23.2 Enthalpy of Solution and Hydration

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🎯 Learning outcomes

Candidates should be able to:

1. Define and use the term enthalpy change with reference to hydration, ΔH_{hyd}, and solution, ΔH_{sol}
2. Construct and use an energy cycle involving the enthalpy change of solution, lattice energy, and enthalpy change of hydration
3. Carry out calculations involving the energy cycles in 23.2
4. Explain, in qualitative terms, the effect of ionic charge and of ionic radius on the numerical magnitude of an enthalpy change of hydration
5. Describe and explain qualitatively the variation in solubility and the enthalpy change of solution, $\Delta H_{\ominus sol}$, of the hydroxides and sulfates of group 2 metals in terms of the relative magnitudes of the enthalpy change of hydration and the lattice energy qualitatively

When an ionic solid dissolves in water, it undergoes a fascinating energetic transformation. This process boils down to two main competing forces: breaking an ionic lattice apart and bonding the free ions to polar water molecules.

Enthalpy Change of Hydration

The **energy released when gaseous ions dissolve in water** is called the **standard enthalpy change of hydration**.

The enthalpy change of hydration, $\Delta H^{\ominus}_{hyd}$, is the enthalpy change when 1 mole of a specified gaseous ion dissolves in sufficient water to form a very dilute solution.

The enthalpy changes of hydration for calcium ions and chloride ions are described by the equations below:

$Ca^{2+}(g) + aq. \rightarrow Ca^{2+}(aq.)\ \Delta H^{\ominus}_{hyd} = -1650\ kJ\ mol^{-1}$

$Cl^{-}(g) + aq. \rightarrow Cl^{-}(aq.)\ \Delta H^{\ominus}_{hyd} = -364\ kJ\ mol^{-1}$

✓ Exam Tip

The word "gaseous" is essential in your definition. The ion must start as a *gaseous* ion. Many students lose marks by writing "ions dissolve in water" without specifying gaseous.

Enthalpy Change of Solution

The standard enthalpy change of solution, $\Delta H^{\ominus}_{sol}$, is the **energy absorbed or released when 1 mole of an ionic solid dissolves in sufficient water** to form a very dilute solution.

The enthalpy changes of solution for magnesium chloride and sodium chloride are described by the equations below:

$MgCl_2(s) + aq \rightarrow MgCl_2(aq);\ \Delta H^{\ominus}_{sol} = -55\ kJ\ mol^{-1}$

Or $MgCl_2(s) + aq \rightarrow Mg^{2+}(aq) + 2Cl^{-}(aq);\ \Delta H^{\ominus}_{sol} = -55\ kJ\ mol^{-1}$

$NaCl(s) + aq \rightarrow NaCl(aq);\ \Delta H^{\ominus}_{sol} = +3.9\ kJ\ mol^{-1}$

Or $NaCl(s) + aq \rightarrow Na+(aq) + Cl-(aq)\ \Delta H^{\ominus}_{sol} = +3.9\ kJ\ mol^{-1}$

Note that:

