Edexcel

A - Level

Chemistry

CODE: (WCH11)

Topic 12

Entropy and energetics

12A 1 Introduction to entropy

WHAT MAKES A REACTION OCCUR?

Perhaps one of the most important questions to ask in chemistry is 'Will a reaction occur?'
We know that, once started, some chemical reactions simply 'go' with no further, continuous help from us.

For example, ammonia gas and hydrogen chloride gas react together at room temperature to form the white solid, ammonium chloride:

$$NH_3(g) + HCl(g) \rightarrow NH_4Cl(s)$$

Magnesium, once ignited, will burn in oxygen to form magnesium oxide:

$$Mg(s) + \tfrac{1}{2}O_2(g) \rightarrow MgO(s)$$

In other reactions, rather than the reactants changing completely into the products, a position of equilibrium is reached, with the final mixture containing a measurable amount of both reactants and products.

There are other types of reactions that simply do not occur at all, at least not without some help. For example:

- ammonium chloride does not spontaneously decompose into ammonia and hydrogen chloride
- magnesium oxide does not break apart to form magnesium and oxygen without some continuous intervention from us in the form of heating.

If we consider all of these types of reaction together, we see that the real difference between them is the position of equilibrium that is established. For some reactions, the position of equilibrium is so far over to the products side that, to all intents and purposes,

EXOTHERMIC AND ENDOTHERMIC REACTIONS

The reaction between magnesium and oxygen is exothermic and can be represented by the enthalpy level diagram shown in fig A.

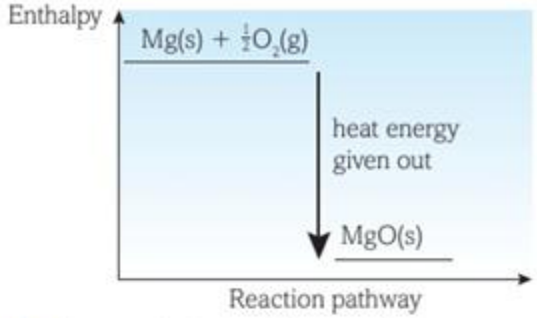


fig A Enthalpy level diagram for the reaction between magnesium and oxygen.

Let us consider the dimerisation of $NO_2(g)$ at 298 K:

$$2NO_2(g) \rightleftharpoons N_2O_4(g)$$

The enthalpy level diagram for this reaction is shown in **fig B**.

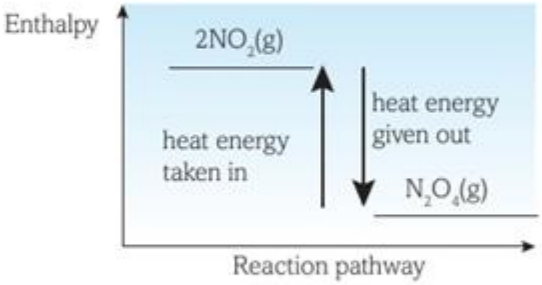


fig B Enthalpy level diagram for the dimerisation of NO_2.

The forward reaction of a reaction, N2O4(g), is exothermic and reaches equilibrium at 298 K. The backward reaction is endothermic, occurring at room temperature without intervention. Spontaneous endothermic reactions are driven by **entropy**, governed by the Second Law of Thermodynamics. Understanding **spontaneous processes** is crucial for understanding the driving force behind these reactions.

SPONTANEOUS PROCESSES

A spontaneous process occurs without continuous intervention, such as freezing water to form ice or mixing gases. The reverse of a spontaneous process cannot occur on its own, as a mixture of gases will never separate on its own. In chemistry, the key question is "Why does a reaction occur?", as spontaneous processes like ice freezing and gas mixing cannot be reversed.

The Second Law of Thermodynamics, introduced in the context of thermodynamics, explains the equilibrium state of a reaction, determining whether it favors the reactants or the products.

ENTROPY

The Second Law of Thermodynamics predicts processes and determines equilibrium positions. It introduces entropy, a property of matter associated with randomness or disorder. Entropy refers to the distribution of molecules and energy in all energy levels. Understanding entropy involves considering gas diffusion and its impact on chemical reactions.

DISTRIBUTION OF MOLECULES

Fig C shows two gas jars. The bottom one contains bromine gas and the top one contains air.

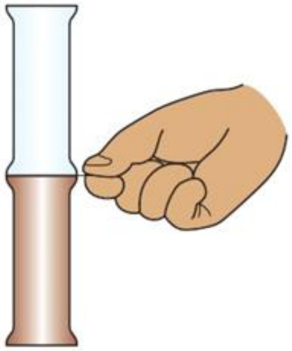
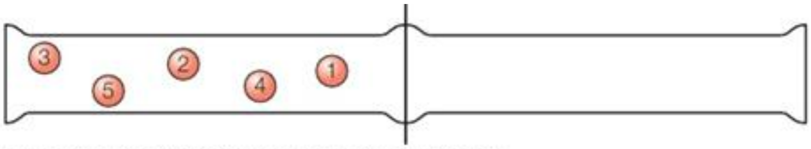
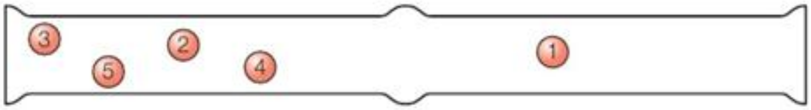


fig C Gas jars containing air and bromine

Remove the cover slip between two gas jars, allowing bromine and air to diffuse evenly. This is demonstrated in Fig D, where only five molecules are present in the left-hand jar.



Five molecules of bromine start off in the left-hand jar



As soon as the cover slip is removed, the molecules are free to move between the jars

▲ **fig D** Diffusion in a gas: one of the ways the molecules might rearrange. Remember that air molecules are also present but have not been shown.

Entropy is measured in units of JK-1mol-'.

Entropy measures the degree of randomness, so you would expect a gas to have a larger entropy than its liquid form, and a liquid to have a larger entropy than its solid form. The figures in table A show that this is the case for water vapour, water and ice.

SUBSTANCE	ENTROPY, S/J K^{-1} mol^{-1}
water vapour	189
water	70
ice	48

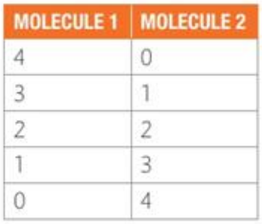
table A Entropies of water vapour, water and ice.

DISTRIBUTION OF ENERGY

The spreading out of molecules in diffusion is an increase in entropy, because the molecules become more randomly dispersed. In the same way, the spreading out of heat energy also represents an increase in entropy. Energy exists in 'packets' called quanta. You can have a whole number of quanta, but not halves or fractions of quanta.

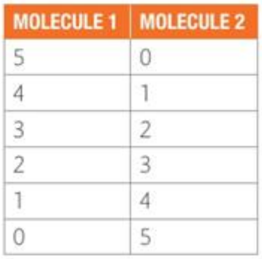
As an example, **table B** shows that there are five possible arrangements of four quanta between two molecules. **Table C** shows that there are six possible arrangements of five quanta between two molecules. **Table D** shows that there are 10 possible arrangements of three quanta between three molecules.

table B



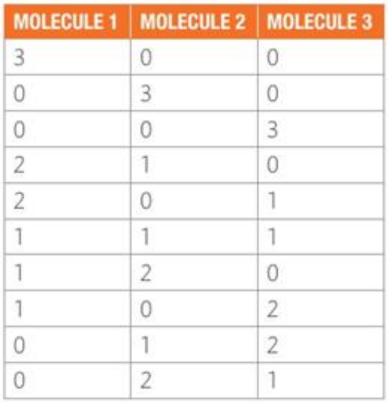
MOLECULE 1	MOLECULE 2
4	0
3	1
2	2
1	3
0	4

table C



MOLECULE 1	MOLECULE 2
5	0
4	1
3	2
2	3
1	4
0	5

table D



MOLECULE 1	MOLECULE 2	MOLECULE 3
3	0	0
0	3	0
0	0	3
2	1	0
2	0	1
1	1	1
1	2	0
1	0	2
0	1	2
0	2	1

table B 2 molecules, 4 quanta, 5 arrangements
table C 2 molecules, 5 quanta, 6 arrangements
table D 3 molecules, 3 quanta, 10 arrangements

PERFECT CRYSTALS

A 'perfect' crystal is one in which the internal lattice structure is the same at all times. In other words, the particles (atoms, molecules or ions) are fixed and are not moving in any way, rotating or vibrating. The Third Law of Thermodynamics states that the entropy of a perfect crystal at the temperature of absolute zero (i.e. 0 K) is zero.

