Lattice energy and Born-Haber cycles

Lattice energy, electron affinity, Born-Haber cycles and calculations, covalent character from experimental versus theoretical values, enthalpies of solution and hydration, and the solubility of ionic compounds.

Definitions

Term	Definition
Enthalpy of atomisation, $\Delta_{at}H$	The enthalpy change when one mole of gaseous atoms forms from an element in its standard state
First ionisation energy	Energy to remove one electron from each atom in one mole of gaseous atoms (endothermic)
First electron affinity	The enthalpy change when one mole of gaseous atoms gains one electron each, to form one mole of gaseous 1− ions (usually **exothermic**)
Second electron affinity	Gaining a second electron, by 1− ions to form 2− ions (**endothermic**, because of repulsion)
Lattice energy (formation), $\Delta_{LE}H$	The enthalpy change when **one mole of an ionic solid forms from its gaseous ions** (exothermic)

Lattice energy as defined here is **exothermic**. (Some books define it for the opposite process, breaking the lattice up, which is endothermic.)

Born–Haber cycles

A **Born–Haber cycle** is a Hess's law cycle for the formation of an ionic compound. For sodium chloride, $\Delta_f H$ is the sum of the steps:

1. Atomisation of sodium: $Na(s) \rightarrow Na(g)$
2. First ionisation of sodium: $Na(g) \rightarrow Na^+(g) + e^-$
3. Atomisation of chlorine: $\frac{1}{2}Cl_2(g) \rightarrow Cl(g)$
4. Electron affinity of chlorine: $Cl(g) + e^- \rightarrow Cl^-(g)$
5. Lattice energy: $Na^+(g) + Cl^-(g) \rightarrow NaCl(s)$

$$\Delta_f H = \Delta_{at}H(Na) + IE_1(Na) + \Delta_{at}H(Cl) + EA_1(Cl) + \Delta_{LE}H$$

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Find the lattice energy of NaCl: $\Delta_f H = -411$, $\Delta_{at}H(Na) = +107$, $IE_1(Na) = +496$, $\Delta_{at}H(Cl) = +122$, $EA_1(Cl) = -349$ kJ mol^{-1}.

$\Delta_{LE}H = -411 - (107 + 496 + 122 - 349) = -411 - 376 = -787$ kJ mol^{-1}.

For compounds like $MgCl_2$ include **two** atomisations of chlorine ($\Delta_{at}H \times 2$), the first **and second** ionisation energies of magnesium, and two electron affinities. For MgO or Na_2O use both electron affinities of oxygen.

NOTE

Draw the cycle with the elements at the bottom, the formation of the compound as a downward arrow, and the other steps as an upward path through gaseous atoms and gaseous ions. Check the state symbols, and multiply by the number of moles.

Experimental and theoretical lattice energies

- The **experimental** lattice energy comes from the Born–Haber cycle.
- The **theoretical** value is calculated from electrostatics, assuming a **perfectly ionic** model (spherical ions with their charge at the centre).

If the two values **agree**, the bonding is close to purely ionic. If the experimental value is **more exothermic** than the theoretical one, there is some **covalent** character, because covalent bonding adds extra attraction. This comes from **polarisation** of the anion by the cation: for example silver iodide has a greater difference than sodium chloride.

A larger difference between the experimental and theoretical lattice energy means a greater degree of covalent character. This is greatest for small, highly charged cations with large, polarisable anions.

Lattice energy trends

The magnitude of lattice energy is larger when:

- the ions have a **higher charge** (the force depends on the product of the charges, so MgO is much greater than $NaCl$), and
- the ions are **smaller** (their centres are closer).

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Enthalpies of solution and hydration

Term	Definition
Enthalpy of solution, $\Delta_{sol}H$	The enthalpy change when **one mole of an ionic solid dissolves in water** to form a solution of infinite dilution
Enthalpy of hydration, $\Delta_{hyd}H$	The enthalpy change when **one mole of gaseous ions** is dissolved in water (always exothermic)

An energy cycle links them:

$$\Delta_{sol}H = -\Delta_{LE}H + \sum \Delta_{hyd}H(\text{ions})$$

(using the lattice energy for forming the solid, so the lattice is broken by $-\Delta_{LE}H$).

> **TRY IT**
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> For $NaCl$: $\Delta_{LE}H = -787$, $\Delta_{hyd}H(Na^+) = -406$, $\Delta_{hyd}H(Cl^-) = -364$ kJ mol^{-1}. Find $\Delta_{sol}H$.

$\Delta_{sol}H = +787 + (-406) + (-364) = +17$ kJ mol^{-1}. It is slightly endothermic.

The enthalpy of hydration is more exothermic for ions with **higher charge** and **smaller radius** (higher charge density) because they attract the polar water molecules more strongly. Lattice energy depends on charge and radius in the same way.

Solubility

Whether a salt dissolves depends on ΔS_{total}, and so on both the enthalpy and entropy changes of solution, not on the enthalpy change alone. A compound can dissolve even when $\Delta_{sol}H$ is positive, if the entropy increase on dissolving is large enough.

Trends in Group 2 compounds can be explained in the same way:

- **Hydroxides** become **more soluble** down the group. The hydroxide ion is small, so the lattice energy depends strongly on the cation radius and falls in magnitude quickly as the cation gets bigger. The hydration enthalpy of the cation falls more slowly, so $\Delta_{sol}H$ becomes more favourable (less endothermic).
- **Sulfates** become **less soluble** down the group. The sulfate ion is large, so the lattice energy hardly changes with cation radius, while the hydration enthalpy of the cation falls markedly as the cation gets bigger. So $\Delta_{sol}H$ becomes less favourable.

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