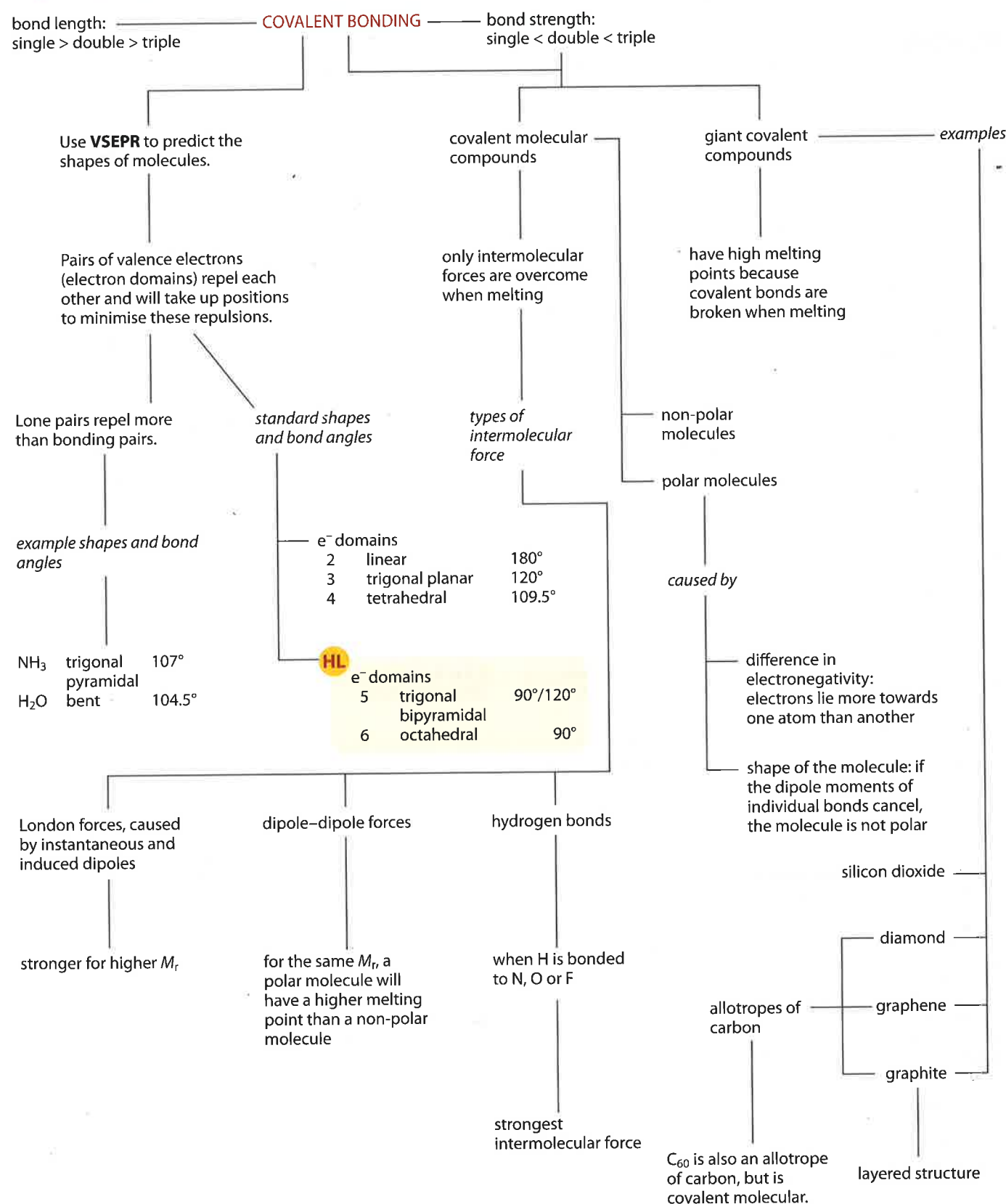


Summary – continued



Energetics/thermochemistry 5

5.1 Measuring energy changes

Heat and temperature

Heat and **temperature** are very different things that often get confused.

Heat is a form of energy that flows from something at a higher temperature to something at a lower temperature.

Temperature is a measure of the average kinetic energy of particles.

Internal energy is the name given to the total amount of energy (kinetic and potential) in a sample of a substance. If a 100 g block of iron at 100 °C is placed in contact with a 50 g block of iron at 50 °C, heat will flow from the hotter block to the colder one until they are at the same temperature. When they are at the same temperature, the 100 g block of iron will have higher internal energy simply because there is more of it, but the average kinetic energy of the particles in the two blocks will be the same because they are at the same temperature.

We often use the words *system* and *surroundings* to describe what is happening in terms of energy flow in chemical reactions.

The 'system' is our chemical reaction and the 'surroundings' is everything else in the Universe (Figure 5.1)!

Exothermic and endothermic reactions and enthalpy changes

Chemical reactions may be classified as either **exothermic** or **endothermic**.

In an exothermic reaction, heat energy is transferred from a system (chemical reaction) to the surroundings (Figure 5.2a) – the surroundings get hotter.

In an endothermic reaction, a system (chemical reaction) takes in heat energy from the surroundings (Figure 5.2b) – the surroundings get cooler.

Learning objectives

- Understand the difference between heat and temperature
- Explain what is meant by exothermic and endothermic reactions
- Draw enthalpy level diagrams for exothermic and endothermic reactions
- Understand what is meant by stability
- Understand the principle of experimental methods for determining enthalpy changes
- Work out enthalpy changes from experimental data

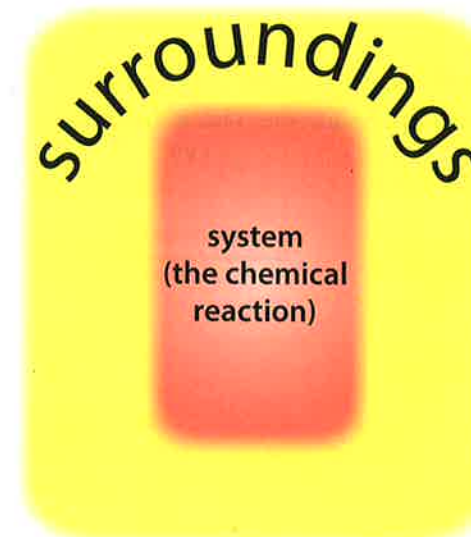


Figure 5.1 The Universe!

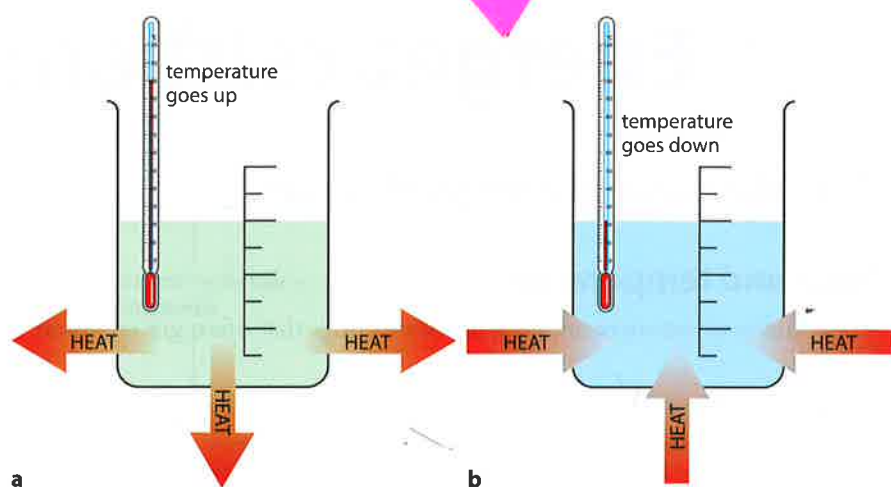


Figure 5.2 **a** The heat energy released in an exothermic reaction comes from the decrease in internal energy (the total energy of all the particles) of the system, for example through the creation of chemical bonds (conversion of chemical energy to heat energy). **b** The heat energy consumed in an endothermic reaction is converted to internal energy, for example through the breaking of chemical bonds (conversion of heat energy to chemical energy).

To be more precise, the enthalpy change is the heat energy exchanged with the surroundings at constant pressure.

Δ means a change in a quantity.

ΔH values are usually quoted under standard conditions. This is discussed in more detail on page 187.

We talk about the **enthalpy change** of a system. The enthalpy change is basically the amount of heat energy taken in/given out in a chemical reaction. Enthalpy is given the symbol **H** and enthalpy change is ΔH .

It is not possible to measure the enthalpy (**H**) of a system (related to the total energy of all the particles making up a substance) only the enthalpy change (ΔH) when the system moves from an initial state to some final state.

ΔH for an exothermic reaction is negative.

ΔH for an endothermic reaction is positive.

Consider a reaction such as methane burning in oxygen:



This reaction is exothermic, because heat is given out to the surroundings.

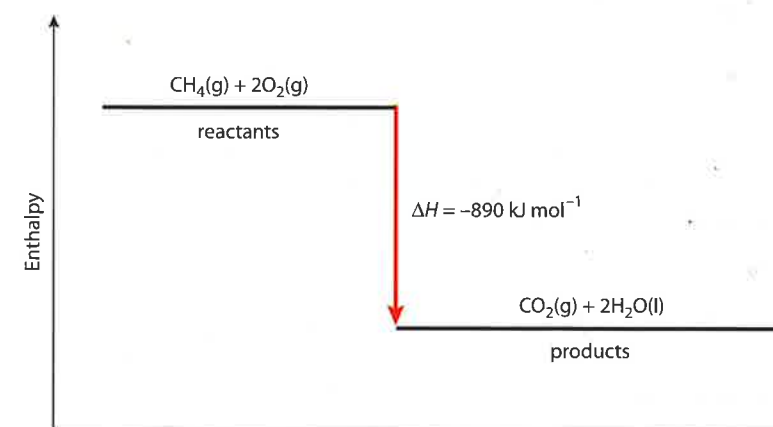


Figure 5.3 An enthalpy level diagram for the combustion of methane. No scale is shown on the vertical axis because we cannot measure the initial enthalpy or final enthalpy of the system.

Figure 5.3 shows an enthalpy level diagram for the combustion of methane. The reaction is exothermic, and the enthalpy of the products is less than that of the reactants. The enthalpy change of a reaction is the amount of heat given out – this is shown by the red arrow. The negative sign for the enthalpy change indicates a decrease in enthalpy.

Because the energy of the products is less than the energy of the reactants, the difference between the two must equal the amount of heat given out. Another way of stating this for an exothermic reaction is:

- total energy of the reactants = total energy of the products + heat given out
- or $\Delta H = \text{enthalpy of products} - \text{enthalpy of reactants}$

In an exothermic reaction the products are at a lower energy (enthalpy) level than the reactants, and we say that the products are more stable than the reactants. This will be discussed further on page 213.

In this section the terms *enthalpy* and *energy* are being used fairly interchangeably. At this level, the enthalpy of a system can be regarded as essentially the total energy stored in a substance – i.e. basically the same as the internal energy. This is not strictly true but it is sufficient for a good understanding of the concepts.

The reaction between nitrogen and oxygen to form nitrogen(II) oxide (nitric oxide) is endothermic:



Energy (heat) flows from the surroundings into the system because the products have a higher energy than the reactants. The sign of ΔH is positive, indicating the increase in enthalpy in an endothermic reaction. In this case:

- total energy of products = total energy of reactants + heat taken in
- or, as above, $\Delta H = \text{enthalpy of products} - \text{enthalpy of reactants}$

The enthalpy level diagram for this reaction is shown in Figure 5.4. The products have higher energy (enthalpy) and are less stable than the reactants.

Some definitions

Enthalpy changes have different values, depending on the conditions under which they are measured. To make them transferable, they are all quoted for the same set of conditions, which is called **standard conditions**. If an enthalpy change is not measured under standard conditions, its value is corrected to that at standard conditions. An enthalpy change under standard conditions is called a **standard enthalpy change** and has the symbol ΔH^\ominus , where the symbol $^\ominus$ means ‘under standard conditions’.

Total energy is conserved in a chemical reaction.

The term **stability** is usually used to describe the relative energies of reactants and products in a chemical reaction. If the products have less energy than the reactants then they are more stable.

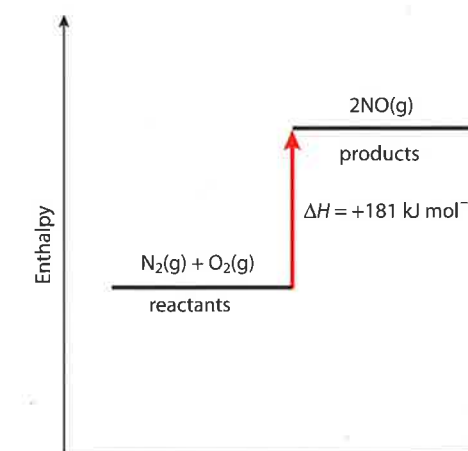


Figure 5.4 An enthalpy level diagram for an endothermic reaction.

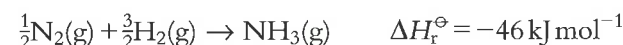
Standard conditions:
pressure = 100 kPa (1.00×10^5 Pa).

There is no mention of temperature in the definition of standard conditions and a temperature should always be specified for a standard enthalpy change. This can then be written as ΔH_{298}^\ominus or $\Delta H^\ominus(298\text{ K})$. Where no temperature is stated we will assume that the temperature is 298 K.

Standard enthalpy change of reaction (ΔH_r^\ominus) is the enthalpy change (heat given out or taken in) when molar amounts of reactants, as shown in the stoichiometric equation, react together under standard conditions to give products.

For example, for the reaction $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightarrow 2\text{NH}_3(\text{g})$, the enthalpy change of reaction is -92 kJ mol^{-1} . This means that 92 kJ of heat energy are given out when 1 mol N_2 reacts with 3 mol H_2 to form 2 mol NH_3 .

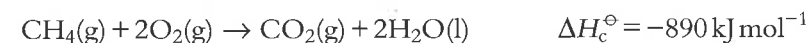
If the equation is written as:



then the enthalpy change of reaction is for 0.5 mol N_2 reacting, and the enthalpy change is half as much.

Standard enthalpy change of combustion (ΔH_c^\ominus) is the enthalpy change when one mole of a substance is completely burnt in oxygen under standard conditions.

A standard enthalpy change of combustion is always negative because combustion is always an exothermic process. For example:



Nature of science

There are certain unifying principles that are fundamental to the study of science. The idea of conservation of energy is one such principle.

Measuring enthalpy changes

In this section we will consider some experimental methods for measuring enthalpy changes of chemical reactions.

Specific heat capacity

We usually take the definition of **specific heat capacity** (c) to be:

The energy required to raise the temperature of 1 g of substance by 1 K (1°C).

It can also be defined as the energy to raise the temperature of 1 kg of substance by 1 K.

The specific heat capacity of aluminium is $0.90\text{ J g}^{-1}\text{ }^\circ\text{C}^{-1}$. Therefore, if 0.90 J of heat energy are put into 1 g of aluminium, the temperature is raised by 1°C (Figure 5.5).

If 1.80 J of heat energy were put into this block of aluminium, the temperature would go up by 2°C . If the 1 g block of aluminium were

replaced by a 2 g block of aluminium, then 1.80 J would be required to raise the temperature by 1°C , because 0.90 J are required to raise the temperature of each 1 g by 1°C . The amount of heat energy required is therefore proportional to the mass and the temperature change. An equation can be derived for how much heat energy (q) must be supplied to raise the temperature of mass m by $\Delta T^\circ\text{C}$:

$$q = mc\Delta T$$

Specific heat capacity indicates how much energy is required to heat up a substance, therefore substances with higher specific heat capacities are more difficult to heat up than substances with lower specific heat capacities. For example, the specific heat capacity of iron is roughly half that of aluminium – therefore if the same amount of heat energy is supplied to 10 g of each metal, the temperature of the iron will go up by twice the amount.

The specific heat capacity also applies when a substance cools. For instance, when 1 g of aluminium cools from 21°C to 20°C , 0.90 J of energy are given out.

Measuring an enthalpy change of combustion

The basic technique is called **calorimetry**. The idea is that the heat given out in a combustion reaction is used to heat another substance of known specific heat capacity, such as water. The equation $q = mc\Delta T$ can be used to calculate the amount of heat given out.

The experimental set-up shown in Figure 5.6 could be used to determine the enthalpy change when one mole of a liquid substance is burnt (the enthalpy change of combustion). The mass and temperature change of the water must be measured, as well as the mass change of the alcohol.

Worked example

5.1 Use the following experimental data to determine the enthalpy change of combustion of ethanol ($\text{C}_2\text{H}_5\text{OH}$) given that the specific heat capacity of water is $4.18\text{ J g}^{-1}\text{ }^\circ\text{C}^{-1}$.

Mass of water = 150.00 g
Initial temperature of water = 19.5°C
Maximum temperature of water = 45.7°C
Initial mass of spirit burner = 121.67 g
Final mass of spirit burner = 120.62 g

The temperature change of the water = $45.7 - 19.5 = 26.2^\circ\text{C}$

The amount of heat energy supplied to the water is given by:

$$q = mc\Delta T$$

$$q = 150.00 \times 4.18 \times 26.2 = 16\,400\text{ J}$$

ΔT is the change in temperature.

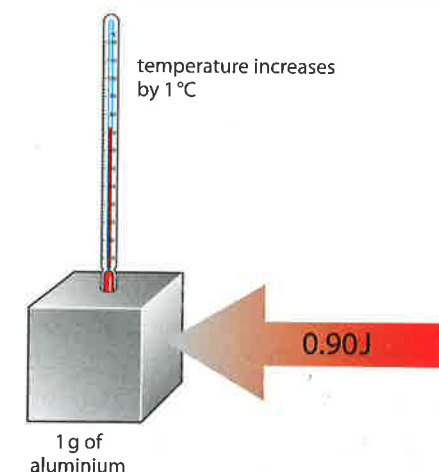


Figure 5.5 The specific heat capacity of aluminium is $0.90\text{ J g}^{-1}\text{ }^\circ\text{C}^{-1}$.

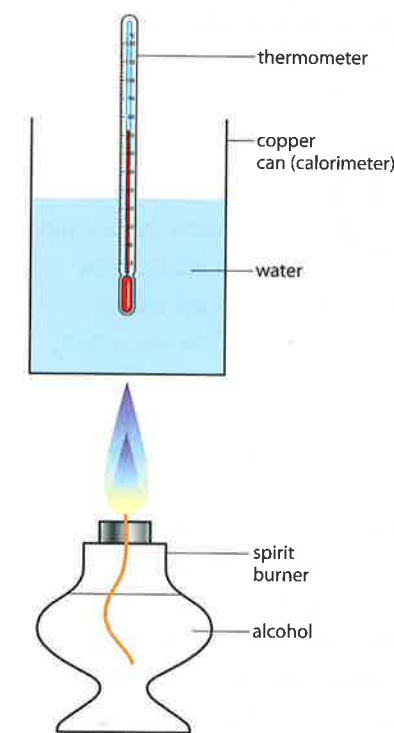


Figure 5.6 An experiment to work out the enthalpy change of combustion of an alcohol.

Exam tip

Note – the mass of water and **not** the mass of ethanol is used here – it is the water that is being heated.

Specific heat capacity has units of $\text{J g}^{-1}\text{ K}^{-1}$ or $\text{J g}^{-1}\text{ }^\circ\text{C}^{-1}$. Units that are also encountered are $\text{kJ kg}^{-1}\text{ K}^{-1}$ or $\text{J kg}^{-1}\text{ K}^{-1}$.

1 K is the same as 1°C when temperature changes are being considered.

This amount of heat energy is supplied by the burning of the ethanol.

$$\text{mass of ethanol burnt} = 121.67 - 120.62 = 1.05 \text{ g}$$

The number of moles of ethanol burnt is given by:

$$\text{number of moles} = \frac{\text{mass}}{\text{molar mass}}$$

The molar mass of ethanol is 46.08 g mol^{-1} . Therefore:

$$\text{number of moles ethanol burnt} = \frac{1.05}{46.08} = 0.0228 \text{ mol}$$

When 0.0228 mol ethanol are burnt, $16\,400 \text{ J}$ of heat energy are produced. Therefore the amount of energy released when one mole is burnt is given by:

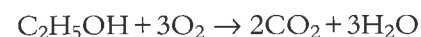
$$\text{energy} = \frac{16\,400}{0.0228} = 721\,000 \text{ J mol}^{-1}$$

The enthalpy change of combustion of ethanol is therefore:

$$\Delta H = -721 \text{ kJ mol}^{-1}$$

The accepted literature value for the enthalpy change of combustion of ethanol is $-1371 \text{ kJ mol}^{-1}$, so it can be seen that this experiment does not give a very accurate answer. There are several major flaws (systematic errors) in the experimental set-up. The most major problem is that of heat loss to the surroundings. Of the heat energy released when the ethanol burns, only some of it goes into heating the water – the rest goes into heating the copper can and the surrounding air. The experiment could have been improved by determining the specific heat capacity of the can and taking this into account when doing the calculation, insulating the can so that less heat is lost through the can to the surroundings, using some sort of draught shield to reduce convection currents around the experiment, etc.