THE SECOND LAW OF THERMODYNAMICS

The Second Law of Thermodynamics is sometimes misquoted. You may have come across the statement that in a spontaneous change, entropy always increases. This cannot be true: if it were, water could never freeze because this change involves a decrease in entropy.

Another example is the reaction between ammonia gas and hydrogen chloride gas:

$$NH_3(g) + HCl(g) \rightarrow NH_4Cl(s)$$

Entropy decreases in spontaneous gas formation at room temperature, but the Second Law of Thermodynamics states that total entropy increases in spontaneous processes, as explained in Section 12A.2.

12A 2 Total entropy

TOTAL ENTROPY CHANGE, ΔS $_{total}$

The total entropy change of a process comprises two components:

- the entropy change of the system, ΔS_{system}, and
- the entropy change of the surroundings, $\Delta S_{surroundings}$.

In a chemical reaction, the system is the species that are taking part in the reaction.
The surroundings is everything else. In practice, this usually means the reaction vessel, e.g. test tube or beaker, and the air in the laboratory.

The total entropy change is defined as the sum of the entropy change of the system and the entropy change of the surroundings. That is:

$$\Delta S_{total} = \Delta S_{system} + \Delta S_{surroundings}$$

For a reaction to be spontaneous, $\Delta_s$total must be positive. This is another way of expressing the Second Law of Thermodynamics.

ENTROPY CHANGE OF THE SYSTEM

Assystem is calculated using the expression:

ΔS_{system} is calculated using the expression:

$$\Delta S_{system} = \Sigma S\,(\text{products}) - \Sigma S\,(\text{reactants})$$

where S represents entropy and Σ represents 'the sum of".
The standard entropy values of some substances are shown in table A
Standard refers to conditions of 100 kPa and 298 K.

GAS	ENTROPY S° /J K^{-1} mol^{-1}
$H_2O(g)$	188.7
H_2	130.6
O_2	205.0
N_2	191.6
Cl_2	165.0
CO_2	213.6
NH_3	192.3

LIQUID	ENTROPY S° /J K^{-1} mol^{-1}
$H_2O(l)$	69.9
CH_3OH	239.7
CH_3CH_2OH	160.7
C_6H_6	172.8

SOLID	ENTROPY S° /J K^{-1} mol^{-1}
$H_2O(s)$	47.9
C(diamond)	2.4
C(graphite)	5.7
CaO	39.7
$CaCO_3$	92.9

table A

ENTROPY CHANGE OF THE SURROUNDINGS

The entropy change of the surroundings, $\Delta S_{surroundings}$, is related to the enthalpy change of the reaction, ΔH, by the expression:

$$\Delta S_{surroundings} = -\frac{\Delta H}{T}$$

where T is the temperature in kelvin.

For an *exothermic* reaction, where ΔH is negative, $\Delta S_{surroundings}$ will always be positive, so the entropy of the surroundings *increases*.

Conversely, for an *endothermic* reaction, $\Delta S_{surroundings}$ will always be negative, so the entropy of the surroundings *decreases*.

CALCULATING THE TOTAL ENTROPY CHANGE, A_S total

Now that we know how to calculate both ΔS_{system} and $\Delta S_{surroundings}$, we are in a position to calculate the total entropy change, ΔS_{total}, for a reaction.

SUMMARY

ΔS_{total} will be positive if:

- both $\Delta S_{surroundings}$ and ΔS_{system} are positive
- $\Delta S_{surroundings}$ is positive and ΔS_{system} is negative, but the magnitude of $\Delta S_{surroundings}$ > the magnitude of ΔS_{system}
- $\Delta S_{surroundings}$ is negative and ΔS_{system} is positive, but the magnitude of $\Delta S_{surroundings}$ < the magnitude of ΔS_{system}.

THERMODYNAMIC AND KINETIC STABILITY

The reaction between methane and oxygen is exothermic, and the total entropy change has a positive value:

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l) \qquad \Delta H_r^\circ = -890.3\ \text{kJ mol}^{-1}$$

$$\Delta S_{total} = +2.95\ \text{kJ mol}^{-1}$$

The added heat energy is required to overcome the high activation energy of the reaction.
A reaction mixture with a high activation energy, where a reaction will not take place spontaneously at room temperature, is said to be kinetically stable.

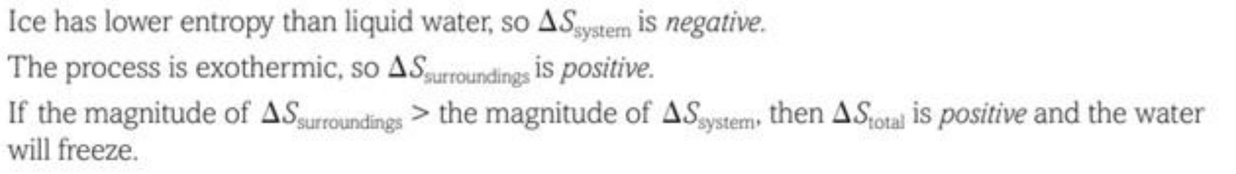
You can see here that a reaction mixture (such as methane and oxygen) can be thermodynamically unstable but kinetically stable, so a reaction does not take place under standard conditions.

THE ROLE OF TEMPERATURE

Entropy increases with heat energy, depending on the temperature of the system. Cold objects have less movement, while hotter objects increase entropy due to vigorous movement. The increase in entropy is less in hotter objects.

WHY DOES WATER FREEZE?

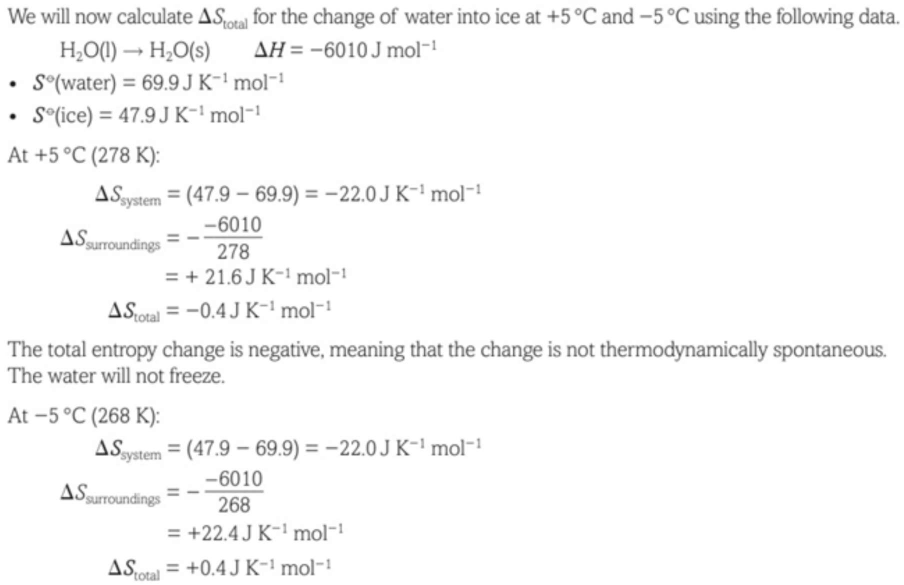
We will now apply these principles to explain why, under certain conditions, water will freeze.



Ice has lower entropy than liquid water, so ΔS_{system} is *negative*.

The process is exothermic, so $\Delta S_{\text{surroundings}}$ is *positive*.

If the magnitude of $\Delta S_{\text{surroundings}}$ > the magnitude of ΔS_{system}, then ΔS_{total} is *positive* and the water will freeze.



We will now calculate ΔS_{total} for the change of water into ice at +5 °C and −5 °C using the following data.

$H_2O(l) \rightarrow H_2O(s) \qquad \Delta H = -6010\ \text{J mol}^{-1}$

- $S^\circ(\text{water}) = 69.9\ \text{J K}^{-1}\ \text{mol}^{-1}$
- $S^\circ(\text{ice}) = 47.9\ \text{J K}^{-1}\ \text{mol}^{-1}$

At +5 °C (278 K):

$$\Delta S_{\text{system}} = (47.9 - 69.9) = -22.0\ \text{J K}^{-1}\ \text{mol}^{-1}$$

$$\Delta S_{\text{surroundings}} = -\frac{-6010}{278}$$

$$= +21.6\ \text{J K}^{-1}\ \text{mol}^{-1}$$

$$\Delta S_{\text{total}} = -0.4\ \text{J K}^{-1}\ \text{mol}^{-1}$$

The total entropy change is negative, meaning that the change is not thermodynamically spontaneous. The water will not freeze.

