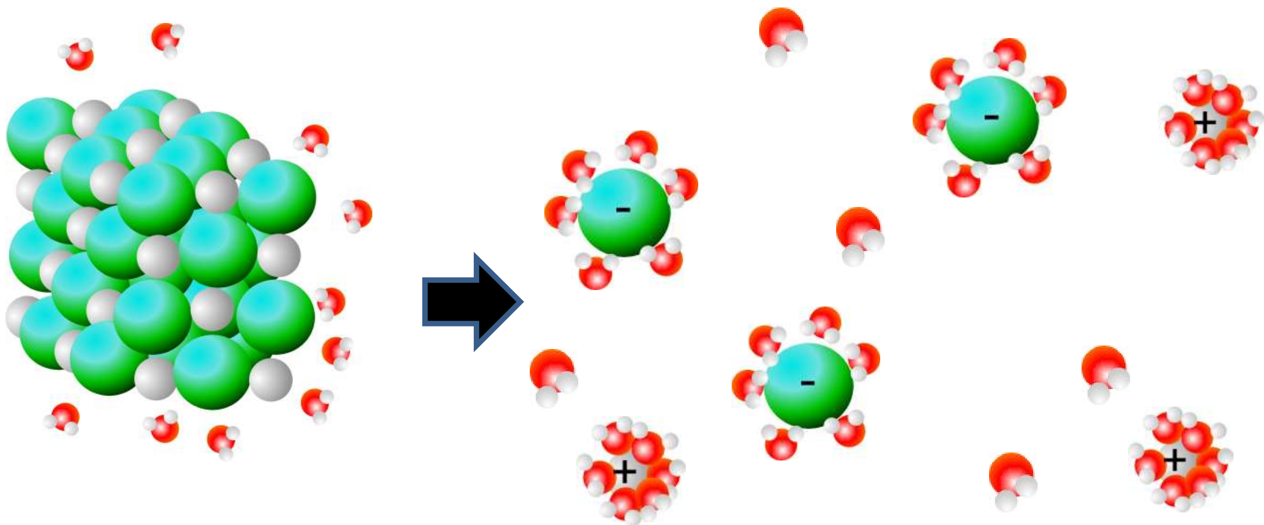
3.17 Enthalpies of solution
Using Hess's law to determine enthalpy changes of solution

Enthalpy of solution
The enthalpy of solution is the standard enthalpy change when one mole of an ionic solid dissolves in a large enough amount of water to ensure that the dissolved ions are well separated and do not interact with one another.

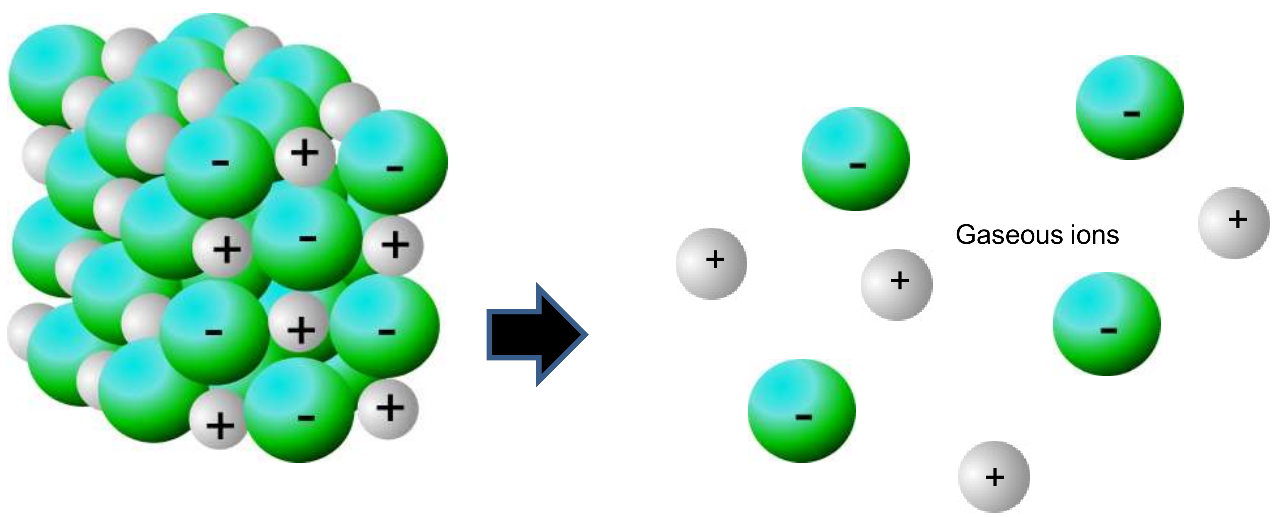
$NaCl\ (s) + aq \rightarrow Na^+\ (aq) + Cl^-(aq)$



