

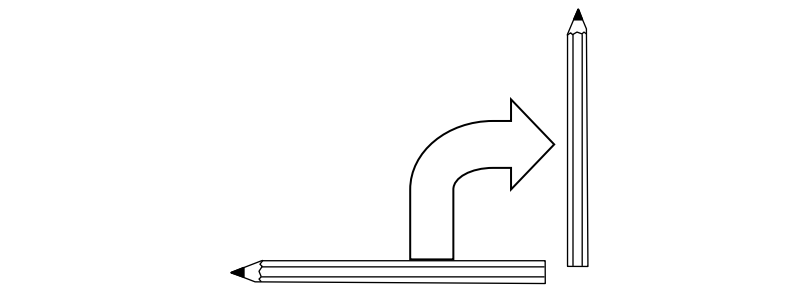
Entropy

Exothermic and Endothermic Reactions

Most chemical reactions give out heat energy as they take place, so the products have less energy (and so are more stable) than the reactants. These are **exothermic** reactions.

When ethanoic acid is added to sodium hydrogencarbonate, a reaction takes place and the temperature decreases, so heat energy is being taken in. This is an example of an endothermic reaction in which the products have more energy (are energetically less stable) than the reactants.

An endothermic reaction can be compared to a ball spontaneously rolling uphill or a pencil lying down springing upright.



What enables chemical reactions to do what is energetically unfavourable?

Energy considerations by themselves are clearly not sufficient to explain why chemical reactions take place.

The other factor that is important for chemical reactions is **entropy**. Essentially materials go to their most likely condition; the most probable situation - that is where there is the maximum freedom.

The greater the freedom molecules have, the greater the entropy. As molecules become more randomly distributed their entropy increases. When molecules gain energy they gain freedom of movement and so their entropy increases.

The symbol used for entropy is S .

Solids have restricted movement for the molecules in them, so they have lower entropies than other states. Perfect crystals at 0 Kelvin have zero entropy.

In liquids, the molecules have greater freedom of movement than solids, so liquids have higher entropies than solids.

This means that dissolved substances will have higher entropies than the solid.

The molecules in gases have much greater freedom of movement and so have comparatively high entropy values.

Complex molecules generally have higher entropies than simple molecules as there are more ways they can arrange themselves.

The table below gives entropy values of selected substances at 298K.

Substance	State	Entropy /JK ⁻¹ mol ⁻¹
Aluminium	Solid	28.3
Silicon dioxide	Solid	41.8
Water	Liquid	70.0
Argon	Gas	154.7
Carbon dioxide	Gas	213.6

It can be seen from this table that the more ordered the state, the lower the value of entropy. The solids have the lowest values. Liquids have higher values and gases have still higher values.

The table below gives entropy values of certain alkanes.

Alkane	State	Entropy /JK ⁻¹ mol ⁻¹
Methane	Gas	186.2
Ethane	Gas	229.5
Propane	Gas	269.9
Butane	Gas	310.1
Pentane	Liquid	261.1

The table of alkanes shows that as the complexity of the gaseous molecules increases so do the entropy values. Pentane has a lower value than butane because it is liquid rather than gas.

When a chemical reaction takes place new substances are formed. The products of a reaction will have different entropy values to the reactants, so the entropy of "the system" changes. The change in entropy can be found using the following equation:

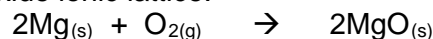
$$\Delta S_{\text{SYSTEM}} = \Delta S_{\text{PRODUCTS}} - \Delta S_{\text{REACTANTS}}$$

For spontaneous change to take place the entropy must increase.

Changes that incur an increase in entropy include:

- ✓ Formation of gas molecules
- ✓ Dissolving of a solid
- ✓ Decomposition of a substance (as the resulting components have greater freedom of movement)
- ✓ Gases becoming more randomly distributed (diffusion)

When magnesium burns the magnesium atoms combine with oxygen molecules to form a magnesium oxide ionic lattice.



In this change a gas is converted to a solid, so the entropy in this change seems to decrease and break our rule about spontaneous change.

Indeed, the entropy change is $-221.5\text{JK}^{-1}\text{mol}^{-1}$.

However as the reaction takes place energy is given out and so the surrounding molecules gain energy and so gain entropy.