At −5 °C (268 K):

$$\Delta S_{\text{system}} = (47.9 - 69.9) = -22.0\ \text{J K}^{-1}\ \text{mol}^{-1}$$

$$\Delta S_{\text{surroundings}} = -\frac{-6010}{268}$$

$$= +22.4\ \text{J K}^{-1}\ \text{mol}^{-1}$$

$$\Delta S_{\text{total}} = +0.4\ \text{J K}^{-1}\ \text{mol}^{-1}$$

The total entropy change is positive, indicating thermodynamic spontaneous freezing. The entropy of the surroundings changes between +5°C and -5°C due to temperature change. Water is placed in a freezer to create ice because the entropy change of the surroundings is large enough to compensate for the decrease in entropy when water freezes.

12A 3 Understanding entropy changes

REACTIONS INVOLVING A CHANGE OF STATE

We have already mentioned that, in general, entropy increases in the order:
solid < liquid < gas
So, we would expect an increase in the entropy of the system if a gas is produced from a reaction involving a solid and/or a liquid.

EXAMPLE 1

When solid ammonium carbonate is added to pure ethanoic acid, bubbles of gas are rapidly produced. Despite its violent appearance, this is an endothermic reaction, as can be shown by placing a thermometer in the acid before the ammonium carbonate is added. The temperature falls considerably as the reaction takes place.

$$2CH_3COOH(l) + (NH_4)_2CO_3(s) \rightarrow 2CH_3COONH_4(aq) + H_2O(l) + CO_2(g)$$

Since the reaction is endothermic, $\Delta S_{surroundings}$ will be negative. However, there is a large increase in the entropy of the system, ΔS_{system}, because a gas is produced from a liquid and a solid. The magnitude of ΔS_{system} is greater than that of $\Delta S_{surroundings}$, and this makes ΔS_{total} positive, so the reaction is thermodynamically spontaneous.

DISSOLVING IONIC SOLIDS IN WATER

When an ionic solid dissolves in water, two changes take place:

- the lattice structure is broken down, and
- the ions become hydrated.

The solubility of an ionic solid is determined by the total entropy change for the solid.

$$\Delta S_{total} = \Delta S_{system} + \Delta S_{surroundings}$$

Since $\Delta S_{surroundings} = -\frac{\Delta_{sol}H}{T}$

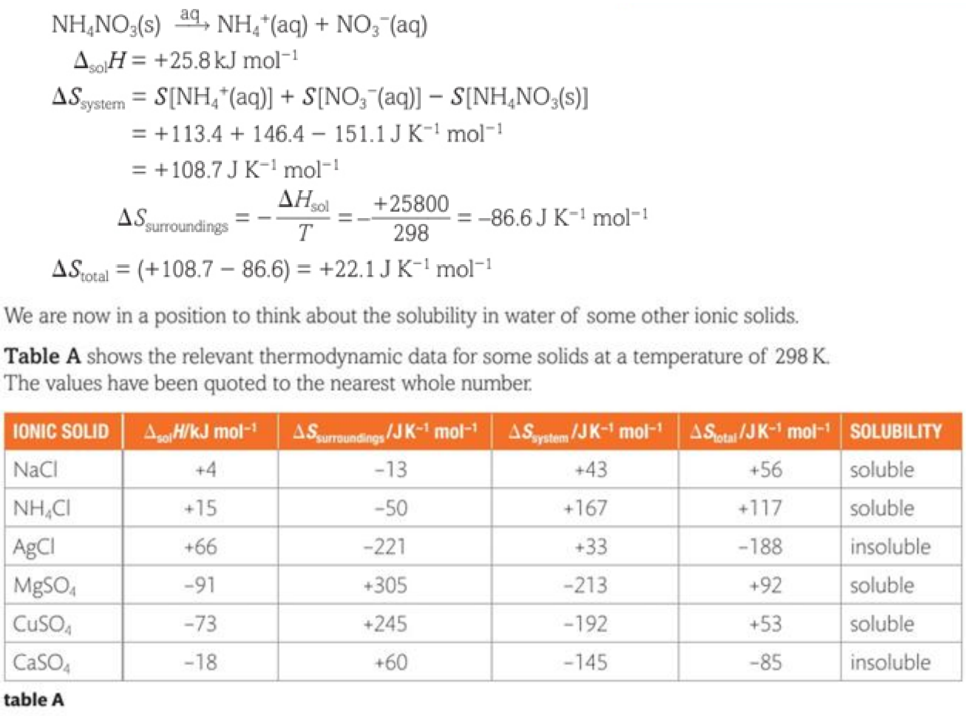
this expression becomes:

$$\Delta S_{total} = \Delta S_{system} - \frac{\Delta_{sol}H}{T}$$

The value of ΔS_{total}, and hence the solubility of the solid, depends on the values of three factors:

- the entropy change of the system, ΔS_{system}
- the enthalpy change of solution, $\Delta_{sol}H$
- the temperature, in kelvin, of the water, T.

Let us have a close look at the dissolving of ammonium nitrate crystals in water at a temperature of 298 K.



$$NH_4NO_3(s) \xrightarrow{aq} NH_4^+(aq) + NO_3^-(aq)$$

$$\Delta_{sol}H = +25.8\text{ kJ mol}^{-1}$$

$$\Delta S_{system} = S[NH_4^+(aq)] + S[NO_3^-(aq)] - S[NH_4NO_3(s)]$$

$$= +113.4 + 146.4 - 151.1\text{ J K}^{-1}\text{ mol}^{-1}$$

$$= +108.7\text{ J K}^{-1}\text{ mol}^{-1}$$

$$\Delta S_{surroundings} = -\frac{\Delta H_{sol}}{T} = -\frac{+25800}{298} = -86.6\text{ J K}^{-1}\text{ mol}^{-1}$$

$$\Delta S_{total} = (+108.7 - 86.6) = +22.1\text{ J K}^{-1}\text{ mol}^{-1}$$

We are now in a position to think about the solubility in water of some other ionic solids.

Table A shows the relevant thermodynamic data for some solids at a temperature of 298 K. The values have been quoted to the nearest whole number.

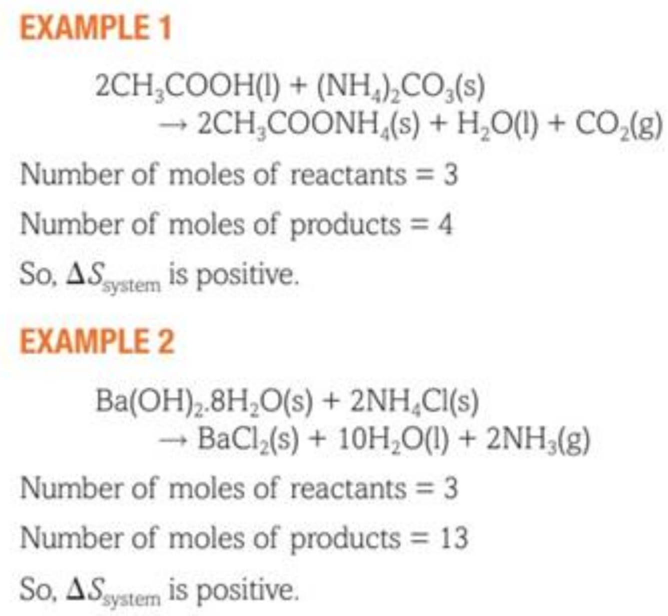
IONIC SOLID	$\Delta_{sol}H$/kJ mol^{-1}	$\Delta S_{surroundings}$/J K^{-1} mol^{-1}	ΔS_{system}/J K^{-1} mol^{-1}	ΔS_{total}/J K^{-1} mol^{-1}	SOLUBILITY
NaCl	+4	-13	+43	+56	soluble
NH_4Cl	+15	-50	+167	+117	soluble
AgCl	+66	-221	+33	-188	insoluble
$MgSO_4$	-91	+305	-213	+92	soluble
$CuSO_4$	-73	+245	-192	+53	soluble
$CaSO_4$	-18	+60	-145	-85	insoluble

table A

REACTIONS INVOLVING A CHANGE IN NUMBER OF MOLES FROM REACTANTS TO PRODUCTS

If you increase the number of moles that you have, you automatically increase the number of particles (i.e. atoms, molecules or ions) present. This will result in an increase in the number of ways that the particles can be arranged, and this increases the entropy of the system, making AS system positive.

We will now look again at the reactions shown above, but this time we will consider the change in the number of moles from reactants to products.



EXAMPLE 1

$$2CH_3COOH(l) + (NH_4)_2CO_3(s) \rightarrow 2CH_3COONH_4(s) + H_2O(l) + CO_2(g)$$

Number of moles of reactants = 3

Number of moles of products = 4

So, ΔS_{system} is positive.