Another major problem with the experiment is incomplete combustion of the ethanol. When ethanol undergoes complete combustion the equation for the reaction is:



However, if there is not a sufficient supply of oxygen to the flame, some of the ethanol can burn to produce carbon monoxide and soot (carbon) as well as water. This is called **incomplete combustion** and gives out less heat than complete combustion. Incomplete combustion causes the flame to be yellow/orange rather than blue because of the presence of soot particles, and the soot can also be seen on the bottom of the copper can.

Other, more minor, problems with the experiment include evaporation of the water and alcohol.

More than three significant figures were carried through on the calculator to give this final answer.

The value of the enthalpy change is negative because the combustion reaction is exothermic.



When we carry out experiments to measure enthalpy changes we often get unexpected values. What criteria do we use when carrying out these experiments to decide whether there are flaws in the experiment or flaws in the theory? This is an example of a more general problem, and it is sometimes too easy to dismiss an 'anomalous' result as being due to systematic errors in the experiment. The opposite also occasionally happens, and a new theory is put forward from an experiment that is possibly flawed – cold fusion is an example of this (originally announced by Pons and Fleischmann in 1989).

More accurate values for the enthalpy change of a combustion reaction require the use of a **bomb calorimeter**. This is a heavily insulated piece of apparatus in which the substance is ignited electronically in a plentiful supply of oxygen.

? Test yourself

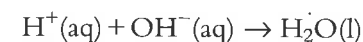
The specific heat capacity of water is $4.18 \text{ J g}^{-1} \text{ }^\circ\text{C}^{-1}$.

- 1 Work out the specific heat capacities of each metal from the data given:
 - a Gold – the temperature of 2.00 g of gold is raised by 11.7°C when 3.00 J of energy is supplied.
 - b Silver – the temperature of 100.0 g of silver is raised by 2.12°C when 50.0 J of energy is supplied.
- 2 a When 1.20 g of hexane (C_6H_{14}) are burnt, the temperature of 250.0 g of water is raised by 56.0°C . Calculate the enthalpy change when one mole of hexane is burnt.
b When 2.00 kg of octane (C_8H_{18}) are burnt, the temperature of 500 kg of water is raised by 46.0°C . Calculate the enthalpy change when one mole of octane is burnt.
- 3 Use the following experimental data to determine the enthalpy change of combustion of propan-1-ol ($\text{C}_3\text{H}_7\text{OH}$):
Mass of water = 200.00 g
Initial temperature of water = 18.2°C
Maximum temperature of water = 38.6°C
Initial mass of spirit burner = 185.51 g
Final mass of spirit burner = 184.56 g
- 4 The actual value for the enthalpy change of combustion of propan-1-ol is $-2010 \text{ kJ mol}^{-1}$. Account for any differences between this value and the one calculated from the experimental data in question 3.

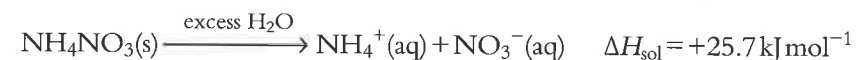
Enthalpy changes in solution

A general method for measuring enthalpy changes involving solutions in the laboratory is to measure out known amounts of reagents, record their initial temperatures, mix together the reagents in a polystyrene cup and record the maximum/minimum temperature observed. The specific heat capacity of the final solution is assumed to be the same as for water. Before we look at some examples of how to do this, we must consider a couple of definitions.

Enthalpy change of neutralisation (ΔH_n) is the enthalpy change when one mole of water molecules are formed when an acid (H^+) reacts with an alkali (OH^-) under standard conditions:



Enthalpy change of solution (ΔH_{sol}) is the enthalpy change when one mole of solute is dissolved in excess solvent to form a solution of 'infinite dilution' under standard conditions, e.g.:



The enthalpy change of neutralisation is always exothermic.

'Infinite dilution' means that any further dilution of the solution produces no further enthalpy change – i.e. the solute particles are assumed not to interact with each other in the solution.

The enthalpy change of solution may be exothermic or endothermic.

Worked examples

5.2 Consider the following experiment: 100.0 cm³ of 1.00 mol dm⁻³ potassium hydroxide solution are measured out and poured into a polystyrene cup and the temperature of the potassium hydroxide solution was measured. Then 120.0 cm³ of 1.00 mol dm⁻³ hydrochloric acid are measured out and the initial temperature was measured. The hydrochloric acid was in excess to make sure that all the potassium hydroxide reacted. The hydrochloric acid was then poured into the polystyrene cup and the mixture stirred rapidly. The maximum temperature was recorded.

The results of this experiment:

Initial temperature of potassium hydroxide solution = 19.7°C

Initial temperature of hydrochloric acid = 19.7°C

Maximum temperature reached = 25.9°C

Use these data to determine the enthalpy change of neutralisation.

Temperature change of the mixture = 6.2°C

Total volume of the reaction mixture = 220.0 cm³

We will assume that the density of the mixture is the same as that of water, and so 220.0 cm³ of solution has a mass of 220.0 g.

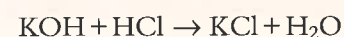
Assumption: the density of the potassium hydroxide and hydrochloric acid solutions are the same as water, so 1 cm³ of solution has a mass of 1 g.

We can work out how much heat (q) has been released in this reaction by using the temperature change of the mixture:

$$q = mc\Delta T = 220 \times 4.18 \times 6.2 = 5700 \text{ J}$$

Assumption: the specific heat capacity of the mixture is the same as that of water. This is a fairly reasonable assumption because the reaction mixture is mostly water.

To work out the enthalpy change of neutralisation, we need to know how many moles of water have been formed. The equation for the reaction is:



number of moles KOH = concentration \times volume in dm³

$$\text{number of moles KOH} = 1.00 \times \frac{100}{1000} = 0.100 \text{ mol}$$

$$\text{number of moles HCl} = 1.00 \times \frac{120}{1000} = 0.120 \text{ mol}$$

The HCl is in excess so the number of moles of water produced is 0.100 mol. Therefore 5700 J of energy is released when 0.100 mol water are formed.

The definition of enthalpy change of neutralisation is the enthalpy change when one mole of water is produced. Therefore, for one mole of water formed:

$$\text{heat energy released} = \frac{1}{0.100} \times 5700 = 57\,000 \text{ J mol}^{-1}$$

This is negative because the reaction is exothermic.

Therefore, the enthalpy change of neutralisation, $\Delta H_n = -57.0 \text{ kJ mol}^{-1}$.

The accepted literature value for the heat of neutralisation of KOH with HCl is $-57.2 \text{ kJ mol}^{-1}$.

Possible errors in this experiment are heat loss to the surroundings and the assumptions that have been made about the specific heat capacities and the density of the solutions. The heat capacity of the calorimeter (polystyrene cup) was also not taken into account – some of the heat energy given out from the reaction was used to heat up the cup.

5.3 a 100.0 cm³ of 1.00 mol dm⁻³ potassium hydroxide solution were reacted with 100.0 cm³ of 1.00 mol dm⁻³ hydrochloric acid. The temperature rise was 6.82°C. Calculate the enthalpy change of neutralisation.

b The experiment in part **a** was repeated with 50.0 cm³ of 1.00 mol dm⁻³ potassium hydroxide solution and 50.0 cm³ of 1.00 mol dm⁻³ hydrochloric acid. Calculate the temperature change of the reaction mixture.

a We can use the method from the previous example to calculate the enthalpy change of neutralisation:

$$q = mc\Delta T = 200 \times 4.18 \times 6.82 = 5700 \text{ J}$$

The number of moles of KOH and HCl in this case are the same, both 0.100 mol. Therefore 0.100 mol water are formed.

$$\text{heat energy released} = \frac{1}{0.100} \times 5700 = 57\,000 \text{ J mol}^{-1}$$

Therefore the enthalpy change of neutralisation, $\Delta H_n = -57.0 \text{ kJ mol}^{-1}$.

b A shortcut can be used to answer this part. The volume of each solution is half that in part **a** but the concentrations are the same. Therefore we can deduce that the number of moles of water formed will be half as much as in part **a**. This means that half as much heat energy will be given out in the neutralisation reaction. However, the total volume of reaction mixture that is being heated is half the original volume – therefore only half as much heat energy will be required to heat it to the same temperature. So the temperature change in this experiment is the same as in part **a**, i.e. 6.82°C.

Exam tip

Some people prefer to use the equation $q = -mc\Delta T$. This avoids the problem of forgetting to add the negative sign for the final enthalpy change for an exothermic reaction. The temperature change for an endothermic reaction must then be taken as negative.

5.4 Consider the following experiment: 100.0 cm³ of water are measured out and poured into a polystyrene cup and the temperature of the water was measured. Then 5.20 g of ammonium chloride are measured out. The ammonium chloride was added to the water and the solution stirred vigorously until all the ammonium chloride had dissolved. The minimum temperature was recorded.

The results of this experiment:

Initial temperature of water = 18.3 °C

Minimum temperature = 15.1 °C

Use the experimental data to determine the enthalpy change of solution of ammonium chloride.

Temperature change of the mixture = 3.2 °C

We will assume that the density of the solution is the same as that of water, and so 100.0 cm³ of solution has a mass of 100.0 g. We can work out how much heat has been absorbed in this reaction by using the temperature change of the mixture:

$$q = mc\Delta T = 100.0 \times 4.18 \times 3.2 = 1340 \text{ J}$$

To work out the enthalpy change of solution, we need to know how many moles of ammonium chloride dissolved:

$$\text{number of moles NH}_4\text{Cl} = \frac{\text{mass}}{\text{molar mass}}$$

$$\text{Therefore, the number of moles of NH}_4\text{Cl that dissolve} = \frac{5.20}{53.50} = 0.0972 \text{ mol.}$$

Therefore 1340 J of energy is absorbed when 0.0972 mol NH₄Cl dissolve.

The definition of enthalpy change of solution is the enthalpy change when one mole of substance dissolves. Therefore, for one mole of NH₄Cl dissolving:

$$\text{heat energy absorbed} = \frac{1}{0.0972} \times 1340 = 13800 \text{ J mol}^{-1}$$

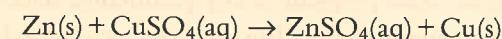
Therefore the enthalpy change of solution, $\Delta H_{\text{sol}} = +13.8 \text{ kJ mol}^{-1}$.

The accepted value for the enthalpy change of solution of ammonium chloride is 15.2 kJ mol⁻¹. Errors in this experiment include the absorption of heat from the surroundings and the assumption about the specific heat capacity of the solution being the same as that of water. The mass of the ammonium chloride was also not taken into account when working out the heat energy released in the experiment (i.e. it was not included in the mass of the solution). The results from this experiment are greatly improved by vigorous stirring of the solution because the ammonium chloride does not dissolve instantaneously. If it is allowed to dissolve slowly, there is more time for heat to be absorbed from the surroundings and the temperature drop is not as large as expected. This effect can be reduced by using the technique of the next experiment.

Assumption: the specific heat capacity of the solution is the same as that of water.

This is positive because the reaction is endothermic.

5.5 The following experiment may be used to determine the enthalpy change of reaction for:



50.0 cm³ of 0.200 mol dm⁻³ copper(II) sulfate solution are placed in a polystyrene cup. The temperature was recorded every 30 s for 2 min. At 2 min 30 s, 1.20 g of powdered zinc are added. The mixture was stirred vigorously and the temperature recorded every half minute for several minutes. The results obtained were then plotted to give the graph shown in Figure 5.7.

Use these data to determine the enthalpy change for this reaction.

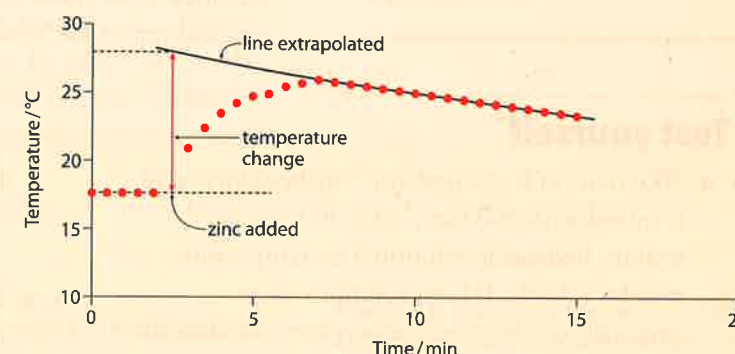


Figure 5.7 Temperature against time for the reaction of zinc with copper sulfate solution.

This type of reaction is called a displacement reaction or a single replacement reaction.

The problem with this reaction is that it does not occur instantaneously, and so although heat is being given out in the reaction, at the same time the reaction mixture is also cooling down by losing heat to the surroundings. From the graph it can be seen that there is an initial rise in temperature, where heat being given out by the reaction is the major factor, but after that the reaction mixture cools. By extrapolating the line back from this cooling part of the curve, we can estimate the temperature from which the mixture appears to be cooling. If we look at the value of the temperature on this curve at 2 min 30 s, the point at which the zinc was added, we should get an estimate of the temperature rise if the reaction had occurred instantaneously. It can be seen that this temperature rise is greater than the temperature rise actually measured in the experiment.

From the graph we estimate the temperature change as 10.3 °C.

The heat given out in the reaction is given by:

$$q = mc\Delta T = 50.0 \times 4.18 \times 10.3 = 2150 \text{ J}$$

To work out the enthalpy change of reaction, we need to know how many moles of copper sulfate reacted (the zinc was in excess).

$$\text{number of moles of CuSO}_4 = \text{concentration} \times \text{volume in dm}^3$$

$$\text{number of moles of CuSO}_4 = 0.200 \times \frac{50.0}{1000} = 0.0100 \text{ mol}$$

Therefore 2150 J of energy are released when 0.0100 mol copper sulfate reacts.

For the reaction of one mole of copper sulfate:

$$\text{heat energy released} = \frac{1}{0.0100} \times 2150 = 215000 \text{ J mol}^{-1}$$

Therefore the enthalpy change of reaction = -215 kJ mol⁻¹.

The extrapolation of the line is very much a matter of judgement and could introduce errors into the calculation.

Assumption: the density of copper sulfate solution is the same as that of water.

This is negative because the reaction is exothermic.

Nature of science

Experimental work and the collection of data is a major part of science. The best data for making accurate predictions are quantitative data. These can be analysed mathematically to allow theories to be developed. Scientists must, however, be aware of the errors and uncertainties in their data and report the results of their experiments appropriately.

? Test yourself

- 5 a 200.0 cm³ of 0.150 mol dm⁻³ hydrochloric acid is mixed with 100.0 cm³ of 0.300 mol dm⁻³ sodium hydroxide solution. The temperature rose by 1.36 °C. If both solutions were originally at the same temperature, calculate the enthalpy change of neutralisation.
- b Predict the temperature rise if the experiment in part a is repeated using:
- 400.0 cm³ of 0.150 mol dm⁻³ hydrochloric acid and 200.0 cm³ of 0.300 mol dm⁻³ sodium hydroxide solution
 - 200.0 cm³ of 0.300 mol dm⁻³ hydrochloric acid and 100.0 cm³ of 0.600 mol dm⁻³ sodium hydroxide solution
 - 50.0 cm³ of 0.300 mol dm⁻³ hydrochloric acid and 25.0 cm³ of 0.600 mol dm⁻³ sodium hydroxide solution.
- 6 a When 1.00 g of magnesium chloride is dissolved in 50.0 cm³ of water the temperature goes up from 21.5 °C to 29.1 °C. Calculate the enthalpy change of solution of magnesium chloride.
- b Predict the temperature change when 2.00 g of magnesium chloride is dissolved in 100 cm³ of water.
- c Predict the temperature change when 2.00 g of magnesium chloride is dissolved in 50.0 cm³ of water.

Learning objectives

- Use Hess's law to calculate enthalpy changes
- Define enthalpy change of formation
- Calculate enthalpy changes from enthalpy change of formation data

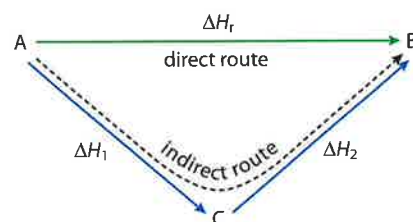


Figure 5.8 An enthalpy cycle.

5.2 Hess's law

It is not always possible to design experiments to measure certain enthalpy changes and so we often have to use data from reactions in which the enthalpy change *can* be measured to work out the enthalpy change for a particular reaction in which it *cannot* be measured directly. In order to do this, we use **Hess's law**:

The enthalpy change accompanying a chemical reaction is independent of the pathway between the initial and final states.

What this basically means is that if we consider the conversion of A into B, the enthalpy change for the reaction is the same if we go directly from A to B or indirectly via other reactions and intermediates (Figure 5.8).

If we know the value for ΔH_1 (for the conversion of A to C) and ΔH_2 (for the conversion of C to B) we can work out the value of the enthalpy change ΔH_r for the conversion of A into B using this cycle. Hess's law states that the enthalpy change for the direct conversion of A to B is exactly the same as the enthalpy change for the indirect route between A and B. Therefore, in this case:

$$\Delta H_r = \Delta H_1 + \Delta H_2$$

Let us consider a slightly different situation in which the enthalpy changes we know are:



This produces a slightly different cycle, in which the arrow for ΔH_2 is the other way around, because the reaction we know is from B to C (Figure 5.9). Now the enthalpy change from A to B is given by $\Delta H_r = \Delta H_1 - \Delta H_2$. We have $-\Delta H_2$ in this case, because the conversion $C \rightarrow B$ on the indirect route ($A \rightarrow C \rightarrow B$) goes in the opposite direction to the arrow we have drawn for ΔH_2 .

Another possible situation is one in which we know:



This is shown in Figure 5.10. Here the enthalpy change for the direct route is given by $\Delta H_r = -\Delta H_1 + \Delta H_2$. In going from $A \rightarrow C \rightarrow B$, we go the wrong way along the ΔH_1 arrow (therefore the sign is negative) but the right way along the ΔH_2 arrow (therefore the sign is positive).

Why Hess's law works

The reason Hess's law works can be understood from Figure 5.11.

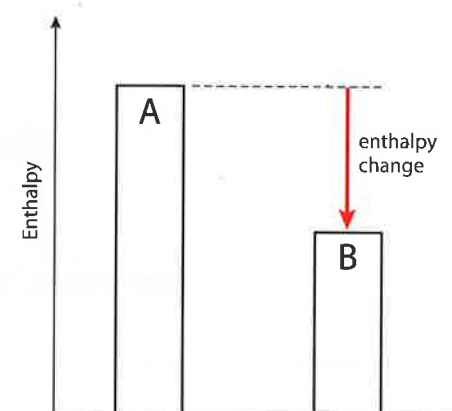


Figure 5.11 Enthalpy is basically a property of a substance under a certain set of conditions. This means that the enthalpy depends on the substance and the conditions. So A has a certain amount of enthalpy, B has a certain amount of enthalpy and these are fixed for a particular set of conditions. The route that is taken between A and B cannot affect the amount of enthalpy A or B has, and therefore the difference in enthalpy between A and B is constant.

Working out enthalpy changes

We are not always able to determine enthalpy changes directly from experiments and Hess's law can then be used to work out unknown enthalpy changes from ones that are known.

Extension

This is basically just a question of vectors:

$$\vec{AB} = \vec{AC} + \vec{CB}$$

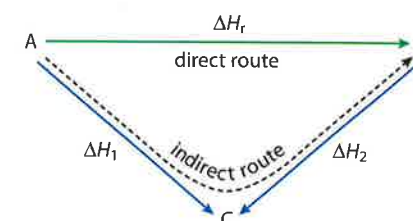


Figure 5.9 If we know the enthalpy change for the conversion $B \rightarrow C$ rather than $C \rightarrow B$, the arrow between B and C is the other way around.

