Dissolving.

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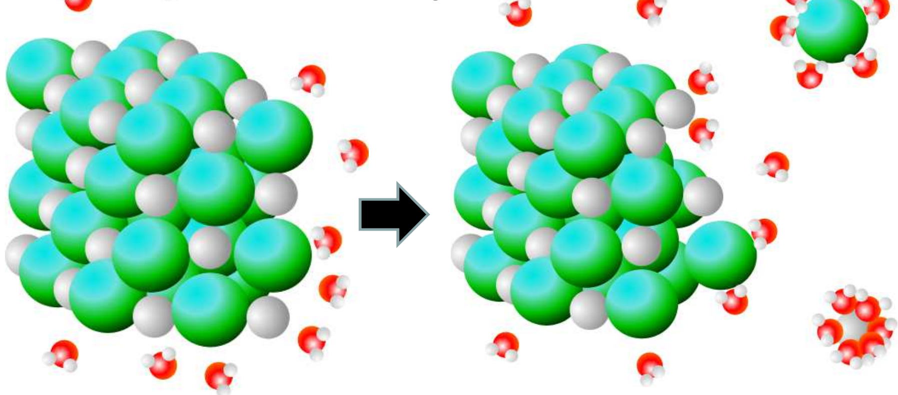
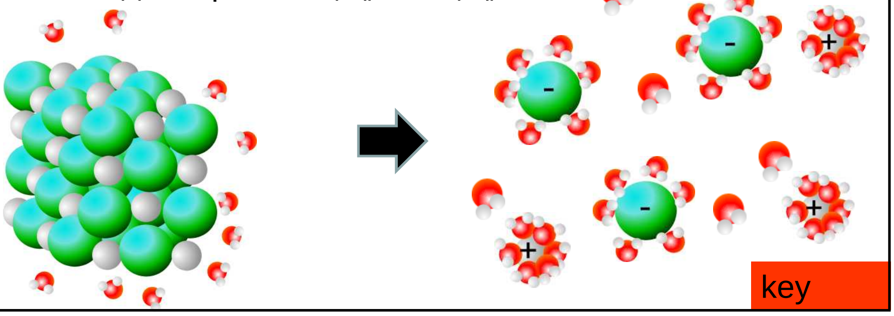
Chemrevise.org



Enthalpy of Solution ΔH_{sol}

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

$NaCl_{(s)} + aq \rightarrow Na^{+}_{(aq)} + Cl^{-}_{(aq)}$



Using Hess's law to determine enthalpy changes of solution

The enthalpy of solution can be calculated from the Enthalpy of lattice dissociation and the enthalpies of hydration using a Hess's law cycle

$$\text{Solute and Solvent} \xrightarrow{\Delta H^{\ominus}_{sol}} \text{Solution}$$

Solute and Solvent → Gaseous ions: $\Delta H^{\ominus}_{L\ dissociation}$

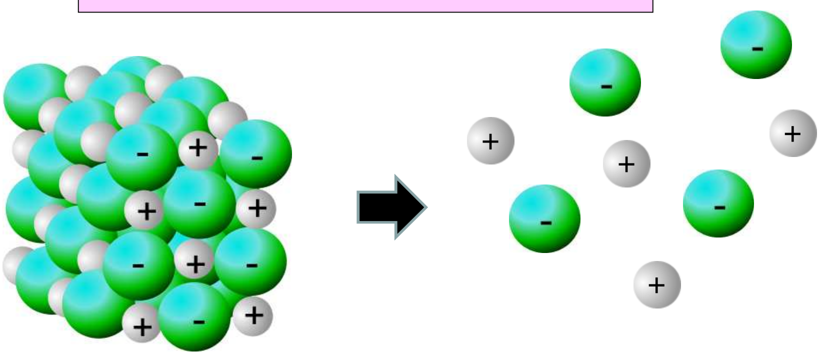
Gaseous ions → Solution: $\Sigma\Delta H^{\ominus}_{hyd}$ anions $+\Sigma\ \Delta H_{hyd}$ cations

In general

$$\Delta H^{\ominus}_{sol} = \Delta H^{\ominus}_{L\ dissociation} + \Sigma\Delta H^{\ominus}_{hyd}$$

key

Breaking up the lattice



The Enthalpy of lattice dissociation is the standard enthalpy change when 1 mole of an ionic crystal lattice is separated into its **constituent ions in gaseous form**

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

Bonds are broken: endothermic process

key

Enthalpy of lattice formation

The Enthalpy of lattice formation is the standard enthalpy change when 1 mole of an ionic crystal lattice is formed from its constituent ions in gaseous form

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

Enthalpy of lattice dissociation

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

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

Note the conflicting definitions and the sign that always accompanies the definitions

