

Entropy: how far?

Chapter

2

Introduction

It is often assumed that exothermic reactions will take place and endothermic reactions will not. This is an oversimplification, as can be seen by studying the solubilities and the enthalpies of solution of many salts. For example:

- ΔH_{soln} of ammonium nitrate is endothermic, yet it is very soluble in water.
- ΔH_{soln} of calcium carbonate is exothermic, yet it is insoluble in water.

During an exothermic process, the energy of the chemicals decreases (ΔH is negative). However, the energy of the surroundings increases by exactly the same amount. In an endothermic reaction, the chemicals gain energy (ΔH is positive) and the surroundings lose an equal quantity of energy. So what is the driving force of spontaneous change?

The answer lies in the simple concept that **energy and matter tend to spread out or disperse**.

When a highly ordered crystalline solid dissolves in water, the solid becomes dispersed throughout the liquid. When the denser gas carbon dioxide is added to air, it does not form a lower layer, but spreads throughout the air. The same happens with energy. If a hot piece of iron is placed in a beaker of water, the heat from the iron disperses into the water until both the iron and the water are at the same temperature. You cannot boil a kettle of water by putting it on a block of ice and expect the ice to become colder as the water heats up. Such a change would not break the first law of thermodynamics (the conservation of energy), but experience tells us that it never happens. Heat spontaneously flows from a hotter body to a colder body.

The spreading out of a solute into water, the spontaneous mixing of carbon dioxide and air, the heat transfer from the hot iron to the colder water are all examples of an increase in disorder. The scientific term for disorder is **entropy**.



*Left: Ordered,
therefore low entropy*

*Right: Disordered,
therefore high entropy*

The second law of thermodynamics states that spontaneous changes result in an increase in disorder or entropy.

The second law of thermodynamics determines:

- whether a physical or chemical change is likely to happen at a particular temperature
- whether redox reactions will take place
- the position of equilibrium

It can be said that the second law of thermodynamics explains all of chemistry.

Care must be taken to include not only the entropy change of the chemicals (ΔS_{system}) but also the entropy change of the surroundings (ΔS_{surr}). For example, when solid sodium hydroxide is added to water, the mixture of the two chemicals is called the system. The test tube and the air in the room are regarded as the surroundings. For a change to happen spontaneously, ΔS_{total} must be positive:

$$\Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{surr}}$$

This is another way of expressing the second law of thermodynamics.

In any spontaneous change, ΔS_{total} will be positive.

Entropy change of the system

A solid is much more ordered (or less disordered) than a liquid, which in turn is more ordered than a gas. So gaseous water is more disordered and has a larger entropy than liquid water, which has a greater entropy than ice. In general, this can be expressed as:

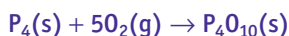
$$S_{\text{solid}} < S_{\text{liquid}} < S_{\text{gas}}$$

Table 2.1 shows the entropy changes for melting and boiling some substances.

	$\Delta S_{\text{melting}}/$ $\text{J K}^{-1} \text{mol}^{-1}$	Melting temperature/K	$\Delta S_{\text{boiling}}/$ $\text{J K}^{-1} \text{mol}^{-1}$	Boiling temperature/K
O_2	8.2	54	76	90
H_2O	22	273	109	373
NH_3	29	195	97	246

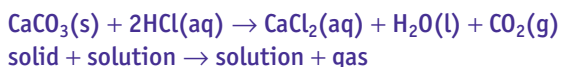
Table 2.1 Some entropy changes

In the combustion of phosphorus, the reaction goes from a solid plus a gas to a solid:



The disorder of a gas is replaced by the order of a solid. Therefore, the extent of disorder decreases and ΔS_{system} is negative.

When dilute hydrochloric acid is added to solid calcium carbonate, carbon dioxide gas is produced:



The disorder increases, so ΔS_{system} is positive.

The entropy change of the system can be calculated from the formula:

$$\Delta S_{\text{system}}^{\circ} = \sum nS^{\circ}(\text{products}) - \sum nS^{\circ}(\text{reactants})$$

In this equation, n represents the stoichiometric numbers in the chemical equation.

e Note the similarity between this expression and the one used to find ΔH_f from enthalpy of formation data:

$$\Delta H_f = \sum n\Delta H_f(\text{products}) - \sum n\Delta H_f(\text{reactants})$$

Table 2.2 shows the standard entropy values of some substances. A more complete list can be found in the Edexcel data booklet that is used in the A2 exam.

Gas	Entropy S^\ominus / $\text{J K}^{-1} \text{mol}^{-1}$	Liquid	Entropy S^\ominus / $\text{J K}^{-1} \text{mol}$	Solid	Entropy S^\ominus / $\text{J K}^{-1} \text{mol}^{-1}$
H_2	131	$\text{C}_2\text{H}_5\text{OH}$	161	P_4	164
O_2	205	CCl_4	216	P_4O_{10}	229
N_2	192	C_6H_6	174	C	5.7
$\text{H}_2\text{O}(\text{g})$	189	$\text{H}_2\text{O}(\text{l})$	70	$\text{H}_2\text{O}(\text{s})$	43
CO_2	214			CaO	40
NH_3	192			CaCO_3	93
CH_4	186				
C_2H_6	230				

Table 2.2
Standard entropies
of some elements and
compounds at 25°C

Table 2.2 shows a second trend, which is that entropy increases as the complexity of a substance increases. For example, the entropy of ethane is greater than that of methane; the entropy of calcium carbonate is greater than that of calcium oxide. Note the difference between this table and one of enthalpies of formation. The standard enthalpy of formation of an element in its standard state is defined as zero. The same is not true about the standard entropy values of an element: ΔH_f^\ominus of $\text{O}_2(\text{g}) = 0 \text{ kJ mol}^{-1}$; S^\ominus of $\text{O}_2(\text{g}) = -205 \text{ J K}^{-1} \text{ mol}^{-1}$.

Effect of temperature on entropy

The third law of thermodynamics states that the entropy of a perfect crystalline substance at absolute zero (0 K or -273°C) is zero. As the crystalline substance is heated, it gains in entropy until its melting temperature is reached. On melting there is a large jump in entropy, followed by a steady increase as the liquid is heated to its boiling temperature. There is another large jump in entropy as its physical state changes, followed by a gradual increase as the gas is heated. This is shown in Figure 2.1.

The values in Table 2.2 are standard entropy values, which means that they are the values at a stated temperature, usually 298 K (25°C), and 1 atm pressure. The entropy of liquid water at 100°C is $80 \text{ J K}^{-1} \text{ mol}^{-1}$, which is $10 \text{ J K}^{-1} \text{ mol}^{-1}$ more than its value at 25°C .

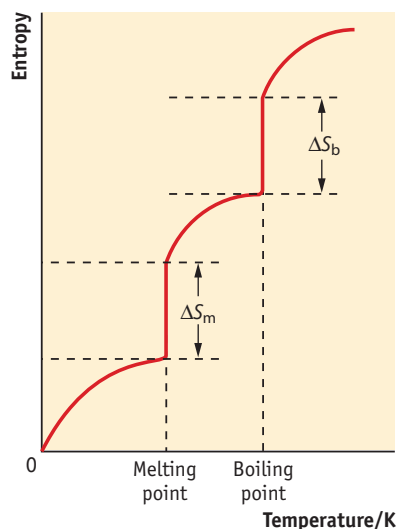
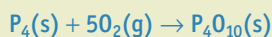


Figure 2.1

Worked example

Use data from Table 2.2 to calculate the standard entropy change of the system for the reaction between phosphorus and oxygen:



Answer

$$\begin{aligned} \Delta S_{\text{system}}^\ominus &= \sum nS^\ominus(\text{products}) - \sum nS^\ominus(\text{reactants}) \\ &= 229 - (+164 + 5 \times 205) = -960 \text{ J K}^{-1} \text{ mol}^{-1} \end{aligned}$$

e Note that S has joules in the units, whereas ΔH has kilojoules.