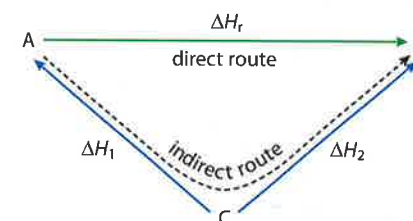


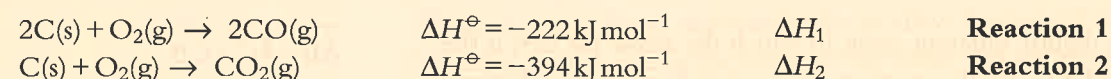
Figure 5.10 If we know the enthalpy change for the conversion $C \rightarrow A$ rather than $A \rightarrow C$, the arrow between A and C is the other way around.

Extension

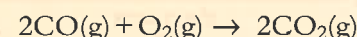
Enthalpy is a state function.

Worked examples

5.6 Given these enthalpy changes:



calculate the enthalpy change for the reaction:



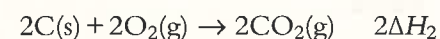
Two methods will be considered for working out the enthalpy change.

Method A (using a cycle)

The enthalpy changes given are used to construct a cycle. The enthalpy change that we have to find is put at the top of the cycle.

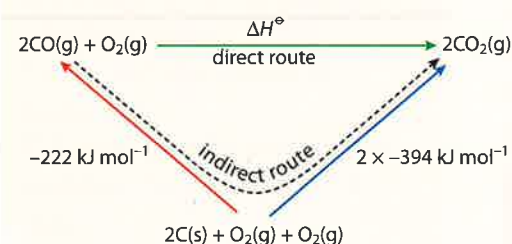
Only the first reaction has been added here. **Reaction 1** is highlighted in yellow and shows the reaction of 2 C and 1 O₂ to form 2 CO. The other O₂, highlighted in orange, remains unchanged, and there is no enthalpy change for this. This means that the total enthalpy change along the red arrow is ΔH_1 .

If **Reaction 2** is now added to complete the cycle, it must be multiplied by two, because we need to form 2 mol CO₂. The enthalpy change must also be multiplied by two, hence $2\Delta H_2$:



Reaction 2 is highlighted in green (Figure 5.12).

The values can now be put into the cycle:



The overall enthalpy change is given by

$$\Delta H^\ominus = -\Delta H_1 + 2\Delta H_2$$

$$\Delta H^\ominus = -(-222) + (2 \times -394) = -566 \text{ kJ mol}^{-1}$$

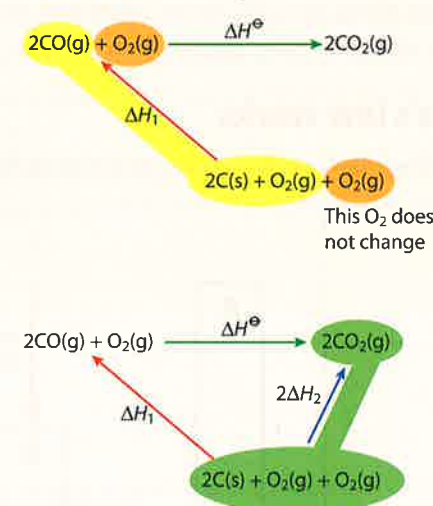


Figure 5.12 Reaction cycles.

This is worked out from Hess's law: the enthalpy change for the direct route is the same as that for the indirect route. Because the direction of the indirect route arrow is opposite to that of the red arrow, the sign of the quantity on the red arrow is reversed.

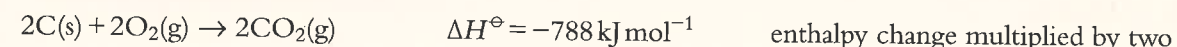
Method B (manipulating the equations)

In this method we rearrange the equations for the data given to produce the equation for the reaction corresponding to the enthalpy change we have to find.

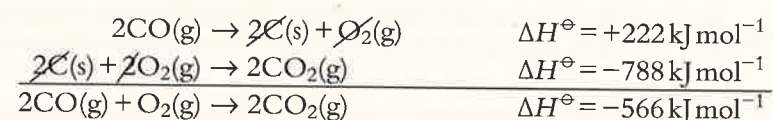
First, **Reaction 1** is reversed to give 2CO on the left-hand side, as in the overall equation:



Now **Reaction 2** is multiplied by two to give 2CO₂ on the right-hand side, as in the overall equation:



We now have 2CO on the left-hand side and 2CO₂ on the right-hand side, as in the overall equations. The two equations and their enthalpy changes are now added together and common terms cancelled to produce the overall equation and its enthalpy change:



This is very similar to methods for solving simultaneous linear equations in mathematics.

The relationship between the various enthalpy changes in the above example can be seen in an enthalpy level diagram (Figure 5.13). Downward arrows represent exothermic processes.

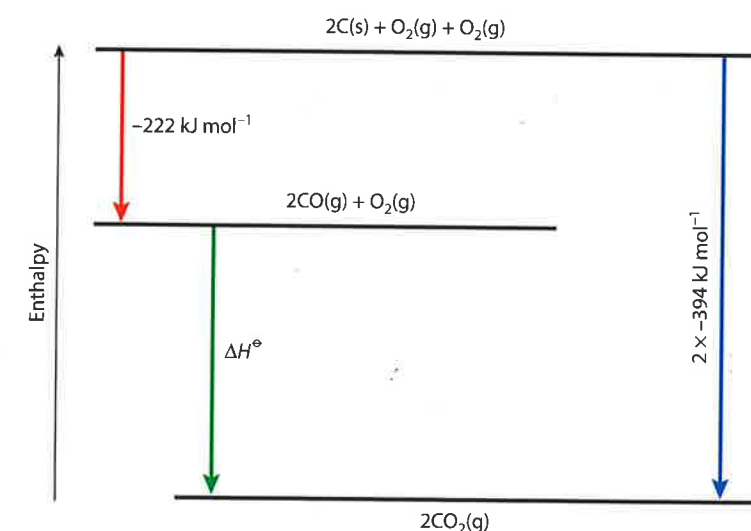


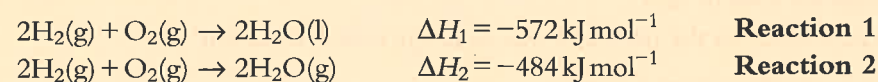
Figure 5.13 An enthalpy level diagram. Exothermic processes are shown as downward arrows – endothermic processes would be shown as upward arrows.

Exam tip

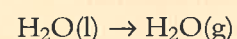
Only one of these methods needs to be understood. Find a method that you are happy with and ignore the other!

Worked example

5.7 Use the following enthalpy change data:

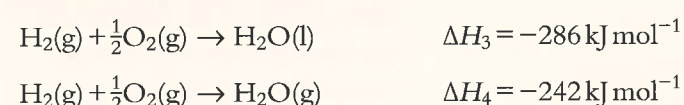


to work out the enthalpy change for the process:



Method A (enthalpy cycle)

Each enthalpy change given should be divided by two, as the enthalpy change for the reaction we have to find just involves one H_2O :



A cycle can be constructed.

The enthalpy change for the direct route is the same as that for the indirect route:

$$\Delta H = -\Delta H_3 + \Delta H_4$$

The indirect route goes in the opposite direction to the ΔH_3 arrow, so the sign is negative.

Substituting values we get:

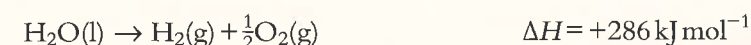
$$\Delta H = -(-286) + (-242) = +44 \text{ kJ mol}^{-1}$$

Method B (manipulating equations)

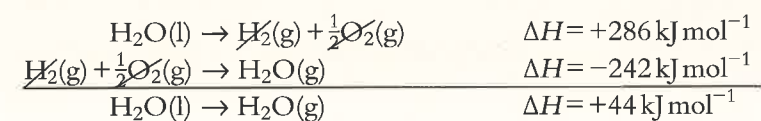
Divide each equation by two to get one H_2O in each:



The first equation must be reversed so that $\text{H}_2\text{O}(\text{l})$ is on the left-hand side, as in the overall equation:



We now have the correct numbers of H_2O on the correct sides and can add the two equations (and the two enthalpy changes) together:



An enthalpy level diagram for the reactions in the above example is shown in Figure 5.14.

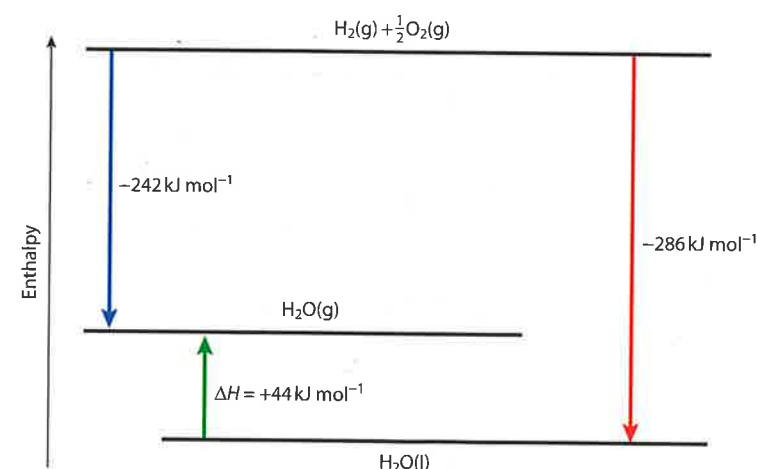
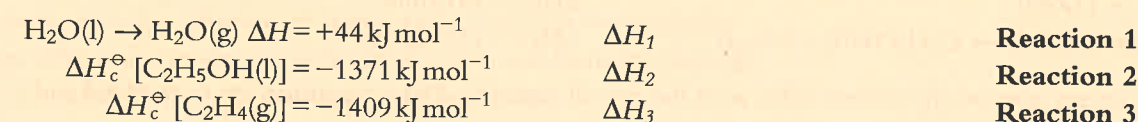
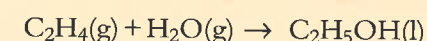


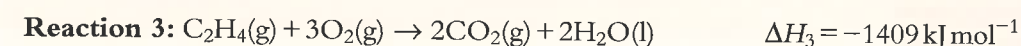
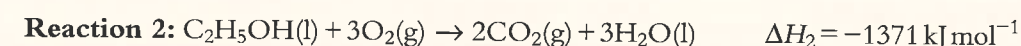
Figure 5.14 An enthalpy level diagram. Exothermic processes are shown as downwards arrows and endothermic reactions are upwards arrows.

Worked example

5.8 Use the information given below to calculate the enthalpy change for the reaction:

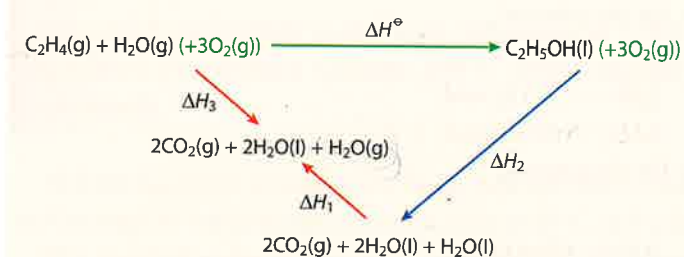


We are given standard enthalpy change of combustion data and so, knowing the definition, we can write out the full chemical equations for the enthalpy changes:



Method A (enthalpy cycle)

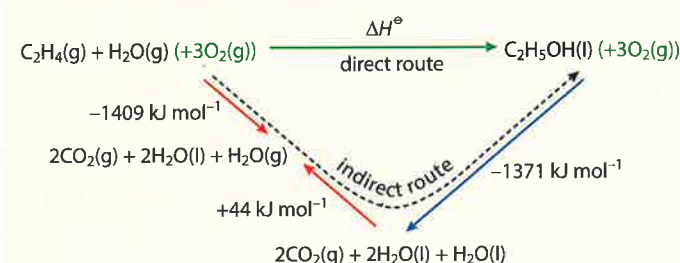
The following cycle can be constructed:



$3\text{O}_2(\text{g})$ has been added to each side of the original equation, but because the same thing has been added to both sides this does not affect the overall enthalpy change.

ΔH_3 is the enthalpy change for the combustion of ethene – $\text{H}_2\text{O}(\text{g})$ does not change in this process.

This cycle shows the individual enthalpy changes involved. All arrows are drawn in the same direction as the equations given. The values can be substituted into the cycle:



The arrow for the indirect route goes in the opposite direction to the arrow for the enthalpy changes ΔH_1 and ΔH_2 .

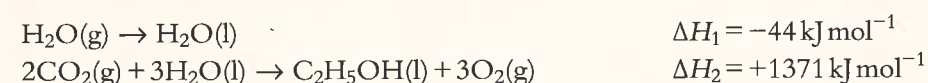
The enthalpy change for the direct route is the same as that for the indirect route.

$$\Delta H^\ominus = -1409 - (+44) - (-1371) = -82 \text{ kJ mol}^{-1}$$

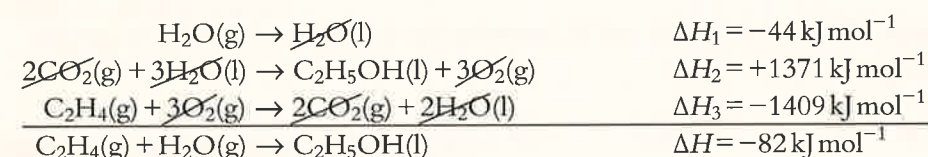
The cycle could have been simplified by reversing the enthalpy change ΔH_1 and incorporating ΔH_1 and ΔH_3 into one step, but care must be then taken with the sign of ΔH_1 .

Method B (manipulating equations)

Reactions 1 and 2 are reversed to give $\text{H}_2\text{O}(\text{g})$ and $\text{C}_2\text{H}_5\text{OH}$ on the correct sides:

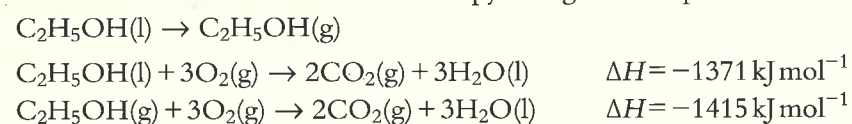


All the species are now on the correct sides, as in the overall equation. These equations are now added and common species cancelled:

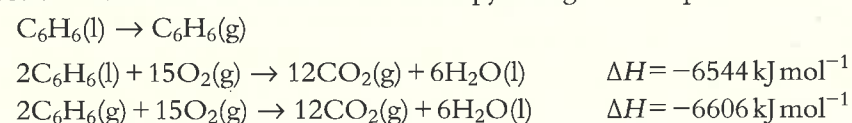


Test yourself

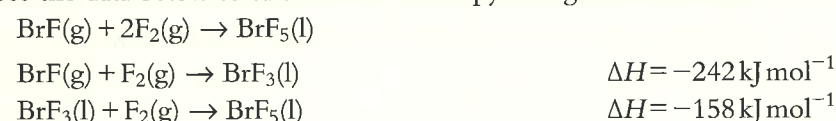
- 7 a Use the data below to calculate the enthalpy change for the process:



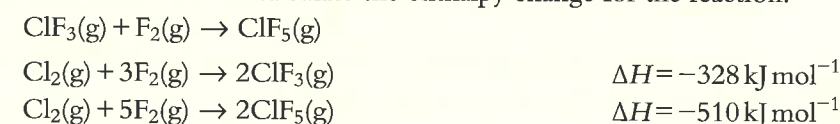
- b Use the data below to calculate the enthalpy change for the process:



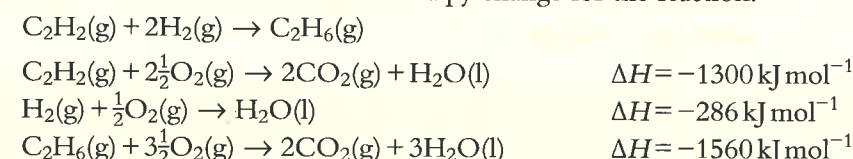
- 8 a Use the data below to calculate the enthalpy change for the reaction:



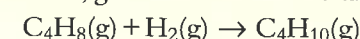
- b Use the data below to calculate the enthalpy change for the reaction:



- 9 Use the data below to work out an enthalpy change for the reaction:



- 10 Calculate the enthalpy change for the following reaction, given the data in the table:

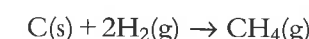


	$\Delta H_f^\ominus / \text{kJ mol}^{-1}$
$\text{C}_4\text{H}_8(\text{g})$	-2717
$\text{C}_4\text{H}_{10}(\text{g})$	-2877
$\text{H}_2(\text{g})$	-286

Standard enthalpy change of formation

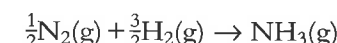
Standard enthalpy change of formation (ΔH_f^\ominus) is the enthalpy change when one mole of a substance is formed from its elements in their standard states under standard conditions.

The equation representing the enthalpy change of formation of methane is:



The carbon here is graphite, which is the most stable form of carbon.

For ammonia, the enthalpy change of formation is for the reaction:

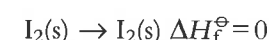


which shows the formation of **one mole** of ammonia.

Standard state refers to the pure substance at 100 kPa and a specified temperature (assume 298 K unless another temperature is specified).

The standard state of nitrogen is $\text{N}_2(\text{g})$, whereas that of iodine is $\text{I}_2(\text{s})$. These are the states in which these substances exist at 25 °C and 100 kPa pressure.

The standard enthalpy change of formation of any element in its standard state is zero because, by definition, no heat energy is taken in or given out when one mole of an element in its standard state is formed from one mole of the element in its standard state:



Extension

Enthalpy changes are not absolute quantities and we can only know the difference in enthalpy between two states. The standard state is chosen as the baseline from which changes are measured.

State symbols must always be included in equations for enthalpy changes because the enthalpy change will be different depending on the state of a substance. For example, the standard enthalpy change of formation of $\text{I}_2(\text{g})$ is not zero.

ΔH_f^\ominus for any element in its standard state is zero.

A standard enthalpy change of formation may be exothermic or endothermic, depending on the substance.

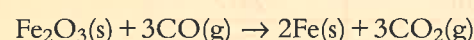
Using standard enthalpy changes of formation to work out enthalpy changes

Worked example

5.9 Given the enthalpy changes (kJ mol^{-1}):

$$\Delta H_f^\ominus [\text{Fe}_2\text{O}_3(\text{s})] = -822; \Delta H_f^\ominus [\text{CO}(\text{g})] = -111; \Delta H_f^\ominus [\text{CO}_2(\text{g})] = -394$$

calculate the standard enthalpy change for the reaction:



This reaction is important in the extraction of iron from its ore.

First we set up an enthalpy change cycle. The equations of the reactions for which we know the enthalpy changes are:



These can be used to construct a cycle (Figure 5.15a) in which the equation for the reaction with the enthalpy change we want to find is along the top and arrows go **up** from the elements to the compounds. The total enthalpy change for the formation of the reactants, $\text{Fe}_2\text{O}_3(\text{s})$ and $3\text{CO}(\text{g})$, from their elements is:

$$\Delta H_f^\ominus [\text{Fe}_2\text{O}_3(\text{s})] + 3\Delta H_f^\ominus [\text{CO}(\text{g})] = -822 + (3 \times -111) = -1155 \text{ kJ mol}^{-1}$$

The total enthalpy change for the formation of the products, $2\text{Fe}(\text{s})$ and $3\text{CO}_2(\text{g})$, from their elements is:

$$2\Delta H_f^\ominus [\text{Fe}(\text{s})] + 3\Delta H_f^\ominus [\text{CO}_2(\text{g})] = 0 + (3 \times -394) = -1182 \text{ kJ mol}^{-1}$$

Note that the standard enthalpy change of formation of $\text{Fe}(\text{s})$ is 0 because it is an element in its standard state. These values can be added to the cycle (Figure 5.15b).

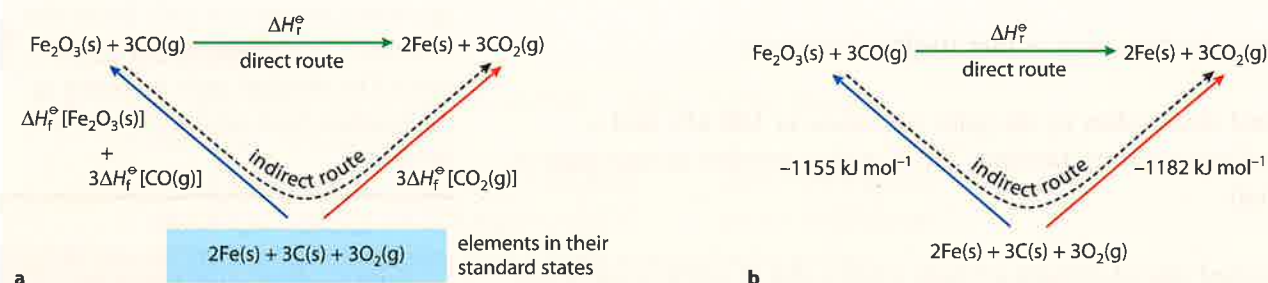


Figure 5.15 Working out an enthalpy change from ΔH_f^\ominus values. **a** Enthalpy cycle for the reaction $\text{Fe}_2\text{O}_3(\text{s}) + 3\text{CO}(\text{g}) \rightarrow 2\text{Fe}(\text{s}) + 3\text{CO}_2(\text{g})$. **b** The same enthalpy cycle with ΔH_f^\ominus values included.

