05 Energetics and thermochemistry

Essential ideas

5.1	The enthalpy changes from chemical reactions can be calculated from their effect on the temperature of their surroundings.
5.2	In chemical transformations energy can neither be created nor destroyed (the first law of thermodynamics).
5.3	Energy is absorbed when bonds are broken and is released when bonds are formed.
15.1	The concept of the energy change in a single step reaction being equivalent to the summation of smaller steps can be applied to changes involving ionic compounds.
15.2	A reaction is spontaneous if the overall transformation leads to an increase in total entropy (system plus surroundings). The direction of spontaneous change always increases the total entropy of the universe at the expense of energy available to do useful work. This is known as the second law of thermodynamics.

The burning of a firework increases the disorder in the universe, as both energy and matter become dispersed. This is the natural direction of change.

All chemical reactions are accompanied by energy changes. Energy changes are vital. Our body's processes are dependent on the energy changes which occur during respiration, when glucose reacts with oxygen. Modern lifestyles are dependent on the transfer of energy that occurs when fuels burn. As we explore the source of these energy changes, we will deepen our understanding of why bonds are broken and formed during a chemical reaction, and why electron transfer can lead to the formation of stable ionic compounds. The questions of why things change will lead to the development of the concept of entropy. We will see that this concept allows us to give the same explanation for a variety of physical and chemical changes: the universe is becoming more disordered. This provides us with a signpost for the direction of all change. The distinction between the quantity and quality of energy will lead to the development of the concept of free energy, a useful accounting tool for chemists to predict the feasibility of any hypothetical reaction.

We will see how creative thinking, accurate calculations, and careful observations and measurement can work together to lead to a deeper understanding of the relationship between heat and chemical change.

James Prescott Joule (1818–89) was devoted to making accurate measurements of heat. The SI unit of energy is named after him.

5.1 Measuring energy changes

Understandings:

- Heat is a form of energy.
- Temperature is a measure of the average kinetic energy of the particles.
- Total energy is conserved in chemical reactions.
- Chemical reactions that involve transfer of heat between the system and the surroundings are described as endothermic or exothermic.
- The enthalpy change (ΔH) for chemical reactions is indicated in kJ mol^{-1}.
- ΔH values are usually expressed under standard conditions, known as $\Delta H^{\ominus}$, including standard states.

Guidance

Enthalpy changes of combustion ($\Delta H_c^{\ominus}$) and formation ($\Delta H_f^{\ominus}$) should be covered.

Applications and skills:

- Calculation of the heat change when the temperature of a pure substance is changed using $q = mc\Delta T$.

Guidance
The specific heat capacity of water is provided in the IB Data booklet in section 2.

- A calorimetry experiment for an enthalpy of reaction should be covered and the results evaluated.

Guidance
- *Consider reactions in aqueous solution and combustion reactions.*
- *Standard state refers to the normal, most pure stable state of a substance measured at 100 kPa.*
- *Temperature is not a part of the definition of standard state, but 298 K is commonly given as the temperature of interest.*
- *Students can assume the density and specific heat capacities of aqueous solutions are equal to those of water, but should be aware of this limitation.*
- *Heat losses to the environment and the heat capacity of the calorimeter in experiments should be considered, but the use of a bomb calorimeter is not required.*

The joule is the unit of energy and work. You do 1 J of work when you exert a force of 1 N over a distance of 1 m. 1 J of energy is expended every time the human heart beats.

Energy is conserved in chemical reactions.

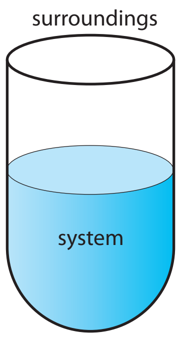


Figure 5.1 The system is the sample or reaction vessel of interest. The surroundings are the rest of the universe.

Enthalpy (*H*) is a measure of the amount of heat energy contained in a substance. It is stored in the chemical bonds and intermolecular forces as potential energy. When substances react, the difference in the enthalpy between the reactants and products (at constant pressure) results in a heat change which can be observed.

Energy and heat transfer energy

Energy is a measure of the ability to do **work**, that is to move an object against an opposing force. It comes in many forms and includes heat, light, sound, electricity, and chemical energy – the energy released or absorbed during chemical reactions. This chapter will focus on reactions which involve heat changes. Heat is a mode of energy transfer which occurs as a result of a temperature difference and produces an increase in disorder in how the particles behave. Heat increases the average kinetic energy of the molecules in a disordered fashion. This is to be contrasted with work, which is a more ordered process of transferring energy. When you do work on a beaker of water, by lifting it from a table, for example, you raise all the molecules above the table in the same way.

System and surroundings

Chemical and physical changes take place in many different environments such as test tubes, polystyrene cups, industrial plants and living cells. It is useful in these cases to distinguish between the **system** – the area of interest and the **surroundings** – in theory everything else in the universe (Figure 5.1). Most chemical reactions take place in an **open system** which can exchange energy and matter with the surroundings. A **closed system** can exchange energy but not matter with the surroundings. Although energy can be exchanged between a system and the surroundings, the total energy cannot change during the process; any energy lost by the system is gained by the surroundings and vice versa.

The heat content of a system is its enthalpy

Although, according to the conservation of energy, the total energy of the system and surroundings cannot change during a process, heat can be transferred between a system and its surroundings energy. The heat content of a system is called its **enthalpy**, a name which comes from the Greek word for 'heat inside'. A system acts like a reservoir of heat. When heat is added to a system from the surroundings its enthalpy increases. Changes in enthalpy are denoted by ΔH. ΔH is positive when heat is added to the system.

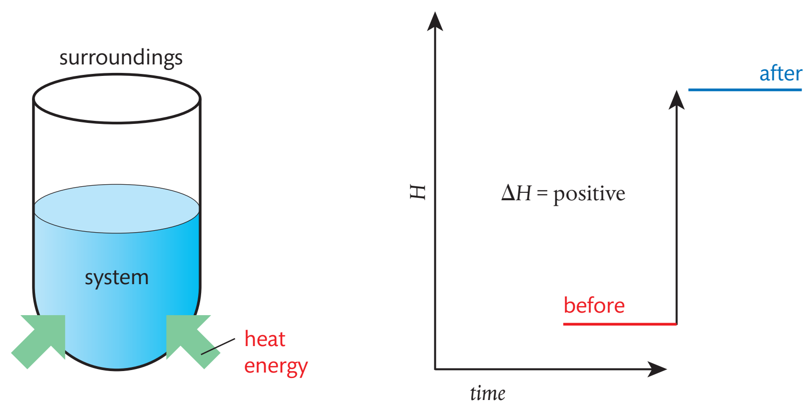


Figure 5.2 When heat is gained by the system from the surroundings, the enthalpy of the system increases and ΔH is positive.

When heat is released from the system to the surroundings the enthalpy of the system decreases and ΔH is negative.

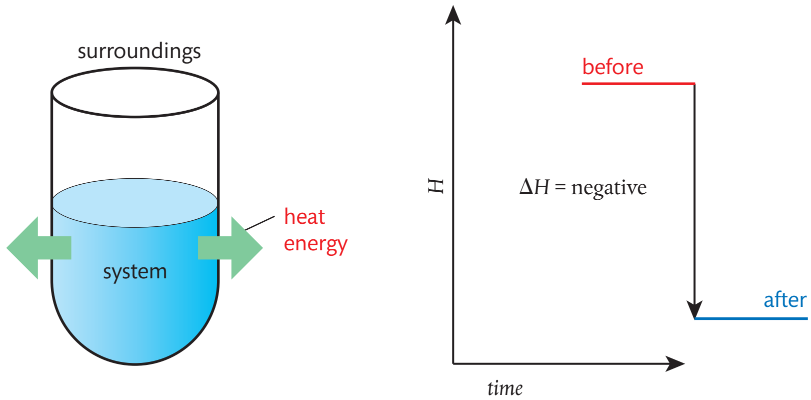


Figure 5.3 When heat is lost from the system to the surroundings the enthalpy of the system decreases and ΔH is negative.

TOK

How important are technical terms such as *enthalpy* in different areas of knowledge? Is their correct use a necessary or sufficient indicator of understanding?

Exothermic and endothermic reactions

The enthalpy (H) of the system is stored in the chemical bonds and intermolecular forces as potential energy. When substances react, the difference in the enthalpy between the reactants and products produces an enthalpy change which can be observed. Most chemical reactions, including most combustion and all neutralization reactions, are exothermic. They give out heat and result in a transfer of enthalpy from the chemicals to the surroundings and $\Delta H_{\text{reaction}}$ is negative.

A few reactions are **endothermic** as they result in an energy transfer from the surroundings to the system. In this case the products have more enthalpy than the reactants and ΔH is positive.

For exothermic reactions heat is given out by the system and ΔH is negative.

For endothermic reactions heat is absorbed by the system and ΔH is positive.

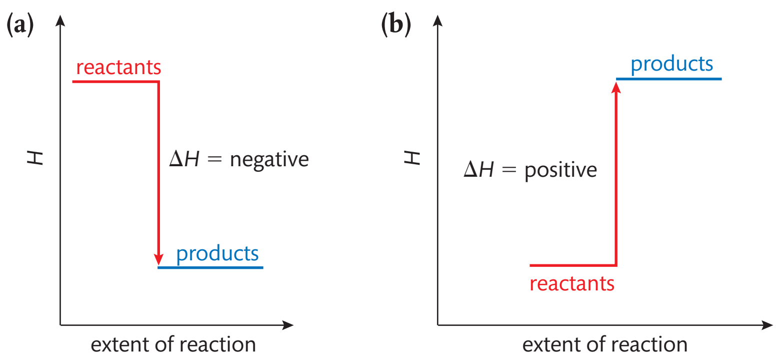


Figure 5.4 (a) An exothermic reaction. The enthalpy of the products is less than the enthalpy of the reactants. (b) An endothermic reaction. The enthalpy of the products is greater than the enthalpy of the reactants.

The standard conditions for enthalpy changes are:

- a pressure of 100 kPa
- concentrations of 1 mol dm^{-3} for all solutions
- all the substances in their standard states.

Standard enthalpy changes

As the enthalpy of a system also depends on the intermolecular forces of the reactants and products, the enthalpy change for a reaction depends on the conditions under which the reaction occurs. The **standard enthalpy changes**, $\Delta H^\ominus$, given in the literature are measured under the following conditions:

- a pressure of 100 kPa
- concentration of 1 mol dm^{-3} for all solutions
- all substances in their standard states.

Temperature is not part of the definition of standard state, but 298K is usually given as the specified temperature.

Thermochemical equations

The combustion of methane can be described by the thermochemical equation:

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l) \qquad \Delta H^\ominus = -890 \text{ kJ mol}^{-1}$$

This is a shorthand way of expressing information that *one mole* of methane gas reacts with *two moles* of oxygen gas to give *one mole* of gaseous carbon dioxide and *two moles* of liquid water and *releases* 890 kJ of heat energy.

The standard state of a substance is the pure form of the substance under standard conditions of 298 K (25 °C) and 1.00 × 10^5 Pa.

The thermochemical equation for photosynthesis can be represented as:

$$6CO_2(g) + 6H_2O(l) \rightarrow C_6H_{12}O_6(aq) + 6O_2(g) \qquad \Delta H^\ominus_{\text{reaction}} = +2802.5 \text{ kJ mol}^{-1}$$

which means that 2802.5 kJ of energy is absorbed when one mole of glucose is formed under standard conditions from gaseous carbon dioxide and liquid water.

It is important to give the state symbols in thermochemical equations as the enthalpy changes depend on the state of the reactants and the products.

Photosynthesis is an endothermic reaction which occurs in green leaves.

NATURE OF SCIENCE

Scientists share their knowledge using a precise language. In everyday language heat and work are both nouns and verbs, whereas in science they are nouns which describe energy transfer processes. Heat is often said to flow from high temperature to low temperature. This image originates from the incorrect outdated view that heat was a liquid, *calorique*, which was included in Lavoisier's list of chemical elements. Heat is now more correctly characterized as a process of energy transfer.

Enthalpy is a word rarely used in non-scientific discourse; it is an abstract entity with a precise mathematical definition. At this level we need not concern ourselves with absolute enthalpy values but only enthalpy changes which can be determined from temperature changes at constant pressure which can be measured.

The use of appropriate terminology is a key issue with scientific literacy and the public understanding of science and scientists need to take this into account when communicating with the public.

	Noms nouveaux.	*Noms anciens correſpondans.*
Subſtances ſimples qui appartiennent aux trois règnes & qu'on peut regarder comme les élémens des corps.	Lumière	Lumière.
	Calorique	Chaleur. Principe de la chaleur. Fluide igné. Feu. Matière du feu & de la chaleur.
	Oxygène	Air déphlogiſtiqué. Air empiréal. Air vital. Baſe de l'air vital.
	Azote	Gaz phlogiſtiqué. Moſete. Baſe de la moſete.
	Hydrogène	Gaz inflammable. Baſe du gaz inflammable.
Subſtances ſimples non métalliques oxidables & acidifiables.	Soufre	Soufre.
	Phoſphore	Phoſphore.
	Carbone	Charbon pur.
	Radical muriatique.	Inconnu.
	Radical fluorique	Inconnu.
	Radical boracique	Inconnu.
Subſtances ſimples métalliques oxidables & acidifiables.	Antimoine	Antimoine.
	Argent	Argent.
	Arſenic	Arſenic.
	Biſmuth	Biſmuth.
	Cobolt	Cobolt.
	Cuivre	Cuivre.
	Etain	Etain.
	Fer	Fer.
	Manganèſe	Manganèſe.
	Mercure	Mercure.
	Molybdène	Molybdène.
	Nickel	Nickel.
	Or	Or.
	Platine	Platine.
	Plomb	Plomb.
	Tungſtène	Tungſtene.
	Zinc	Zinc.
Subſtances ſimples ſalifiables terreuſes.	Chaux	Terre calcaire, chaux.
	Magnéſie	Magnéſie, baſe du ſel d'Epſom.
	Baryte	Barote, terre peſante.
	Alumine	Argile, terre de l'alun, baſe de l'alun.
	Silice	Terre ſiliceuſe, terre vitrifiable.

CHALLENGE YOURSELF

1 Most combustion reactions are exothermic but there are exceptions. Find an element in the second period which has a positive enthalpy of combustion.

Lavoisier's list of chemical elements includes heat (*calorique*) which was thought to be a liquid.

Temperature is a measure of average kinetic energy

The movement or kinetic energy of the particles of a substance depends on the temperature. If the temperature of a substance is decreased, the average kinetic energy of the particles also decreases. **Absolute zero** (–273 °C) is the lowest possible temperature attainable as this is the temperature at which all movement has stopped. The **Kelvin scale** emphasizes this relationship between average kinetic energy and temperature. The absolute temperature, measured in kelvin, is directly proportional to the average kinetic energy of its particles.

The SI unit of temperature is the kelvin (K), but the Celsius scale (°C), which has the same incremental scaling, is commonly used in most countries. The USA, however, continues to use the Fahrenheit (°F) scale for all non-scientific communication.

Heat changes can be calculated from temperature changes

If the same amount of heat is added to two different objects, the temperature change will not be the same, as the average kinetic energy of the particles will not increase by the same amount. The object with the smaller number of particles will experience the larger temperature increase, as the same energy is shared amongst a smaller collection of particles.

In general, the increase in temperature when an object is heated depends on:

- the mass of the object
- the heat added
- the nature of the substance.

The specific heat capacity is the property of a substance which gives the heat needed to increase the temperature of unit mass by 1 K. The specific heat capacity depends on the number of particles present in a unit mass sample, which in turn will depend on the mass of the individual particles.

heat change (q) = mass (m) × specific heat capacity (c) × temperature change (ΔT)

heat change = $m \times c \times \Delta T$

heat change (J) = m (g) × c (J g^{-1} K^{-1}) × ΔT (K)

When the heat is absorbed by water, c = 4.18 J g^{-1} K^{-1}

This value is given in the IB data booklet.

It takes considerably more heat energy to increase the temperature of a swimming pool by 5 °C than boil a kettle of water from room temperature. The swimming pool contains more water molecules and so has a larger heat capacity.

This relationship allows the heat change in a material to be calculated from the temperature change.

The water in the kettle has a higher temperature but the water in the swimming pool has more heat energy. Temperature is a measure of the average kinetic energy of the molecules.

When considering the relationship between different objects the **heat capacity** is often a more convenient property. The heat capacity (C) is defined as the heat needed to increase the temperature of an object by 1 K.

$$\text{heat capacity } (C) = \frac{\text{heat change } (q)}{\text{temperature change } (\Delta T)}$$

A swimming pool has a larger heat capacity than a kettle.

A temperature rise of 1 K is the same as a temperature rise of 1 °C.

- **The specific heat capacity (c) is defined as the heat needed to increase the temperature of unit mass of material by 1 K.**

$$\textbf{specific heat capacity } (c) = \frac{\textbf{heat change } (q)}{\textbf{mass } (m) \times \textbf{temperature change } (\Delta T)}$$

- **The heat capacity (C) is defined as the heat needed to increase the temperature of an object by 1 K.**

$$\textbf{heat capacity } (C) = \frac{\textbf{heat change } (q)}{\textbf{temperature change } (\Delta T)}$$

TOK

Our shared knowledge is passed on from one generation to the next by language. The language we use today is often based on the shared knowledge of the past which can sometimes be incorrect. What do such phrases as "keep the heat in and the cold out" tell us about previous concepts of heat and cold? How does the use of language hinder the pursuit of knowledge?

NATURE OF SCIENCE

Although heat is a concept that is familiar to us all – we need it to cook our food and to keep us warm – it is a subject that has proved to be difficult for science to understand. We are equipped by our sense of touch to distinguish between high and low temperature but heat has proved challenging on a more fundamental level. The development of different temperature scales was an important technological and scientific step as it recognized the need for objectivity in scientific measurement, and the need to calibrate the instruments to one or more one fixed points. However, scientific understanding in this area was still confused at the time. The original Celsius scale, for example, had the boiling point of water at a lower temperature than its melting point, so it was not clear what it was quantifying and other scales used arbitrary fixed points such as the melting points of butter, or the temperatures of the Paris wine cellars.

The observation that heat can be added to melting ice or boiling water without changing its temperature was a significant observation in the distinction between the heat and temperature.

Our modern distinction is based on our particulate theory of matter. Temperature is a measure of the individual particle's kinetic energy and heat, a process by which energy is transferred.

Worked example

How much heat is released when 10.0 g of copper with a specific heat capacity of 0.385 J g^{-1} °C^{-1} is cooled from 85.0 °C to 25.0 °C?

Solution

$$\text{heat change} = m \times c \times \Delta T$$
$$= 10.0\text{ g} \times 0.385\text{ J g}^{-1}\text{ °C}^{-1} \times -60.0\text{ °C}$$ (the value is negative as the Cu has lost heat)
$$= -231\text{ J}$$

Exercises

1 When a sample of NH_4SCN is mixed with solid $Ba(OH)_2.8H_2O$ in a glass beaker, the mixture changes to a liquid and the temperature drops sufficiently to freeze the beaker to the table. Which statement is true about the reaction?

A The process is endothermic and ΔH is –
B The process is endothermic and ΔH is +
C The process is exothermic and ΔH is –
D The process is exothermic and ΔH is +

2 Which one of the following statements is *true* of all exothermic reactions?

A They produce gases.
B They give out heat.
C They occur quickly.
D They involve combustion.

3 If 500 J of heat is added to 100.0 g samples of each of the substances below, which will have the largest temperature increase?

	Substance	Specific heat capacity / J g^{-1} K^{-1}
A	gold	0.129
B	silver	0.237
C	copper	0.385
D	water	4.18

4 The temperature of a 5.0 g sample of copper increases from 27 °C to 29 °C. Calculate how much heat has been added to the system. (Specific heat capacity of Cu = 0.385 J g^{-1} K^{-1})

A 0.770 J **B** 1.50 J **C** 3.00 J **D** 3.85 J

5 Consider the specific heat capacity of the following metals.

Metal	Specific heat capacity / J g^{-1} K^{-1}
Al	0.897
Be	1.82
Cd	0.231
Cr	0.449

1 kg samples of the metals at room temperature are heated by the same electrical heater for 10 min. Identify the metal which has the highest final temperature.

A Al **B** Be **C** Cd **D** Cr

6 The specific heat of metallic mercury is 0.138 J g^{-1} °C^{-1}. If 100.0 J of heat is added to a 100.0 g sample of mercury at 25.0 °C, what is the final temperature of the mercury?

CHALLENGE YOURSELF

2 Suggest an explanation for the pattern in specific heat capacities of the metals in Exercise 3.

Enthalpy changes and the direction of change

There is a natural direction for change. When we slip on a ladder, we go down, not up. The direction of change is in the direction of lower stored energy. In a similar way, we expect methane to burn when we strike a match and form carbon dioxide and water. The chemicals are changing in a way which reduces their enthalpy (Figure 5.5).

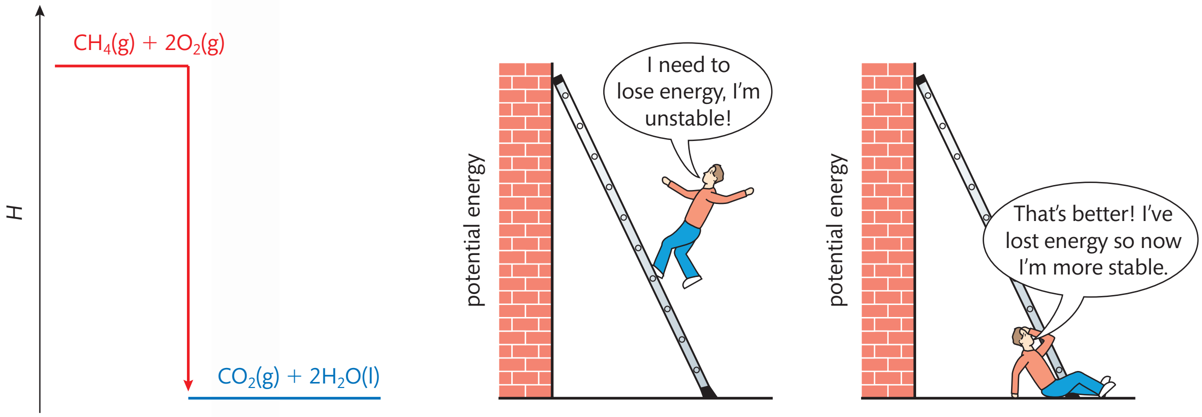


Figure 5.5 An exothermic reaction can be compared to a person falling off a ladder. Both changes lead to a decrease in stored energy. The state of lower energy is more stable. The mixture of carbon dioxide and water is more stable than a mixture of methane and oxygen.

