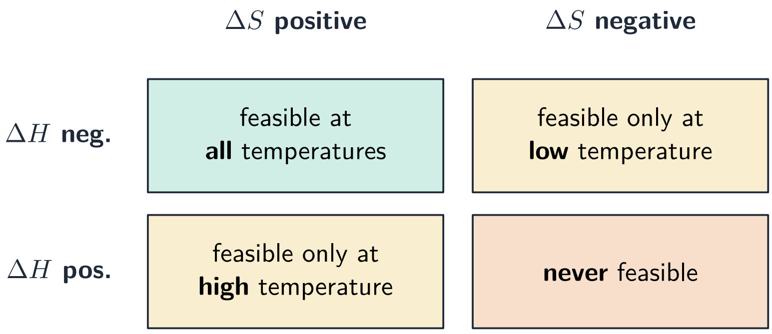
Gibbs free energy change, ΔG

The **Gibbs free energy** 吉布斯自由能 change decides whether a reaction can happen on its own:

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

Here T is the temperature in kelvin. A reaction is **feasible** (it can happen) when ΔG is negative or zero. The **feasibility** 可行性 therefore depends on temperature:

ΔH	ΔS	**When feasible**
negative	positive	at all temperatures
positive	positive	only at high temperature
negative	negative	only at low temperature
positive	negative	never



	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** $\Delta G \leq 0$

Whether a reaction is feasible ($\Delta G \leq 0$) depends on the signs of ΔH and ΔS, and sometimes on temperature

To find the changeover temperature, set $\Delta G = 0$, which gives $T = \Delta H/\Delta S$.