The enthalpy change for the direct route is the same as the enthalpy change for the indirect route. The indirect route goes in the opposite direction to the blue arrow and therefore the sign of this enthalpy change is reversed:

$$\Delta H_r^\ominus = -(-1155) + (-1182) = -27 \text{ kJ mol}^{-1}$$

Therefore the enthalpy change of reaction is -27 kJ mol^{-1} .

What we have actually done in this cycle is to subtract the total enthalpy change of the reactants from the total enthalpy change of the products to give the overall enthalpy change. This can be shown as:

$$\Delta H_r = \Sigma \Delta H_f^\ominus (\text{products}) - \Sigma \Delta H_f^\ominus (\text{reactants})$$

Σ means 'sum of'.

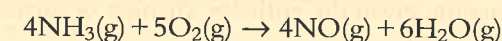
Using this equation is by far the easiest way of solving problems involving enthalpy changes of formation.

Worked example

5.10 Given these standard enthalpy change values (kJ mol^{-1}):

$$\Delta H_f^\ominus [\text{NH}_3(\text{g})] = -46; \Delta H_f^\ominus [\text{NO}(\text{g})] = 90; \Delta H_f^\ominus [\text{H}_2\text{O}(\text{g})] = -242$$

calculate the enthalpy change for the reaction:



Using $\Delta H_r = \Sigma \Delta H_f^\ominus (\text{products}) - \Sigma \Delta H_f^\ominus (\text{reactants})$

$$\Sigma \Delta H_f^\ominus (\text{products}) = (4 \times 90) + (6 \times -242) = -1092 \text{ kJ mol}^{-1}$$

$$\Sigma \Delta H_f^\ominus (\text{reactants}) = 4 \times -46 = -184 \text{ kJ mol}^{-1}$$

Note: ΔH_f^\ominus for $\text{O}_2(\text{g})$ is zero because it is an element in its standard state.

$$\Delta H_r^\ominus = -1092 - (-184) = -908 \text{ kJ mol}^{-1}$$

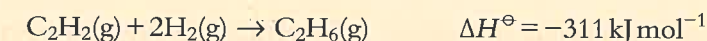
So the enthalpy change for this reaction is -908 kJ mol^{-1} .

Determining an enthalpy change of formation from an enthalpy change of reaction

If you are given an enthalpy change of reaction and some enthalpy changes of formation, it may be possible to work out a missing enthalpy change of formation.

Worked example

5.11 Given that the standard enthalpy change of formation of ethane ($\text{C}_2\text{H}_6(\text{g})$) is -85 kJ mol^{-1} and this equation:



work out the enthalpy change of formation of ethyne, $\text{C}_2\text{H}_2(\text{g})$.

$$\Delta H^\ominus = \Sigma \Delta H_f^\ominus (\text{products}) - \Sigma \Delta H_f^\ominus (\text{reactants})$$

$$-311 = -85 - (\Delta H_f^\ominus [\text{C}_2\text{H}_2(\text{g})] + [2 \times 0])$$

Rearranging the equation gives:

$$\Delta H_f^\ominus [\text{C}_2\text{H}_2(\text{g})] = -85 + 311 = +226 \text{ kJ mol}^{-1}$$

Nature of science

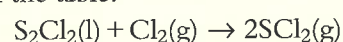
Hess carried out a series of experiments looking at how the amount of heat energy given out in chemical reactions depended on whether the reaction occurred directly or indirectly in a series of steps. His experiments required careful measurements and an awareness of the limitations of his data. He published his work in 1840 and proposed a general law that for a chemical reaction, the heat energy evolved is constant and does not depend on whether substances combine directly or indirectly. His hypothesis could be tested by further experimental work and a theory based on the principle of conservation of energy developed.

Test yourself

- 11 Write equations for the enthalpy change of formation of the following:

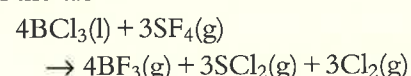
- HF(g)
- CH₃Cl(g)
- H₂O(l)
- C₅H₁₁OH(l)

- 12 Calculate the enthalpy change for the following reaction, given the enthalpy changes of formation in the table:



	$\Delta H_f^\circ / \text{kJ mol}^{-1}$
S ₂ Cl ₂ (l)	-59.4
SCl ₂ (g)	-19.7

- 13 Calculate the enthalpy change for the following reaction, given the enthalpy changes of formation in the table:



	$\Delta H_f^\circ / \text{kJ mol}^{-1}$
BCl ₃ (l)	-427
SCl ₂ (g)	-19.7
SF ₄ (g)	-775
BF ₃ (g)	-1137

- 14 Calculate the enthalpy change of formation of NO₂(g) from the following data:
- $$2\text{Pb}(\text{NO}_3)_2(\text{s}) \rightarrow 4\text{NO}_2(\text{g}) + 2\text{PbO}(\text{s}) + \text{O}_2(\text{g})$$
- $$\Delta H = +602 \text{ kJ mol}^{-1}$$

	$\Delta H_f^\circ / \text{kJ mol}^{-1}$
Pb(NO ₃) ₂ (s)	-452
PbO(s)	-217

5.3 Bond enthalpies

Enthalpy changes for reactions in the gas phase can be worked out if we know the amount of energy required/released when bonds are broken/made. To be able to do this we must first consider the definition of bond enthalpy (also just called **bond energy**):

Bond enthalpy is the enthalpy change when one mole of covalent bonds, in a gaseous molecule, is broken under standard conditions.

For example, the H–H bond enthalpy is 436 kJ mol⁻¹, which can be represented by the equation:



One mole of H₂ molecules is broken apart to give two moles of gaseous hydrogen atoms.

The H–Cl bond enthalpy is 431 kJ mol⁻¹, which is represented by:

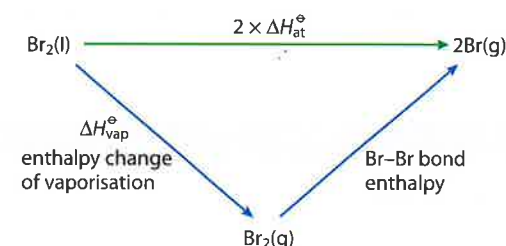


Bond enthalpies are used for reactions occurring in the gaseous state.

If we consider the process:



this does not represent the bond enthalpy of the Br–Br bond, because this reaction can be broken down into two processes:



The process Br₂(l) → 2Br(g) is called atomisation, and energy must be supplied to overcome the London forces between the bromine molecules as well as to break the Br–Br bonds.

Energy must be supplied to break apart two atoms in a molecule against the attractive force holding them together. Therefore, the process of breaking bonds must be endothermic – the enthalpy change is positive.

Energy is released when two atoms come together to form a bond. Therefore, the process of making bonds is exothermic – the enthalpy change is negative.

Some average bond enthalpies are shown in Table 5.1.

Learning objectives

- Define average bond enthalpy
- Use bond energies to calculate enthalpy changes

Exam tip

HCl(g) → ½H₂(g) + ½Cl₂(g) does **not** represent the bond enthalpy of HCl. ½H₂(g) represents half a mole of H₂ molecules and is not the same as H(g), which is one mole of gaseous H atoms.

The Br–Br bond enthalpy is 193 kJ mol⁻¹, and the **standard enthalpy change of vaporisation** (for the formation of one mole of gaseous molecules) is 31 kJ mol⁻¹.

The enthalpy change for the process Br₂(l) → 2Br(g) is actually **twice** the enthalpy change of atomisation (ΔH_{at}) as the enthalpy change of atomisation is defined as the enthalpy change for formation of one mole of gaseous atoms.

Bond breaking requires energy (endothermic): ΔH positive.

Bond making releases energy (exothermic): ΔH negative.

Bond enthalpies are defined in terms of **breaking** bonds and therefore, have **positive** values.

Bond	Bond enthalpy / kJ mol ⁻¹	Bond	Bond enthalpy / kJ mol ⁻¹	Bond	Bond enthalpy / kJ mol ⁻¹	Bond	Bond enthalpy / kJ mol ⁻¹
H-H	436	C-H	412	O-O	146	C-O	360
C-C	348	Si-H	318	O=O	496	C=O	743
C=C	612	N-H	388	Si-O	374	C≡O	1070
C≡C	837	P-H	322	F-F	158	C-N	305
Si-Si	226	O-H	463	Cl-Cl	242	C=N	613
N-N	163	S-H	338	Br-Br	193	C≡N	890
N=N	409	F-H	562	I-I	151	C-F	484
N≡N	944	Cl-H	431	N-Cl	200	C-Cl	338
P-P	172	Br-H	366	Si-F	590	C-Br	276
S-S	264	I-H	299	N-F	278	C-I	238

Table 5.1 Some average bond enthalpies.

The bond energies given in tables are **average** values. For example, the C-H bond energy in ethane (C₂H₆) is slightly different from that in benzene (C₆H₆) so the value quoted in the table is an average value, averaged over the values for C-H bonds in many compounds. This can introduce some inaccuracies into calculations involving bond energies. Bond energy calculations are therefore most accurate when they involve breaking/making only a few bonds.

Exam tip

This is important when answering examination questions.

Exam tip

When defining 'average bond enthalpy' it is important to define 'bond enthalpy' as well as explaining 'average'.

Average bond enthalpy is the average amount of energy required to break one mole of covalent bonds, in gaseous molecules under standard conditions. 'Average' refers to the fact that the bond enthalpy is different in different molecules and therefore the value quoted is the average amount of energy to break a particular bond in a range of molecules.

Extension

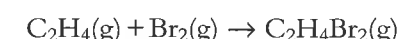
Why is bond making exothermic?

When two atoms are a long way apart, the electrical potential energy of the two together is a maximum (consider separating the two atoms from where they are bonded together to where they are an infinite distance apart – work must be done against the force holding them together, so the potential energy increases). As they approach closer together, because of the attractive force between them, the potential energy decreases and this energy is released as heat. This can be likened to a ball falling to Earth – as the ball and the Earth come together, the potential energy of the system is first of all converted to kinetic energy and then to heat as the two collide.

Using bond enthalpies to work out enthalpy changes for reactions

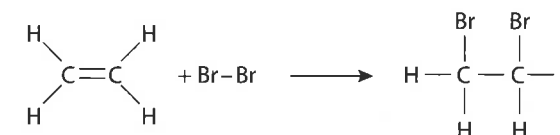
Example

Consider the reaction between ethene and bromine to produce 1,2-dibromoethane:

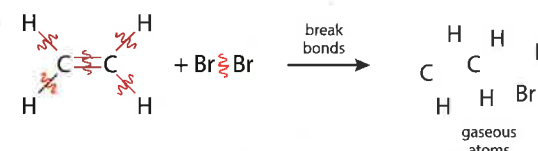


What is the enthalpy change for this reaction?

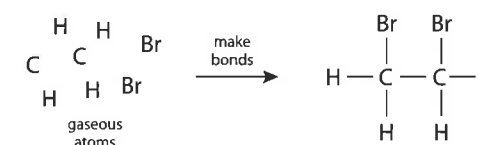
If the species are drawn as structural formulas, then all the bonds can be seen clearly:



We imagine the reaction happening with all the bonds in the reactants being broken:



Then new bonds form to make the products:



The bond energies can be added up (Tables 5.2 and 5.3) to work out the enthalpy change.

Bond broken	Bond energy / kJ mol ⁻¹	Number of bonds	Total energy / kJ mol ⁻¹
C-H	412	4	1648
C=C	612	1	612
Br-Br	193	1	193
Total energy to break all bonds			2453

Table 5.2 Calculation of the enthalpy change when all bonds are broken in ethene and bromine.

The total enthalpy change when all the bonds are broken is +2453 kJ mol⁻¹. This is positive because breaking bonds is an endothermic process.

Bond made	Bond energy / kJ mol ⁻¹	Number of bonds	Total energy / kJ mol ⁻¹
C-H	412	4	1648
C-C	348	1	348
C-Br	276	2	552
Total energy released when bonds made			2548

Table 5.3 Calculation of the enthalpy change when bonds are formed in C₂H₄Br₂.

Bromine and 1,2-dibromoethane are both liquids under standard conditions. The equation here is for the reaction in the gas phase, and the enthalpy change will not be the same as for the reaction involving liquid bromine to form C₂H₄Br₂(l).

The total enthalpy change when all the bonds are made is $-2548 \text{ kJ mol}^{-1}$. This is negative because making bonds is an exothermic process.

If we add up these enthalpy changes, we get the overall enthalpy change for the reaction:

$$\Delta H^\ominus = 2453 - 2548 = -95 \text{ kJ mol}^{-1}$$

The overall process is sometimes summarised as:

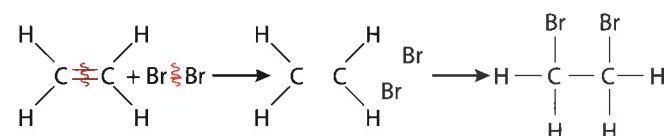
$$\Delta H_r = \Sigma(\text{bonds broken}) - \Sigma(\text{bonds made})$$

where the bond energies are taken directly from Table 5.1 and no signs changed, i.e. all values are put in as positive.

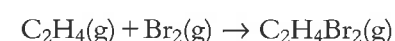
This approach would give:

$$\Delta H^\ominus = [(4 \times 412) + (1 \times 612) + (1 \times 193)] - [(4 \times 412) + (1 \times 348) + (2 \times 276)]$$

A shortcut for doing this question would be to realise that there are four C–H bonds in ethene and four C–H bonds in 1,2-dibromoethane, and therefore there is no need to make or break these bonds:



If the enthalpy change for:

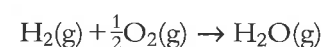


is calculated using enthalpy changes of formation the value obtained is -121 kJ mol^{-1} , which is different from the value of -95 kJ mol^{-1} obtained using bond enthalpy calculations. The value obtained using enthalpy changes of formation is expected to be more reliable, because enthalpy changes of formation are specific to the particular substances, whereas bond enthalpies are average values. The C–H bond energies in C_2H_4 and $\text{C}_2\text{H}_4\text{Br}_2$ would not be expected to be the same, and the values used for the C=C and C–C bonds are not necessarily the actual bond energies in these compounds.

Using a cycle in calculations involving bond enthalpies

Example

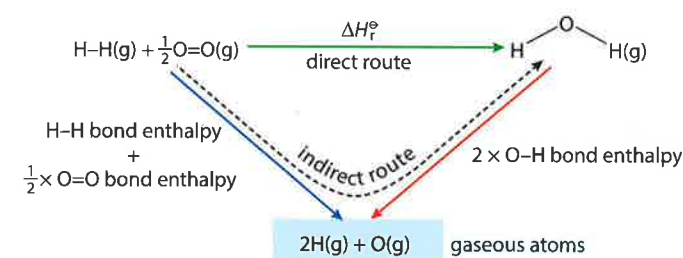
Using bond enthalpies given in Table 5.4, we can calculate the enthalpy change for the reaction:



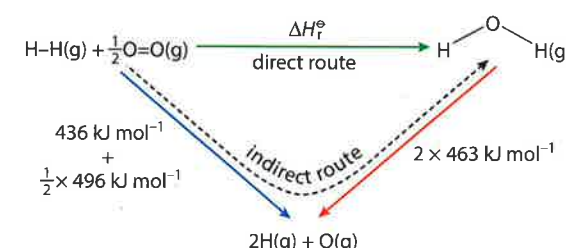
Bond	Bond enthalpy / kJ mol^{-1}
H–H	436
O=O	496
O–H	463

Table 5.4 Bond enthalpies.

A cycle can be drawn:



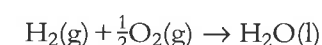
The values can be substituted into the cycle:



The enthalpy change for the direct route is the same as that for the indirect route. The direction of the arrow for the indirect route is opposite to that of the red arrow, and therefore the sign of this enthalpy change must be reversed:

$$\Delta H_r^\ominus = (436 + \frac{1}{2} \times 496) - (2 \times 463) = -242 \text{ kJ mol}^{-1}$$

In order to use bond enthalpies, the substances must be in the gas phase. This is because intermolecular forces must also be taken into account in the liquid and solid states. So, in order to use bond enthalpies with solids and liquids we must first generate gaseous species. If we wanted to find the enthalpy change for the formation of *liquid* water from its elements – i.e. for the process:



we would also have to know the enthalpy change of vaporisation of water – i.e. the enthalpy change for the process:



Figure 5.16 shows how this can be incorporated into the cycle.

The enthalpy change for the reaction is: $\Delta H_r^\ominus = 684 - 926 - 41 = -283 \text{ kJ mol}^{-1}$

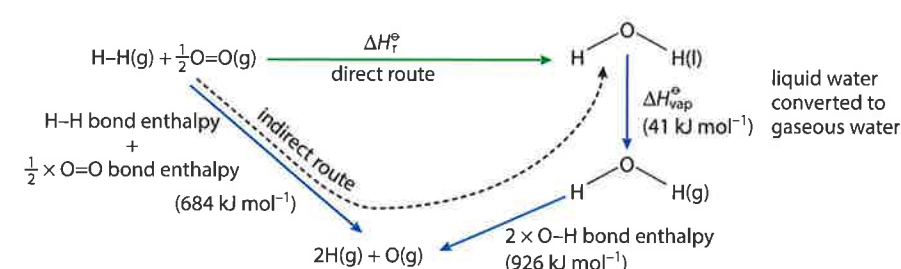


Figure 5.16 Including the enthalpy of vaporisation in an enthalpy cycle.

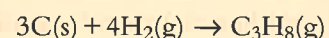
A reaction in the gas phase will be endothermic if less energy is released when bonds are formed (exothermic) than is required to break bonds (endothermic). This could be the case if stronger/more bonds are broken than are formed.

A reaction in the gas phase will be exothermic if more energy is released when bonds are formed (exothermic) than is required to break bonds (endothermic). This could be the case if stronger/more bonds are made than are broken.

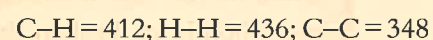
It is important to note that bond energies can only be used to decide whether a reaction in the gas phase is exothermic or endothermic. For reactions involving solids and liquids, other interactions, such as intermolecular forces, must also be taken into account.

Worked example

5.12 Calculate the enthalpy change for the process:

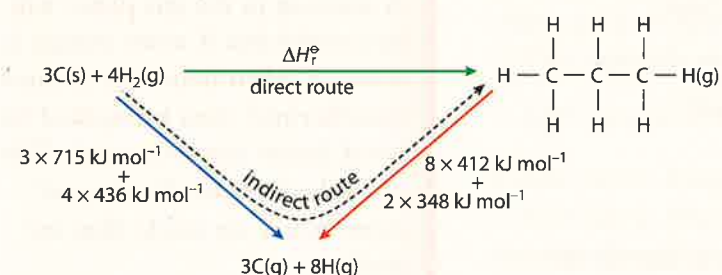


using the following bond energies (kJ mol^{-1}):



and the enthalpy change $\text{C(s)} \rightarrow \text{C(g)}$ $\Delta H^\ominus = +715 \text{ kJ mol}^{-1}$

A cycle can be used to work out the overall enthalpy change:



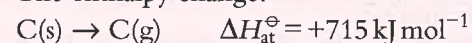
In the left-hand process, represented by the blue arrow, three moles of solid carbon are converted into gaseous atoms and four moles of H-H bonds are broken. In the right-hand process (red arrow), eight moles of C-H bonds and two moles of C-C bonds are broken to generate gaseous atoms.

The value of the unknown enthalpy change is given by:

$$\begin{aligned} \Delta H^\ominus &= [(3 \times 715) + (4 \times 436)] - [(8 \times 412) + (2 \times 348)] \\ &= -103 \text{ kJ mol}^{-1} \end{aligned}$$

The published value for this enthalpy change is -104 kJ mol^{-1} , so in this case there is fairly good agreement between data worked out using bond enthalpies and in other ways.

The enthalpy change:



is the enthalpy change of atomisation for carbon – the enthalpy change for the formation of one mole of gaseous atoms.