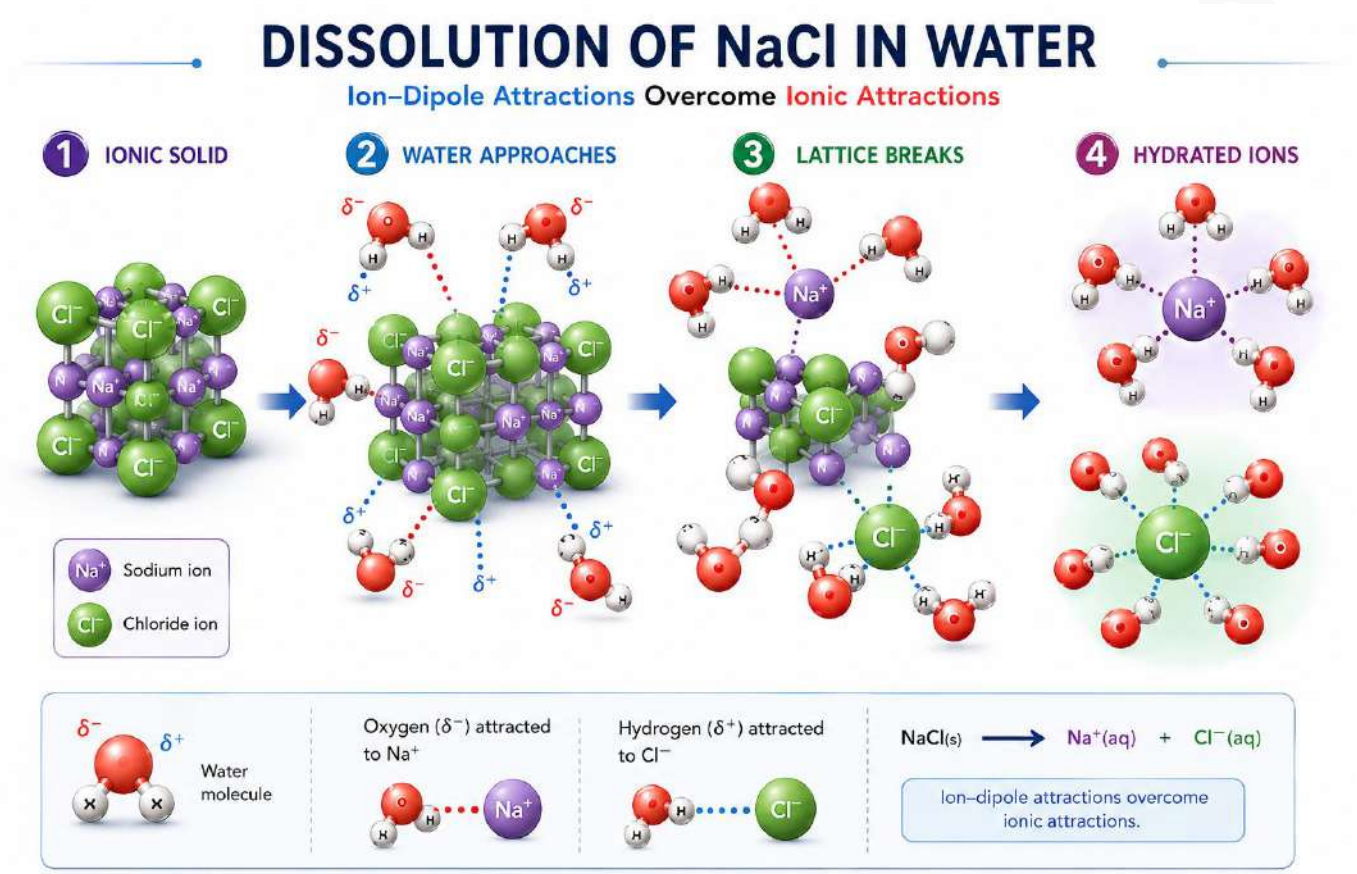
- the symbol for the enthalpy change of solution is $\Delta H^{\ominus}_{sol}$
- The symbol 'aq' represents the very large amount of water used
- Enthalpy changes of solution can be positive (endothermic) or negative (exothermic)
- A compound is likely to be soluble in water only if $\Delta H^{\ominus}_{sol}$ is negative or has a small positive value; substances with large positive values of $\Delta H^{\ominus}_{sol}$ are relatively insoluble.

Chemistry at the Molecular Level

Water molecules are polar: the oxygen end carries a partial negative charge (δ–) and the hydrogen ends carry partial positive charges (δ+). This polarity is what makes water such an effective solvent for ionic compounds:

- **Cations** are surrounded by the δ– oxygen atoms of water molecules.
- **Anions** are surrounded by the δ+ hydrogen atoms of water molecules.

These attractive forces are called **ion–dipole interactions**, and the energy they release is the **hydration enthalpy**.



Summary of the three key terms:

Term	Symbol	Always exo-/endothermic?	Key phrase in the definition
Enthalpy change of hydration	ΔH°_{hyd}	Always exothermic (–)	1 mol of gaseous ions → very dilute solution
Enthalpy change of solution	ΔH°_{sol}	Can be either	1 mol of ionic solid → very dilute solution
Lattice energy (formation)	ΔH°_{latt}	Always exothermic (–)	1 mol of ionic solid formed from gaseous ions

Constructing energy cycles

By Hess's Law, we can link these three quantities in an energy cycle. Dissolving an ionic solid can be thought of as two steps:

1. **Step 1 — Lattice breaking:** The ionic lattice is broken apart to give gaseous ions. This is the *reverse* of lattice energy formation, so the value is $+\Delta H^\circ_{latt}$

2. **Step 2 — Hydration:** The gaseous ions are hydrated by water molecules. The energy released = sum of all hydration enthalpies.