Diamonds are not forever as they are unstable relative to graphite.

C(diamond) → C(graphite)

$\Delta H = -1.9$ kJ mol^{-1}

However, the change is very slow.

Diamond is a naturally occurring form of carbon that has crystallized under great pressure. It is unstable relative to graphite.

There are many examples of exothermic reactions and we generally expect a reaction to occur if it leads to a reduction in enthalpy. In the same way that a ball is more stable on the ground than in mid-air, we can say that the products in an exothermic reaction are more stable than the reactants. It is important to realize that stability is a relative term. Hydrogen peroxide, for example, is stable with respect to its elements but unstable relative to its decomposition to water and oxygen (Figure 5.6).

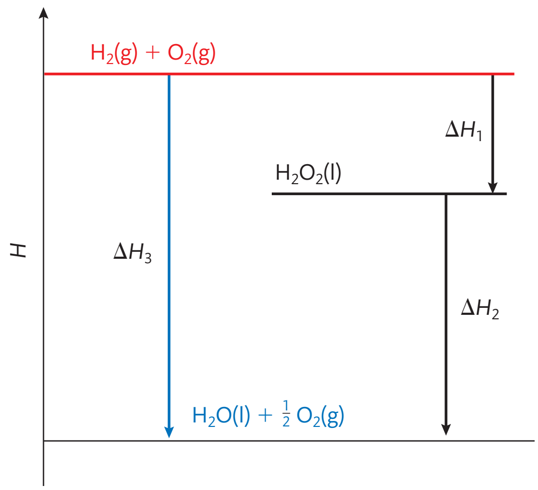


Figure 5.6 Hydrogen peroxide is stable relative to the hydrogen and oxygen but unstable relative to water.

The sign of ΔH is a guide for the likely direction of change but it is not completely reliable. We do not expect a person to fall up a ladder but some endothermic reactions can occur. For example, the reaction:

$$6SOCl_2(l) + FeCl_3.6H_2O(s) \rightarrow FeCl_3(s) + 6SO_2(g) + 12HCl(g) \qquad \Delta H = +11271 \text{ kJ mol}^{-1}$$

is extremely endothermic. Endothermic reactions are less common and occur when there is an increase in disorder of the system, for example owing to the production of gas. This is discussed in more detail later in the chapter.

Measuring enthalpy changes of combustion

For liquids such as ethanol, the enthalpy change of combustion can be determined using the simple apparatus shown in Figure 5.7.

The standard enthalpy change of combustion ($\Delta H_c^\ominus$) is the enthalpy change for the complete combustion of one mole of a substance in its standard state in excess oxygen under standard conditions.

Sherbet contains sodium hydrogencarbonate and tartaric acid. When sherbet comes into contact with water on the tongue an endothermic reaction takes place. The sherbet absorbs heat energy from the water on the tongue creating a cold sensation.

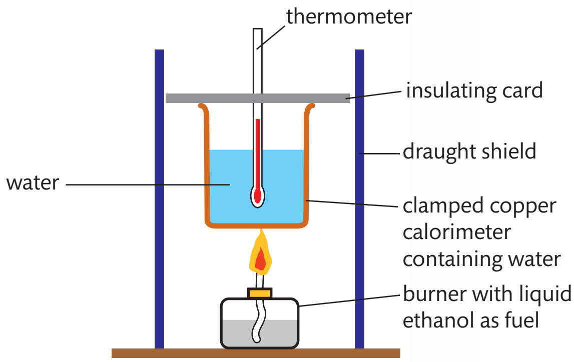


Figure 5.7 The heat produced by the combustion of the fuel is calculated from the temperature change of the water in the metal calorimeter. Copper is a good conductor of heat, so heat from the flame can be transferred to the water.

The temperature of the water increases as it has increased its heat content, owing to the heat released by the combustion reaction. There is a decrease of enthalpy during the reaction.

Calculating enthalpies of reaction from temperature changes

When the heat released by an exothermic reaction is absorbed by water, the temperature of the water increases. The heat produced by the reaction can be calculated if it is assumed that all the heat is absorbed by the water.

$$\Delta H_{\text{reaction}} = -\Delta H(\text{water}) = -m(H_2O) \times c(H_2O) \times \Delta T(H_2O)$$

As the water has gained the heat produced by the reaction, the enthalpy change of reaction is negative when the temperature of the water increases.

When an endothermic reaction is carried out in solution, the heat absorbed by the reaction is taken from the water so the temperature of the water decreases. As the reaction has taken in the heat lost by the water, the enthalpy change of reaction is positive.

As the heat change observed depends on the amount of reaction, for example the number of moles of fuel burned, enthalpy changes are usually expressed in kJ mol^{-1}.

It is important to state all assumptions when processing data. Simple treatments of heat of combustion reactions assume that all the heat is absorbed by the water, but the heat absorbed by the copper calorimeter can also be calculated.

The energy content of different foods and fuels could also be investigated.

Worked example

Calculate the enthalpy of combustion of ethanol from the following data. Assume all the heat from the reaction is absorbed by the water. Compare your value with the IB data booklet value and suggest reasons for any differences.

Mass of water in copper calorimeter / g	200.00
Temperature increase in water / °C	13.00
Mass of ethanol burned / g	0.45

Solution

$$\text{number of moles of ethanol} = \frac{m(C_2H_5OH)}{M(C_2H_5OH)}\ \text{mol}$$

$$M(C_2H_5OH) = (12.01 \times 2) + (6 \times 1.01) + 16.00 = 46.08\ \text{g mol}^{-1}$$

$$\Delta H_{\text{reaction}} = -m(H_2O) \times c(H_2O) \times \Delta T(H_2O)$$

$$\Delta H_c = \Delta H_{\text{reaction}}\ \text{(for one mole of ethanol)}$$

$$= \frac{-m(H_2O) \times c(H_2O) \times \Delta T(H_2O)}{m(C_2H_5OH) / M(C_2H_5OH)}\ \text{J mol}^{-1}$$

$$= \frac{-200\ \text{g} \times 4.18\ \text{J g}^{-1}\ {}^\circ\text{C}^{-1} \times 13.00^\circ\text{C}}{0.45\text{g} / 46.08\ \text{g mol}^{-1}}\ \text{J mol}^{-1}$$

$$= -1112\,883\ \text{J mol}^{-1}$$

$$= -1112.883\ \text{kJ mol}^{-1}$$

$$= -1100\ \text{kJ mol}^{-1}$$

The precision of the final answer is limited by the precision of the mass of the ethanol (see Chapter 11).

The IB data booklet value is -1367 kJ mol^{-1}. The difference between the values can be accounted for by any of the following factors:

- Not all the heat produced by the combustion reaction is transferred to the water. Some is needed to heat the copper calorimeter and some has passed to the surroundings.
- The combustion of the ethanol is unlikely to be complete owing to the limited oxygen available, as assumed by the literature value.
- The experiment was not performed under standard conditions.

It is important that you record qualitative as well as quantitative data when measuring enthalpy changes – for example, evidence of incomplete combustion in an enthalpy of combustion determination. When asked to evaluate experiments and suggest improvements, avoid giving trivial answers such as incorrect measurement. Incomplete combustion, for example, can be reduced by burning the fuel in oxygen. Heat loss can be reduced by insulating the apparatus.

Combustion reactions are generally exothermic, so ΔH_c values are generally negative.

Exercises

7 The mass of the burner and its content is measured before and after the experiment. The thermometer is read before and after the experiment. What are the expected results?

	Mass of burner and contents	Reading on thermometer
A	decreases	increases
B	decreases	stays the same
C	increases	increases
D	increases	stays the same

8 The experimental arrangement in Figure 5.7 is used to determine the enthalpy of combustion of an alcohol. Which of the following would lead to an experimental result which is **less** exothermic than the literature value?

I Heat loss from the sides of the copper calorimeter.
II Evaporation of alcohol during the experiment.
III The thermometer touches the bottom of the calorimeter.

A I and II only **B** I and III only **C** II and III only **D** I, II, and III

9 A copper calorimeter was used to determine the enthalpy of combustion of butan-1-ol. The experimental value obtained was −2100 ± 200 kJ mol^{-1} and the data booklet value is −2676 kJ mol^{-1}. Which of the following accounts for the difference between the two values?

I random measurement errors
II incomplete combustion
III heat loss to the surroundings

A I and II only **B** I and III only **C** II and III only **D** I, II, and III

10 1.10 g of glucose was completely burnt in a copper calorimeter. The temperature of the water increased from 25.85 °C to 36.50 °C.

(a) Calculate the enthalpy of combustion of glucose from the data below.

Mass of water / g	200.00
Specific heat capacity of water / g^{-1} K^{-1}	4.18
Mass of copper / g	120.00
Specific heat capacity of copper / g^{-1} K^{-1}	0.385

(b) Draw an enthalpy level diagram to represent this reaction.

11 The heat released from the combustion of 0.0500 g of white phosphorus increases the temperature of 150.00 g of water from 25.0 °C to 31.5 °C. Calculate a value for the enthalpy change of combustion of phosphorus. Discuss possible sources of error in the experiment.

Calorimetry – comparing pentane and hexane

Full details of how to carry out this experiment with a worksheet are available online.

A common error when calculating heat changes is using the incorrect mass of substance heated.

NATURE OF SCIENCE

Qualitative and quantitative experimental data are the lifeblood of science. The best data for making accurate and precise descriptions and predictions are often quantitative data that are amenable to mathematical analysis but qualitative observations always have a role in chemistry: the lower than expected exothermic value for a heat of combustion of a hydrocarbon for example is often as a result of incomplete combustion. The evidence for this comes from any black soot and residue observed during the experiment.

The combustion of fossil fuel, which meets many of our energy needs, produces carbon dioxide which is a greenhouse gas. It is important we are aware of how our lifestyle contributes to global warming. It is a global problem but we need to act locally to solve it. Global warming is discussed in more detail in Chapter 12.

Enthalpy changes of reaction in solution

The enthalpy changes of reaction in solution can be calculated by carrying out the reaction in an insulated system, for example, a polystyrene cup (Figure 5.8). The heat released or absorbed by the reaction can be measured from the temperature change of the water.

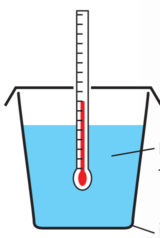


Figure 5.8 A simple calorimeter. The polystyrene is a very good thermal insulator with a low heat capacity.

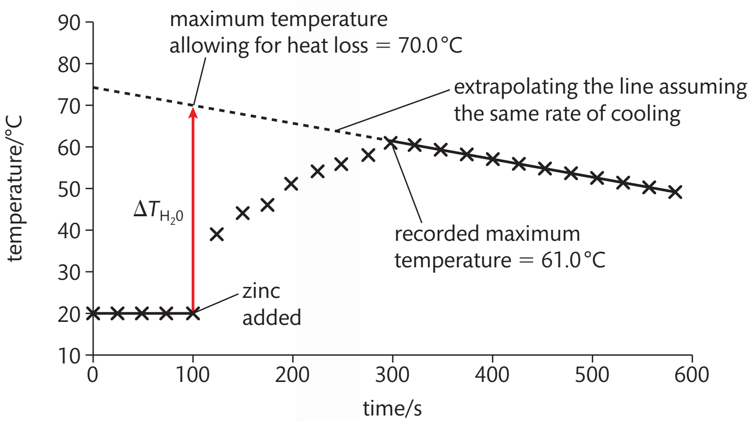


Figure 5.9 A known volume of copper sulfate solution is added to the calorimeter and its temperature measured every 25 s. Excess zinc powder is added after 100 s and the temperature starts to rise until a maximum after which it falls in an approximately linear fashion.

In the previous calculation, we assumed that all the heat produced in the reaction is absorbed by water. One of the largest sources of error in experiments conducted in a polystyrene cup is heat loss to the environment. Consider, for example, the exothermic reaction between zinc and aqueous copper sulfate (Figure 5.9):

$$Cu^{2+}(aq) + Zn(s) \rightarrow Cu(s) + Zn^{2+}(aq)$$

Heat is lost from the system as soon as the temperature rises above the temperature of the surroundings, in this case 20 °C, and so the maximum recorded temperature is lower than the true value obtained in a perfectly insulated system. We can make some allowance for heat loss by extrapolating the cooling section of the graph to the time when the reaction started (100 s).

To proceed we can make the following assumptions:

1. no heat loss from the system
2. all the heat goes from the reaction to the water
3. the solution is dilute: $V(CuSO_4) = V(H_2O)$
4. water has a density of 1.00 g cm^{-3}.

$$\Delta H(\text{system}) = 0 \text{ (assumption 1)}$$

$$\Delta H(\text{system}) = \Delta H(\text{water}) + \Delta H_{\text{reaction}} \text{ (assumption 2)}$$

$$\Delta H_{\text{reaction}} = -\Delta H(\text{water})$$

For an exothermic reaction, $\Delta H_{\text{reaction}}$ is negative as heat has passed from the reaction into the water.

$$\Delta H(\text{water}) = m(H_2O) \times c(H_2O) \times \Delta T(H_2O)$$

The limiting reactant must be identified in order to determine the molar enthalpy change of reaction.

$$\Delta H_{\text{reaction}} = \frac{-m(H_2O) \times c(H_2O) \times \Delta T(H_2O)}{\text{moles of limiting reactant}}$$

As the zinc was added in excess, the copper sulfate is the limiting reactant. From Chapter 1 (page 30):

$$\text{number of moles } (n) = \text{concentration (mol dm}^{-3}) \times \text{volume } (V \text{ cm}^3)$$

There are 1000 cm^3 in 1 dm^3

$$\text{volume } (V \text{ dm}^3) = \text{volume } (V \text{ cm}^3) / 1000 \text{ (cm}^3 \text{ dm}^{-3})$$

$$\text{number of moles of } CuSO_4 \; (n(CuSO_4)) = [CuSO_4] \times \frac{V(CuSO_4)}{1000} \text{ mol}$$

$$\Delta H_{\text{reaction}} = \frac{-m(H_2O) \times c(H_2O) \times \Delta T(H_2O)}{n(CuSO_4)} \text{ J mol}^{-1}$$

$$= \frac{-m(H_2O) \times c(H_2O) \times \Delta T(H_2O)}{[CuSO_4] \times V(CuSO_4)/1000} \text{ J mol}^{-1}$$

$$\Delta H_{reaction} = \frac{-m(H_2O) \times c(H_2O) \times \Delta T(H_2O)}{[CuSO_4] \times V(CuSO_4)/1000} \text{ J (assumption 3)}$$

$$\Delta H_{reaction} = \frac{c(H_2O) \times \Delta T(H_2O)}{[CuSO_4]/1000} \text{ (assumption 4)}$$

$$\Delta H_{reaction} = \frac{c(H_2O) \times \Delta T(H_2O)}{[CuSO_4]} \text{ kJ mol}^{-1}$$

Worked example

The neutralization reaction between solutions of sodium hydroxide and sulfuric acid was studied by measuring the temperature changes when different volumes of the two solutions were mixed. The total volume was kept constant at 120.0 cm^3 and the concentrations of the two solutions were both 1.00 mol dm^{-3} (Figure 5.10).

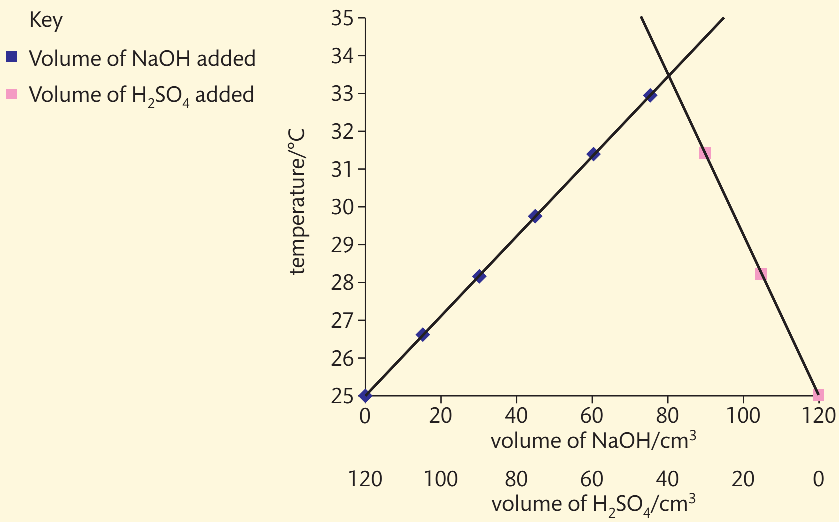


Figure 5.10 Temperature changes produced when different volumes of sodium hydroxide and sulfuric acid are mixed.

(a) Determine the volumes of the solutions which produce the largest increase in temperature.

(b) Calculate the heat produced by the reaction when the maximum temperature was produced.

(c) Calculate the heat produced for one mole of sodium hydroxide.

(d) The literature value for the enthalpy of neutralization is = −57.5 kJ mol^{-1}.

Calculate the percentage error value and suggest a reason for the discrepancy between the experimental and literature values.

Solution

(a) From the graph: $V(NaOH) = 80.0\ cm^3$

$V(H_2SO_4) = 40.0\ cm^3$

(b) Assuming 120.0 cm^3 of the solution contains 120.0 g of water and all the heat produced by the neutralization reaction passes into the water.

$$\Delta H_{reaction} = -m(H_2O) \times c(H_2O) \times \Delta T(H_2O) \text{ J}$$

$$= -120.0 \text{ g} \times 4.18 \text{ J g}^{-1} \text{ K}^{-1} \times (33.5 - 25.0) \text{ K}$$

$$= -4264 \text{ J}$$

(c) $\Delta H_{reaction} = \dfrac{-4264}{n(NaOH)}\ J\ mol^{-1}$

$$= \frac{-4264}{1.00 \times 80.0/1000}\ J\ mol^{-1}$$

$$= \frac{-4264}{80.0}\ kJ\ mol^{-1}$$

$$= -53.3\ kJ\ mol^{-1}$$

(d) $\%\ error = \dfrac{-57.5 - -53.3}{-57.5} \times 100\% = 7\%$

The calculated value assumes:

- no heat loss from the system
- all heat is transferred to the water
- the solutions contain 120 g of water.
- There are also uncertainties in the temperature, volume, and concentration measurements.

The literature value assumes standard conditions.

TOK

What criteria do we use in judging whether discrepancies between experimental and theoretical values are due to experimental limitations or theoretical assumptions?

Being courageous is one element of the IB Learner Profile. When is a scientist justified in rejecting the literature value in favour of their experimentally determined value?

A common error is to miss out or incorrectly state the units and to miss out the negative sign for ΔH.

NATURE OF SCIENCE

The accurate determination of enthalpy changes involves making careful observations and measurements, which inevitably have experimental uncertainties. The calculated enthalpy values are also dependent on the assumptions made. All these elements should be considered when reporting and evaluating experimental enthalpy values.

Mathematics is a powerful tool in the sciences, but scientific systems are often too complex to treat rigorously. These underlying assumptions, made to make a problem solvable, should not be ignored when evaluating quantitative data generated by a mathematical model.

CHALLENGE YOURSELF

3 A piece of brass is held in the flame of a Bunsen burner for several minutes. The brass is then quickly transferred into an aluminium calorimeter which contains 200.00 g of water. Determine the temperature of the Bunsen flame from the following data.

m(brass) / g	21.20
m(aluminium calorimeter) / g	80.00
c(brass) / J g^{-1} K^{-1}	0.400
c(Al) / J g^{-1} K^{-1}	0.900
Initial temperature of water / °C	24.50
Final temperature of water / °C	77.50

Exercises

12 Calculate the molar enthalpy change from the data in Figure 5.9. The copper sulfate has a concentration of 1.00 mol dm^{-3} and a volume of 1.00 dm^3.

13 Calculate the enthalpy of neutralization based on the following data.

Initial temperature of solutions / °C	24.5
Concentration of KOH(aq) / mol dm^{-3}	0.950
Concentration of HNO_3(aq) / mol dm^{-3}	1.050
Volume of HCl(aq) / cm^3	50.00
Volume of NaOH(aq) / cm^3	50.00
Final temperature of mixture / °C	32.3

State the assumptions you have made in your calculation.

14 A student added 5.350 g of ammonium chloride to 100.00 cm^3 of water. The initial temperature of the water was 25.55 °C but it decreased to 21.79 °C. Calculate the enthalpy change that would occur when 1 mol of the solute is added to 1.000 dm^3 of water.

15 Explain the meaning of the term ΔH and describe how it is measured.

The temperature of the Bunsen flame and the enthalpy of fusion can be investigated.

5.2 Hess's law

Understandings:

- The enthalpy change for a reaction that is carried out in a series of steps is equal to the sum of the enthalpy changes for the individual steps.

Applications and skills:

- Application of Hess's law to calculate enthalpy changes.
- Calculation of ΔH reactions using $\Delta H_f^{\ominus}$ data.

Guidance

- *Enthalpy of formation data can be found in the data booklet in section 12.*
- An application of Hess's law is

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

- Determination of the enthalpy change of a reaction that is the sum of multiple reactions with known enthalpy changes.