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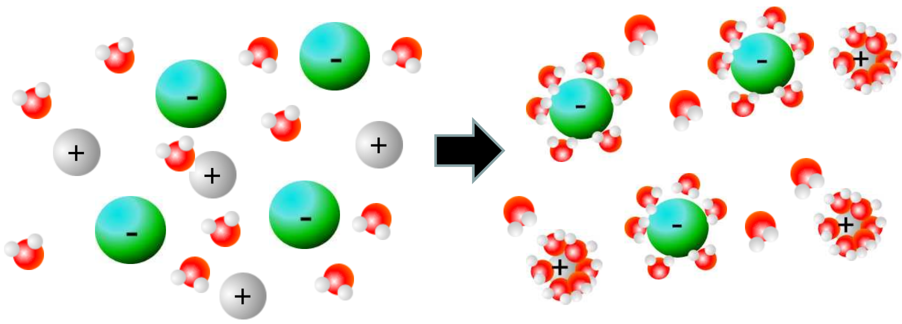
Making new bonds with water



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

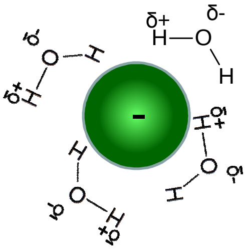
Hydration enthalpy is the enthalpy change when **one mole of gaseous ions** become **aqueous ions** .

key

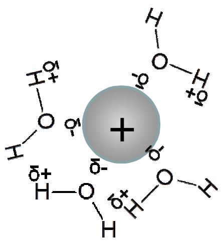
Hydration Enthalpy

$Li^+_{(g)} + aq \rightarrow Li^+_{(aq)}$ $\Delta H_{hyd} = -519\ kJ\ mol^{-1}$

$F^-_{(g)} + aq \rightarrow F^-_{(aq)}$ $\Delta H_{hyd} = -506\ kJ\ mol^{-1}$



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 on the ion the greater the hydration enthalpy.

-smaller ions and ions with higher charges have more exothermic hydration enthalpies