Working out a bond enthalpy from an enthalpy change of reaction

Example

Using the bond enthalpies for the F-F and Br-Br bonds and the enthalpy change of reaction given, we can calculate the mean Br-F bond energy in BrF_3 :



This is most easily done using the equation:

$$\Delta H_r = \Sigma(\text{bonds broken}) - \Sigma(\text{bonds made})$$

$$-545 = [193 + (3 \times 158)] - [6 \times \text{Br-F}]$$

Rearranging this we get:

$$6 \times \text{Br-F} = 193 + (3 \times 158) + 545$$

$$6 \times \text{Br-F} = 1212$$

Therefore the Br-F bond enthalpy is $\frac{1212}{6}$, i.e. 202 kJ mol^{-1} .

Potential energy profiles and stability

A potential energy diagram (profile) can be used to show the energy changes occurring during a chemical reaction. The potential energy diagrams for exothermic and endothermic reactions are shown in Figure 5.17. A reaction coordinate represents the progress of a reaction from reactants to products. As reactant particles approach each other, repulsion between the particles and the partial breaking of bonds causes the potential energy of the system to increase. The activation energy is the minimum energy that colliding particles must have before a collision results in a chemical reaction – this will be considered in more detail on page 246.

In an exothermic reaction, the products are at lower energy than the reactants and are therefore said to be **more stable** than the reactants. For an endothermic reaction, the products are at higher energy and are **less stable** than the reactants.

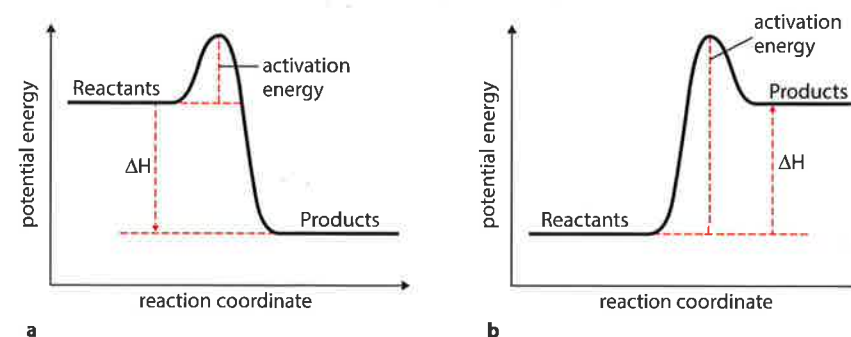
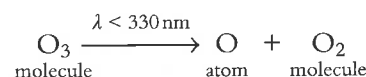
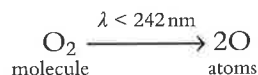


Figure 5.17 **a** Potential energy diagram for an exothermic reaction; **b** potential energy diagram for an endothermic reaction.

Potential energy diagrams are often used in discussions about rate of reaction and will be discussed later, on page 246.

Absorption of UV light in the atmosphere

Ozone (O₃) and oxygen (O₂) in the atmosphere are important in protecting the surface of the Earth from the damaging effects of ultraviolet radiation. UV radiation is absorbed by molecules of O₂ and/or O₃ as they undergo dissociation – breaking the bond between oxygen atoms:



O₂ molecules absorb higher energy UV radiation than O₃ because the bond between the oxygen atoms in O₂ is stronger than that between the oxygen atoms in O₃.

The UV radiation required to break the bond in O₂ (double bond) is in the UV-C part of the spectrum and must have a wavelength shorter than 242 nm to provide sufficient energy to break the bond. The bond in ozone is between a single bond and double bond (see page 170) and the absorption of lower energy, UV-B, radiation will break the bond. A more detailed account is given in the Higher Level section on page 174.

Nature of science

Scientists use models to explain experimental data and to make predictions. Here we are using a very simple model in terms of breaking bonds and making bonds to make predictions about enthalpy changes for reactions. Agreement between a theoretical model and the experimental data is used to evaluate models.

? Test yourself

- 15 Use the bond enthalpies in Table 5.1 on page 208 to work out the enthalpy changes for the following reactions:
 - a $\text{CH}_4(\text{g}) + \text{Cl}_2(\text{g}) \rightarrow \text{CH}_3\text{Cl}(\text{g}) + \text{HCl}(\text{g})$
 - b $\text{C}_2\text{H}_2(\text{g}) + 2\text{H}_2(\text{g}) \rightarrow \text{C}_2\text{H}_6(\text{g})$
 - c $\text{CO}(\text{g}) + \text{Cl}_2(\text{g}) \rightarrow \text{COCl}_2(\text{g})$
- 16 Calculate the mean Cl–F bond enthalpy, given the following data:

$$\text{Cl}_2(\text{g}) + 3\text{F}_2(\text{g}) \rightarrow 2\text{ClF}_3(\text{g}) \quad \Delta H^\ominus = -164 \text{ kJ mol}^{-1}$$
 and the Cl–Cl and F–F bond enthalpies in Table 5.1 (page 208).
- 17 Calculate the mean Cl–F bond enthalpy, given the following data:

$$\text{ClF}_3(\text{g}) + \text{F}_2(\text{g}) \rightarrow \text{ClF}_5(\text{g}) \quad \Delta H^\ominus = -91 \text{ kJ mol}^{-1}$$
 and the F–F bond enthalpy in Table 5.1 (page 208).
- 18 Work out the enthalpy change for the reaction:

$$\text{S}(\text{s}) + \text{F}_2(\text{g}) \rightarrow \text{SF}_2(\text{g})$$
 given the bond energies:

$$\text{S–F} = 327 \text{ kJ mol}^{-1} \text{ and } \text{F–F} = 158 \text{ kJ mol}^{-1}$$
 and this enthalpy change:

$$\text{S}(\text{s}) \rightarrow \text{S}(\text{g}) \quad \Delta H = +223 \text{ kJ mol}^{-1}$$

Both ClF₃ and ClF₅ just contain single bonds between Cl and F.

5.4 Energy cycles (HL)

So far, the energy cycles we have drawn have been for covalent substances. In this section we will consider an enthalpy level diagram for ionic substances. Before we look at this we must consider some definitions.

Standard enthalpy change of atomisation ($\Delta H_{\text{at}}^\ominus$) – this is the enthalpy change when one mole of gaseous atoms is formed from an element under standard conditions.

ΔH_{at} is always endothermic – for example:



The values for the enthalpy changes of atomisation of hydrogen and chlorine are half the bond enthalpy values given in Table 5.1 on page 208. The bond enthalpy for Cl₂ refers to breaking of one mole of covalent bonds to produce two moles of gaseous atoms:



whereas the enthalpy change of atomisation for Cl₂ refers to breaking half a mole of covalent bonds to produce one mole of gaseous atoms.

First ionisation energy is the enthalpy change when one electron is removed from each atom in one mole of gaseous atoms under standard conditions:



Second ionisation energy is the enthalpy change for the process:



First electron affinity is the enthalpy change when one electron is added to each atom in one mole of gaseous atoms under standard conditions:



Second electron affinity is enthalpy change for the process:



Learning objectives

- Define the enthalpy changes involved in the formation and dissolution of ionic substances
- Understand how to draw a Born–Haber cycle
- Understand how to construct energy cycles for ionic substances dissolving in water

All ionisation energies are endothermic.

The (g) symbol is essential in these equations.

The first electron affinity is exothermic for virtually all elements; it is a favourable process to bring an electron from infinity to where it feels the attractive force of the nucleus in an atom.

The second electron affinity is always endothermic. It is an unfavourable process to add an electron to an ion which is already negatively charged, due to repulsion between the negative charges.

Look carefully to determine whether lattice enthalpy is exothermic or endothermic – as it can be defined in either direction, i.e. as the making or breaking of the lattice. Here it is defined as the breaking of the lattice and is an endothermic process because energy must be supplied to separate the ions against the attractive forces holding them in the lattice.

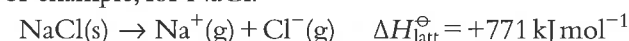


The Born–Haber cycle was developed by two Nobel-prize-winning German scientists: Fritz Haber (1868–1934) and Max Born (1882–1970).

The arrow for ΔH_{latt} goes upwards, indicating an endothermic process.

Lattice enthalpy ($\Delta H_{\text{latt}}^{\ominus}$) is the enthalpy change when one mole of an ionic compound is broken apart into its constituent gaseous ions under standard conditions.

For example, for NaCl:

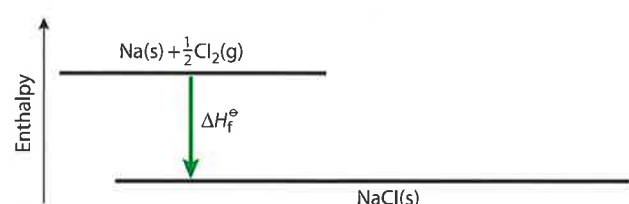


Note, for ammonium nitrate the equation is:



Born–Haber cycles

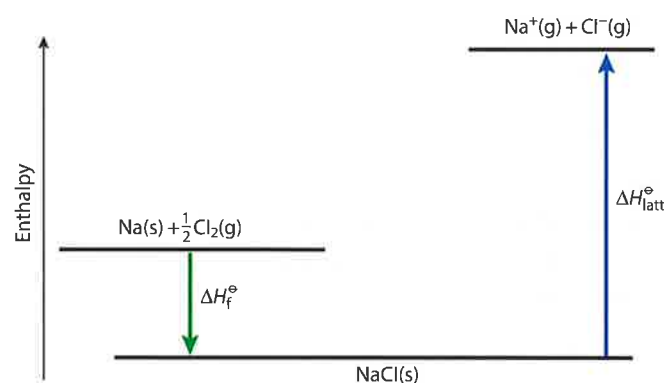
A **Born–Haber cycle** is an enthalpy level diagram breaking down the formation of an ionic compound into a series of simpler steps. For example, for sodium chloride, we will show the stages in construction of the cycle. The first step we put in is the equation for the enthalpy change of formation:



The enthalpy change of formation for NaCl(s) is exothermic and the (green) arrow is shown in the downward, negative, direction.

The aim now is to construct a cycle that gives us an alternative route between the elements, $\text{Na(s)} + \frac{1}{2}\text{Cl}_2(\text{g})$, and the ionic compound NaCl(s).

NaCl(s) can be broken apart into its constituent gaseous ions – this is the lattice enthalpy:



Putting the lattice enthalpy into the cycle gives us an idea of what we are aiming at so, to complete the cycle, Na(s) and $\frac{1}{2}\text{Cl}_2(\text{g})$ must be converted into gaseous ions. This and the other stages are detailed in the full Born–Haber cycle shown in Figure 5.18. Na(s) is first converted into $\text{Na}^+(\text{g})$ in two steps – these are shown as steps 1 and 2 in Figure 5.18.

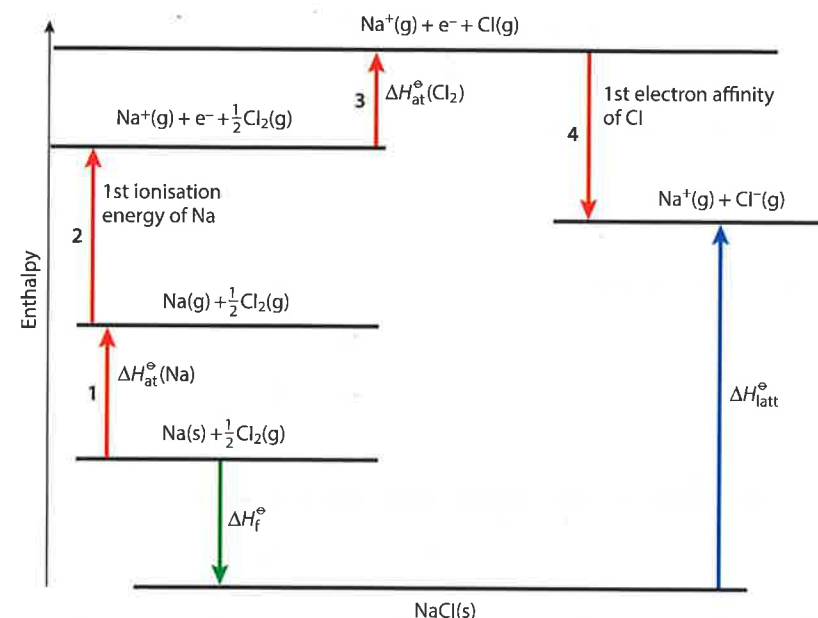
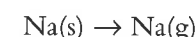


Figure 5.18 The Born–Haber cycle for NaCl. Upward arrows represent endothermic processes; downward arrows represent exothermic processes.

Step 1 involves the enthalpy change of atomisation for sodium:

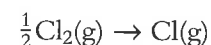


Step 2 involves the first ionisation energy of sodium:

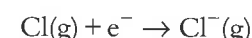


The sodium must be converted to gaseous atoms before it can be ionised because the definition of ionisation energy involves removal of an electron from a **gaseous** atom.

The sodium has been converted into the required species, $\text{Na}^+(\text{g})$, and now we must do the same with the chlorine. Step 3 is the atomisation of chlorine:



The cycle is then completed in step 4 by adding the electron removed from the sodium atom to the chlorine atom. This process is the first electron affinity of chlorine and is exothermic, so the arrow goes downwards:



If all the quantities in the cycle except one are known, then application of Hess's law allows the missing quantity to be worked out. For example, let us calculate the lattice enthalpy of sodium chloride using the data in Table 5.5.

The values can be put into the diagram (Figure 5.19) and Hess's law used to calculate the missing lattice energy.

$\Delta H_{\text{at}} [\text{Na(s)}]$	109 kJ mol^{-1}
$\Delta H_{\text{at}} [\text{Cl}_2(\text{g})]$	121 kJ mol^{-1}
first ionisation energy (Na)	494 kJ mol^{-1}
first electron affinity (Cl)	-364 kJ mol^{-1}
$\Delta H_{\text{f}} [\text{NaCl(s)}]$	-411 kJ mol^{-1}

Table 5.5 Data for the calculation of the lattice enthalpy of sodium chloride.

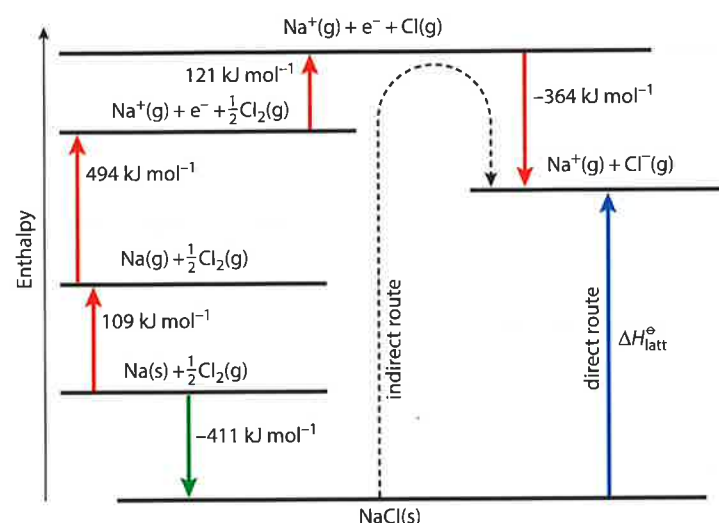


Figure 5.19 Working out a missing value – the lattice energy.

The enthalpy change for the direct route is the same as that for the indirect route. Therefore:

$$\Delta H_{\text{latt}}^{\circ} = 411 + 109 + 494 + 121 - 364$$

$$\Delta H_{\text{latt}}^{\circ} = 771 \text{ kJ mol}^{-1}$$

The sign of -411 was reversed because the direction of the indirect route arrow goes against the direction of this arrow.

Worked example

5.13 Draw a Born–Haber cycle for magnesium oxide and use it to work out the second electron affinity of oxygen.

Enthalpy term	Enthalpy change / kJ mol ⁻¹
ΔH _{at} ^o [Mg(s)]	150
ΔH _{at} ^o [O ₂ (g)]	248
first ionisation energy (Mg)	736
second ionisation energy (Mg)	1450
first electron affinity (O)	-142
ΔH _f ^o (MgO)	-602
ΔH _{latt} ^o (MgO)	3889

The Born–Haber cycle is shown in Figure 5.20.

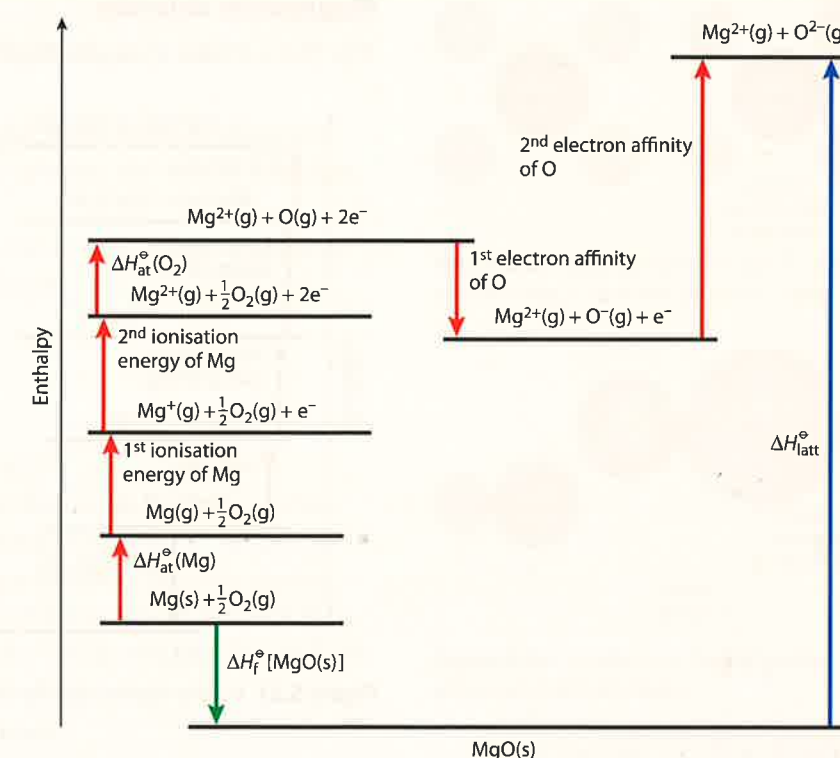


Figure 5.20 A Born–Haber cycle for MgO. The first electron affinity for O(g) is negative, but the second electron affinity is positive.

The second electron affinity of O is worked out most easily by applying Hess's law and looking at the enthalpy change for the direct route and the indirect route (Figure 5.21).

The signs of the enthalpy changes highlighted in Figure 5.21 are reversed, as the direction of the indirect route is in the opposite direction to the arrows on the diagram. The enthalpy change for the direct route is the same as that for the indirect route: second electron affinity of O = 142 - 248 - 1450 - 736 - 150 - 602 + 3889 = 845 kJ mol⁻¹.

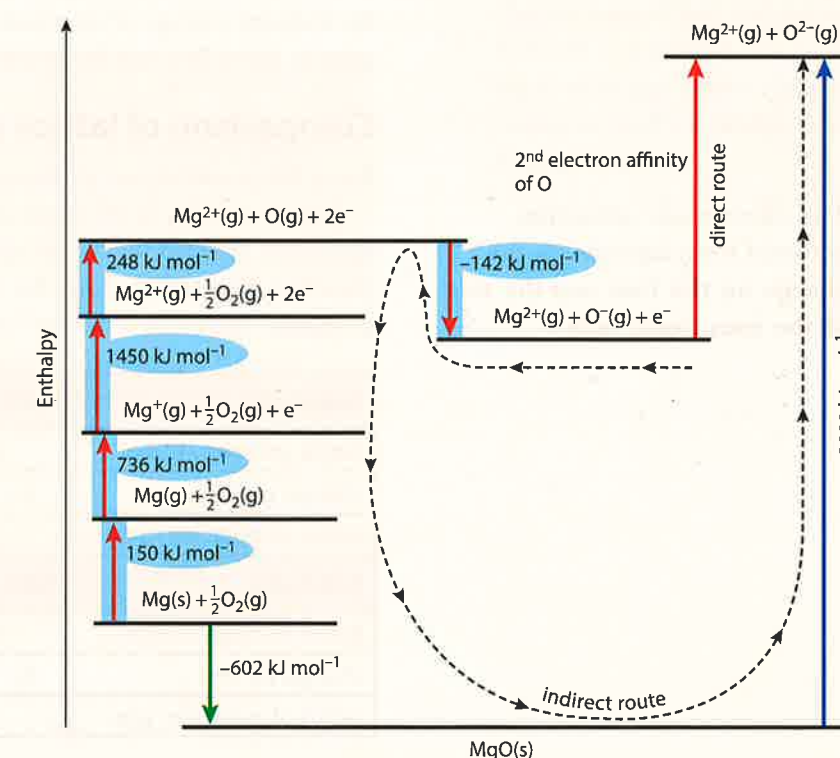


Figure 5.21 The Born–Haber cycle for MgO, showing the enthalpy changes for which the sign must be changed to work out the second electron affinity of oxygen.