Enthalpy cycles

As it is sometimes difficult to measure the enthalpy change of a reaction directly, chemists have developed a method which uses an indirect route. The enthalpy change for a particular reaction is calculated from the known enthalpy change of other reactions. Consider the **energy cycle** in Figure 5.11: in the clockwise route, the carbon and hydrogen are first combined to form ethanol and then ethanol is burned. In the anticlockwise route, the elements are burned separately. The experimentally determined enthalpy changes are included in the figure.

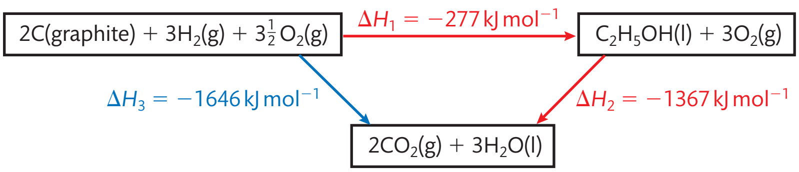


Figure 5.11 In the clockwise route, the elements are first combined to form ethanol and then ethanol is burned. In the anticlockwise route, the elements are burned separately.

Consider the clockwise route:

$$\Delta H_1 + \Delta H_2 = -277 + -1367 = -1644 \text{ kJ mol}^{-1}$$

Consider the anticlockwise route:

$$\Delta H_3 = -1646 \text{ kJ mol}^{-1}$$

Given the uncertainty of the experimental values, we can conclude that:

$$\Delta H_3 = \Delta H_1 + \Delta H_2$$

The values are the same as both changes correspond to the combustion of two moles of carbon and three moles of hydrogen. The result is a consequence of the law of conservation of energy, otherwise it would be possible to devise cycles in which energy was created or destroyed (Figure 5.12). Consider a clockwise cycle in which carbon and hydrogen and oxygen are converted to ethanol and then carbon dioxide and water, which are then converted to the original elements.

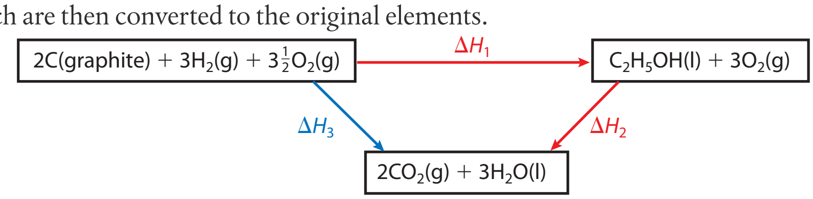


Figure 5.12 There is no net chemical change in a complete cycle as the starting reactants and final products are the same.

Hess's law is a natural consequence of the law of conservation of energy. If you know the law of conservation of energy, do you automatically know Hess's law?

From the law of conservation of energy:

in Figure 5.12, the enthalpy change in a complete cycle = 0

$$= \Delta H_1 + \Delta H_2 - \Delta H_3$$

therefore $\Delta H_1 + \Delta H_2 = \Delta H_3$

This result can be generalized and is known as **Hess's law**.

Using Hess's law

Hess's law states that the enthalpy change for any chemical reaction is independent of the route provided the starting conditions and final conditions, and reactants and products, are the same.

Hess's law states that the enthalpy change for any chemical reaction is independent of the route, provided the starting conditions and final conditions, and reactants and products, are the same.

The importance of Hess's law is that it allows us to calculate the enthalpy changes of reactions that we cannot measure directly in the laboratory. For example, although the elements carbon and hydrogen do not combine directly to form propane, C_3H_8, the enthalpy change for the reaction:

$$3C(graphite) + 4H_2(g) \rightarrow C_3H_8(g)$$

can be calculated from the enthalpy of combustion data of the elements and the compound (Figure 5.13).

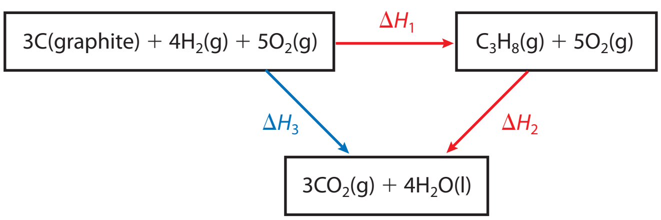


Figure 5.13 $\Delta H_1 + \Delta H_2 = \Delta H_3$, therefore $\Delta H_1 = \Delta H_3 - \Delta H_2$. Although ΔH_1 cannot be measured directly it can be calculated from the enthalpy of combustion of carbon, hydrogen, and propane.

The steps in an enthalpy cycle may be hypothetical and may refer to reactions that do not actually take place. The only requirement is that the individual chemical reactions in the sequence must balance. The relationship between the different reactions is clearly shown in an energy level diagram (Figure 5.14).

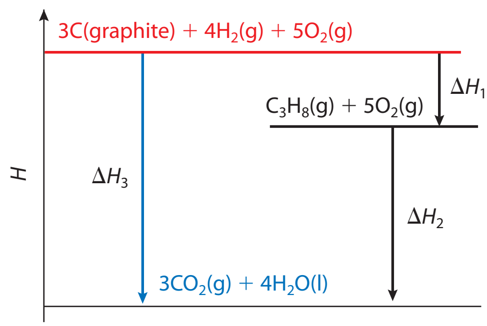


Figure 5.14 Energy level diagram used to obtain the enthalpy of formation of propane indirectly.

Reversing the direction of a reaction reverses the sign of ΔH.

Worked example

$$S(s) + 1\tfrac{1}{2}O_2(g) \rightarrow SO_3(g) \qquad \Delta H^{\ominus} = -395\ \text{kJ} \qquad (1)$$

$$SO_2(g) + \tfrac{1}{2}O_2(g) \rightarrow SO_3(g) \qquad \Delta H^{\ominus} = -98\ \text{kJ} \qquad (2)$$

Calculate the standard enthalpy change, $\Delta H^{\ominus}$, for the reaction:

$$S(s) + O_2(g) \rightarrow SO_2(g)$$

Solution

We can think of the reaction as a journey from S(s) to $SO_2(g)$. As the standard enthalpy change cannot be measured directly, we must go by an alternative route suggested by the equations given.

Reaction 1 starts from the required starting point:

$$S(s) + 1\tfrac{1}{2}O_2(g) \rightarrow SO_3(g) \qquad \Delta H^\ominus = -395\ \text{kJ} \qquad (1)$$

Reaction 2 relates $SO_3(g)$ to $SO_2(g)$. To finish with the required product, we reverse the chemical change and the sign of enthalpy change:

$$SO_3(g) \rightarrow SO_2(g) + \tfrac{1}{2}O_2(g) \qquad \Delta H^\ominus = +98\ \text{kJ} \qquad (2)$$

We can now combine these equations:

$$S(s) + \tfrac{3}{2}O_2(g) + SO_3(g) \rightarrow SO_3(g) + SO_2(g) + \tfrac{1}{2}O_2(g) \qquad \Delta H^\ominus = -395 + 98\ \text{kJ}$$

Simplifying:

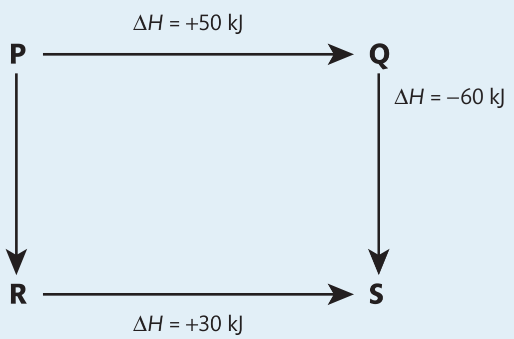
$$S(s) + \frac{\cancel{3}^{2}}{2}O_2(g) + \cancel{SO_3(g)} \rightarrow \cancel{SO_3(g)} + SO_2(g) + \cancel{\tfrac{1}{2}O_2(g)} \qquad \Delta H^\ominus = -297\ \text{kJ}$$

$$S(s) + O_2(g) \rightarrow SO_2(g) \qquad \Delta H^\ominus = -297\ \text{kJ}$$

The enthalpy change for the decomposition of metal carbonates can be determined by adding the metal carbonate and metal oxide to dilute acids using Hess's Law.

Exercises

16 The diagram illustrates the enthalpy changes of a set of reactions.



Which of the following statements are correct?

I	$P \rightarrow S$	$\Delta H = -10$ kJ
II	$R \rightarrow Q$	$\Delta H = +90$ kJ
III	$P \rightarrow R$	$\Delta H = +20$ kJ

A I and II only **B** I and III only **C** II and III only **D** I, II, and III

17 Calculate the enthalpy change, $\Delta H^\ominus$, for the reaction:

$$C(\text{graphite}) + \tfrac{1}{2}O_2(g) \rightarrow CO(g)$$

from the information below:

$$C(\text{graphite}) + O_2(g) \rightarrow CO_2(g) \qquad \Delta H^\ominus = -394\ \text{kJ}$$

$$CO(g) + \tfrac{1}{2}O_2(g) \rightarrow CO_2(g) \qquad \Delta H^\ominus = -283\ \text{kJ}$$

18 Calculate the enthalpy change, $\Delta H^\ominus$, for the reaction:

$$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$$

from the information below:

$$N_2(g) + O_2(g) \rightarrow 2NO(g) \qquad \Delta H^\ominus = +180.5\ \text{kJ}$$

$$N_2(g) + 2O_2(g) \rightarrow 2NO_2(g) \qquad \Delta H^\ominus = +66.4\ \text{kJ}$$

19 Calculate the enthalpy change for the dimerization of nitrogen dioxide:

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

It is good practice to give the enthalpy changes for endothermic reactions have an explicitly + value.

from the following data:

$$\tfrac{1}{2}N_2(g) + O_2(g) \rightarrow NO_2(g) \qquad \Delta H^\ominus = +33.2 \text{ kJ mol}^{-1}$$

$$N_2(g) + 2O_2(g) \rightarrow N_2O_4(g) \qquad \Delta H^\ominus = +9.16 \text{ kJ mol}^{-1}$$

20 The thermochemical equations for three related reactions are shown.

$$CO(g) + \tfrac{1}{2}O_2(g) \rightarrow CO_2(g) \qquad \Delta H_1 = -283 \text{ kJ mol}^{-1}$$

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(l) \qquad \Delta H_2 = -572 \text{ kJ mol}^{-1}$$

$$CO_2(g) + H_2(g) \rightarrow CO(g) + H_2O(l) \qquad \Delta H_3 = ???$$

Determine ΔH_3

A +289 kJ mol^{-1} **B** −3 kJ mol^{-1} **C** −289 kJ mol^{-1} **D** −855 kJ mol^{-1}

The standard enthalpy of formation of a substance is the enthalpy change that occurs when one mole of the substance is formed from its elements in their standard states under standard conditions of 298 K (25 °C) and 1.00 × 10^5 Pa.

Standard enthalpy changes of reaction

As discussed earlier, the enthalpy change of a reaction depends on the physical state of the reactants and the products and the conditions under which the reaction occurs. For this reason, **standard enthalpy changes, $\Delta H^\ominus$**, which are measured under standard conditions of 298 K (25 °C) and 1.00 × 10^5 Pa, are generally tabulated.

The **standard enthalpy change of formation, $\Delta H_f^\ominus$**, of a substance is the enthalpy change that occurs when one mole of the substance is formed from its elements in their standard states. These standard measurements are taken at a temperature of 298 K (25 °C) and a pressure of 1.00 × 10^5 Pa. They are important as they:

- give a measure of the stability of a substance relative to its elements
- can be used to calculate the enthalpy changes of all reactions, either hypothetical or real.

Be careful with definitions of all key terms. Many students have difficulty defining standard enthalpy of formation – they refer to the energy required rather than enthalpy change and do not refer to the formation of one mole of substance in its standard state.

Worked example

The enthalpy of formation of ethanol is given in section 12 of the IB data booklet. Give the thermochemical equation which represents the standard enthalpy of formation of ethanol.

Solution

The value from the IB data booklet = −278 kJ mol^{-1}

Ethanol (C_2H_5OH) is made from the elements (C(graphite)) and hydrogen ($H_2(g)$) and oxygen ($O_2(g)$).

$$\_\_C(graphite) + \_\_H_2(g) + \_\_O_2(g) \rightarrow C_2H_5OH(l)$$

Balance the equation:

$$2C(graphite) + 3H_2(g) + \tfrac{1}{2}O_2(g) \rightarrow C_2H_5OH(l) \qquad \Delta H = -278 \text{ kJ mol}^{-1}$$

Note that as the enthalpy change of formation refers to one mole of product, there are fractional coefficients in the balanced equation.

The standard enthalpy change of formation of an element in its most stable form is zero. There is no chemical change and so no enthalpy change when an element is formed from itself.

Exercises

21 Which of the following does **not** have a standard heat of formation value of **zero** at 25 °C and 1.00 × 10^5 Pa?

A $Cl_2(g)$ **B** $I_2(s)$ **C** $Br_2(g)$ **D** Na(s)

22 Which of the following does **not** have a standard heat of formation value of **zero** at 25 °C and 1.00 × 10^5 Pa?

A H(g) **B** Hg(s) **C** C(diamond) **D** Si(s)

23 For which equation is the enthalpy change described as an enthalpy change of formation?

A $CuSO_4(aq) + Zn(s) \rightarrow ZnSO_4(aq) + Cu(s)$
B $Cu(s) + S(s) + 2O_2(g) \rightarrow CuSO_4(aq)$
C $5H_2O(l) + CuSO_4(s) \rightarrow CuSO_4.5H_2O(s)$
D $Cu(s) + S(s) + 2O_2(g) \rightarrow CuSO_4(s)$

24 **(a)** Write the thermochemical equation for the standard enthalpy of formation of propanone (CH_3COCH_3).

(b) State the conditions under which standard enthalpy changes are measured.

Using standard enthalpy changes of formation

Standard enthalpy changes of formation can be used to calculate the standard enthalpy change of any reaction. Consider the general energy cycle in Figure 5.15.

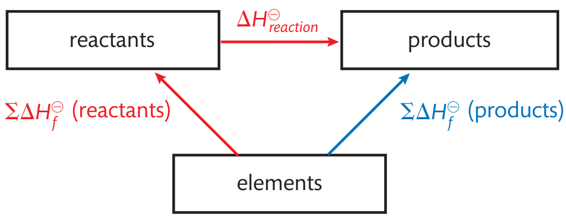


Figure 5.15 The chemical change elements → products can either occur directly or indirectly. The total enthalpy change must be the same for both routes. ∑ means 'the sum of '.

We have from the diagram:

$$\sum\Delta H^\ominus_f(\text{reactants}) + \Delta H_{\text{reaction}} = \sum\Delta H^\ominus_f(\text{products})$$

This gives the general expression for $\Delta H_{\text{reaction}}$ of any reaction

$$\Delta H_{\text{reaction}} = \sum\Delta H^\ominus_f(\text{products}) - \sum\Delta H^\ominus_f(\text{reactants})$$

$\Delta H_{\text{reaction}} = \sum\Delta H^\ominus_f(\text{products}) - \sum\Delta H^\ominus_f(\text{reactants})$

Worked example

Calculate the enthalpy change for the reaction

$$C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(g)$$

from the following standard enthalpy changes of formation.

Substance	$\Delta H^\ominus_f$/ kJ mol^{-1}
$C_3H_8(g)$	–105
$CO_2(g)$	–394
$H_2O(l)$	–286

Solution

First, write down the equation with the corresponding enthalpies of formation underneath:

$C_3H_8(g)$	+	$5O_2(g)$	→	$3CO_2(g)$	+	$4H_2O(g)$	
–105		>0		3(–394)		4(–286)	$\Delta H^\ominus_f$ / kJ mol^{-1}

As the standard enthalpies of formation are given per mole they must be multiplied by the number of moles in the balanced equation, shown in red above.

Write down the general expression for the $\Delta H_{\text{reaction}}$

$$\Delta H_{\text{reaction}} = \sum\Delta H^\ominus_f(\text{products}) - \sum\Delta H^\ominus_f(\text{reactants})$$

and express $\Delta H_{reaction}$ in terms of the data given:

$$\Delta H^{\ominus}_{reaction} = 3(-394) + 4(-286) - (-105)$$
$$= -2221 \text{ kJ mol}^{-1}$$

NATURE OF SCIENCE

Heat is a tool that drives a country's industrial development and an individual's life, and a concept that has enlightened our understanding of why things change in the natural world.

The scientific understanding and harnessing of the energy has helped make the modern world what it is. The conservation of energy, on which Hess's law is based, developed as a result of practical considerations about the use and effect of heat and work. Hess's law is now important on both a practical and theoretical level as it allows us to predict the energy changes of possible and impossible reactions. The study of energetics shows how scientific theories evolve and generally accommodate the assumptions and premises of other theories, creating a consistent understanding across a range of phenomena and disciplines.

Exercises

25 Calculate $\Delta H^{\ominus}$ (in kJ mol^{-1}) for the reaction

$$Fe_3O_4(s) + 2C(graphite) \rightarrow 3Fe(s) + 2CO_2(g)$$

from the data below:

	$\Delta H_f^{\ominus}$ / kJ mol^{-1}
$Fe_3O_4(s)$	−1118
$CO_2(g)$	−394

26 Calculate $\Delta H^{\ominus}$ (in kJ mol^{-1}) for the reaction

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

from the data below:

	$\Delta H_f^{\ominus}$ / kJ mol^{-1}
$NO_2(g)$	+33.2
$N_2O_4(g)$	+9.2

27 Hydrogen peroxide slowly decomposes into water and oxygen:

$$2H_2O_2(l) \rightarrow 2H_2O(l) + O_2(g)$$

Calculate the enthalpy change of this reaction from the data table.

	$\Delta H_f^{\ominus}$ / kJ mol^{-1}
$H_2O_2(l)$	−188
$H_2O(l)$	−286

A +98 kJ mol^{-1} **B** −98 kJ mol^{-1} **C** +196 kJ mol^{-1} **D** −196 kJ mol^{-1}

28 Calculate the enthalpy change for the hypothetical reduction of magnesium oxide by carbon, according to the equation below from the data given. Comment on its feasibility.

$$2MgO(s) + C(s) \rightarrow CO_2(g) + 2Mg(s)$$

	$\Delta H_f^{\ominus}$ / kJ mol^{-1}
$CO_2(g)$	−394
MgO(l)	−602

5.3 Bond enthalpies

Understandings:

- Bond forming releases energy and bond breaking requires energy.
- Average bond enthalpy is the energy needed to break one mole of a bond in a gaseous molecule averaged over similar compounds.

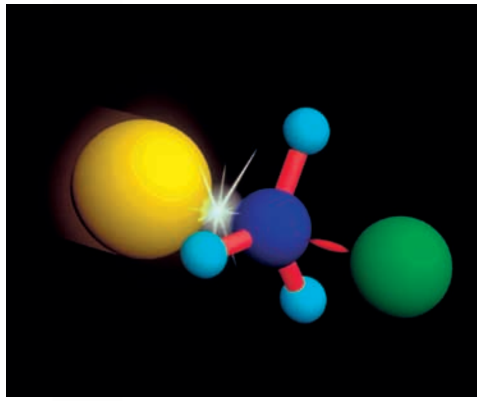
Applications and skills:

- Calculation of the enthalpy changes from known bond enthalpy values and comparison of these to experimentally measured values.

Guidance

- _Bond enthalpy values are given in the data booklet in section 11._
- Average bond enthalpies are only valid for gases and calculations involving bond enthalpies may be inaccurate because they do not take into account intermolecular forces.
- Sketching and evaluation of potential energy profiles in determining whether reactants or products are more stable and if the reaction is exothermic or endothermic.
- Discussion of the bond strength in ozone relative to oxygen in its importance to the atmosphere.

Chemical reactions involve the breaking and making of bonds. To understand the energy changes in a chemical reaction, we need to look at the energies needed to break the bonds that hold the atoms together in the reactants and the energy released when new bonds are formed in the products.



A chemical reaction involves the breaking and making of bonds. 500 to 1000 kJ of heat are typically needed to break one mole of chemical bonds. This image shows a change in the bond between the atoms represented by the yellow and the dark blue.

Breaking bonds is an endothermic process

A covalent bond is due to the electrostatic attraction between the shared pair of electrons and the positive nuclei of the bonded atoms. Energy is needed to separate the atoms in a bond.

The bond enthalpy is the energy needed to break one mole of bonds in gaseous molecules under standard conditions.

The energy change, for example, during the formation of two moles of chlorine atoms from one mole of chlorine molecules can be represented as:

$$Cl_2(g) \rightarrow 2Cl(g) \qquad \Delta H^{\ominus} = +242 \text{ kJ mol}^{-1}$$

The situation is complicated in molecules which contain more than two atoms. Breaking the first O–H bond in a water molecule requires more heat energy than breaking the second bond:

$$H_2O(g) \rightarrow H(g) + OH(g) \qquad \Delta H^{\ominus} = +502 \text{ kJ mol}^{-1}$$

$$OH(g) \rightarrow H(g) + O(g) \qquad \Delta H^{\ominus} = +427 \text{ kJ mol}^{-1}$$

Similarly the energy needed to break the O–H in other molecules such as ethanol, C_2H_5OH, is different. In order to compare bond enthalpies which exist in different environments, **average bond enthalpies** are tabulated.

Using Hess's law:

$$H_2O(g) \rightarrow H(g) + OH(g) \qquad \Delta H = +502 \text{ kJ mol}^{-1}$$

$$OH(g) \rightarrow H(g) + O(g) \qquad \Delta H = +427 \text{ kJ mol}^{-1}$$

Average bond enthalpy over numbers on right

$$H_2O(g) \rightarrow H(g) + H(g) + OH(g) \qquad \Delta H = +502 + 427 \text{ kJ mol}^{-1}$$

$$\text{Average bond enthalpy } E(\text{O–H}) = \frac{+502 + 427}{2} \text{ kJ mol}^{-1}$$

$$= \frac{929}{2}$$

$$= 464.5 \text{ kJ mol}^{-1}$$

This value should be compared with the bond enthalpies given in the table on page 232 which are calculated from a wide range of molecules. Multiple bonds generally have higher bond enthalpies and shorter bond lengths than single bonds.