When an ionic lattice dissolves in water to form a solution it involves breaking up the forces of attraction in the lattice and forming new forces of attraction between the metal ions and water molecules.
There are enthalpy changes for both these processes of bond breaking and making.

Enthalpy of lattice dissociation- This is the process of breaking up the lattice.
The enthalpy of lattice dissociation is the standard enthalpy change when 1 mole of an ionic crystal lattice form is separated into its constituent ions in gaseous form.

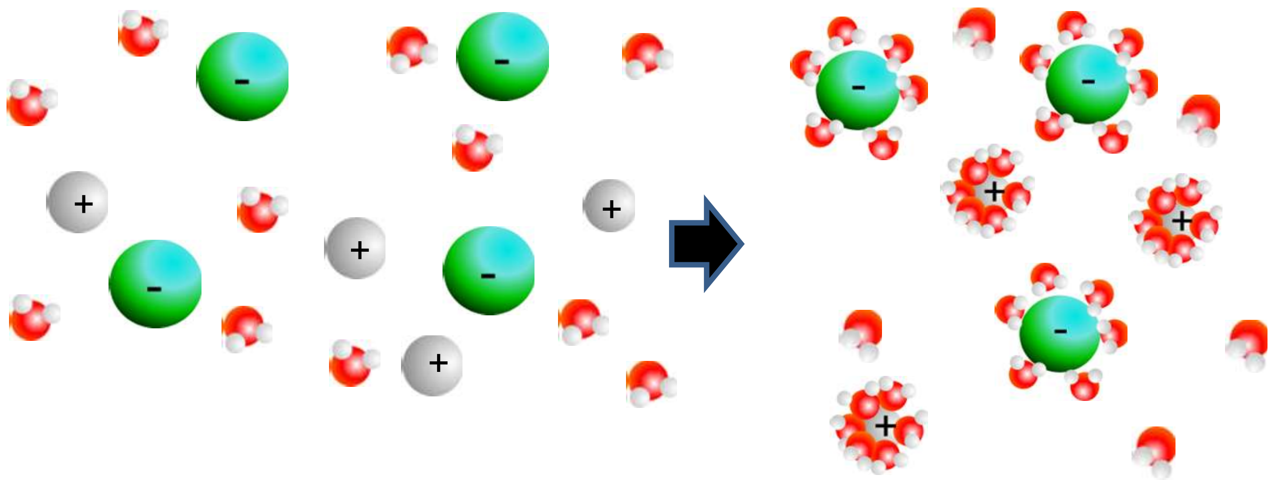
$NaCl\ (s) \rightarrow Na^+\ (g) + Cl^-\ (g)$ [$\Delta H_{Latt} = +787$ kJ mol^{-1}]



When an ionic substance dissolves the lattice must be broken up. The enthalpy of lattice dissociation is equal to the energy needed to break up the lattice (to gaseous ions). This step is **endothermic.**

The size of the lattice enthalpy depends on the size and charge on the ion. The smaller the ion and the higher the ionic charge the stronger the lattice.

Making new bonds with water



New forces of attraction are formed between the water molecules and the ions. Energy is given out in this step.

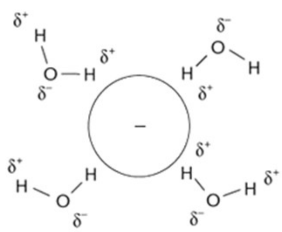
Hydration enthalpy is the enthalpy change when one mole of gaseous ions become aqueous ions.