When considering entropy in changes, it is necessary to consider what happens to the surroundings as well as the system (chemical reaction) itself.

$$\Delta S_{\text{TOTAL}} = \Delta S_{\text{SYSTEM}} + \Delta S_{\text{SURROUNDINGS}}$$

Any entropy increase in the surroundings comes from the energy which the system gives out. The increase in entropy depends upon the proportional increase in energy of particles in the surroundings. If for example the surroundings gain 20kJ of energy, the proportional increase is greater if the surroundings originally have low energy. Temperature is a measure of the energy of molecules, so the change in entropy in the surroundings is;

$$\Delta S_{\text{SURROUNDINGS}} = \frac{-\Delta H}{T}$$

It can be seen from this that as the temperature becomes higher, the value of $\Delta S_{\text{SURROUNDINGS}}$ decreases.

A reaction is feasible if ΔS_{TOTAL} is positive. This will depend upon the change in entropy of the system and the change in entropy of the surroundings.

$$\Delta S_{\text{TOTAL}} = -\Delta H/T + \Delta S_{\text{SYSTEM}}$$

The table below shows the various possibilities.

ΔS_{SYSTEM}	$\Delta S_{\text{SURROUNDING S}}$	Comparative values	ΔS_{TOTAL}	Feasibility of reaction
+	+		+	Yes
-	+	$\Delta S_{\text{SYSTEM}} > \Delta S_{\text{SURROUNDINGS}}$	-	No
-	+	$\Delta S_{\text{SYSTEM}} < \Delta S_{\text{SURROUNDINGS}}$	+	Yes
+	-	$\Delta S_{\text{SYSTEM}} > \Delta S_{\text{SURROUNDINGS}}$	+	Yes
+	-	$\Delta S_{\text{SYSTEM}} < \Delta S_{\text{SURROUNDINGS}}$	-	No
-	-		-	No

For the example of burning magnesium $\Delta H = -1204\text{kJmol}^{-1}$ at 298K.

$$\text{So } \Delta S_{\text{SURROUNDINGS}} = -(-1204)/298 = +4.0403\text{kJK}^{-1}\text{mol}^{-1}$$

$$\text{Using } \Delta S_{\text{TOTAL}} = \Delta S_{\text{SYSTEM}} + \Delta S_{\text{SURROUNDINGS}}$$

$$\text{Converting } +4.0403\text{kJK}^{-1}\text{mol}^{-1} \text{ to } +4,040.3 \text{ JK}^{-1}\text{mol}^{-1}$$

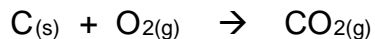
$$\Delta S_{\text{TOTAL}} = (-221.1) + (+4,040.3) = 3,818.8 \text{ JK}^{-1}\text{mol}^{-1}$$

Notice that the units of S are in $\text{JK}^{-1}\text{mol}^{-1}$. In particular J not kJ

It can now be seen that the overall entropy change is positive, showing that the reaction is feasible.

Other examples

Combustion of carbon



ΔS_{SYSTEM}	$+3.02 \text{ JK}^{-1}\text{mol}^{-1}$
ΔH	$-393.5 \text{ kJmol}^{-1}$

$$\Delta S_{\text{SURROUNDINGS}} = -(-393.5)/298 = +1.32047 \text{ kJK}^{-1}\text{mol}^{-1} \text{ (or } +1,320.47 \text{ JK}^{-1}\text{mol}^{-1}\text{)}$$

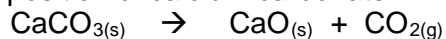
$$\text{Using } \Delta S_{\text{TOTAL}} = \Delta S_{\text{SYSTEM}} + \Delta S_{\text{SURROUNDINGS}}$$

$$\Delta S_{\text{TOTAL}} = (+3.02) + (+1,320.47) = +1,323.49 \text{ JK}^{-1}\text{mol}^{-1}$$

The positive value shows that this reaction is feasible.