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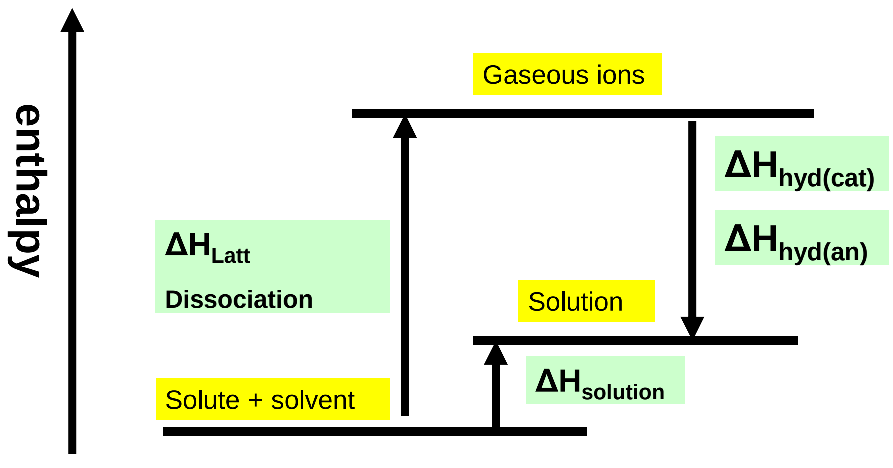
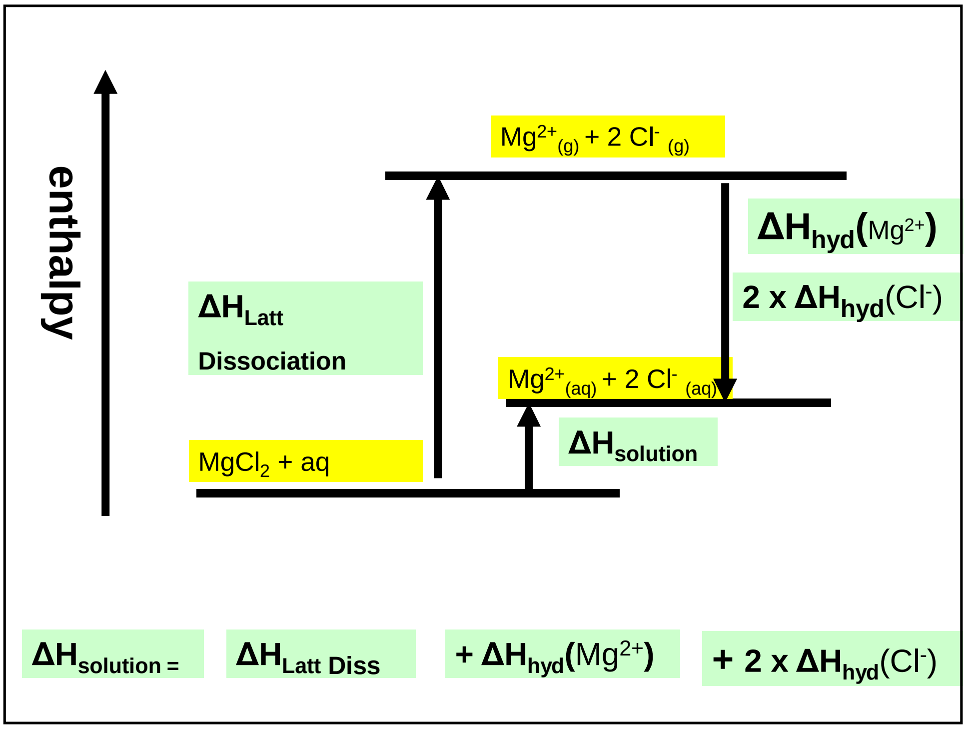
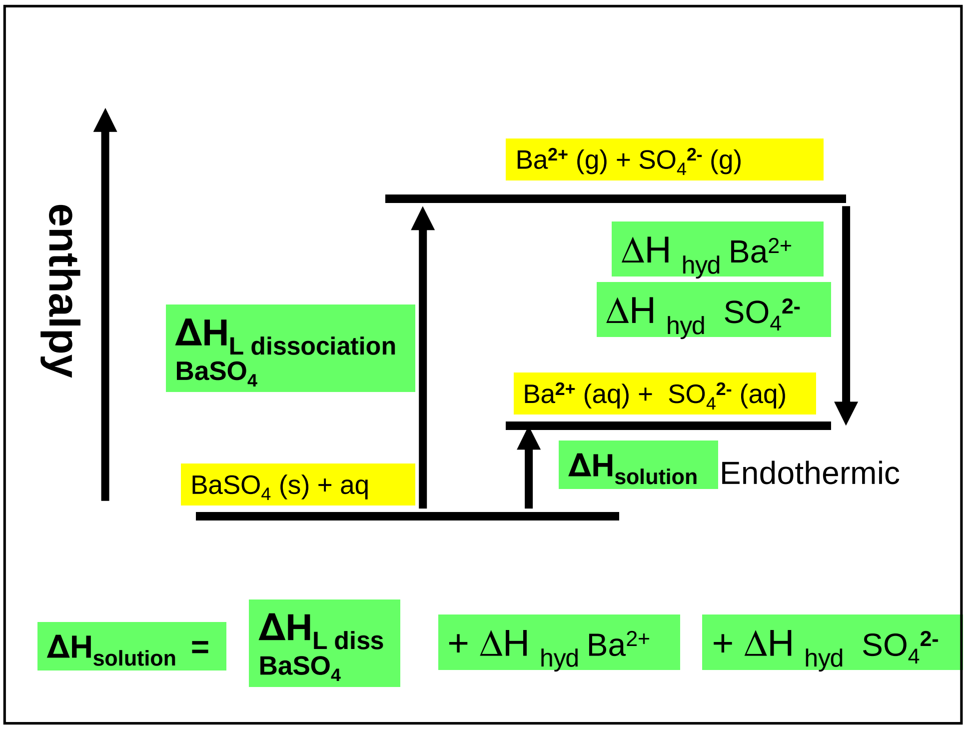


$\Delta H_{solution} = \Delta H_{Latt\ Diss} + \Delta H_{hyd(cat)} + \Delta H_{hyd(an)}$


enthalpy
$Mg^{2+}_{(g)} + 2\ Cl^-_{(g)}$
$\Delta H_{hyd}(Mg^{2+})$
$2 \times \Delta H_{hyd}(Cl^-)$
ΔH_{Latt} Dissociation
$Mg^{2+}_{(aq)} + 2\ Cl^-_{(aq)}$
$\Delta H_{solution}$
$MgCl_2$ + aq
$\Delta H_{solution} = \Delta H_{Latt\ Diss} + \Delta H_{hyd}(Mg^{2+}) + 2 \times \Delta H_{hyd}(Cl^-)$


enthalpy
Ba^{2+} (g) + SO_4^{2-} (g)
$\Delta H_{hyd}\ Ba^{2+}$
$\Delta H_{hyd}\ SO_4^{2-}$
$\Delta H_{L\ dissociation}$ $BaSO_4$
Ba^{2+} (aq) + SO_4^{2-} (aq)
$\Delta H_{solution}$ Endothermic
$BaSO_4$ (s) + aq
$\Delta H_{solution} = \Delta H_{L\ diss}\ BaSO_4 + \Delta H_{hyd}\ Ba^{2+} + \Delta H_{hyd}\ SO_4^{2-}$

What does $\Delta H_{solution}$ tell us?

