# 20 Further energy changes

*In Topic 5, we showed how we could measure the standard enthalpy change, $\Delta H^\ominus$, of a reaction, and at how this value is determined by the relative bond strengths in the reactants and in the products. In this topic, we look how the $\Delta H^\ominus$ values for ionic reactions are determined by the forces of attraction between the ions. We then show how energy considerations can explain some trends in the properties of Group 2 compounds. The criteria that $\Delta H$ is negative cannot be used for endothermic reactions. The concept of entropy as a measure of disorder is introduced and the fact that the total entropy change must be positive for a spontaneous process is discussed. For chemical changes, the concept of Gibbs free energy provides a simpler method of determining the feasibility of a reaction.*

## Learning outcomes

By the end of this topic you should be able to:

**2.3g)** explain and use the term *electron affinity* (part, see also Topic 2)

**5.1b)** explain and use the term *lattice energy* ($\Delta H$ negative, i.e. gaseous ions to solid lattice) (part, see also Topic 5)

**5.1d)** explain, in qualitative terms, the effect of ionic charge and of ionic radius on the numerical magnitude of a lattice energy

**5.2a)** apply Hess's Law to construct simple energy cycles, and carry out calculations involving such cycles and relevant energy terms, with particular reference to the formation of a simple ionic solid and of its aqueous solution, and Born–Haber cycles (including ionisation energy and electron affinity) (part, see also Topic 5)

**5.3a)** explain that entropy is a measure of the 'disorder' of a system, and that a system becomes more stable when its energy is spread out in a more disordered state

**5.3b)** explain the entropy changes that occur during a change in state, e.g. (s) → (l); (l) → (g); (s) → (aq), during a temperature change, and during a reaction in which there is a change in the number of gaseous molecules

**5.3c)** predict whether the entropy change for a given process is positive or negative

**5.3d)** calculate the entropy change for a reaction, $\Delta S^\ominus$, given the standard entropies, $S^\ominus$, of the reactants and products

**5.4a)** define standard Gibbs free energy change of reaction by means of the equation $\Delta G^\ominus = \Delta H^\ominus - T\Delta S^\ominus$

**5.4b)** calculate $\Delta G^\ominus$ for a reaction using the equation $\Delta G^\ominus = \Delta H^\ominus - T\Delta S^\ominus$

**5.4c)** state whether a reaction or process will be spontaneous by using the sign of $\Delta G^\ominus$

**5.4d)** predict the effect of temperature change on the spontaneity of a reaction, given standard enthalpy and entropy changes

**10.1f)** interpret and explain qualitatively the trend in the thermal stability of the Group 2 nitrates and carbonates in terms of the charge density of the cation and the polarisability of the large anion

**10.1g)** interpret and explain qualitatively the variation in solubility of the Group 2 hydroxides and sulfates in terms of relative magnitudes of the enthalpy change of hydration and the corresponding lattice energy.
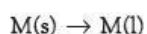
## 20.1 The Born–Haber cycle – finding the strengths of ionic bonds
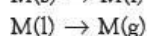
### Lattice enthalpy

In Topic 5 we saw that the following enthalpy changes are measures of the strengths of different types of bonding:

● intermolecular forces:

$$M(s) \rightarrow M(l) \qquad \text{enthalpy change of fusion, } \Delta H^\ominus_m$$
$$M(l) \rightarrow M(g) \qquad \text{enthalpy change of vaporisation, } \Delta H^\ominus_{vap}$$

- metallic:

$$M(s) \rightarrow M(g) \qquad \text{enthalpy change of atomisation, } \Delta H^{\ominus}_{at}$$

- covalent:

$$X\text{—}Y(g) \rightarrow X(g) + Y(g) \qquad \text{bond enthalpy, } E(X\text{—}Y)$$

In the same way, we could use the enthalpy change for the following process:

$$M^+X^-(s) \rightarrow M^+(g) + X^-(g)$$

as a measure of the strength of ionic bonding. It does not measure the strength of a *single* ionic bond between two ions, because there are many ionic bonds of different strengths in all directions in an ionic lattice (in NaCl, for example, each Na$^+$ ion is surrounded by six Cl$^-$ ions, and it is attracted to each of them), but nevertheless it allows useful comparisons to be made. The convention usually used is to quote the enthalpy change for the reverse process, that is, the enthalpy change when one mole of ionic solid is formed from its isolated gaseous ions. This quantity is known as the **lattice enthalpy (LE)** (or lattice energy). It has a large negative value because the formation of an ionic compound is a strongly exothermic process. For example, for sodium chloride:

$$Na^+(g) + Cl^-(g) \rightarrow NaCl(s) \qquad LE = -787\,kJ\,mol^{-1}$$
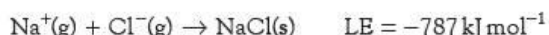
The **lattice enthalpy** is the enthalpy change when one mole of the solid is formed from its isolated ions in the gas phase.

Lattice enthalpies are calculated in a similar way to bond enthalpies, except that the additional factor of electron transfer must be taken into account. For sodium chloride, the energy associated with this process is the sum of the following two energies:

- the ionisation energy (IE) of sodium, for the process $Na(g) \rightarrow Na^+(g) + e^-$
- the electron affinity (EA) of chlorine, for the process $Cl(g) + e^- \rightarrow Cl^-(g)$.

We met ionisation energies in section 2.13. The definition of electron affinity is as follows.

The **electron affinity** (EA) of an atom (or ion) is defined as the energy change that occurs when one mole of electrons combines with one mole of gaseous atoms (or ions). That is, the electron affinity is the energy change for the following process:

$$X(g) + e^- \rightarrow X^-(g)$$
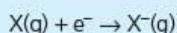
If there is a space in an atom's outer shell for an extra electron, the effective nuclear charge usually attracts an electron sufficiently strongly to make its electron affinity exothermic. However, a second electron affinity is always positive because the negative charge on the ion repels the second electron. For example, for oxygen:

$$O(g) + e^- \rightarrow O^-(g) \qquad \Delta H = -141\,kJ\,mol^{-1}$$
$$O^-(g) + e^- \rightarrow O^{2-}(g) \qquad \Delta H = +790\,kJ\,mol^{-1}$$
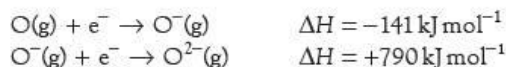
Adding these two gives:

$$O(g) + 2e^- \rightarrow O^{2-}(g) \qquad \Delta H = +649\,kJ\,mol^{-1}$$



**Figure 20.1** The Born–Haber cycle for sodium chloride

Figure 20.1 shows how the lattice enthalpy of sodium chloride may be worked out. Such a cycle constructed to find a lattice enthalpy is called a **Born–Haber cycle**.

The values of all the terms in this Born–Haber cycle can be measured, with the exception of the lattice enthalpy. (It is not physically possible to produce a mole of isolated gaseous ions – the electrostatic forces would be too great – let alone
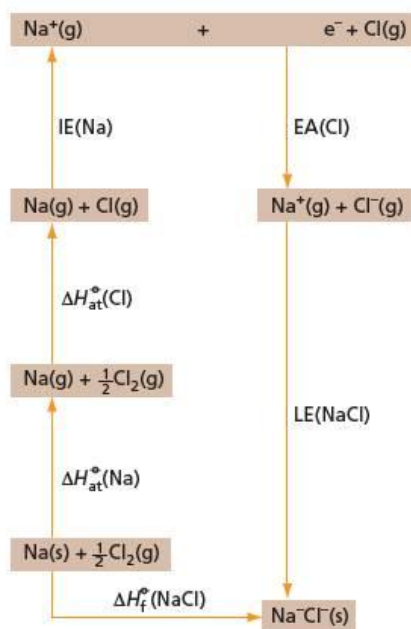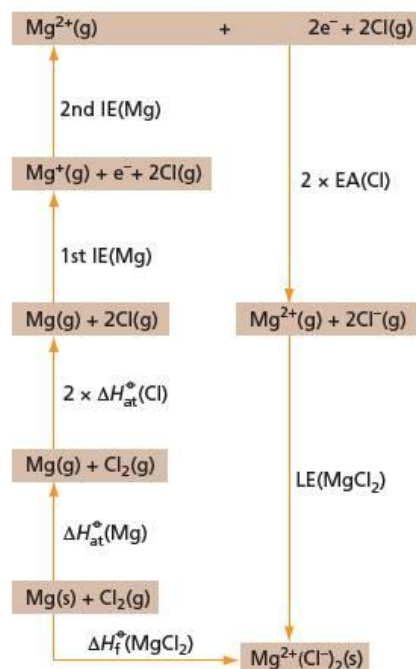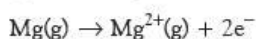
**Figure 20.2** The Born–Haber cycle for magnesium chloride

condense them into a mole of solid lattice.) But the lattice enthalpy can be calculated as follows:

$$\Delta H_{at}^{\ominus}(Na) + \Delta H_{at}^{\ominus}(Cl) + IE(Na) + EA(Cl) + LE(NaCl) = \Delta H_f^{\ominus}(NaCl)$$
$$+107.3 + 121.3 + 495.8 + (-348.6) + LE(NaCl) = -411.2$$
$$LE(NaCl) = -411.2 - (+375.8)$$
$$= -787\,kJ\,mol^{-1}$$