Notice that the units of S are in $\text{JK}^{-1}\text{mol}^{-1}$. In particular J not kJ

Decomposition of calcium carbonate



ΔS_{SYSTEM}	$+165 \text{ JK}^{-1}\text{mol}^{-1}$
ΔH	$+178 \text{ kJmol}^{-1}$

$$\Delta S_{\text{SURROUNDINGS}} = -(+178)/298 = -0.597 \text{ kJK}^{-1}\text{mol}^{-1} \text{ (or } -597 \text{ JK}^{-1}\text{mol}^{-1}\text{)}$$

$$\text{Using } \Delta S_{\text{TOTAL}} = \Delta S_{\text{SYSTEM}} + \Delta S_{\text{SURROUNDINGS}}$$

$$\Delta S_{\text{TOTAL}} = (+165) + (-597) = -432 \text{ JK}^{-1}\text{mol}^{-1}$$

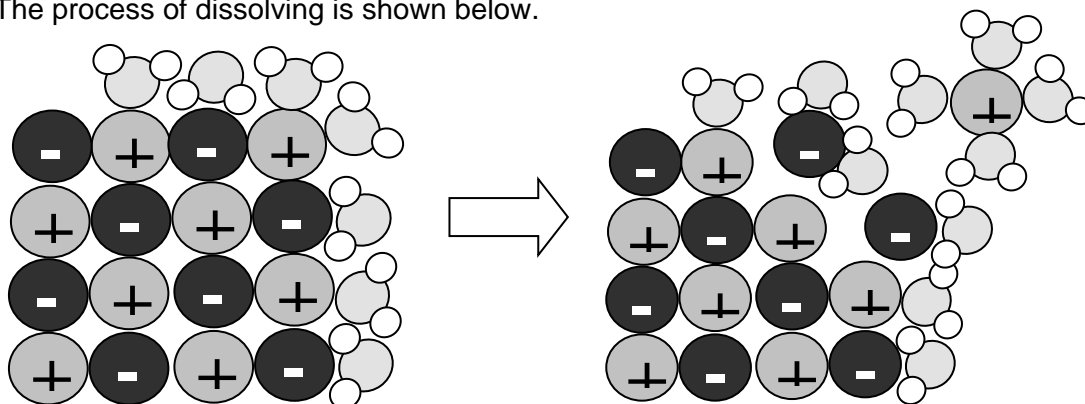
The negative value shows that this reaction is not feasible at room temperature.

Solutions

When an ionic substance is placed in water, the water molecules, being highly polar, are attracted to the ions. The oxygen in the water molecule carries a partial negative charge and is attracted to cations. The hydrogen in the water molecule carries a partial positive charge and is attracted to anions.

The process of water molecules linking to ions is called hydration of ions. The water molecules are vibrating, so as they bond to the ions they shake the ions free from the lattice.

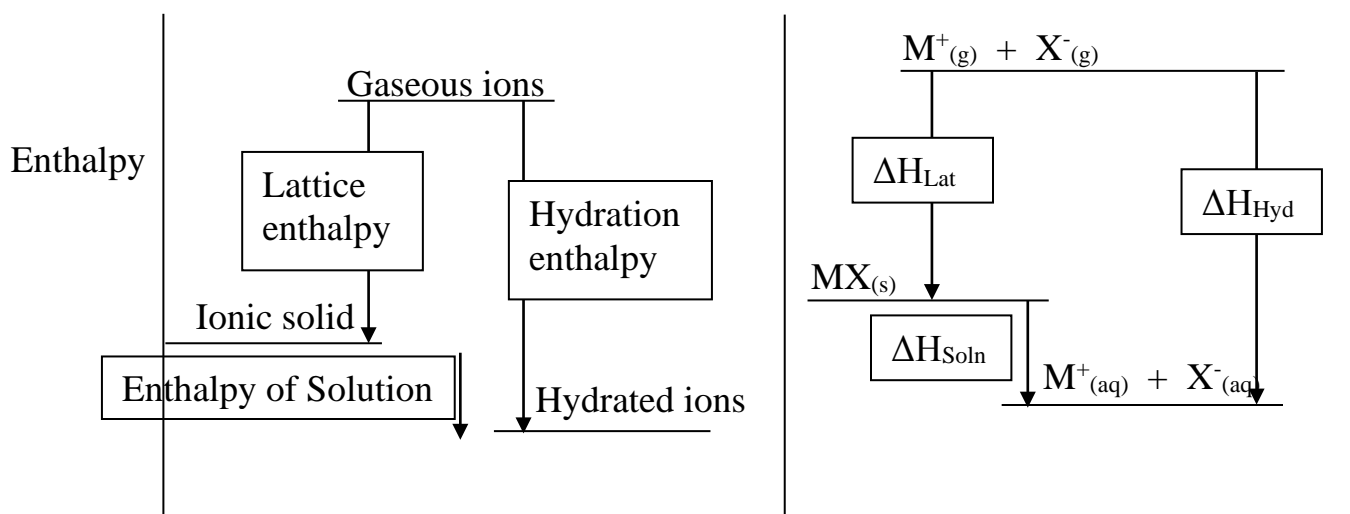
The process of dissolving is shown below.