At first sight you might think that the reaction in the worked example should not take place because the entropy decreases. However, this is only the entropy change of the *system*. Both this reaction (negative ΔS value) and the reaction of acid with calcium carbonate (positive ΔS value) take place spontaneously. What has not been taken into account is the entropy change of the surroundings (the reactions are exothermic).

Entropy change of the surroundings

When an exothermic reaction takes place, heat energy is transferred to the surrounding air, causing an increase in disorder of the air molecules. This can be seen from the Maxwell–Boltzmann distribution of energies at two temperatures.

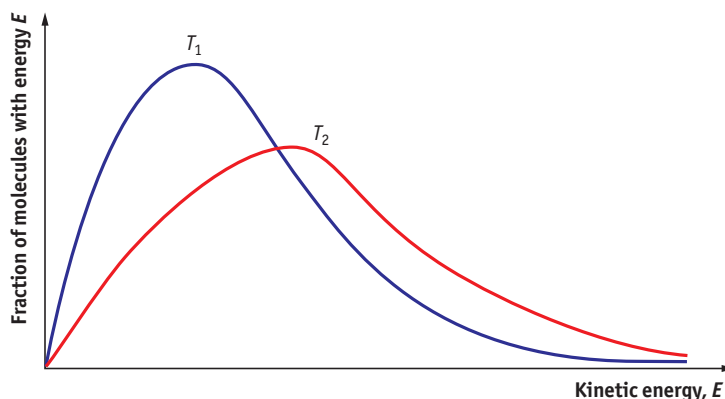


Figure 2.2
Maxwell–Boltzmann distribution of molecular energies at two temperatures ($T_2 > T_1$)

At the higher temperature (T_2), the molecules have a much greater range of energy and so are more random or disordered. This leads to the important conclusions:

- $\Delta S_{\text{surr}}^{\circ}$ is positive for all exothermic reactions.
- $\Delta S_{\text{surr}}^{\circ}$ is negative for all endothermic reactions.

This is shown pictorially in Figure 2.3.

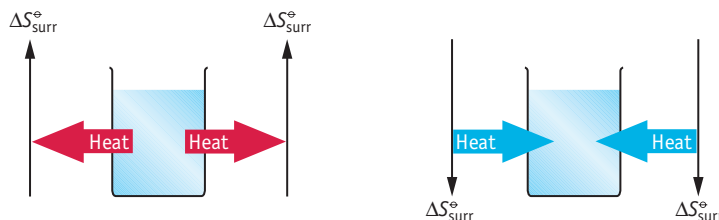


Figure 2.3 $\Delta S_{\text{surr}}^{\circ}$ and exothermic and endothermic reactions

If the surroundings are hot, the entropy increase is small because the molecules have high entropy and are already in chaotic motion. Conversely, if the surroundings are cold, the entropy change is much greater. The entropy change in the surroundings, caused by transfer of heat, depends on the value of the heat change and is also inversely proportional to the temperature of the surroundings. The heat change of the surroundings is the negative of the enthalpy change of the system:

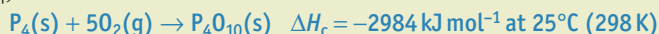
$$\Delta S_{\text{surr}}^{\circ} = \frac{-\Delta H^{\circ}}{T}$$

e If the system is exothermic, it loses enthalpy which is transferred as heat to the surroundings.

The temperature is given in kelvin ($K = ^{\circ}\text{C} + 273$).

Worked example

Calculate the entropy change of the surroundings when 1 mol of phosphorus, P_4 , burns in air.



Answer

$$\begin{aligned}\Delta S_{\text{surr}}^\ominus &= \frac{-\Delta H^\ominus}{T} \\ &= \frac{-(-2984)}{298} = +10.0 \text{ kJ K}^{-1} \text{ mol}^{-1} = +10\,000 \text{ J K}^{-1} \text{ mol}^{-1}\end{aligned}$$

e As with ΔH calculations, you should always include a sign in the answer for ΔS .

Total entropy change

The total entropy change (sometimes called the entropy change of the universe) is the sum of the entropy changes of the system and the surroundings:

$$\Delta S_{\text{total}}^\ominus = \Delta S_{\text{system}}^\ominus + \Delta S_{\text{surr}}^\ominus$$

Worked example

Calculate the total entropy change for the combustion of phosphorus. The entropy change of the *system* is $-960 \text{ J K}^{-1} \text{ mol}^{-1}$ and the entropy change of the *surroundings* is $+10\,000 \text{ J K}^{-1} \text{ mol}^{-1}$.

Answer

$$\begin{aligned}\Delta S_{\text{total}}^\ominus &= \Delta S_{\text{system}}^\ominus + \Delta S_{\text{surr}}^\ominus = -960 + (+10\,000) \\ &= +9040 \text{ J K}^{-1} \text{ mol}^{-1}\end{aligned}$$

Note that entropy data are in joules (per kelvin per mole) and enthalpy data are in kilojoules (per mole). You must either divide the entropy value by 1000 or multiply the enthalpy value by 1000.

Changes are thermodynamically feasible if the *total* entropy change is positive.

This means that an unfavourable (negative) entropy change of the system can be compensated for by a favourable (positive) entropy change of the surroundings.

$\Delta S_{\text{system}}^\ominus$	$\Delta S_{\text{surr}}^\ominus$	Feasible
Positive	Positive (exothermic reaction)	Always
Negative	Negative (endothermic reaction)	Never
Negative	Positive (exothermic reaction)	If the value of $\Delta H/T > \Delta S_{\text{system}}^\ominus$ (more likely at low temperatures)
Positive	Negative (endothermic reaction)	If the value $\Delta S_{\text{system}}^\ominus > \Delta H/T$ (more likely at high temperatures)

Table 2.3
Entropy changes
and feasibility

Direction of change

If ΔS_{total} is positive the change is said to be thermodynamically spontaneous. Thus the change will occur, providing that the kinetics of the change are favourable. If ΔS_{total} is negative, the reverse reaction is thermodynamically spontaneous. The value of ΔS_{total} can be altered by altering the temperature. For an exothermic reaction an increase in temperature will cause ΔS_{surr} to become less positive, which in turn will make ΔS_{total} less positive.

Worked example

Calculate the value of ΔS_{surr} at 25°C and at 100°C for a reaction with $\Delta H = -123 \text{ kJ mol}^{-1}$.

Answer

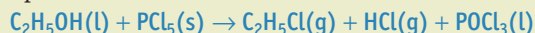
$$\Delta S_{\text{surr}} = -\Delta H/T = -(-123\,000 \text{ J mol}^{-1})/298 \text{ K} = +413 \text{ J K}^{-1} \text{ mol}^{-1} \text{ at } 25^\circ\text{C}$$

$$\Delta S_{\text{surr}} = -(-123\,000 \text{ J mol}^{-1})/373 \text{ K} = +330 \text{ J K}^{-1} \text{ mol}^{-1} \text{ at } 100^\circ\text{C}$$

The value of ΔS_{total} also determines the extent of the reaction. The more positive its value, the more the position of equilibrium will lie to the right. This is explained in more detail in Chapter 3.

Worked example 1

Comment on the feasibility of the following reaction occurring at a temperature of 298 K:



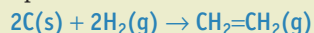
$$\Delta H = -107 \text{ kJ mol}^{-1}; \Delta S_{\text{system}} = +368 \text{ J K}^{-1} \text{ mol}^{-1}$$

Answer

As ΔH is negative, ΔS_{surr} will be positive. Both ΔS_{surr} and ΔS_{system} are favourable (positive), so the reaction is thermodynamically feasible (spontaneous) at all temperatures.

Worked example 2

Comment on the feasibility of the following reaction occurring at a temperature of 298 K:



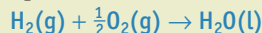
$$\Delta H = +52.2 \text{ kJ mol}^{-1}; \Delta S_{\text{system}} = -184 \text{ J K}^{-1} \text{ mol}^{-1}$$

Answer

Both ΔH and ΔS_{system} are unfavourable, so the reaction will not take place. Carbon and hydrogen are thermodynamically stable relative to ethene at all temperatures.