The situation is slightly more complicated if the ions carry more than one charge. For example, for magnesium chloride, the energy change associated with the process:

$$Mg(g) \rightarrow Mg^{2+}(g) + 2e^-$$

is the sum of the first and second ionisation energies of magnesium (it is *not* just the second ionisation energy of magnesium). In addition, as the formula is $MgCl_2$, we need to produce two moles of chloride ions. The Born–Haber cycle is shown in Figure 20.2.

$$\Delta H_{at}^{\ominus}(Mg) + 2 \times \Delta H_{at}^{\ominus}(Cl) + 1st\ IE(Mg) + 2nd\ IE(Mg) + 2 \times EA(Cl) + LE(MgCl_2)$$
$$= \Delta H_f(MgCl_2)$$
$$+147.1 + 2 \times 121.3 + 737.7 + 1450.7 + (2 \times -348.6) + LE(MgCl_2)$$
$$= -641.3$$
$$LE(MgCl_2) = -641.3 - (+1880.9)$$
$$= -2522\,kJ\,mol^{-1}$$

> **Now try this**
>
> Construct a Born–Haber cycle for each of the following compounds, and use it to calculate the lattice energy. Use the data given below in your calculations (all in $kJ\,mol^{-1}$).
> 1 $Na_2O$
> 2 $MgO$
>
> [$IE(Na) = +494$; $IE(Mg) = +736$; $IE(Mg^+) = +1450$; $EA(O) = -141$; $EA(O^-) = +790$; $\Delta H_f^{\ominus}(Na_2O) = -414$; $\Delta H_f^{\ominus}(MgO) = -602$; $\Delta H_{at}^{\ominus}(Na) = +107$; $\Delta H_{at}^{\ominus}(Mg) = +147$; $E(O=O) = +496$]

## The magnitude of the lattice enthalpy

The value of the lattice enthalpy of magnesium chloride is much larger than that for sodium chloride. There are two reasons for this. The first is that there are more cation-to-anion attractions because there are twice as many chloride ions. The second reason is that each of these attractions is much stronger, because the magnesium ion carries twice the charge of the sodium ion.

There are other factors that determine the size of the lattice enthalpy. The most important of these is how closely the ions approach each other (the sum of their ionic radii). The effects on the lattice enthalpy of the distance between the ions and the charges on the ions are illustrated in Table 20.1.

**Table 20.1** For ionic compounds of the same type, the shorter the inter-ionic distance, the greater the value of the lattice enthalpy. Compounds containing doubly or triply charged ions have much larger values of lattice energy.

| Compound | Inter-ionic distance/nm | Charges on ions | Lattice energy/kJ mol$^{-1}$ |
|---|---|---|---|
| LiF | 0.211 | 1, 1 | −1036 |
| NaCl | 0.279 | 1, 1 | −787 |
| CsI | 0.385 | 1, 1 | −604 |
| BeF$_2$ | 0.167 | 2, 1 | −3505 |
| MgCl$_2$ | 0.259 | 2, 1 | −2522 |
| BaI$_2$ | 0.363 | 2, 1 | −1877 |
| Li$_2$O | 0.210 | 1, 2 | −2814 |
| MgO | 0.210 | 2, 2 | −3791 |
| Al$_2$O$_3$ | 0.189 | 3, 2 | −16470 |

Lattice enthalpies are determined by the magnitudes of:
- the charges on the ions
- the inter-ionic distance
- the type of lattice.

## Worked example

**a** Write an equation that represents the chemical change associated with the lattice enthalpy of calcium fluoride.

**b** Which two elements, one from Group 1 and the other from Group 17, form a compound with the most negative value of lattice enthalpy?

### Answer

**a** $Ca^{2+}(g) + 2F^-(g) \rightarrow CaF_2(s)$

**b** Lithium and fluorine, because they have the smallest ionic radii.

## Now try this

**1 a** Draw a Born–Haber cycle for barium sulfide, BaS.

**b** Use the following values (all in $kJ\,mol^{-1}$) to calculate the lattice enthalpy of barium sulfide:

$\Delta H_{at}(Ba) = +180$; $\Delta H_{at}(S) = +249.2$; 1st IE(Ba) = +502; 2nd IE(Ba) = 966; 1st EA(S) = −141.4; 2nd EA(S) = +790.8; $\Delta H_f(BaS) = −595.8$

**2** Explain why the following substances have different values of lattice enthalpy from that of sodium chloride:

**a** potassium chloride     **b** magnesium sulfide     **c** calcium chloride.

## Ceramics

**Ceramics** are substances with giant structures that contain either strong covalent bonds with some ionic character (e.g. $SiO_2$) or strong ionic bonds with some covalent character (e.g. MgO and $Al_2O_3$). They are hard but brittle. They are hard because of the strong interatomic forces that hold the crystal together, and brittle because any deformation brings similarly charged ions closer together and leads to increased repulsion. If the ions have multiple charges, the lattice energy, melting point and Young modulus (a measure of stiffness) all increase, as Table 20.2 shows.

**Table 20.2** The properties of some ionic substances

| Substance | Charges on ions | Lattice energy/ $kJ\,mol^{-1}$ | Melting point/°C | Young modulus/ $GN\,m^{-2}$ |
|---|---|---|---|---|
| NaCl | 1, 1 | −787 | 801 | 44 |
| MgO | 2, 2 | −3791 | 2852 | 245 |
| $Al_2O_3$ | 3, 2 | −16470 | 2072 | 525 |

The high melting points mean that ceramics are used for furnace linings. The linings for blast furnaces are made of bricks with a high content of aluminium oxide, and those for steel converters are mainly magnesium oxide, made by heating magnesium carbonate (see section 10.4).

As the charges in the ionic substance increase, so does the covalent character of the bonds. By the time the charge reaches +4, as in $Si^{4+}$, the bond can be considered to be almost totally covalent. Ceramics such as silicon(IV) oxide, $SiO_2$, silicon(IV) nitride, $Si_3N_4$, silicon(IV) carbide, SiC, and tungsten carbide, WC, have high Young moduli, and are useful in adding stiffness to plastics or metals. For example:

- glass fibres embedded in epoxy resins ('glass-reinforced plastic', GRP) are used in boat construction
- the tiles covering the space shuttle contain silicon(IV) oxide fibres
- the blades in some jet engines are stiffened with silicon(IV) carbide.

**Figure 20.3** Ceramics provide many useful properties.
**a** Fine china is hard but brittle.
**b** The tiles covering the space shuttle have an extremely low thermal conductivity, and so insulate the inside of the shuttle from the heat at re-entry.
**c** GRP is tough and does not corrode, and so is used extensively in boat-building.

Some ceramics can lose their electrical resistance completely when cooled and act as **superconductors** while still at relatively high temperatures compared to those near to absolute zero that are needed to cause superconductivity in metals. These ceramics are mixtures of metal oxides, usually including copper oxide. One of them, with the approximate formula $YBa_2Cu_3O_7$, is a superconductor at 90 K. In the future, these superconducting ceramics could be used to transmit electricity over large distances without any loss in energy, or to make highly efficient electrical devices.

## 20.2 Enthalpy changes of solution and hydration

### Enthalpy change of solution

The solubilities of salts in water show wide variations, with no obvious pattern. One of the factors determining solubility is whether the **enthalpy change of solution**, $\Delta H_{sol}$, of the salt is positive or negative. This enthalpy change is the energy associated with the process:

$$M^+X^-(s) \rightarrow M^+(aq) + X^-(aq)$$

We must be careful to specify the dilution of the final solution when quoting this enthalpy change. On dilution, the ions in a solution become more extensively hydrated (an exothermic process) and also move further apart (an endothermic process). The relative importance of these two effects changes with dilution, affecting the values of $\Delta H_{sol}$ in a complicated way. A quoted single value of $\Delta H_{sol}$ refers to an 'infinitely dilute' solution. This value cannot be determined directly by experiment and must be found by a process of extrapolation. In practice, there comes a point when further dilution has no measurable effect on the value of $\Delta H_{sol}$, and this may be taken as infinite dilution.

The **enthalpy change of solution**, $\Delta H_{sol}$, is the enthalpy change when one mole of solute dissolves in an infinite volume of water.

If $\Delta H_{sol}$ is positive, the salt is likely to be insoluble or of very low solubility. If $\Delta H_{sol}$ is approximately zero or negative, then the salt is likely to be soluble or very soluble.

### Enthalpy change of hydration

The value of $\Delta H_{sol}$ depends on two energy changes. The first is the energy that holds the lattice together, that is, the lattice energy. The second is the energy given out when gaseous ions are hydrated. This is called the **enthalpy change of hydration**, $\Delta H_{hyd}$.