EXAMPLE 2

$$Ba(OH)_2.8H_2O(s) + 2NH_4Cl(s) \rightarrow BaCl_2(s) + 10H_2O(l) + 2NH_3(g)$$

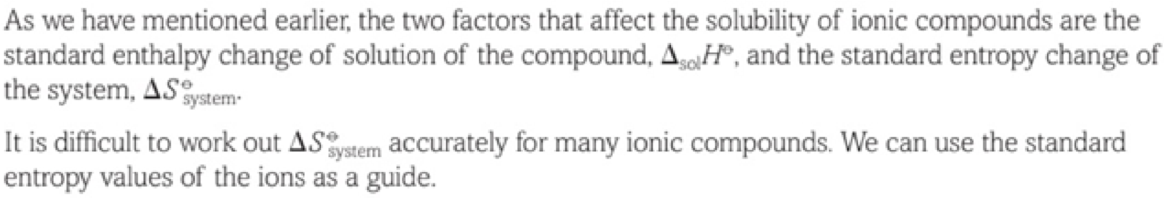
Number of moles of reactants = 3

Number of moles of products = 13

So, ΔS_{system} is positive.

SOLUBILITY TRENDS IN GROUP 2

In Topic 8 (Book 1: IAS), we mentioned that for Group 2 the solubility of the metal hydroxides increases down the group and the solubility of the metal sulfates decreases down the group. We can now explain the reason for these trends in solubility.

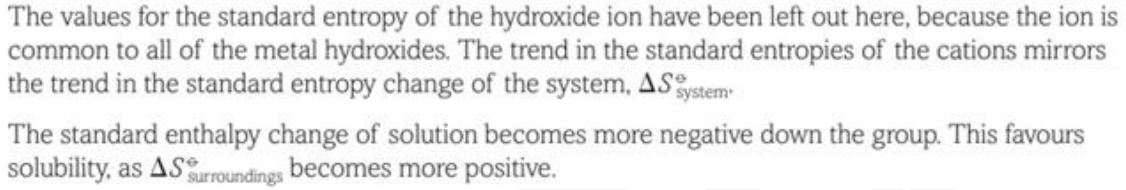


As we have mentioned earlier, the two factors that affect the solubility of ionic compounds are the standard enthalpy change of solution of the compound, $\Delta_{sol}H^\circ$, and the standard entropy change of the system, ΔS°_{system}.

It is difficult to work out ΔS°_{system} accurately for many ionic compounds. We can use the standard entropy values of the ions as a guide.

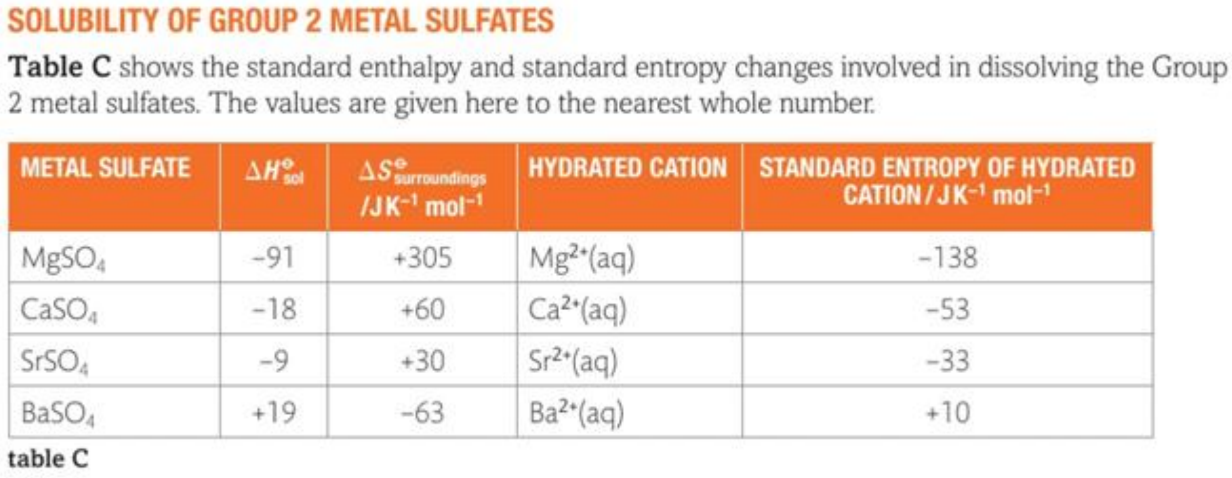
SOLUBILITY OF GROUP 2 METAL HYDROXIDES

Table B shows the standard enthalpy and standard entropy changes involved in dissolving the Group 2 metal hydroxides. The values are given here to the nearest whole number.



The values for the standard entropy of the hydroxide ion have been left out here, because the ion is common to all of the metal hydroxides. The trend in the standard entropies of the cations mirrors the trend in the standard entropy change of the system, ΔS°_{system}.

The standard enthalpy change of solution becomes more negative down the group. This favours solubility, as $\Delta S^\circ_{surroundings}$ becomes more positive.

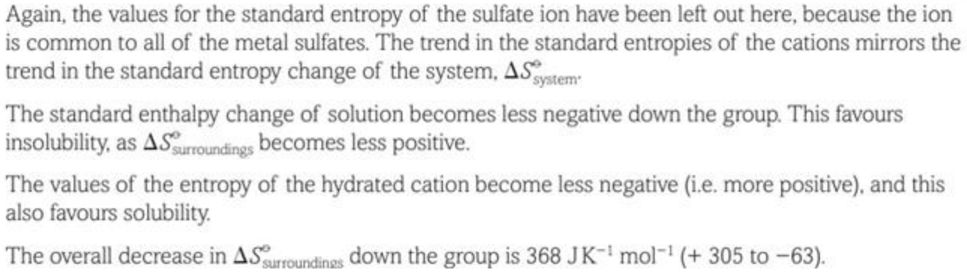


SOLUBILITY OF GROUP 2 METAL SULFATES

Table C shows the standard enthalpy and standard entropy changes involved in dissolving the Group 2 metal sulfates. The values are given here to the nearest whole number.

METAL SULFATE	ΔH°_{sol}	$\Delta S^\circ_{surroundings}$ /J K^{-1} mol^{-1}	HYDRATED CATION	STANDARD ENTROPY OF HYDRATED CATION / J K^{-1} mol^{-1}
$MgSO_4$	−91	+305	$Mg^{2+}(aq)$	−138
$CaSO_4$	−18	+60	$Ca^{2+}(aq)$	−53
$SrSO_4$	−9	+30	$Sr^{2+}(aq)$	−33
$BaSO_4$	+19	−63	$Ba^{2+}(aq)$	+10

table C



Again, the values for the standard entropy of the sulfate ion have been left out here, because the ion is common to all of the metal sulfates. The trend in the standard entropies of the cations mirrors the trend in the standard entropy change of the system, ΔS°_{system}.

The standard enthalpy change of solution becomes less negative down the group. This favours insolubility, as $\Delta S^\circ_{surroundings}$ becomes less positive.

The values of the entropy of the hydrated cation become less negative (i.e. more positive), and this also favours solubility.

The overall decrease in $\Delta S^\circ_{surroundings}$ down the group is 368 J K^{-1} mol^{-1} (+ 305 to −63).

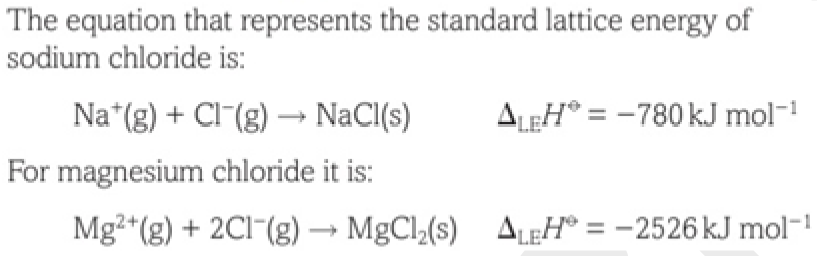
12B 1 LATTICE ENERGY, A_{LE}H AND BORN-HABER CYCLES

LATTICE ENERGY

In Book 1, we saw that bond enthalpies can be used as a measure of the strength of the covalent bonding in molecules. The equivalent energy change for ionic bonding in ionic compounds is lattice energy, ALEH (or lattice enthalpy).