The average bond enthalpy is the energy needed to break one mole of bonds in gaseous molecules under standard conditions averaged over similar compounds.

Note carefully the definition of bond enthalpy. A common error is to fail to indicate that all the species have to be in the gaseous state.

Bond	E(X–Y) / kJ mol^{-1}	Bond length / 10^{-9} m
H–H	+436	0.074
C–C	+347	0.154
C=C	+614	0.134
C–H	+414	0.108
O=O	+498	0.121
O–H	+463	0.097
C=O	+804	0.122
Cl–Cl	+242	0.199

All bond enthalpies refer to reactions in the gaseous state so that the enthalpy changes caused by the formation and breaking of intermolecular forces can be ignored.

Making bonds is an exothermic process

The same amount of energy is absorbed when a bond is broken as is given out when a bond is made (Figure 5.16). For example:

$$H(g) + H(g) \rightarrow H_2(g)$$

$$\Delta H^\ominus = -436 \text{ kJ mol}^{-1}$$

Endothermic processes involve the separation of particles which are held together by a force of attraction.

Exothermic processes involve the bringing together of particles which have an attractive force between them.

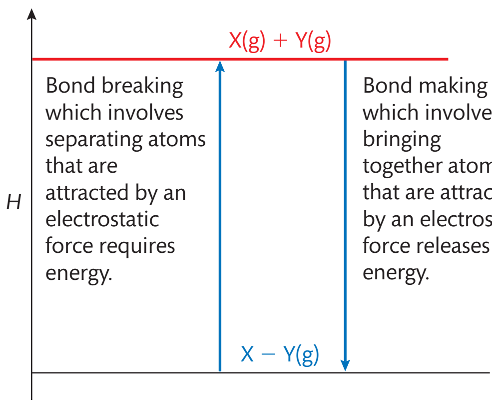


Figure 5.16 The energy changes that occur when bonds are broken and bonds are formed.

Worked example

Which of the following processes are endothermic?

A $2Cl(g) \rightarrow Cl_2(g)$

B $Na(g) \rightarrow Na^+(g) + e^-$

C $Na^+(g) + Cl^-(g) \rightarrow NaCl(s)$

D $Na(g) \rightarrow Na(s)$

Solution

Only one of the processes involves the separation of particles:

$$Na(g) \rightarrow Na^+(g) + e^-$$

In this case, a negatively charged electron is separated from a positive ion $Na^+(g)$.

Answer = B

Exercises

29 Which of the following processes are endothermic?

I $H_2O(s) \rightarrow H_2O(g)$
II $CO_2(g) \rightarrow CO_2(s)$
III $O_2(g) \rightarrow 2O(g)$

A I and II only **B** I and III only **C** II and III only **D** I, II, and III

30 Identify the equation which represents the bond enthalpy for the H–Cl bond.

A $HCl(g) \rightarrow H(g) + Cl(g)$
B $HCl(g) \rightarrow \frac{1}{2}H_2(g) + \frac{1}{2}Cl_2(g)$
C $HCl(g) \rightarrow H^+(g) + Cl^-(g)$
D $HCl(aq) \rightarrow H^+(aq) + Cl^-(aq)$

31 Which of the following processes are endothermic?

I $CO_2(g) \rightarrow CO_2(s)$
II $H_2O(s) \rightarrow H_2O(g)$
III $O_2(g) \rightarrow 2O(g)$

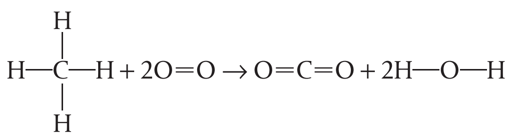
A I and II only **B** I and III only **C** II and III only **D** I, II, and III

32 Identify the bonds which are broken in the following process.

$$C_2H_6(g) \rightarrow 2C(g) + 6H(g)$$

Using bond enthalpies to calculate the enthalpy changes of reaction

We are now in a position to understand how energy changes occur in chemical reactions. Consider, for example, the complete combustion of methane when we use a Bunsen burner:



Energy is needed to break the C—H and O═O bonds in the reactants, but energy is given out when the C═O and O—H bonds are formed. The reaction is exothermic overall as the bonds which are formed are stronger than the bonds which are broken. A reaction is endothermic when the bonds broken are stronger than the bonds which are formed.

Worked example

Use bond enthalpies to calculate the heat of combustion of methane, the principal component of natural gas.

Solution

1 Write down the equation for the reaction showing all the bonds. This has already been done above.

2 Draw a table which shows the bonds which are broken and those that are formed during the reaction with the corresponding energy changes.

CHALLENGE YOURSELF

4 Compare the value of the enthalpy of combustion of methane obtained in the worked example to that in section 13 of the IB data booklet and use Hess's law to estimate the strength of a hydrogen bond.

Bonds broken	ΔH / kJ mol^{-1} (endothermic)	Bonds formed	ΔH / kJ mol^{-1} (exothermic)
4 C–H	4 (+414)	2 C=O	2 (–804)
2 O=O	2 (+498)	4 O–H	4 (–463)
Total	= +2652		= +3460

$$\Delta H = \sum E(\text{bonds broken}) - \sum E(\text{bonds formed})$$

$$\Delta H^{\ominus} = +2652 + (-3460)\ \text{kJ mol}^{-1} = -808\ \text{kJ mol}^{-1}$$

The value calculated from the bond enthalpies should be compared with the experimental value of –891 kJ mol^{-1} measured under standard conditions given in section 13 of the IB data booklet. The values are different because the standard state of water is liquid and the bond enthalpy calculation assumes that the reaction occurs in the gaseous state. The use of average bond enthalpies is an additional approximation.

Make sure that you select the correct values for the bond enthalpies. For example don't confuse C=C with C—C, and use the correct coefficients for the number of bonds broken and formed.

Exercises

33 Which of the following is equivalent to the bond enthalpy of the carbon–oxygen bond in carbon monoxide?

A $CO(g) \rightarrow C(s) + O(g)$
B $CO(g) \rightarrow C(g) + O(g)$
C $CO(g) \rightarrow C(s) + \frac{1}{2}O_2(g)$
D $CO(g) \rightarrow C(g) + \frac{1}{2}O_2(g)$

34 Use the bond enthalpies below to calculate $\Delta H^{\ominus}$ for the reaction:

$$H_2C{=}CH_2 + H_2 \rightarrow H_3C{-}CH_3$$

Bond	Bond enthalpy / kJ mol^{-1}
C—C	+347
C=C	+612
H—H	+436
C—H	+413

35 Use the bond enthalpies below to calculate $\Delta H^{\ominus}$ for the reaction:

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(g)$$

Bond	Bond enthalpy / kJ mol^{-1}
O=O	+498
H—H	+436
O—H	+464

36 The hydrogenation of the alkene double bond in unsaturated oils is an important reaction in margarine production. Calculate the enthalpy change when one mole of C=C bonds is hydrogenated from the bond energy data shown.

Bond	Bond enthalpy / kJ mol^{-1}
H—H	436
C—C	347
C—H	412
C=C	612

A –224 kJ mol^{-1} **B** –123 kJ mol^{-1} **C** +123 kJ mol^{-1} **D** +224 kJ mol^{-1}

37 Use the bond enthalpy data given to calculate the enthalpy change of reaction between methane and fluorine:

$$C_2H_4(g) + F_2(g) \rightarrow CH_2FCH_2F(g)$$

Bond	Bond enthalpy / kJ mol^{-1}
C—C	347
C=C	612
F—F	158
H—F	568
C—F	467

A +776 **B** +164 **C** –511 **D** –776

38 Use the bond enthalpies given in section 11 of the IB data booklet to estimate the enthalpy of combustion of ethanol and comment on the reliability of your result.

CHALLENGE YOURSELF

5 Suggest, based on the discussion of bonding and structure in Chapter 4, why graphite is more stable than diamond.

Don't confuse the different methods of calculating enthalpy changes. A common error when using bond enthalpies is the reversal of the sign.

The correct expression is:

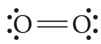
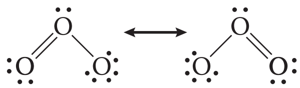
$\Delta H = \sum E(\text{bonds broken}) - \sum E(\text{bonds formed})$

This should be contrasted with the expression using standard enthalpies of formation:

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

Ozone depletion

The Earth is unique among the planets in having an atmosphere that is chemically active and rich in oxygen. Oxygen is present in two forms, normal oxygen (O_2) and ozone (O_3), and both forms play a key role in protecting life on the Earth's surface from harmful ultraviolet (UV) radiation. They form a protective screen which ensures that radiation that reaches the surface of the Earth is different from that emitted by the Sun. As discussed in Chapter 4, O_2 and O_3 differ in their bonding as follows:

	
O_2; double bonds	O_3; the oxygen to oxygen bond is between a single bond and a double bond

The bonds in oxygen and ozone are broken by UV of different wavelengths

The bonds in oxygen and ozone are both broken when they absorb UV radiation of sufficient energy. The double bond in O_2 is stronger than the 1.5 bond in ozone and so is broken by radiation of higher energy and shorter wavelengths.

The energy E_{photon} of a photon of light is related to its frequency ν by Planck's equation (see Chapter 2):

$$E_{\text{photon}} = h\nu$$

The wavelength λ is related to the frequency: $\nu = c/\lambda$ where c is the speed of light. Substituting for ν in Planck's equation:

$$E_{\text{photon}} = \frac{h \times c}{\lambda}$$

As oxygen has the strongest bond, shorter wavelength radiation is needed to break its bonds. The wavelengths of light needed to break the bonds in ozone are calculated in the following example.

The depletion of the ozone layer is an important transdisciplinary topic. It is also discussed in Chapter 4.

Worked example

The bond energy in ozone is 363 kJ mol^{-1}. Calculate the wavelength of UV radiation needed to break the bond.

Solution

One mole of photons are needed to break one mole of bonds. The energy of a mole of photons is the energy of one photon multiplied by Avogadro's number (L) (page 15).

$$L \times E_{\text{photon}} = 363\text{ kJ} = 363\,000\text{ J}$$

$$E_{\text{photon}} = \frac{363\,000}{6.02 \times 10^{23}}\text{ J}$$

$$\lambda = \frac{hc}{E_{\text{photon}}}$$

$$= 6.63 \times 10^{-34}\text{ Js} \times 3.00 \times 10^{8}\text{ ms}^{-1} \times \frac{6.02 \times 10^{23}}{363000}\text{ J}^{-1}$$

$$= 3.30 \times 10^{-7}\text{ m}$$

$$= 330\text{ nm}$$

Any radiation in the UV region with a wavelength smaller than 330 nm breaks the bond in ozone.

The natural formation and depletion of ozone

The temperature of the atmosphere generally decreases with height but at 12 km above the Earth's surface the temperature starts to rise because ultraviolet radiation is absorbed in a number of photochemical reactions.

In the stratosphere, the strong covalent double bond in normal oxygen O_2 is broken by high-energy UV radiation with a wavelength shorter than 242 nm to form two oxygen atoms:

A free radical is a species with an unpaired electron.

$$O_2(g) \xrightarrow{\text{UV light, } \lambda < 242\text{ nm}} O\bullet(g) + O\bullet(g)\text{(atomic oxygen)}$$

The oxygen atoms have unpaired electrons. They are reactive **free radicals** and so react with another oxygen molecule to form ozone.

$$O\bullet(g) + O_2(g) \rightarrow O_3(g)$$

This second step is *exothermic*; bonds are formed and the energy given out raises the temperature of the stratosphere.

As the bonds in ozone are weaker than the double bond in oxygen, ultraviolet light of lower energy is needed to break them:

$$O_3(g) \xrightarrow{\text{UV light, } \lambda < 330\text{ nm}} O\bullet(g) + O_2(g)$$

The oxygen atoms then react with another ozone molecule to form two oxygen molecules.

$$O_3(g) + O\bullet(g) \rightarrow 2O_2(g)$$

As bonds are formed this is another exothermic reaction which produces heat that maintains the relatively high temperature of the stratosphere. The level of ozone in the

CHALLENGE YOURSELF

6 Explain why oxygen behaves as a free radical despite having an even number of electrons.

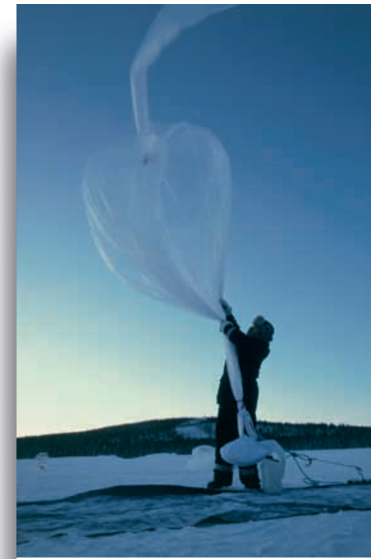
stratosphere – less than 10 ppm – stays at a constant level if the rate of formation of ozone is balanced by its rate of removal. This is known as a **steady state**. The whole process is described by the Chapman Cycle.

$$O_2 \xrightarrow[\text{high energy UV } \lambda < 242\text{nm}]{\text{Step 1}} 2\,O^{\bullet}$$

$$O^{\bullet} + O_2 \underset{\text{Step 3 lower energy}}{\overset{\text{Step 2}}{\rightleftarrows}} O_3$$

$$O_3 + O^{\bullet} \xrightarrow[\text{(slow)}]{\text{Step 4}} 2\,O_2$$

This cycle of reactions is significant because dangerous ultraviolet light has been absorbed and the stratosphere has become warmer. Both these processes are essential for the survival of life on Earth.



Technician releasing a balloon to measure stratospheric ozone over the Arctic. This research was part of a joint project by NASA and the European Union to look at the amount and rate of stratospheric ozone depletion.

Exercises

39 The concentration of ozone in the upper atmosphere is maintained by the following reactions.

I $O_2 \rightarrow 2O\bullet$
II $O_2 + O\bullet \rightarrow O_3$
III $O_3 \rightarrow O_2 + O\bullet$

The presence of chlorofluorocarbons (CFCs) in the upper atmosphere has led to a reduction in ozone concentration.

(a) Identify the step which is exothermic.
(b) Identify with reference to the bonding in O_2 and O_3, the most endothermic step.

40 Use section 11 of the IB data booklet to calculate the minimum wavelength of radiation needed to break the O═O double bond in O_2.

41 Explain why ozone can be decomposed by light with a longer wavelength than that required to decompose oxygen.

Ozone depletion is a global political issue. Consider the following quote from Maneka Gandhi, former Indian Minister of the Environment and delegate to the *Montreal Protocol*. 'India recognizes the threat to the environment and the necessity for a global burden sharing to control it. But is it fair that the industrialized countries who are responsible for the ozone depletion should arm-twist the poorer nations into bearing the cost of their mistakes?'

Stratospheric ozone depletion is a particular concern in the polar regions of the planet, although the pollution that causes it comes from a variety of regions and sources. International action and cooperation have helped to ameliorate the ozone depletion problem.

15.1 Energy cycles

Understandings:

- Representative equations (e.g. $M^+(g) \rightarrow M^+(aq)$) can be used for enthalpy/energy of hydration, ionization, atomization, electron affinity, lattice, covalent bond, and solution.
- Enthalpy of solution, hydration enthalpy, and lattice enthalpy are related in an energy cycle.

Applications and skills:

- Construction of Born–Haber cycles for Group 1 and 2 oxides and chlorides.
- Construction of energy cycles from hydration, lattice, and solution enthalpy. For example, dissolution of solid NaOH or NH_4Cl in water.
- Calculation of enthalpy changes from Born–Haber or dissolution energy cycles.

Guidance

- *The following enthalpy/energy terms should be covered: ionization, atomization, electron affinity, lattice, covalent bond, hydration, and solution.*
- *Values for lattice enthalpies (section 18), enthalpies of aqueous solutions (section 19), and enthalpies of hydration (section 20) are given in the data booklet.*

- Relate size and charge of ions to lattice and hydration enthalpies.

Guidance

Polarizing effect of some ions producing covalent character in some largely ionic substances will not be assessed.

- Perform lab experiments which could include single replacement reactions in aqueous solutions.

First ionization energies and electron affinities

In Chapter 4 we discussed the formation of ionic compounds such as sodium chloride. Metal atoms lose electrons and non-metal atoms gain electrons.

The first ionization energy is the minimum energy required to remove one mole of electrons from one mole of gaseous atoms.

The first ionization energy ($\Delta H_i^\ominus$) corresponds to the energy needed to form the positive ion.

$$Na(g) \rightarrow Na^+(g) + e^-(g) \qquad \Delta H_i^\ominus = +496\ kJ\ mol^{-1}$$

This process was discussed in Chapters 2 and 3, where we saw that sodium, which is on the left of the Periodic Table, has a relatively low ionization energy. The first **electron affinity** ($\Delta H_e^\ominus$) is the enthalpy change when one mole of gaseous atoms attracts one mole of electrons. Values are tabulated in section 7 of the IB data booklet. For chlorine:

The first electron affinity is the enthalpy change when one mole of gaseous electrons is added to one mole of gaseous atoms.

$$Cl(g) + e^-(g) \rightarrow Cl^-(g) \qquad \Delta H_e^\ominus = -349\ kJ\ mol^{-1}$$

As the electron is attracted to the positively charged nucleus of the Cl atom, the process is exothermic.

Lattice enthalpies

Add the equations for first ionization energy and first electron affinity:

$$Na(g) + Cl(g) \rightarrow Na^+(g) + Cl^-(g) \qquad \Delta H^\ominus = -349 + 496 = +147\ kJ\ mol^{-1}$$

We can now see that the electron transfer process is endothermic overall and so energetically unfavourable, despite the fact that it leads to the formation of ions with stable noble gas electron configurations. To understand the formation of ionic compounds, we need to look deeper. The oppositely charged gaseous ions come together to form an **ionic lattice**; this is a very exothermic process as there is strong attraction between the oppositely charged ions:

The lattice enthalpy is the enthalpy change that occurs when one mole of a solid ionic compound is separated into gaseous ions under standard conditions.

$$Na^+(g) + Cl^-(g) \rightarrow NaCl(s) \qquad \Delta H^\ominus = -790\ kJ\ mol^{-1}$$

Although some texts use an exothermic definition of lattice energy, it is the endothermic definition which is given in section 18 of the IB data booklet.

It is this step of the process which explains the readiness of sodium and chlorine to form an ionic compound.

The **lattice enthalpy** ($\Delta H_{lat}^\ominus$) expresses this enthalpy change in terms of the reverse endothermic process. The lattice enthalpy relates to the formation of gaseous ions from one mole of a solid crystal breaking into gaseous ions. For example, sodium chloride:

$$NaCl(s) \rightarrow Na^+(g) + Cl^-(g) \qquad \Delta H^\ominus_{lat} = +790\ \text{kJ mol}^{-1}$$

Experimental lattice enthalpies and the Born–Haber cycle

Experimental lattice energies cannot be determined directly. An energy cycle based on Hess's law, known as the **Born–Haber cycle** is used. The formation of an ionic compound from its elements is supposed to take place in a number of steps including the formation of the solid lattice from its constituent gaseous ions. From Hess's law, the enthalpy change for the overall formation of the solid must be equal to the sum of the enthalpy changes accompanying the individual steps.

Consider, for example, the formation of sodium chloride:

$$Na(s) + \tfrac{1}{2}Cl_2(g) \rightarrow NaCl(s) \qquad \Delta H^\ominus_f(NaCl) = -411\ \text{kJ mol}^{-1}$$

This can be considered to take place in several steps as shown in the table below.

Step	$\Delta H^\ominus$ / kJ mol^{-1}
Sodium is atomized to form one mole of gaseous ions: $Na(s) \rightarrow Na(g)$ The corresponding enthalpy change is known as the enthalpy change of atomization.	$\Delta H^\ominus_{atom}(Na) = +107$
One mole of chlorine atoms is formed as ½ mole of Cl—Cl bonds break: $\tfrac{1}{2}Cl_2(g) \rightarrow Cl(g)$ E = bond enthalpy, page 233 Enthalpy of atomization of chlorine	$\tfrac{1}{2}E(Cl{-}Cl) = \tfrac{1}{2}(+242)$
One electron is removed from the outer shell of the gaseous sodium atom: $Na(g) \rightarrow Na^+(g) + e^-$ Ionization energy of sodium	$\Delta H^\ominus_i(Na) = +496$
One electron is added to the outer shell of the gaseous chlorine atom: $Cl(g) + e^- \rightarrow Cl^-(g)$ Electron affinity of chlorine	$\Delta H^\ominus_e(Cl) = -349$
The gaseous ions come together to form one mole of solid sodium chloride: $Na^+(g) + Cl^-(g) \rightarrow NaCl(s)$ – Lattice enthalpy of sodium chloride	$-\Delta H^\ominus_{lat}$ = ???

These changes are best illustrated using an energy level diagram (Figure 5.17).

The enthalpy change of atomization $\Delta H^\ominus_{atom}$ is the enthalpy change that occurs when one mole of gaseous atoms is formed from the element in its standard state.

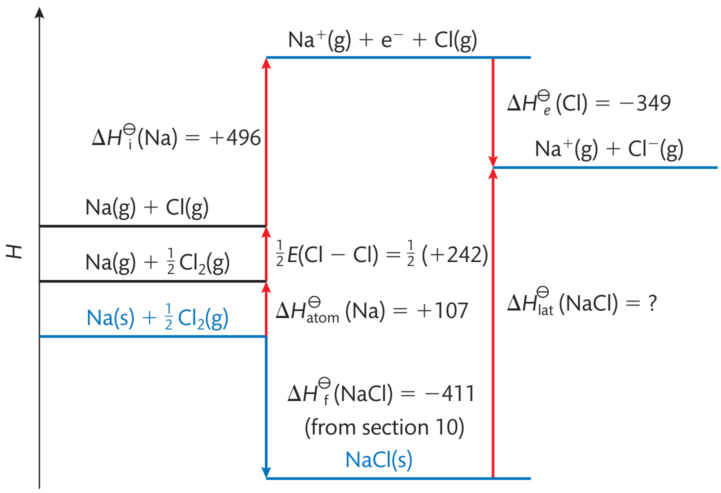


Figure 5.17 Born–Haber cycle for sodium chloride. The enthalpy change of formation of sodium chloride, shown in blue, can be equated to a combination of the enthalpy changes associated with the changes shown in red.

