Heinemann
CHEMISTRY 2

5TH EDITION

VCE Units 3 & 4

Written for the VCE Chemistry Study Design 2017–2021

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CHEMISTRY 2
5TH EDITION

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The Chemistry Education Association was formed in 1977 by a group of chemistry teachers from secondary and tertiary institutions. It aims to promote the teaching of chemistry, particularly in secondary schools. The CEA has established a tradition of providing up-to-date text and electronic material and support resources for both students and teachers and professional development opportunities for teachers.

The CEA offers scholarships and bursaries to students and teachers to further their interest in chemistry. The CEA supports STAV with sponsorship for the Chemistry Conference, Science Drama Awards and The Science Talent Search.

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AREA OF STUDY 1

How can the diversity of carbon compounds be explained and categorised?

AREA OF STUDY 2

What is the chemistry of food?

How to use this book

Heinemann Chemistry 2 5th edition

Heinemann Chemistry 2 5th Edition has been written to the new VCE Chemistry Study Design 2017–2021. The book covers Units 3 and 4 in an easy-to-use resource. Explore how to use this book below.

Extension

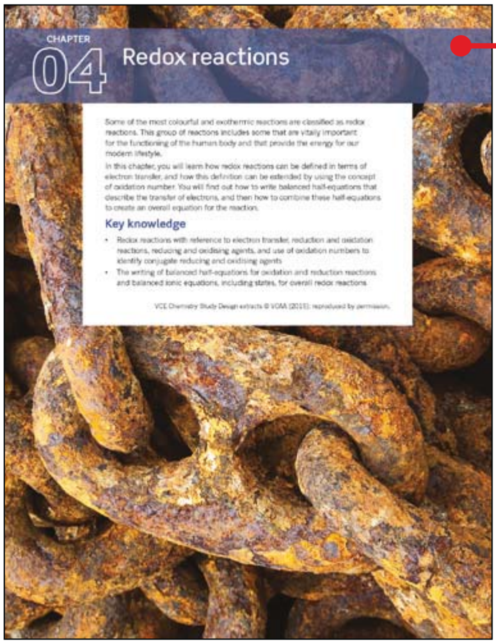
The extension boxes include material that goes beyond the core content of the Study Design and are intended for students who wish to expand their depth of understanding.

Highlight

The highlight boxes provide important information such as key definitions, formulas and summary points.

Chapter opener

Chapter opening pages link the Study Design to the chapter content. Key knowledge addressed in the chapter is clearly listed.



CHAPTER 04 Redox reactions

Some of the most colourful and exothermic reactions are classified as redox reactions. This group of reactions includes some that are vitally important for the functioning of the human body and that provide the energy for our modern lifestyle.

In this chapter, you will learn how redox reactions can be defined in terms of electron transfer, and how this definition can be extended by using the concept of oxidation number. You will find out how to write balanced half-equations that describe the transfer of electrons, and then how to combine these half-equations to create an overall equation for the reaction.

Key knowledge

- Redox reactions with reference to electron transfer, reduction and oxidation reactions, reducing and oxidising agents, and use of oxidation numbers to identify conjugate reducing and oxidising agents
- The writing of balanced half-equations for oxidation and reduction reactions and balanced ionic equations, including states, for overall redox reactions

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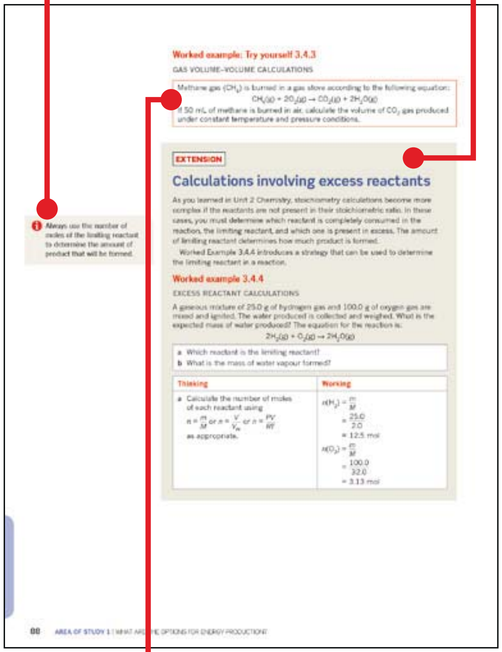
ChemFile

ChemFiles include a range of interesting information and real-world examples.

Chemistry in Action

Chemistry in Action boxes place chemistry in an applied situation or relevant context. These boxes refer to the nature and practice of chemistry, applications of chemistry and the associated issues and the historical development of concepts and ideas.



Worked example: Try yourself 3.4.3

GAS VOLUME–VOLUME CALCULATIONS

Methane gas (CH_4) is burned in a gas stove according to the following equation:

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$$

If 50 mL of methane is burned in air, calculate the volume of CO_2 gas produced under constant temperature and pressure conditions.

EXTENSION

Calculations involving excess reactants

As you learned in Unit 2 Chemistry, stoichiometry calculations become more complex if the reactants are not present in their stoichiometric ratio. In these cases, you must determine which reactant is completely consumed in the reaction, the limiting reactant, and which one is present in excess. The amount of limiting reactant determines how much product is formed.

Worked Example 3.4.4 introduces a strategy that can be used to determine the limiting reactant in a reaction.

Worked example 3.4.4

EXCESS REACTANT CALCULATIONS

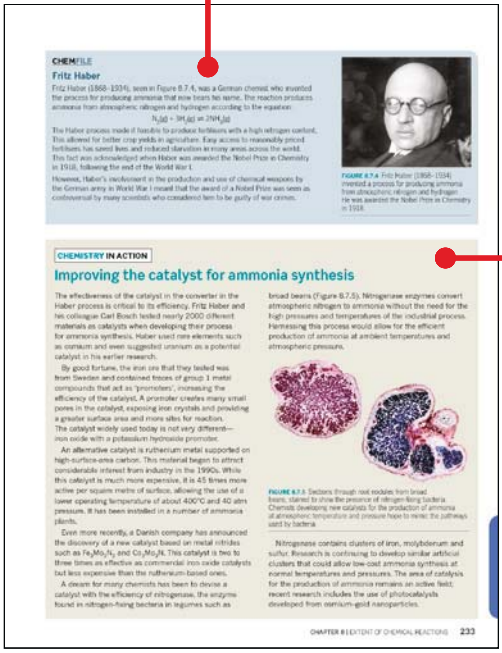
A gaseous mixture of 25.0 g of hydrogen gas and 100.0 g of oxygen gas are mixed and ignited. The water produced is collected and weighed. What is the expected mass of water produced? The equation for the reaction is:

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

a Which reactant is the limiting reactant?
b What is the mass of water vapour formed?

Thinking	Working
a Calculate the number of moles of each reactant using $n = \frac{m}{M}$ or $n = \frac{V}{V_m}$ or $n = \frac{PV}{RT}$ as appropriate.	$n(H_2) = \frac{m}{M}$ $= \frac{25.0}{2.0}$ $= 12.5$ mol $n(O_2) = \frac{m}{M}$ $= \frac{100.0}{32.0}$ $= 3.13$ mol

Always use the number of moles of the limiting reactant to determine the amount of product that will be formed.



CHEMFILE

Fritz Haber

Fritz Haber (1868–1934), seen in Figure 8.7.4, was a German chemist who invented the process for producing ammonia that now bears his name. The reaction produces ammonia from atmospheric nitrogen and hydrogen according to the equation:

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

The Haber process made it feasible to produce fertilisers with a high nitrogen content. This allowed for better crop yields in agriculture. Easy access to reasonably priced fertilisers has saved lives and reduced starvation in many areas across the world. This fact was acknowledged when Haber was awarded the Nobel Prize in Chemistry in 1918, following the end of the World War I.

However, Haber's involvement in the production and use of chemical weapons by the German army in World War I meant that the award of a Nobel Prize was seen as controversial by many scientists who considered him to be guilty of war crimes.

FIGURE 8.7.4 Fritz Haber (1868–1934) invented a process for producing ammonia from atmospheric nitrogen and hydrogen. He was awarded the Nobel Prize in Chemistry in 1918.

CHEMISTRY IN ACTION

Improving the catalyst for ammonia synthesis

Worked examples

Worked examples are set out in steps that show thinking and working. This enhances student understanding by linking underlying logic to the relevant calculations.

Each **Worked example** is followed by a **Worked example: Try yourself**. This mirror problem allows students to immediately test their understanding.

Fully worked solutions to all **Worked examples: Try yourself** are available on *Heinemann Chemistry 2 5th Edition ProductLink*.

Glossary

Key terms are shown in bold and listed at the end of each chapter. A comprehensive glossary at the end of the book provides comprehensive definitions for all key terms.

Chapter review

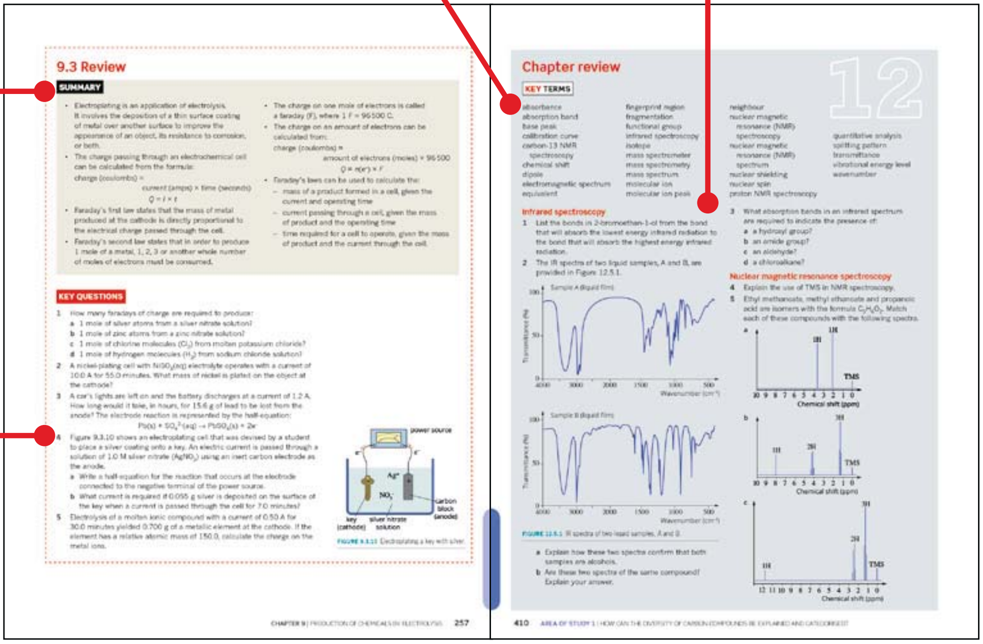
Each chapter concludes with a set of higher order questions to test students' ability to apply the knowledge gained from the chapter.

Section summary

A summary is provided at the end of each section to assist students consolidate key points and concepts.

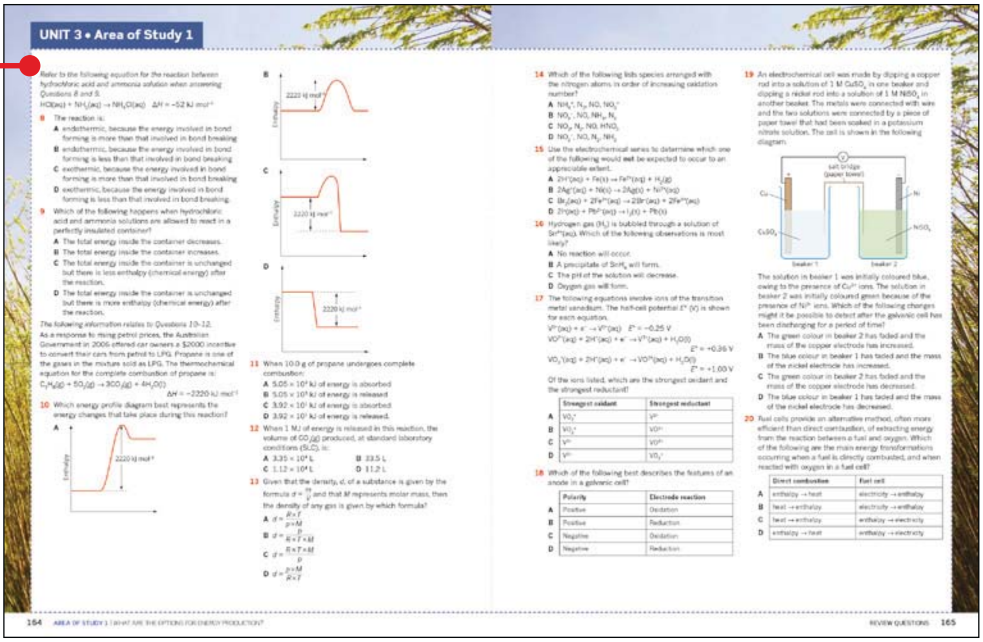
Section review

A set of key questions is provided at the end of each section to test students' understanding and ability to recall the key concepts of the section.



Area of Study review

A comprehensive set of exam-style questions, including multiple choice and extended response questions, are provided at the end of each Area of Study section. The questions are designed to assist students to apply their knowledge and understanding across the entire Area of Study.



Answers

Numerical answers and key short response answers are included at the back of the book. Comprehensive answers and fully worked solutions for all section review questions, Worked examples: Try yourself, chapter review questions and Area of Study review questions are provided via *Heinemann Chemistry 2 5th Edition ProductLink.*

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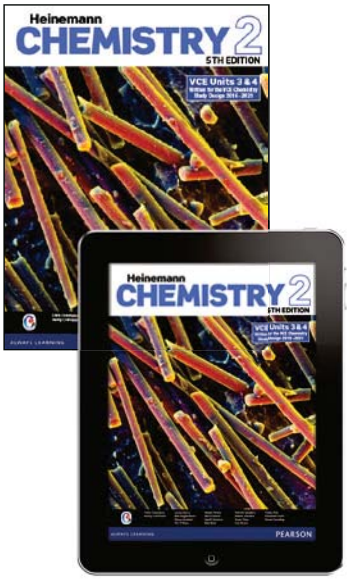

Student Book

Heinemann Chemistry 2 5th Edition has been written to fully align with the VCE Chemistry Study Design 2017–2021. The series includes the very latest developments and applications of chemistry and incorporates best practice literacy and instructional design to ensure the content and concepts are fully accessible to all students.

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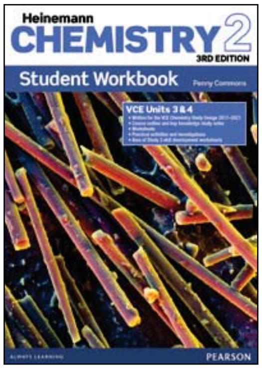
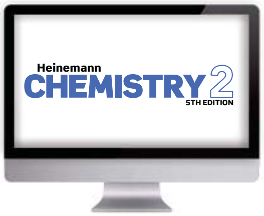
Pearson eBook 3.0 is the digital version of the student book. It retains the integrity of the printed page and is available online or offline on any device—PC/Mac, Android tablet and iPad.



Student Workbook

Heinemann Chemistry 2 Student Workbook 3rd edition will give students the edge in preparing for all forms of assessment. New content has been written to ensure the workbook is fully aligned to the 2017–2021 Chemistry Study Design. Key features include study notes, worksheets, practical activities and guidance, and assessment practice and opportunities.



ProductLink

Heinemann Chemistry 2 5th Edition ProductLink provides comprehensive support for teachers and students completely free of charge. *ProductLink* includes comprehensive answers and worked solutions to all student book questions, tests, quizzes and practice exams, teaching programs and risk assessments. *Heinemann Chemistry 2 5th Edition ProductLink* provides extensive support material for Unit 4 Area of Study 3 Practical Investigation. This includes teacher notes and advice, logbook template and sample logbook, poster template and sample poster, rubrics, checklists and more.