Worked example 3

Comment on the feasibility of the following reaction occurring at a temperature of 298 K:



$$\Delta H = -286 \text{ kJ mol}^{-1}; \Delta S_{\text{system}} = -45 \text{ J K}^{-1} \text{ mol}^{-1}$$

Answer

ΔH is favourable (exothermic) but ΔS_{system} is unfavourable (negative). The reaction will take place only if $\Delta H/T$ is greater than ΔS_{system} .

$$\begin{aligned} \Delta S_{\text{total}} &= \Delta S_{\text{system}} + \Delta S_{\text{surr}} = \Delta S_{\text{system}} - \Delta H/T \\ &= -45 \text{ J K mol}^{-1} - (-286\,000 \text{ J K}^{-1} \text{ mol}^{-1})/298 \text{ K} = +915 \text{ J K}^{-1} \text{ mol}^{-1} \end{aligned}$$

This is a positive value and so the reaction is thermodynamically feasible at 298 K. At very high temperatures the value of $-\Delta H/T$ will become too small to overcome the negative value of ΔS_{system} and the reaction will not be feasible.

Note that the value of ΔH was converted from kJ to J and the temperature from °C to K.

ΔS_{system} is positive because the reaction involves liquid + solid \rightarrow two gases + liquid (getting more random).

e As both factors are favourable, there is no need to work out the value of ΔS_{total} . However, the reaction may be too slow (reactants kinetically stable) at low temperatures.

e As both factors are unfavourable, there is no need to work out the value of ΔS_{total} .

This reaction mixture is kinetically stable at room temperature. Either a catalyst or a spark is needed for reaction to occur. Water decomposes into its elements only at very high temperatures.

Worked example 4

Comment on the feasibility of the following reaction occurring at a temperature of 298 K:



$$\Delta H = +178 \text{ kJ mol}^{-1}; \Delta S_{\text{system}} = +164 \text{ J K}^{-1} \text{ mol}^{-1}$$

Answer

ΔH is unfavourable (endothermic), but ΔS_{system} is favourable (positive). Therefore, the reaction will only be thermodynamically feasible when ΔS_{system} is greater than $\Delta H/T$.

$$\begin{aligned} \Delta S_{\text{total}} &= \Delta S_{\text{system}} + \Delta S_{\text{surr}} = \Delta S_{\text{system}} - \Delta H/T \\ &= +164 \text{ J K mol}^{-1} - (+178000 \text{ J K}^{-1} \text{ mol}^{-1})/298 \text{ K} = -433 \text{ J K}^{-1} \text{ mol}^{-1} \end{aligned}$$

This is a negative value and so the reaction is not feasible at 298 K.

This reaction occurs at high temperatures because the value of ΔS_{surr} becomes less negative and eventually smaller than 164. Thus, calcium carbonate is both thermodynamically and kinetically stable at room temperature, but will decompose on strong heating.

e Calcium carbonate is kinetically stable as the activation energy for its decomposition is high.

e At A-level, it is normally assumed that an increase in temperature results in negligible change in the value of ΔS_{system} because the entropies of the reactants and products change by similar amounts.

At a higher temperature, the magnitude of ΔS_{surr} always gets smaller. Thus a negative ΔS_{surr} becomes less negative and a positive ΔS_{surr} becomes less positive.

e Thermodynamics gives no information about reaction rate. A thermodynamically feasible reaction might have such high activation energy that it does not proceed at room temperature.

Spontaneous endothermic reactions

When solid ammonium carbonate is added to pure ethanoic acid, bubbles of gas are rapidly produced. This appears to be a violent reaction, but if a thermometer is placed in the acid before the ammonium carbonate is added, it will be observed that the temperature falls considerably as the reaction takes place.



Even though the reaction is endothermic, there is a considerable increase in entropy of the system because a gas is produced. This makes ΔS_{total} positive and the reaction thermodynamically spontaneous.

Hydrated barium hydroxide reacts with solid ammonium chloride in a rapid endothermic reaction at room temperature:



As with the previous example, the driving force of the reaction is ΔS_{system} , which overcomes the endothermic nature of the reaction. The reactants are solids and the products are a solid, a liquid and a gas, and three substances make 13 substances, so there is a considerable gain in disorder.

Another easily observed endothermic change is the dissolving of ammonium nitrate in water.



As the reaction is spontaneous, the negative value of ΔS_{surr} must be outweighed by the positive value of ΔS_{system} .

All three of the above examples are thermodynamically spontaneous. The activation energies are low and so all three reactions take place rapidly at room temperature. They are examples of reactants that are thermodynamically and kinetically unstable relative to their products.

- A positive ΔS_{total} means that the reactants are thermodynamically unstable relative to the products.
- A negative ΔS_{total} means that the reactants are thermodynamically stable relative to the products.
- A small activation energy means that the reactants are kinetically unstable relative to the products.
- A large activation energy means that the reactants are kinetically stable relative to the products.

Solubility

Dissolving a gas always results in a negative ΔS_{system} because the system becomes more ordered. Therefore, for a gas to be soluble it must always dissolve exothermically (the surroundings become more disordered). This means that the equilibrium:



is driven to the left by an increase in temperature. Gases, such as carbon dioxide, are less soluble in hot water than in cold water.



An interesting point follows about global warming. The accepted theory is that, historically, periods of high levels of atmospheric carbon dioxide produced high temperatures. This is questionable for a number of reasons. First, there is some evidence from ice cores that implies that the warming *preceded* the rise in carbon dioxide levels, rather than following it. This can be explained easily. As the sea temperature rises, due to changes in activity of the sun, the equilibrium shown above is driven to the left (the endothermic direction), so more carbon dioxide enters the atmosphere. The second flaw in the argument that carbon dioxide caused higher temperatures before the industrial revolution is that there is no reason why the atmospheric carbon dioxide level should have varied before man started to burn fossil fuels in large quantities.

Contrary to the expected approach to entropy, dissolving solids does not always result in a positive $\Delta S_{\text{system}}^\circ$ (the system becoming more disordered). The solute becomes more disordered as it goes from highly ordered solid to a more random solution, but the solvent can become more ordered due to the forces of attraction between solute and solvent. This is particularly the case when compounds

containing ions of high charge density dissolve in water (see p. 44). $\Delta H_{\text{soln}}^{\circ}$ can be either negative (hence the surroundings also become more disordered) or slightly positive (hence the surroundings become slightly less disordered). The equilibrium:



is driven to the left (less soluble) if $\Delta H_{\text{soln}}^{\circ}$ is exothermic and to the right (more soluble) if $\Delta H_{\text{soln}}^{\circ}$ is endothermic.

Solubility of ionic compounds

When an ionic solid dissolves in water, the lattice breaks down and the ions are separated. This is very endothermic, so you might expect that ionic solids would not dissolve in water. To explain this apparent paradox, you must think about what happens to the ions as the solid dissolves.

Cations become surrounded by water molecules. Strong ion-dipole forces act between the positive cations and the δ^- oxygen atoms in the water. Similarly, the anions become surrounded by water molecules with the δ^+ hydrogen atoms of the water molecules being strongly attracted to the negative anions. This process is called **hydration**. It is the highly exothermic nature of hydration that compensates for the endothermic break-up of the lattice.

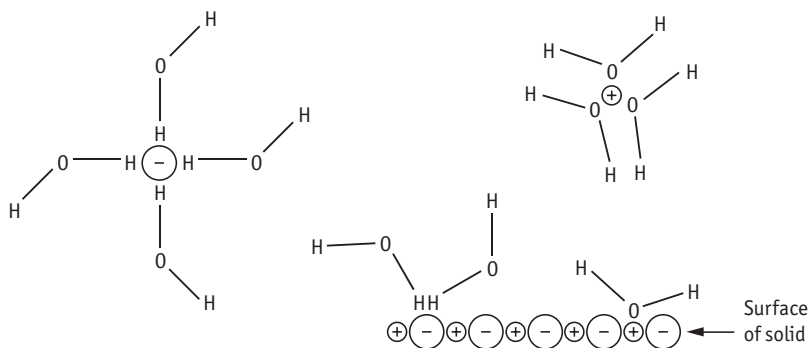


Figure 2.4 An ionic solid dissolving

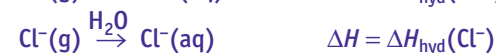
The enthalpy of solution of a solid, ΔH_{soln} , is the enthalpy change when 1 mol of the solid is dissolved in sufficient solvent to give an infinitely dilute solution.