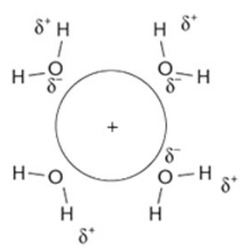
Enthalpy of hydration ΔH_{hyd}
Enthalpy change when **one mole of gaseous ions** become **aqueous ions**.
$X^{+}_{(g)}$ + aq → $X^{+}_{(aq)}$ For Li^{+} ΔH_{hyd} = -519 kJ mol $^{-1}$
or
$X^{-}_{(g)}$ + aq → $X^{-}_{(aq)}$ For F^{-} ΔH_{hyd} = -506 kJ mol $^{-1}$

This always gives out energy (exothermic, -ve) because bonds are made between the ions and the water molecules.

Hydration enthalpies are **exothermic** as energy is given out as water molecules bond to the metal ions.

The **negative** ions are attracted to the **δ^{+} hydrogens** on the **polar water** molecules and the positive ions are attracted to the δ^{-} oxygen on the polar water molecules.



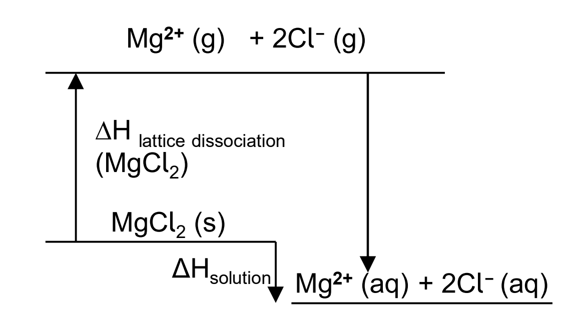


The higher the **charge density** the greater the hydration enthalpy (e.g. **smaller ions** or **ions with larger charges**) as the ions attract the water molecules more strongly.

e.g. Fluoride ions have more negative hydration enthalpies than chloride ions.

Magnesium ions have a more negative hydration enthalpy than barium ions.

For $MgCl_2$ **the ionic equation** for the dissolving is $\mathbf{MgCl_{2\,(s)} + aq \rightarrow Mg^{2+}_{(aq)} + 2Cl^-_{(aq)}}$



Sometimes in questions $\Delta H_{Latt\ formation}$ is given instead of $\Delta H_{Latt\ dissociation}$ in order to catch you out. Remember the difference between the two.

In general

$\Delta H_{solution} = \Delta H_{L\ dissociation} + \Sigma\Delta H_{hyd}$

OR

$\Delta H_{solution} = -\Delta H_{L\ formation} + \Sigma\Delta H_{hyd}$

Example. Calculate the enthalpy of solution of NaCl given that the lattice enthalpy of formation of NaCl is − 771 kJ mol^{-1} and the enthalpies of hydration of sodium and chloride ions are −406 and − 364 kJ mol^{-1} respectively

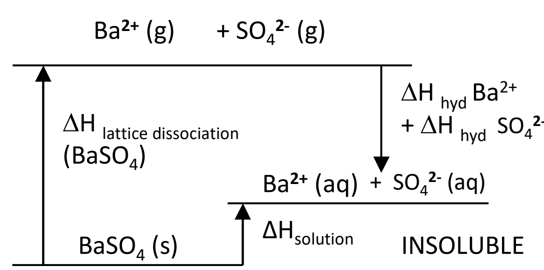
$\Delta H\ sol = -\Delta H_{Latt\ formation} + \Sigma\Delta H_{hyd}$

$= -(-771) + (-406 - 364)$

$= +1\ kJmol^{-1}$

What does $\Delta H_{Solution}$ tell us?
Generally **ΔH solution** is not very exothermic or endothermic so the hydration enthalpy is about the same as lattice enthalpy.
In general the substance is more likely to **be soluble** if the **ΔH solution is exothermic.**
If a substance is insoluble it is often because the lattice enthalpy is much larger than the hydration enthalpy and it is not energetically favourable to break up the lattice, making **ΔH solution endothermic**.