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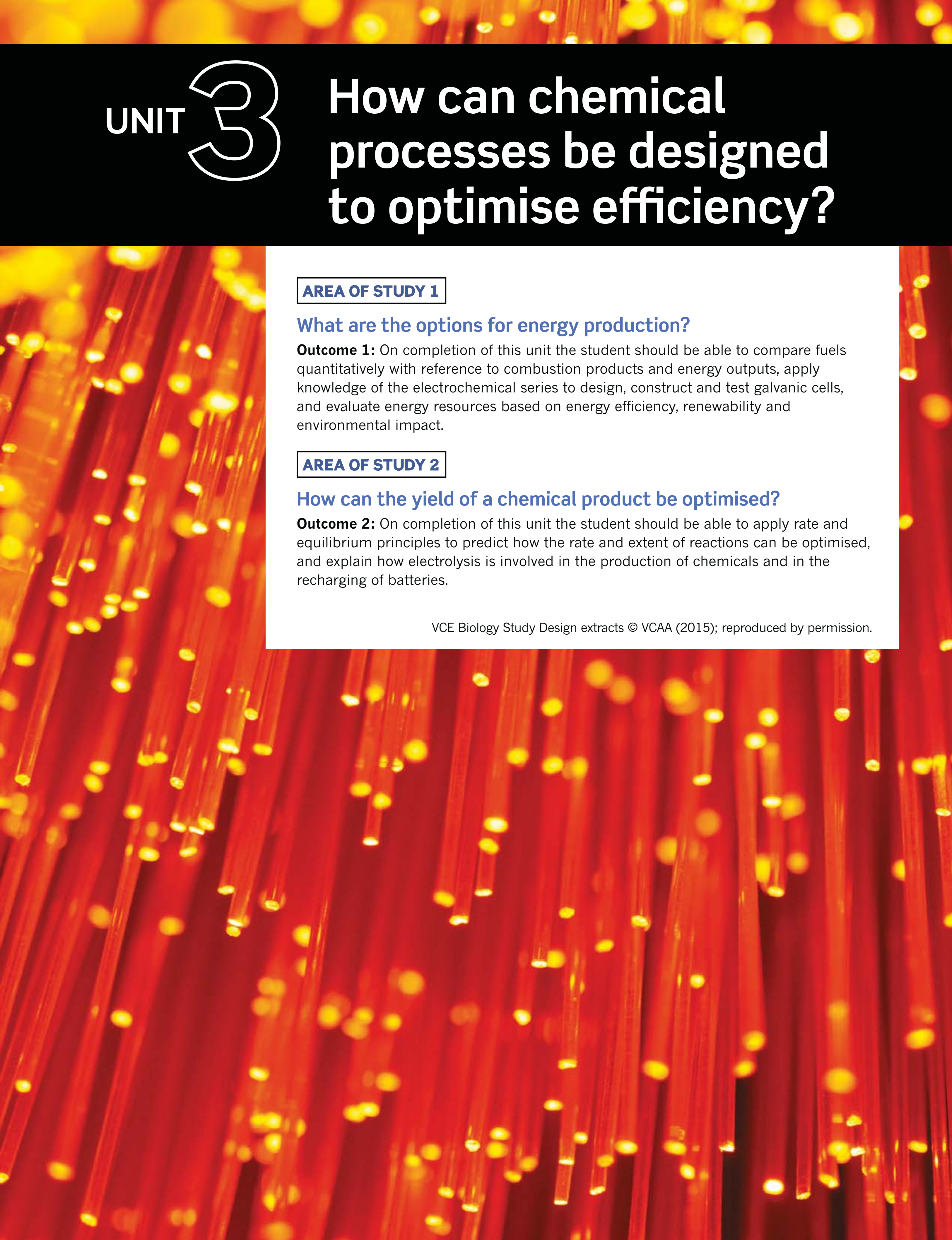


UNIT 3

How can chemical processes be designed to optimise efficiency?

AREA OF STUDY 1

What are the options for energy production?

Outcome 1: On completion of this unit the student should be able to compare fuels quantitatively with reference to combustion products and energy outputs, apply knowledge of the electrochemical series to design, construct and test galvanic cells, and evaluate energy resources based on energy efficiency, renewability and environmental impact.

AREA OF STUDY 2

How can the yield of a chemical product be optimised?

Outcome 2: On completion of this unit the student should be able to apply rate and equilibrium principles to predict how the rate and extent of reactions can be optimised, and explain how electrolysis is involved in the production of chemicals and in the recharging of batteries.

CHAPTER

01

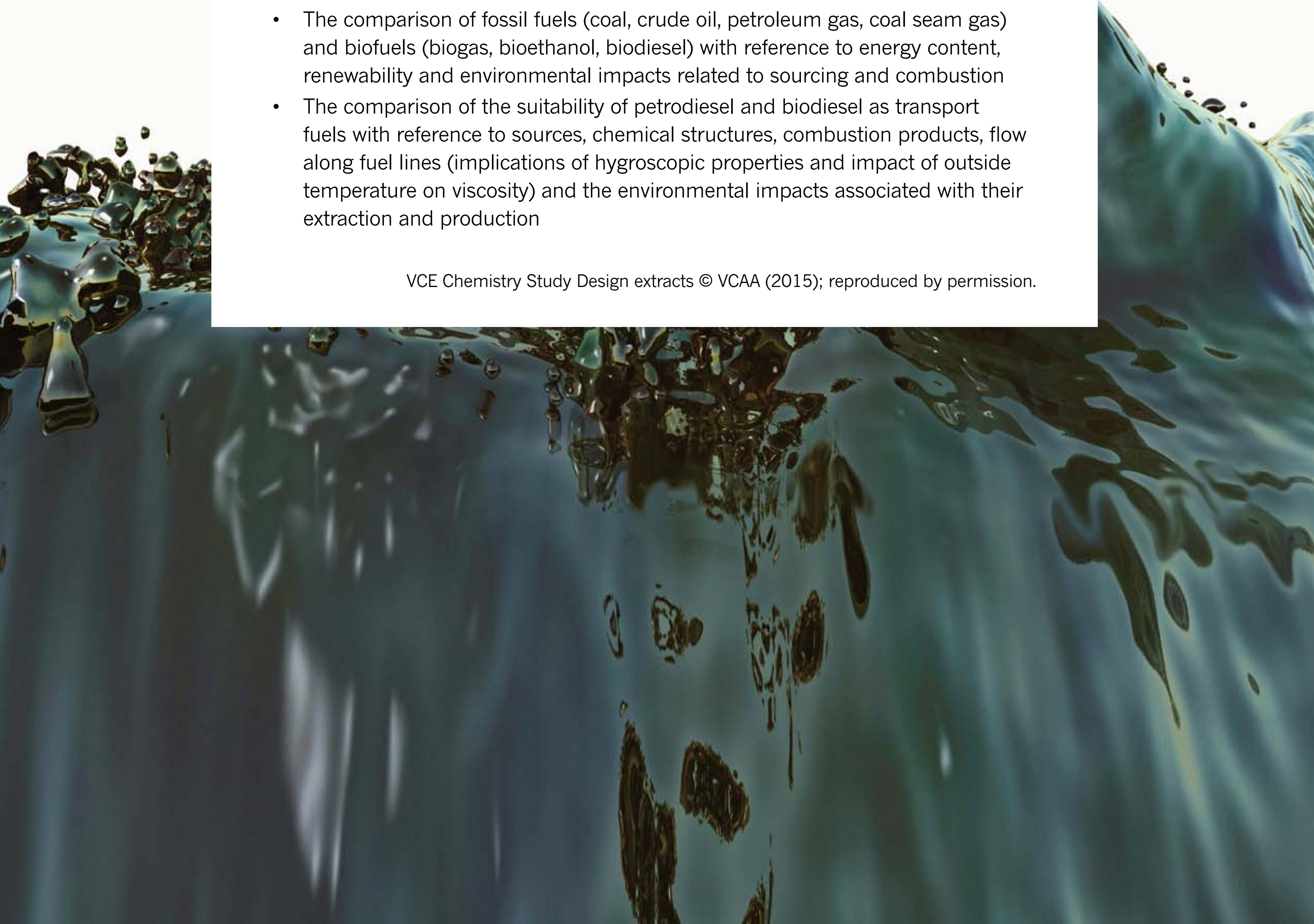
Fuels

In this chapter, you will learn how fuels are used to meet global energy needs and you will gain an appreciation of the chemistry that underpins decisions about the use of fuels. Combustion reactions are used to release useful heat energy from the chemical energy stored in fuels. You will explore how fuels vary in terms of the energy that they produce when they are burnt.

You will consider the environmental impact of using different types of fuels, including their carbon emissions as well as the other pollutants they release into the atmosphere. Current research being conducted into the production of renewable fuels and the potential for reducing the harmful impact of fossil fuels will also be discussed.

Key knowledge

- The definition of a fuel, including the distinction between fossil fuels and biofuels with reference to origin and renewability (ability of a resource to be replaced by natural processes within a relatively short period of time)
- Combustion of fuels as exothermic reactions with reference to the use of the joule as the SI unit of energy, energy transformations and their efficiencies
- The comparison of fossil fuels (coal, crude oil, petroleum gas, coal seam gas) and biofuels (biogas, bioethanol, biodiesel) with reference to energy content, renewability and environmental impacts related to sourcing and combustion
- The comparison of the suitability of petrodiesel and biodiesel as transport fuels with reference to sources, chemical structures, combustion products, flow along fuel lines (implications of hygroscopic properties and impact of outside temperature on viscosity) and the environmental impacts associated with their extraction and production



1.1 Types of fuels

FIGURE 1.1.1 Sugars, such as sucrose, are fuels for your body.

FIGURE 1.1.2 Petrol is just one type of fuel that is used each day to meet our energy needs.

Fuels provide you with energy. They are substances that have chemical energy stored within them. All chemicals contain stored energy. What makes a **fuel** special is that this stored chemical energy can be released relatively easily.

Sugar is an example of a common fuel (Figure 1.1.1). A cube of table sugar (sucrose) can provide your body with 82 kilojoules of energy. This is about 1% of your daily energy needs. If sucrose is burnt, this energy is released as heat. The combustion of 1 kilogram of sucrose releases sufficient energy to melt more than 5 kilograms of ice and then boil all the liquid water produced.

Although sugars provide energy for your body, you do not heat your home, power cars or produce electricity by burning sugar. A range of other fuels such as wood, coal, oil, natural gas, LPG, ethanol and petrol (Figure 1.1.2) are used for these energy needs.

In this section, you will explore the range of fuels available and how they are sourced.

THE NEED FOR FUELS

A fuel is a substance with stored energy that can be released relatively easily for use as heat or power. Although this chapter will focus on fuels with stored chemical energy, the term 'fuel' is also applied to sources of nuclear energy, such as uranium.

The use of fuels by society can be considered from a number of points of view, including at a:

- local level (e.g. the type of petrol used in your car)
- national level (e.g. whether Australia's use of energy resources is **sustainable**)
- global level (e.g. whether the use of **fossil fuels** (coal, oil and natural gas) is contributing to the **enhanced greenhouse effect**).

These are not separate issues. Choices made locally have regional and global effects. The decisions of global and national governments affect how and which fuels are used.

Units of energy

The international system of units (**SI units**) is a widely used system of measurement that specifies units for a range of quantities. The SI unit for energy is the joule, symbol J. As 1 J of energy is a relatively small amount, it is common to see the following units in use:

- kilojoules, 1 kJ = 10^3 J
- megajoules, 1 MJ = 10^6 J
- gigajoules, 1 GJ = 10^9 J
- terajoules, 1 TJ = 10^{12} J.

Use of energy in Australia and the world

World energy consumption is around 4×10^{20} joules per year. The United States consumes a quarter of the world's energy. Australia consumes about one-hundredth of the world's energy. But energy consumption per person in Australia is only just below that of the United States. Figure 1.1.3 shows the ways in which Australians use energy. As you can see, heating and transportation account for 87% of Australia's total energy consumption.

In Australia and around the world, most of the energy used for heating, electricity generation and powering vehicles comes from fossil fuels. About 86% of Australian electricity is generated from these fuels, with 73% from coal and 13% from natural gas.

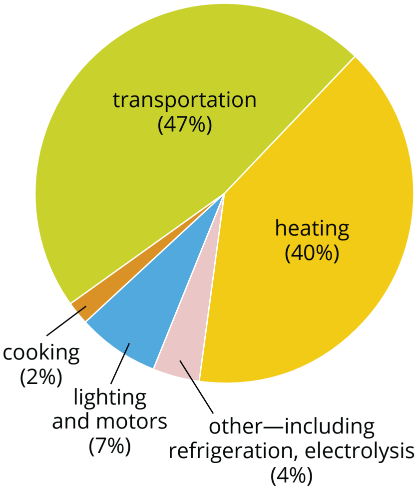


FIGURE 1.1.3 This pie chart shows where energy is used in Australia.

Coal-fired power stations are the dominant source of the world's electricity because they are often the cheapest form of generation. Electricity from coal-fired power stations is reliable and coal is very abundant.

About 14% of Australia's electricity comes from renewable energy sources. Hydroelectricity contributes 7% of total electricity and wind, biofuels and solar energy make up the other 7%.

Future energy needs

Burning wood was the dominant method of obtaining energy up to the middle of the 19th century. Wood supplies once seemed unlimited and, like fossil fuels today, satisfied most of the demands of the time.

Fossil fuels now provide nearly 90% of the world's energy needs. As members of a society that is heavily dependent on fossil fuels as a source of energy, we can find it hard to imagine obtaining energy from elsewhere.

The world first became aware that fossil fuels are a finite energy reserve during the 'oil crisis' of the early 1970s. Several Middle Eastern oil exporters restricted production for political reasons. This dramatically increased the cost of crude oil and caused huge increases in the price of petrol around the world.

Given the limited reserves and concerns about the link between fossil fuels and climate change, there is considerable interest in identifying and developing new energy sources. Many countries are already considering alternative sources of energy. The development of alternative sources for large-scale energy production is not a simple task. Replacement energy sources need to meet a range of requirements, such as being reliable, sustainable and cost-effective. Figure 1.1.4 shows the increase in world energy production from different sources.

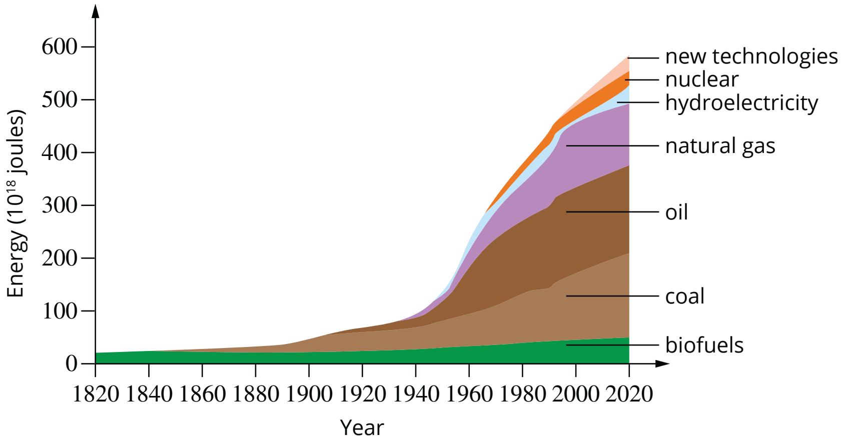


FIGURE 1.1.4 This graph shows the increase in world energy production.

FOSSIL FUELS

Non-renewable resources are those that are used faster than they can be replaced. Coal, oil and natural gas are non-renewable fuels. Reserves of fossil fuels are limited and they could eventually be exhausted.