The lattice energy of a compound is the energy change when one mole of the ionic solid is formed from its gaseous ions. If standard conditions of 100 kPa and a stated temperature (usually 298 K) are applied then the energy change is called the **standard lattice energy.**

The equation that represents the standard lattice energy of sodium chloride is:



The equation that represents the standard lattice energy of sodium chloride is:

$$Na^+(g) + Cl^-(g) \rightarrow NaCl(s) \qquad \Delta_{LE}H^{\ominus} = -780\,kJ\,mol^{-1}$$

For magnesium chloride it is:

$$Mg^{2+}(g) + 2Cl^-(g) \rightarrow MgCl_2(s) \qquad \Delta_{LE}H^{\ominus} = -2526\,kJ\,mol^{-1}$$

FACTORS AFFECTING THE MAGNITUDE OF LATTICE ENERGY

The lattice energy of magnesium chloride is larger than that of sodium chloride due to factors such as the charge of magnesium ions, the number of cation-to-anion interactions, and the distance between cations and anions. These factors are influenced by the relative sizes of the ions and the type of lattice structure, as shown in Table A.

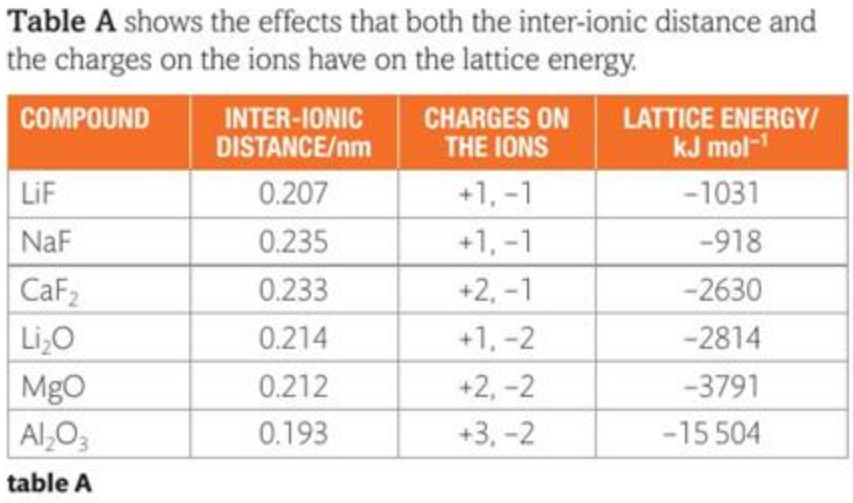


Table A shows the effects that both the inter-ionic distance and the charges on the ions have on the lattice energy.

COMPOUND	INTER-IONIC DISTANCE/nm	CHARGES ON THE IONS	LATTICE ENERGY/ kJ mol^{-1}
LiF	0.207	+1, −1	−1031
NaF	0.235	+1, −1	−918
CaF_2	0.233	+2, −1	−2630
Li_2O	0.214	+1, −2	−2814
MgO	0.212	+2, −2	−3791
Al_2O_3	0.193	+3, −2	−15 504

table A

STANDARD ENTHALPY CHANGE OF ATOMISATION, Δ_{at} Hɵ

The enthalpy change measured at a stated temperature (usually 298 K) and 100 kPa when one mole of gaseous atoms is formed from an element in its standard state is called the standard enthalpy change of atomisation of the element (see Topic 6 (Book 1: IAS)). It is given the symbol Δ_{at} Hɵ

Equations representing some standard enthalpy changes of atomisation at 298 K are given below.

$\text{C(s)} \rightarrow \text{C(g)}$ $\Delta_{at}H^{\ominus} = +717\ \text{kJ mol}^{-1}$

$\text{Na(s)} \rightarrow \text{Na(g)}$ $\Delta_{at}H^{\ominus} = +107\ \text{kJ mol}^{-1}$

$\frac{1}{2}\text{H}_2\text{(g)} \rightarrow \text{H(g)}$ $\Delta_{at}H^{\ominus} = +218\ \text{kJ mol}^{-1}$

$\frac{1}{2}\text{Cl}_2\text{(g)} \rightarrow \text{Cl(g)}$ $\Delta_{at}H^{\ominus} = +122\ \text{kJ mol}^{-1}$

ELECTRON AFFINITY

The first **electron affinity** of an element, 1st *EA*, is the energy change when each atom in one mole of atoms in the gaseous state gains an electron to form a −1 ion.

The equations below represent the first electron affinities of som elements.

$\text{Cl(g)} + e^- \rightarrow \text{Cl}^-\text{(g)}$ $1^{st}\ EA = -349\ \text{kJ mol}^{-1}$

$\text{Br(g)} + e^- \rightarrow \text{Br}^-\text{(g)}$ $1^{st}\ EA = -325\ \text{kJ mol}^{-1}$

$\text{O(g)} + e^- \rightarrow \text{O}^-\text{(g)}$ $1^{st}\ EA = -141\ \text{kJ mol}^{-1}$

The first electron affinity has a negative value for many elements, including the alkali metals. Examples include:

$\text{Li(g)} + e^- \rightarrow \text{Li}{-}\text{(g)}$ $1^{st}\ EA = -60\ \text{kJ mol}^{-1}$

and

$\text{Na(g)} + e^- \rightarrow \text{Na}^-\text{(g)}$ $1^{st}\ EA = -53\ \text{kJ mol}^{-1}$

BORN-HABER CYCLES

We are now in a position to consider the overall energy changes that take place when an ionic compound is made from its elements. These energy changes are summarised in an energy level diagram called the Born-Haber cycle. Fig A shows the Born-Haber cycle for sodium chloride.

The cycle includes the following energy changes, all of which can be determined experimentally:

- The enthalpy change of formation of NaCl(s), $\Delta_f H[\text{NaCl(s)}] = -411\ \text{kJ mol}^{-1}$
- $\Delta_{at}H[\text{Na(s)}] = +107\ \text{kJ mol}^{-1}$
- the first ionisation energy, $1^{st}\ IE[\text{Na(g)}] = +496\ \text{kJ mol}^{-1}$
- $\Delta_{at}H[\text{Cl}_2\text{(g)}] = +122\ \text{kJ mol}^{-1}$
- $EA[\text{Cl(g)}] = -349\ \text{kJ mol}^{-1}$

Applying Hess's Law to the cycle gives us:

$$+107 + 496 + 122 + (-349) + \Delta_{LE}H = -411$$

Hence:

$$\begin{aligned}\Delta_{LE}H[\text{NaCl(s)}] &= -411 - 107 - 496 - 122 + 349\ \text{kJ mol}^{-1}\\ &= -787\ \text{kJ mol}^{-1}\end{aligned}$$

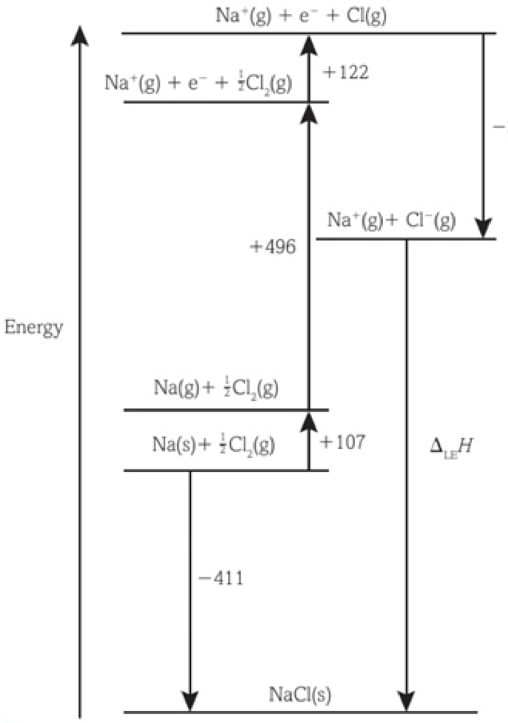
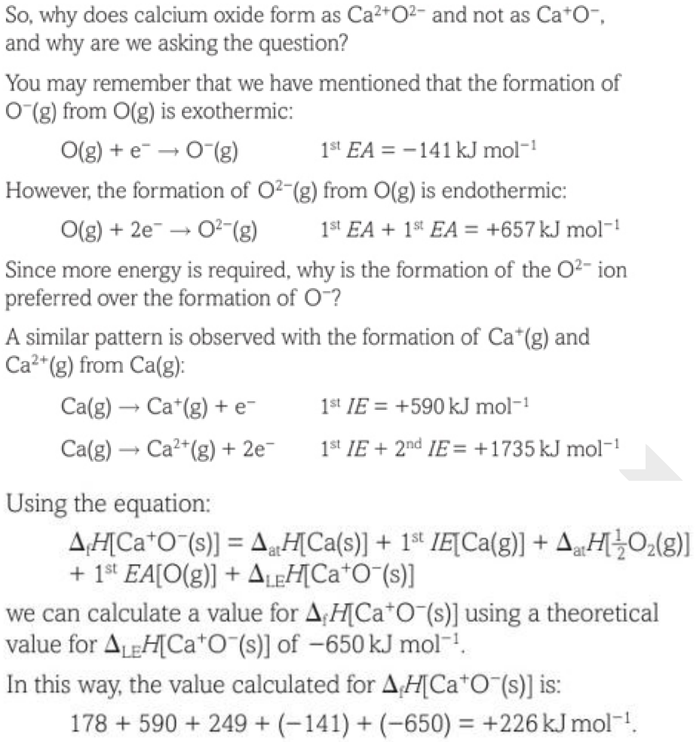


fig A Born-Haber cycle for sodium chloride.