The hydration enthalpy of an ion, ΔH_{hyd} , is the enthalpy change when 1 mol of **gaseous** ions is dissolved in sufficient solvent to give an infinitely dilute solution.

Step 1:



Step 2:

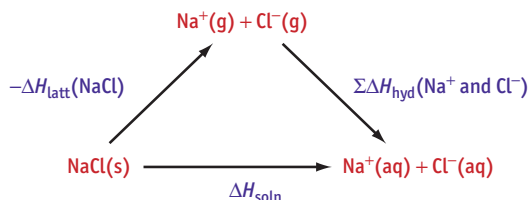


On addition, the gaseous ions cancel, giving:



e An infinitely dilute solution can be thought of as one in which further dilution does not cause a heat change.

This can be shown as a Hess's law cycle:

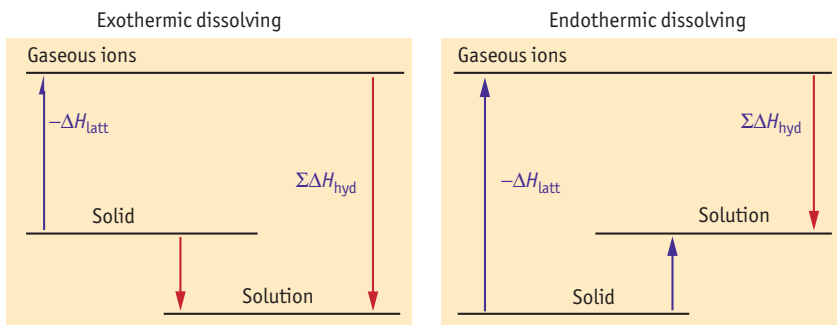


$$\Delta H_{\text{soln}} = -\Delta H_{\text{latt}} + \Delta H_{\text{hyd}}(\text{Na}^+) + \Delta H_{\text{hyd}}(\text{Cl}^-)$$

From this equation, it can be seen that:

- the more exothermic the lattice energy, the more endothermic the enthalpy of solution
- the more exothermic either of the hydration enthalpies, the more exothermic the enthalpy of solution

The sign of the enthalpy of solution is determined by the difference in magnitude between the lattice energy and the sum of the hydration energies.



If the magnitude of the lattice enthalpy (blue arrow) is *less* than the sum of the hydration enthalpies of the two ions (red arrow), dissolving will be exothermic.

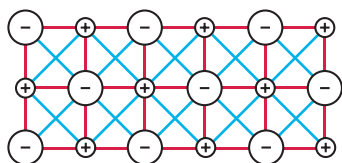
If the magnitude of the lattice enthalpy is *greater* than the sum of the hydration enthalpies of the two ions, dissolving will be endothermic.

A general relationship can be deduced from the energy-level diagrams above:

$$\Delta H_{\text{soln}} = -\text{lattice energy} + \text{the sum of the hydration energies of all the ions}$$

Factors that affect lattice energy

The magnitude of the lattice energy depends on the strength of the forces acting on the ions. In a lattice, each ion is surrounded by a number of ions of opposite charge, resulting in strong forces of attraction (red) and some forces of repulsion (blue). This is illustrated in Figure 2.5.



e Remember that the lattice energy is defined in the exothermic direction. It is the energy change when 1 mol of an ionic solid is formed from its constituent gaseous ions infinitely far apart.

Figure 2.5 The forces acting between the ions in a planar slice through a crystal of sodium chloride

The strength of these forces depends mainly on:

- the product of the charges on the ions — the larger the product, the greater is the magnitude of the lattice energy
- the sum of the radii of the cation and the anion — the larger the sum, the smaller the magnitude of the lattice energy
- the extent of covalency (a small effect) — the greater the extent of covalency, the greater is the magnitude of the lattice energy

Worked example 1

Explain why the lattice energy of sodium fluoride is more exothermic than the lattice energy of potassium chloride.

Answer

It is because Na^+ has a smaller ionic radius than K^+ , and F^- is smaller than Cl^- . Therefore, the forces between sodium ions and fluoride ions are stronger than those between potassium ions and chloride ions.

Worked example 2

Explain why the lattice energy of calcium oxide is approximately four times larger than that of potassium fluoride.

Answer

This is because in calcium oxide the product of the ionic charges is 4, whereas in potassium fluoride it is 1. The sums of the ionic radii of the two compounds are not very different. However, the value is smaller in CaO than in KF , so the lattice energy ratio is further increased from 4.

Table 2.4 shows lattice energies for some ionic solids.

Lattice energy/ kJ mol^{-1}					
Halides	LiF	NaF	KF	RbF	CsF
	-1022	-902	-801	-767	-716
	LiCl	NaCl	KCl	RbCl	CsCl
	-846	-771	-701	-675	-645
	LiBr	NaBr	KBr	RbBr	CsBr
	-800	-733	-670	-647	-619
	LiI	NaI	KI	RbI	CsI
	-744	-684	-629	-609	-585
	BeCl_2	MgCl_2	CaCl_2	SrCl_2	BaCl_2
	-3006	-2500	-2237	-2112	-2018
Oxides	Li_2O	Na_2O	K_2O	Rb_2O	Cs_2O
	-2814	-2478	-2232	-2161	-2063
	BeO	MgO	CaO	SrO	BaO
	-4444	-3890	-3513	-3310	-3152
Sulfides	Li_2S	Na_2S	K_2S	Rb_2S	Cs_2S
	-2500	-2200	-2052	-1944	-1850
	BeS	MgS	CaS	SrS	BaS
	-3832	-3300	-3013	-2850	-2725
Hydroxides		$\text{Mg}(\text{OH})_2$	$\text{Ca}(\text{OH})_2$	$\text{Sr}(\text{OH})_2$	$\text{Ba}(\text{OH})_2$
		-2842	-2553	-2354	-2228

Table 2.4 Some lattice energies

Table 2.4 shows that:

- the magnitude of the lattice energy steadily decreases down a group of the periodic table as the size of the cation increases
- the magnitude of the lattice energy steadily decreases down the group as the size of the anion increases
- the magnitude of the lattice energy increases as the charge on either or both the cation and the anion increases

Factors that affect hydration enthalpy

The magnitude of the hydration enthalpy of an ion depends on the strength of the force between the ion and the water molecules surrounding it. Positive ions are attracted to the δ^- oxygen atoms of the water and negative ions to the δ^+ hydrogen atoms.

The strength of the forces depends on:

- the magnitude of the charge on the ion — the greater the charge, the greater is the force
- the radius of the ion — the smaller the radius, the greater is the force

Hydration enthalpies of some gaseous ions are shown in Table 2.5.

Cation	$\Delta H_{\text{hyd}}/\text{kJ mol}^{-1}$	Anion	$\Delta H_{\text{hyd}}/\text{kJ mol}^{-1}$
Li^+	-519	F^-	-506
Na^+	-406	Cl^-	-364
K^+	-322	Br^-	-335
Mg^{2+}	-1920	I^-	-293
Ca^{2+}	-1650	OH^-	-460
Sr^{2+}	-1480		
Ba^{2+}	-1360		

Table 2.5 Hydration enthalpies of ions

Table 2.5 shows that

- the hydration energies become less exothermic as the radius of the ions in a group increases
- the magnitude of the hydration energy increases as the charge on the cation increases

Calculation of enthalpy of solution

Worked example

Use data from Tables 2.4 and 2.5 to predict the enthalpy of solution of sodium chloride.