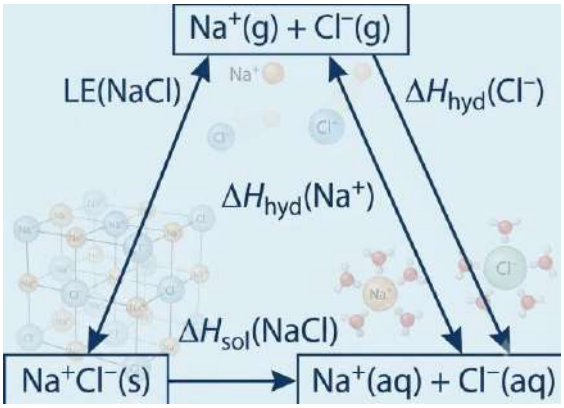


Figure: Hess's Law cycle for the dissolution in water of sodium chloride

$$\Delta H^{\theta}_{sol} = -\Delta H^{\theta}_{latt} + \Delta H^{\theta}_{hyd}$$

⚠ **Exam Tip:** Remember that $\Delta H^{\ominus}_{hyd}$ **is the sum of both individual ions**. Always pay close attention to the stoichiometry of the salt formula! For example, $MgCl_2$ produces **2 moles** of Cl^- ions, so you must multiply the hydration enthalpy of Cl^- by 2 in your calculations.

✎ Worked Example: Calculating ΔH°sol for NaCl

Given: $\Delta H°_{latt}(NaCl) = -787$ kJ mol^{-1}, $\Delta H°_{hyd}(Na^+) = -406$ kJ mol^{-1}, $\Delta H°_{hyd}(Cl^-) = -364$ kJ mol^{-1}

Find $\Delta H°_{sol}(NaCl)$.

Step 1 — Apply Hess's Law:

$\Delta H°_{sol} = -\Delta H°_{latt} + \Sigma\Delta H°_{hyd}$

$\Delta H°_{sol} = -(-787) + (-406) + (-364)$

$\Delta H°_{sol} = +787 + (-770)$

$\Delta H°_{sol} = +17$ kJ mol^{-1}

NaCl is slightly endothermic to dissolve, but the value is small – NaCl is soluble.

✎ Worked Example: Calculating ΔH°sol for $MgCl_2$ (Watch the stoichiometry!)

Given: $\Delta H°_{latt}(MgCl_2) = -2\,526$ kJ mol^{-1}, $\Delta H°_{hyd}(Mg^{2+}) = -1\,920$ kJ mol^{-1}, $\Delta H°_{hyd}(Cl^-) = -364$ kJ mol^{-1}

$MgCl_2$ gives 1 mol Mg^{2+} and 2 mol Cl^- — so multiply $\Delta H°_{hyd}(Cl^-)$ by 2!

$\Delta H°_{sol} = -(-2526) + (-1920) + 2\times(-364)$

$\Delta H°_{sol} = +2526 + (-1920) + (-728)$

$\Delta H°_{sol} = -122$ kJ mol^{-1}

✓ Exam Tip

Always check the formula! For salts such as $MgCl_2$, $AlCl_3$, and $CaCl_2$, you must multiply $\Delta H°_{hyd}$ of the anion by the number of anions produced from one formula unit. Forgetting this is the most common calculation error in this topic.

Effect of ionic charge and of ionic radius on the enthalpy change of hydration

$\Delta H_{hyd}°$ becomes **more exothermic (more negative)** when:

Factor	Why?
Smaller ionic radius	Higher charge density → stronger ion-dipole attractions with water → more energy released.
Higher ionic charge	Greater electrostatic attraction to polar water molecules → more energy released.

📌 *An insight:* Hydration enthalpy is a measure of **ion–dipole bond strength** between ions and water. It's always exothermic because bonds form.

★ **Key Point**

Charge density = ionic charge ÷ ionic radius. A small, highly charged ion has a very high charge density, and therefore a very large (very exothermic) hydration enthalpy.

Comparison: Mg^{2+} ($\Delta H°_{hyd}$ = −1 920 kJ mol^{-1}) vs Ba^{2+} ($\Delta H°_{hyd}$ = − 1 305 kJ mol^{-1}). Both have charge 2+, but Mg^{2+} is much smaller → much more negative $\Delta H°_{hyd}$.

Solubility of group 2 sulfates- Decreases Down the Group

The following table shows the solubility of some Group 2 sulfates in water. The solubility decreases as the radius of the metal ion increases. We can explain this variation in solubility in terms of the relative values of the enthalpy change of hydration and the corresponding lattice energy.