The **enthalpy change of hydration**, $\Delta H_{hyd}$, is the enthalpy change when one mole of gaseous ions dissolves in an infinite volume of water.
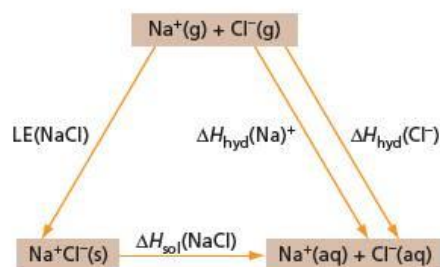
**Figure 20.4** Hess's Law cycle for the dissolving in water of sodium chloride

**Table 20.3** Absolute enthalpy changes of hydration for some common ions

| Ion | $\Delta H_{hyd}$/kJmol$^{-1}$ |
|---|---|
| H$^+$ | −1120 |
| Li$^+$ | −544 |
| Na$^+$ | −435 |
| Mg$^{2+}$ | −1980 |
| Ca$^{2+}$ | −1650 |
| Al$^{3+}$ | −4750 |
| F$^-$ | −473 |
| Cl$^-$ | −339 |



**Figure 20.5**

For sodium chloride, we can construct the cycle shown in Figure 20.4. The value of the lattice enthalpy is found using the Born–Haber cycle (see Figure 20.1); it is −787 kJ mol$^{-1}$. $\Delta H_{sol}$ can be found experimentally: its value is +3.9 kJ mol$^{-1}$. Therefore:

$$\Sigma(\Delta H_{hyd}) = LE(NaCl) + \Delta H_{sol}(NaCl)$$
$$= -787 + 3.9$$
$$= -783.1 \text{ kJ mol}^{-1}$$

where $\Sigma(\Delta H_{hyd}) = \Delta H_{hyd}(Na^+) + \Delta H_{hyd}(Cl^-)$.

We can now see why similar substances can show wide variations in solubility. Both the lattice enthalpy and the enthalpy change of hydration are large negative quantities. A small percentage change in either of these has a very large effect on the difference between the two terms: a 0.5% change in LE would alter $\Delta H_{sol}$ by 100%, for example. These variations can be used to explain the differences in solubility of some compounds of Group 2 (see section 20.6).

The Hess's Law cycle does not enable us to find $\Delta H_{hyd}$ for the individual ions, because it provides only the *sum* of the enthalpy changes of hydration for the cation and anion. In order to find their individual values, we must assign a value to one of the ions. The value for the H$^+$ ion is generally agreed to be −1120 kJ mol$^{-1}$ and, by using this value, we can calculate the **absolute enthalpy change of hydration** of ions, as shown in Table 20.3.

The values in Table 20.3 show that the absolute enthalpy change of hydration depends on the ability of the ion to attract water molecules. Small, highly charged ions have the most negative values of $\Delta H_{hyd}$ (see section 4.9).

Enthalpy changes of hydration are more negative:
- if the ion is small
- if the ion has two or three units of charge on it.

## Worked example

**a** Draw an energy cycle to show the connection between solid magnesium chloride, its gaseous ions and its aqueous ions.
**b** Use the following values to calculate the value of $\Delta H_{hyd}(MgCl_2)$:

LE(MgCl$_2$) = −2375 kJ mol$^{-1}$; $\Delta H_{sol}(MgCl_2)$ = −155.1 kJ mol$^{-1}$

**c** Compare this value with the value obtained from the separate absolute enthalpy changes of hydration for Mg$^{2+}$ and Cl$^-$ in Table 20.3.

**Answer**
**a** See Figure 20.5.
**b** From Figure 20.5:

$$\Delta H_{hyd}(MgCl_2) = \Delta H_{hyd}(Mg^+) + 2\Delta H_{hyd}(Cl^-)$$
$$= LE + \Delta H_{sol}$$
$$= -2375 - 155.1$$
$$= \mathbf{-2530 \text{ kJ mol}^{-1}}$$

**c** From Table 20.3:

$$\Delta H_{hyd}(Mg^+) + 2\Delta H_{hyd}(Cl^-) = -1980 + 2 \times (-339)$$
$$= \mathbf{-2658 \text{ kJ mol}^{-1}}$$

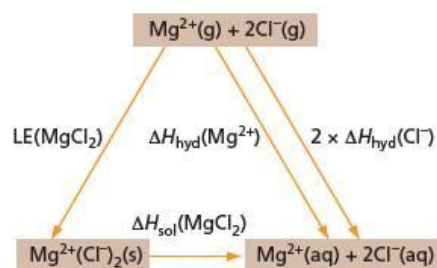This value agrees with that in **b** to within 5%: a fair agreement

1 Draw a Born–Haber cycle for aluminium fluoride, $AlF_3(s)$.
2 Use the following values (all in $kJ\,mol^{-1}$) to calculate the lattice energy of aluminium fluoride:

$\Delta H_f^{\ominus}(AlF_3) = -1504.1$; $\Delta H_a^{\ominus}(Al) = 324.3$; $\Delta H_a^{\ominus}(F) = 79.0$; 1st IE(Al) = 577;
2nd IE(Al) = 1820; 3rd IE(Al) = 2740; EA(Cl) = −328

3 Draw an energy diagram to show the connection between $AlF_3(s)$, its gaseous ions and its aqueous ions.
4 Use the figures in Table 20.3 and the lattice enthalpy value obtained in 2 to calculate $\Delta H_{sol}(AlF_3)$.

## 20.3 The concept of entropy

### Spontaneous and reversible processes

A **spontaneous change** is one that, in the absence of any barrier, such as activation energy, takes place naturally in the direction stated. Not all chemical changes that occur spontaneously are exothermic, and so the principle that $\Delta H$ is negative cannot always be used as the criterion of feasibility. In order to find a more general principle, which will enable us to predict if a reaction is spontaneous or not, we need to consider what happens to the energy that is released or absorbed in a chemical reaction.

Spontaneous processes often take place because the potential energy of the system decreases – for example, a weight falls to the ground or an electric current flows through a resistor from a point of high potential to one of lower potential. In both these examples, the reduction in potential energy is accompanied by an increase in heat, which is random kinetic energy. Potential energy is much more ordered than heat energy. In potential energy the energy mostly moves in a definite direction: in heat energy the energy is random and moves in every direction. Random motion is much more probable than directed motion and that is why systems tend to become more disordered.

The measure of this disorder is called **entropy**, and is given the symbol $S$. Formally a change of entropy is defined using the equation $\Delta S = q/T$, where $q$ is the amount of heat transferred at an absolute temperature $T$. We can see why the temperature is important. An amount of random heat energy $q$ added to a relatively ordered system at a low temperature $T_1$ causes more disorder than if the same amount of heat was added to a much less ordered system at a higher temperature $T_2$. An analogy that has been used is that a sneeze or cough causes more disturbance in a quiet library than a sneeze or cough in a noisy, busy street.

The general principle for a spontaneous change is that the **total entropy change** $\Delta S_{tot}$ **is positive**. This is known as the Second Law of Thermodynamics (the Law of Conservation of Energy being the first). We know that heat spontaneously flows from a hot body at temperature $T_2$ to a cold body at temperature $T_1$. The removal of an amount of energy at temperature $T_2$ is accompanied by an entropy decrease $-q/T_2$. The addition of this energy to a cold body at temperature $T_2$ is accompanied by an entropy increase of $+q/T_2$. The total entropy change is $-q/T_2 + q/T_1$ (see Figure 20.6). This is positive if $T_2 > T_1$, which agrees with the observation that heat flows spontaneously form a hot to a cold body. If $T_2 = T_1$, the system is in equilibrium but any heat transfer is so infinitely slow that no useful work can be obtained from it. This special condition when $\Delta S_{tot} = 0$ is known as a **reversible change**.

**Figure 20.6** When a quantity of heat $q$ flows from a hot body at temperature $T_2$ to a cold body at temperature $T_1$, $\Delta S_{tot} = -q/T_2 + q/T_1$. This is positive if $T_2 > T_1$.

| hot body at temperature $T_2$ | entropy change $-q/T_2$ |

amount of heat energy $q$

| cold body at temperature $T_1$ | entropy change $+q/T_1$ |
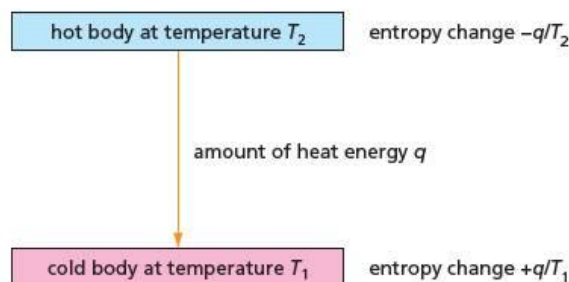
## Entropy values

Unlike $H$, $S$ can be given an absolute value. Using the Third Law of Thermodynamics, which states that **at absolute zero the entropy of a pure, crystalline substance is zero**, we have a base from which we can measure absolute entropy values. This law fits in with our idea that under these conditions a system is at the most ordered that it can be; it also has experimental support from measurements at very low temperatures. Values for some elements are listed in Table 20.4. As entropy change is $q/T$, its units are $J\,mol^{-1}\,K^{-1}$.

**Table 20.4** Values of absolute entropies $S^\ominus$ for some elements. These are at 298 K and 1.0 bar.

| Element | He | Ar | C(diamond) | C(graphite) | Na | K | Mg | Fe |
|---|---|---|---|---|---|---|---|---|
| $S^\ominus/J\,mol^{-1}\,K^{-1}$ | 126.0 | 154.7 | 2.4 | 5.7 | 51.2 | 64.2 | 32.7 | 27.3 |

If we look at Table 20.4, we can find some trends about absolute entropies. These may be summarised as follows. $S^\ominus$ values:

- increase as $A_r$ increases
- increase from solids to liquids to gases
- decrease if the element is soft.