Formation of fossil fuels

Coal, oil and natural gas were formed from ancient plants, animals and microorganisms. Buried under tonnes of mud, sand and rock, this once biological material has undergone complex changes to become the fossil fuels used by societies today. The organic matter still retains some of the chemical energy the plants originally accumulated by carrying out **photosynthesis**. Chemical energy in fossil fuels can be considered to be trapped solar energy.

Fossil fuel formation occurs over millions of years. This is why these fuels are considered non-renewable. Once reserves of the fossil fuels have been used, they will not be replaced in the foreseeable future.

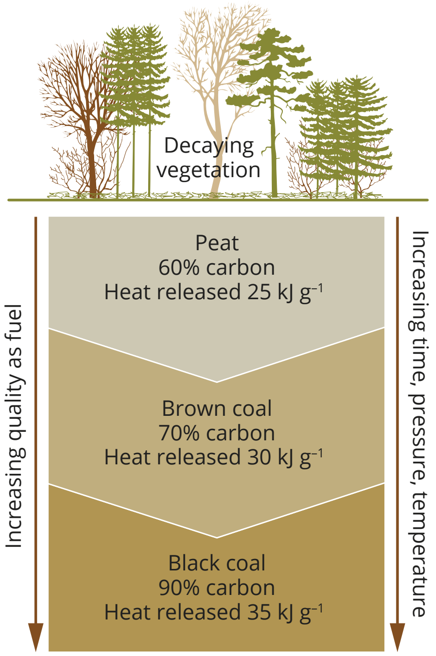


FIGURE 1.1.5 Steps in the formation of coal. Values of the carbon content and heat released upon combustion are for dried coal.

Coal

As wood and other plant material turn into coal, gradual chemical changes occur. Wood is about 50% carbon. As wood is converted into coal, the carbon content increases and the proportion of hydrogen and oxygen decreases. The wood progressively becomes peat, brown coal and then black coal (see Figure 1.1.5). Coal is a mixture of large molecules made from carbon, hydrogen, nitrogen, sulfur and other elements.

The amount of water in coal decreases as these changes occur. When coal is burnt, the energy released causes the water to vaporise, reducing the net amount of heat released. Black coal, which contains the least water and therefore the highest percentage of carbon, is a better fuel than brown coal or peat.

Although black coal is usually buried further underground than brown coal, its higher heat value often makes it economical to mine. Black coal is mined in Queensland and New South Wales. It is used for domestic power generation or exported overseas.

Large brown coal deposits are located in the Latrobe Valley in Victoria (see Figure 1.1.6). The power stations located next to these open-cut mines burn brown coal to generate electricity. Australia is the fifth largest producer of coal and the second largest exporter of coal in the world.

FIGURE 1.1.6 In Australia, brown coal is mined in the Latrobe Valley in Victoria.

CHEMFILE

Forming crude oil

The main deposits of crude oil were formed from small marine animals (zooplankton) and plants (phytoplankton) that lived up to 1 billion years ago. Some crude oil deposits are estimated to be even older, as much as 3–4 billion years old. If a deposit of crude oil was trapped beneath a layer of impermeable rock, then a layer of natural gas would also form.

The first deposits of crude oil were discovered at the end of the 19th century in the United States. Today, the largest crude oil deposits are in Russia, Iran, Iraq and Saudi Arabia. New crude oil deposits are still being found throughout the world. The oldest deposits found so far are in Venezuela, where the oil is estimated to be almost 4 billion years old. However, only about 10% of the oil discovered is profitable to extract.

Permeable rocks contain tiny spaces through which liquid substances can move. Crude oil has a lower density than water, so oil migrates upwards through permeable rocks over time. Large deposits of oil are formed when portions of this migrating oil become trapped under impermeable rocks. To extract the crude oil, drilling into the impermeable rock has to take place (see Figure 1.1.7). In most cases, the oil flows up by itself under high pressure that has gradually built up from when the oil was formed. As the extraction continues, the overall pressure drops and pumps are needed to extract the remaining deposit.

FIGURE 1.1.7 Operating drill during oil and gas exploration.

Fuels from crude oil

Crude oil (petroleum) is a mixture of hydrocarbon molecules that are mostly members of the **homologous series** of **alkanes**. Crude oil itself is of no use as a fuel, but it contains many useful compounds.

Crude oil is separated into a range of fractions by **fractional distillation**. Fractional distillation does not produce pure substances. Each fraction is still a mixture of hydrocarbon compounds. These fractions can be used as fuels, or treated further to produce more specific products through chemical processes.

The relative amounts of different alkanes in crude oil vary with the deposit. For example, oil from Bass Strait and the Carnarvon Basin, Western Australia, contains relatively few of the larger molecules needed to form lubricants and bitumen.

ℹ Alkanes are hydrocarbons with the general formula C_nH_{2n+2}. Alkanes are commonly found in crude oil.

CHEMISTRY IN ACTION

Fractional distillation of crude oil

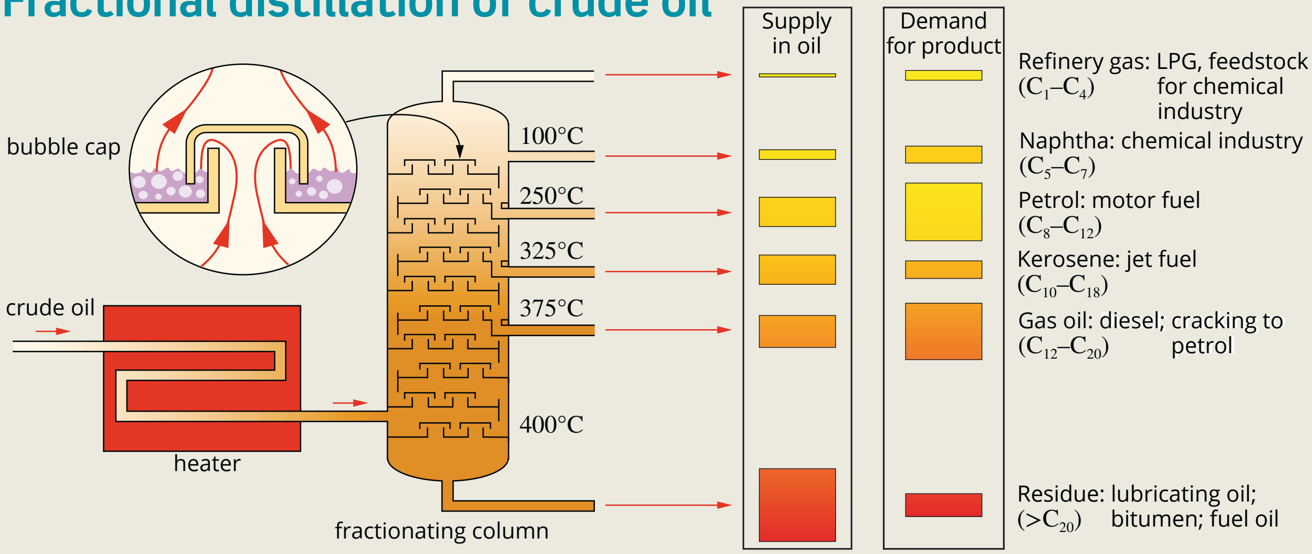


FIGURE 1.1.8 Fractional distillation of oil, and the bubble caps that stop the upward movement of gases.

Fractional distillation uses heat to separate a mixture into a number of different parts or fractions. A number of different temperatures are produced because of the nature of the column in which the crude oil is placed. The temperature of the tower decreases gradually with increasing height. Within the tower are horizontal trays, each containing hundreds of bubble caps. Bubble caps impede (stop) the upwards movement of gases (see Figure 1.1.8). As the vapour rises, it forces the caps up and it bubbles through condensed liquid in the trays. Those substances in the vapour that have boiling points almost equal to the temperature of the liquid in the trays condense and are collected. Consequently, fractions collected from trays higher in the tower will have lower boiling points.

The boiling point of a molecular compound depends on the strength of its intermolecular forces. Attractions between non-polar alkane molecules arise from weak dispersion forces, which are stronger with increasing molecular mass. As a result, each fraction consists of alkanes within a specific mass range. Lighter alkanes condense near the top of the tower, whereas heavier alkanes condense near the bottom. The composition and boiling range of each fraction are summarised in Figure 1.1.8. For example, the petrol fraction that boils (and condenses) between 100°C and 250°C consists of alkanes containing 8–12 carbon atoms; that is, C_8H_{18} to $C_{12}H_{26}$.

Oil reserves

Australia's relatively small oil reserves are likely to be exhausted later this century. Figure 1.1.9 (page 6) shows the current locations of Australian oil, gas and coal fields. These reserves are associated with giant offshore gas fields near the northern Western Australian coast, and in reserves in outback South Australia and Bass Strait. Australia already imports over 90% of the crude oil it uses. Importation of large amounts of oil has a significant impact on Australia's economy.

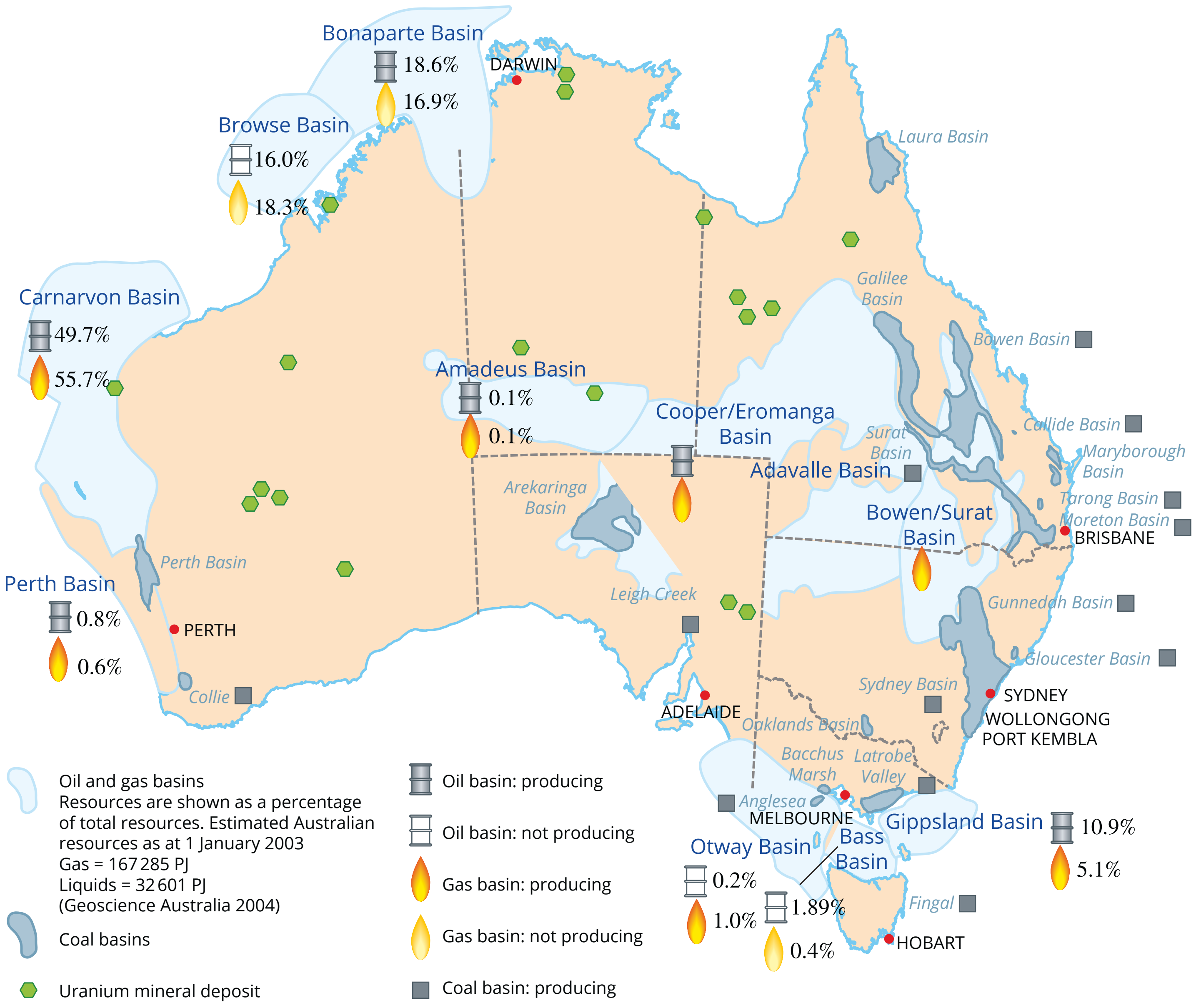


FIGURE 1.1.9 Australian oil, gas and coal fields.

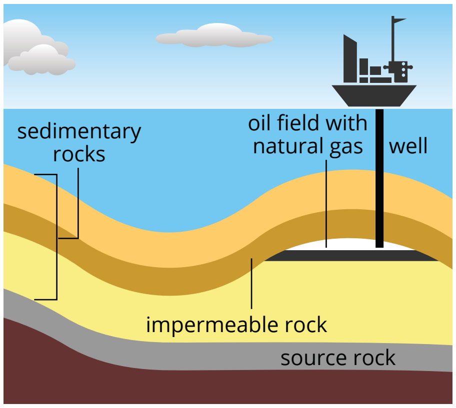


FIGURE 1.1.10 Natural gas deposits are often found trapped above crude oil. Once a well is sunk into the deposit, the natural gas flows to the surface.

Natural gas

Natural gas is another fossil fuel found in deposits in the Earth's crust. It is mainly composed of methane (CH_4) together with small amounts of other hydrocarbons such as ethane (C_2H_6) and propane (C_3H_8). Water, sulfur, carbon dioxide and nitrogen may also be present in natural gas.

Natural gas can be found:

- in gas reservoirs trapped between layers of rocks
- as a component of petroleum deposits
- in coal deposits where it is bonded to the surface of the coal. Coal seams usually contain water and the pressure of the water can keep the gas adsorbed to the coal surface. Natural gas found this way is known as **coal seam gas** or CSG. It is a major component of the energy supplies of Queensland
- trapped in shale rock, where it is referred to as **shale gas**. Shale gas is mined in many parts of the United States.

Natural gas is accessed by drilling as with crude oil; drilling causes the natural gas to flow to the surface (see Figure 1.1.10).

Fracking

The extraction of natural gas from coal or shale deposits usually involves a process called **fracking**. Under pressure, the natural gas is adsorbed on the surface of the coal or shale. Fracking is used to fracture the rock or coal to release the natural gas.

Fracking begins with drilling a well into the deposit to access the trapped gas. The well is encased in steel and concrete to prevent leakage into local water supplies. Fracking fluid is then pumped down the well at extremely high pressures. This high-pressure fluid fractures the surrounding rock or coal, creating fissures through which gas can flow. This process is shown in Figure 1.1.11.

Materials used for fracking include sand, water and other chemicals. There are concerns about the potential impact of this process on the local environment and underground water supplies.

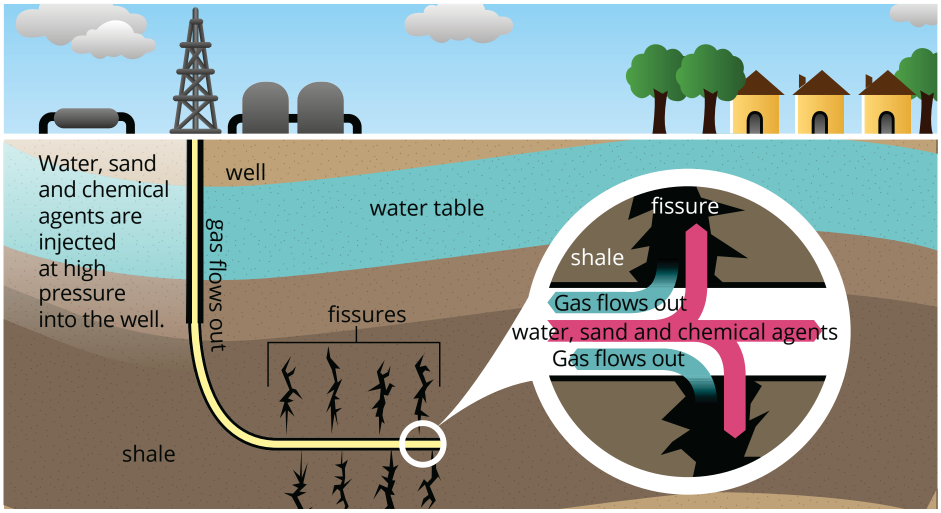


FIGURE 1.1.11 The fracking process: sand, water and other chemicals are injected into the deposit at high pressure to free the gas from the coal or shale.