Note changes from original bond energy for Cl_2 = 242 and the arrow for lattice energy has been inverted.

$$\Delta H^\ominus_f(NaCl) = \Delta H^\ominus_{atom}(Na) + \Delta H^\ominus_i(Na) + \tfrac{1}{2}E(Cl{-}Cl) + \Delta H^\ominus_e(Cl) - \Delta H^\ominus_{lat}(NaCl)$$

This allows an equation for the lattice enthalpy to be expressed in terms of experimentally verifiable quantities:

$$\Delta H^\ominus_{lat}(NaCl) = \Delta H^\ominus_{atom}(Na) + \Delta H^\ominus_i(Na) + \tfrac{1}{2}E(Cl{-}Cl) + \Delta H^\ominus_e(Cl) - \Delta H^\ominus_f(NaCl)$$

$$\Delta H^\ominus_{lat}(NaCl) = +107 + 496 + \tfrac{1}{2}(+242) - 349 - (-411)\ \text{kJ mol}^{-1}$$

$$= +786\ \text{kJ mol}^{-1}$$

Worked example

(a) Write an equation to represent the lattice energy of magnesium oxide, MgO.

(b) Write an equation to represent the second electron affinity of oxygen and comment on the relative values of the first and second values given in section 8 of the IB data booklet.

(c) Use the following data, and further information from sections 8 and 11 of the IB data booklet to construct a Born–Haber cycle for magnesium oxide.

(d) Calculate the lattice energy of magnesium oxide.

Additional data:

- enthalpy change of atomization for Mg(s) = +148 kJ mol^{-1}
- second ionization energy of magnesium = +1451 kJ mol^{-1}
- enthalpy change of formation of MgO(s) = −602 kJ mol^{-1}

Solution

(a) $MgO(s) \rightarrow Mg^{2+}(g) + O_2(g)$

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

The first electron affinity corresponds to the attraction of an outer electron into the outer energy level of an oxygen atom. This is an exothermic process.

The second electron affinity corresponds to a negatively charged oxide ion accepting an additional outer electron into an outer energy level despite the mutual repulsion between the negatively charged species. This is an endothermic process.

(c) Note the enthalpy change of atomization for oxygen = half the bond energy for O_2 (Figure 5.18).

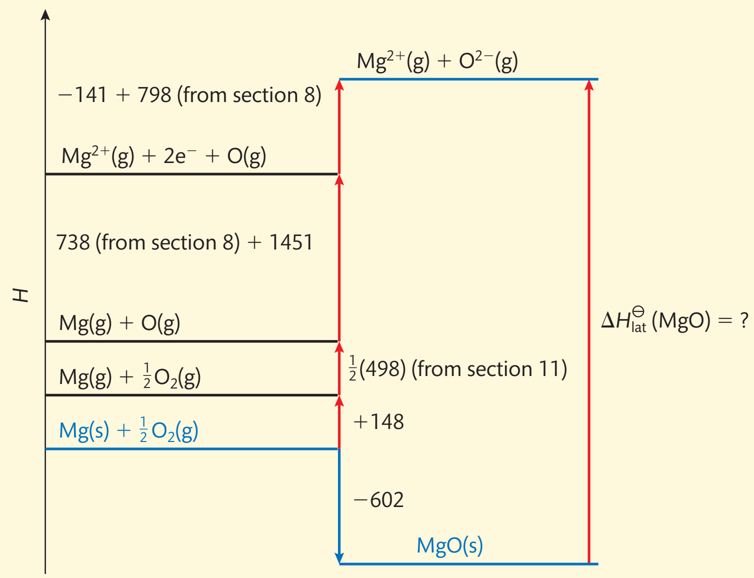


Figure 5.18 Born–Haber cycle for magnesium oxide.

(d) From the diagram we have

$$\Delta H^{\ominus}_{lat}(MgO) = +602 + 148 + ½(498) + (738 + 1451) + (753 - 142)\ kJ\ mol^{-1}$$

$$\Delta H^{\ominus}_{lat}(MgO) = +3799\ kJ\ mol^{-1}$$

Exercises

42 Identify the process which has the sign of its associated enthalpy change different from the rest.

A $Cl(g) + e^- \rightarrow Cl^-(g)$ **C** $KCl(g) \rightarrow K^+(g) + Cl^-(g)$
B $K(g) \rightarrow K^+(g) + e^-$ **D** $Cl_2(g) \rightarrow 2Cl(g)$

43 Which equation represents the electron affinity of potassium?

A $K(g) \rightarrow K^+(g) + e^-$ **B** $K(g) \rightarrow K^-(g) + e^-$ **C** $K(g) + e^- \rightarrow K^-(g)$ **D** $K^+(g) + e^- \rightarrow K(g)$

44 Identify the process which corresponds to the standard enthalpy change of atomization of bromine.

A $Br_2(g) \rightarrow 2Br(g)$ **B** $Br_2(l) \rightarrow 2Br(g)$ **C** $½Br_2(g) \rightarrow Br(g)$ **D** $½Br_2(l) \rightarrow Br(g)$

45 **(a)** Write an equation to represent the lattice energy of potassium oxide, K_2O.
(b) The Born–Haber cycle shown may be used to calculate the lattice energy of potassium oxide (Figure 5.19).

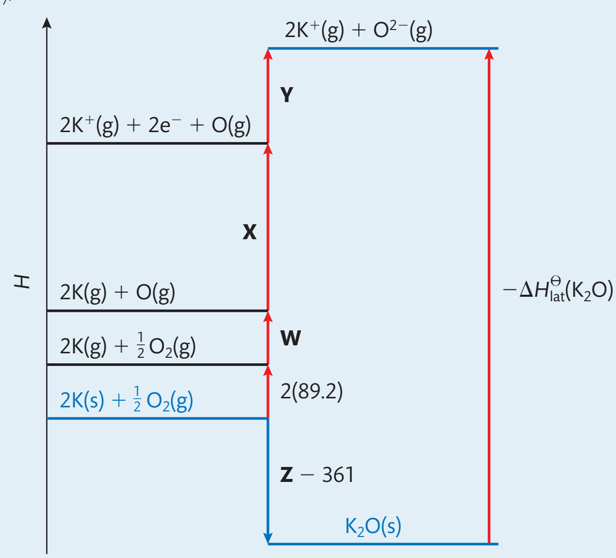


Figure 5.19 Born–Haber cycle for potassium oxide.

Identify the enthalpy changes labelled by the letters **W**, **X**, **Y** and **Z**.

(c) Use the energy cycle, and further information from sections 8 and 11 of the IB data booklet to calculate an experimental value for the lattice energy of potassium oxide.

Theoretical lattice enthalpies can be calculated from the ionic model

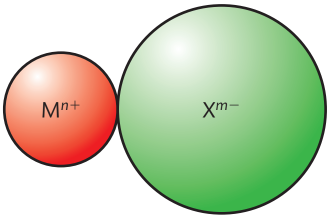


Figure 5.20 An ion pair of cation and anion. Note that both ions are spherical. This is one of the assumptions of the ionic model.

Theoretical lattice enthalpies can be calculated by assuming the crystal is made up from perfectly spherical ions. This **ionic model** assumes that the only interaction is due to electrostatic forces between the ions. Consider, for example, the formation of the ion pair in Figure 5.20.

The energy needed to separate the ions depends on the product of the ionic charges and the sum of the ionic radii.

- An increase in the ionic radius of one of the ions decreases the attraction between the ions.
- An increase in the ionic charge increases the ionic attraction between the ions.

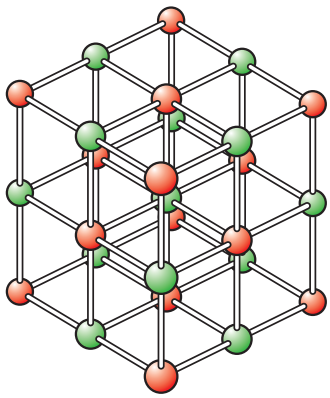


Figure 5.21 The cubic crystal consists of an ionic lattice of sodium (Na^+) and chloride (Cl^-) ions. Sodium ions are represented by red spheres, chloride ions as green spheres. Ionic crystals tend to be hard and brittle, due to the strong electrostatic forces between the constituent ions.

To calculate the lattice energy for one mole, more ion interactions need to be considered as a solid crystal forms (Figure 5.21). The overall attraction between the positive and negative ions predominates over the repulsion of ions with the same charge as ions are generally surrounded by neighbouring ions of opposite charge.

This leads to the general expression:

$$\Delta H^{\ominus}_{\text{lat}} = \frac{Knm}{R_{M^{n+}} + R_{X^{m-}}}$$

where K is a constant that depends on geometry of the lattice and n and m are the magnitude of charges on the ions. As the ionic radii ($R_{M^{n+}} + R_{X^{m-}}$) can be determined from X-ray diffraction measurements of the crystal, theoretical values can be calculated once the geometry of the solid lattice is known.

Exercises

46 Which one of the following compounds would be expected to have the highest lattice enthalpy?

A Na_2O **B** MgO **C** CaO **D** KCl

47 Theoretical lattice enthalpies can be calculated on the ionic model. The values for the sodium halides are tabulated below.

Halide	$\Delta H^{\ominus}_{\text{lat}}$/ kJ mol^{-1}
NaF	+910
NaCl	+769
NaBr	+732
NaI	+682

Explain the trend in lattice enthalpies of sodium halides.

48 The theoretical lattice enthalpies, based on the ionic model, of sodium chloride and magnesium oxide are shown below.

Compound	$\Delta H^{\ominus}_{\text{lat}}$ / kJ mol^{-1}
NaCl	+769
MgO	+3795

Explain why magnesium oxide has the higher lattice enthalpy compared to sodium chloride.

Lattice enthalpies depend on the size and charge of the ions.

The lattice enthalpies of the group 1 halides are given below. Remember from Chapter 3 that ion radius increases going down a group of the Periodic Table.

	F^-	Cl^-	Br^-	I^-
Li^+	1049	864	820	764
Na^+	930	790	754	705
K^+	829	720	691	650
Rb^+	795	695	668	632
Cs^+	759	670	647	613

The lattice enthalpies of the Group 1 halides

We can see that the lattice enthalpies decrease as the size of the cation or anion increases. LiF contains the ions with the smallest ionic radii and has the highest lattice enthalpy, and CsI contains the largest ions and the smallest lattice enthalpy.

The effect of charge is seen in the following comparisons.

	$\Delta H^{\ominus}_{lattice}$ (kJ mol^{-1})		$\Delta H^{\ominus}_{lattice}$ (kJ mol^{-1})	Explanation of difference
NaCl	1049	$MgCl_2$	2540	$MgCl_2$ has more than double the lattice enthalpy of NaCl as Mg^{2+} has double the charge of Na^+ and a smaller ionic radius.
CaF_2	2651	CaO	3401	CaO has higher lattice enthalpy than CaF_2 as O^{2-} has double the charge of F^-. The value is less than double as O^{2-} has a larger ionic radius than F^-

So overall, we can see that lattice enthalpies are greater when ionic compounds form between smaller, more highly charged ions, that is those with the greatest charge density.

Lattice enthalpy decreases with increasing ion radius and increases with increasing ion charge.

NATURE OF SCIENCE

The trend in lattice enthalpies described here does not apply universally. A comparison of the lattice enthalpies of AgI and NaI shows that AgI has the larger lattice enthalpy, despite Ag^+ having a larger ion radius than Na^+. So the bonding in AgI is stronger than accounted for by a purely ionic model. We know from Chapter 4 that the covalent character of a bond increases as the difference in electronegativity decreases, and in AgI the bonding is intermediate in character. The additional contribution from covalent bonding accounts for the higher than expected lattice enthalpy.

Compound	Ionic radius of M^+/ 10^{-12} m	$\Delta H^{\ominus}_{lat}$/kJ mol^{-1} (Born–Haber)
NaI	102	705
AgI	115	892

The enthalpy change of solution is the enthalpy change when one mole of a solute is dissolved in a solvent to infinite dilution under standard conditions of temperature (298 K) and pressure (1.0×10^5 Pa).

Exercises

49 Identify the compound which has the greatest lattice energy.

A sodium chloride
B potassium chloride
C magnesium bromide
D calcium bromide

50 The lattice enthalpy values for sodium fluoride and magnesium chloride are shown below.

$$NaF(s) \quad \Delta H^{\ominus} = +930 \text{ kJ mol}^{-1}$$
$$MgCl_2(s) \quad \Delta H^{\ominus} = +2540 \text{ kJ mol}^{-1}$$

Identify which of the following statements help(s) to explain the relative value of the lattice enthalpies.

I The ionic charge of sodium is less than that of magnesium.
II The ionic radius of the chloride is larger than that of flouride.

A I only **B** II only **C** I and II **D** Neither I nor II

51 The lattice enthalpies of silver bromide and sodium bromide are given below.

	$\Delta H^{\ominus}$/ kJ mol^{-1}		$\Delta H^{\ominus}$/ kJ mol^{-1}
AgBr	905	KBr	691

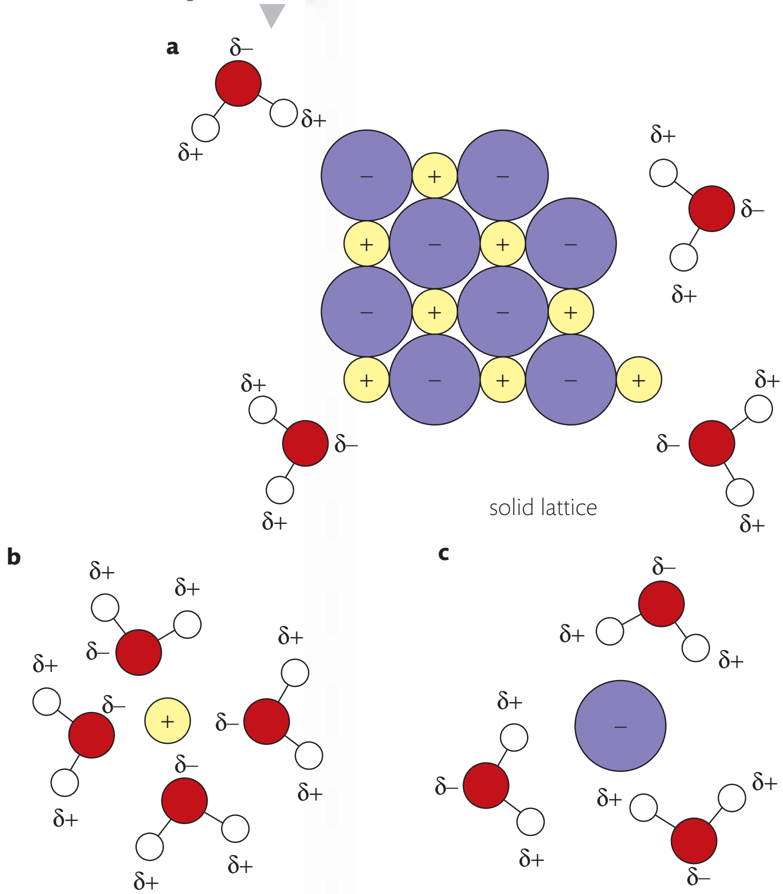
Explain the relative values of the lattice enthalpies with reference to the bonding.

Enthalpies of solution

In exercise 14 you were asked to calculate the enthalpy change that occurs when ammonium chloride is added to 1 dm^3 of water:

$$NH_4Cl(s) \xrightarrow{H_2O} NH_4^+(aq) + Cl^-(aq) \qquad \Delta H^{\ominus}_{sol} = +14.78 \text{ kJ mol}^{-1}$$

Figure 5.22 Ionic compounds generally dissolve in the polar solvent water. (a) Ionic lattice are often broken up by polar water molecules. At the contact surface, partial charges in the water molecules are attracted to ions of opposite charge in the lattice, which may cause them to dislodge from their positions. (b) The partially negatively oxygen atoms in the polar water molecules are attracted to the positive ions. (c) The partially positively hydrogen atoms in the polar water molecules are attracted to the negative ions.



As the exercise demonstrates, these enthalpies of solutions can calculated by measuring the temperature change in solution. As the interaction between the solute and the solvent water molecules depends on the concentration of the solution; the enthalpy of solution strictly refers to the ideal situation of infinite dilution. The enthalpy of solution is obtained practically by measuring enthalpy changes for solutions with increasing volumes of water until a limit is reached.

Ionic compounds like NaCl and NH_4Cl dissolve very readily in water as the ions are strongly attracted to the polar solvent water. The partial positive charge on the hydrogen atoms in the water molecules are attracted to the negative ions and the partial negative change of the oxygen is attracted to the positive ions.

Ions separated from the lattice in this way become surrounded by water molecules and are said to be **hydrated**. The strength of interaction between the polar water molecules and the separated ions is given by their **hydration enthalpies**.

The hydration enthalpy of an ion depends on the attraction between the ions and the polar water molecules

The enthalpy of hydration of a compound is the enthalpy change that occurs when one mole of its constituent gaseous ions is dissolved to form an infinitely dilute solution. The enthalpy of hydration of individual ions, although more useful, cannot generally be measured directly; as positive ions and negative ions are both present in a compound and it is difficult to disentangle the contribution of each ion.

This problem is resolved by measuring the enthalpy of hydration of the H^+ ion separately using an indirect spectral technique:

$$H^+(g) \rightarrow H^+(aq) \qquad \Delta H^\ominus_{hyd} = -1130 \text{ kJ mol}^{-1}$$

and then combining this value with the hydration enthalpy of different compounds to obtain values for individual ions.

The enthalpy change of hydration of an ion is the enthalpy change that occurs when one mole of gaseous ions is dissolved to form an infinitely dilute solution of one mole of aqueous ions.

$$M^{n+}(g) \rightarrow M^{n+}(aq) \qquad \Delta H^\ominus_{hyd}(M^{n+})$$

$$X^{m-}(g) \rightarrow X^{m-}(aq) \qquad \Delta H^\ominus_{hyd}(X^{m-})$$

As there is a force of attraction between the ions and the polar water molecules, it is an exothermic process and the enthalpy changes are negative.

Consider the following hydration energies of the Group 1 cations and Group 17 anions.

Cations	$\Delta H^\ominus_{hyd}$ / kJ mol^{-1}	Anions	$\Delta H^\ominus_{hyd}$ / kJ mol^{-1}
Li^+	−538	F^-	−504
Na^+	−424	Cl^-	−359
K^+	−340	Br^-	−328
Rb^+	−315	I^-	−287

The values become less exothermic as the groups are descended and the ionic radius increases. The electrostatic attraction between the ions and the water molecule decreases with increasing distance.

The hydration enthalpies of the ions are approximately inversely proportional to the ionic radii:

$$\Delta H^\ominus_{hyd} \approx \frac{-A}{R_{ionic}}$$

where A is a constant. So the smallest ion, Li^+, has the most exothermic hydration ion and the largest ion, I^-, has the least exothermic value.

Similarly across periods 3: the hydration enthalpies of the metal become more exothermic as the ionic charge increases and the ionic radius decreases. Both changes lead to increased attraction between the positive ion and the partially negatively charged oxygen atoms in the water molecules.

This suggests a relationship of the form:

$$\Delta H^\ominus_{hyd} \approx -Bn / R_{ionic}$$

where n is the charge of the ion and B is a constant. Al^{3+} has the most exothermic hydration enthalpy because it has the highest charge and the smallest radius.

The heat produced when water is added to anhydrous copper(II) sulfate (white) is enough to produce steam and disturb the powder. The hydrated ions can remain in the solid lattice as blue crystals or form a solution if more water is added.

The enthalpy change of hydration of an ion is the enthalpy change that occurs when one mole of gaseous ions is dissolved to form an infinitely dilute solution of one mole of aqueous ions under standard conditions of temperature and pressure.

CHALLENGE YOURSELF

7 Ag^+ has a more exothermic enthalpy of hydration than Na^+ but has a larger ionic radius. Suggest an explanation for this.

Cations	$\Delta H^{\ominus}_{hyd}$ / kJ mol^{-1}
Na^+	−424
Mg^{2+}	−1963
Al^{3+}	−4741

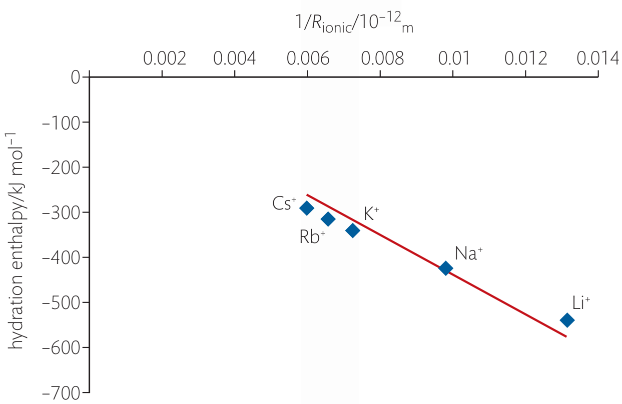


Figure 5.23 The hydration enthalpies of the Group 1 metal ions plotted against $1/R_{ionic}$. The hydration enthalpies of the ions are approximately inversely proportional to the ionic radii: $\Delta H^{\ominus}_{hyd} \approx -A/R_{ionic}$.