We find similar trends in the entropies of the compounds listed in Table 20.5.

**Table 20.5** Values of absolute entropies for some compounds

| Compound | NaCl(s) | $Na_2CO_3$(s) | KCl(s) | $H_2O$(l) | $C_2H_5OH$(l) | CO(g) | $CO_2$(g) |
|---|---|---|---|---|---|---|---|
| $S^\ominus/J\,mol^{-1}\,K^{-1}$ | 72.1 | 135.0 | 82.6 | 69.9 | 160.7 | 197.6 | 213.6 |

## Some entropy changes

An entropy change is defined as $q/T$. We can use this to calculate the increase in entropy when 10 kJ of heat flows from a hot body at 500 K to a cold body at 400 K. We have:

$$\text{entropy change of hot body} = \frac{-10\,000}{500} = -200\,J\,mol^{-1}\,K^{-1}$$

$$\text{entropy change of cold body} = \frac{+10\,000}{400} = +250\,J\,mol^{-1}\,K^{-1}$$

$$\text{total entropy change} = -200 + 250 = +50\,J\,mol^{-1}\,K^{-1}$$

Another example when it is easy to calculate the entropy change is the melting of a solid at its melting point or the evaporation of a liquid at its boiling point. Under these conditions the change is reversible and so $\Delta S_{tot}$ is zero. This means that $\Delta S = q/T$, where $q$ is the molar latent heat. At 273 K, the latent heat of fusion of ice is $6.01\,kJ\,mol^{-1}$. This gives the entropy change as $6010/273 = 22.0\,J\,mol^{-1}\,K^{-1}$.

## Entropy change of a chemical reaction

The entropy change of chemical reaction can be calculated in a similar way to that used for calculating enthalpy changes. But we must remember that although the standard enthalpy change of formation of elements is zero, their standard entropies are not.

> **Now try this**
>
> What is the entropy change when 30 kJ of heat flows from a hot body at 100 °C to a cold body at 27 °C?

> **Now try this**
>
> 1 The latent heat of vaporisation of water is $2260\,J\,g^{-1}$. What is its entropy change of evaporation at 100 °C in $J\,mol^{-1}\,K^{-1}$?
> 2 The latent heat of fusion of lead is $23.0\,J\,g^{-1}$ at 327 °C. What is its entropy of fusion?

## Worked example

What is $\Delta S^\ominus$ for the reaction $2Na(s) + Cl_2(g) \rightarrow 2NaCl(s)$?

### Answer

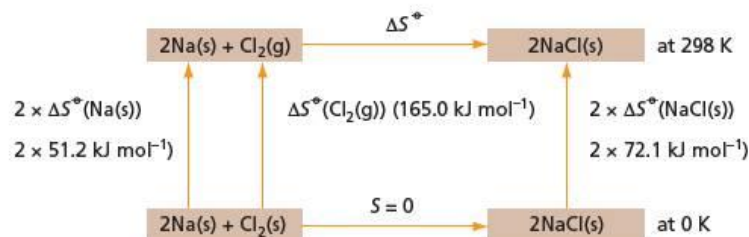Figure 20.7 shows the entropy changes for the reaction.

**Figure 20.7** Calculating the entropy change for the formation of sodium chloride. At 0 K, $\Delta S = 0$ as $\Delta S$ for all the substances = 0.



From Figure 20.7:

$$2 \times 51.2 + 165.0 + \Delta S^\ominus = 2 \times 72.1$$
$$\Delta S^\ominus = 142.2 - 267.4 = -125.2$$
$$= -125.2\,J\,mol^{-1}\,K^{-1}$$

It is not surprising that the reaction is accompanied by an entropy decrease as a gas is being used up. This entropy decrease is only possible because the reaction is so exothermic that the entropy of the heat given off more than compensates for this decrease.

### Now try this

What is $\Delta S^\ominus$ for the following reactions?

1 $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$
2 $C_2H_4(g) + H_2O(l) \rightarrow C_2H_5OH(l)$
3 $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$
[$\Delta S^\ominus$/J mol$^{-1}$ K$^{-1}$: $CaCO_3(s)$ 92.9; $CaO(s)$ 39.7; $H_2O(l)$ 69.9; $C_2H_5OH(l)$ 160.7; $H_2O(g)$ 130.6; $H_2(g)$ 130.6; $N_2(g)$ 191.6; $NH_3(g)$ 192.3; $C_2H_4(g)$ 219.5]

Some other examples of entropy changes for different types of reactions are given in Table 20.6.

**Table 20.6** Some examples of entropy changes

| Example | $\Delta S^\ominus$/J K$^{-1}$ mol$^{-1}$ | Type of change |
|---|---|---|
| mixing two gases (one mole of each) | 22 | mixing |
| $C_6H_6(s) \rightarrow C_6H_6(l)$ | 3.6 | melting |
| $C_6H_{14}(l) \rightarrow C_6H_{14}(g)$ | 88 | evaporation |
| $K(s) + I_2(s) \rightarrow KI(s)$ | −17 | combination |
| $MgCO_3(s) \rightarrow MgO(s) + CO_2(g)$ | 175 | decomposition |
| $NaCl(s) \rightarrow Na^+(aq) + Cl^-(aq)$ | 43 | solution |
| $Ca^{2+}(aq) + CO_3^{2-}(aq) \rightarrow CaCO_3(s)$ | −204 | precipitation |

## 20.4 Gibbs free energy

In a chemical reaction, we have to consider the entropy changes that take place both in the system (that is the reaction that is happening) and in the surroundings (which absorbs or gives out heat). Many chemical reactions are exothermic and the entropy increase in the surroundings more than compensates for any entropy decrease that may be taking place in the system. We have:

$$\Delta S^\ominus_{total} = \Delta S^\ominus_{system} + \Delta S^\ominus_{surroundings}$$
$$\Delta S^\ominus_{surroundings} = \frac{q}{T} = \frac{-\Delta H}{T}$$

It is always possible to calculate the total entropy change from these two terms but it is more convenient if they are combined together in a single function. This function is called the Gibbs free energy function after Josiah Willard Gibbs (see Figure 20.8) is given the symbol $\Delta G$.



**Figure 20.8** Josiah Willard Gibbs (1839–1903), the father of chemical thermodynamics

It is a measure of the total entropy increase associated with the reaction and is a measure of the driving force of that reaction. If the reaction has a decrease in free energy, it is feasible. We have:

$$\Delta S^{\ominus}_{total} = \Delta S^{\ominus}_{system} + \Delta S^{\ominus}_{surroundings}$$

$$\frac{-\Delta G^{\ominus}}{T} = \Delta S^{\ominus}_{system} - \frac{\Delta H^{\ominus}}{T}$$

This equation can be written in the more familiar form:

$$\Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus}$$

We can use this equation as follows:

- if $\Delta G^{\ominus}$ is negative, the reaction is feasible
- if $\Delta G^{\ominus} = 0$, the reaction is in equilibrium
- if $\Delta G^{\ominus}$ is positive, the reaction will not go spontaneously to completion.

The entropy increase associated with a decrease in $\Delta G^{\ominus}$ can be given another interpretation. Whereas $-\Delta H^{\ominus}$ is a measure of the total heat energy $q$ lost from the system, $-\Delta G^{\ominus}$ is the *maximum* amount of that total energy that is available to do work. Usually $\Delta G^{\ominus}$ is less negative than $\Delta H^{\ominus}$ but occasionally the reverse is true.

## Calculating $\Delta G^{\ominus}$

We can calculate $\Delta G^{\ominus}$ for a reaction in a similar way to that we calculated $\Delta H^{\ominus}$, using free energies of formation rather than enthalpies of formation.

### Worked example

Calculate $\Delta G^{\ominus}$ for the reaction $C_2H_6(g) + 4\frac{1}{2}O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l)$

#### Answer
Figure 20.9 shows the free energies of formation for the reaction.
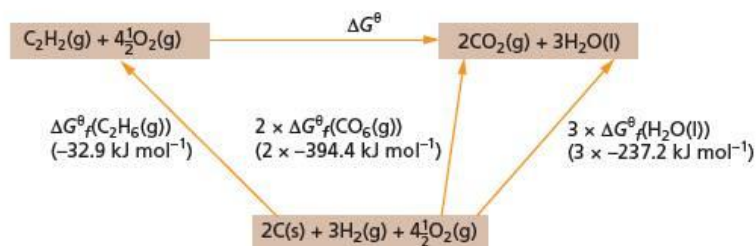
**Figure 20.9** Calculating $\Delta G^{\ominus}$ from $\Delta G^{\ominus}_f$ values



From Figure 20.9:

$$-32.9 + \Delta G^{\ominus} = -788.8 - 711.6$$
$$\Delta G^{\ominus} = -1500.4 - (-32.9)$$
$$= -1467.5 \text{ kJ mol}^{-1}$$

(We should not be surprised that $\Delta G^{\ominus}$ is so large and negative. The reaction is highly exothermic and this more than compensates for $\Delta S^{\ominus}$ being negative because of the reduction in the number of gas molecules.)