Compound	Solubility / mol dm^{-3} (25°C)
Magnesium sulfate, $MgSO_4$	1.83
Calcium sulfate, $CaSO_4$	4.66×10^{-2}
Strontium sulfate, $SrSO_4$	7.11×10^{-4}
Barium sulfate, $BaSO_4$	9.43×10^{-6}

Table: Solubilities in water of some Group 2 sulfates.

Change in hydration enthalpy down the group

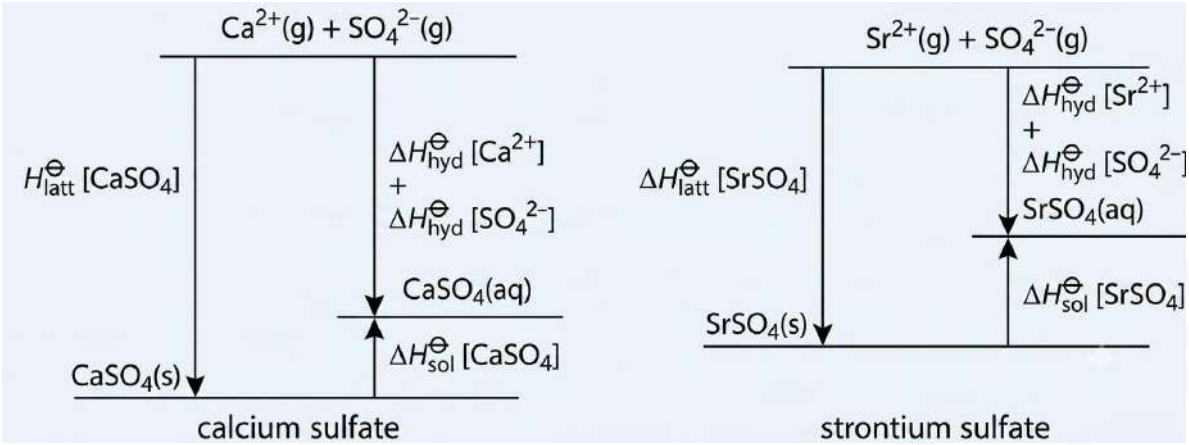
- Smaller ions (with the same charge) have greater enthalpy changes of hydration
- So, the enthalpy change of hydration decreases (gets less exothermic) in the order: $Mg^{2+} > Ca^{2+} > Sr^{2+} > Ba^{2+}$
- This decrease is relatively large down the group, and it depends entirely on the increase in the size of the cation, as the anion is unchanged (it is the sulfate ion in every case).

Change in lattice energy down the group

- Lattice energy is greater if the ions (with the same charge) forming the lattice are small so the lattice energy decreases in the order: $Mg^{2+} > Ca^{2+} > Sr^{2+} > Ba^{2+}$
- The lattice energy is also inversely proportional to the sum of the radii of the anion and cation. The sulfate ion is much larger than the Group 2 cations
- So, the sulfate ion contributes a relatively greater part to the change in the lattice energy down the group
- So, the decrease in lattice energy is relatively smaller down the group, and it is determined more by the size of the large sulfate ion than the size of the cations.

Difference in the enthalpy change of the solution of Group 2 sulfates

Earlier, we saw that substances that have a very low solubility in water are likely to have $\Delta H^{\ominus}_{sol}$, with a high positive (endothermic) value. As a rough guide, the higher the positive value of $\Delta H^{\ominus}_{sol}$, the less soluble the salt.



We have seen that:

- The lattice energy of the sulfates decreases (gets less exothermic) by relatively smaller values down the group
- the enthalpy change of hydration decreases (gets less exothermic) by relatively larger values down the group
- So, applying Hess's law, the value of $\Delta H^{\ominus}_{sol}$, gets more endothermic down the group (Figure above)
- So, the solubility of the Group 2 sulfates decreases down the group.

Once Again:

- **Hydration enthalpy decreases (becomes less exothermic)** as cation size increases from $Mg^{2+} \rightarrow Ba^{2+}$. This is a **large** decrease because it depends entirely on cation size.
- **Lattice energy also decreases (becomes less exothermic)** as cation size increases, but by a **smaller** amount. This is because the sulfate ion (SO_4^{2-}) is *much larger* than any of the Group 2 cations, so it dominates the lattice energy term. Changing the cation size has less impact.
- **Net result (Hess's Law):** $\Delta H°_{sol} = -\Delta H°_{latt} + \Sigma\Delta H°_{hyd}$. Since $\Delta H°_{hyd}$ falls faster than $\Delta H°_{latt}$, $\Delta H°_{sol}$ becomes increasingly endothermic (more positive) down the group.
- **Therefore:** as $\Delta H°_{sol}$ becomes more positive → solubility **decreases** down the group.