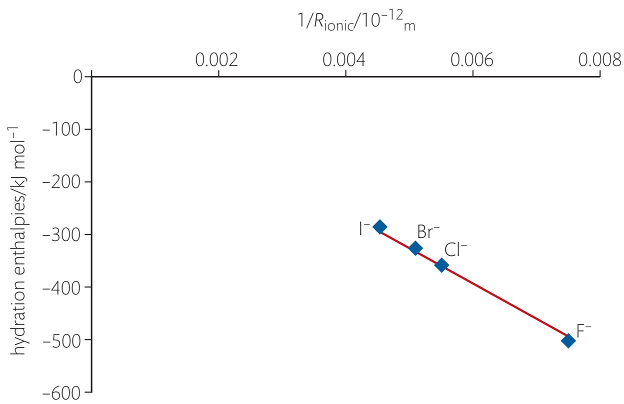


Figure 5.24 The hydration enthalpies of the halides (Group 17) ions plotted against $1/R_{ionic}$. The hydration enthalpies of the ions are approximately inversely proportional to the ionic radii: $\Delta H^{\ominus}_{hyd} \approx -A/R_{ionic}$.

Calculation of enthalpy changes in aqueous solution

Full details of how to carry out this experiment with a worksheet are available online.

The enthalpy change of solution is related to the lattice enthalpy and the hydration enthalpies of the constituent ions

The solution of a substance can be understood by imagining that the solid is first sublimed into gaseous ions, which are then plunged into water.

$$\begin{aligned}\Delta H^{\ominus}_{sol}(\text{NaCl}) &= \Delta H^{\ominus}_{lattice}(\text{NaCl}) + \Delta H^{\ominus}_{hyd}(\text{Na}^+) + \Delta H^{\ominus}_{hyd}(\text{Cl}^-)\\ &= +790 - 424 - 359 \text{ kJ mol}^{-1}\\ &= +7 \text{ kJ mol}^{-1}\end{aligned}$$

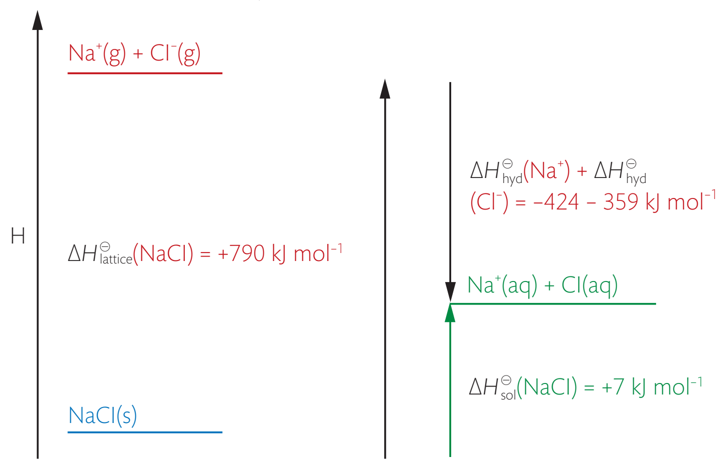


Figure 5.25 An energy cycle which relates the enthalpy of solution of an ionic compound to its lattice enthalpy and the hydration enthalpies of its constituent ions.

The value obtained by the energy cycle should be compared with the value in the data booklet in section 19, which is $\Delta H^{\ominus}_{sol}(\text{NaCl}) = +3.88$ kJ mol^{-1}. The disagreement between the two values illustrates a general problem when a small numerical value is calculated from the difference of two large numerical values.

Exercises

52 Discuss the relative enthalpies of hydration of the K^+ and F^- ions in relation to their ionic radii.

53 **(a)** Use an energy cycle to calculate the enthalpy of solution of potassium chloride from data in sections 18 and 20 of the IB data booklet.

(b) Calculate the % inaccuracy of your value by comparing with the value in section 19 and comment on the disagreement between the two values.

NATURE OF SCIENCE

A UK newspaper, in an attempt to gauge scientific literacy amongst some prominent public figures asked the question: Why does salt dissolve in water?

Here are some of their answers:

Geologist/ TV presenter: The chlorine joins with the water and the sodium ions float free.

Writer/Critic broadcaster: It must be because it absorbs water to the point at which it disintegrates.

TV Presenter/Poet: It forms another compound.

Cultural historian: The sodium molecules join up with the hydrogen and oxygen molecules.

Brain scientist: Because sodium and chloride disassociate and H_2O is hydrogen and oxygen.

Political journalist: Because it's less dense.

Human fertility expert and science TV presenter: It's to do with ions isn't it? Do you know, I'm not sure I can really explain it.

Author, broadcaster: No idea.

The article argued that despite the importance of science to people's lives most adults have very little understanding of how the world works. An understanding of the nature of science is vital when society needs to make decisions involving scientific findings and issues. Scientists are well placed to explain to the public their issues and findings, but outside their specializations, as some of these responses show, they may be no more qualified than ordinary citizens to advise others on scientific issues.

NATURE OF SCIENCE

Making quantitative measurements which can be replicated improves the reliability of data but it should not be forgotten that there are still significant discrepancies in values for enthalpy terms like lattice enthalpies or hydration enthalpies from different sources due to the difficulty of measuring the values directly, and these are being continually revised. Theoretical values are also available based on different models. Care should be taken when comparing data from different sources.

CHALLENGE YOURSELF

8 So why does salt dissolve in water?

15.2 Entropy and spontaneity

Understandings:

- Entropy (S) refers to the distribution of available energy among the particles. The more ways the energy can be distributed the higher the entropy.
- Gibbs free energy (G) relates the energy that can be obtained from a chemical reaction to the change in enthalpy (ΔH), change in entropy (ΔS), and absolute temperature.

  Guidance
  ΔG is a convenient way to take into account both the direct entropy change resulting from the transformation of the chemicals, and the indirect entropy change of the surroundings as a result of the gain/loss of heat energy. Examine various reaction conditions that affect ΔG.
- Entropy of gas > liquid > solid under same conditions.

Applications and skills:

- Prediction of whether a change will result in an increase or decrease in entropy by considering the states of the reactants and products.
- Calculation of entropy changes (ΔS) from given values ($S^\ominus$).
- Application of $\Delta G^\ominus = \Delta H^\ominus - T\Delta S^\ominus$ in predicting spontaneity and calculation of various conditions of enthalpy and temperature that will affect this.

  Guidance
  Thermodynamic data are given in section 12 of the data booklet.
- Relation of ΔG to position of equilibrium.

Entropy is a more complete direction of change

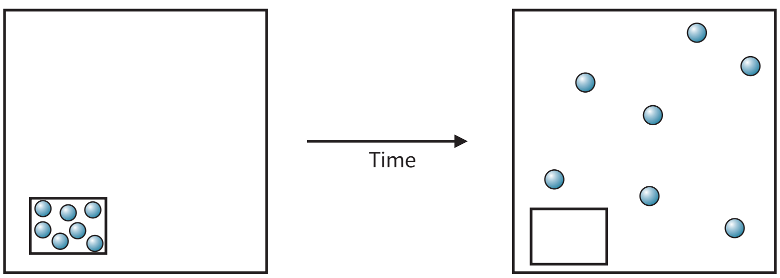
If a bottle of a carbonated drink is left open, we expect it to find it ‘flat’ after a couple of days. The carbon dioxide escapes from solution and diffuses or spreads out into the wider surroundings. We do not expect all the carbon dioxide to return at a later date. In a similar way, a hot cup of coffee will cool down and lose some heat to the surroundings. The heat will not return. Both these examples illustrate a general principle: energy and matter tend to disperse and the universe becomes more disordered. These are both examples of **spontaneous change**; they occur naturally without the need to do work. We can reverse the natural tendency of change but only at the expense of doing work. Similarly, sodium and chlorine have a natural tendency to react together to form sodium chloride. We can reverse this process and split sodium chloride into its constituents, but only at the expense of using valuable electrical energy, as discussed in Chapter 9.

Spontaneous changes occur without the need to do work. A spontaneous reaction occurs without adding energy (beyond that required to overcome the activation energy barrier – see Chapter 6).

Bubbles rise and escape from a carbonated drink. This illustrates a general principle: matter and energy tend to disperse and become more disordered. Such everyday experiences can be expressed more precisely when the degree of disorder of a system is quantified by its **entropy** (S). Entropy (S) refers to the distribution of available energy among the particles. The more ways the energy can be distributed the higher the entropy. Ordered states, with a small energy distribution are said to have low entropy; disordered states, with a high energy distribution, have high entropy. As time moves forward, matter and energy become more disordered, and the total entropy of the universe increases.

Entropy (S) refers to the distribution of available energy among the particles.

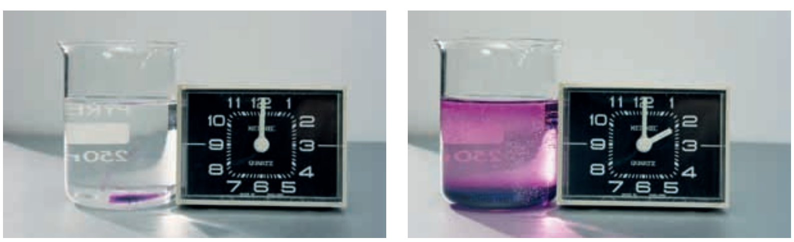
This is an expression of the Second Law of Thermodynamics, which is one of the most important laws in science (Figure 5.26).



All gas particles are concentrated in small volume. This is an ordered state with low entropy.

The gas particles are dispersed throughout the room. This is a disordered state with high entropy.

Figure 5.26 Particles naturally adopt a more disordered state with higher entropy. A mixed up system allows the energy to be distributed in more ways than one in which different particles are separated. This illustrates the Second Law of Thermodynamics: spontaneous processes always occur with an increase of entropy in the universe.



A piece of potassium manganate(VII) was placed at the bottom of the beaker at 12 o’clock. Two hours later it has diffused throughout the water:

$KMnO_4(s) \rightarrow K^+(aq) + MnO_4^-(aq)$

The aqueous ions have higher entropy than the solid crystal. Entropy increases with time.

NATURE OF SCIENCE

The Second Law of Thermodynamics has been called the most fundamental law in all of science and some, including Albert Einstein, have argued that it is one of the few laws which will never be overthrown. It is important, however, to understand that it is a statement of experience which cannot be proved. It has been shown to apply to all known spontaneous changes. It is not impossible for the disordered arrangement in Figure 5.26 to spontaneously change into the more ordered arrangement, but it is statistically unlikely that the motion of all the particles would be spontaneously coordinated to find them all back in the box at the same instant. This is particularly true given that even a small volume of gas contains a very large number of molecules. The Second Law of Thermodynamics was first formulated to explain how steam engines work, but is now used to explain the big bang, and the expansion of the universe. It is one of the most fundamental scientific laws, and it has been said that 'not knowing the Second Law of Thermodynamics is like never having read a work of Shakespeare'.

To get a better understanding of the statistical nature of the Second Law developed by Ludwig Boltzmann, we need to adopt a statistical approach based on the number of different microscopic arrangements of the same macroscopic state.

Consider the example of an idealized hot cup of coffee with all the stored heat 4*Q* localized in the four cells of the cup. Each cell can only hold a maximum of one unit *Q* of energy. There is only one microscopic state consistent with this macroscopic state.

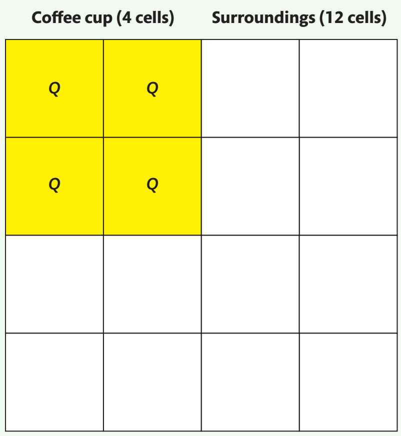


Figure 5.27 The hot cup of coffee is a low entropy state: $W = 1$.

We now allow one unit of heat *Q* to flow from the cup to the surroundings. We have the possibilities of four different microscopic states with 3*Q* in the cup, as we can have one of any four boxes empty and twelve different microscopic states with unit *Q* spread around the room, in any of twelve possible cells. The mixed-up state has more possible distributions and so a higher entropy.

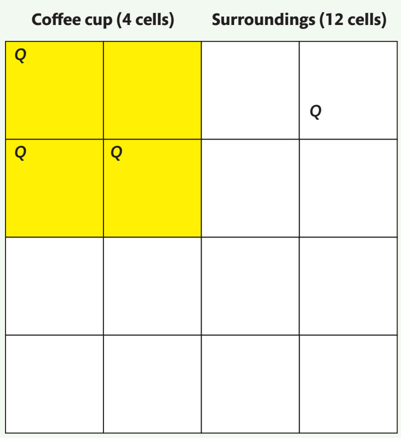


Figure 5.28 A cooler cup of coffee. There are 4×12 different states with 3*Q* in the cup 1*Q* in the surroundings. $W = 48$. The entropy has increased.

In this approach:

$$W(\text{total}) = W(\text{surroundings}) \times W(\text{coffee cup})$$

continued ...

TOK

Which ways of knowing have been used to construct the Second Law of Thermodynamics? To what extent is certainty attainable within each of the ways of knowing or within each of the areas of knowledge?

Ludwig Boltzmann (1844–1906). Boltzmann extended the kinetic theory of gases and used the mechanics and statistics of large numbers of particles to give definitions of heat and entropy. Boltzmann suffered life-long depression and he committed suicide at age 62. Boltzmann's formula is engraved on his tombstone.

NATURE OF SCIENCE

continued ...

A more convenient approach, adopted by Ludwig Boltzmann, is to use a function (S) based on the natural logarithms of W:

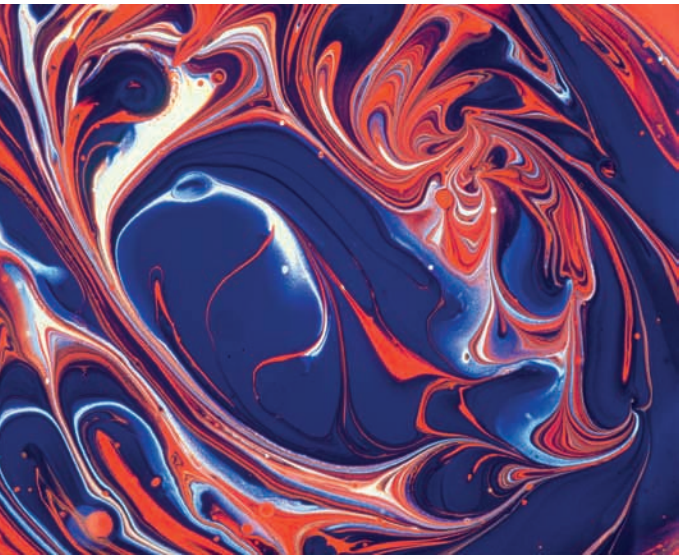
$$S = k \ln W \text{ with } k \text{ being a constant}$$

This gives the property:

$$S(\text{total}) = k \ln W(\text{total}) = k \ln W(\text{coffee cup}) \times W(\text{surroundings})$$
$$= k \ln W(\text{coffee cup}) + k \ln W\, W(\text{surroundings})$$
$$S(\text{total}) = S(\text{coffee cup}) + S(\text{surroundings})$$

The function S is consistent with our previous interpretation of entropy, with the Boltzmann constant k.

The same diagrams and mathematics can essentially be used to explain why perfume molecules spread around a room. The use of abstract mathematics may make the subject more challenging but it does broaden the scope of scientific understanding.



The entropy of the universe increases as the red and blue paints are mixed.

The power of the Second Law of Thermodynamics is that it offers an explanation for all change. For example, a hot cup of coffee naturally cools when left, for essentially the same reason that a gas disperses – the energy disperses so as to lead to the situation with the widest energy distribution. This change results in an increase in entropy of the universe. Another example is seen in the mixing of different colours of paint.

Predicting entropy changes

As the solid state is the most ordered state and the gaseous state the most disordered, we can predict that the entropy of a system increases as a solid changes to a liquid and as a liquid changes to a gas.

Similarly, doubling the number of particles present in a sample also increases the opportunity for a system to become disordered and for its entropy to increase. More precisely, it can be shown that doubling the amount of a substance doubles the entropy. Similar considerations allow us to predict the entropy changes of the system (ΔS) during any physical or chemical change. Some examples are tabulated below.

Change	ΔS
solid → liquid	increase (+)
solid → gas	increase (+)
liquid → gas	increase (+)
liquid → solid	decrease (–)
gas → solid	decrease (–)
gas → liquid	decrease (–)

When predicting entropy changes, the change due to a change in the number of particles in the gaseous state is usually greater than any other possible factor.

Worked example

Predict the entropy change ΔS for the following changes.

(a) $Br_2(l) \rightarrow Br_2(g)$
(b) $2Cu(s) + O_2(g) \rightarrow 2CuO(s)$
(c) $Ag^+(aq) + Br^-(aq) \rightarrow AgBr(s)$
(d) $H_2(g) + Cl_2(g) \rightarrow 2HCl(g)$
(e) $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$
(f) $Cu^{2+}(aq) + Zn(s) \rightarrow Cu(s) + Zn^{2+}(aq)$

Solution

(a) One mole of liquid is changing into one mole of gas. There is an increase in disorder and an increase in entropy. ΔS is positive.

(b) There is decrease in the number of moles of gas during the reaction. This leads to a reduction in disorder in the products. ΔS is negative.

(c) There are two moles of aqueous ions on the left-hand side and one mole of solid on the right-hand side. There is a decrease in disorder and there will be a decrease in entropy. ΔS is negative.

(d) There are two moles of gas in the reactants and in the products. There is no significant change in disorder. The entropy change will be close to zero. $\Delta S \approx 0$.

(e) There are three moles of gas in the reactants and one mole of gas in the products. There is a decrease in disorder and so there will be a decrease in entropy. ΔS is negative.

(f) One mole of solid and one mole of aqueous ions are changed into one mole of solid and one mole of aqueous ions. The entropy change will be close to zero. $\Delta S \approx 0$.

TOK

Entropy is a technical term which has a precise meaning. How important are such technical terms in different areas of knowledge?

Exercises

54 Identify the process expected to have a value of ΔS closest to zero?

A $C_2H_4(g) + H_2(g) \rightarrow C_2H_6(g)$
B $H_2(g) + Cl_2(g) \rightarrow 2HCl(g)$
C $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$
D $H_2O(l) \rightarrow H_2O(g)$

55 Identify the processes which have an associated increase in entropy.

I $Br_2(g) \rightarrow Br_2(l)$
II $Br_2(g) \rightarrow 2Br(g)$
III $KBr(s) \rightarrow K^+(aq) + Br^-(aq)$

A I and II **B** I and III **C** II and III **D** I, II, and III

56 Which is the best description of the entropy and enthalpy changes accompanying the sublimation of iodine: $I_2(s) \rightarrow I_2(g)$?

A ΔS +, ΔH +, reaction is endothermic
B ΔS +, ΔH –, reaction is exothermic
C ΔS –, ΔH +, reaction is endothermic
D ΔS –, ΔH –, reaction is exothermic

57 Identify the reaction which has the largest increase in entropy?

A $AgNO_3(aq) + NaCl(aq) \rightarrow AgCl(s) + NaNO_3(aq)$
B $H_2(g) + Cl_2(g) \rightarrow 2HCl(g)$
C $C_2H_4(g) + H_2(g) \rightarrow C_2H_6(g)$
D $Mg(s) + H_2SO_4(aq) \rightarrow MgSO_4(aq) + H_2(g)$

58 Predict the entropy change ΔS for the following reactions.

(a) $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$
(b) $3Fe(s) + 4H_2O(g) \rightarrow Fe_3O_4(s) + 4H_2(g)$
(c) $Ba(OH)_2{\cdot}8H_2O(s) + 2NH_4SCN(s) \rightarrow Ba(SCN)_2(aq) + 2NH_3(aq) + 10H_2O(l)$

Explanations to changes in entropy must refer to changes in state and the number of moles. Change in number of moles of gas is often the key factor.

Absolute entropy

The absolute entropy of different substances can be calculated. As entropy depends on the temperature and pressure, tabulated entropy values refer to standard conditions and are represented as $S^{\ominus}$. Some values are shown in the table below.

A perfectly ordered solid at absolute zero has zero entropy. All other states, which are more disordered, have positive entropy values.

Substance	Formula	$S^{\ominus}$ / J K^{-1} mol^{-1}
hydrogen	$H_2(g)$	+131
oxygen	$O_2(g)$	+205
nitrogen	$N_2(g)$	+191
graphite	C(graphite)	+5.7
methane	$CH_4(g)$	+186
ammonia	$NH_3(g)$	+193
water	$H_2O(l)$	+70.0
steam	$H_2O(g)$	+188.8
ethane	$C_2H_6(g)$	+230
ethene	$C_2H_4(g)$	+220
ethanol	$C_2H_5OH(l)$	+161

Section 12 of the IB data booklet has a list of values for organic compounds. The units will be explained later.

As expected, the entropy values increase in the order: solid, liquid, gas. It should be noted that all entropy values are positive. A perfectly ordered solid at absolute zero has an entropy of zero. All other states, which are more disordered, have positive entropy values.

Calculating entropy changes

The entropy change of the system during a reaction can be calculated from the differences between the total entropy of the products and the total entropy of the reactants.

$$\sum S^{\ominus}(\text{reactants}) \xrightarrow{\Delta S^{\ominus}_{\text{reaction}}} \sum S^{\ominus}(\text{products})$$

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

The strategy and potential pitfalls of solving problems related to entropy change are similar to those discussed when calculating enthalpy changes.

Worked example

Calculate the entropy change for the hydrogenation of ethene

$$C_2H_4(g) + H_2(g) \rightarrow C_2H_6(g)$$

using the entropy values given in section 12 in the IB data booklet and the table above.

Solution

When asked to calculate an entropy change it is always a good idea to start by predicting the sign of $\Delta S^{\ominus}_{\text{reaction}}$.

$$C_2H_4(g) + H_2(g) \rightarrow C_2H_6(g)$$

Two moles of gas are converted to one mole of gas: there will be a decrease in disorder and a decrease in entropy. So $\Delta S^{\ominus}_{\text{reaction}}$ will be negative.