Magnesium chloride

The Born–Haber cycle for MgCl_2 is shown in Figure 5.22.

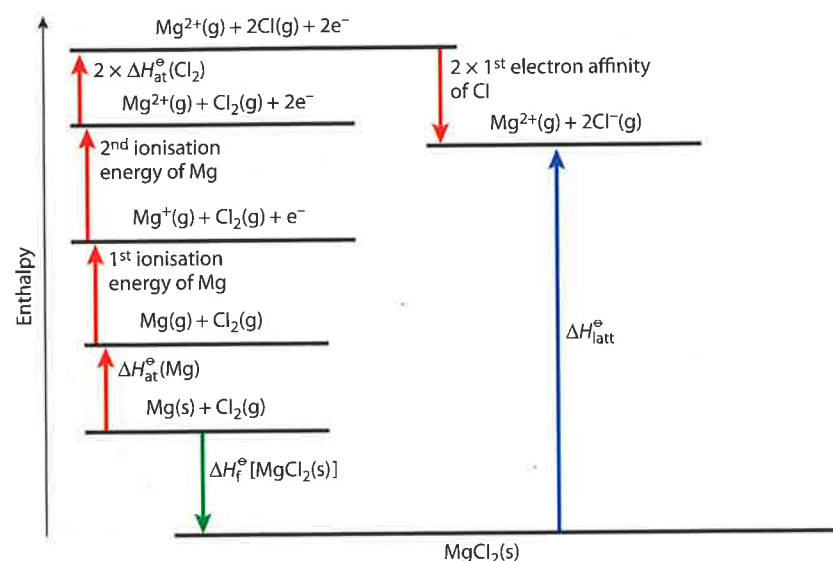


Figure 5.22 A Born–Haber cycle for MgCl_2 .

The only difference here from the other Born–Haber cycles considered above is that the enthalpy change of atomisation and the electron affinity of chlorine are both multiplied by two. Remember that the definition of the enthalpy change of atomisation refers to the formation of one mole of gaseous atoms and not the breaking of one mole of covalent bonds.

Comparison of lattice enthalpies

Some lattice enthalpies are shown in Table 5.6.

Lattice enthalpy is the result of electrostatic attractions between oppositely charged ions in the giant lattice. The greater the electrostatic attraction between the ions, the more energy has to be supplied to break the lattice apart.

Substance	NaCl		MgCl ₂		MgO	
lattice enthalpy / kJ mol^{-1}	+771		+2526		+3791	
charges on ions	1+	1-	2+	1-	2+	2-
radius of metal ion / pm	95		65		65	
Substance	CsCl		BaCl ₂		BaO	
lattice enthalpy / kJ mol^{-1}	+645		+2056		+3054	
charges on ions	1+	1-	2+	1-	2+	2-
radius of metal ion / pm	169		135		135	

Table 5.6 Some lattice enthalpies.

The electrostatic attraction between ions depends on the charge on the ions and the size of the ions (ionic radii).

The effect of charge

MgCl_2 has a higher lattice enthalpy than NaCl (Figure 5.23).

The higher the charges on the ions, the more strongly they will attract each other – and therefore the greater the lattice enthalpy.

The force between ions is proportional to the product of the charges, so the force of attraction increases along the series:

$$1+/1- < 1+/2- < 2+/2-$$

The effect of size

CsCl has a smaller lattice enthalpy than NaCl .

Ions act like point charges – a positive ion such as Na^+ behaves as if its ionic charge all acts at its centre and a negative ion such as Cl^- behaves as if a $1-$ charge exists at its centre. The bigger the ionic radii, the greater the distance between the centres of the ions and, therefore, the smaller the attraction between the ions and the smaller the lattice enthalpy (Figure 5.24).

Lattice enthalpy is larger for smaller ions.

We can see that MgCl_2 has a larger lattice enthalpy than NaCl , not just because the Mg^{2+} ion has a higher charge than the Na^+ ion, but also because the Mg^{2+} ion is smaller.

Worked example

5.14 Arrange the following compounds in order of increasing lattice enthalpy:

BaCl_2 LiF ZnS

The most important factor in determining lattice enthalpy is the charge on the ions. ZnS contains $2+$ and $2-$ ions, BaCl_2 contains $2+$ and $1-$ ions and LiF contains $1+$ and $1-$ ions. The order of increasing lattice enthalpy is:

$$\text{LiF} < \text{BaCl}_2 < \text{ZnS}$$

The attraction between $2+/2-$ ions in ZnS is greater than that between $2+/1-$ ions in BaCl_2 , which is greater than between $1+/1-$ ions in LiF .

Because the melting point of an ionic substance depends on the force of attraction between ions, a substance with a high lattice enthalpy would also be expected to have a high melting point (Table 5.7).

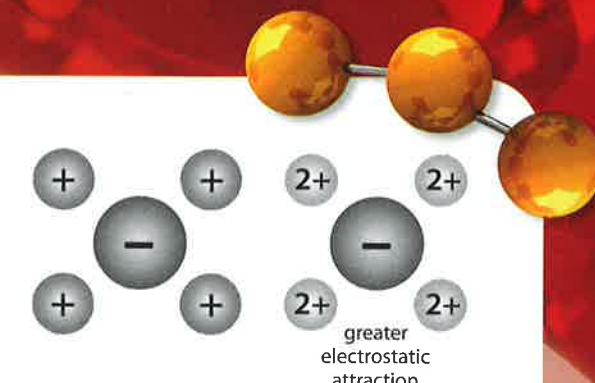


Figure 5.23 NaCl contains $1+$ and $1-$ ions, whereas MgCl_2 contains $2+$ and $1-$ ions.

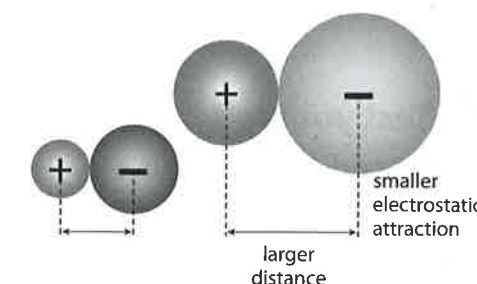


Figure 5.24 Smaller ions have a greater attraction between them.

Exam tip

The largest lattice enthalpy is obtained for small, highly charged ions. When comparing different compounds, the effect of charge causes a larger change in lattice enthalpy than do size variations.

Substance	Lattice enthalpy / kJ mol ⁻¹	Melting point / °C
NaCl	+771	801
MgO	+3791	2852
KCl	+711	770
CaO	+3401	2614
CsCl	+645	645
BaO	+3054	1918

Table 5.7 The lattice enthalpies and melting points of some substances.

? Test yourself

- 19 Use the data in the table to calculate the first electron affinity of Br.

	/kJ mol ⁻¹
ΔH_{at} [K(s)]	90
ΔH_{at} [Br ₂ (l)]	112
first ionisation energy (K)	418
ΔH_{latt} (KBr)	670
ΔH_{f} (KBr(s))	-394

- 20 Use the data in the table to calculate the lattice enthalpy of BaF₂.

	/kJ mol ⁻¹
ΔH_{at} [Ba(s)]	176
ΔH_{at} [F ₂ (g)]	79
first ionisation energy (Ba)	502
second ionisation energy (Ba)	966
first electron affinity (F)	-348
ΔH_{f} (BaF ₂ (s))	-1201

- 21 Arrange the following in order of increasing lattice enthalpy (smallest first):

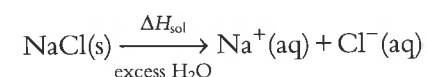
LiF KCl CaO
CaS CaCl₂

- 22 State whether the following enthalpy changes are *always exothermic*, *always endothermic* or *sometimes exothermic and sometimes endothermic*:

- first ionisation energy
- second ionisation energy
- enthalpy change of atomisation
- enthalpy change of formation
- first electron affinity
- second electron affinity

Dissolving ionic substances

In this section, we will consider the enthalpy changes that occur when ionic substances dissolve in water. The equation for sodium chloride dissolving in water is:



The enthalpy change represented here is called the **enthalpy change of solution** (ΔH_{sol}) and is defined as:

The enthalpy change when one mole of solute is dissolved in excess solvent to form a solution of 'infinite dilution' under standard conditions.

The dissolving of sodium chloride in water can be broken down in to two separate processes and an energy cycle drawn (Figure 5.25).

Stage 1: lattice enthalpy (ΔH_{latt}) – breaking apart the lattice into gaseous ions – an endothermic process.

Stage 2: hydration of the ions (ΔH_{hyd}) – surrounding the gaseous ions by water molecules – an exothermic process.

Enthalpy change of hydration (ΔH_{hyd}) is defined as:

The enthalpy change when one mole of gaseous ions is surrounded by water molecules to form an 'infinitely dilute solution' under standard conditions.

For example:



Ion–dipole forces (Figure 5.26) are formed between the ions and water molecules and **hydration enthalpies are always exothermic**. So the dissolving process (Figure 5.27) involves an endothermic process (ΔH_{latt}) and an exothermic process (ΔH_{hyd}).

Overall, an enthalpy change of solution will be exothermic if the total enthalpy change of hydration is more negative than the lattice enthalpy is positive.

Working out the value of the enthalpy change of solution for sodium chloride:

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

$$\Delta H_{\text{sol}} = 771 + (-406) + (-364)$$

$$\Delta H_{\text{sol}} = +1 \text{ kJ mol}^{-1}$$

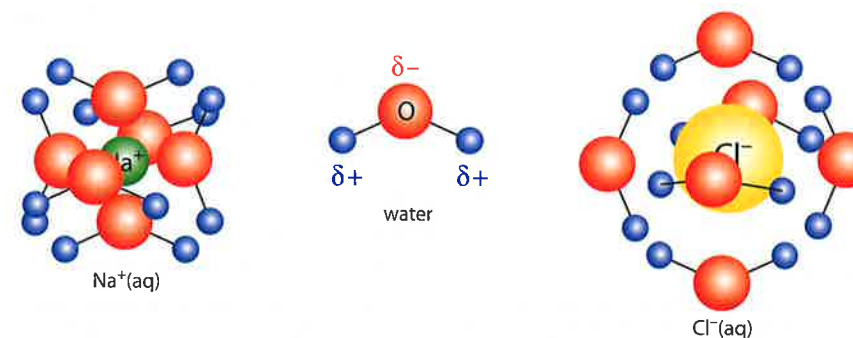


Figure 5.26 Hydrated Na⁺ and Cl⁻ ions.

'Infinite dilution' means that any further dilution of the solution produces no further enthalpy change – i.e. the solute particles are assumed not to interact with each other in the solution.

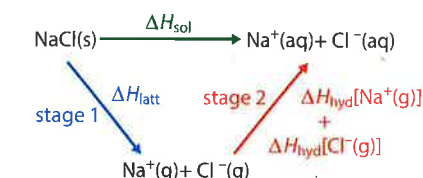


Figure 5.25 Dissolving and energy.

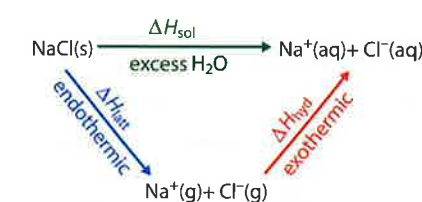


Figure 5.27 The energy changes involved in dissolving.

So, the dissolving of sodium chloride in water is an endothermic process (just). For dissolving magnesium chloride (MgCl_2) the enthalpy change of solution would be given by the equation:

$$\Delta H_{\text{sol}} = \Delta H_{\text{latt}} + \Delta H_{\text{hyd}}(\text{Mg}^{2+}) + 2\Delta H_{\text{hyd}}(\text{Cl}^-)$$

In general:

$$\Delta H_{\text{sol}}(\text{X}_n\text{Y}_m) = \Delta H_{\text{latt}} + n\Delta H_{\text{hyd}}(\text{X}^{m+}) + m\Delta H_{\text{hyd}}(\text{Y}^{n-})$$

Hydration enthalpies

Some hydration enthalpies are shown in Table 5.8. It can be seen from the values in the table that the enthalpy change of hydration depends on the size of an ion and its charge.

Positive ion	$\Delta H_{\text{hyd}}/\text{kJ mol}^{-1}$	Negative ion	$\Delta H_{\text{hyd}}/\text{kJ mol}^{-1}$
Li^+	-519	Cl^-	-364
Na^+	-406	Br^-	-335
K^+	-322	I^-	-293
Mg^{2+}	-1920		
Ca^{2+}	-1650		

Table 5.8 Enthalpy of hydration values for some ions.

More highly charged ions have a more exothermic enthalpy change of hydration because of a stronger electrostatic attraction between the ion and water molecules. Ca^{2+} and Na^+ ions are roughly the same size, but Ca^{2+} has a much more exothermic enthalpy change of hydration because of its higher charge.

Smaller ions have more exothermic enthalpy changes of hydration because of a stronger electrostatic attraction between the ion and water molecules. Ca^{2+} and Mg^{2+} ions have the same charge but Mg^{2+} has a more exothermic enthalpy change of hydration because of its smaller size.

As for lattice enthalpy, the magnitude of the charge has a greater effect on the enthalpy change of hydration than does the size of the ions. So, the hydration enthalpies of all 2+ ions will be more exothermic than those of 1+ ions.

Nature of science

Data is very important in science. The use of energy cycles allows the calculations of energy changes for reactions which cannot be measured directly.

? Test yourself

- 23 Use the values given in the table to work out the enthalpy change of solution of potassium iodide.

Lattice enthalpy of KI(s) / kJ mol^{-1}	629
Enthalpy change of hydration of $\text{K}^+(\text{g})$ / kJ mol^{-1}	-322
Enthalpy change of hydration of $\text{I}^-(\text{g})$ / kJ mol^{-1}	-293

- 24 Use the values given in the table to work out the enthalpy change of solution of magnesium chloride.

Lattice enthalpy of $\text{MgCl}_2(\text{s})$ / kJ mol^{-1}	2493
Enthalpy change of hydration of $\text{Mg}^{2+}(\text{g})$ / kJ mol^{-1}	-1920
Enthalpy change of hydration of $\text{Cl}^-(\text{g})$ / kJ mol^{-1}	-364

5.5 Entropy and spontaneity (HL)

The dissolving of sodium chloride (common salt) in water is an example of an endothermic process that occurs spontaneously at room temperature. The idea of an endothermic reaction occurring spontaneously goes against our experience from everyday life that things do not seem to move spontaneously from a lower to a higher energy state (a book does not jump from a lower shelf (lower potential energy) to a higher one (higher potential energy) but will fall to a lower shelf if the shelf it is on breaks. Endothermic processes such as the melting of ice at room temperature and water evaporating are relatively common, however, and this suggests that it is not just a consideration of the energy changes involved that must be used to predict whether a reaction occurs spontaneously. The examples of endothermic processes mentioned here all have one thing in common: they all involve an increase in **disorder**. In a sodium chloride solution, the Na^+ and Cl^- ions are dispersed throughout the solution and are moving around, which is a much more disordered, or random, arrangement than a separate crystal of sodium chloride and a beaker of pure water. Similarly, liquid water is much more disordered than a solid lump of ice, as in the liquid form all the molecules are moving around each other randomly. To understand why these processes occur we need to introduce a new term called **entropy (S)**.

Entropy is a measure of how the available energy is distributed among the particles.

When a system becomes more disordered, the energy in it can be distributed in more ways among the available particles and the entropy of the system is higher.

Imagine 100 people sitting on chairs in a hall – there is only a limited number of ways in which they can move but still remain seated. However, if you have the same 100 people running around in the hall there is an absolutely enormous number of different ways in which they can move.

The first situation can be likened to a solid and the second to a gas. In a gas, all the particles are moving at different speeds in different directions, and also rotating and vibrating, and there is a huge number of ways (high entropy) in which the energy could be distributed among all the different particles still giving the same total energy. In a solid, the particles are more constrained and there are fewer ways in which the energy could be distributed among the particles (lower entropy).

Entropy is given the symbol S . The units of entropy are $\text{J K}^{-1} \text{mol}^{-1}$. S^\ominus is called **standard entropy**. It is possible to work out values for standard entropies for substances – for example, the standard entropy of $\text{H}_2(\text{g})$ is $131 \text{ J K}^{-1} \text{mol}^{-1}$, and the standard entropy of NaCl(s) is $72.4 \text{ J K}^{-1} \text{mol}^{-1}$.

Learning objectives

- Understand what is meant by entropy
- Predict the sign of the entropy change for a given reaction
- Work out entropy changes from standard entropy values
- Calculate values of ΔG for a reaction
- Work out whether or not a reaction is spontaneous from the sign of ΔG
- Predict how the spontaneity of a reaction varies with temperature

Extension

A better (more correct) way of saying this is that entropy is a measure of the ways in which the available energy could be distributed among the available energy states. All molecular motion (translational, vibrational, rotational) is quantised – entropy relates to the probability of distributing the energy across the energy microstates that are available.

Joules and not kilojoules.

Actual values of entropy can be calculated from experimental data – as opposed to enthalpy, for which only enthalpy changes can be measured.

The Austrian physicist Ludwig Boltzmann (1844–1906) developed a statistical approach to entropy. His famous equation, $S = k \log W$, is inscribed on his gravestone – W represents the possible energy states over which the energy can be distributed and k is the Boltzmann constant.

An entropy change is represented by the symbol ΔS^\ominus .

A positive value for ΔS^\ominus indicates an increase in entropy – the energy is more spread out (can be distributed over a larger number of possible energy states). This corresponds to an increase in disorder.

For example, ΔS^\ominus for the process $\text{H}_2\text{O}(\text{l}) \rightarrow \text{H}_2\text{O}(\text{g})$ is $+119 \text{ J K}^{-1} \text{ mol}^{-1}$. The disorder of the system has increased. The particles in a gas have complete freedom of movement in three dimensions and, therefore, the energy can be distributed in more ways between the particles (higher entropy). The movement of the particles in a liquid is more constrained and so there are not as many ways to distribute the energy among the particles (lower entropy).

A negative value for ΔS^\ominus indicates a decrease in entropy – a decrease in the number of ways the available energy can be distributed among the particles. This corresponds to a decrease in disorder.

For example, ΔS^\ominus for the process $\text{NH}_3(\text{g}) + \text{HCl}(\text{g}) \rightarrow \text{NH}_4\text{Cl}(\text{s})$ is $-285 \text{ J K}^{-1} \text{ mol}^{-1}$. Two moles of gas being converted into a solid results in a decrease in disorder. The particles in a solid have less freedom of movement, and so there are fewer ways of distributing the energy among the particles and, therefore, the solid has lower entropy than the gas.

How to predict the sign of an entropy change

Gases have higher entropy than liquids, which have higher entropy than solids (Figure 5.28).

Table 5.9 shows the values of standard entropies for elements across period 2 in the periodic table. Lithium to carbon are all solid elements and have low entropy values at 298 K, but nitrogen to neon are all gases and have much higher entropy values.

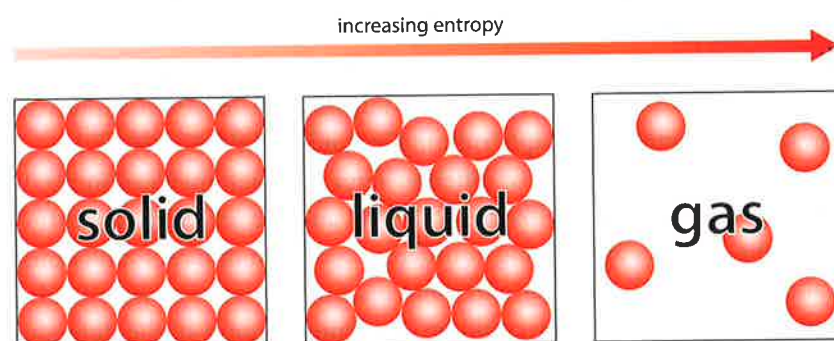


Figure 5.28 In a solid the particles vibrate about mean positions; in a liquid the particles move around each other; in a gas the particles move at high speeds in all directions.