Answer

$$\begin{aligned}\Delta H_{\text{soln}} &= -\Delta H_{\text{latt}} + \Delta H_{\text{hyd}}(\text{Na}^+) + \Delta H_{\text{hyd}}(\text{Cl}^-) \\ &= -(-771) + (-406) + (-364) = +1 \text{ kJ mol}^{-1}\end{aligned}$$

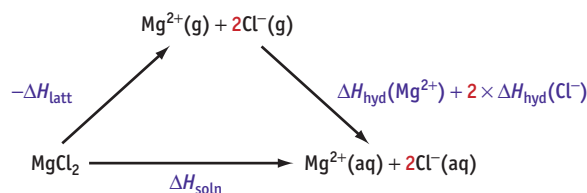
Using lattice energies and hydration energies to predict the enthalpy of solution may be inaccurate, because slight errors in any of the quantities could result in an answer with the wrong sign. For example, if the data in the above

worked example had been taken from a different source, the calculation could have been:

$$\begin{aligned}\Delta H_{\text{soln}} &= -\Delta H_{\text{latt}} + \Delta H_{\text{hyd}}(\text{Na}^+) + \Delta H_{\text{hyd}}(\text{Cl}^-) \\ &= -(-780) + (-444) + (-340) = -4 \text{ kJ mol}^{-1}\end{aligned}$$

The true value of ΔH_{soln} of NaCl(s) is $+3.9 \text{ kJ mol}^{-1}$.

Extra care must be taken with ionic compounds of formula MX_2 . This can be illustrated using a Hess's law cycle:



$$\begin{aligned}\Delta H_{\text{soln}} &= -\Delta H_{\text{latt}}(\text{MgCl}_2) + \Delta H_{\text{hyd}}(\text{Mg}^{2+}) + 2 \times \Delta H_{\text{hyd}}(\text{Cl}^-) \\ &= -(-2500) + (-1920) + 2(-364) = -148 \text{ kJ mol}^{-1}\end{aligned}$$

As can be seen from Table 2.6, many ionic solids have endothermic enthalpies of solution and are still soluble. Others have exothermic enthalpies of solution and are insoluble. The concept that exothermic changes will take place spontaneously and endothermic changes will not is an oversimplification. The criteria for spontaneity include the **entropy** change of the system (p. 31).

The hydration enthalpy of the chloride ion must be multiplied by two, because there are two Cl^- ions in the equation.

Cation	Anion							
	F ⁻	Cl ⁻	Br ⁻	I ⁻	OH ⁻	CO ₃ ²⁻	NO ₃ ⁻	SO ₄ ²⁻
Li ⁺	+4.9**	-37	-49	-63	-24	-18	-3	-30
Na ⁺	+1.9	+3.9	-0.6	-7.5	-45	-27	+21	-2.4
K ⁺	-18	+17	+20	+20	-57	-31	+35	+24
NH ₄ ⁺	-1.2	+15	+16	+14	-	-	+26	+6.6
Ag ⁺	-23	+66*	+84*	+112*	-	+42*	+23	+18
Mg ²⁺	-18*	-160	-186	-213	+2.3*	-25.3*	-91	-91
Ca ²⁺	+12*	-81	-103	-120	-16.7**	-13*	-19	-18**
Al ³⁺	-27**	-330	-370	-390	*	-	-	-350

* insoluble
** slightly soluble

Table 2.6 Enthalpies (kJ mol^{-1}) of solutions of anhydrous compound at 25°C

Extent of solubility

Solubility of a solid is determined by the total entropy change for 1 mol of that solid.

$$\Delta S_{\text{total}}^\ominus = \Delta S_{\text{system}}^\ominus + \Delta S_{\text{surr}}^\ominus = \Delta S_{\text{system}}^\ominus + (-\Delta H_{\text{soln}}^\ominus/T)$$

For an ionic solid to dissolve significantly, $\Delta S_{\text{total}}^\ominus$ must be positive. Its value depends on both the entropy change of the system and the enthalpy change.

Entropy changes on dissolving an ionic solid

When ammonium chloride dissolves in water, the enthalpy change is $+15 \text{ kJ mol}^{-1}$.

This is endothermic and the system moves spontaneously to a state of higher enthalpy. The entropy of the surroundings *decreases* by $15\,000/298 = 50\text{ JK}^{-1}\text{ mol}^{-1}$ ($\Delta S_{\text{surr}}^{\circ} = -50\text{ JK}^{-1}\text{ mol}^{-1}$). However, this is balanced by an increase in the entropy of the system, as the ordered ammonium chloride lattice is broken down and the ions dispersed into the solvent. The value of $\Delta S_{\text{system}}^{\circ}$ is $+167\text{ JK}^{-1}\text{ mol}^{-1}$. The total entropy change is:

$$\Delta S_{\text{total}}^{\circ} = \Delta S_{\text{system}}^{\circ} + \Delta S_{\text{surr}}^{\circ} = +167 + (-50) = +117\text{ JK}^{-1}\text{ mol}^{-1}$$

This is a positive number and so the dissolving of ammonium chloride is thermodynamically spontaneous.

Entropy of the surroundings

Because $\Delta S_{\text{surr}}^{\circ} = -\Delta H_{\text{soln}}^{\circ}/T$, the sign of the entropy change depends on the sign of the enthalpy change:

- For endothermic enthalpies of solution, $\Delta S_{\text{surr}}^{\circ}$ is negative

Some ionic solids have an endothermic enthalpy of solution (see Table 2.6). This means that $\Delta S_{\text{surr}}^{\circ}$ is negative. If these compounds are to be soluble, $\Delta S_{\text{system}}^{\circ}$ must be positive and must outweigh the negative $\Delta S_{\text{surr}}^{\circ}$. Examples of soluble substances with endothermic $\Delta H_{\text{soln}}^{\circ}$ are sodium chloride ($\Delta H_{\text{soln}}^{\circ} = +3.9\text{ kJ mol}^{-1}$), potassium sulfate ($\Delta H_{\text{soln}}^{\circ} = +23.8\text{ kJ mol}^{-1}$) and ammonium nitrate ($\Delta H_{\text{soln}}^{\circ} = +25.8\text{ kJ mol}^{-1}$).

Many insoluble substances have positive enthalpies of solution and hence negative $\Delta S_{\text{surr}}^{\circ}$. Because they are insoluble, $\Delta S_{\text{total}}^{\circ}$ is negative. An example is silver chloride: $\Delta H_{\text{soln}}^{\circ} = +66\text{ kJ mol}^{-1}$; $\Delta S_{\text{surr}}^{\circ} = -66\,000/298 = -220\text{ JK}^{-1}\text{ mol}^{-1}$. This means that $\Delta S_{\text{system}}^{\circ}$ must either have a smaller positive value than $220\text{ JK}^{-1}\text{ mol}^{-1}$ or be negative. (In fact, the value of $\Delta S_{\text{system}}^{\circ}$ for silver chloride is $+33\text{ JK}^{-1}\text{ mol}^{-1}$.)

- For exothermic enthalpies of solution, $\Delta S_{\text{surr}}^{\circ}$ is positive.

Some ionic solids have an exothermic enthalpy of solution and so $\Delta S_{\text{surr}}^{\circ}$ is positive. At first sight, it might be expected that these solids would be soluble. This is the case if $\Delta S_{\text{system}}^{\circ}$ is positive. An example is sodium hydroxide, $\Delta H_{\text{soln}}^{\circ} = -32.7\text{ kJ mol}^{-1}$. It is also the case if $\Delta S_{\text{system}}^{\circ}$ is negative but its magnitude is less than $\Delta S_{\text{surr}}^{\circ}$. An example is barium chloride, $\Delta H_{\text{soln}}^{\circ} = -13.2\text{ kJ mol}^{-1}$.