Some ionic compounds do not dissolve in water because the electrostatic attraction between the ions is too great for the water molecules to overcome.

There are two key energy processes taking place as an ionic substance dissolves. The lattice has to be broken apart. This is an endothermic process. As new bonds form between the water

molecules and the ions an exothermic process takes place. The energy change that takes place when a solution dissolves is a balance of these two energy changes. This is illustrated in the diagram below.

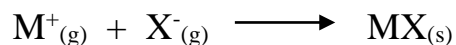


Definitions for Enthalpy Change in Solution

Lattice Enthalpy,

The heat energy given out (exothermic enthalpy change), when one mole of a crystal lattice is formed from separate, gaseous ions at an infinite distance apart under standard conditions.

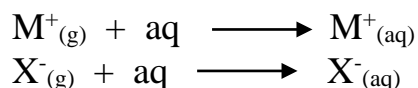
For one mole



Enthalpy of Hydration,

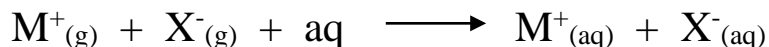
The heat energy given out when one mole of gaseous ions dissolve in an excess of water to form an infinitely dilute solution under standard conditions.

For one mole



Enthalpy of Solution,

The solution enthalpy is a measure of the amount of heat energy change when one mole of substance is dissolved in excess water.



Lattice Enthalpy

The lattice enthalpy is a measure of the strength of an ionic lattice. Some values of lattice enthalpy are given below.

Compound	Lattice energy/ kJmol^{-1}
NaF	-923
NaCl	-776
NaBr	-742
NaI	-699
KCl	-701
RbCl	-675
CsCl	-645
MgCl ₂	-2493
CaCl ₂	-2237
MgO	-3933
CaO	-3513

It can be seen that as the size of the anion increases, the value of the lattice energy drops. This is because the sum of the radii increases (distance between the centres of charge increases), and so electrostatic attraction decreases as and the lattice enthalpy decreases a consequence. Increasing size of cation also causes a decrease in the lattice enthalpy.

The higher the charge on either or both of the ions, the greater the lattice enthalpy. As the charge on the ion increases the electrostatic attraction also increases, so the lattice energy becomes greater.

Hydration Enthalpy

The hydration enthalpy is a measure of the attraction between an ion and water molecules. Some values of hydration enthalpy are given below.

Ion	Hydration enthalpy/ kJmol^{-1}	Ion	Hydration enthalpy/ kJmol^{-1}
Li ⁺	-499	F ⁻	-457
Na ⁺	-390	Cl ⁻	-381
K ⁺	-305	Br ⁻	-351
Mg ²⁺	-1891	I ⁻	-307
Ca ²⁺	-1562		
Al ³⁺	-4613		

It can be seen that as the size of the cation increases, the value of the hydration enthalpy drops. This is because the distance between the centre of ionic charge and the water molecule increases, and so electrostatic attraction decreases as and the hydration enthalpy decreases a consequence. Increasing size of anion also causes a decrease in the hydration enthalpy for similar reasons.