Element	Li	Be	B	C	N ₂	O ₂	F ₂	Ne
State	solid	solid	solid	solid	gas	gas	gas	gas
$S^\ominus / \text{J K}^{-1} \text{ mol}^{-1}$	29	10	6	6	192	205	203	146

Table 5.9 Standard entropies for elements across period 2.

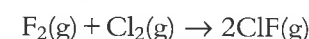
Reaction	Entropy	ΔS^\ominus	Explanation
$\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightarrow 2\text{NH}_3(\text{g})$	decrease	–	Four moles of gas on the left-hand side are converted to two moles of gas on the right-hand side; a decrease in the number of moles of gas is a decrease in disorder; therefore the energy can be distributed in fewer ways in the products (energy is less spread out).
$\text{CaCO}_3(\text{s}) \rightarrow \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$	increase	+	One mole of solid becomes one mole of solid and one mole of gas; the number of moles of gas increases.
$\text{CH}_4(\text{g}) + 2\text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l})$	decrease	–	Three moles of gas are converted to one mole of gas.
$\text{C}_2\text{H}_4(\text{g}) + \text{H}_2(\text{g}) \rightarrow \text{C}_2\text{H}_6(\text{g})$	decrease	–	Two moles of gas are converted to one mole of gas.

Table 5.10 Entropy changes for some reactions.

To predict the sign of the entropy change in a reaction, the easiest way to think about it is in terms of **disorder**. If there is an increase in disorder the energy is more spread out at the end than at the beginning, and so the entropy is higher at the end. Because gases have significantly higher entropy than solids and liquids, the most important factor in determining whether a chemical reaction involves an increase or decrease in entropy is whether there is an increase or decrease in the number of moles of gas (Table 5.10).

- An **increase** in number of moles of **gas**: ΔS^\ominus +ve (entropy **increases**).
- A **decrease** in number of moles of **gas**: ΔS^\ominus –ve (entropy **decreases**).

If the number of moles of gas is the same on both sides of an equation, for example:



the prediction could be made that the entropy change would be approximately zero.

Calculating an entropy change for a reaction

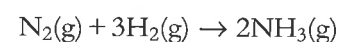
Values of ΔS^\ominus can be worked out from standard entropies, S^\ominus :

entropy change = total entropy of products – total entropy of reactants

$$\Delta S^\ominus = \sum S^\ominus_{\text{products}} - \sum S^\ominus_{\text{reactants}}$$

Example

Calculate the standard entropy change for this reaction:



$$\Delta S^\ominus = (2 \times 193) - [192 + (3 \times 131)]$$

$$\Delta S^\ominus = -199 \text{ J K}^{-1} \text{ mol}^{-1}$$

The decrease in entropy corresponds to the prediction made above based on the number of moles of gas (four moles of gas go to two moles of gas).

The entropy of a system is also changed by other factors as follows:

- entropy increases as the temperature increases
- entropy increases as the pressure decreases
- the entropy of a mixture is higher than the entropy of pure substances.

	$S^\ominus / \text{J K}^{-1} \text{ mol}^{-1}$
N ₂	192
H ₂	131
NH ₃	193

The standard entropy values are multiplied by the appropriate coefficients in the equation.

? Test yourself

25 Work out whether each of the following processes involves an increase or a decrease in entropy:

- a $\text{C}_2\text{H}_2(\text{g}) + 2\text{H}_2(\text{g}) \rightarrow \text{C}_2\text{H}_6(\text{g})$
- b $2\text{C}_2\text{H}_6(\text{g}) + 7\text{O}_2(\text{g}) \rightarrow 4\text{CO}_2(\text{g}) + 6\text{H}_2\text{O}(\text{l})$
- c $\text{COCl}_2(\text{g}) \rightarrow \text{CO}(\text{g}) + \text{Cl}_2(\text{g})$
- d $2\text{C}(\text{s}) + \text{O}_2(\text{g}) \rightarrow 2\text{CO}(\text{g})$

26 Use the entropy values in the table to calculate the standard entropy change in each of the following reactions:

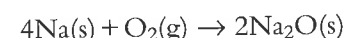
- a $\text{CH}_4(\text{g}) + 2\text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l})$
- b $2\text{Cu}(\text{NO}_3)_2(\text{s}) \rightarrow 2\text{CuO}(\text{s}) + 4\text{NO}_2(\text{g}) + \text{O}_2(\text{g})$
- c $4\text{BCl}_3(\text{l}) + 3\text{SF}_4(\text{g}) \rightarrow 4\text{BF}_3(\text{g}) + 3\text{SCl}_2(\text{g}) + 3\text{Cl}_2(\text{g})$

Substance	$S^\ominus / \text{JK}^{-1} \text{mol}^{-1}$
$\text{CH}_4(\text{g})$	186
$\text{O}_2(\text{g})$	103
$\text{CO}_2(\text{g})$	214
$\text{H}_2\text{O}(\text{l})$	70
$\text{Cu}(\text{NO}_3)_2(\text{s})$	193
$\text{CuO}(\text{s})$	43
$\text{NO}_2(\text{g})$	240
$\text{BCl}_3(\text{l})$	206
$\text{SF}_4(\text{g})$	292
$\text{BF}_3(\text{g})$	254
$\text{SCl}_2(\text{g})$	282
$\text{Cl}_2(\text{g})$	83

Predicting whether a reaction will be spontaneous

Spontaneous reaction: one that occurs without any outside influence.

If sodium and oxygen are put together in an isolated container at 25°C , they will react spontaneously to produce sodium oxide:



This reaction will occur by itself – nothing has to be done to make the reaction occur. This is an example of a spontaneous reaction.

If methane and oxygen are put into an isolated container at 25°C , they will react together spontaneously to form carbon dioxide and water. This reaction, although it is spontaneous, is not a very fast reaction at room temperature (unless a spark is supplied) and would have to be left for a very long time before a significant amount of carbon dioxide and water could be detected. Similarly, the conversion of diamond to graphite at room temperature is a spontaneous process, but luckily occurs immeasurably slowly!

Whether a reaction will be spontaneous or not under a certain set of conditions can be deduced by looking at how the **entropy of the Universe** changes as the reaction occurs. The second law of thermodynamics states that for a process to occur spontaneously it must result in an increase in the entropy of the Universe.

A spontaneous reaction does not have to happen quickly.

The first law of thermodynamics is basically a statement of the principle of conservation of energy: the energy of the Universe remains constant.

This can be understood in terms of the spreading out of energy. A system will tend to move spontaneously from where the energy is concentrated (low entropy) to where it is more spread out (higher entropy). Where the energy is concentrated (low entropy) it is useful and can bring about change, but where it is spread out (higher entropy) it is less useful and cannot bring about change.

The Universe may be regarded as being composed of the system (the chemical reaction) and the surroundings. The entropy change of the Universe is given by:

$$\Delta S_{\text{Universe}} = \Delta S_{\text{surroundings}} + \Delta S_{\text{system}}$$

If, during a reaction, the value of $\Delta S_{\text{Universe}}$ is positive, the entropy of the Universe increases and the reaction occurs spontaneously.

When heat is given out in a chemical reaction, the surroundings get hotter and the particles move around more – therefore the entropy of the surroundings increases. So the entropy change of the surroundings can be related to the enthalpy change of the system. A new equation can be derived from the equation of the entropy change of the Universe given above. The new equation is:

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

ΔG is called the change in **Gibbs free energy**, or just the **free energy change**. Under standard conditions, we have ΔG^\ominus , which is the **standard free energy change**.

ΔG is related to the entropy change of the Universe and, from the condition that for a reaction to occur spontaneously the entropy of the Universe must increase, we can derive the condition:

for a reaction to be spontaneous, ΔG for the reaction must be negative.

Calculating ΔG^\ominus

The standard free energy change for a reaction can be calculated using the equation:

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

The units of ΔG are usually kJ mol^{-1} .

T must be in K.

The subscripts are now omitted, because both ΔH and ΔS refer to the system, i.e. the chemical reaction.

Extension

The entropy change of the surroundings depends on the temperature and is given by:

$$\Delta S_{\text{surroundings}} = \frac{-\Delta H_{\text{system}}}{T}$$

$[-\Delta H$ because an exothermic reaction (ΔH negative) causes the entropy of the surroundings to increase ($\Delta S_{\text{surroundings}}$ positive)]

$$\Delta S_{\text{Universe}} = \Delta S_{\text{surroundings}} + \Delta S_{\text{system}}$$

$$\Delta S_{\text{Universe}} = \frac{-\Delta H_{\text{system}}}{T} + \Delta S_{\text{system}}$$

$$-T\Delta S_{\text{Universe}} = \Delta H_{\text{system}} - T\Delta S_{\text{system}}$$

$-T\Delta S_{\text{Universe}}$ is given the symbol ΔG .

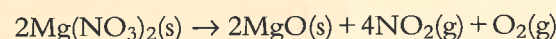
Exam tip

You must remember to divide the entropy value by 1000 – this is a very common mistake.

Note: temperature must be in kelvin.

Worked example

5.15 Consider the decomposition of $\text{Mg}(\text{NO}_3)_2(\text{s})$:



- a Use the following data to work out ΔG^\ominus and hence whether or not the reaction will be spontaneous at 25°C .
- b As the temperature is increased from absolute zero, work out the temperature (in $^\circ\text{C}$) at which the reaction first becomes spontaneous.

	$\text{Mg}(\text{NO}_3)_2(\text{s})$	$\text{MgO}(\text{s})$	$\text{NO}_2(\text{g})$	$\text{O}_2(\text{g})$
$\Delta H_f^\ominus/\text{kJ mol}^{-1}$	-790	-602	34	0
$S^\ominus/\text{J K}^{-1}\text{mol}^{-1}$	164	27	240	205

- a To calculate the enthalpy change, we have been given ΔH_f^\ominus and so can use:

$$\Delta H = \sum \Delta H_f^\ominus(\text{products}) - \sum \Delta H_f^\ominus(\text{reactants})$$

$$\Delta H^\ominus = [(2 \times -602) + (4 \times 34) + 0] - [(2 \times -790)] = 512 \text{ kJ mol}^{-1}$$

To calculate the entropy change we use:

$$\Delta S = \sum S^\ominus(\text{products}) - \sum S^\ominus(\text{reactants})$$

$$\Delta S^\ominus = [(2 \times 27) + (4 \times 240) + 205] - [(2 \times 164)] = 891 \text{ J K}^{-1} \text{ mol}^{-1}$$

At 298 K:

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

$$\Delta G^\ominus = 512 - 298 \times \frac{891}{1000} = 246 \text{ kJ mol}^{-1}$$

At 298 K the reaction is **not** spontaneous because ΔG is positive.

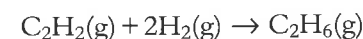
ΔS^\ominus is divided by 1000 to convert to kJ.

- b Because ΔS is positive, as the temperature is increased $T\Delta S$ will become larger until it is eventually bigger than ΔH and the reaction will become spontaneous.

We can estimate the temperature at which this reaction is going to become spontaneous. As the temperature is increased, ΔG will become less and less positive, until it becomes zero, and then it will be negative. So if we work out the temperature at which ΔG becomes zero, the reaction will be spontaneous at any temperature above that.

Example

We can calculate ΔG^\ominus at 298 K for:



given the following information:

$$\Delta H^\ominus = -313 \text{ kJ K}^{-1} \text{ mol}^{-1} \quad \Delta S^\ominus = -233 \text{ J K}^{-1} \text{ mol}^{-1}$$

ΔH^\ominus is in kJ but ΔS^\ominus is in J, and in order to combine them they must be converted so they are both in kJ or J. As ΔG^\ominus is usually quoted in kJ, ΔS^\ominus will be converted to kJ. Therefore:

$$\Delta S^\ominus = \frac{-233}{1000} = -0.233 \text{ kJ K}^{-1} \text{ mol}^{-1}$$

$$\Delta G^\ominus = -313 - 298 \times (-0.233) = -244 \text{ kJ mol}^{-1}$$

Because the value of ΔG is negative, the reaction is spontaneous.

Using

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

$$0 = 512 - T \times \frac{891}{1000}$$

Rearranging the equation gives:

$$T = 575 \text{ K}$$

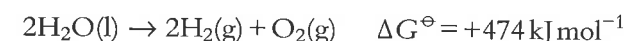
This means that this reaction is likely to become spontaneous above 575 K, that is 302°C .

This calculation is only approximate because the values of ΔH and ΔS change with temperature, and we have used ΔH^\ominus and ΔS^\ominus , i.e. the values at 298 K.

Non-spontaneous reactions

If a reaction is non-spontaneous it does not mean that it can never happen – it just means that it will not happen without external influence. For instance, in the above worked example we can increase the temperature to make the reaction spontaneous.

Consider the following reaction:



This reaction is not spontaneous at 25°C , but it can be made to happen at this temperature by the continuous passage of an electric current (electrolysis).

The effect of changing temperature on the spontaneity of a reaction

We will use the equation $\Delta G = \Delta H - T\Delta S$ to explain the effect of temperature on the value of ΔG and hence on the spontaneity of a reaction.

Consider a reaction for which ΔH is positive and ΔS is positive. If $T\Delta S$ is smaller than ΔH , ΔG will be positive and the reaction will **not** be spontaneous. So a reaction like this is non-spontaneous at low temperatures (when $T\Delta S$ is smaller than ΔH). As the temperature is raised, $T\Delta S$ becomes larger and, because this is being subtracted from ΔH , ΔG becomes less positive/more negative – the reaction becomes more spontaneous as the temperature is raised. Eventually, when $T\Delta S$ becomes greater than ΔH , ΔG will be negative and the reaction will be spontaneous.

Now consider a reaction for which ΔH is positive and ΔS is negative. Because ΔS is negative $-T\Delta S$ in the equation is positive. ΔH is also positive, so overall ΔG is positive and the reaction is not spontaneous. Because both ΔH and $-T\Delta S$ are positive, this reaction is non-spontaneous at all temperatures: ΔG can never be negative.

Both reactions considered so far have been endothermic and it can be seen that an endothermic reaction can only occur spontaneously if it involves an increase in entropy (and the temperature is sufficiently high).

ΔH	ΔS	$-T\Delta S$	ΔG	Spontaneous?
negative	positive	negative	negative	at all temperatures
positive	positive	negative	becomes more negative as temperature increases	becomes more spontaneous as temperature increases
negative	negative	positive	becomes less negative as temperature increases	becomes less spontaneous as temperature increases
positive	negative	positive	positive	never

Table 5.11 Determining if a reaction will be spontaneous.

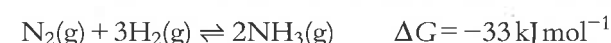
An exothermic reaction (ΔH negative) will always be spontaneous at some temperature or other. If the reaction involves an increase in entropy (ΔS positive) then $-T\Delta S$ will be negative. Because ΔH is also negative, ΔG will always be negative and the reaction will always be spontaneous.

If the reaction involves a decrease in entropy (ΔS negative), the reaction will be spontaneous at low temperatures, when ΔH is more negative than $-T\Delta S$ is positive. It will, however, become less spontaneous as the temperature increases (because $-T\Delta S$ is positive and becomes more positive as the temperature increases). At higher temperatures, $-T\Delta S$ will be more positive than ΔH is negative, and therefore ΔG will be positive and the reaction will be non-spontaneous.

Table 5.11 gives an overview of this discussion.

Gibbs free energy and equilibrium

Consider the Haber process for the production of ammonia:



According to the discussion above, this reaction will proceed from left to right – nitrogen and hydrogen will spontaneously become ammonia – but the reverse reaction ($\Delta G = +33 \text{ kJ mol}^{-1}$) will not occur spontaneously. However, equilibrium can be reached in either direction – if we start with nitrogen and hydrogen, the system will form an equilibrium mixture in which nitrogen, hydrogen and ammonia are present; if we start with pure ammonia, some will spontaneously react to form nitrogen and hydrogen so that all three are present in the equilibrium mixture. This does not, however, violate the second law of thermodynamics because the value of ΔG that was calculated was for complete conversion of one mole of nitrogen and three moles of hydrogen to two moles of ammonia. The equilibrium mixture always has a lower Gibbs free energy (higher entropy) than either the pure reactants or the pure products (a mixture has higher entropy than pure substances) therefore the conversion of either reactants or products into the equilibrium mixture results in a process in which ΔG is negative (Figure 5.29).

The overall Gibbs free energy of a system (note that we are looking at the Gibbs free energy (G) here and not the **change** in Gibbs free energy (ΔG)) depends on how much of each substance is present, and the equilibrium mixture represents the composition that gives the minimum value of the Gibbs free energy (maximum value of entropy). When the system is at equilibrium, the Gibbs free energy of the amount of reactants

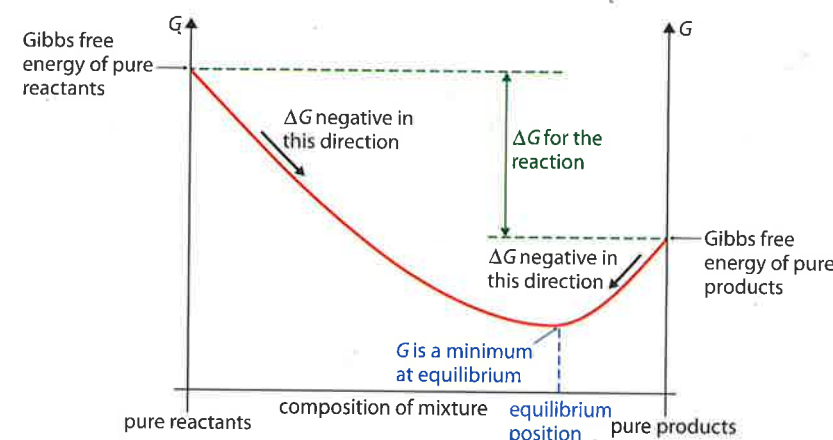


Figure 5.29 Variation in the Gibbs free energy for a reaction for which ΔG is negative overall.

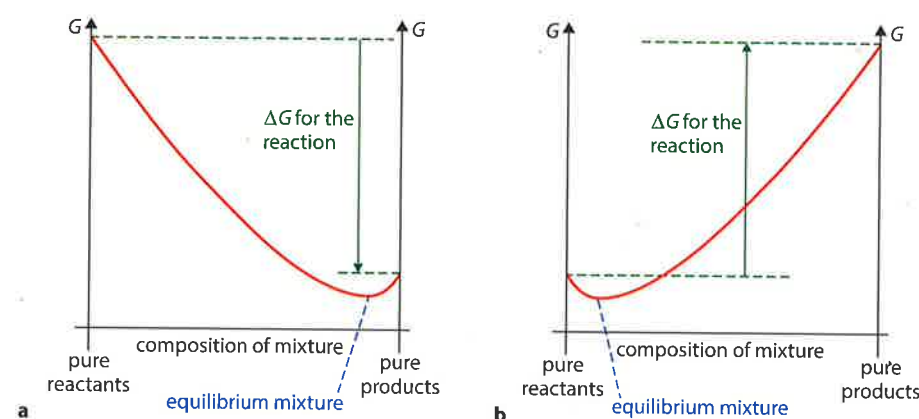


Figure 5.30 **a** ΔG is negative and the position of equilibrium lies closer to the products; **b** ΔG is positive and the position of equilibrium lies closer to the reactants.

present is the same as that of however much of the products is present, and so ΔG is zero and there is no tendency to spontaneously move in either direction away from equilibrium. Any shift away from the equilibrium position results in an increase in G and therefore a process for which ΔG is positive – i.e. non-spontaneous.

The value and sign of ΔG give us information about the position of equilibrium. If ΔG is negative then the position of equilibrium will lie closer to the products than the reactants (Figure 5.30a). The more negative the value of ΔG , the closer the position of equilibrium lies towards the products. If ΔG is numerically very large and negative then the position of equilibrium lies very close to pure products, which corresponds to the idea discussed above – a reaction for which ΔG is negative proceeds spontaneously from reactants to products. If ΔG is positive then the position of equilibrium lies more towards the reactants (Figure 5.30b) – the more positive the value, the closer the position of equilibrium lies towards pure reactants.

A value of ΔG of -30 kJ mol^{-1} (or more negative) indicates that a reaction essentially goes to completion at around room temperature; one of $+30 \text{ kJ mol}^{-1}$ (or more positive) indicates a reaction that does not really proceed towards products at all.

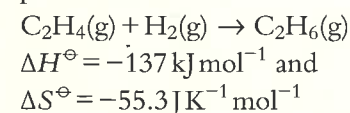
Nature of science

The word **spontaneous** has a specific meaning in science which is not the same as how it is used in everyday life. Words sometimes have a different meaning in science from the same word in everyday life. Scientists must agree on the meaning of these words and many professional bodies, such as IUPAC, provide the final word on the use of scientific terms. The meaning of terms can also change – for instance, ‘standard conditions’ used to be defined in terms of atmospheric pressure but has now changed to 100 kPa. The whole scientific community must agree to such changes because scientists must understand what other scientists mean – everybody cannot use their own definition!