If the solid is *insoluble*, $\Delta S_{\text{total}}^{\circ}$ is negative. This means that $\Delta S_{\text{system}}^{\circ}$ must be negative and its magnitude must outweigh the positive $\Delta S_{\text{surr}}^{\circ}$. An example is calcium carbonate, $\Delta H_{\text{soln}}^{\circ} = -12.3\text{ kJ mol}^{-1}$ and $\Delta S_{\text{surr}}^{\circ} = +41\text{ JK}^{-1}\text{ mol}^{-1}$. For $\Delta S_{\text{total}}^{\circ}$ to be negative, $\Delta S_{\text{system}}^{\circ}$ must be more negative than $-41\text{ JK}^{-1}\text{ mol}^{-1}$. (Its value is $-202\text{ JK}^{-1}\text{ mol}^{-1}$.)

Entropy of the system

This is made up of the entropy change of the solute and the entropy change of the solvent.

$$\Delta S_{\text{system}}^{\circ} = \Delta S_{\text{solute}}^{\circ} + \Delta S_{\text{solvent}}^{\circ}$$

When any solute is dissolved, its entropy increases as the particles go from being arranged in a regular pattern in the solid to being distributed randomly in

Values of enthalpy and entropy changes in dissolving are shown in Table 2.7.

the solution. This applies to both covalent substances, such as glucose, and to ionic substances such as sodium chloride.

$$\Delta S_{\text{solute}}^{\circ} > 0 \text{ (}\Delta S_{\text{solute}}^{\circ} \text{ positive)}$$

In the case of many solutions, there is also an increase in the entropy of the solvent as it becomes mixed with solute particles. However, when anhydrous ionic substances are dissolved in water, there is also a certain amount of ordering of water molecules. The positive ions become surrounded by water molecules, as the δ^- oxygen atoms in the water bond with the positive cations. This makes the δ^+ hydrogen atoms more positive causing them to bind a second sphere of water molecules. The extent to which this happens depends on the charge density of the cation. The charge density of the ammonium ion is small because the single positive charge is delocalised over the whole ion and so the entropy of the water is not significantly altered. The lithium ion, Li^+ , decreases the entropy of the solvent water to a greater extent than the other group 1 ions, as its ionic radius is much smaller. The group 2 cations have a much larger charge density than group 1 ions. They are doubly charged and, for each, the ionic radius is much less than that of the group 1 ion in the same period. The extent to which the $\Delta S_{\text{water}}^{\circ}$ is negative (more ordered) decreases as the group is descended. Thus barium ions, Ba^{2+} , order the water less than magnesium ions, Mg^{2+} .

Negative ions also cause a slight ordering of water molecules, as the negative ions are surrounded by δ^+ hydrogen atoms in water molecules.

For the process:



the following assumptions can be made:

- Dissolving group 1 compounds, ammonium compounds and silver compounds causes only a small change in the entropy of the water, so $\Delta S_{\text{system}}^{\circ}$ is always positive.
- Dissolving compounds containing doubly charged cations, such as those of the group 2 metals, causes a large decrease in the entropy of the water, so $\Delta S_{\text{system}}^{\circ}$ is negative.

It is possible to calculate the value of $\Delta S_{\text{system}}^{\circ}$. It has been estimated that $\Delta S_{\text{system}}^{\circ}$ for dissolving ammonium chloride in water is $+167 \text{ J K}^{-1} \text{ mol}^{-1}$; the theoretical value for barium sulfate is $-104 \text{ J K}^{-1} \text{ mol}^{-1}$.

Some enthalpy and entropy changes for ionic solids dissolving in water, i.e. for the change



are shown in Table 2.7.

It can be seen from the table that all the compounds containing singly charged cations have a positive $\Delta S_{\text{system}}^{\circ}$. This is the main reason why group 1 compounds are water soluble, the exception being lithium fluoride. This is caused by the fluoride ion forming strong hydrogen bonds with water molecules and by the

This can be demonstrated by filling a burette with water and then adding some anhydrous aluminium chloride or iron(III) chloride. The volume of the water shrinks noticeably as water molecules bond to the ions and become less randomly arranged. The high charge density of Al^{3+} ions means that when aluminium chloride is dissolved, $\Delta S_{\text{system}}^{\circ}$ is negative.

Substance	$\Delta H_{\text{soln}}^{\circ}$ / kJ mol^{-1}	$\Delta S_{\text{surr}}^{\circ}$ / $\text{J K}^{-1} \text{mol}^{-1}$	$\Delta S_{\text{system}}^{\circ}$ / $\text{J K}^{-1} \text{mol}^{-1}$	$\Delta S_{\text{total}}^{\circ}$ / $\text{J K}^{-1} \text{mol}^{-1}$	Solubility
LiCl(s)	-37	+124	+11	+135	Soluble
NaCl(s)	+4	-13	+43	+30	Soluble
KCl(s)	+17	-57	+77	+20	Soluble
LiF(s)	+5	-17	-37	-54	Insoluble
$\text{NH}_4\text{Cl}(s)$	+15	-51	+167	+116	Soluble
AgCl(s)	+66	-221	+33	-188	Insoluble
$\text{MgSO}_4(s)$	-91	+305	-213	-92	Soluble
$\text{CaSO}_4(s)$	-18	+60	-145	-85	Insoluble
$\text{BaSO}_4(s)$	+19	-65	-104	-169	Insoluble
$\text{CuSO}_4(s)$	-73	+245	-192	+53	Soluble

high charge density of the small Li^+ ion. Both these factors cause a more ordered arrangement of the water molecules. Silver chloride is insoluble in spite of the favourable $\Delta S_{\text{system}}^{\circ}$, because its $\Delta H_{\text{soln}}^{\circ}$ is highly endothermic.

The reverse is true for compounds containing doubly positive cations. All have a negative $\Delta S_{\text{system}}^{\circ}$. This is why many of their compounds (carbonates, phosphates and hydroxides) are insoluble. They are only soluble if the enthalpy of solution is sufficiently exothermic. This is the case with magnesium sulfate and copper sulfate, but not with calcium sulfate. For barium sulfate, $\Delta H_{\text{soln}}^{\circ}$ is endothermic and $\Delta S_{\text{system}}^{\circ}$ is negative, so it is extremely insoluble.

The relationship between enthalpy of solution, solubility and the entropy of the system is summarised in Table 2.8.

$\Delta H_{\text{soln}}^{\circ}$	Solubility	$\Delta S_{\text{system}}^{\circ}$
Endothermic (+)	Soluble	Must be more positive than $\Delta H_{\text{soln}}^{\circ}/T$
Endothermic (+)	Insoluble	Negative or less positive than $\Delta H_{\text{soln}}^{\circ}/T$
Exothermic (-)	Soluble	Positive or less negative than $\Delta H_{\text{soln}}^{\circ}/T$
Exothermic (-)	Insoluble	Must be more negative than $\Delta H_{\text{soln}}^{\circ}/T$

Solubility trends in a group

The enthalpy of solution of an ionic solid can be calculated by means of a Hess's law cycle (p. 42). The reason for the trend in the value of $\Delta H_{\text{soln}}^{\circ}$ is found in the way that the lattice energies and hydration energies change down a group.

The enthalpy of solution is a balance between lattice energy and the sum of the hydration energies of the ions:

$$\Delta H_{\text{soln}} = -\text{lattice energy} + \text{sum of the hydration energies of the ions}$$

In any group of the periodic table:

- The lattice energies become less exothermic as the group is descended.
- The hydration energies of the cations become less exothermic down the group.

Therefore, the change in $\Delta H_{\text{soln}}^{\circ}$ down the group is determined by which quantity shows the *greater decrease*.

Table 2.7
Enthalpy and entropy changes for ionic solids dissolving in water

The substances with an exothermic $\Delta H_{\text{soln}}^{\circ}$ are shown in red; those that with an endothermic $\Delta H_{\text{soln}}^{\circ}$ are in blue.

e Exothermic indicates a positive $\Delta S_{\text{surr}}^{\circ}$; endothermic indicates a negative $\Delta S_{\text{surr}}^{\circ}$

Table 2.8
Enthalpy, solubility and entropy

If the lattice energy decreases more than the hydration energy, the process of dissolving is more exothermic (or less endothermic).