ΔH solution endothermic.



We must consider **entropy**, however, to give us the full picture about solubility.
When a solid dissolves into ions the **entropy increases** as there is **more disorder** as solid changes to solution and **number of particles increases**.
This positive ΔS can make ΔG negative even if ΔH solution is endothermic, especially at higher temperatures.

For salts where ΔH solution is exothermic the salt will always dissolve at all temperatures.

$$\mathbf{\Delta G = \Delta H - T\Delta S}$$

ΔG is always negative

ΔH is negative

ΔS is positive due to the increased disorder as more particles so **$-T\Delta S$** always negative

For salts where ΔH solution is endothermic the salt may dissolve depending on whether the **$-T\Delta S$** value is more negative than ΔH is positive.

$$\mathbf{\Delta G = \Delta H - T\Delta S}$$

Will dissolve if ΔG is negative

ΔH is positive

ΔS is positive due to the increased disorder as more particles so **$-T\Delta S$** always negative

Increasing the temperature will make it more likely that ΔG will become negative, making the reaction feasible and the salt dissolve.

Explaining trends in solubility

Hydroxides

Group 2 hydroxides become more soluble down the group.

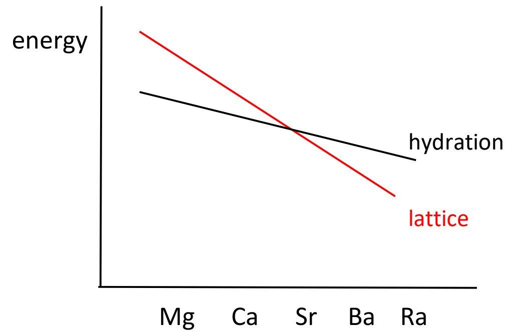
This can be explained by changes in the lattice enthalpy and hydration enthalpy.

Lattice enthalpy drops down the group because the cations get bigger leading to a weaker ionic attraction.

Water molecules are more strongly attracted to smaller ions with a larger charge.

Hydration enthalpy drops because the cations becomes bigger and less polarising so they attract the water molecules less.

The hydroxides become more soluble because the lattice enthalpy drops more than the hydration enthalpy.



For magnesium hydroxide the lattice enthalpy is larger than the hydration enthalpy leading to an endothermic enthalpy of solution which makes it less likely to dissolve.

For barium hydroxide the lattice enthalpy is smaller than the hydration enthalpy leading to an exothermic enthalpy of solution which makes it more likely to dissolve.

Sulfates

Group 2 sulfates become **less** soluble down the group.

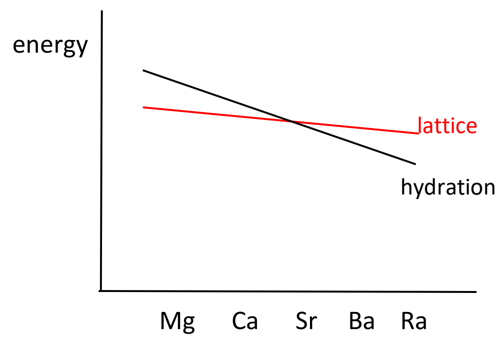
This can be explained by same changes in the lattice enthalpy and hydration enthalpy as the above case.

Lattice enthalpy drops down the group because the cations get bigger leading to a weaker ionic attraction. The key difference between sulfates and hydroxides is the sulfate ion is much larger than the metal ions (and hydroxide ion). The decreasing size of the cation has less of an effect in this case and the lattice enthalpy falls less going down the group.

Water molecules are more strongly attracted to smaller ions with a larger charge.

Hydration enthalpy drops because the cations becomes bigger and less polarising so they attract the water molecules less.

The hydroxides become less soluble because the lattice enthalpy drops less than the hydration enthalpy.



For magnesium sulfate the lattice enthalpy is smaller than the hydration enthalpy leading to an exothermic enthalpy of solution which makes it more likely to dissolve.

For barium sulfate the lattice enthalpy is larger than the hydration enthalpy leading to an endothermic enthalpy of solution which makes it less likely to dissolve.