WHY IS CALCIUM OXIDE $Ca^{2+}O^{2-}$ AND NOT $Ca^{+}O^{-}$?

Calcium oxide is not necessarily Ca2+02- due to its stable noble gas electronic configuration. Many ions exist in stable compounds, especially transition metal cations, which do not have a noble gas electronic configuration. The reason for calcium oxide's formation as Ca2+02- is that the formation of O(g) from O(g) is exothermic.



So, why does calcium oxide form as $Ca^{2+}O^{2-}$ and not as $Ca^{+}O^{-}$, and why are we asking the question?

You may remember that we have mentioned that the formation of $O^{-}(g)$ from O(g) is exothermic:

$$O(g) + e^- \rightarrow O^-(g) \qquad 1^{st}\ EA = -141\ kJ\ mol^{-1}$$

However, the formation of $O^{2-}(g)$ from O(g) is endothermic:

$$O(g) + 2e^- \rightarrow O^{2-}(g) \qquad 1^{st}\ EA + 1^{st}\ EA = +657\ kJ\ mol^{-1}$$

Since more energy is required, why is the formation of the O^{2-} ion preferred over the formation of O^-?

A similar pattern is observed with the formation of $Ca^+(g)$ and $Ca^{2+}(g)$ from Ca(g):

$$Ca(g) \rightarrow Ca^+(g) + e^- \qquad 1^{st}\ IE = +590\ kJ\ mol^{-1}$$

$$Ca(g) \rightarrow Ca^{2+}(g) + 2e^- \qquad 1^{st}\ IE + 2^{nd}\ IE = +1735\ kJ\ mol^{-1}$$

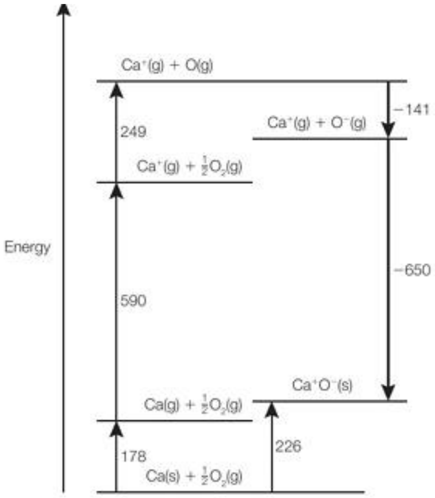
Using the equation:

$$\Delta_f H[Ca^+O^-(s)] = \Delta_{at}H[Ca(s)] + 1^{st}\ IE[Ca(g)] + \Delta_{at}H[\tfrac{1}{2}O_2(g)] + 1^{st}\ EA[O(g)] + \Delta_{LE}H[Ca^+O^-(s)]$$

we can calculate a value for $\Delta_f H[Ca^+O^-(s)]$ using a theoretical value for $\Delta_{LE}H[Ca^+O^-(s)]$ of $-650\ kJ\ mol^{-1}$.

In this way, the value calculated for $\Delta_f H[Ca^+O^-(s)]$ is:

$$178 + 590 + 249 + (-141) + (-650) = +226\ kJ\ mol^{-1}.$$



ig B Born-Haber cycle for $Ca^+O^-(s)$.

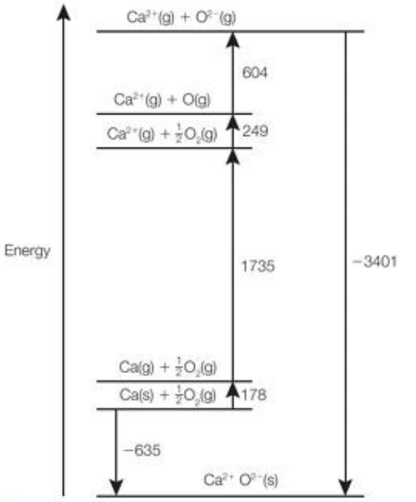


fig C Born-Haber cycle for $Ca^{2+}O^{2-}(s)$.

12B 2 Experimental and theoretical lattice energy

EXPERIMENTAL LATTICE ENERGY

The Born-Haber cycle allows us to calculate a value for the lattice energy of an ionic compound from knowledge of the other energy changes, all of which can be determined experimentally. The value of the lattice energy calculated this way is called the experimental lattice energy.

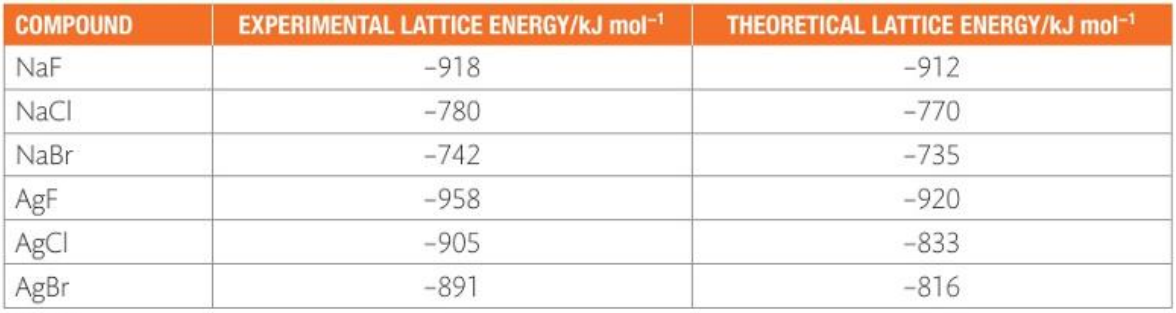
THEORETICAL LATTICE ENERGY

The type of lattice structure and the inter-ionic distance can be found by X-ray crystallography. Using this information, it is possible for us to calculate a value for the lattice energy of an ionic compound. However, we first need to make the following assumptions.

- The ions are in contact with one another.
- The ions are perfectly spherical.
- The charge on each ion is evenly distributed around the centre so that each ion can be considered as point charges.

A value for the theoretical lattice energy can be calculated using the principles of electrostatics. There are three main methods for performing such calculations. If you are interested, you can research them under the headings of the 'Born-Landé equation', the 'Born-Mayer equation' and the 'Kapustinskii equation'.

Table A shows a comparison of the experimental lattice energies (obtained by using a Born-Haber cycle) with the theoretical lattice energies (calculated using the principles of electrostatics) for various compounds.



COMPOUND	EXPERIMENTAL LATTICE ENERGY/kJ mol^{-1}	THEORETICAL LATTICE ENERGY/kJ mol^{-1}
NaF	–918	–912
NaCl	–780	–770
NaBr	–742	–735
AgF	–958	–920
AgCl	–905	–833
AgBr	–891	–816

table A

The covalency in bonding is caused by polarisation of the anion by the cation. Polarisation results in distortion of the electron density within the anion, resulting in a higher electron density near the cation. This means that there is some electron density existing between the two ions. In other words, there will be a degree of covalent bonding in the compound.

EXTENT OF COVALENT CHARACTER: POLARISATION OF THE ANION

In an ionic lattice, the positive ion (cation) will attract the electrons of the anion. If the electrons are pulled towards the cation, the anion is said to be polarised because the even distribution of its electron density has been distorted (fig A).

The extent to which an anion is polarised by a cation depends on several factors. The two main factors are summarised below. These are known as Fajan's Rules.

Polarisation will be increased by:

- a high charge and small size of the cation (i.e. a high charge density of the cation)
- a high charge and large size of the anion.

HIGH CHARGE AND SMALL SIZE OF CATION

The ability of a cation to attract electrons from the anion towards itself is called its 'polarising power'. A cation with a high charge and a small radius has a large polarising power. An approximate value for the polarising power of a cation can be obtained by calculating its charge density (sometimes called surface charge density).