Write down the equation with the corresponding entropy values below:

$C_2H_4(g)$	+	$H_2(g)$	$\rightarrow$	$C_2H_6(g)$	
220		131		230	$S^{\ominus}$/ J K^{-1} mol^{-1}

$$\Delta S^{\ominus}_{\text{reaction}} = \sum S^{\ominus}(\text{products}) - \sum S^{\ominus}(\text{reactants})$$
$$= 230 - (220 + 131) = -121 \text{ J K}^{-1}\text{ mol}^{-1}$$

Exercises

59 Sketch a graph to show how the entropy of a solid changes as the temperature increases.

60 Calculate the entropy change ΔS for the Haber process, shown below, using tabulated standard molar entropies at 25 °C.

$$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$$

61 Calculate the standard entropy change associated with the formation of methane from its elements.

Spontaneity

This discussion of the direction of change based on entropy changes is incomplete. Earlier in the chapter, we suggested that enthalpy changes could be used as an indicator of the direction of change; but this left endothermic reactions unexplained. Similarly, we have also discussed the need for the entropy to increase during spontaneous changes, but we have seen that many reactions occur with a decrease of entropy. This section resolves these issues.

Entropy changes of the surroundings

So far, our discussion of entropy has focussed on the entropy of the substances present in the system. To consider the total entropy change of a reaction, we must also consider the accompanying entropy change in the surroundings.

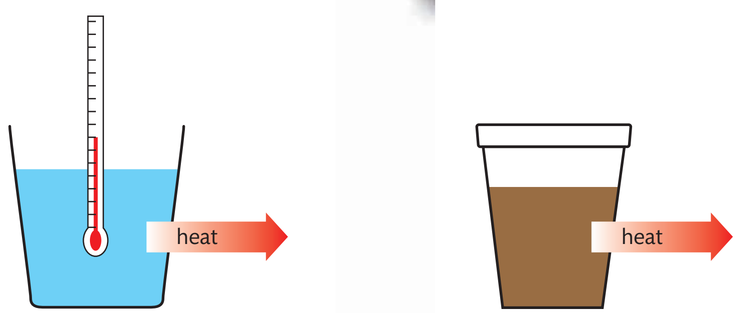
Consider again the reaction between zinc and copper sulfate, discussed earlier.

$$Cu^{2+}(aq) + Zn(s) \rightarrow Cu(s) + Zn^{2+}(aq) \qquad \Delta H^{\ominus}_{\text{reaction}} = -217 \text{ kJ mol}^{-1}, \Delta S^{\ominus}_{\text{reaction}} \approx 0$$

How does this reaction increase the total entropy of the universe?

The key to answering this question is an appreciation that adding heat to the surroundings results in a general dispersal of heat into the surrounding universe. The reaction can be compared to the cooling of a hot cup of coffee discussed earlier. Both result in an increase in total entropy as heat is dispersed.

The change of the entropy of the surroundings, ΔS(surroundings), can be calculated from the enthalpy change in the system, ΔH(system), and the absolute temperature, T.



The entropy of the surroundings increases as the heat given out by the reaction increases the disorder of the surroundings.

The entropy of the surroundings increases as the heat given out by the hot coffee increases the disorder of the surroundings.

Figure 5.29 Both an exothermic reaction and a cooling coffee cup increase the entropy of the universe.

The change in entropy of the surroundings is proportional to $-\Delta H$(system)

We have seen that exothermic reactions, with a negative value for ΔH(system) result in an increase in the entropy of the surroundings. This explains the inclusion of the negative sign when relating ΔH(system) to ΔS(surroundings).

$$\Delta S(\text{surroundings}) \propto -\Delta H(\text{system})$$

We are now in a position to understand why exothermic reactions are generally more common than endothermic reactions. The key is not the decrease in energy of the system but the associated increase in entropy of the surroundings.

The change in entropy is inversely proportional to the absolute temperature

To understand the relationship between the enthalpy change of reaction and the entropy change of the surroundings, it is helpful to recognize that the impact of a transfer of heat to the surroundings depends on the current state of disorder in the surroundings. If the surroundings are hot, the addition of a little extra heat makes little difference to the disorder. But if the surroundings are cold, the same amount of heat could cause a dramatic change in entropy. This explains the inclusion of absolute temperature, T, in the denominator in the expression:

$$\Delta S(\text{surroundings}) \propto 1/T$$

The impact of an addition of heat depends on the present state of disorder, as indicated by the absolute temperature.

A busy street is a 'hot' and disordered environment; a quiet library is a 'cold' and ordered environment. Which do you think would cause more disruption: sneezing in a busy street or in a quiet library?

ΔS(surroundings) and an explanation of the units of entropy

An expression consistent with the above discussion is

$$\Delta S(\text{surroundings}) = \frac{-\Delta H(\text{system})}{T} \ (T \text{ must be measured in K})$$

For the displacement reaction discussed, at $T = 25\ °\text{C} = 298\ \text{K}$

$$\Delta S(\text{surroundings}) = -\frac{-217\ \text{kJ mol}^{-1}}{298\ \text{K}} = +0.729\ \text{kJ K}^{-1}\ \text{mol}^{-1} = 729\ \text{J K}^{-1}\ \text{mol}^{-1}$$

We can now see the origins of the units used for entropy in the values tabulated earlier.

Entropies are generally expressed in the units J K^{-1} mol^{-1}.

These are consistent with its characterization as a distribution of available energy.

If a system were at absolute zero, an additional small amount of heat energy would lead to an infinite increase in entropy. Such a state is impossible. Absolute zero can never be achieved.

Calculating total entropy changes and understanding endothermic reactions

The Second Law of Thermodynamics tells us that for a spontaneous change:

$$\Delta S(\text{total}) = \Delta S(\text{system}) + \Delta S(\text{surroundings}) > 0$$

Substitute for ΔS(surroundings) from the expression developed earlier:

$$\Delta S(\text{total}) = \Delta S(\text{system}) - \frac{\Delta H(\text{system})}{T} > 0$$

This equation allows us to understand how endothermic reactions can occur. Endothermic reactions occur if the change of entropy of the system can compensate for the negative entropy change of the surroundings produced as the heat flows from the surroundings to the system. For example, the strongly endothermic reaction

$$Ba(OH)_2{\cdot}8H_2O(s) + 2NH_4SCN(s) \rightarrow Ba(SCN)_2(aq) + 2NH_3(aq) + 10H_2O(l)$$

is possible as there is a very large increase in disorder and entropy of the system. Three moles of solid are converted to ten moles of liquid and three moles of compounds in aqueous solution.

This emphasizes a general point. We must consider the universe (i.e. both the system and the surroundings) when applying the Second Law of Thermodynamics. Order may increase in local areas but only at the expense of greater disorder elsewhere in the universe. For chemical reactions, neither ΔH(system) nor ΔS(system) alone can reliably be used to predict the feasibility of a reaction.

Such local manifestations of order as the development of life, and the construction of beautiful buildings, are only possible at the expense of greater disorder generated elsewhere in the universe.

Photosynthesis is a remarkable reaction. There is a decrease in entropy of the system as the particles adopt more ordered structures and the reaction is endothermic as the system absorbs energy:

$$6CO_2(g) + 6H_2O(l) \rightarrow C_6H_{12}O_6(g) + 6H_2O(l)$$

This does not break the Second Law of Thermodynamics as the increase in entropy of the Sun more than compensates for the local decrease in entropy in a green leaf.

Gibbs free energy is a useful accounting tool

We have seen that for chemical reactions neither ΔH(system) nor ΔS(system) alone can reliably be used to predict the feasibility of a reaction. The ultimate criterion for the feasibility of a reaction is:

$$\Delta S(\text{total}) = \Delta S(\text{system}) - \frac{\Delta H(\text{system})}{T} > 0$$

This expression can be tidied up. Multiplying by T (as they are always positive)

$$T\Delta S(\text{total}) = T\Delta S(\text{system}) - \Delta H(\text{system}) > 0$$

Multiplying by −1 and reversing the inequality:

$$-T\Delta S(\text{total}) = -T\Delta S(\text{system}) + \Delta H(\text{system}) < 0$$

ΔG(system) must be negative for a spontaneous process.

This combination of entropy and enthalpy of a system gives a new function known as the **Gibbs free energy** (ΔG(system)):

$$\Delta G(\text{system}) = \Delta H(\text{system}) - T\Delta S(\text{system}) < 0$$

That is, ΔG(system) must be negative for a spontaneous process.

Whereas ΔH(system) is a measure of the *quantity* of heat change during a chemical reaction, ΔG(system) gives a measure of the *quality* of the energy available. It is a measure of the energy which is free to do useful work rather than just leave a system as heat. Spontaneous reactions have negative free energy changes because they can do useful work. Josiah Willard Gibbs (1839–1903) was the first to develop this concept.

Using ΔG(system) to predict the feasibility of a change

We can use the expression ΔG(system) to predict how a system changes as the temperature is changed. We generally assume that both the enthalpy and entropy changes of the system do not change with temperature.

Using the expression:

$$\Delta G(\text{system}) = \Delta H(\text{system}) - T\Delta S(\text{system}) < 0$$

we can think of the temperature, T, as a tap which adjusts the significance of the term ΔS(system) in determining the value of ΔG(system).

- At low temperature:

  $\Delta G(\text{system}) \approx \Delta H(\text{system})$, as $T\Delta S(\text{system}) \approx 0$

  That is, all exothermic reactions can occur at low temperatures.
- At high temperature:

  $\Delta G(\text{system}) \approx -T\Delta S(\text{system})$, as the temperature is sufficiently high to make the term ΔH(system) negligible.

  This means all reactions which have a positive value of ΔS(system) can be feasible at high temperatures even if they are endothermic.

Worked example

(a) Give an equation for the boiling of water.

(b) Predict a sign for the enthalpy change and entropy change for this process.

(c) Predict a value for the sign of ΔG at low and high temperatures.

(d) Suggest why water boils at 100 °C.

(e) Use the entropy values in the table on page 252 to calculate the entropy change for this process.

(f) Use the data below to calculate the enthalpy change for the process.

	$\Delta H_f^\ominus$ / kJ mol^{-1}
$H_2O(l)$	–286
$H_2O(g)$	–242

(g) Deduce the boiling point of water from your calculations. Describe any assumptions you have made.

Solution

(a)

$$H_2O(l) \rightarrow H_2O(g)$$

(b) As there is an increase in moles of gas, ΔS(system) is positive. The process involves the breaking of intermolecular (hydrogen) bonds so ΔH(system) is positive.

(c) At low temperature: ΔG(system) ≈ ΔH(system) and so is positive.

At high temperature: ΔG(system) ≈ $-T\Delta S$(system) and so is negative.

(d) The change only occurs at higher temperatures where ΔG is negative.

$$\Delta G = 0 \text{ at } 100\ °\text{C}$$

(e)

$$\begin{array}{ccc} H_2O(l) & \rightarrow & H_2O(g) \\ +70.0 & & +188.8 \end{array}$$

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

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

$$= +188.8 - (70) = +118.8 \text{ J K}^{-1}\text{ mol}^{-1}$$

(f)

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

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

(g) At the boiling point: $\Delta G(\text{system}) = \Delta H(\text{system}) - T\Delta S(\text{system}) = 0$

$$T = \frac{\Delta H(\text{system})}{\Delta S(\text{system})}$$

$$T = \frac{44 \text{ kJ mol}^{-1}}{118.8 \times 10^{-3} \text{ kJ K}^{-1}\text{ mol}^{-1}} = 370 \text{ K}$$

It is assumed that ΔH(system) and ΔS(system) do not change with temperature.

Exercises

62 Ammonium chloride dissolves in water spontaneously in an endothermic process. Identify the best explanation for these observations.

A Endothermic processes are energetically favourable.
B The bonds in solid NH_4Cl are very weak.
C The entropy change of the system drives the process.
D The entropy change of the surroundings drives the process

63 **(a)** Use data from section 12 of the IB data booklet and additional data ($\Delta H_f^\ominus(H_2O(s)) = -292$ kJ mol^{-1}) to calculate the enthalpy change that occurs when ice melts.
(b) The entropy change when ice melts is 22.0 J K^{-1} mol^{-1}. Deduce a value for the melting point of ice.

64 Identify the combination of ΔH and ΔS which results in a reaction being spontaneous at low temperatures but non-spontaneous at higher temperatures?

A ΔS – and ΔH – **B** ΔS + and ΔH – **C** ΔS – and ΔH + **D** ΔS + and ΔH +

65 Identify the combination of ΔH and ΔS which leads to a reaction that is **not** spontaneous at low temperatures but becomes spontaneous at higher temperatures?

A ΔH – and ΔS – **B** ΔH – and ΔS + **C** ΔH + and ΔS – **D** ΔH + and ΔS +

66 The ΔH and ΔS values for the combustion of hydrogen are both negative. Which is the correct description of this reaction at different temperatures?

	Low temperature	High temperature
A	not spontaneous	not spontaneous
B	spontaneous	not spontaneous
C	spontaneous	spontaneous
D	not spontaneous	spontaneous

67 The decomposition of limestone can be represented by the equation:

$$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$$

(a) Predict a sign for the enthalpy change of the reaction.
(b) Predict a sign for the entropy change of the reaction.
(c) Deduce how the stability of limestone changes with temperature.

The effect of $\Delta H^\ominus$, $\Delta S^\ominus$, and T on the spontaneity of reaction

The effect of temperature on the spontaneous reactions for different reactions is summarized in the table below.

$\Delta H^\ominus$	$\Delta S^\ominus$	T	ΔG	Spontaneity
positive (endothermic)	positive (more disordered products)	low	positive $\approx \Delta H^\ominus$	not spontaneous
positive (endothermic)	positive (more disordered products)	high	negative $\approx -T\Delta S^\ominus$	spontaneous
positive (endothermic)	negative (more ordered products)	low	positive $\approx \Delta H^\ominus$	not spontaneous
positive (endothermic)	negative (more ordered products)	high	positive $\approx -T\Delta S^\ominus$	not spontaneous
negative (exothermic)	positive (more disordered products)	low	negative $\approx \Delta H^\ominus$	spontaneous
negative (exothermic)	positive (more disordered products)	high	negative $\approx -T\Delta S^\ominus$	spontaneous
negative (exothermic)	negative (more ordered products)	low	negative $\approx -T\Delta S^\ominus$	spontaneous
negative (exothermic)	negative (more ordered products)	high	positive $\approx -T\Delta S^\ominus$	not spontaneous

Work through all the different set of conditions to make sure that you agree with the results of this table. Do not memorize it!

Calculating ΔG values

There are two routes to calculating changes in Gibbs free energy during a reaction. ΔG (at 298 K) can be calculated from tabulated values of $\Delta G_f^\ominus$ in the same way enthalpy changes are calculated. ΔG values are, however, very sensitive to changes to temperature, and ΔG values calculated using this method are not applicable when the temperature is changed. Changes in free energy at other temperatures can be obtained by applying the equation:

$$\Delta G(\text{system}) = \Delta H(\text{system}) - T\Delta S(\text{system})$$

Calculating $\Delta G_{\text{reaction}}$ from $\Delta G_f^\ominus$

$\Delta G_{\text{reaction}}$ for reactions at 298 K can be calculated from $\Delta G_f^\ominus$ values in the same way $\Delta H_{\text{reaction}}$ can be calculated from $\Delta H_f^\ominus$ values (Figure 5.30).

> Values of ΔG can only give information about the feasibility of a reaction. They give no information about the reaction's rate. Some spontaneous reactions need to be heated to occur. The reactants need energy to overcome the activation energy barrier. This is discussed further in Chapter 6.

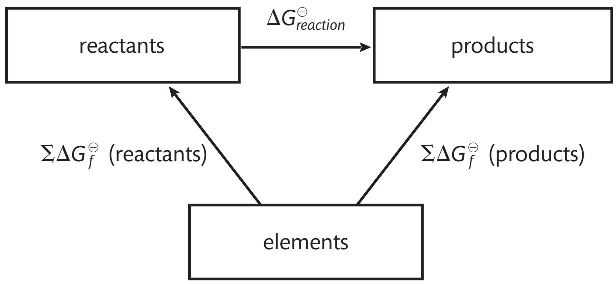


Figure 5.30 A Gibbs free energy cycle.

$$\Delta G_{\text{reaction}} = \sum\Delta G_f^\ominus(\text{products}) - \sum\Delta G_f^\ominus(\text{reactants})$$

Worked example

Calculate $\Delta G_{\text{reaction}}$ for the reaction

$$2Al(s) + Fe_2O_3(s) \rightarrow 2Fe(s) + Al_2O_3(s)$$

from the following data.

Compound	$\Delta G_f^\ominus$/kJ mol^{-1}
$Fe_2O_3(s)$	−742
$Al_2O_3(s)$	−1582

Comment on the significance of the value obtained.

Solution

First, write the chemical equation with the values below:

2Al(s)	+	$Fe_2O_3(s)$	→	2Fe(s)	+	$Al_2O_3(s)$	
2 × 0		−742		2 × 0		−1582	$\Delta G_f^\ominus$/ kJ mol^{-1}

Note: $\Delta G_f^\ominus$(element) is zero by definition just as it is for $\Delta H_f^\ominus$(element).

$$\Delta G_{\text{reaction}} = \sum\Delta G_f^\ominus(\text{products}) - \sum\Delta G_f^\ominus(\text{reactants})$$
$$= -1582 - -742 \text{ kJ mol}^{-1}$$
$$= -840 \text{ kJ mol}^{-1}$$

The reaction is spontaneous under standard conditions.

Exercises

68 The enthalpy and entropy changes for the reaction

$$A(s) + B(aq) \rightarrow C(aq) + D(g)$$

are $\Delta H^\ominus = 100$ kJ mol^{-1} and $\Delta S^\ominus = 100$ J K^{-1} mol^{-1}

A The reaction is not spontaneous at any temperature.
B The reaction is spontaneous at all temperatures.
C The reaction is spontaneous at all temperatures below 1000 °C.
D The reaction is spontaneous at all temperatures above 1000 K.

69 Magnesium carbonate, $MgCO_3$, is a white solid that occurs in nature as the mineral magnesite. Magnesite decomposes to the oxide at temperatures above 540 °C.

$$MgCO_3(s) \rightarrow MgO(s) + CO_2(g)$$

Identify the correct description of this reaction at 800 °C.

	ΔG	ΔH	ΔS
A	+	+	+
B	+	−	−
C	−	+	+
D	−	+	−

70 Calculate $\Delta G_{reaction}$ for the thermal decomposition of calcium carbonate

$$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$$

from the following data, and comment on the significance of the value obtained.

Compound	$\Delta G_f^\ominus$ / kJ mol^{-1}
$CaCO_3(s)$	−1129
$CaO(s)$	−604
$CO_2(g)$	−394

Using $\Delta S^\ominus_{reaction}$ and $\Delta H^\ominus_{reaction}$ values to calculate $\Delta G^\ominus_{reaction}$ at all temperatures

As the standard values of $\Delta G_f^\ominus$ refer to standard conditions, they can only be used to calculate $\Delta G^\ominus_{reaction}$ at 298 K.

When the system is the reaction we have:

$$\Delta G_{reaction} = \Delta H_{reaction} - T\Delta S_{reaction}$$

Here $\Delta G_{reaction}$ can now be calculated at any temperature with $\Delta H_{reaction} = \Delta H^\ominus_{reaction}$ and $\Delta S_{reaction} = \Delta S^\ominus_{reaction}$ effectively constant.

$$\Delta G_{reaction} = \Delta H^\ominus_{reaction} - T\Delta S^\ominus_{reaction}$$

Worked example

Calculate $\Delta G_{reaction}$ at 298 K for the thermal decomposition of calcium carbonate from the following data.

Compound	$\Delta H_f^\ominus$/ kJ mol^{-1}	$S^\ominus$/ J K^{-1} mol^{-1}
$CaCO_3(s)$	−1207	+92.9
$CaO(s)$	−635	+39.7
$CO_2(g)$	−394	+214

Solution

First calculate $\Delta H_{reaction}$. Write the chemical equation with the $\Delta H_f^\ominus$ values in the appropriate places.

$CaCO_3(s)$	$\rightarrow$	$CaO(s)$	+	$CO_2(g)$	
−1207		−635		−394	$\Delta H_f^\ominus$/ kJ mol^{-1}

Using the equation

$$\Delta H^{\ominus}_{reaction} = \sum\Delta H^{\ominus}_{f}(\text{products}) - \sum\Delta H^{\ominus}_{f}(\text{reactants})$$
$$= (-635 + -394) - (-1207)\ \text{kJ mol}^{-1}$$
$$= +178\ \text{kJ mol}^{-1}$$

Now calculate the standard entropy change of reaction. As always predict whether the value is positive or negative.

One mole of solid is converted to one mole of solid and one mole of gas. There is an increase in disorder and an increase in entropy. $\Delta S^{\ominus}_{reaction}$ is positive.

And now do the calculation:

$CaCO_3(s)$	$\rightarrow$	$CaO(s)$	+	$CO_2(g)$	$\Delta S^{\ominus}$ / J K^{-1} mol^{-1}
+92.9		+39.7		+214	

Using the equation:

$$\Delta S^{\ominus}_{reaction} = \sum S^{\ominus}(\text{products}) - \sum S^{\ominus}(\text{reactants})$$
$$= (39.7 + 214) - (+92.9)\ \text{J K}^{-1}\ \text{mol}^{-1}$$
$$= +160.8\ \text{J K}^{-1}\ \text{mol}^{-1}$$

Now calculate the change in Gibbs free energy of the reaction.

$$\Delta G_{reaction} = \Delta H^{\ominus}_{reaction} - T\Delta H^{\ominus}_{reaction}$$
$$= +178 - (298 \times 160.8 \times 10^{-3})\ \text{kJ mol}^{-1}$$
$$= +130\ \text{kJ mol}^{-1}$$

Note as the temperature is 298 K this value agrees with that calculated in the previous exercise using free energy of formation data.

Don't forget to convert so as to use consistent units for $\Delta H^{\ominus}_{reaction}$ and $\Delta S^{\ominus}_{reaction}$ when calculating $\Delta G_{reaction}$. Temperatures in all free energy calculations must be in kelvin. Note also the use of J and kJ.