The lattice energy and hydration enthalpy values for group 2 hydroxides and sulfates are shown in Table 2.9.

Substance	Lattice energy/ kJ mol ⁻¹	Hydration enthalpy of cation/kJ mol ⁻¹
Mg(OH) ₂ (s)	-2842	-1920
Ca(OH) ₂ (s)	-2553	-1650
Sr(OH) ₂ (s)	-2354	-1480
Ba(OH) ₂ (s)	-2228	-1360
Change down the group	614	560
MgSO ₄ (s)	-2874	-1920
CaSO ₄ (s)	-2677	-1650
SrSO ₄ (s)	-2516	-1480
BaSO ₄ (s)	-2424	-1360
Change down the group	450	560

Table 2.9 Lattice energy and hydration enthalpy values for group 2 hydroxides and sulfates.

Table 2.9 shows that, for the hydroxides of group 2, on descending the group there is a greater change in lattice energy than there is in hydration enthalpy. This results in the enthalpy of solution becoming steadily more exothermic.

The lattice energy changes more than the hydration enthalpy because of the way in which the two factors depend on the ionic radius:

- The hydration energy of a cation depends upon its charge density — the charge divided by the radius.
- The lattice energy depends upon the charges of the two ions multiplied together divided by the sum of the two ionic radii — $\{r(+)+r(-)\}$.
- The OH⁻ ion is a small anion, similar in size to the group 2 cations. Therefore, the value of $\{r(+)+r(-)\}$ increases considerably as the value of the radius of the cation, $r(+)$, increases.

The opposite is true for the group 2 sulfates. The sulfate ion is much larger than any of the group 2 cations. Therefore, as $r(-) \gg r(+)$, the value of $\{r(+)+r(-)\}$ changes by only a small amount. This means that the decrease in the value of the lattice energy is more than the decrease of the hydration enthalpy of the ions. This makes the enthalpy of solution increasingly less exothermic as the group is descended.

The values of $\Delta H_{\text{soln}}^{\circ}$ are shown in Table 2.10.

The value of $\Delta H_{\text{soln}}^{\circ}$ is not the only factor determining solubility. The other factor is the change in entropy of the system. For many ionic solids, this is difficult to determine accurately. A guide is the relative entropy values of the ions, which are also shown in Table 2.10. Note how the entropy of the ion increases as the ionic radius increases.

Solubility of silver halides

Substance	$\Delta H_{\text{soln}}^{\circ}$ /kJ mol ⁻¹	$\Delta S_{\text{surr}}^{\circ} = -\Delta H_{\text{soln}}^{\circ}/T$ /J K ⁻¹ mol ⁻¹	Hydrated ion	Relative* entropy value of hydrated ion/J K ⁻¹ mol ⁻¹
AgF	-20	+67	F ⁻ (aq)	-14
AgCl	+66	-221	Cl ⁻ (aq)	+57
AgBr	+85	-285	Br ⁻ (aq)	+82
AgI	+113	-379	I ⁻ (aq)	+111
Change down the group from F to I	More endothermic	-446, so less likely to dissolve	Change down the group from F ⁻ (aq) to I ⁻ (aq)	-125, so more likely to dissolve

The change in value of $\Delta H_{\text{soln}}^{\circ}$ and hence of $\Delta S_{\text{surr}}^{\circ}$ indicates that the solubility should decrease from silver fluoride, AgF, to silver iodide, AgI. The change in entropy of the halide ion indicates the opposite, because the values become more favourable. However, the change in the entropy of the hydrated ions (125 J K⁻¹ mol⁻¹) is significantly less than the change in $\Delta S_{\text{surr}}^{\circ}$ (446 J K⁻¹ mol⁻¹). This explains the fall in solubility of silver fluoride to silver iodide.

Solubility of group 2 hydroxides

Substance	$\Delta H_{\text{soln}}^{\circ}$ /kJ mol ⁻¹	$\Delta S_{\text{surr}}^{\circ} = -\Delta H_{\text{soln}}^{\circ}/T$ /J K ⁻¹ mol ⁻¹	Hydrated ion	Relative* entropy value of hydrated ion/J K ⁻¹ mol ⁻¹
Mg(OH) ₂	+3	-10	Mg ²⁺ (aq)	-138
Ca(OH) ₂	-16	+54	Ca ²⁺ (aq)	-53
Sr(OH) ₂	-46	+154	Sr ²⁺ (aq)	-33
Ba(OH) ₂	-52	+174	Ba ²⁺ (aq)	+10
Change down the group from Mg to Ba	More exothermic	-184, so more likely to dissolve	Change down the group from Mg ²⁺ (aq) to Ba ²⁺ (aq)	-148, so more likely to dissolve

The enthalpy of solution becomes more negative down the group. This means that $\Delta S_{\text{surr}}^{\circ}$ becomes more positive and so favours solubility. The change in the entropy of the cation gets less negative and this also favours solubility. As both factors favour an increase in solubility, barium hydroxide is more soluble than magnesium hydroxide.

Solubility of group 2 sulfates

Substance	$\Delta H_{\text{soln}}^{\circ}$ /kJ mol ⁻¹	$\Delta S_{\text{surr}}^{\circ} = -\Delta H_{\text{soln}}^{\circ}/T$ /J K ⁻¹ mol ⁻¹	Hydrated ion	Relative* entropy value of hydrated ion/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
Change down the group from Mg to Ba	Less exothermic	-368, so less likely to dissolve	Change down the group from Mg ²⁺ (aq) to Ba ²⁺ (aq)	+148, so more likely to dissolve

Table 2.10 Enthalpy and entropy changes involved in dissolving ionic solids

* The values of the entropy of hydrated ions are relative to the value for H⁺(aq).

Note that the change in $\Delta S_{\text{surr}}^{\circ}$ down a group is more than the change in $\Delta S_{\text{system}}^{\circ}$. This means that the change in enthalpy of solution is the main factor determining the change in solubility down a group.

The enthalpy of solution becomes *less* negative down the group. This means that $\Delta S_{\text{surr}}^{\circ}$ becomes less positive and, therefore, favours insolubility. The change in the entropy of the cation gets less negative, which favours solubility, but the change in entropy of the hydrated cation ($148 \text{ J K}^{-1} \text{ mol}^{-1}$) is much less than the change in entropy of the surroundings ($368 \text{ J K}^{-1} \text{ mol}^{-1}$). This results in the solubility of the sulfates decreasing down the group.

Melting and boiling points

At equilibrium, the value of ΔS_{total} is zero. At 0°C , there is equilibrium between ice and water. The ice does not melt, nor does the water freeze, unless heat is added to or taken from the system. Neither direction is thermodynamically feasible, so the two forms of water remain in equilibrium:

$$\begin{aligned}\Delta S_{\text{total}} &= \Delta S_{\text{system}} + \Delta S_{\text{surr}} \\ &= \Delta S_{\text{system}} - \frac{\Delta H}{T} = 0\end{aligned}$$

$$\Delta S_{\text{system}} = \frac{\Delta H}{T} \quad \text{or} \quad T = \frac{\Delta H}{\Delta S_{\text{system}}}$$

$$\Delta H \text{ for ice melting} = +6012 \text{ J mol}^{-1}$$

$$\Delta S_{\text{system}} = S(\text{water}) - S(\text{ice}) = +22 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\text{melting temperature of ice} = \frac{\Delta H}{\Delta S_{\text{system}}} = \frac{6012}{22} = 273 \text{ K} = 0^{\circ}\text{C}$$

$$\Delta H \text{ for water boiling} = +40\,700 \text{ J mol}^{-1}$$

$$\Delta S_{\text{system}} = S(\text{steam}) - S(\text{water}) = +109 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\text{boiling temperature of water} = \frac{\Delta H}{\Delta S_{\text{system}}} = \frac{40\,700}{109} = 373 \text{ K} = 100^{\circ}\text{C}$$

It can be seen from the expression $T = \Delta H/\Delta S$, that the melting or boiling temperature depends upon the amount of energy required for the change of state. This explains why boiling and melting temperatures depend on the strength of the forces between the particles:

strong force = large amount of energy needed to separate the particles
= high melting or boiling temperature

Summary

- The reactants are thermodynamically unstable relative to the products if ΔS_{total} for the change is positive. This means that the reaction is thermodynamically feasible.
- Endothermic reactions can happen only if the entropy change of the system is positive.
- Endothermic reactions are more likely to take place at higher temperatures.
- Exothermic reactions are always thermodynamically favourable if the entropy change of the system is positive.
- Exothermic reactions are thermodynamically favourable even when the entropy of the system is negative, if the entropy change of the surroundings outweighs the entropy change of the system.