CHEMISTRY IN ACTION

Debate surrounding coal seam gas

Coal seam gas (CSG) is a natural gas that is extracted from underground coal seams, where it is trapped in pores in the coal. Almost 30% of Australia's natural gas reserves come from coal seam gas. Reserves of CSG are found in New South Wales and Queensland. It is predicted that the reserves of CSG could supply the eastern states of Australia for over 25 years.

Various chemicals have been used as fracking fluids. Fracking fluids increase the permeability of the rock and therefore flow of gas to the surface. Fluids such as benzene, toluene, xylene and ethylbenzene were once commonly used. The use of these fluids has been banned in both New South Wales and Queensland because of concern over their effect on the environment. For example, these potentially carcinogenic compounds may escape and contaminate groundwater.

Water is now commonly used as a fracking fluid. Generally, large amounts of water are not available at the fracking site, so water needs to be transported in, which can have significant economic and environmental costs.

In 2015, there was a moratorium (ban) on coal seam gas exploration and fracking in Victoria. In September 2015, protestors rallied in the streets of Melbourne to express their concerns about the process (see Figure 1.1.12). The Victorian Government agreed to examine the science and impact of the CSG industry and methods while they extended their ban on the process.

FIGURE 1.1.12 Hundreds of protestors against fracking marching towards Parliament House in Melbourne in 2015.

Liquefied petroleum gas

Propane and butane gases can be separated from natural gas by fractional distillation. Propane and butane become liquids under pressure and are sold as **liquefied petroleum gas** (LPG). LPG is used as a fuel in cars and in home gas bottles. The natural gas remaining after the removal of propane and butane is used widely as a fuel for home heating and cooking.

BIOFUELS

Governments and industry are exploring alternatives to fossil fuels in order to meet our future energy needs and limit the impact of fossil fuels on the environment. Ideally, new sources of energy will be **renewable**. Renewable energy is energy that can be obtained from natural resources that can be constantly replenished.

Biochemical fuels (or **biofuels**) are fuels derived from plant materials such as grains (maize, wheat, barley or sorghum), sugar cane (Figure 1.1.13) and vegetable waste, and vegetable oils. The three main biofuels are **biogas**, **bioethanol** and **biodiesel**. They can be used alone or blended with fossil fuels such as petrol and diesel.

FIGURE 1.1.13 Harvesting sugar cane in Queensland. Sugar cane can be a source of the raw materials for the production of bioethanol.

As well as being renewable, biofuels are predicted to have less impact on the environment than fossil fuels. The plant materials used in the generation of biofuels are produced by photosynthesis, which removes carbon dioxide from the atmosphere and produces glucose ($C_6H_{12}O_6$) in the following reaction:

$$6CO_2(g) + 6H_2O(l) \rightarrow C_6H_{12}O_6(aq) + 6O_2(g)$$

The plants convert the glucose into cellulose and starch. Although carbon dioxide is released back into the atmosphere when the biofuel is burnt, the net impact should be less than for fossil fuels. You will compare fossil fuels and biofuels in more detail in later sections of this chapter.

Bioethanol

For thousands of years, humans have employed biological catalysts (**enzymes**) from yeasts to convert starches and sugars to ethanol. Enzymes catalyse the breakdown of the starch in grain crops (such as barley and wheat) to glucose. Other enzymes in yeasts then convert glucose and other small sugar molecules to ethanol (CH_3CH_2OH) and carbon dioxide in the **fermentation** reaction:

$$C_6H_{12}O_6(aq) \rightarrow 2CH_3CH_2OH(aq) + 2CO_2(g)$$

Bioethanol is used extensively in Australia. This includes E10 petrol, which contains 10% ethanol. This mix can be used by most modern car engines and its use reduces the consumption of petrol derived from crude oil.

Biogas

Biogas is gas that is released in the breakdown of organic waste by **anaerobic** bacteria. These bacteria decompose the complex molecules contained in substances such as carbohydrates and proteins into the simple molecular compounds carbon dioxide and methane. A digester (Figure 1.1.14) is a large tank filled with the anaerobic bacteria that digest (consume) the complex molecules to form biogas.

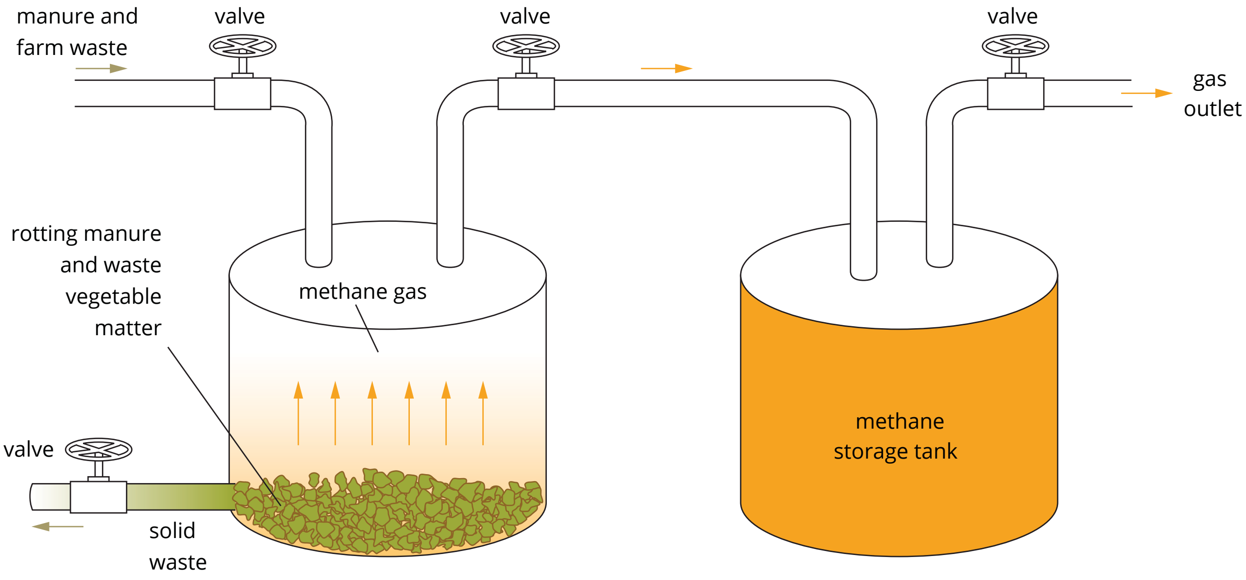


FIGURE 1.1.14 A digester is used in the production of biogas.

A range of materials, including rotting rubbish (such as that seen in Figure 1.1.15) and decomposing plant material, can be used to produce biogas.

The composition of biogas depends on the original material from which it is obtained and the method of decomposition. The typical composition of a sample of biogas is shown in Table 1.1.1.

FIGURE 1.1.15 Pipes buried in this rubbish tip collect biogas.

TABLE 1.1.1 Typical percentage composition of different molecules found in biogas

Gas	Formula	Percentage composition (by volume)
Methane	CH_4	60
Carbon dioxide	CO_2	32
Nitrogen	N_2	4.5
Hydrogen sulfide	H_2S	2
Oxygen	O_2	1
Hydrogen	H_2	0.5

As you can see from Table 1.1.1, biogas consists mainly of methane and carbon dioxide. Biogas can be used for heating and to power homes and farms. There are more than 7 million biogas generators in China. Biogas generators are particularly suited to farms, as the waste from a biogas generator makes a rich fertiliser.

In the future, it is likely more energy will be obtained from biogas generated at sewage works, chicken farms, piggeries and food-processing plants. Your local rubbish tip also has the potential to supply biogas. The gas can be used directly for small-scale heating or to generate electricity.

Biodiesel

Biodiesel is a mixture of organic compounds called esters. These esters are produced by a chemical reaction between vegetable oils or animal fats and an alcohol (most commonly methanol (CH_3OH)).

The usual raw material for the production of biodiesel is vegetable oil from sources such as soyabean, canola or palm oil. Recycled vegetable oil or animal fats can also be used. The structure of a typical biodiesel molecule is shown in Figure 1.1.16. (The production of biodiesel is discussed in section 1.3 on page 24.)

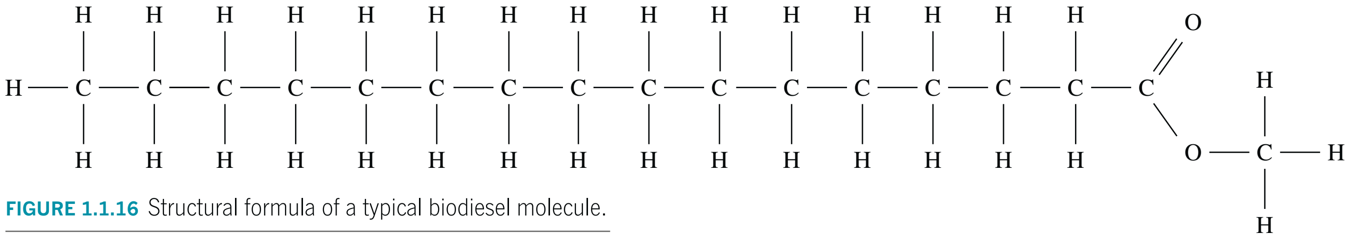


FIGURE 1.1.16 Structural formula of a typical biodiesel molecule.

1.1 Review

SUMMARY

- A fuel is a substance with stored energy that can be released relatively easily for use as heat or power.
- A fuel is considered to be non-renewable if it cannot be replenished at the rate at which it is consumed. Fossil fuels such as coal, oil and natural gas are non-renewable.
- Fossil fuels are produced over millions of years by the breakdown of biomass at high temperatures and pressures underground. Australia has large reserves of coal and natural gas.
- A fuel is considered to be renewable if it can be replenished at the rate at which it is consumed. Biofuels such as biogas, bioethanol and biodiesel are renewable.
- Biogas is formed by the anaerobic breakdown of organic waste.
- Bioethanol can be produced by fermentation of starches and sugars.
- Biodiesel is produced in a reaction between a vegetable oil or an animal fat and a small alcohol molecule such as methanol.
- Some of the non-renewable and renewable fuels in use in Australia are listed in Table 1.1.2.

TABLE 1.1.2 Types of renewable and non-renewable fuels in use in Australia

Non-renewable fuels	Renewable fuels
Coal Oil Liquefied petroleum gas (LPG) Natural gas Coal seam gas (CSG)	Bioethanol Biogas Biodiesel

KEY QUESTIONS

1 What is the difference between a renewable and non-renewable fuel?

2 Give an example of a renewable fuel source and a non-renewable fuel source used in Australia.

3 In Australia, which resource is likely to last longer before it is depleted: coal, oil or natural gas? Explain your answer.

4 Wood from forests is a renewable resource that supplied global energy needs for thousands of years.

   a Why is wood no longer sustainable as the major energy source for today's society?

   b Is it possible to have a non-renewable and sustainable energy source? Explain.

5 Why is it necessary to treat crude oil by fractional distillation?

1.2 Fossil fuels and biofuels

Fuels contain stored chemical energy that can be harnessed to perform useful functions. The heat energy released when fuels are burnt provides heat for warmth and cooking, as well as acting as the source of electrical energy and mechanical energy for transport.

In this section, you will look at the different fuels used to produce electricity or power vehicles and compare the environmental impact of these fuels.

ENERGY TRANSFORMATIONS

All substances contain chemical energy. The chemical energy of a substance is referred to as its **energy content**. Fuels are examples of substances with high energy contents.

When fuels are used, their chemical energy is converted to a different form of energy. For example, a competitive cyclist may eat energy bars. Much of the chemical energy of the food is converted in the cyclist's body to mechanical and kinetic energy.

The conversion of chemical energy to kinetic energy in the cyclist is an example of an **energy transformation**—energy is converted from one form to a different form. The use of fuels involves energy transformations. The chemical energy in a log on a fire can be converted to thermal energy to heat a room of a house.

FIGURE 1.2.1 Commercial solar cells convert solar energy to electrical energy with an efficiency of 12–18%.

When energy transformations occur, the total amount of energy is unchanged because energy cannot be created or destroyed. However, not all of the energy is converted to one specific form. In the case of the solar power cells shown in Figure 1.2.1, not all of the energy of the sunlight is converted to electrical energy.

The term **energy efficiency** is used to describe the percentage of energy from a source that is converted to useful energy. For example, if the efficiency of a solar panel on a roof is listed as 17%, it means that 17% of the energy arriving on the panel from the Sun is transformed to electrical energy. The other 83% is converted to other forms of energy. The largest proportion of the Sun's energy reaching the solar cells is converted into heat energy that simply increases the temperature of the cells.

ELECTRICITY PRODUCTION

Chemical energy from most fuels is harnessed through **combustion** of the fuel. In combustion reactions, the reactant combines with oxygen to produce carbon dioxide and water. Thermal energy released from the combustion of fuels can be converted into electrical energy. In Australia, electrical energy is produced from several different fuels.

Electricity from coal

The combustion of coal generates over three-quarters of Australia's electricity. Rather than transport coal to every factory, office and household, the chemical energy is converted to electrical energy at a power station. Electricity is transmitted easily from the power station by metal cables and wires to other regions. The reaction occurring when coal burns can be written as:

$$C(s) + O_2(g) \rightarrow CO_2(g)$$

The energy released from the combustion of coal is about 32 kJ g^{-1}.

A number of energy transformations occur in a coal-fired power station.

- Coal is burnt—chemical energy in coal is converted to thermal energy.
- Heat from the burning coal is used to boil water—thermal energy from the burning coal becomes thermal energy in steam.
- Steam is passed through a turbine—thermal energy in the steam becomes mechanical energy as the turbine spins. (This is the least efficient energy transformation in the sequence.)
- Electricity is produced from a generator that is driven by the turbine—mechanical energy is converted to electrical energy.

Figure 1.2.2 illustrates how the thermal energy released by the coal is converted to electrical energy.