- Generally $\Delta H_{solution}$ is not very exo or endothermic so the hydration enthalpy is about the same as lattice enthalpy.
- If a substance is insoluble it is often because the lattice enthalpy is larger than the hydration enthalpy and it is not energetically favourable to break up the lattice.
- We must consider entropy, however, to give us the full picture about solubility

When a solid dissolves into ions the entropy increases **(*ΔS +ve)*** as the disorder increases with the change from solid to solution and the number of particles increases. This will contribute towards making **ΔG** negative

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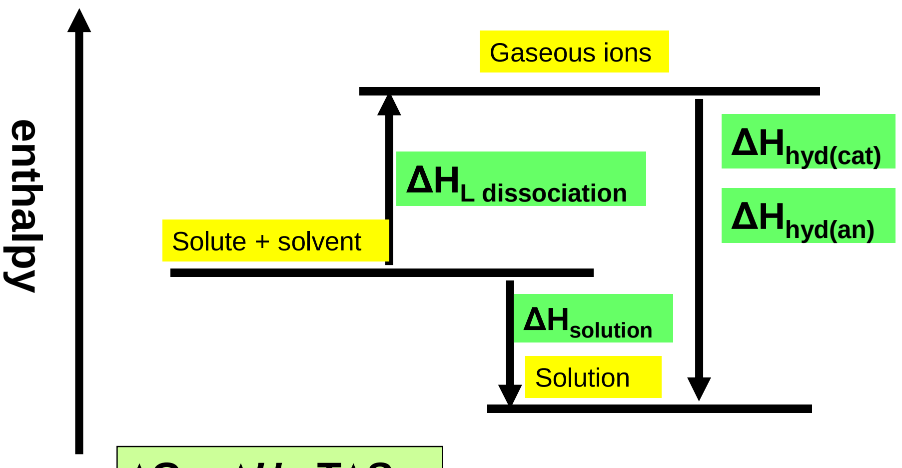
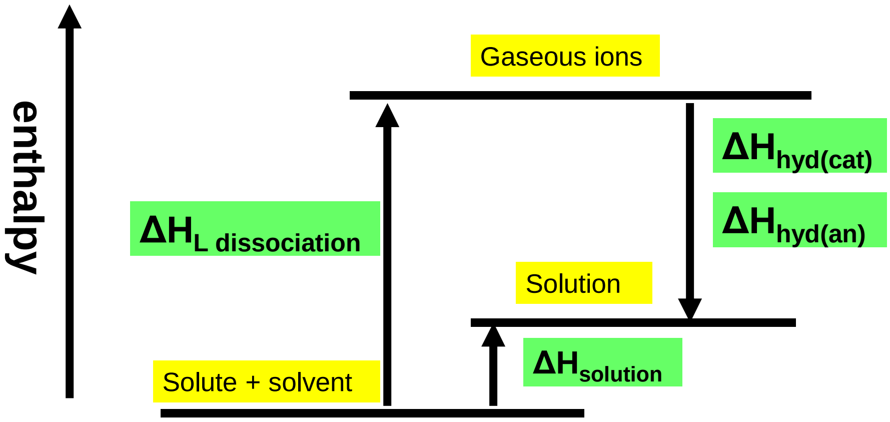


$$\Delta G = \Delta H - T\Delta S$$

$\Delta H_{solution}$ is exothermic. **ΔS is positive**

Δ**G** will be negative at all temperatures so always soluble



$\Delta G = \Delta H - T\Delta S$

$\Delta H_{solution}$ is endothermic.

ΔS is positive

Δ**G** will be only be negative if **-TΔS** is more negative than ΔH is positive. Increasing temperature will make it more likely to occur.

Entropy and solubility

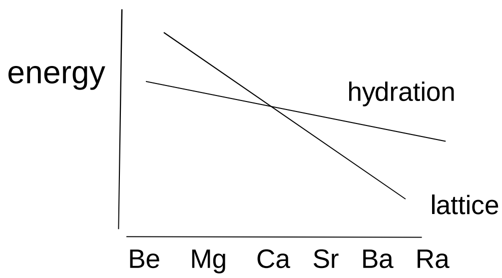
1. The enthalpy of solution for silver fluoride in water is -20 kJ mol^{-1}. Explain why the dissolving of silver fluoride in water is always a spontaneous process at any temperature

2. Why does the solubility of potassium chlorate in water increase with increasing temperature?

3. Why do gases get less soluble as temperature increases?

Explaining a trend in solubility

- Group 2 hydroxides become more soluble down the group.
- This can be explained by changes in the lattice enthalpy and hydration enthalpy



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Lattice enthalpy drops down the group because the cations get bigger.

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 quicker than the hydration enthalpy

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