Questions

1 Give an example of an endothermic reaction that takes place rapidly at room temperature.

2 What is the entropy of a perfect crystal of helium at absolute zero? Would a perfect crystal of sodium chloride have a different entropy value at absolute zero? Explain your answer.

3 State and explain which of the following would have the higher entropy:

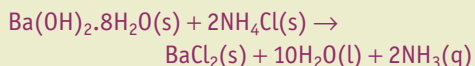
- a** an aqueous solution of glucose, $C_6H_{12}O_6$, or an aqueous solution of carbon dioxide at $25^\circ C$
- b** a solution of sodium chloride at $50^\circ C$ or a solution of sodium chloride at $25^\circ C$

4 Explain why the copper sulfate in a solution of copper sulfate does not spontaneously sink to the bottom even though it is denser than water.

5 Use the data in Table 2.2 to calculate the thermodynamic feasibility of the following reactions at 298 K.

- a** $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$ $\Delta H = -92 \text{ kJ mol}^{-1}$
- b** $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$ $\Delta H = +178 \text{ kJ mol}^{-1}$

6 Hydrated barium hydroxide reacts with solid ammonium chloride according to the equation:



The total standard entropy change at 298 K = $+150 \text{ J K}^{-1} \text{ mol}^{-1}$

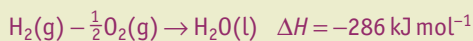
Some enthalpy and entropy data are given in the table.

Substance	Standard enthalpy of formation / kJ mol^{-1}	Standard entropy / $\text{J K}^{-1} \text{ mol}^{-1}$
$Ba(OH)_2 \cdot 8H_2O(s)$	-3245	
$NH_4Cl(s)$	-315	92
$BaCl_2(s)$	-860	130
$H_2O(l)$	-286	70
$NH_3(g)$	-46	193

Use the data to:

- a** Calculate ΔH° for this reaction
- b** Calculate ΔS_{system} and hence calculate the standard entropy of hydrated barium hydroxide.

7 The reaction between hydrogen and oxygen does not take place at a temperature of 298 K.



Use the data above and that in Table 2.2 to explain the concepts of thermodynamic stability and kinetic inertness.

8 Draw a Hess's law diagram, and use it together with the data here, to calculate ΔH_{soln} of lithium fluoride, LiF.

	Enthalpy change / kJ mol^{-1}
$\Delta H_{\text{hyd}}(\text{Li}^+(g))$	-519
$\Delta H_{\text{hyd}}(\text{F}^-(g))$	-506
$\Delta H_{\text{latt}}(\text{LiF}(s))$	-1022

Comment on the likely solubility of lithium fluoride in water.

9 Draw a Hess's law diagram for dissolving calcium chloride. Use it and the data here to calculate ΔH_{hyd} of a chloride ion, Cl^- .

	Enthalpy change / kJ mol^{-1}
$\Delta H_{\text{hyd}}(\text{Ca}^{2+}(g))$	-1650
$\Delta H_{\text{latt}}(\text{CaCl}_2(s))$	-2237
$\Delta H_{\text{soln}}(\text{CaCl}_2(s))$	-83

10 Given the ionic radii of the ions M^{2+} and Q^{3+} , explain which ion would have a higher exothermic hydration enthalpy.

Ion	Ionic radius/nm
M^{2+}	0.031
Q^{3+}	0.095

11 Study the data in the table.

Substance	$\Delta H_{\text{soln}}^{\circ}/\text{kJ mol}^{-1}$	Ion	$S^{\circ}/\text{J K}^{-1} \text{mol}^{-1}$
MgF ₂ (s)	-18	Mg ²⁺ (aq)	-138
CaF ₂ (s)	+13	Ca ²⁺ (aq)	-55
AgBr(s)	+85	Br ⁻ (aq)	+57
AgI(s)	+112	I ⁻ (aq)	+111

- a** Use the data to suggest and explain the relative solubility of the group 2 fluorides, magnesium fluoride, MgF₂, and calcium fluoride, CaF₂.
- b** Use the data to suggest and explain the relative solubility of the silver halides, silver bromide, AgBr, and silver iodide, AgI.

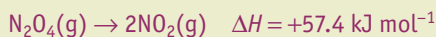
12 State and explain:

- a** whether H₂O(l) at 25°C has a higher or lower entropy than H₂O(l) at 35°C
- b** whether H₂O(l) at 100°C has a higher or lower entropy than H₂O(g) at 100°C

13 Use the following equations to state and explain whether the reactions result in an increase or decrease in the entropy of the systems:

- a** $\text{SO}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{SO}_3(\text{g})$
- b** $\text{NH}_4\text{Cl}(\text{s}) + \text{OH}^-(\text{aq}) \rightarrow \text{NH}_3(\text{g}) + \text{Cl}^-(\text{aq}) + \text{H}_2\text{O}(\text{l})$
- c** $\text{CaCO}_3(\text{s}) \rightarrow \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$
- d** $\text{NH}_4\text{NO}_3(\text{s}) + \text{aq} \rightarrow \text{NH}_4^+(\text{aq}) + \text{NO}_3^-(\text{aq})$
- e** $\text{Ca}(\text{NO}_3)_2(\text{s}) + \text{aq} \rightarrow \text{Ca}^{2+}(\text{aq}) + 2\text{NO}_3^-(\text{aq})$

14 a Calculate ΔS_{system} for the following reaction at 85°C:



Compound	Entropy, S , at 85°C/J K ⁻¹ mol ⁻¹
N ₂ O ₄ (g)	325
NO ₂ (g)	256

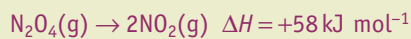
- b** Calculate ΔS_{total} for the reaction at 85°C.
- c** Comment on the feasibility of this reaction.
- d** Explain the term **thermodynamic stability** with reference to this reaction.

15 a Predict which of the following changes, W to Z, will take place at a temperature of 298 K.

Change	$\Delta H/\text{kJ mol}^{-1}$	$\Delta S_{\text{system}}/\text{J K}^{-1} \text{mol}^{-1}$
W	-170	+500
X	-170	-500
Y	+170	-500
Z	+170	+500

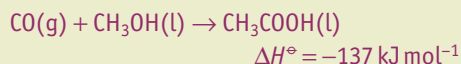
- b** Which of the changes W to Z will become more favourable when the temperature is increased?

16 Dinitrogen tetroxide decomposes spontaneously at 50°C:



State and explain the sign of ΔS_{system} for this reaction.

17 Ethanoic acid can be prepared from carbon monoxide and methanol



The standard entropy values, at 298 K, of these substances are given in the table.

Substance	$S^{\circ}/\text{J K}^{-1} \text{mol}^{-1}$
CO(g)	198
CH ₃ OH(l)	127
CH ₃ COOH(l)	160

- a** Suggest why the standard entropy of ethanoic acid is greater than that of methanol.
- b** Calculate the entropy change of the system for this reaction.
- c** Calculate the entropy change of the surroundings.
- d** Show, by calculation, whether this reaction is thermodynamically spontaneous at 298 K.
- e** This reaction does not take place at room temperature unless a catalyst is present. Use this fact and your answer from part **d** to explain the terms **thermodynamic stability** and **kinetic inertness**.

18 Ludwig Boltzmann could be described as the 'father of entropy'. Refer to the web and write a few lines about him. What was written on his tombstone?