### Now try this

Calculate $\Delta G^{\ominus}$ for

1 the combustion of propane
[$\Delta G^{\ominus}_f (C_3H_8(g)) = -23.4$ kJ mol$^{-1}$]
2 the chlorination of ethane to give ethyl chloride.
[$\Delta G^{\ominus}_f$/kJ mol$^{-1}$: $C_2H_6(g)$ –32.9; $C_2H_5Cl(g)$ –52.9; $HCl(g)$ –95.2]

## Variation of $\Delta G^{\ominus}$ with temperature

The values of $\Delta H^{\ominus}$ and $\Delta S^{\ominus}$ for a reaction vary slightly with changes in temperature, but the effect is very small compared to the effect that changes in temperature have on $\Delta G^{\ominus}$. Increasing temperature makes the $T\Delta S^{\ominus}$ term increasingly important. For example, over the temperature range 298 K to 1500 K, $\Delta H^{\ominus}$ and $\Delta S^{\ominus}$ for the decomposition of calcium carbonate change by only a few per cent but $\Delta G^{\ominus}$ changes from +131 kJ mol$^{-1}$ at 298, to +16 kJ mol$^{-1}$ at 1000 K and –64 kJ mol$^{-1}$ at 1500 K. To a good approximation, we can regard $\Delta H^{\ominus}$ and $\Delta S^{\ominus}$ as constant and calculate how $\Delta G^{\ominus}$ changes with temperature using the equation $\Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus}$.

## Worked example

For the reaction $C_2H_4(g) + HCl(g) \rightarrow C_2H_5Cl(g)$, at 298 K,
$\Delta H^\ominus = -96.7\,kJ\,mol^{-1}$ and $\Delta G^\ominus = -25.9\,kJ\,mol^{-1}$.
Calculate the value of $\Delta G^\ominus$ at 1000 K.

### Answer

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

At 298 K, $-T\Delta S^\ominus = -25.9 - (-96.7) = +70.8\ kJ\,mol^{-1}$

$$\Delta S^\ominus = \frac{-70\,800}{298} = -239\,J\,mol^{-1}\,K^{-1}$$

At 1000 K, $\Delta G^\ominus = -96.7 - \left(1000 \times \frac{-239}{1000}\right)$

$$= +142\,kJ\,mol^{-1}$$

This shows that as the temperature increases, the addition reaction becomes less feasible.

## Now try this

1 Calculate the temperature at which $\Delta G^\ominus$ for the addition of HCl to ethene becomes zero.

2 When $KNO_3$ dissolves in water at 298 K, $\Delta H^\ominus = +34.8\,kJ\,mol^{-1}$ and $\Delta G^\ominus = +0.3\,kJ\,mol^{-1}$.
   a Calculate $\Delta S^\ominus$.
   b Calculate $\Delta G^\ominus$ at 320 K.
   c Comment on the effect of temperature on the solubility of $KNO_3$.

3 Heptane is converted into methylbenzene industrially:

   $$C_7H_{16}(l) \rightarrow C_7H_8(l) + 4H_2(g)$$

   At 300 K, $\Delta H^\ominus = +211\,kJ\,mol^{-1}$ and $\Delta G^\ominus = +110\,kJ\,mol^{-1}$.

   Estimate $\Delta G^\ominus$ at:
   a 600 K
   b 900 K
   c Explain why your estimated values will be unreliable.

# Applying free energy changes

The free energy of a reaction tells us whether the reaction proceeds spontaneously and this depends on the signs and magnitudes of both $\Delta H^\ominus$ and $\Delta S^\ominus$ for the reaction. As $\Delta H^\ominus$ and $\Delta S^\ominus$ can each be positive or negative, there are four possibilities.

## $\Delta H^\ominus$ and $\Delta S^\ominus$ both positive

These reactions are said to be entropy driven. These endothermic reactions, which may not be feasible at room temperature, become feasible if the temperature is raised (Le Chatelier's Principle). The following are some examples:

- melting and boiling
- decomposition reactions
- electrolysis
- dissolving (in some cases).

It is easy to see why both $\Delta H^\ominus$ and $\Delta S^\ominus$ are positive for melting and boiling (see Figure 20.10). The change is endothermic because intermolecular bonds are being broken. There is an increase in the entropy because disorder increases from solid to liquid to gas.

Most decomposition reactions (for example, the cracking of alkanes and the thermal decomposition of calcium carbonate) are endothermic because the total bond enthalpy in the products is less than that in the reactants. The energy required to break relatively strong bonds is not recovered by the formation of fewer or weaker bonds. Decomposition reactions are accompanied by an increase in entropy because the change in number of molecules, $\Delta n$, is positive.

**Figure 20.10** $\Delta H$ and $\Delta S$ both positive: **a** melting ice and **b** boiling water



Decomposition may be brought about by electrolysis rather than by heating. The reaction can then take place at a temperature at which $\Delta G^\ominus$ is positive, because it is being driven by the passage of an electric current through a potential difference. For the electrolysis of water, the minimum voltage needed to bring about decomposition is 1.23 V. This point is discussed in more detail in Topic 23.

Liquids of similar polarity (for example, hexane and heptane) mix together in all proportions. If the polarity of the liquids is different, however, $\Delta H^\ominus$ becomes so large and positive that they may be only partially miscible (for example, butan-1-ol and water). The solubility then increases if the temperature is raised. This is usually the situation when a covalent solid dissolves in a liquid (for example, benzoic acid in water).

The dissolving of ionic solids in water is an extremely complex process. Because ions hydrate to a greater extent in dilute solution, dissolving an ionic solid in water may be exothermic when the solution is dilute, but endothermic when it becomes saturated. Two entropy terms operate:

- an entropy increase because the ions in the solid are free to move in solution
- an entropy decrease because water molecules that were originally free to move become restricted by hydration of the ions.

This complex interplay between enthalpy and entropy factors makes it very difficult to explain why some ionic compounds are very soluble in water while others are highly insoluble. For ions with a single charge, the overall entropy change is usually positive and this means that compounds of Group 1 are water soluble, even when the enthalpy of solution is positive. For ions with a multiple charge, the overall entropy change is usually negative. Many compounds in Group 2 have a positive enthalpy of solution and combining this with an adverse entropy term makes them insoluble (see page 345).

## $\Delta H^\ominus$ and $\Delta S^\ominus$ both negative

These reactions are said to be enthalpy driven. These exothermic reactions are feasible at low temperatures. Here are some common examples:

- condensation and freezing (see Figure 20.11)
- addition and combination reactions
- electrochemical cells
- precipitation.

These reactions are the reverse of the reactions in which both $\Delta H^{\ominus}$ and $\Delta S^{\ominus}$ are positive. Although addition and combination reactions are feasible at room temperature, it may be that the rate of reaction is then so slow that a catalyst has to be used. An example of this is the catalytic hydrogenation of an alkene.

**a**



**b**
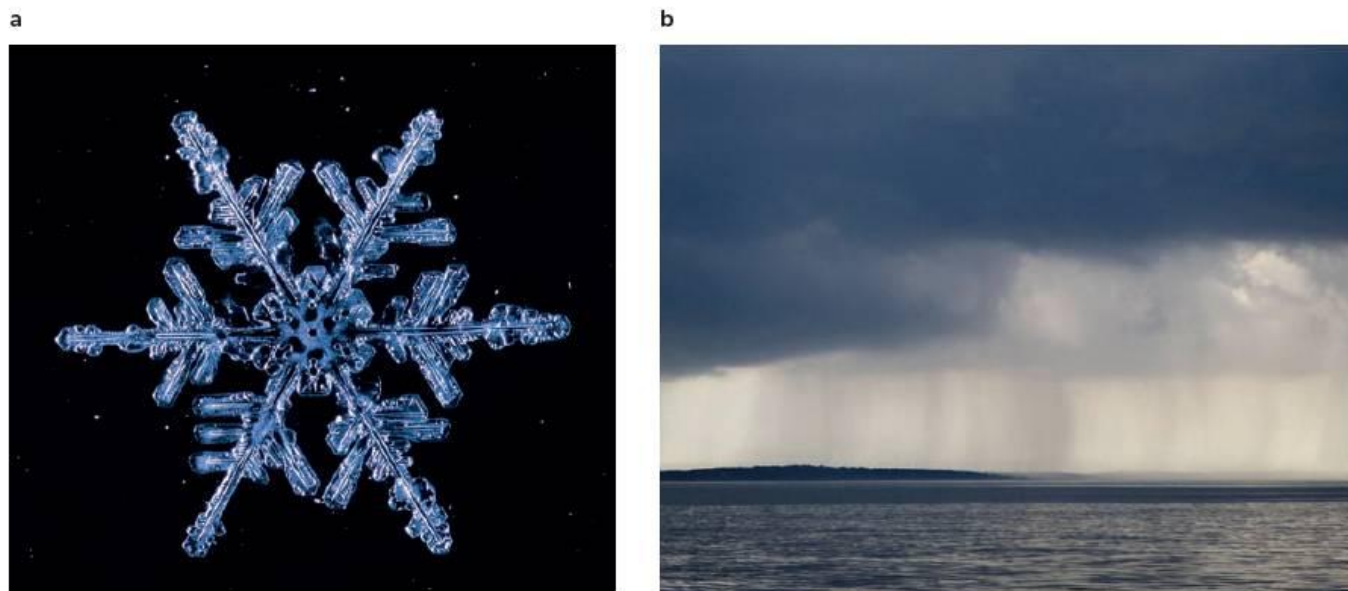


**Figure 20.11** $\Delta H$ and $\Delta S$ both negative: **a** formation of a snow crystal and **b** rain from clouds

## $\Delta H^{\ominus}$ negative and $\Delta S^{\ominus}$ positive

These reactions are feasible at all temperatures. The reactants are said to be **metastable** under all conditions because they exist only because the activation energy of the reaction is so high. They are thermodynamically unstable, but kinetically inert. The following are some examples:

- a few decomposition reactions
- organic combustion reactions
- combustion of explosives (see Figure 20.12 and the panel on page 343).