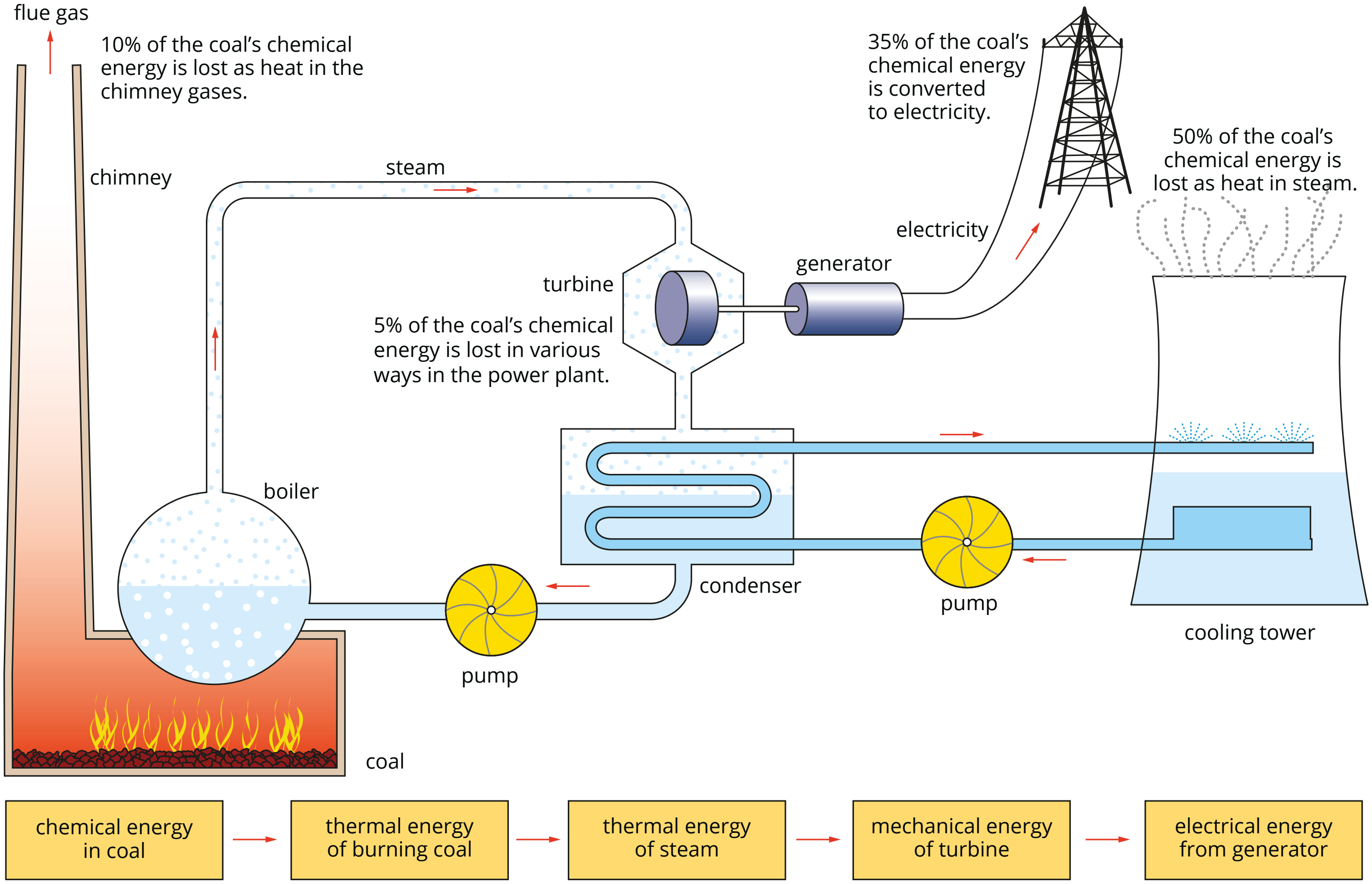


FIGURE 1.2.2 A representation of the process of burning coal to produce electricity. The chemical energy in the coal undergoes several transformations before electricity is produced.

The overall efficiency of a coal-fired power station is 30–40%. The combustion of brown coal is usually at the lower end of this efficiency range. Energy is lost during each step of the process, mainly as heat.

Electricity from natural gas

Natural gas is also used in Victoria to generate electricity for the power grid. In a gas-fired power plant, methane and other small alkanes are burnt to release energy. As shown in Figure 1.2.3, the hot gases produced by combustion cause air to expand in a combustion turbine to generate electrical energy. This is a simpler process than in a coal-fired plant where the thermal energy is used to produce steam.

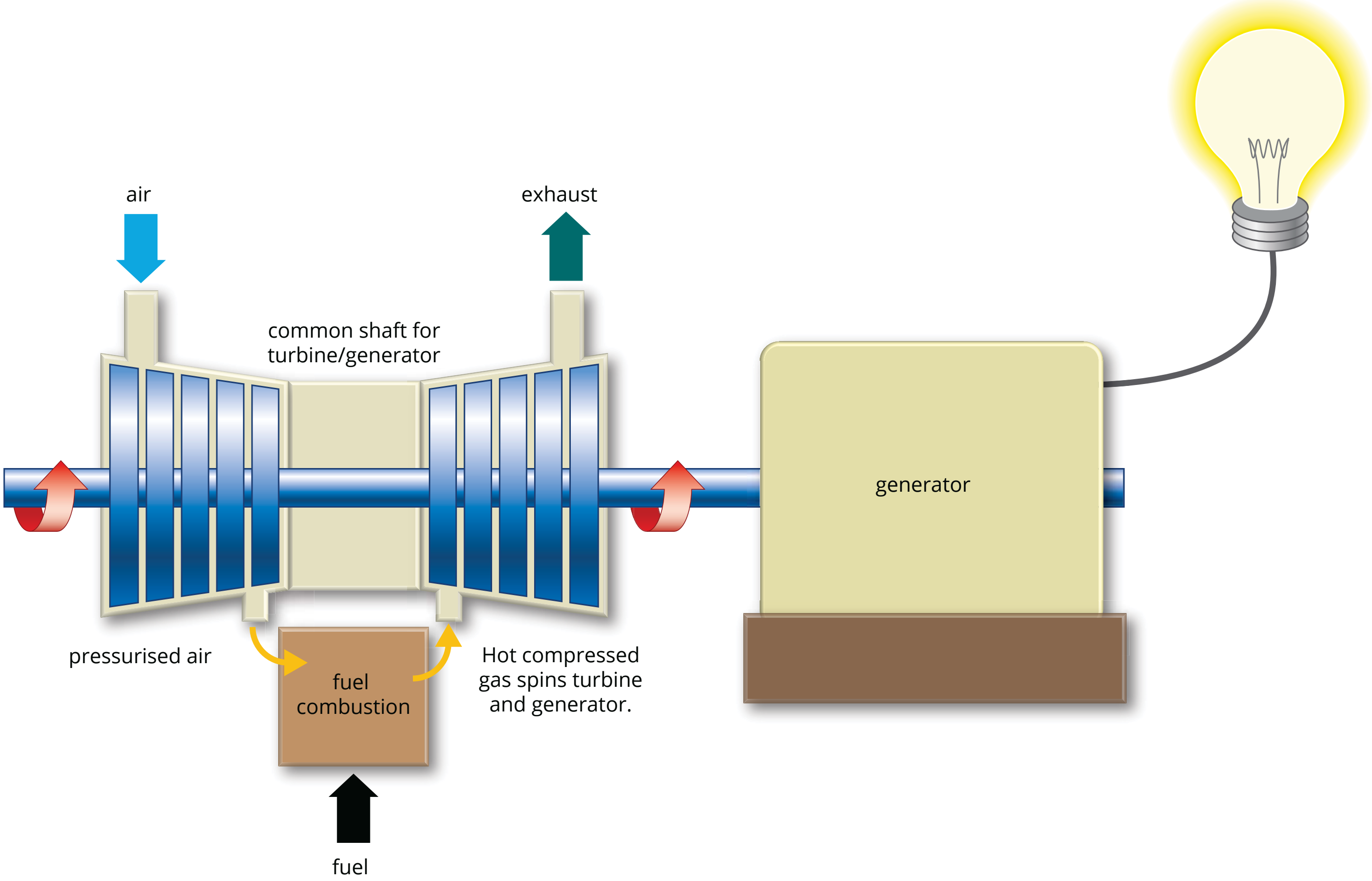


FIGURE 1.2.3 In a gas-fired power plant, the hot gases produced expand air in a combustion turbine to generate electricity.

The composition of natural gas varies but the main combustion reaction involves methane. The equation is:

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$$

The combustion of 1 mole of methane releases 890 kJ of energy, equivalent to 55.6 kJ g^{-1}. This is a significantly higher value than that of coal.

A gas-fired plant is more efficient than a coal-fired power station, reaching efficiencies just over 40%. Gas-fired plants also emit less carbon dioxide and particulate matter (small solid particles of solid combustion products) per unit of energy released. An added advantage of gas-fired plants is that the output can be varied at short notice. This allows the operators to adjust to the fluctuating power usage of consumers.

The largest gas-fired power station in Victoria, shown in Figure 1.2.4 (page 14), is operated by Origin Energy at Mortlake in south-west Victoria. The plant uses natural gas collected from off the nearby coast to generate electricity. Most Australian states have gas-fired plants but many of the plants are small-scale ones. Coal seam gas is the source of methane used in some states.

FIGURE 1.2.4 The Mortlake gas-fired power station, 200 km west of Melbourne, was opened in 2012. Natural gas from the Otway Basin is piped to this facility where it is burnt to produce electricity.

Electricity from biogas

Biogas is a renewable fuel that can be used to generate electricity, usually in small-scale electricity generators rather than large power plants. These smaller generators are often located at the site where the biogas is produced. For example, sewage works commonly burn biogas produced in a generator to supply some of their power needs.

The main reaction occurring in the combustion of biogas is the same reaction of methane burning in a gas-fired power station. The energy released per gram of biogas is less than that of natural gas because the methane content in biogas is significantly lower.

Berrybank Farm near Ballarat is an example of the innovative use of biogas. Over $2 million has been spent on building infrastructure to collect the manure from 20 000 pigs. The manure is fed into a digester that produces two useful products: biogas and fertiliser. The biogas is used to fire generators, like the one shown in Figure 1.2.5, that produce an estimated $180 000 of electricity annually.

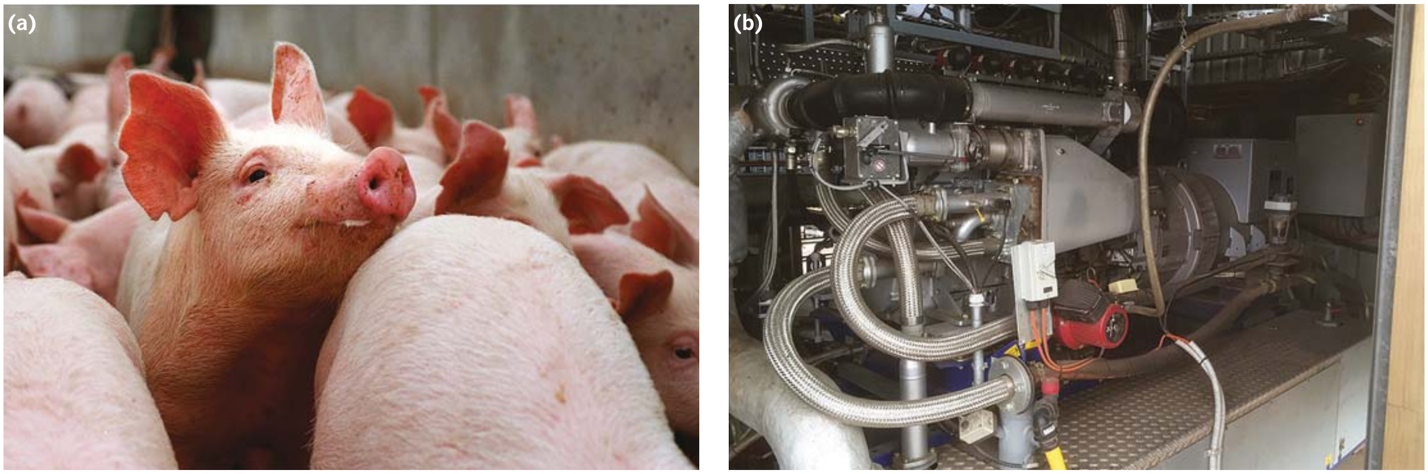


FIGURE 1.2.5 (a) Some of the pigs on the Berrybank Farm near Ballarat; (b) one of the generators that uses the biogas fuel.

FUEL FOR TRANSPORT

Crude oil is the source of most of the fuel we use for transport. Crude oil is a mix of alkanes. The alkanes in crude oil are separated into a series of fractions (parts) by fractional distillation. Some of these fractions are important fuels, such as liquid petroleum gas (LPG), petrol, kerosene and petrodiesel. LPG can also be separated from natural gas.

Petrol

Perhaps the most important of all hydrocarbon combustion reactions are those that occur when petrol is burnt. Petrol is a mixture of hydrocarbons, including octane, and the combustion reactions of these chemicals power most of Australia's 17.6 million motor vehicles. The equation for the combustion of octane is:

$$2C_8H_{18}(l) + 25O_2(g) \rightarrow 16CO_2(g) + 18H_2O(l)$$

The combustion of 1 mole of octane releases 5450 kJ of energy, equivalent to 47.8 kJ g^{-1}. Combustion occurs in the cylinder of a car engine. The hot gases formed push the piston in the engine, enabling the car to move. A typical piston is shown in Figure 1.2.6.

The efficiency of a petrol engine in a new car can be as high as 25%. The operation of a piston in a car engine can be seen in Figure 1.2.7.

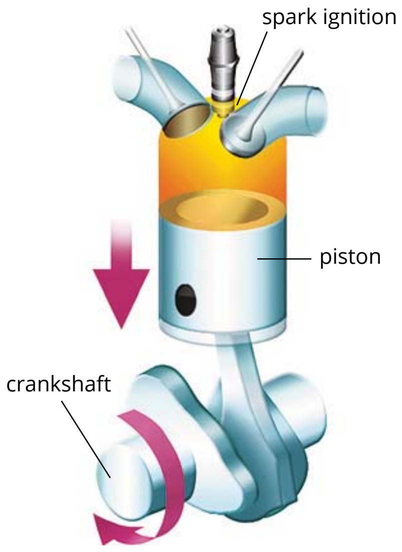


FIGURE 1.2.6 The combustion of octane (C_8H_{18}) and the other hydrocarbons in petrol pushes the pistons in internal combustion engines.

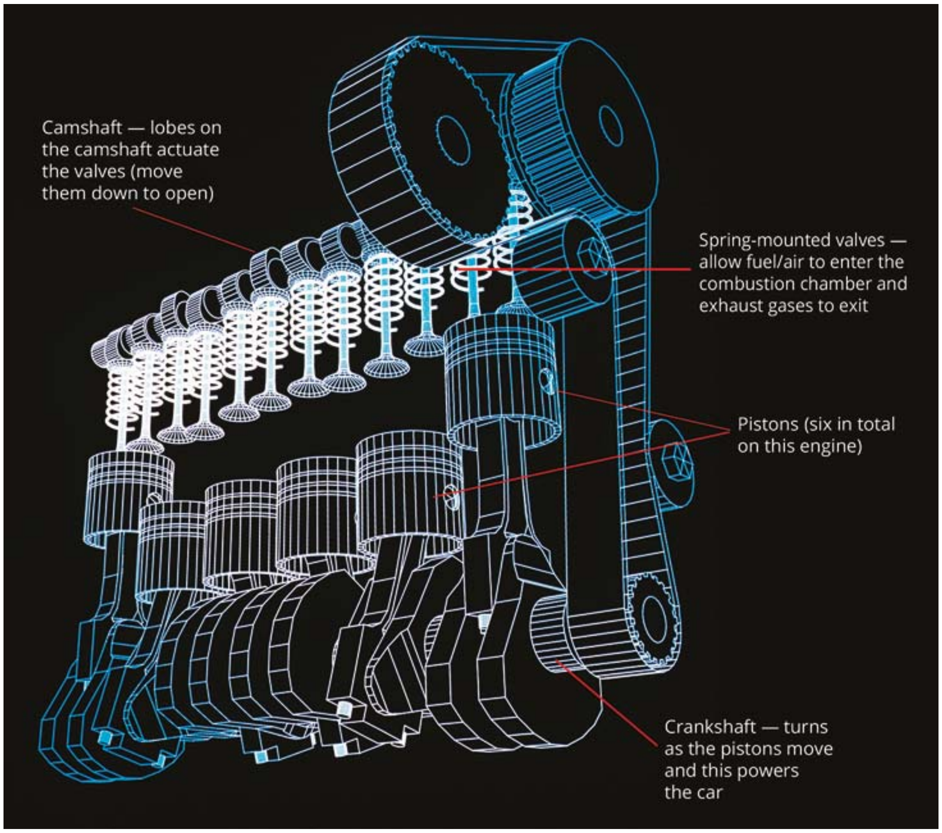


FIGURE 1.2.7 In a standard engine, fuel and air are mixed in cylinders and then compressed, and the mixture is ignited. The explosion drives the piston down, which turns the crankshaft and powers the car. The flow of fuel and exhaust gases is controlled by spring-mounted valves shown in the centre.