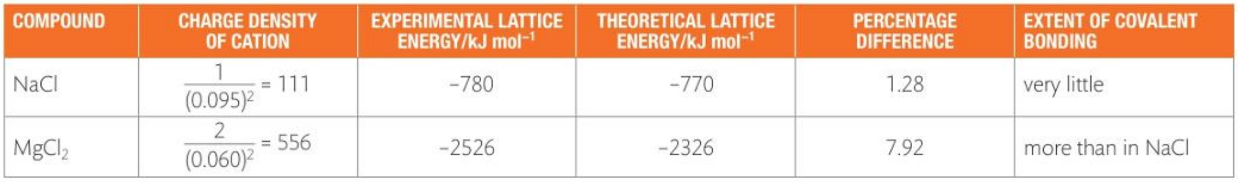
The charge density of a cation is the charge divided by the surface area of the ion. If the ion is assumed to be a sphere, its surface area is equal to 4πr2, where r is the ionic radius.

A rough approximation of the charge density can be determined by dividing the charge by the square of its ionic radius. This calculation is beyond the scope of your International A Level course.

$$\text{charge density} \sim \frac{\text{charge}}{r^2}$$

Table B compares the extent of covalent bonding in sodium chloride and magnesium chloride.

an anion in an ionic lattice.



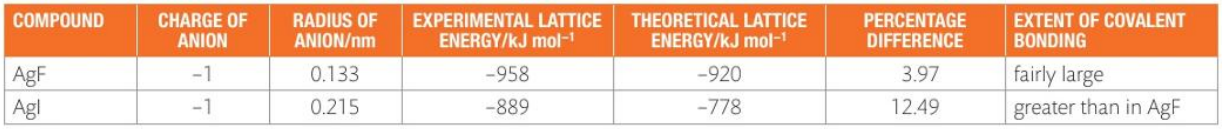
COMPOUND	CHARGE DENSITY OF CATION	EXPERIMENTAL LATTICE ENERGY/kJ mol^{-1}	THEORETICAL LATTICE ENERGY/kJ mol^{-1}	PERCENTAGE DIFFERENCE	EXTENT OF COVALENT BONDING
NaCl	$\frac{1}{(0.095)^2} = 111$	−780	−770	1.28	very little
$MgCl_2$	$\frac{2}{(0.060)^2} = 556$	−2526	−2326	7.92	more than in NaCl

table B

HIGH CHARGE AND LARGE SIZE OF THE ANION

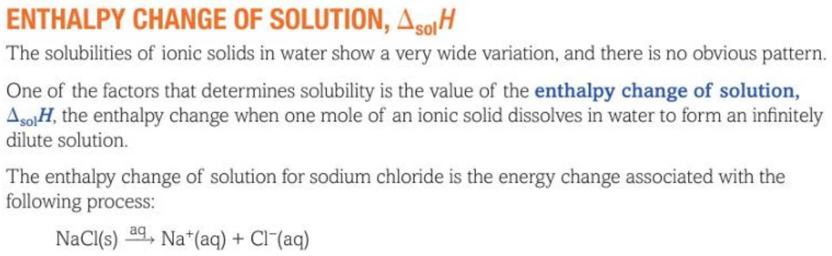
The ease with which an anion is polarised depends on its charge and its size. Anions with a large charge and a large size are polarised most easily.
Table C compares the extent of covalent bonding in silver fluoride and silver iodide.

Table C compares the extent of covalent bonding in silver fluoride and silver iodide.



COMPOUND	CHARGE OF ANION	RADIUS OF ANION/nm	EXPERIMENTAL LATTICE ENERGY/kJ mol^{-1}	THEORETICAL LATTICE ENERGY/kJ mol^{-1}	PERCENTAGE DIFFERENCE	EXTENT OF COVALENT BONDING
AgF	−1	0.133	−958	−920	3.97	fairly large
AgI	−1	0.215	−889	−778	12.49	greater than in AgF

table C



ENTHALPY CHANGE OF SOLUTION, $\Delta_{sol}H$

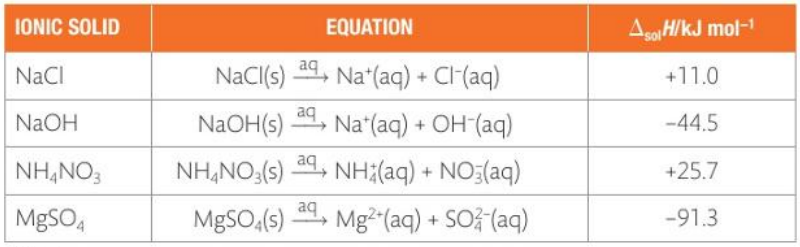
The solubilities of ionic solids in water show a very wide variation, and there is no obvious pattern.

One of the factors that determines solubility is the value of the **enthalpy change of solution,** $\Delta_{sol}H$, the enthalpy change when one mole of an ionic solid dissolves in water to form an infinitely dilute solution.

The enthalpy change of solution for sodium chloride is the energy change associated with the following process:

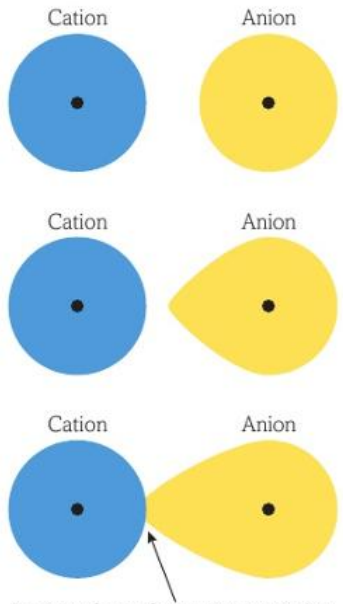
$$NaCl(s) \xrightarrow{aq} Na^+(aq) + Cl^-(aq)$$

The relative importance of these two processes (endothermic and exothermic) changes with dilution, and they affect the value of $\Delta_{sol} H$ in a complicated way. For this reason, the quoted values for $\Delta_{sol} H$ refer to an infinitely dilute solution. This value cannot be determined experimentally and is found by a process of extrapolation.



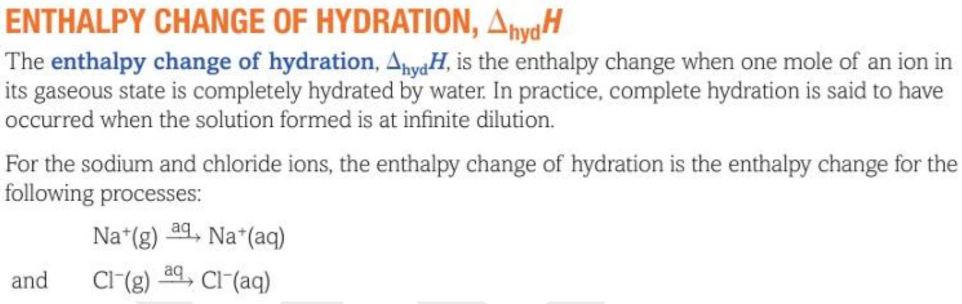
IONIC SOLID	EQUATION	$\Delta_{sol}H$/kJ mol^{-1}
NaCl	$NaCl(s) \xrightarrow{aq} Na^+(aq) + Cl^-(aq)$	+11.0
NaOH	$NaOH(s) \xrightarrow{aq} Na^+(aq) + OH^-(aq)$	−44.5
NH_4NO_3	$NH_4NO_3(s) \xrightarrow{aq} NH_4^+(aq) + NO_3^-(aq)$	+25.7
$MgSO_4$	$MgSO_4(s) \xrightarrow{aq} Mg^{2+}(aq) + SO_4^{2-}(aq)$	−91.3

table A



Region where electrons are existing in an area of orbital overlap

▲ **fig A** A representation of a cation attracting the electrons of an anion in an ionic lattice.



ENTHALPY CHANGE OF HYDRATION, $\Delta_{hyd}H$

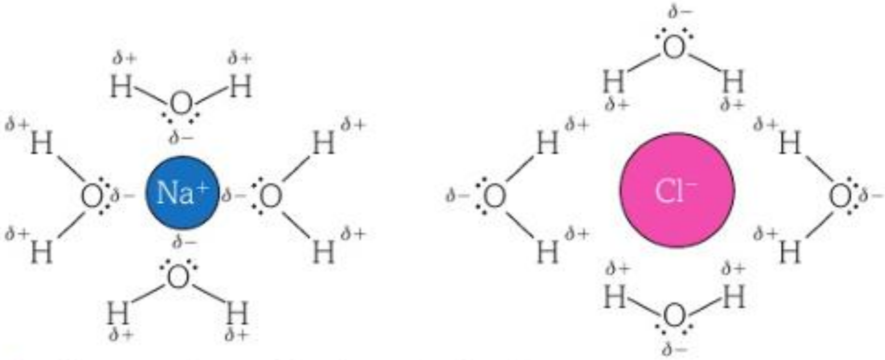
The **enthalpy change of hydration**, $\Delta_{hyd}H$, is the enthalpy change when one mole of an ion in its gaseous state is completely hydrated by water. In practice, complete hydration is said to have occurred when the solution formed is at infinite dilution.