Exercises

71 Calculate $\Delta G_{reaction}$ at 2000 K for the thermal decomposition of calcium carbonate from the data given in the worked example.

72 Which property of an element has a value of zero in its standard state?

I $\Delta H^{\ominus}_{f}$
II $S^{\ominus}$
III $\Delta G^{\ominus}_{f}$

A I and II **B** I and III **C** II and III **D** I, II, and III

73 The standard enthalpy change for the formation of ethanol, $C_2H_5OH(l)$, and its molar entropy are given in section 12 of the IB data booklet.

(a) Write an equation for the formation of ethanol.
(b) Calculate the entropy change for this process. The entropies of its constituent elements are:
C(graphite) = 5.7 J K^{-1} mol^{-1}
$H_2(g)$ = 65.3 J K^{-1} mol^{-1}
$O_2(g)$ = 102.5 J K^{-1} mol^{-1}
(c) Calculate the standard free energy change of formation of ethanol at 500 K.
(d) Deduce whether the reaction is spontaneous at 500 K, and give a reason.
(e) Predict the effect, if any, of an increase in temperature on the spontaneity of this reaction.

Gibbs free energy and equilibrium

So far we have considered reactions in which it is assumed that all the reactants are converted into products. Many reactions do not go to completion but instead reach equilibrium, as will be discussed in Chapter 7. The extent of reaction can be quantified by the ratio of the concentrations: [products]/[reactants]. The boundary between partial and complete reaction is of course not clearly defined, but as $\Delta G^\circ_{reaction}$ becomes more negative, the reaction favours products. When $\Delta G^\circ_{reaction}$ is below −30 kJ mol^{-1} the reaction can considered as complete.

For values of $\Delta G^\circ_{reaction}$ between −30 and 0 kJ mol^{-1} there will be an equilibrium mixture with products predominating.

The table below summarizes the relationship between $\Delta G^\circ_{reaction}$ and the extent of reaction.

$\Delta G^\ominus_{reaction}$	Extent of reaction
$\Delta G^\ominus_{reaction} > +30$ kJ mol^{-1}	spontaneous change impossible : no reaction $\frac{[products]}{[reactants]} \ll 1$
0 kJ mol^{-1} $< \Delta G^\ominus_{reaction} <$ +30 kJ mol^{-1}	partial reaction producing equilibrium mixture $\frac{[products]}{[reactants]} < 1$
$\Delta G^\ominus_{reaction} = 0$ kJ mol^{-1}	partial reaction producing equilibrium mixture $\frac{[products]}{[reactants]} = 1$
0 kJ mol^{-1} $> \Delta G^\ominus_{reaction} >$ −30 kJ mol^{-1}	partial reaction producing equilibrium mixture $\frac{[products]}{[reactants]} > 1$
$\Delta G^\ominus_{reaction} < -30$ kJ mol^{-1}	complete reaction $\frac{[products]}{[reactants]} \gg 1$

The relationships between free energy, entropy and equilibrium are discussed more fullly in Chapter 7, page 335.

CHALLENGE YOURSELF

9 For the reaction A → B, $K_c = \frac{[products]}{[reactants]} = \frac{[B]}{[A]}$

Find a mathematical function of K_c which gives values of $\Delta G^\ominus_{reaction}$ consistent with the table.

Exercises

74 What signs of $\Delta H^{\ominus}_{reaction}$ and $\Delta S^{\ominus}_{reaction}$ for a reaction result in a complete reaction at all temperatures?

	$\Delta H^{\ominus}_{reaction}$	$\Delta S^{\ominus}_{reaction}$
A	–	–
B	+	–
C	–	+
D	+	+

75 Which conditions correspond to a system of equilibrium?

I The entropy of the system is at a maximum.
II The free energy of a system is at a minimum.
III $\Delta G^{\ominus}_{reaction} = 0$

A I and II only **B** I and III only **C** II and III only **D** I, II, and III

76 Which values correspond to a reaction that can be reversed by changing the temperature.

	$\Delta H^{\ominus}_{reaction}$	$\Delta S^{\ominus}_{reaction}$
I	–	–
II	+	–
III	+	+

A I and II only **B** I and III only **C** II and III only **D** I, II, and III

77 Propene reacts with hydrogen in the presence of a nickel catalyst to form propane.

$$C_3H_6(g) + H_2(g) \rightarrow C_3H_8(g)$$

$\Delta H^{\ominus}_{reaction} = -123$ kJ mol^{-1}; $\Delta S^{\ominus}_{reaction} = -128$ J K mol^{-1}

Estimate the temperature range in which a mixture of all three gases will be present.

78 The Haber process is an important process in which ammonia is formed from nitrogen and hydrogen:

$$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$$

$\Delta S^{\ominus}_{reaction} = -198$ J K^{-1} mol^{-1}; $\Delta H^{\ominus}_{reaction} = -93$ J K^{-1} mol^{-1}

Estimate the temperature range in which a mixture of all three gases will be present.

Practice questions

1 A pure aluminium block with a mass of 10 g is heated so that its temperature increases from 20 °C to 50 °C. The specific heat capacity of aluminium is 8.99×10^{-1} J g^{-1} K^{-1}. Which expression gives the heat energy change in kJ?

A $10 \times 8.99 \times 10^{-1} \times 303$

B $10 \times 8.99 \times 10^{-1} \times 30$

C $\dfrac{10 \times 8.99 \times 10^{-1} \times 303}{1000}$

D $\dfrac{10 \times 8.99 \times 10^{-1} \times 30}{1000}$

2 Which processes have a negative enthalpy change?

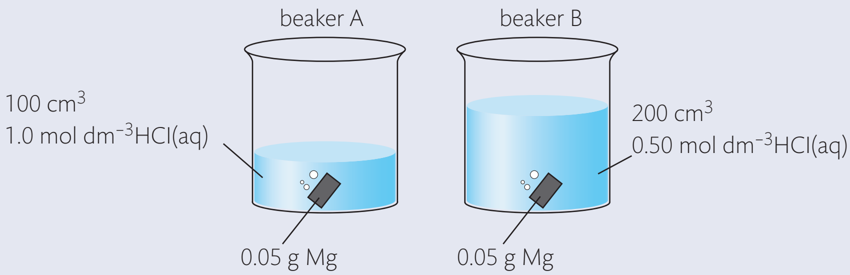
I $2CH_3OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 4H_2O(l)$

II $HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l)$

III $H_2O(g) \rightarrow H_2O(l)$

A I and II only **B** I and III only **C** II and III only **D** I, II, and III

3 Identical pieces of magnesium are added to two beakers, A and B, containing hydrochloric acid. Both acids have the same initial temperature but their volumes and concentrations differ.



Which statement is correct?

A The maximum temperature in A will be higher than in B.
B The maximum temperature in A and B will be equal.
C It is not possible to predict whether A or B will have the higher maximum temperature.
D The temperature in A and B will increase at the same rate.

4 Consider the following reactions.

$Cu_2O(s) + \frac{1}{2}O_2(g) \rightarrow 2CuO(s)$ $\quad \Delta H^\ominus = -144$ kJ

$Cu_2O(s) \rightarrow Cu(s) + CuO(s)$ $\quad \Delta H^\ominus = +11$ kJ

What is the value of $\Delta H^\ominus$, in kJ, for this reaction?

$$Cu(s) + \tfrac{1}{2}O_2(g) \rightarrow CuO(s)$$

A −144 + 11 **B** +144 − 11 **C** −144 − 11 **D** +144 + 11

5 Which equation best represents the bond enthalpy of HCl?

A $HCl(g) \rightarrow H^+(g) + Cl^-(g)$
B $HCl(g) \rightarrow H(g) + Cl(g)$
C $HCl(g) \rightarrow \frac{1}{2}H_2(g) + \frac{1}{2}Cl_2(g)$
D $2HCl(g) \rightarrow H_2(g) + Cl_2(g)$

6 Consider the equations below.

$CH_4(g) + O_2(g) \rightarrow HCHO(l) + H_2O(l)$ $\quad \Delta H^\ominus = x$

$HCHO(l) + \frac{1}{2}O_2(g) \rightarrow HCOOH(l)$ $\quad \Delta H^\ominus = y$

$2HCOOH(l) + \frac{1}{2}O_2(g) \rightarrow (COOH)_2(s) + H_2O(l)$ $\quad \Delta H^\ominus = z$

What is the enthalpy change of the reaction below?

$$2CH_4(g) + 3\tfrac{1}{2}O_2(g) \rightarrow (COOH)_2(s) + 3H_2O(l)$$

A $x + y + z$ **B** $2x + y + z$ **C** $2x + 2y + z$ **D** $2x + 2y + 2z$

7 Which process represents the C–Cl bond enthalpy in tetrachloromethane?

A $CCl_4(g) \rightarrow C(g) + 4Cl(g)$
B $CCl_4(g) \rightarrow CCl_3(g) + Cl(g)$
C $CCl_4(l) \rightarrow C(g) + 4Cl(g)$
D $CCl_4(l) \rightarrow C(s) + 2Cl_2(g)$

8 What is the energy, in kJ, released when 1.00 mol of carbon monoxide is burned according to the following equation?

$2CO(g) + O_2(g) \rightarrow 2CO_2(g)$ $\quad \Delta H^\ominus = -564$ kJ

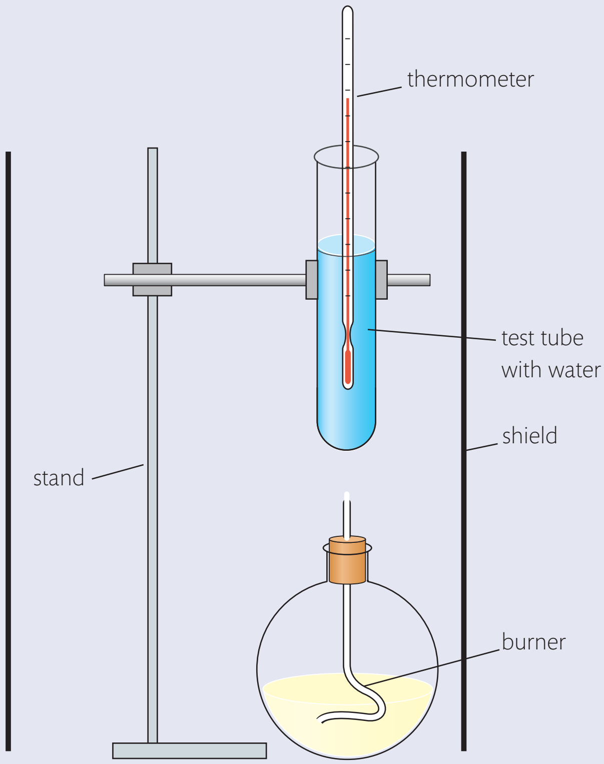
A 141 **B** 282 **C** 564 **D** 1128

9 Methanol is made in large quantities as it is used in the production of polymers and in fuels. The enthalpy of combustion of methanol can be determined theoretically or experimentally.

$$CH_3OH(l) + 1\tfrac{1}{2}O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$$

(a) Using the information from section 11 of the IB data booklet, determine the theoretical enthalpy of combustion of methanol. (3)

(b) The enthalpy of combustion of methanol can also be determined experimentally in a school laboratory. A burner containing methanol was weighed and used to heat water in a test tube, as illustrated below.



The following data were collected.

Initial mass of burner and methanol / g	80.557
Final mass of burner and methanol / g	80.034
Mass of water in test tube / g	20.000
Initial temperature of water / °C	21.5
Final temperature of water / °C	26.4

(i) Calculate the amount, in mol, of methanol burned. (2)

(ii) Calculate the heat absorbed, in kJ, by the water. (3)

(iii) Determine the enthalpy change, in kJ mol^{-1}, for the combustion of 1 mole of methanol. (2)

(c) The data booklet value for the enthalpy of combustion of methanol is –726 kJ mol^{-1}. Suggest why this value differs from the values calculated in parts (a) and (b).

(i) Part (a) (1)

(ii) Part (b) (1)

(*Total 12 marks*)

10 The data below are from an experiment to measure the enthalpy change for the reaction of aqueous copper(II) sulfate, $CuSO_4$(aq), and zinc, Zn(s).

$$Cu^{2+}(aq) + Zn(s) \rightarrow Cu(s) + Zn^{2+}(aq)$$

50.0 cm^3 of 1.00 mol dm^{-3} copper(II) sulfate solution was placed in a polystyrene cup and zinc powder was added after 100 seconds. The temperature–time data were taken from a data-logging software program. The table shows the initial 23 readings.

	A	B	C	D	E	F	G	H
1	**time/s**	**temperature/°C**						
2	0.0	24.8						
3	1.0	24.8						
4	2.0	24.8						
5	3.0	24.8						
6	4.0	24.8						
7	5.0	24.8						
8	6.0	24.8						
9	7.0	24.8						
10	8.0	24.8						
11	9.0	24.8						
12	10.0	24.8						
13	11.0	24.8						
14	12.0	24.8						
15	13.0	24.8						
16	14.0	24.8						
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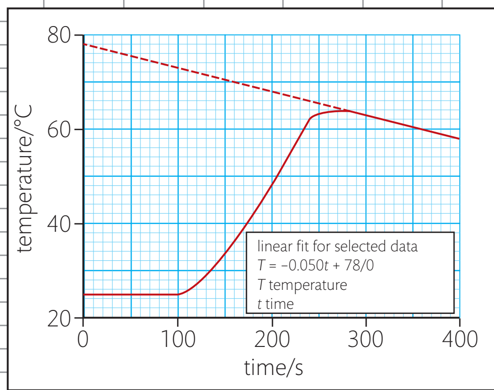


A straight line has been drawn through some of the data points. The equation for this line is given by the data-logging software as

$$T = -0.050t + 78.0$$

where T is the temperature at time t.

(a) The heat produced by the reaction can be calculated from the temperature change, ΔT, using the expression below.

heat change = volume of $CuSO_4$(aq) × specific heat capacity of H_2O × ΔT

Describe **two** assumptions made in using this expression to calculate heat changes. (2)

(b) (i) Use the data presented by the data-logging software to deduce the temperature change, ΔT, which would have occurred if the reaction had taken place instantaneously with no heat loss. (2)

(ii) State the assumption made in part (b)(i). (1)

(iii) Calculate the heat, in kJ, produced during the reaction using the expression given in part (a). (1)

(c) The colour of the solution changed from blue to colourless. Deduce the amount, in moles, of zinc which reacted in the polystyrene cup. (1)

(d) Calculate the enthalpy change, in kJ mol^{-1}, for this reaction. (1)

(Total 8 marks)

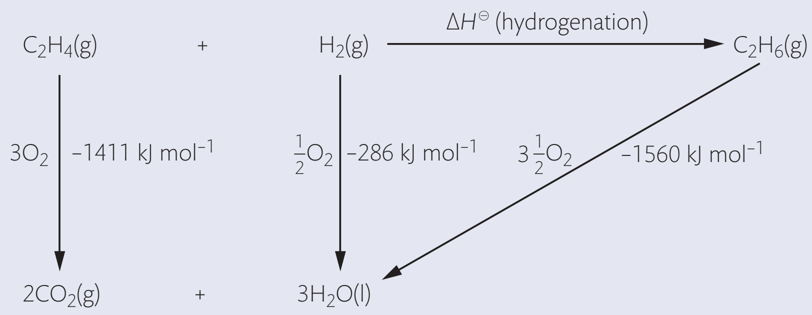
11 Two students were asked to use information from the data booklet to calculate a value for the enthalpy of hydrogenation of ethene to form ethane.

$$C_2H_4(g) + H_2(g) \rightarrow C_2H_6(g)$$

John used the average bond enthalpies from section 10. Marit used the values of enthalpies of combustion from section 13.

(a) Calculate the value for the enthalpy of hydrogenation of ethene obtained using the average bond enthalpies given in section 11. (2)

(b) Marit arranged the values she found in section 12 into an energy cycle.



Calculate the value for the enthalpy of hydrogenation of ethene from the energy cycle. (1)

(c) Suggest **one** reason why John's answer is slightly less accurate than Marit's answer. (1)

(d) John then decided to determine the enthalpy of hydrogenation of cyclohexene to produce cyclohexane.

$$C_6H_{10}(l) + H_2(g) \rightarrow C_6H_{12}(l)$$

(i) Use the average bond enthalpies to deduce a value for the enthalpy of hydrogenation of cyclohexene. (1)

(ii) The percentage difference between these two methods (average bond enthalpies and enthalpies of combustion) is greater for cyclohexene than it was for ethene. John's hypothesis was that it would be the same. Determine why the use of average bond enthalpies is less accurate for the cyclohexene equation shown above, than it was for ethene. Deduce what extra information is needed to provide a more accurate answer. (2)

(*Total 7 marks*)

12 Hydrazine is a valuable rocket fuel. The equation for the reaction between hydrazine and oxygen is given below.

$$N_2H_4(l) + O_2(g) \rightarrow N_2(g) + 2H_2O(l)$$

Use the bond enthalpy values from section 10 of the data booklet to determine the enthalpy change for this reaction. (3)

13 The following reactions take place in the ozone layer by the absorption of ultraviolet light.

I $O_3 \rightarrow O_2 + O\bullet$

II $O_2 \rightarrow O\bullet + O\bullet$

State and explain, by reference to the bonding, which of the reactions, I or II, requires a shorter wavelength. (2)

14 Which ionic compound has the greatest lattice enthalpy?

A MgO **B** CaO **C** NaF **D** KF

15 Which step(s) is/are endothermic in the Born–Haber cycle for the formation of LiCl?

A $\frac{1}{2}Cl_2(g) \rightarrow Cl(g)$ and $Li(s) \rightarrow Li(g)$
B $Cl(g) + e^- \rightarrow Cl^-(g)$ and $Li(g) \rightarrow Li^+(g) + e^-$
C $Li^+(g) + Cl^-(g) \rightarrow LiCl(s)$
D $\frac{1}{2}Cl_2(g) \rightarrow Cl(g)$ and $Cl(g) + e^- \rightarrow Cl^-(g)$

16 Which reaction has the greatest increase in entropy?

A $SO_2(g) + 2H_2S(g) \rightarrow 2H_2O(l) + 3S(s)$
B $CaO(s) + CO_2(g) \rightarrow CaCO_3(s)$
C $CaC_2(s) + 2H_2O(l) \rightarrow Ca(OH)_2(s) + C_2H_2(g)$
D $N_2(g) + O_2(g) \rightarrow 2NO(g)$

17 Which change will **not** increase the entropy of a system?

A increasing the temperature
B changing the state from liquid to gas
C mixing different types of particles
D a reaction where four moles of gaseous reactants changes to two moles of gaseous products

18 What is the standard free energy change, $\Delta G^\ominus$, in kJ, for the following reaction?

$$C_2H_5OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(g)$$

Compound	$\Delta G_f^\ominus$ / kJ mol^{-1}
$C_2H_5OH(l)$	−175
$CO_2(g)$	−394
$H_2O(g)$	−229
$O_2(g)$	0

A −1650 **B** −1300 **C** −448 **D** +1300

19 What is the standard entropy change, $\Delta S^\ominus$, for the following reaction?

$$2CO(g) + O_2(g) \rightarrow 2CO_2(g)$$

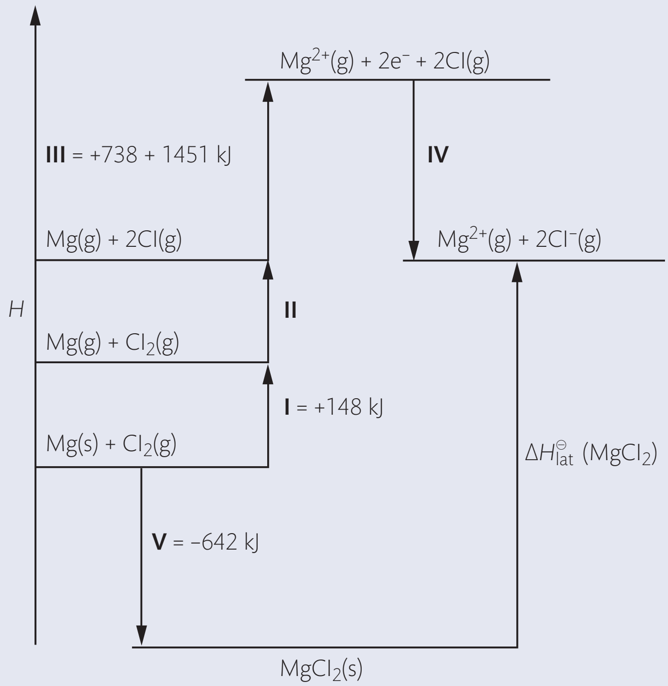
	$CO(g)$	$O_2(g)$	$CO_2(g)$
$S^\ominus$ / J K^{-1} mol^{-1}	198	205	214

A −189 **B** −173 **C** +173 **D** +189

20 A reaction has a standard enthalpy change, $\Delta H^\ominus$, of +10.00 kJ mol^{-1} at 298 K. The standard entropy change, $\Delta S^\ominus$, for the same reaction is +10.00 J K^{-1} mol^{-1}. What is the value of $\Delta G^\ominus$ for the reaction in kJ mol^{-1}?

A +9.75 **B** +7.02 **C** −240 **D** −2970

21 The lattice enthalpy of magnesium chloride can be calculated from the Born–Haber cycle shown below.



(a) Identify the enthalpy changes labelled **I** and **V** in the cycle. (2)

(b) Use the ionization energies given in the cycle above and further data from the data booklet to calculate a value for the lattice enthalpy of magnesium chloride. (4)

(c) The theoretically calculated value for the lattice enthalpy of magnesium chloride is +2326 kJ. Explain the difference between the theoretically calculated value and the experimental value. (2)

(d) The experimental lattice enthalpy of magnesium oxide is given in section 18 of the data booklet. Explain why magnesium oxide has a higher lattice enthalpy than magnesium chloride. (2)

(*Total 10 marks*)

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