# Group 2 (A Level)

Explaining the thermal stability of Group 2 nitrates and carbonates by polarisation, and the trends in solubility and enthalpy of solution of the hydroxides and sulfates.

## 27.1 Similarities and trends in the properties of the Group 2 metals, magnesium to barium, and their compounds

### Thermal stability of carbonates and nitrates

Thermal stability **increases down the group**: $MgCO_3$ decomposes at a lower temperature than $BaCO_3$. The same is true of the nitrates, which give the metal oxide, brown $NO_2$ and oxygen.

**Explanation (polarisation):** the small $Mg^{2+}$ ion has a **high charge density** (charge divided by radius), so it **polarises** the large carbonate or nitrate anion, distorting its electron cloud towards the cation and weakening a C–O (or N–O) bond. Down the group the cation is **larger**, the charge density is lower, so the anion is **less polarised**, the bonds are stronger, and **more energy** is needed to decompose the compound.

> **Use the words charge density, polarise and distort the electron cloud of the anion. The ionic radius of the cation is what changes down the group; the anion is the same.**

Group 1 compounds are more stable than Group 2 for the same reason (a lower charge and a larger radius). Lithium's carbonate is the exception in Group 1, as $Li^+$ is small.

### Solubility and the enthalpy of solution

- **Hydroxides:** solubility **increases** down the group.
- **Sulfates:** solubility **decreases** down the group.

These trends can be explained using the enthalpy cycle for $\Delta H_{sol}$:

$$\Delta H_{sol} = -\Delta H_{latt} + \Delta H_{hyd}(M^{2+}) + \Delta H_{hyd}(\text{anion})$$

Both the **lattice energy** and the **hydration enthalpy of** $M^{2+}$ become less exothermic down the group, because the cation gets larger. What matters is **which decreases faster**.

- **Hydroxides** ($OH^-$ is small): the lattice energy is affected a lot by the size of the cation, since the anion is so small, so the **lattice energy falls faster** than the hydration enthalpy, and $\Delta H_{sol}$ becomes **more negative (more favourable)** down the group, so solubility increases.

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- **Sulfates** ($SO_4^{2-}$ is large): the lattice energy hardly changes with the size of the cation, since the large anion dominates the distance, so the **hydration enthalpy falls faster** than the lattice energy, and $\Delta H_{sol}$ becomes **less negative (more positive)** down the group, so solubility decreases.

Solubility also depends on entropy, but the trend in $\Delta H_{sol}$ is the explanation required.

> **TRY IT**
>
> Why is $BaSO_4$ much less soluble than $MgSO_4$?

The hydration enthalpy of the small $Mg^{2+}$ is very exothermic and offsets the lattice energy, so $MgSO_4$ dissolves. For $Ba^{2+}$ the hydration enthalpy is far smaller, but the lattice energy stays about the same, so the dissolving is much less favourable and $BaSO_4$ is insoluble.

## Polarisation is distortion of the anion

Charge density is a measure of charge concentrated into a given ionic size, not a literal universal formula of charge divided by radius. For ions with the same 2+ charge, the smaller ion has the stronger electric field near its surface and greater polarising power. It distorts the carbonate or nitrate electron cloud more strongly, making decomposition to oxide and gas easier.

The anion is the same in a comparison down one series. Do not explain a magnesium-to-barium carbonate trend by saying that carbonate becomes larger: the important changing species is the **cation**. Also distinguish polarising power of a cation from polarizability of an anion. A large, diffuse anion is more readily distorted, whereas a small high-charge cation is better at causing the distortion.

**Worked explanation:** $Mg^{2+}$ is smaller than $Ba^{2+}$ and has the same charge. It more strongly polarises $CO_3^{2-}$, weakening the anion's bonding and favouring decomposition to MgO and $CO_2$ at a lower temperature. For barium carbonate, weaker polarisation means a higher temperature is needed. The argument does not require carbonate to be free in the gas phase.

> **TRY IT**
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> A student says barium carbonate is more thermally stable because barium's larger nucleus attracts carbonate more strongly. Correct the argument.

**Answer:** The larger ionic radius of $Ba^{2+}$ lowers its charge density and polarising power despite the increased proton number. The carbonate electron cloud is less distorted, so thermal decomposition is harder.