**Figure 20.12** $\Delta H$ negative and $\Delta S$ positive: **a** fireworks and **b** explosive decomposition of ammonium nitrate

**a**



**b**

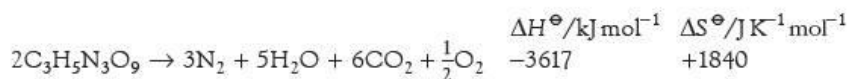Some substances decompose exothermically because the total bond enthalpy in the products is higher than that in the reactants. Examples include the decomposition of ozone and dinitrogen oxide:

|  | $\Delta H^{\ominus}/\text{kJ mol}^{-1}$ | $\Delta S^{\ominus}/\text{J K}^{-1}\text{mol}^{-1}$ |
|---|---|---|
| $O_3(g) \rightarrow 1\frac{1}{2}O_2(g)$ | $-142.7$ | $+68.7$ |
| $N_2O(g) \rightarrow N_2(g) + \frac{1}{2}O_2(g)$ | $-82.0$ | $+74.4$ |

This means that ozone and dinitrogen oxide cannot be synthesised directly by the reverse of the reactions above. Ozone is made by the combination of oxygen atoms with oxygen molecules, and dinitrogen oxide is made by the thermal decomposition of ammonium nitrate:

$$NH_4NO_3(s) \rightarrow N_2O(g) + 2H_2O(g)$$
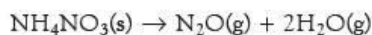
If the reaction rapidly gives off large quantities of gas at high temperature, an explosion may result. An example is the decomposition of propane-1,2,3-trinitrate (commonly called nitroglycerine):

|  | $\Delta H^{\ominus}/\text{kJ mol}^{-1}$ | $\Delta S^{\ominus}/\text{J K}^{-1}\text{mol}^{-1}$ |
|---|---|---|
| $2C_3H_5N_3O_9 \rightarrow 3N_2 + 5H_2O + 6CO_2 + \frac{1}{2}O_2$ | $-3617$ | $+1840$ |

## $\Delta H^{\ominus}$ positive and $\Delta S^{\ominus}$ negative

Reactions of this type are not spontaneously feasible and have to be driven. An example is photosynthesis (see Figure 20.13), which must be continuously supplied with energy from sunlight.

|  | $\Delta H^{\ominus}/\text{kJ mol}^{-1}$ | $\Delta S^{\ominus}/\text{J K}^{-1}\text{mol}^{-1}$ |
|---|---|---|
| $6CO_2(g) + 6H_2O(l) \rightarrow C_6H_{12}O_6(s) + 6O_2(g)$ | $+2803$ | $-225$ |
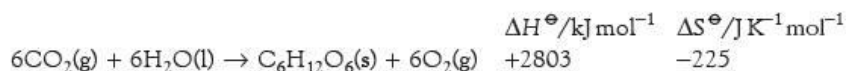
**Figure 20.13** $\Delta H$ positive and $\Delta S$ negative: photosynthesis in chloroplasts

## Worked example

For the following processes, explain why $\Delta H^{\ominus}$ and $\Delta S^{\ominus}$ have the signs (positive or negative) shown.

a $Mg(s) + O_2(g) \rightarrow MgO(s)$ $\qquad\qquad$ $\Delta H^{\ominus}$ –ve, $\Delta S^{\ominus}$ –ve

b $C_2H_5OH(l) \rightarrow C_2H_4(g) + H_2O(l)$ $\qquad$ $\Delta H^{\ominus}$ +ve, $\Delta S^{\ominus}$ +ve
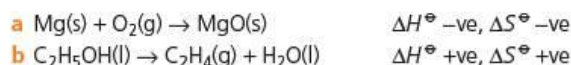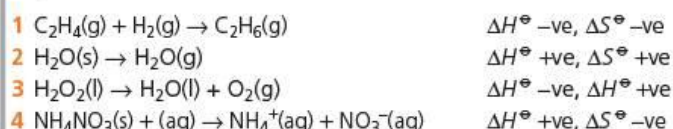
**Answer**

a $\Delta H^{\ominus}$ is negative because relatively weak bonds in magnesium and oxygen are converted into strong ionic bonds in magnesium oxide. $\Delta S^{\ominus}$ is negative because $\Delta n = -1$.

b $\Delta H^{\ominus}$ is positive because a relatively weak $\pi$ bond is being formed. $\Delta S^{\ominus}$ is positive because $\Delta n = +1$.
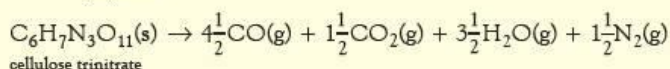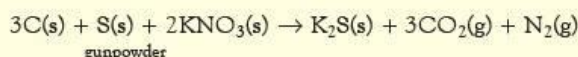
## Now try this

For the following processes, explain why $\Delta H^{\ominus}$ and $\Delta S^{\ominus}$ have the signs (positive or negative) shown.

1 $C_2H_4(g) + H_2(g) \rightarrow C_2H_6(g)$ $\qquad\qquad$ $\Delta H^{\ominus}$ –ve, $\Delta S^{\ominus}$ –ve
2 $H_2O(s) \rightarrow H_2O(g)$ $\qquad\qquad\qquad\qquad$ $\Delta H^{\ominus}$ +ve, $\Delta S^{\ominus}$ +ve
3 $H_2O_2(l) \rightarrow H_2O(l) + O_2(g)$ $\qquad\qquad$ $\Delta H^{\ominus}$ –ve, $\Delta H^{\ominus}$ +ve
4 $NH_4NO_3(s) + (aq) \rightarrow NH_4^+(aq) + NO_3^-(aq)$ $\qquad$ $\Delta H^{\ominus}$ +ve, $\Delta S^{\ominus}$ –ve

## Explosives

An explosion is a chemical reaction that produces sound, as well as a great deal of heat and light. Sound is produced if the speed of the ejected gases exceeds the speed of sound, $330\,\text{m s}^{-1}$ in air, resulting in the propagation of a shock wave.

Some explosions are produced by **propellants**, fuels used to drive rockets (Figure 20.14a) or to set in motion a shell or bullet in the barrel of a gun. These reactions must take place quickly and smoothly. This is achieved by using a source of heat near one small part of the propellant to initiate the reaction and then the heat produced by the reaction here sets off the propellant in contact with it. The speed of propagation is comparatively slow, probably only a few metres per second, and lasts all the time the bullet or shell is in the barrel of the gun. Propagation of the explosion by heat is a characteristic of **low explosives**. Common examples of low explosives include gunpowder (used in firework rockets) and cellulose trinitrate (used as cordite in the cartridges of shells or bullets). Low explosives may be set off using a match and fuse, or by being hit with a percussion cap. The simplified equations for the decompositions are as follows:

$$3C(s) + S(s) + 2KNO_3(s) \rightarrow K_2S(s) + 3CO_2(g) + N_2(g)$$
gunpowder

$$C_6H_7N_3O_{11}(s) \rightarrow 4\tfrac{1}{2}CO(g) + 1\tfrac{1}{2}CO_2(g) + 3\tfrac{1}{2}H_2O(g) + 1\tfrac{1}{2}N_2(g)$$
cellulose trinitrate

Cellulose trinitrate contains enough oxygen for all the products to be gaseous. The carbon monoxide produced burns to form carbon dioxide in the air around the explosion.

Other types of explosive are set off by a shock wave. This process is called **detonation** and is characteristic of **high explosives** (see Figure 20.14b). The whole explosion is nearly instantaneous as the shock wave travels at the speed of sound, which in a solid can be as high as $1000\,\text{m s}^{-1}$. The explosion produced is much more intense than that from a low explosive. High explosives are used in mining, for the demolition of buildings and in the warheads of shells. A high explosive would be disastrous if used in the cartridge of a rifle – the explosion would be so violent that the gun would explode instead of the bullet being sent out of the barrel.

**Figure 20.14 a** Ariane rocket. Liquid hydrogen is used as fuel in the rocket engine. The two rocket boosters either side of the main body add to the thrust of the engine. **b** High explosive is used to demolish this warehouse. **c** Airbags in cars require rapid release of nitrogen to inflate.