Liquid petroleum gas

Liquid petroleum gas (LPG) can also be used in cars. Most of the vehicles that use LPG as a fuel have a standard petrol engine with a fuel tank and fuel injection system modified to suit a gaseous fuel. The equation for the combustion of propane, a major component of LPG, is:

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

The combustion of 1 mole of propane releases 2220 kJ of energy, equivalent to 50.5 kJ g^{-1}.

In Australia, LPG is a significantly cheaper fuel than petrol, yet its popularity is still limited. Some of the reasons for this are:

- most new vehicles are designed to run on petrol; therefore, the owner has to pay around $2000 for a conversion
- the LPG fuel tank takes up boot space

- there are fears that LPG cylinders might explode if the vehicle crashes
- the prices of fuels fluctuate, so often it is difficult to do meaningful price comparisons.

Bioethanol

Australia imports over 90% of its fuel requirements. This reliance on other countries, combined with concerns over the greenhouse emissions of fossil fuels, has sparked interest in the production of the renewable biofuels, bioethanol and biodiesel. Biodiesel is discussed in detail in the next section of this chapter.

Bioethanol can be produced from crops such as sugar cane. However, sugar cane is also needed for sugar production so there are limits to the amounts of bioethanol that can be produced in this way. Instead, researchers are trialling less valuable sources of sugar and starch for bioethanol production.

The Manildra plant at Nowra in New South Wales, shown in Figure 1.2.8, is one of Australia's largest ethanol refineries. At this plant, flour and starch are produced from wheat and sold for use in food manufacture. The waste that remains still contains high levels of starch, which is converted to ethanol.

FIGURE 1.2.8 Ethanol refinery in Manildra at Nowra, New South Wales.

Ethanol can be blended with petrol for use in motor vehicles. Australian government regulations limit the proportion of ethanol in petrol to 10%. This petrol blend is labelled E10 and sold at most Australian service stations. The presence of ethanol reduces the emissions of particulates and gases such as oxides of nitrogen, but higher levels of ethanol can damage engines, especially in older vehicles.

The equation for the combustion of ethanol is:

$$C_2H_5OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l)$$

The combustion of 1 mole of ethanol releases 1367 kJ of energy, equivalent to 29.7 kJ g^{-1}. As Table 1.2.1 shows, the energy content of ethanol is about 62% that of petrol, so a larger mass (and volume) of ethanol is required to provide the same amount of energy. At a simple level, the lower energy content of ethanol can be regarded as the result of the carbon atoms in an ethanol molecule being partly oxidised ('partly burnt'). This is due to the presence of oxygen in the ethanol molecule.

TABLE 1.2.1 Energy content and energy density of vehicle fuels

Fuel	Energy content (kJ g^{-1})	Energy density (kJ L^{-1})
Methane	55.6	23 500 (liquefied)
Propane (LPG component)	50.5	29 400 (liquefied)
Butane (LPG component)	49.6	29 800 (liquefied)
Octane (petrol fraction)	47.8	33 400
Ethanol	29.7	23 400

ENVIRONMENTAL IMPACT

A discussion of the environmental impact of fuels needs to consider both the impact of emissions from the combustion of the fuel, and the impact on the environment of obtaining the fuel in the first place.

Emissions from fuel combustion

Carbon dioxide

Because large quantities of fuel are burnt every day to meet society's energy needs, the level of carbon dioxide production is high. This is a concern because carbon dioxide is a **greenhouse gas**.

Energy from the Sun heats the surface of the Earth. The Earth in turn radiates energy back towards space but greenhouse gases in the atmosphere absorb and re-radiate the energy in a process known as the **greenhouse effect**. The higher the concentration of greenhouse gas, the more energy is trapped.

The greenhouse effect occurs naturally due to the gases present in the atmosphere. However, scientists are concerned that increasing levels of greenhouse gases produced by our use of fossil fuels are causing global warming and triggering consequential shifts in weather patterns and climate. This is referred to as the enhanced greenhouse effect.

Methane, water vapour, nitrogen oxides and ozone are also greenhouse gases. Methane is 21 times more effective at trapping heat than carbon dioxide. The way in which greenhouse gases restrict heat radiation leaving the Earth is shown in Figure 1.2.9.

The greenhouse effect is caused by heat being trapped in the Earth's atmosphere by greenhouse gases, which causes an increase in temperatures at the Earth's surface. As the amount of greenhouse gases in the Earth's atmosphere increases due to human activities, more heat is trapped, which is predicted to cause global changes in climate.

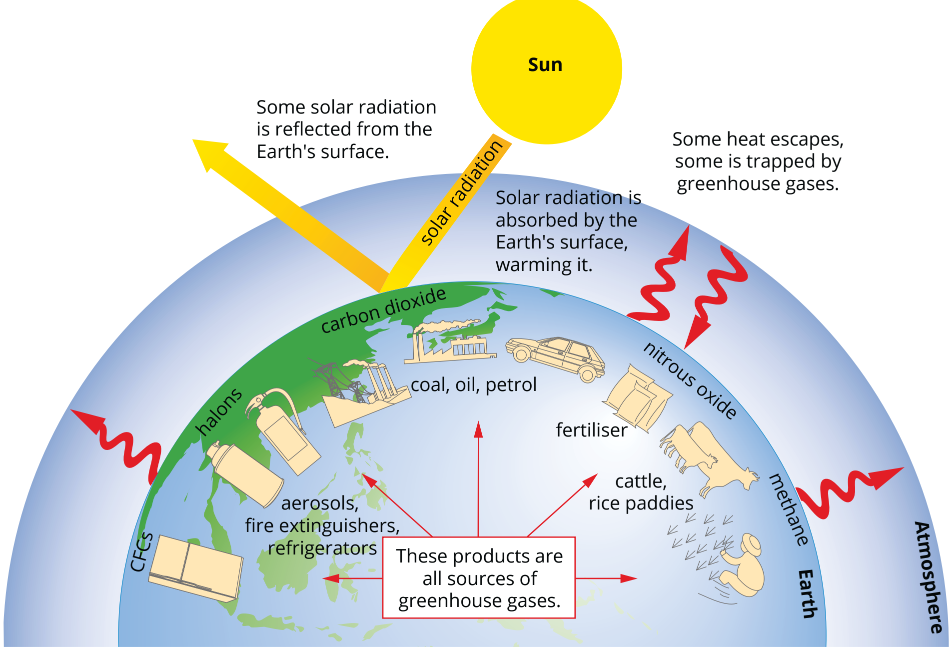


FIGURE 1.2.9 The greenhouse effect. Greenhouse gases help to maintain the temperature at the Earth's surface. Increased quantities of these gases as a result of human activities create an enhanced greenhouse effect.

The graph shown in Figure 1.2.10 supports concerns that the Earth is warming. Many countries are choosing alternatives to fossil fuels to address these fears.

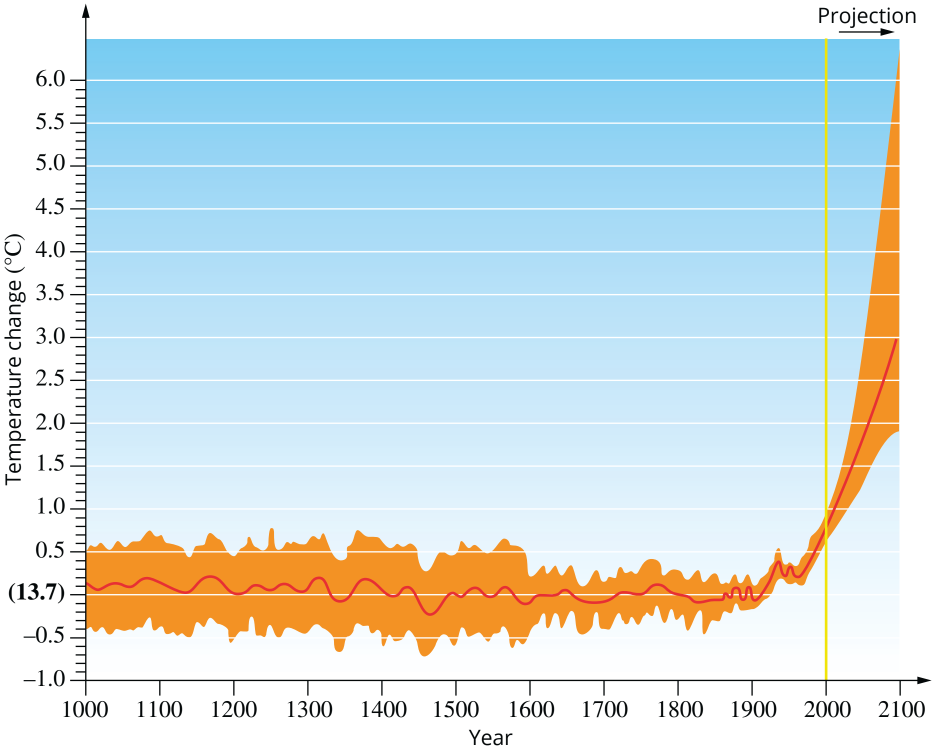


FIGURE 1.2.10 Change in the average surface temperature of the Earth from the year 1000 projected to 2100. Estimates of future temperature increases vary, depending on what assumptions are made.

Each fuel discussed in this section produces carbon dioxide when it burns. Table 1.2.2 compares the theoretical mass of carbon dioxide produced from the complete combustion of 1 gram of each fuel and per unit of energy produced.

TABLE 1.2.2 Mass of CO_2 produced from the combustion of 1 gram of fuel

Fuel	Mass of CO_2 (g) emitted per gram of fuel	Mass of CO_2 (g) per megajoule of energy produced (approx.)
Coal	3.7	93
Natural gas	2.8	56
LPG	3.0	65
Petrol	3.1	73
Ethanol	1.9	72

Bioethanol is a renewable fuel derived from plants. Although carbon dioxide is produced when bioethanol burns, carbon dioxide is also absorbed by the plants as they grow. For this reason, the widespread use of bioethanol should lead to a net reduction in the levels of carbon dioxide emitted.

However, bioethanol is not **carbon neutral**. This is because energy is required, and emissions are produced, in the growing, transport and refining of the fuel. Note also that although a relatively low mass of carbon dioxide is emitted per gram of fuel burnt, because bioethanol produces much less energy than the same mass or volume of petrol, a similar mass of carbon dioxide is emitted to produce the same quantity of energy.

CHEMFILE

Cleaner coal

Research is being conducted into ways of reducing carbon dioxide emissions from coal-fired power stations. These include:

- storing carbon dioxide deep underground (geosequestration)
- removing water from brown coal by heating; the volatile hydrocarbons that are driven off are also burnt to produce electricity
- absorbing carbon dioxide into solvents (chemical capture).

There are several methods for converting coal to liquid and gaseous fuels. Flash pyrolysis has been developed by CSIRO for converting coal to oil. In this process, crushed coal is heated to 600°C. The tar that forms is reacted with hydrogen to give a type of crude oil.

Other emissions

Carbon dioxide and water vapour are not the only products formed when fuels are burnt. Fuels may contain elements such as sulfur, which burns to form sulfur dioxide, or the high temperatures of combustion can lead to reactions with nitrogen in air. Table 1.2.3 lists the more common pollutants formed.

TABLE 1.2.3 Pollutants formed from fuel combustion

Emission	Formation	Comments
Sulfur dioxide (SO_2)	Sulfur in fuel reacts with oxygen: $S(s) + O_2(g) \rightarrow SO_2(g)$	Causes respiratory problems. Leads to the formation of **acid rain**
Nitrogen oxides (NO and NO_2)	Nitrogen in fuel reacts with oxygen, or nitrogen in air reacts due to high temperatures: $N_2(g) + O_2(g) \rightarrow 2NO(g)$ $2NO(g) + O_2(g) \rightarrow 2NO_2(g)$	Causes respiratory problems. Leads to the formation of other pollutants and acid rain
Ozone (O_3)	Nitrogen oxides react with oxygen at high temperatures	Causes respiratory problems
Particulates, such as ash	Combustion of impurities in fuel	Irritant. Adheres to houses and plants
Carbon monoxide	Incomplete combustion of fuel	Poisonous gas
Organic chemicals such as methanal and ethanal	Reactions of other organic chemicals in fuel	Toxic and carcinogenic compounds

The levels of each pollutant mentioned in Table 1.2.3 vary with the composition of the fuel and the efficiency of the particular combustion process. However, it is possible to generalise.

- Ash is usually more of a problem with coal than other fuels. Ash is produced when coal is burnt without any purification or removal of impurities.
- Sulfur levels are lower in natural gas and LPG than in liquid or solid fossil fuels.
- The molecules in petrol are larger than the molecules in natural gas, LPG and ethanol. As a consequence, the combustion of petrol tends to be less complete. This produces more carbon monoxide and particulates.
- Although biofuels are renewable, they can still produce the same pollutants as fossil fuels when burnt.

Environmental impact of sourcing the fuel

All fuels have to be mined or produced and the environmental impact of sourcing a fuel needs to be considered. Table 1.2.4 shows some of the sources of the fuels described in this chapter.

TABLE 1.2.4 Sources of fuels

Fuel source	Notes
 Biogas collected under domes from a sewage plant	Biogas is often collected from sewage farms and rubbish tips. The gas collection minimises emissions associated with these sites. Because methane is much more effective as a greenhouse gas than carbon dioxide, it is better to collect the methane in biogas and combust it to produce carbon dioxide than to release it directly to the atmosphere.
 Oil rig	Oil rigs, once in place, can operate with low impact on the environment but the issues created when a spill or explosion occurs can be significant.
 Open-cut coal mine	Coal mines can be open cut or underground. Open-cut mines, such as in the Latrobe Valley in Victoria, are damaging to the local environment.
 Harvesting a wheat crop for bioethanol production	Bioethanol is produced from crops. Growing crops requires energy expenditure and the use of resources such as water and fertiliser. Intensive farming can lead to land degradation and erosion. These are larger issues if crops are grown solely to produce ethanol, but of less concern if waste from food crops is used as a raw material. Diverting crops from fuel production could also drive up the cost of food produced from those crops.

CHEMFILE

The Hazelwood coal mine fire

On a very hot day, on 9 February 2014, the Hazelwood open-cut coal mine in Victoria caught fire (see Figure 1.2.11). Normal bushfires are difficult to manage, but it soon became apparent that a fire in a coal mine presented unprecedented problems. Coal is a good fuel and a very large surface of coal was exposed at the mine. The smoke from the burning coal was toxic and it was difficult for firefighters to work near the front of the fire.

The adverse health effects of the Hazelwood mine fire were significant. In the short term, residents experienced headaches, sore throats and respiratory difficulties. Residents and workers will be monitored over the next 20 years for signs of more permanent damage to the lungs and circulatory systems.

The fire burnt for 45 days. During that time:

- vulnerable residents were evacuated from nearby Morwell
- school children were transported to schools further from the mine
- many firefighters were treated for smoke inhalation
- residents were advised to stay indoors.

FIGURE 1.2.11 Smoke from the Hazelwood coal mine fire blowing over the nearby town of Morwell.

RENEWABILITY

Fossil fuels are a non-renewable source of energy. It took millions of years for their formation in the Earth's crust, so the likelihood of new deposits forming cannot be considered. The reserves of each fossil fuel are summarised below.