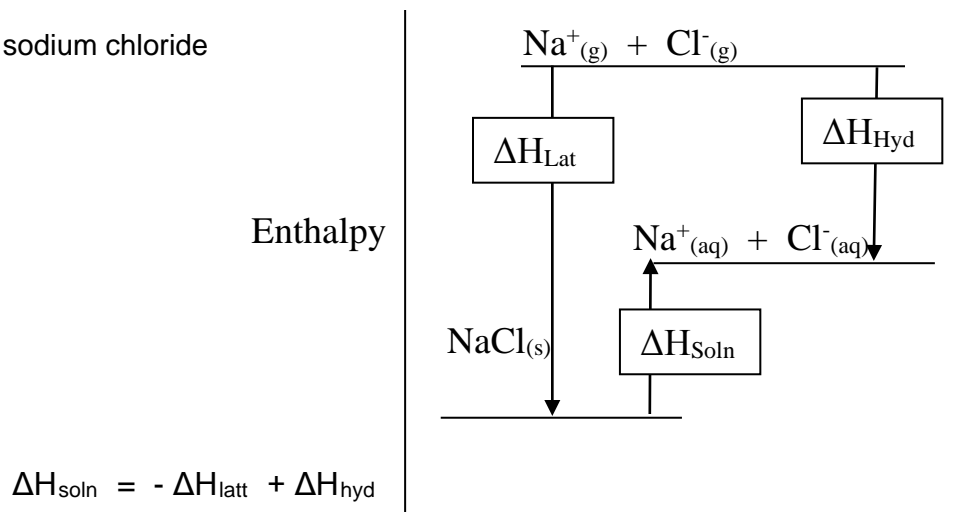
The higher the charge on the ion, the greater the hydration enthalpy. As the charge on the ion increases the electrostatic attraction also increases, so the hydration enthalpy becomes greater.

Enthalpy of Solution

The enthalpy of solution is related to the lattice and hydration enthalpies as follows:

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

Considering sodium chloride



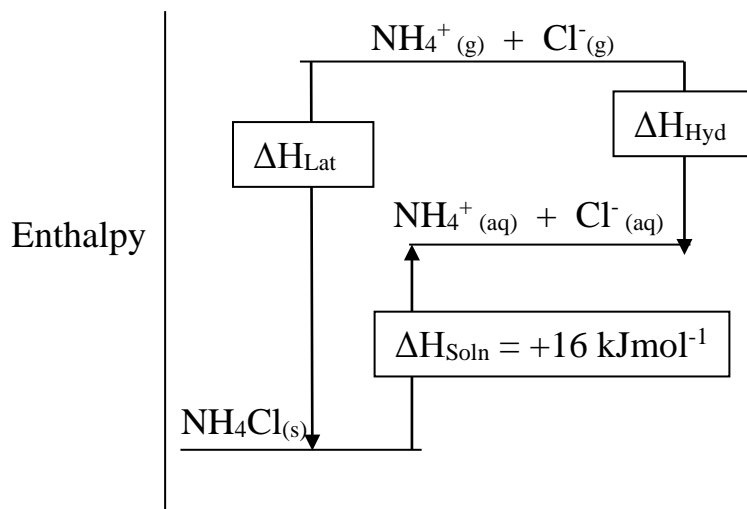
$$\Delta H_{\text{soln}}(\text{NaCl}) = -(-776) + (-390 + -381) = +5\text{kJmol}^{-1}$$

It can be seen that the enthalpy of solution for sodium chloride is endothermic. To understand why the process of dissolving occurs spontaneously it is necessary to look at the entropy changes involved in the process.

$$\Delta S_{\text{TOTAL}} = \Delta S_{\text{SYSTEM}} + \Delta S_{\text{SURROUNDINGS}}$$

Although this is an endothermic reaction making $\Delta S_{\text{SURROUNDINGS}}$ negative, the ΔS_{SYSTEM} has a high positive value because the process of dissolving means that a highly ordered ionic lattice becomes a much less ordered solution of ions.

The dissolving of ammonium chloride is even more endothermic with a ΔH_{soln} of $+16\text{kJmol}^{-1}$.



The values of system entropy and enthalpy of solution are shown below.

ΔS_{SYSTEM}	$+278.5 \text{ JK}^{-1}\text{mol}^{-1}$
ΔH_{soln}	$+16 \text{ kJmol}^{-1}$

So $\Delta S_{\text{SURROUNDINGS}} = -(+16)/298 = -0.0537 \text{ kJK}^{-1}\text{mol}^{-1}$ (or $-53.7 \text{ JK}^{-1}\text{mol}^{-1}$)

Calculating ΔS_{TOTAL} .

$$\Delta S_{\text{TOTAL}} = \Delta S_{\text{SYSTEM}} + \Delta S_{\text{SURROUNDINGS}}$$

$$\Delta S_{\text{TOTAL}} = (+278.5) + (-53.7) = +224.8 \text{ JK}^{-1}\text{mol}^{-1}$$

The positive value of ΔS_{TOTAL} allows us to predict that ammonium chloride will be soluble.