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## Decomposition equations and quantitative evidence

For Group 2 carbonates, $MCO_3 \rightarrow MO + CO_2$. For nitrates, $2M(NO_3)_2 \rightarrow 2MO + 4NO_2 + O_2$. Loss of mass in an open container reflects the gaseous products leaving, not disappearance of matter. A thermal-stability experiment compares onset or extent of decomposition under controlled heating; particle size, sample amount and heating rate can affect observations.

**Worked example:** 0.0100 mol of a Group 2 nitrate gives 0.0100 mol oxide, 0.0200 mol nitrogen dioxide and 0.00500 mol oxygen. The total gas amount is 0.0250 mol. By contrast, 0.0100 mol carbonate produces only 0.0100 mol gas. A comparison of gas volumes must account for these different stoichiometries rather than assuming more gas means less stable material.

> **TRY IT**
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> Why should equal masses of different Group 2 carbonates not automatically be expected to give equal total carbon dioxide volumes on complete decomposition?

**Answer:** Their molar masses differ, so equal masses contain different numbers of moles. Each mole carbonate gives one mole $CO_2$; compare equal amounts in moles or correct for the amounts used.

## Competing lattice and hydration changes

Dissolution separates lattice ions, costing energy, then hydrates them, releasing energy. Moving down Group 2 makes the cation larger. Its attractions to anions in the solid and to water molecules both weaken. It is insufficient to mention only the increasingly easy lattice breakup: loss of hydration energy can outweigh that benefit.

For hydroxides, the increase in cation size changes separation between the cation and relatively small hydroxide ions significantly. The reduction in lattice-dissociation cost can outweigh the reduction in hydration benefit. For sulfates, the large anion already dominates the interionic separation, so changing cation size has a smaller relative lattice effect; the reduced hydration benefit is more important. This provides the syllabus-level energetic account of the opposing trends, while entropy is also relevant to full solubility thermodynamics.

## A numerical cycle as a reasoning exercise

**Worked example:** consider illustrative 1 : 1 salts with the same anion. Salt A needs +2000 kJ mol$^{-1}$ to separate its lattice and releases −2050 kJ mol$^{-1}$ on total hydration, giving $\Delta H_{sol} = -50$. Salt B needs +1900 and releases −1850, giving $\Delta H_{sol} = +50$. Although B's lattice is easier to break, its hydration loses more benefit than the lattice step saves. Looking at lattice energy alone would predict the wrong energetic direction.

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For an actual Group 2 hydroxide, include **two** hydroxide hydration terms in the cycle. For a sulfate, there is one sulfate per cation. When a source uses a negative lattice-formation enthalpy, reverse it before adding hydration. "Lattice energy falls" can be ambiguous: specify **smaller magnitude** or **less exothermic** for formation, or a reduced positive dissociation cost.

> **TRY IT**
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> A hydroxide has lattice formation −2500 kJ mol$^{-1}$, cation hydration −1700, and hydroxide hydration −450 per mole. Find its solution enthalpy.

**Answer:** $\Delta H_{sol} = +2500 - 1700 - 2(450) = \mathbf{-100}$ kJ mol$^{-1}$. Using only one hydroxide term would not represent one mole of $M(OH)_2$.

## Solubility, pH and experimental conclusions

A saturated solution of the more soluble Group 2 hydroxide generally contains more hydroxide ions, so has higher pH at the same temperature. Compare saturated solutions when using this trend: two deliberately prepared equal-concentration solutions do not automatically have different pH solely because their salts have different maximum solubilities.

The sulfate trend explains why barium salts precipitate sulfate efficiently. However, "insoluble" in qualitative chemistry means **very sparingly soluble**, not exactly zero dissolved ions. A solubility-product calculation can quantify the remaining concentrations. Solubility depends on temperature and any common ions already present, so those conditions must be held constant in comparisons.

> **TRY IT**
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> Does a positive enthalpy of solution prove that a salt cannot dissolve?

**Answer:** No. Entropy also contributes through $\Delta G = \Delta H - T\Delta S$. An endothermic dissolution can still be favourable if the entropy contribution is sufficient. Use the enthalpy trend as part of the explanation, not a universal yes/no solubility rule.

**Chapter check:** distinguish cation polarising power from anion polarizability, write the correct decomposition stoichiometry, and compare both lattice and hydration contributions. Review **energy cycles** and **solubility equilibria** for the quantitative links.

### References and further reading

Scope follows section 27 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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