- Coal—reserves are extensive but low efficiency and concerns about emissions are making coal increasingly less popular as a fuel.
- Crude oil—reserves are more limited than those of coal and availability is likely to decline in coming decades.
- Natural gas—deposits are likely to be exhausted over the coming decades but reserves of coal seam gas and shale gas could potentially provide natural gas into the next century. Concerns over fracking need to be resolved if natural gas is to be sourced from these reserves.

Biofuels are renewable and current production levels are sustainable. However, biofuels produce only a small percentage of Australia's fuel needs.

If biofuel production were to increase significantly, we could need to grow crops specifically for this purpose. This would present a number of issues, including land degradation, clearing of forest and bushland, and ensuring food supplies are maintained.

1.2 Review

SUMMARY

- Fuels such as petrol, natural gas, biogas and bioethanol undergo combustion reactions in excess oxygen to form carbon dioxide and water.
- The combustion reactions of fuels are used to produce electricity and to power vehicles.
- In a coal-fired power station, thermal energy from coal creates steam that is used to turn a turbine and generate electricity. The efficiency of this process is between 30 and 40%.
- Electricity can also be produced from the combustion of natural gas or biogas.
- Petrol engines can use petrol or petrol blended with ethanol. Engines can also be modified to run on LPG.
- The combustion of fuels produces a range of other pollutants such as carbon monoxide, sulfur dioxide, nitrogen oxides and particulates.
- Petrol produces more energy per gram than LPG or bioethanol. However, bioethanol and LPG produce less carbon dioxide and particulates in emissions.
- Biofuels offer several environmental advantages: CO_2 is absorbed during the growth of crops used in their production, they can be replenished and they can be produced from material that would have otherwise been waste.
- A shift to large-scale production of biofuels could place a strain on resources and available farmland.
- Table 1.2.5 compares the advantages and disadvantages of some fuels.

TABLE 1.2.5 Advantages and disadvantages of fuels described in this section

Fuel	Advantages	Disadvantages
Coal	• Large reserves • Less easily transported than liquid or gaseous fuels • Relatively high energy content	• Non-renewable • High level of emissions
Natural gas	• More efficient than coal for electricity production • Easy to transport through pipes • Relatively high energy content	• Non-renewable • Limited reserves • Polluting but less than coal and petrol
Biogas	• Renewable • Made from waste • Reduces waste disposal • Low running costs • CO_2 absorbed during photosynthesis	• Low energy content • Supply of waste raw materials limited
Petrol	• High energy content • Ease of transport	• Non-renewable • Polluting but less than coal • Limited reserves
LPG	• Low cost • Easily separated from natural gas • Relatively high energy content; fewer particulates produced than petrol	• Non-renewable • Polluting but less than petrol
Bioethanol	• Renewable • Can be made from waste • CO_2 absorbed during photosynthesis • Burns smoothly • Fewer particulates produced than petrol	• Limited supply of raw materials from which to produce it • Lower energy content than petrol • May require use of farmland otherwise used for food production

KEY QUESTIONS

1 The following processes are all part of the production of electrical energy from coal. Arrange these processes in order of occurrence.
- Energy released from coal is transferred to water.
- Steam spins a turbine.
- Coal is added to a furnace.
- Coal is excavated, crushed and dried.
- Steam is produced.
- Electricity is generated.

2 Classify each of the following as an advantage or a disadvantage of the use of bioethanol compared to petrol as an energy source.

a Less CO_2 impact overall
b Lower energy content (kJ g^{-1})
c Can be produced from waste products
d Renewable resource
e Greater amount of CO_2 emitted to travel a set distance

3 Methane can be sourced from crude oil, coal seam gas, sewage and gas wells.

Complete the following table that describes the sources of methane and the process used to extract or separate the methane.

Source	Composition of source	Extraction process
Crude oil		
Coal seam gas		
Sewage		
Gas well		

4 **a** The water content of brown coal is 60–70%. What implications does this high water content have for the energy released from burning the coal?
b What pre-treatment could raise the energy content per gram of brown coal consumed in a power station?
c If some electricity produced from burning coal was used to reduce its water content, then how could this energy cost be minimised?
d What impact do impurities such as sulfur have on generating electricity from brown coal?

1.3 Petrodiesel and biodiesel

The high energy content of diesel makes it an excellent fuel for transportation and equipment designed to do heavy work. For many years, **petrodiesel**, which is produced from crude oil, has been the primary source of fuel for diesel engines. Some of the uses of diesel in transport are in ocean liners, farming machinery and the engines that provide the energy for the large hauling capacity of mining trucks (Figure 1.3.1).

In the last 20 years, biodiesel has emerged as an alternative to petrodiesel. In this section, you will compare the sourcing, performance and environmental impact of these two fuels.

FIGURE 1.3.1 (a) The largest ocean liners resemble floating cities. They are powered by enormous diesel engines like this one. (b) Diesel engines provide the power necessary for heavy-duty tractors. (c) Diesel engines provide the energy for the large hauling capacity of mining trucks.

CHEMFILE

Rudolf Diesel

Rudolf Diesel (1858–1913) (Figure 1.3.2) was a German engineer who invented the 'oil engine' that was named after him. His prototype engine first operated in 1893 and was powered by peanut oil. Diesel was well aware of the potential value of an engine that could run on renewable fuel. He demonstrated his engine at the World Exhibition in Paris in 1900 and was awarded the Grand Prix—the highest prize.

Just before his death in 1913, Diesel stated: 'The diesel engine can be fed with vegetable oils and would help considerably in the development of agriculture of the countries which use it.'

Diesel also predicted that: 'The use of vegetable oils for engine fuels may seem insignificant today. But such oils may become, in course of time, as important as petroleum and the coal tar products of the present time.'

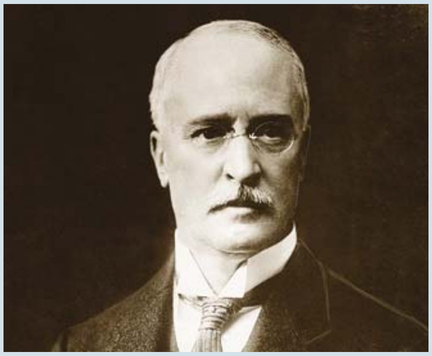


FIGURE 1.3.2 Rudolf Diesel invented the diesel engine.

DIESEL PRODUCTION AND STRUCTURE

A diesel engine is a form of internal combustion engine that does not require a spark to ignite the fuel in the engine cylinder. Diesel engines are favoured in situations requiring high fuel efficiencies and for heavy haulage vehicles.

Diesel engines have a 20–40% better fuel economy than petrol engines because:

- diesel engines are typically more energy efficient than petrol engines
- diesel fuel has a higher density than petrol, so although the energy content of diesel and petrol, measured in kJ g^{-1}, is similar, diesel fuel yields more energy per litre.

The most common form of diesel fuel is petrodiesel, which is produced from crude oil. However, biodiesel is increasingly being manufactured as an alternative. The two pathways for producing diesel are shown in Figure 1.3.3.

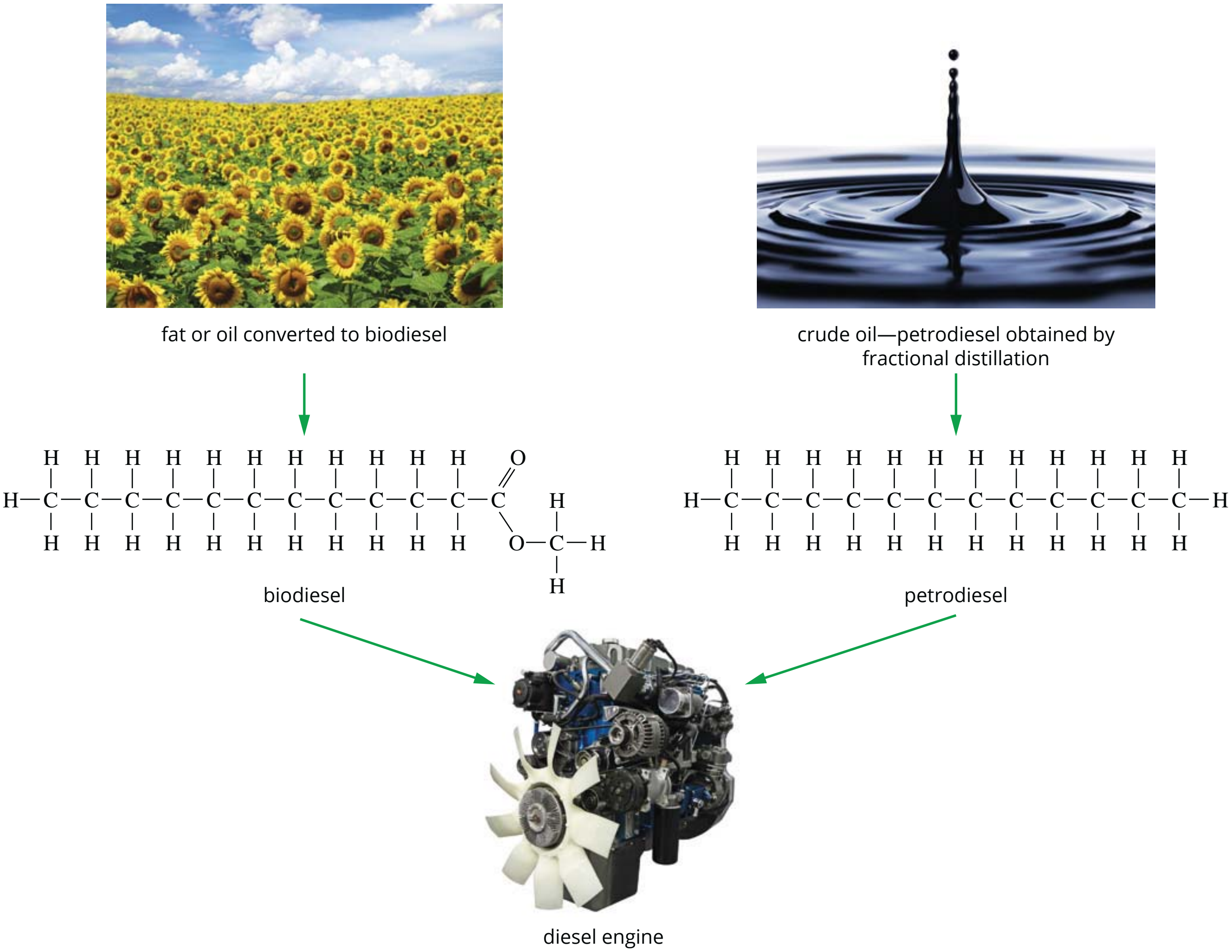
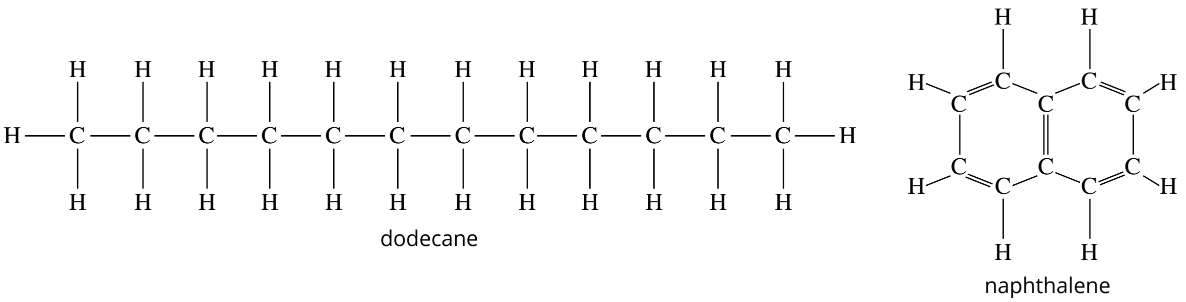


FIGURE 1.3.3 Two methods of producing diesel fuel. Biodiesel can be produced from the oil of crops such as sunflowers. Petrodiesel is produced through fractional distillation of crude oil. Pure forms of biodiesel and petrodiesel can be used in a diesel engine or they can be blended together.

Petrodiesel

Petrodiesel is one of the products of the fractional distillation of oil. It is not a pure substance. Different manufacturers produce petrodiesel of different compositions, but petrodiesel is generally around 75% alkanes and 25% **aromatic hydrocarbons**. The alkanes range from $C_{10}H_{22}$ to $C_{15}H_{32}$. Aromatic hydrocarbons contain molecules made up of six-membered carbon rings with alternating single and double bonds. You can see the structures of both alkanes and aromatic hydrocarbons found in petrodiesel in Figure 1.3.4.



dodecane

naphthalene

FIGURE 1.3.4 Components of petrodiesel include alkanes, such as dodecane, and aromatic compounds, such as naphthalene.

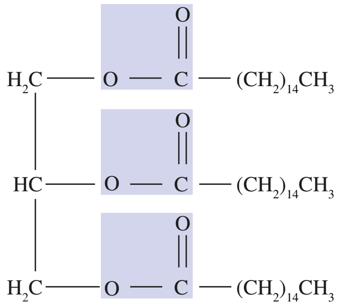


FIGURE 1.3.5 The structure of a triglyceride molecule. There are three ester functional groups in the molecule. The ester groups are shaded.

Biodiesel

Fats and oils are **triglycerides** with a molecular structure consisting of three hydrocarbon chains attached by ester functional groups to a backbone of three carbon atoms, as shown in Figure 1.3.5.

The triglyceride is converted into biodiesel by warming it with an alcohol, usually methanol, in a process known as **transesterification**. Potassium hydroxide solution acts as a **catalyst** in this reaction. A catalyst is a substance that increases the rate of a reaction without being consumed itself.

In the transesterification reaction, the triglyceride is converted into a small molecule called glycerol and three ester molecules with long carbon chains. The ester molecules are the biodiesel product. The reaction is shown in Figure 1.3.6.

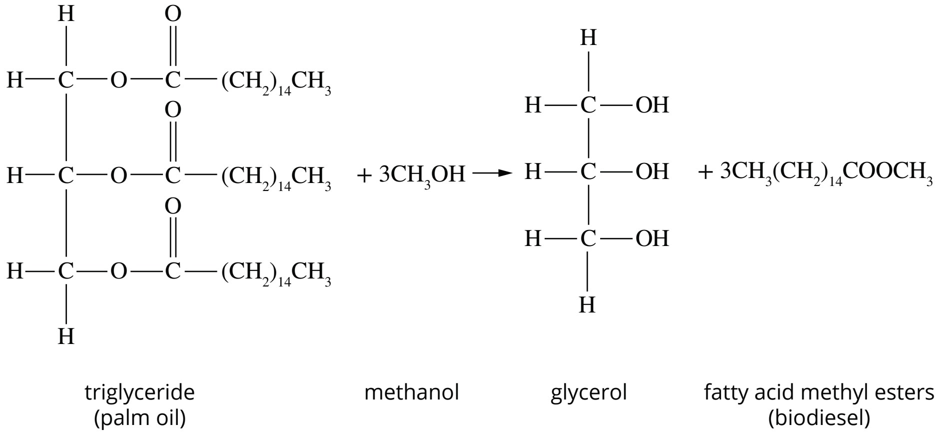


FIGURE 1.3.6 The reaction of a triglyceride with alcohol to form fatty acid esters (biodiesel) and glycerol.

The structure of a typical biodiesel molecule is shown in Figure 1.3.7. Molecules of this type are sometimes referred to as **fatty acid esters**, because carboxylic acids with relatively long hydrocarbon chains are referred to as **fatty acids**.