Common examples of high explosives include TNT (see section 25.3) and propane-1,2,3-trinitrate. The latter, by itself, is highly dangerous and sensitive to shock. Alfred Nobel made his fame and fortune by showing that when it was absorbed in clay, a much more stable explosive is produced, called **dynamite**. Propane-1,2,3-trinitrate contains enough oxygen for complete combustion, but TNT needs additional oxygen, often supplied by ammonium nitrate. A simplified equation representing the decompositions of TNT and ammonium nitrate is as follows:

$$C_7H_5N_3O_6(s) + 3\tfrac{1}{2}NH_4NO_3(s) \rightarrow 7CO(g) + 5N_2(g) + 9\tfrac{1}{2}H_2O(g)$$
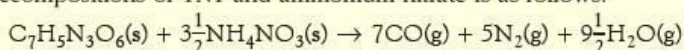
High explosives must be set off with a detonator. This contains a small quantity of a high explosive, such as mercury fulminate or lead azide, that is very sensitive to shock. Detonators can be used to set off either high explosives or low explosives, because the shock wave produced is sufficiently intense to set off a high explosive and enough heat is given out to set off a low explosive.

$$Hg(CNO)_2(s) \rightarrow Hg(l) + 2CO(g) + N_2(g)$$
mercury fulminate

$$Pb(N_3)_2(s) \rightarrow Pb(s) + 3N_2(g)$$
lead azide
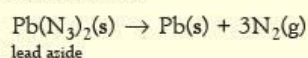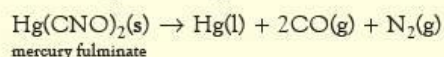
This rapid release of nitrogen is used to inflate airbags in cars, using sodium azide, $NaN_3$ (see Figure 20.14c).

**The manufacture of explosives is very dangerous and these chemicals have caused many fatal accidents. On no account should their preparation be attempted in the laboratory.**
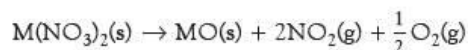
## 20.5  Trends in Group 2 compounds

### Thermal stability of the carbonates and nitrates

We have already pointed out that the carbonates and nitrates of Group 2 require increasingly higher temperatures before they break down (see section 10.4). If we look at the general reactions

$$MCO_3(s) \rightarrow MO(s) + CO_2(g)$$

and

$$M(NO_3)_2(s) \rightarrow MO(s) + 2NO_2(g) + \tfrac{1}{2}O_2(g)$$

we can see that the entropy changes for both reactions will be positive because one mole of each of the carbonates gives off one mole of gas and one mole of each of the nitrates gives off 2½ moles of gas. Because the number of moles of gas evolved is the same for all the carbonates, their entropy change of decomposition should be similar; a similar argument applies to the entropy change of decomposition for all the nitrates. This means that the ease of decomposition of the carbonates and nitrates is largely determined by their enthalpy changes. This is shown by the data in Tables 20.7 and 20.8.

**Table 20.7** Values of $\Delta H$, $\Delta G$ and $\Delta S$ for the decomposition of the Group 2 carbonates

| | Mg | Ca | Sr | Ba |
|---|---|---|---|---|
| $\Delta H/\text{kJ mol}^{-1}$ | +100.3 | +178.3 | +234.6 | +269.3 |
| $\Delta G/\text{kJ mol}^{-1}$ | +48.3 | +130.4 | +184.1 | +218.1 |
| $\Delta S/\text{J mol}^{-1}\text{K}^{-1}$ | +174 | +161 | +168 | +172 |

**Table 20.8** Values of $\Delta H$, $\Delta G$ and $\Delta S$ for the decomposition of anhydrous Group 2 nitrates. Group 2 nitrates are usually obtained as hydrated salts, which will make the actual values different, but the general trend should remain the same

| | Mg | Ca | Sr | Ba |
|---|---|---|---|---|
| $\Delta H/\text{kJ mol}^{-1}$ | +255.4 | +369.7 | +452.6 | +505.0 |
| $\Delta G/\text{kJ mol}^{-1}$ | +122.7 | +241.8 | +320.8 | +374.2 |
| $\Delta S/\text{J mol}^{-1}\text{K}^{-1}$ | +445 | +429 | +442 | +439 |

At room temperature $\Delta G$ for all the reactions is positive. If we assume that the values of $\Delta H$ and $\Delta S$ do not change much with temperature, $\Delta G$ will approach zero when $T\Delta S \approx \Delta H$. The temperature at which this occurs will be lowest when $\Delta H$ has the smallest positive value, that is at the top of the group. This agrees with the observation that the carbonates and nitrates at the top of the group decompose at a lower temperature than those at the bottom.

The reason why $\Delta H$ becomes more positive as the proton number increases is because the size of the cation increases. During decomposition, the large carbonate and nitrate ions become converted into oxide ions at the same time as carbon dioxide or nitrogen dioxide and oxygen are being given off. The ease with which this happens is affected by the cations that are next to the carbonate or nitrate ions. The two charges on the small magnesium cation create a much stronger electrostatic field than the two charges on the much larger barium cation. We say that the magnesium ion has a higher *charge density*. This high charge density changes the shape of the anion making it more like the shapes of the products (Figure 20.15). This change in shape of the anion is most marked when the anion is large and its electrons are not so firmly attracted to the nucleus. We say that the carbonate and nitrate ions are easily *polarised*.

**Figure 20.15** The small magnesium ion has a high charge density and changes the shape of the carbonate ion to a greater degree than does the much larger barium ion. A similar change in shape happens with the nitrate ion.
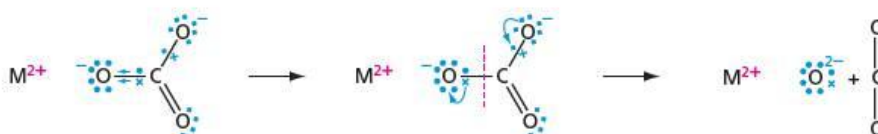


**Now try this**

Assuming that $\Delta H$ and $\Delta S$ remain constant, use the data in Table 20.7 to calculate the temperatures at which $\Delta G$ for the decomposition of magnesium carbonate and barium carbonate become zero.

## Solubility of Group 2 sulfates and hydroxides

The solubility of the sulfates in Group 2 is in the order $MgSO_4 > CaSO_4 > SrSO_4 > BaSO_4$ (see section 10.4). These are determined by the free energy of solution. The entropy changes for the dissolving will be very similar as in all cases $MSO_4(s)$ is being converted into $M^{2+}$ and $SO_4^{2-}$ ions. The solubility changes are, therefore, largely determined by the enthalpy changes of solution. These can be calculated using the thermochemical cycle shown in Figure 20.16. This shows us that:

$$\Delta H_{sol} = +\Delta H_{hyd}(M^{2+}) + \Delta H_{hyd}(SO_4^{2-}) - LE(MSO_4)$$

For the sulfates, the values of lattice energies are dominated by the large sulfate ion, so there is a comparatively small change from magnesium to barium: they vary by only $500\,\text{kJ mol}^{-1}$ from magnesium sulfate to barium sulfate (see Table 20.9). The enthalpy changes of hydration change to a greater extent (by $617\,\text{kJ mol}^{-1}$) from the small magnesium ion to the much larger barium ion. The value for $\Delta H_{hyd}^{\ominus}(SO_4^{2-})$
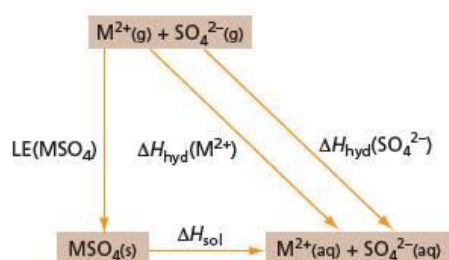
**Figure 20.16** Thermochemical cycle for the solubility of Group 2 sulfates

is constant, $-1160\,\text{kJ}\,\text{mol}^{-1}$. So the general trend is for $\Delta H^{\ominus}_{\text{sol}}$ to become more positive (by $117\,\text{kJ}\,\text{mol}^{-1}$) going down the group. This is the principal reason for the decreasing solubility.

**Table 20.9** Thermochemical data for the solubilities of the Group 2 sulfates

| M | $-\text{LE(MSO}_4)/$ $\text{kJ}\,\text{mol}^{-1}$ | $\Delta H_{\text{hyd}}(M^{2+})/$ $\text{kJ}\,\text{mol}^{-1}$ | $\Delta H_{\text{hyd}}(SO_4{}^{2-})/$ $\text{kJ}\,\text{mol}^{-1}$ | $\Delta H_{\text{sol}}/$ $\text{kJ}\,\text{mol}^{-1}$ | Solubility/mol in 100g of water |
|---|---|---|---|---|---|
| Mg | 2959 | −1890 | −1160 | −91 | $2.2 \times 10^{-1}$ |
| Ca | 2704 | −1562 | −1160 | −18 | $1.5 \times 10^{-3}$ |
| Sr | 2572 | −1414 | −1160 | −2 | $7.1 \times 10^{-4}$ |
| Ba | 2459 | −1273 | −1160 | +26 | $1.1 \times 10^{-6}$ |

The solubility of the hydroxides is in the opposite order, that is Mg < Ca < Sr < Ba. If we apply a similar Born–Haber cycle to the hydroxides as we did for the sulfates, we have:

$$\Delta H_{\text{sol}} = \Delta H_{\text{hyd}}(M^{2+}) + 2\Delta H_{\text{hyd}}(OH^-) - \text{LE(MOH)}$$

$2 \times \Delta H_{\text{hyd}}(OH^-)$ has the constant value $-1100\,\text{kJ}\,\text{mol}^{-1}$. The lattice enthalpies for the hydroxides change more down the group than do the lattice enthalpies for the sulfates, and this is the reason for the reversed trend in solubility (see Table 20.10).