For the sodium and chloride ions, the enthalpy change of hydration is the enthalpy change for the following processes:

$$Na^+(g) \xrightarrow{aq} Na^+(aq)$$

and

$$Cl^-(g) \xrightarrow{aq} Cl^-(aq)$$

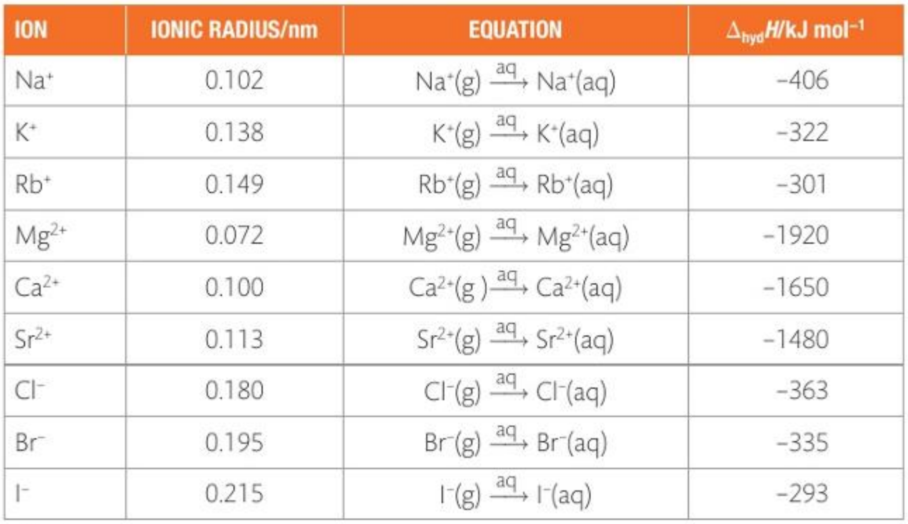


▲ **fig A** Hydration of sodium and chloride ions.

In the case of the sodium ion, the interaction is the result of the attraction between the δ- oxygen atom of the water molecule and the cation. Such an interaction is often referred to as an ion-dipole interaction. With some other positive ions, notably those of the transition metals, a dative covalent bond is formed between the water molecule and the cation using one of the lone pairs of electrons on the oxygen atom.

Ion-dipole interactions exist in the hydrated chloride ion, but some hydrogen bonds are also formed between the δ+ hydrogen atoms of the water molecules and the chloride ion, making use of the lone pairs of electrons on the chloride ion (see Topic 7 (Book 1: IAS)).

Enthalpy changes of hydration are always negative. Some examples are given in table B.



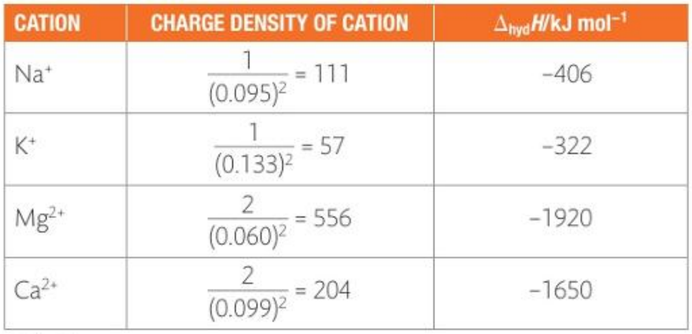
ION	IONIC RADIUS/nm	EQUATION	$\Delta_{hyd}H$/kJ mol^{-1}
Na^+	0.102	$Na^+(g) \xrightarrow{aq} Na^+(aq)$	−406
K^+	0.138	$K^+(g) \xrightarrow{aq} K^+(aq)$	−322
Rb^+	0.149	$Rb^+(g) \xrightarrow{aq} Rb^+(aq)$	−301
Mg^{2+}	0.072	$Mg^{2+}(g) \xrightarrow{aq} Mg^{2+}(aq)$	−1920
Ca^{2+}	0.100	$Ca^{2+}(g) \xrightarrow{aq} Ca^{2+}(aq)$	−1650
Sr^{2+}	0.113	$Sr^{2+}(g) \xrightarrow{aq} Sr^{2+}(aq)$	−1480
Cl^-	0.180	$Cl^-(g) \xrightarrow{aq} Cl^-(aq)$	−363
Br^-	0.195	$Br^-(g) \xrightarrow{aq} Br^-(aq)$	−335
I^-	0.215	$I^-(g) \xrightarrow{aq} I^-(aq)$	−293

table B

FACTORS AFFECTING THE MAGNITUDE OF THE HYDRATION ENTHALPY

The magnitude of hydration energy is more negative for 2+ ions than 1+ ions, due to the stronger interaction between them and water molecules. As ionic radius increases, the magnitude of Δ_{hyd} H decreases, indicating an increase in ionic radius. This can be explained using an electrostatic model for hydration, where larger ions decrease the electrostatic force of attraction, resulting in decreased energy released during hydration.

As with lattice energy, there is a strong correlation between $\Delta_{hyd}H$ and the charge densities of the ions. **Table C** shows this for four cations.



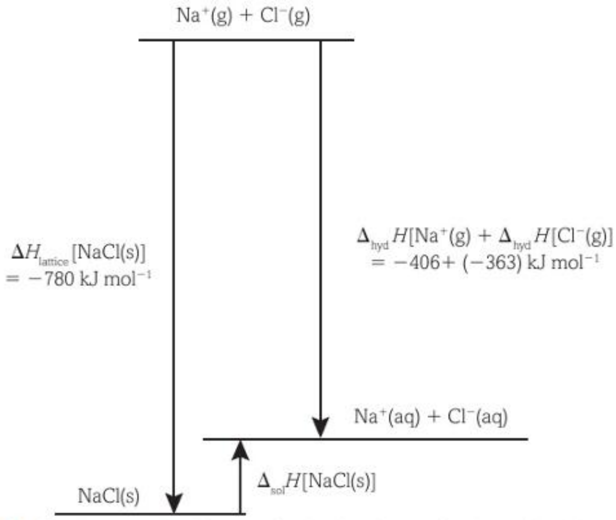
CATION	CHARGE DENSITY OF CATION	$\Delta_{hyd}H$/kJ mol^{-1}
Na^+	$\frac{1}{(0.095)^2} = 111$	−406
K^+	$\frac{1}{(0.133)^2} = 57$	−322
Mg^{2+}	$\frac{2}{(0.060)^2} = 556$	−1920
Ca^{2+}	$\frac{2}{(0.099)^2} = 204$	−1650

table C

The greater the charge density of the cation, the more negative the value of $\Delta_{hyd}H$.

RELATIONSHIP BETWEEN $\Delta_{sol}H$, $\Delta_{hyd}H$ AND $\Delta_{LE}H$

The relationship between $\Delta_{sol}H$, $\Delta_{hyd}H$ and $\Delta_{LE}H$ is best shown by an energy level diagram similar to that of a Born–Haber cycle as shown in **fig B**.



▲ **fig B** Energy level diagram for the dissolution of sodium chloride.

Applying Hess's Law:

$$\Delta_{LE}H[NaCl(s)] + \Delta_{sol}H[NaCl(s)] = \Delta_{hyd}H[Na^+(g)] + \Delta_{hyd}H[Cl^-(g)]$$

$$\Delta_{sol}H[NaCl(s)] = -406 + (-363)\,kJ\,mol^{-1} - (-780)\,kJ\,mol^{-1}$$

$$= +11\,kJ\,mol^{-1}$$

The relationship can also be shown in the form of a Hess cycle (shown in question 3 below).

SUBJECT VOCABULARY

enthalpy change of solution, $\Delta_{sol}H$ the enthalpy change when one mole of an ionic solid dissolves in water to form an infinitely dilute solution

infinitely dilute solution a solution in which there is so much water that adding any more does not cause a further enthalpy change

enthalpy change of hydration, $\Delta_{hyd}H$ is the enthalpy change when one mole of an ion in its gaseous state is completely hydrated by water

ion–dipole interaction the attraction in aqueous solution between ions and polar water molecules