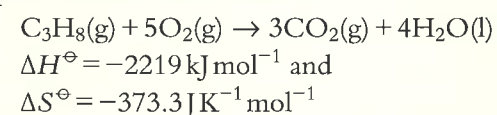
Science involves a constantly changing body of knowledge. Our understanding of entropy has evolved since the term was first used by Rudolf Clausius in a paper in 1865 and now we discuss entropy from a probability/statistical point of view.

? Test yourself

- 27 Given the data below, calculate ΔG^\ominus for the following reaction at 298 K and state whether it is spontaneous or not:



- 28 Given the data below, calculate ΔG^\ominus for the following reaction and state whether it is spontaneous or not at 298 K:



- 29 Consider the decomposition of $\text{Pb}(\text{NO}_3)_2(\text{s})$:
- $$2\text{Pb}(\text{NO}_3)_2(\text{s}) \rightarrow 2\text{PbO}(\text{s}) + 4\text{NO}_2(\text{g}) + \text{O}_2(\text{g})$$
- $$\Delta H^\ominus = +598 \text{ kJ mol}^{-1} \quad \Delta G^\ominus = +333 \text{ kJ mol}^{-1}$$

- a Work out the value for ΔS^\ominus at 298 K.
b Assuming that ΔH and ΔS do not change with temperature, calculate the temperature, in $^\circ\text{C}$, above which this reaction will become spontaneous.

- 30 For each of the following reactions, predict whether it becomes more or less spontaneous as temperature increases:

- a $\text{N}_2\text{O}_4(\text{g}) \rightarrow 2\text{NO}_2(\text{g})$
b $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightarrow 2\text{NH}_3(\text{g})$
c $2\text{KNO}_3(\text{s}) \rightarrow 2\text{KNO}_2(\text{s}) + \text{O}_2(\text{g})$
d $2\text{AgNO}_3(\text{s}) \rightarrow 2\text{Ag}(\text{s}) + 2\text{NO}_2(\text{g}) + \text{O}_2(\text{g})$

- 31 Consider the equilibrium
 $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$ $\Delta G^\ominus = 5 \text{ kJ mol}^{-1}$
Does the position of equilibrium lie more towards the reactants (N_2O_4) or the products (NO_2)?

Exam-style questions

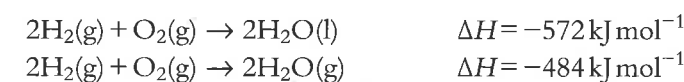
- 1 The specific heat capacity of a liquid is $4.00 \text{ J g}^{-1} \text{ K}^{-1}$; 2000 J of heat energy are supplied to 100.0 g of the liquid. By how much would the temperature of the liquid increase?

A 278 K B 5 K C 80 K D 20 K

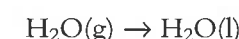
- 2 Which of the following is correct about endothermic reactions?

- A Heat energy is taken in and the temperature increases.
B Heat energy is given out and the temperature increases.
C Heat energy is taken in and the temperature decreases.
D Heat energy is given out and the temperature decreases.

- 3 Use the following information:

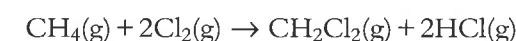


to calculate the enthalpy change for the process:



- A -88 kJ mol^{-1} C $+88 \text{ kJ mol}^{-1}$
B -44 kJ mol^{-1} D $+44 \text{ kJ mol}^{-1}$

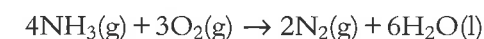
- 4 Use the bond enthalpies in the table to calculate the enthalpy change (in kJ mol^{-1}) for the reaction:



Bond	Bond enthalpy / kJ mol^{-1}
C-H	410
Cl-Cl	240
C-Cl	340
H-Cl	430

- A -720 B +240 C +620 D -240

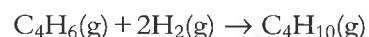
- 5 Use the enthalpy change of formation values in the table to calculate the enthalpy change for the following reaction:



Substance	$\Delta H_f^\ominus / \text{kJ mol}^{-1}$
$\text{NH}_3(\text{g})$	-46
$\text{H}_2\text{O}(\text{l})$	-286

- A -240 kJ mol^{-1} C $-1532 \text{ kJ mol}^{-1}$
B -332 kJ mol^{-1} D $-1900 \text{ kJ mol}^{-1}$

6 Use the enthalpy changes given in the table to calculate the enthalpy change (in kJ mol^{-1}) for the reaction:



Substance	$\Delta H_c^\ominus / \text{kJ mol}^{-1}$
$\text{C}_4\text{H}_6(\text{g}) + 5\frac{1}{2}\text{O}_2(\text{g}) \rightarrow 4\text{CO}_2(\text{g}) + 3\text{H}_2\text{O}(\text{l})$	-2595
$\text{C}_4\text{H}_{10}(\text{g}) + 6\frac{1}{2}\text{O}_2(\text{g}) \rightarrow 4\text{CO}_2(\text{g}) + 5\text{H}_2\text{O}(\text{l})$	-2875
$\text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{l})$	-285

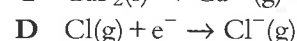
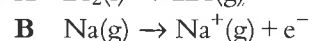
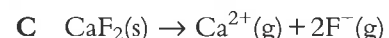
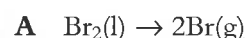
A 290

B -290

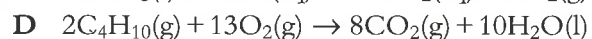
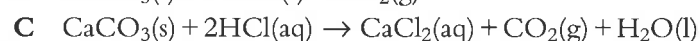
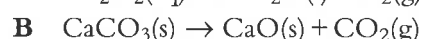
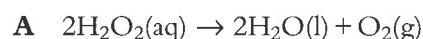
~~C -5~~

D 5

HL 7 Which of the following processes is exothermic?



HL 8 Which of the following reactions has a ΔS^\ominus value that is negative?



HL 9 Which of the following will have the largest value of lattice enthalpy?

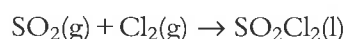
A NaCl

B MgO

C CaO

D MgBr_2

HL 10 Using the data given below, calculate the value of ΔG^\ominus for the following reaction at 298 K:



$$\Delta H^\ominus = -97.3 \text{ kJ mol}^{-1} \text{ and } \Delta S^\ominus = -254.4 \text{ J K}^{-1} \text{ mol}^{-1}$$

A $-21.5 \text{ kJ mol}^{-1}$

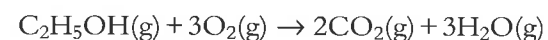
C $-173.1 \text{ kJ mol}^{-1}$

B $75714 \text{ kJ mol}^{-1}$

D $-97.0 \text{ kJ mol}^{-1}$

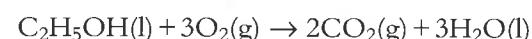
11 a Explain what you understand by the term 'average bond enthalpy'. [2]

b Use the average bond enthalpies given in the table to calculate the enthalpy change for the combustion of ethanol vapour, according to the equation: [3]



Bond	C-H	C-C	C-O	O-H	O=O	C=O
Bond enthalpy / kJ mol^{-1}	412	348	360	463	496	743

c Explain why bond enthalpies could not be used to work out the enthalpy change for the reaction: [2]



d Consider the reaction: [2]

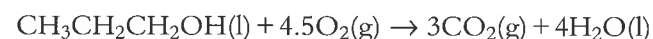


Draw a potential energy profile for this reaction and explain whether NO_2 or N_2O_4 is more stable. [3]

12 a Define 'standard enthalpy change of formation'. [2]

b Write a chemical equation for the standard enthalpy change of formation of propan-1-ol. [2]

c The equation for the combustion of propan-1-ol is:



Use the enthalpy change of formation values in the table to calculate the enthalpy change for this reaction.

Substance	$\Delta H_f^\ominus / \text{kJ mol}^{-1}$
$\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}(\text{l})$	-316
$\text{CO}_2(\text{g})$	-394
$\text{H}_2\text{O}(\text{l})$	-286

HL d Use the standard entropy values in the table below to calculate the entropy change for the complete combustion of propan-1-ol and justify the sign of the entropy change. [3]

Substance	$S^\ominus / \text{J K}^{-1} \text{ mol}^{-1}$
$\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}(\text{l})$	196.6
$\text{CO}_2(\text{g})$	214
$\text{H}_2\text{O}(\text{l})$	69.9
$\text{O}_2(\text{g})$	205

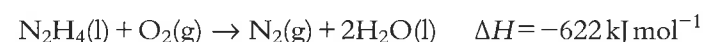
HL e Calculate the standard free energy change, ΔG^\ominus , for the complete combustion of propan-1-ol and explain whether the reaction will be spontaneous at 25 °C. [3]

13 Hydrazine, N_2H_4 , has been used as a rocket fuel.

- Draw a Lewis structure for hydrazine.
- Write a chemical equation to represent the enthalpy change of formation of gaseous hydrazine.
- Use bond enthalpies from the table to calculate the enthalpy change of formation of gaseous hydrazine.

Bond	$\text{N}\equiv\text{N}$	$\text{N}=\text{N}$	$\text{N}-\text{N}$	$\text{H}-\text{H}$	$\text{N}-\text{H}$
Bond enthalpy / kJ mol^{-1}	944	409	163	436	388

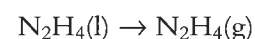
d The equation for the combustion of liquid hydrazine is:



The enthalpy change of formation of $\text{H}_2\text{O}(\text{l})$ is -286 kJ mol^{-1} .

Use these data to calculate the enthalpy change of formation of liquid hydrazine.

e Calculate the enthalpy change for the process:



HL 14 a Define 'lattice enthalpy'.

b Write chemical equations to represent the following enthalpy changes:

- the lattice enthalpy of potassium chloride
- the first electron affinity of chlorine
- the first ionisation energy of potassium

c Construct a Born-Haber cycle for the formation of potassium chloride and use it and the values in the table to calculate the lattice enthalpy of potassium chloride.

Process	Enthalpy change / kJ mol^{-1}
$\Delta H_{\text{at}} [\text{K}(\text{s})]$	90
$\Delta H_{\text{at}} [\text{Cl}_2(\text{g})]$	121
first ionisation energy (K)	418
first electron affinity (Cl)	-364
$\Delta H_f [\text{KCl}(\text{s})]$	-436

d Explain why the value of the lattice enthalpy for calcium chloride is substantially greater than that for potassium chloride.

e The enthalpy changes of hydration of potassium ions and chloride ions are given in the table. Use these values and other value(s) from part c to calculate the enthalpy change of solution of potassium chloride.

Ion	Enthalpy change of hydration / kJ mol^{-1}
$\text{K}^+(\text{g})$	-340
$\text{Cl}^-(\text{g})$	-359

Summary

ENERGETICS

exothermic reaction — gives out heat to surroundings — Products have lower energy than reactants, so are more stable.

endothermic reaction — takes in heat from surroundings — Products have higher energy than reactants, so are less stable.

To ENTROPY on next page

To SPONTANEOUS REACTIONS on next page

enthalpy change, ΔH

standard enthalpy change:
enthalpy change for molar amounts of substance under standard conditions

standard conditions:
 $P = 100 \text{ kPa}$

indicated by the symbol \ominus

— negative for exothermic reaction
— positive for endothermic reaction

heat energy exchanged with surroundings at constant pressure

types of enthalpy change

tools for enthalpy calculations

$$q = mc\Delta T$$

specific heat capacity:
energy required to raise the temperature of 1 g of substance by 1 K

Hess's law:
the enthalpy change accompanying a reaction is independent of the pathway taken from reactants to products

To IONIC COMPOUNDS on next page

enthalpy change of combustion (ΔH_c):
heat given out when one mole of substance is completely burnt in oxygen

enthalpy change of reaction (ΔH_r):
heat given out or taken in when molar amounts of reactants react together

enthalpy change of formation (ΔH_f):
heat given out or taken in when one mole of substance is formed from its elements in their standard states

$\Delta H_r^\ominus = \sum \Delta H_f^\ominus(\text{products}) - \sum \Delta H_f^\ominus(\text{reactants})$
The **standard state** of an element is the pure substance at 100 kPa and a specified temperature.

For an element in its standard state:
 $\Delta H_f^\ominus = 0$

bond enthalpy:
heat taken in when one mole of covalent bonds, in a gaseous molecule, are broken

— bond breaking is endothermic
— bond making is exothermic

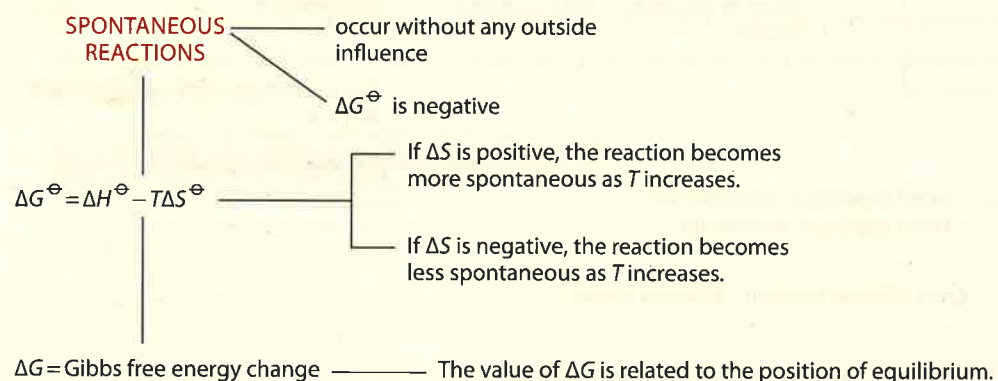
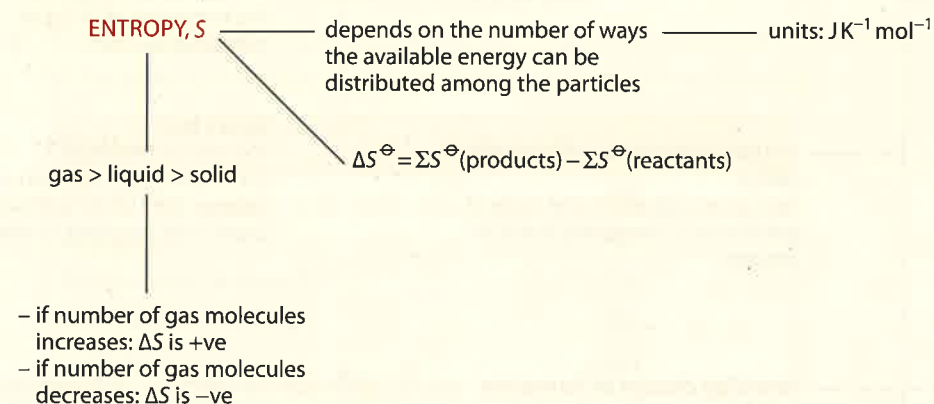
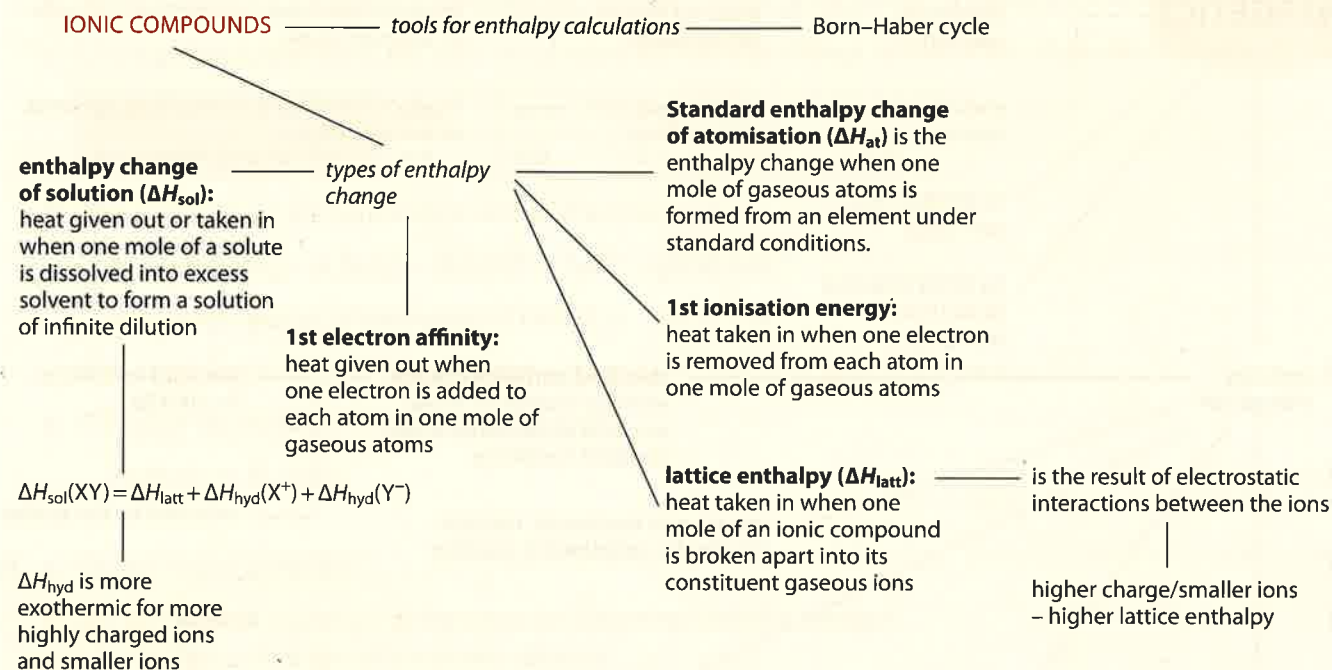
$$\Delta H_r = \sum(\text{bonds broken}) - \sum(\text{bonds made})$$

bond enthalpy values for a given type of bond are averaged over many compounds

O_2 has a higher bond enthalpy than O_3 and so absorbs shorter wavelength UV radiation

Summary – continued

HL



Chemical kinetics 6

6.1 Collision theory and rate of reaction

6.1.1 What is 'rate of reaction'?

When we consider the rate of a chemical reaction what we are looking at is how fast or slow the reaction is (Figures 6.1 and 6.2). This can be thought of in terms of how quickly the reactants are used up or how quickly the products are formed.

Rate of reaction is the speed at which reactants are used up or products are formed.

Experiments to measure the rate of reaction

Consider the reaction between calcium carbonate and hydrochloric acid:



The rate of this reaction can be measured in various ways, two of which will be considered for this experiment:

- 1 measurement of the rate at which CO_2 is produced
- 2 measurement of the rate at which the mass decreases.

Measurement of the rate at which CO_2 is produced

The apparatus is set up as shown in Figure 6.3 without the calcium carbonate. The bung in the conical flask (Erlenmeyer flask) is removed, the calcium carbonate added, the bung quickly replaced and the timer started. This experiment can be used to generate a graph of volume of carbon dioxide produced against time by noting the volume on the measuring cylinder every ten seconds and then plotting the data. Sample data for this experiment are shown in Table 6.1.

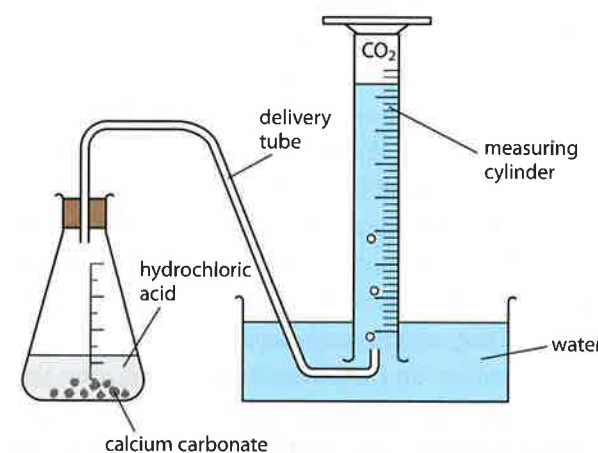


Figure 6.3 An experiment to measure rate of CO_2 production.

Learning objectives

- Understand what is meant by and define the rate of a chemical reaction
- Describe experimental methods for measuring the rates of various types of chemical reactions
- Analyse numerical and graphical data from rate experiments



Figure 6.1 Rusting is a very slow chemical reaction but one that costs economies billions of dollars each year.



Figure 6.2 An explosion is a very fast reaction – gases and a great deal of heat are generated very quickly.

Instead of a measuring cylinder, a gas burette or a gas syringe could be used.