**Table 20.10** Thermochemical data for the solubilities of the Group 2 hydroxides

| M | $-\text{LE(M(OH)}_2)/$ $\text{kJ}\,\text{mol}^{-1}$ | $\Delta H_{\text{hyd}}(M^{2+})/$ $\text{kJ}\,\text{mol}^{-1}$ | $2 - \Delta H_{\text{hyd}}(OH^-)/$ $\text{kJ}\,\text{mol}^{-1}$ | $\Delta H_{\text{sol}}/$ $\text{kJ}\,\text{mol}^{-1}$ | Solubility/mol in 100g of water |
|---|---|---|---|---|---|
| Mg | 2993 | −1890 | −1100 | 3 | $1.6 \times 10^{-5}$ |
| Ca | 2644 | −1562 | −1100 | −18 | $2.5 \times 10^{-3}$ |
| Sr | 2467 | −1414 | −1100 | −47 | $3.4 \times 10^{-3}$ |
| Ba | 2320 | −1273 | −1100 | −53 | $4.1 \times 10^{-2}$ |

Because the hydroxide ion is small, the lattice enthalpies of the Group 2 hydroxides are sensitive to changes in size of the cation and vary in value by $673\,\text{kJ}\,\text{mol}^{-1}$ from magnesium hydroxide to barium hydroxide. The changes in $\Delta H^{+}_{\text{hyd}}(M^{2+})$ are less than this ($617\,\text{kJ}\,\text{mol}^{-1}$). So in contrast to the sulfates, $\Delta H^{+}_{\text{sol}}$ becomes more negative, by $56\,\text{kJ}\,\text{mol}^{-1}$, on descending the group and the solubility increases.

## Summary

- Experimentally-derived lattice enthalpies can be found using a **Born–Haber cycle**.
- The **enthalpy change of solution** is determined by the lattice enthalpy and the **enthalpy change of hydration**.
- Polarisation of the large anion by the doubly charged cation determines the stability of the Group 2 nitrates and carbonates.
- There is an entropy change $\Delta S$ when a quantity of heat $q$ is passed at an absolute temperature $T$.
- There is an entropy increase when a system becomes more disordered, for example melting, boiling, and increase in the number of gas molecules.
- The total entropy of the system plus surroundings must increase for a spontaneous reaction.
- This total entropy increase is related to the Gibbs free energy $\Delta G^{\ominus}$. The more negative $\Delta G^{\ominus}$ is, the greater the driving force of the reaction.
- The solubility of Group 2 sulfates decrease with increasing proton number. This is because the enthalpy change of solution

becomes increasingly unfavourable. The reverse effect is shown by the Group 2 hydroxides.

### Some key definitions
- The **lattice enthalpy**, LE, is the enthalpy change when one mole of the solid is formed from its isolated ions in the gas phase.
- The **ionisation energy**, IE, is the minimum energy change required to remove one mole of electrons from one mole of atoms in the gas phase.
- The **electron affinity**, EA, is the energy change when one mole of electrons is added to one mole of atoms in the gas phase.
- The **enthalpy change of solution**, $\Delta H^{\ominus}_{\text{sol}}$, is the enthalpy change when one mole of solute is dissolved in an infinite volume of water.
- The **enthalpy change of hydration**, $\Delta H^{\ominus}_{\text{hyd}}$, is the enthalpy change when one mole of isolated ions in the gas phase is dissolved in an infinite volume of water.

# Examination practice questions

Please see the data section of the CD for any $A_r$ values you may need.

**1** Calcium chloride, $CaCl_2$, is an important industrial chemical used in refrigeration plants, for de-icing roads and for giving greater strength to concrete.
  **a** Show by means of an equation what is meant by the lattice energy of calcium chloride. [1]
  **b** Suggest, with an explanation, how the lattice energies of the following salts might compare in magnitude with that of calcium chloride.
    **i** calcium fluoride, $CaF_2$     **ii** calcium sulfide, $CaS$ [3]
  **c** Use the following data, together with additional data from the data section on the CD, to calculate the lattice energy of $CaCl_2$.

| | |
|---|---|
| standard enthalpy change of formation of $CaCl_2$ | $-796\,kJ\,mol^{-1}$ |
| standard enthalpy change of atomisation of $Ca(s)$ | $+178\,kJ\,mol^{-1}$ |
| electron affinity per mole of chlorine atoms | $-349\,kJ\,mol^{-1}$ |

enthalpy

$\underline{Ca(s) + Cl_2(g)}$

[3]

  **d** When a solution of $CaCl_2$ is added to a solution of the dicarboxylic acid, malonic acid, the salt calcium malonate is precipitated as a white solid. The solid has the following composition by mass: Ca, 28.2%; C, 25.2%; H, 1.4%; O, 45.2%.
    **i** Calculate the empirical formula of calcium malonate from these data.
    **ii** Suggest the structural formula of malonic acid. [3]
    *[Cambridge International AS & A Level Chemistry 9701, Paper 41 Q2 November 2009]*

**2 a i** What is meant by the term *enthalpy change of hydration, $\Delta H^{\ominus}_{hyd}$?*
    **ii** Write an equation that represents the $\Delta H^{\ominus}_{hyd}$ of the $Mg^{2+}$ ion.
    **iii** Suggest a reason why $\Delta H^{\ominus}_{hyd}$ of the $Mg^{2+}$ ion is greater than $\Delta H^{\ominus}_{hyd}$ of the $Ca^{2+}$ ion.
    **iv** Suggest why it is impossible to determine the enthalpy change of hydration of the oxide ion, $O^{2-}$. [5]

**b** The enthalpy change of solution for $MgCl_2$, $\Delta H^{\ominus}_{sol}$ $(MgCl_2(s))$, is represented by the following equation.
$MgCl_2(s) + aq \rightarrow Mg^{2+}(aq) + 2Cl^-(aq)$
Describe the simple apparatus you could use, and the measurements you would make, in order to determine a value for $\Delta H^{\ominus}_{sol}$ $(MgCl_2(s))$ in the laboratory. [4]
**c** The table below lists data relevant to the formation of $MgCl_2(aq)$.

| enthalpy change | value/kJ mol$^{-1}$ |
|---|---|
| $\Delta H^{\ominus}_f\,(MgCl_2(s))$ | $-641$ |
| $\Delta H^{\ominus}_f\,(MgCl_2(aq))$ | $-801$ |
| lattice energy of $MgCl_2(s)$ | $-2526$ |
| $\Delta H^{\ominus}_{hyd}\,(Mg^{2+}(g))$ | $-1890$ |

By constructing relevant thermochemical cycles, use the above data to calculate a value for
  **i** $\Delta H^{\ominus}_{sol}\,(MgCl_2\,(s))$,
  **ii** $\Delta H^{\ominus}_{hyd}\,(Cl^-(g))$. [3]
**d** Describe and explain how the solubility of magnesium sulfate compares to that of barium sulfate. [4]
*[Cambridge International AS & A Level Chemistry 9701, Paper 42 Q1 June 2012]*

**3 a** Describe and explain how the solubilities of the sulfates of the Group 2 elements vary down the group. [3]
**b** The following table lists some enthalpy changes for magnesium and strontium compounds.

| Enthalpy change | Value for magnesium/ kJ mol$^{-1}$ | Value for strontium/ kJ mol$^{-1}$ |
|---|---|---|
| lattice enthalpy of $M(OH)_2$ | $-2993$ | $-2467$ |
| enthalpy change of hydration of $M^{2+}(g)$ | $-1890$ | $-1414$ |
| enthalpy change of hydration of $OH^-(g)$ | $-550$ | $-550$ |

  **i** Use the above data to calculate values of $\Delta H^{\ominus}_{sol}$ for $Mg(OH)_2$ and $Sr(OH)_2$.

**ii** Use your results in **i** to suggest whether $Sr(OH)_2$ is more or less soluble in water than is $Mg(OH)_2$. State any assumptions you make.

**iii** Suggest whether $Sr(OH)_2$ would be more or less soluble in hot water than in cold. Explain your reasoning. [5]

**c** Calcium hydroxide, $Ca(OH)_2$, is slightly soluble in water.

**i** Write an expression for $K_{sp}$ for calcium hydroxide, and state its units.

**ii** 25.0 cm³ of a saturated solution of $Ca(OH)_2$ required 21.0 cm³ of 0.0500 mol dm⁻³ HCl for complete neutralisation. Calculate the $[OH^-(aq)]$ and the $[Ca^{2+}(aq)]$ in the saturated solution, and hence calculate a value for $K_{sp}$.

**iii** How would the solubility of $Ca(OH)_2$ in 0.1 mol dm⁻³ NaOH compare with that in water? Explain your answer.

[6]

*[Cambridge International AS & A Level Chemistry 9701, Paper 42 Q2 June 2010]*