

Group 2

A-Level Chemistry

Thermal stability of the nitrates and carbonates

The **thermal stability** 热稳定性 of the Group 2 **nitrates** 硝酸盐 and **carbonates** 碳酸盐 **increases** down the group. Here is the reason, in terms of how the ions affect each other.

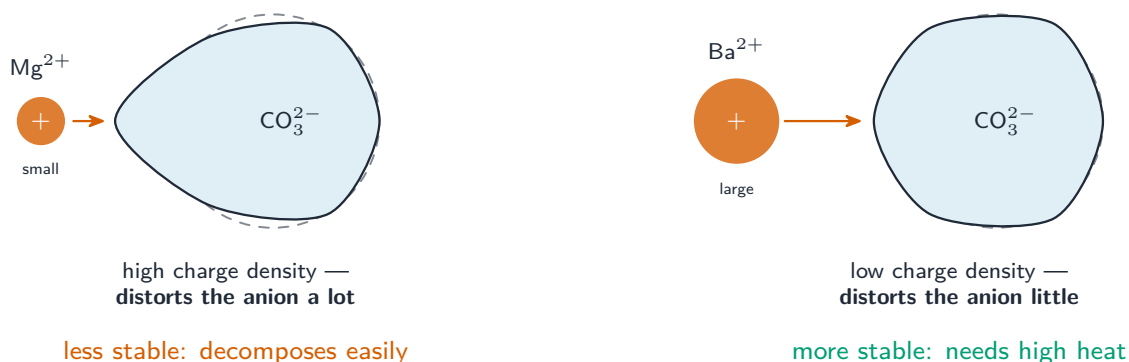


Heating limestone (calcium carbonate) in a kiln decomposes it to calcium oxide — a thermal decomposition

Image: Martinvl, CC BY-SA 4.0 (commons.wikimedia.org)

A small **cation** 阳离子 with a small **ionic radius** 离子半径 has a high charge density. It pulls on the electrons of the nearby anion and distorts its shape — this is **polarisation** 极化. Distorting the large **anion** 阴离子 (the carbonate or nitrate ion) weakens a bond inside it, so the compound breaks down more easily.

Going down the group, the cation gets larger. Its charge density drops, so it polarises the anion **less**. The anion is less distorted, so the compound is harder to break down — it is more thermally stable and needs a higher temperature to decompose.



A small cation has a high charge density, so it distorts (polarises) the large anion more —weakening it, so the compound is less stable

Worked example. Down Group 2 the **hydroxides** become **more** soluble while the **sulfates** become **less** soluble. Explain why the two trends run in opposite directions. Solubility is a contest between the **lattice energy** holding the solid together and the **hydration energy** rewarding the ions for dissolving. Both get less exothermic as the cation grows, so whichever falls **faster** decides the trend. With the **small** hydroxide ion, the lattice energy depends strongly on the cation's size, so it falls faster than the hydration energy: the lattice gets relatively easier to break and solubility **rises**. With the **large** sulfate ion, the lattice energy is already dominated by that big anion and barely changes down the group, while the cation's hydration energy still falls - so solubility **falls**. Name **both** energies and say which one falls faster; simply restating the trends earns no explanation marks.

Solubility of the hydroxides and sulfates

When an ionic solid dissolves, two energy changes compete. The **enthalpy change of solution** 溶解焓变 is the sum of them:

hydroxides
get *more* soluble
down the group

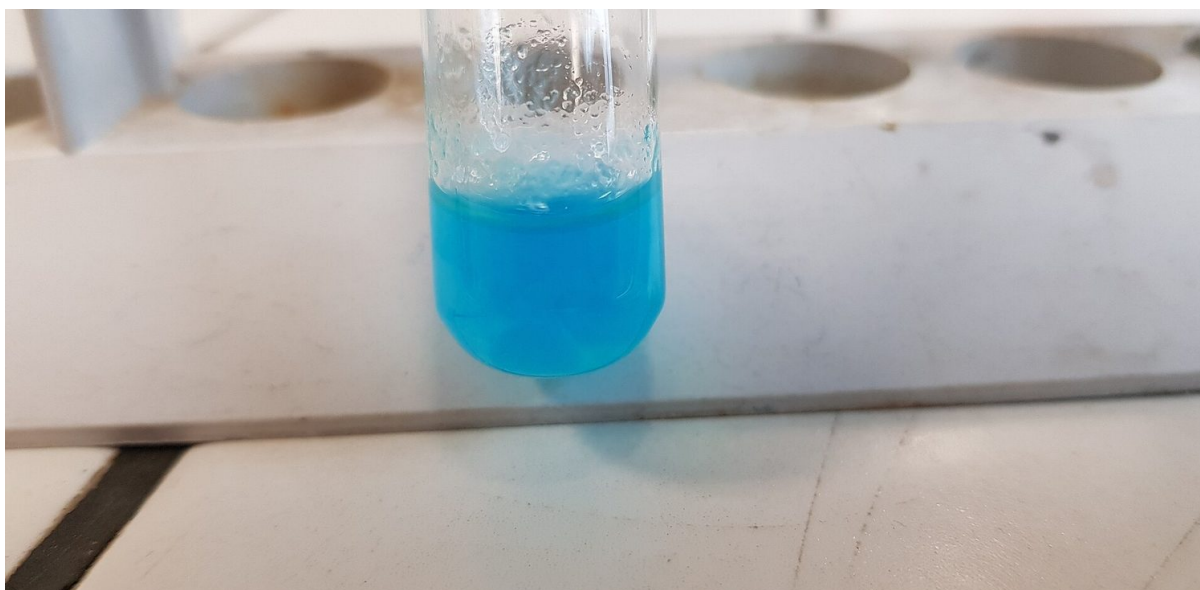
sulfates
get *less* soluble
down the group

Down Group 2 the hydroxides get more soluble but the sulfates less

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

- you must first pull the lattice apart (this needs the **lattice energy** 晶格能).
- then water surrounds the ions (this releases the **enthalpy change of hydration** 水合焓变).

If the energy released on hydration roughly matches (or beats) the energy needed to break the lattice, the solid dissolves easily.



An insoluble metal hydroxide forms as a gelatinous precipitate when its lattice energy is too large to be repaid by hydration

Image: Alvy16, CC BY 4.0 (commons.wikimedia.org)

Going down the group, both the lattice energy and the hydration enthalpy get **smaller** (less negative), because the cation is larger. But they shrink at different rates, and this explains the opposite trends:

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

hydroxides (small OH^-):
lattice energy falls *a lot* down the group
 $\Rightarrow$ outweighs the smaller hydration fall → more soluble

sulfates (large SO_4^{2-}):
lattice energy stays almost constant
 $\Rightarrow$ the hydration fall then dominates → less soluble

Why the trends are opposite: the small OH^- lattice energy falls a lot down the group (hydroxides dissolve more), but the large SO_4^{2-} lattice energy barely changes (sulfates dissolve less)

Compound	Trend in solubility 溶解度 down the group	Why
hydroxides 氢氧化物	increases	the OH^- ion is small, so the lattice energy falls a lot down the group; this change outweighs the fall in hydration energy
sulfates 硫酸盐	decreases	the SO_4^{2-} ion is large, so the lattice energy stays almost the same; the fall in hydration energy then dominates, so dissolving becomes less favourable

Exam tips

- Thermal stability of carbonates and nitrates **increases down** the group —larger cations polarise the anion less.
- Give the **decomposition products**: carbonates $\rightarrow$ oxide + CO_2 ; nitrates $\rightarrow$ oxide + NO_2 + O_2 (brown gas).

- Hydroxides get **more soluble** and sulfates **less soluble** down the group.
- Explain trends with **cation charge density (polarising power)**, not just size.