✓ Exam Tip:

In exam answers, you must explicitly state: (1) how $\Delta H°_{hyd}$ and $\Delta H°_{latt}$ each change, (2) which changes *more*, and (3) the resulting effect on $\Delta H°_{sol}$ and solubility. Simply saying 'the lattice energy decreases' will not score full marks.

1. The solubility of the Group 2 sulfates decreases down the group.
   Explain this trend. [3]

   Marking Scheme

   M1 ΔH_{latt} and ΔH_{hyd} decrease / both become less exothermic / less negative
   M2 ΔH_{latt} decreases / changes less/becomes less exothermic by a smaller extent
   OR ΔH_{hyd} decreases / changes more / dominant factor
   M3 ΔH_{sol} becomes less exothermic / less negative, **OR** ΔH_{sol} becomes (more) endothermic / (more) positive
   OR $\Delta H_{sol} = \Delta H_{hyd} - \Delta H_{latt}$ expression **AND** reaction becomes less exothermic

Group 2 Hydroxides — Solubility Increases Down the Group

The hydroxide ion (OH^-) is **much smaller** than the sulfate ion. This changes the analysis:

- **Lattice energy decreases (becomes less exothermic)** as cation size increases from $Mg^{2+} \rightarrow Ba^{2+}$. Because the hydroxide ion is small, the changing cation size has a **large, proportionally significant** effect on lattice energy — it decreases by a **large** amount.
- **Hydration enthalpy also decreases (becomes less exothermic)** as cation size increases, but by a **smaller** amount. (Note: the hydration enthalpy of OH^- is constant for all four hydroxides.)
- **Net result (Hess's Law):** Since $\Delta H°_{latt}$ falls faster than $\Delta H°_{hyd}$, $\Delta H°_{sol}$ becomes less endothermic (or more negative) down the group.
- **Therefore:** as $\Delta H°_{sol}$ becomes less positive (or more negative) → solubility **increases** down the group.

> ⚠ **Common Confusion: Sulfates vs Hydroxides**
>
> The trends are opposite for sulfates and hydroxides. The key is the **size of the anion:**
>
> - **Large anion (SO_4^{2-}):** $\Delta H°_{latt}$ is relatively insensitive to cation size → $\Delta H°_{hyd}$ decreases faster → solubility decreases down the group.
> - **Small anion (OH^-):** $\Delta H°_{latt}$ is more sensitive to cation size → $\Delta H°_{latt}$ decreases faster → solubility increases down the group.

2. The solubility of the Group 2 hydroxides increases down the group.
Explain this trend. [3]

Marking Scheme
M1 ΔH_{latt} and ΔH_{hyd} both become less exothermic / less negative
M2 ΔH_{hyd} changes less / becomes less exothermic by a smaller extent
OR ΔH_{latt} changes more / dominant factor/changes faster
M3 ΔH_{sol} becomes more exothermic / more negative
OR ΔH_{sol} becomes less endothermic / less positive

Core Definitions (Must Know Exactly)

Term	Symbol	Definition	Sign
Standard enthalpy change of solution	$\Delta H_{sol}°$	Enthalpy change when 1 mole of an ionic substance dissolves in **sufficient water** to form a **very dilute solution** under standard conditions (298 K, 100 kPa, 1 mol dm^{-3}).	Can be **exothermic (-)** or **endothermic (+)**
Standard enthalpy change of hydration	$\Delta H_{hyd}°$	Enthalpy change when 1 mole of **specified gaseous ions** dissolves in sufficient water to form a **very dilute solution** under standard conditions.	**Always exothermic (–)**
Lattice energy (formation)	$\Delta H_{latt}°$	Enthalpy change when 1 mole of an **ionic lattice** is formed from its **gaseous ions** under standard conditions.	**Always exothermic (–)**

Exam Tips

- ✅ **Always state standard conditions** (298 K, 100 kPa, 1 mol dm^{-3} solution).
- ✅ **Draw the energy cycle clearly** with arrows and labels – examiners award marks for the cycle.
- ✅ **Check signs:** Lattice formation is (–), breaking it is (+).
- ✅ **Watch out for $MgCl_2$, $AlCl_3$, etc.** – multiply hydration enthalpy by the number of ions.
- ✅ **Define hydration as "gaseous ions → aqueous ions"** – many students miss "gaseous".
- ✅ **Explain factors using "charge density" and "ion-dipole attractions"** – not just "size" or "charge" alone.