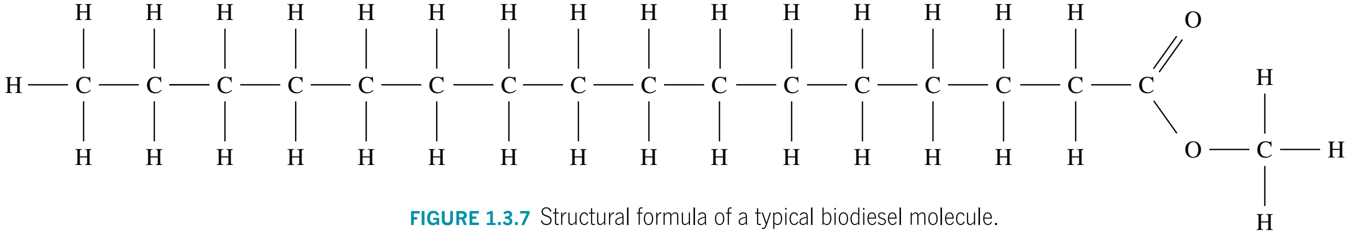


FIGURE 1.3.7 Structural formula of a typical biodiesel molecule. Biodiesel molecules are often longer than petrodiesel molecules.

Like petrodiesel, biodiesel is not a pure substance. The structure of the triglyceride varies depending on the particular plant or animal used as the source. Triglycerides produced by animals, such as tallow, usually form **saturated esters**, which have only carbon–carbon single bonds in the hydrocarbon chain. However, triglycerides produced by plants often form **unsaturated esters** like the one shown in Figure 1.3.8.

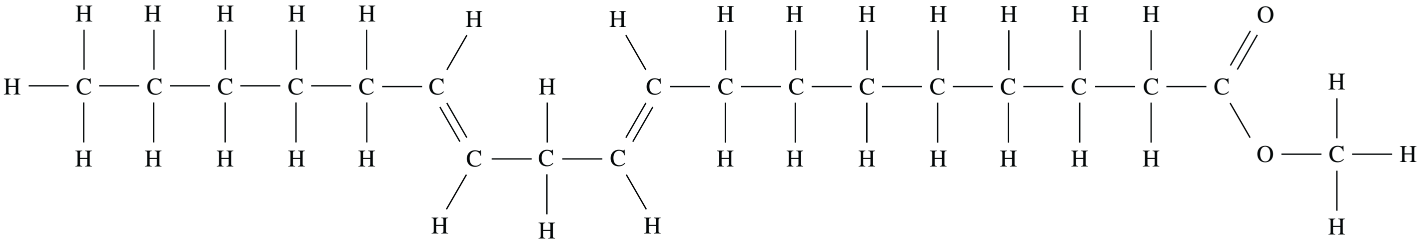


FIGURE 1.3.8 Biodiesel molecules derived from plants often contain carbon–carbon double bonds.

ⓘ The term 'saturated' refers to hydrocarbons that contain only single bonds between the carbon atoms. They are said to be saturated because each carbon atom is bonded to as many hydrogen atoms as possible. 'Unsaturated' means that there is at least one carbon–carbon double or triple bond within the hydrocarbon chain.

The presence of double bonds in the hydrocarbon chain changes the shape of the molecules, making it more difficult for them to pack together. This weakens the dispersion forces between neighbouring molecules of unsaturated esters. As a result, biodiesel produced from plant oil usually has a lower melting point than biodiesel produced from animal fats.

At present, far more petrodiesel is consumed than biodiesel, both locally and internationally (Figure 1.3.9). Australia's total diesel consumption is over 23 000 megalitres of diesel per year. Biodiesel comprises only 400 megalitres of this total. This gap is likely to close in the future as the biodiesel industry is the subject of extensive scientific research.

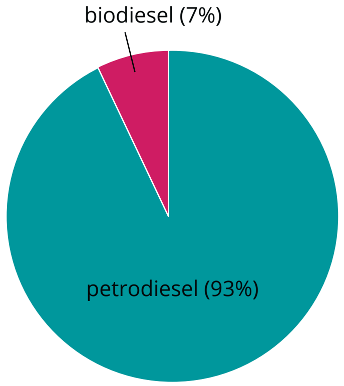


FIGURE 1.3.9 This pie chart shows world diesel consumption. Petrodiesel dominates world diesel consumption (2015 data).

COMPARISON OF PETRODIESEL AND BIODIESEL

Properties and performance

Some of the properties of petrodiesel and biodiesel are compared in Table 1.3.1.

TABLE 1.3.1 Properties of petrodiesel and biodiesel compared

Property	Explanation of property	Petrodiesel	Biodiesel
Density (kg L^{-1})	Mass of fuel in a given volume	0.84	0.87
Viscosity (cSt)	Measure of a fluid's resistance to flow at 40°C	2.5	4.9
Cloud point (°C)	Lowest temperature at which crystals start to form	–15 to 5	–3 to 12
Energy content (kJ g^{-1})	Energy released per gram of fuel	48	41
Energy density (kJ L^{-1})	Energy released per litre of fuel	40	36

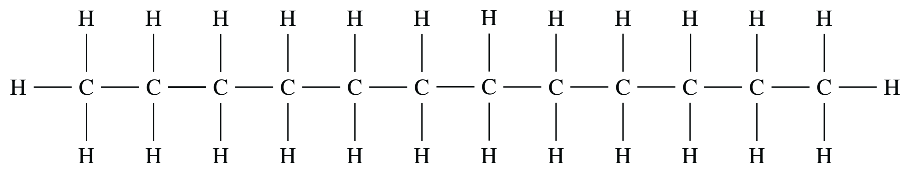
The energy contents of petrodiesel and biodiesel are comparable and also similar to that of petrol (47 kJ g^{-1}). However, because both forms of diesel have higher densities than petrol, the energy released per litre of diesel fuel is higher than for petrol (34 kJ L^{-1}).

Examination of the data in Table 1.3.1 assists in understanding the following key points.

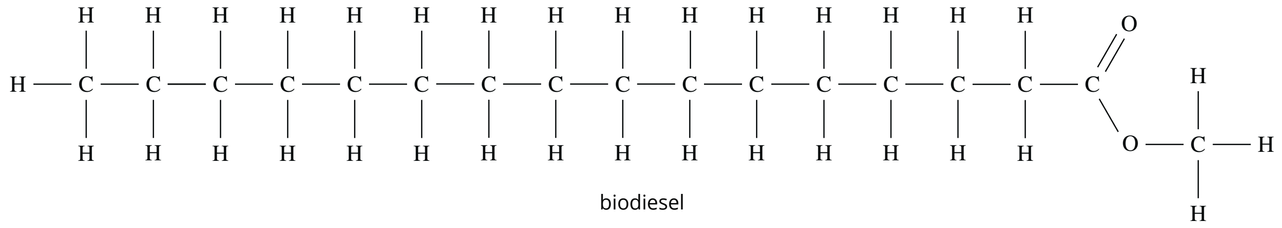
- Petrodiesel produces up to 10% more energy than biodiesel (this is offset by the fact that biodiesel burns more smoothly and efficiently).
- Biodiesel has a higher **viscosity** than petrodiesel. Biodiesel does not flow as easily along fuel lines and through filters.
- In very cold climates, biodiesel can lose its ability to flow, or worse still, it can solidify. The **cloud point** is a measure of performance at low temperature. Cloud point refers to the temperature at which small crystals start to form. Obviously, an engine will not run if the fuel will not flow on a cold day.

The differences in viscosity and flow under cold conditions are related to the chemical structures of the two forms of diesel. Petrodiesel consists of smaller, non-polar molecules (see Figure 1.3.10, page 28). The only forces present between neighbouring petrodiesel molecules are weak **dispersion forces**.

However, the hydrocarbon chain in biodiesel is often longer and each molecule also contains two highly **electronegative** oxygen atoms (see Figure 1.3.10).



petrodiesel



biodiesel

FIGURE 1.3.10 Petrodiesel and biodiesel molecules. Petrodiesel molecules are shorter than biodiesel molecules and are non-polar. Biodiesel molecules are longer and contain polar C–O bonds. As a result, biodiesel is more viscous than petrodiesel.

The oxygen atoms create dipoles at one end of the molecule, with the result that **dipole–dipole bonds** form between neighbouring molecules. These stronger intermolecular bonds cause the viscosity and melting point of biodiesel to be greater than for petrodiesel.

The presence of polar bonds in biodiesel molecules also explains why biodiesel has a greater tendency than petrodiesel to absorb water. Water is a polar molecule and is more attracted to the slightly polar biodiesel molecules than to non-polar petrodiesel molecules. A substance that absorbs water easily is said to be more **hygroscopic** than one that does not. The water content of biodiesel needs to be low for efficient combustion to occur.

For the motorist, the differences in the properties of the two fuels imply that:

- diesel blends containing up to 20% biodiesel have a similar performance to petrodiesel and the engines do not need to be modified
- in cold climates, additives need to be added to motor fuel containing high levels of biodiesel. Service stations also need to ensure the pump is kept warmer than the surroundings. Biodiesel sourced from plants has fewer cold-flow issues than biodiesel produced from animal fats.

Biodiesel also has the potential to keep fuel systems cleaner, but higher quality seals and fuel hoses may be required. Biodiesel cannot be stored for as long as petrodiesel because it is more likely to react with atmospheric oxygen and biodegrade. **Biodegradation** is the breakdown of a substance by the action of living organisms, such as bacteria and fungi.

Environmental impact

When comparing the two forms of diesel, you need to consider the emissions produced when the fuels are burnt, as well as the impact on the environment of producing the fuel in the first place.

Combustion and emissions

The main combustion products of both forms of diesel are carbon dioxide and water. The combustion reactions of typical components of the fuels are represented by the equations:

Petrodiesel: $2C_{12}H_{26}(l) + 37O_2(g) \rightarrow 24CO_2(g) + 26H_2O(g)$

Biodiesel: $2C_{17}H_{34}O_2(l) + 49O_2(g) \rightarrow 34CO_2(g) + 34H_2O(g)$

The carbon dioxide emissions from both petrodiesel and biodiesel are about 73 g MJ^{-1}, which is almost the same as for petrol. However, diesel vehicles produce 10–20% less carbon dioxide emissions than petrol vehicles because of their higher fuel efficiency. In the case of biodiesel, carbon dioxide is absorbed in the growth of the plant or animal the biodiesel is derived from, reducing the net impact on greenhouse gas levels.

As with petrol engines, use of either form of diesel leads to emissions of pollutants such as nitrogen oxides, carbon monoxide and unburnt hydrocarbons.

Petrodiesel also produces some sulfur dioxide (SO_2) emissions. Whether biodiesel produces SO_2 depends upon the origins of the triglycerides that it is produced from. For example, soyabean oil does not contain sulfur but canola oil does.

Biodiesel exhaust contains up to 20% less particulate matter than diesel.

There is considerable debate about which fuel, diesel or petrol, is the cleanest in terms of emissions. The answer is not clear-cut. Diesel engines produce less carbon dioxide, carbon monoxide and unburnt hydrocarbons. But petrol engines produce virtually no particulates and emit less nitrogen oxides.

Fuel production and the environment

Both types of diesel impact on the environment from where they are sourced and the environment around the industrial plants where they are refined. Some of these impacts are illustrated in Table 1.3.2.

TABLE 1.3.2 A comparison of the impacts of sourcing and producing petrodiesel and biodiesel

	Petrodiesel	Biodiesel
Impacts of sourcing	 • Crude oil can be mined on land or at sea. • Crude oil is non-renewable. • Oil deposits are often located in environmentally sensitive locations and mining approval is often contested. • Spills or leaks could significantly damage local ecology. • Oil is a flammable liquid with associated fire risks.	 • Increased biodiesel production requires intensive farming. • Crops such as canola are renewable because they can be harvested each year. • Growing crops requires resources such as water and fertiliser. The quality of the soil deteriorates if the same crops are grown each year. • Farm machinery produces CO_2 and other pollutants that reduce the net benefits of renewable fuels. • High-quality farmland is used for growing fuels instead of food.
Impacts of production	 • Oil refineries can produce significant emissions due to the burning of excess hydrocarbons. • Energy is required to operate the refinery.	 • Biodiesel plants should produce less emissions than oil refineries do. • Energy is required to operate the plant.

In the immediate future, the growth of biodiesel production may depend upon economics. If biodiesel manufacturers cannot produce biodiesel from canola for a price lower than the market price of petrodiesel, then the industry is unlikely to expand. A complicating factor is the fluctuations that occur in the price of diesel as shown in Figure 1.3.11.

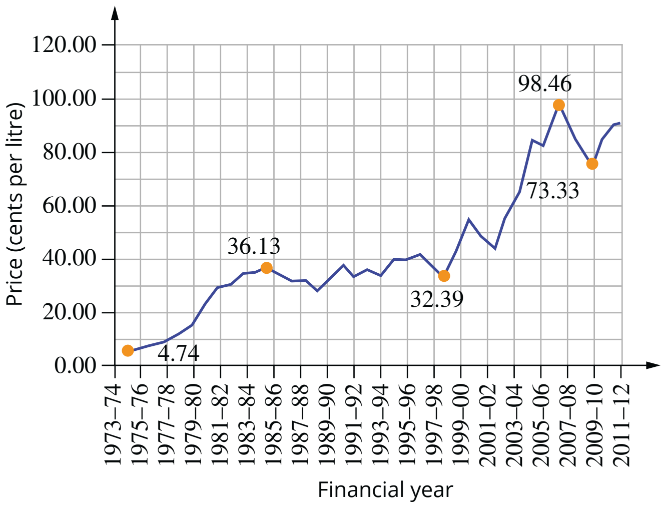


FIGURE 1.3.11 Fluctuations in the Australian diesel price make the feasibility of manufacturing biodiesel challenging.

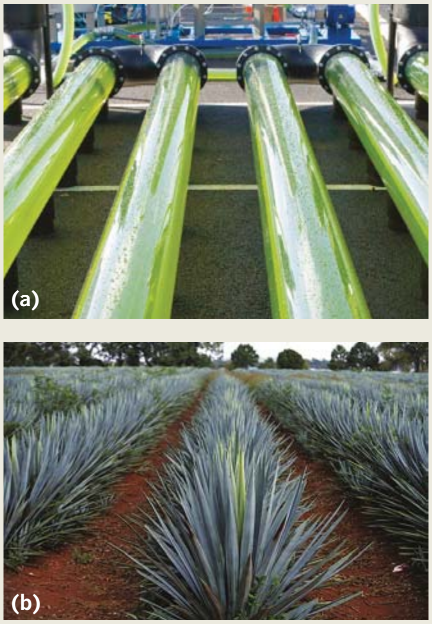


FIGURE 1.3.12 (a) A pilot plant investigating the feasibility of producing biodiesel from algae. Farmland is not required and algae can be harvested many times per year. (b) The agave plant shows promise as a source of biofuels. It is best known as the raw material for making tequila in Mexico.

EXTENSION

Biodiesel production using alternative feedstocks

Several innovative Australian companies are successfully trialling new processes to avoid using food-grade crops as the source of triglycerides for biodiesel.

- Biomax in Laverton, Victoria, produces biodiesel from poppy seed oil. Tasmania has a licence to grow opium poppies for the production of morphine. The company was not allowed to sell the oil on the open market due to fears it might contain illegal substances. However, they were permitted to make biodiesel from oil that would otherwise have been a waste product.
- Biomax is also involved in a trial in Victoria's Latrobe Valley at a cooling pond for a power station. Carbon dioxide produced in the coal-fired power station nearby is used to promote the growth of algae with a high oil content (Figure 1.3.12a).
- Australian Renewable Fuels Limited manufactures 150 million litres of biofuel each year at a northeastern Victorian plant in Barnawartha. The raw materials are tallow from local abattoirs and used cooking oil, which would otherwise be difficult to dispose of.
- Juncea (a close relative to canola) and agave crops are being trialled on marginal farmland in several locations (Figure 1.3.12b). These crops have a high oil yield but don't have to grow on farmland that could be used for food crops.

1.3 Review

SUMMARY

- Diesel engines are used in many forms of transport and in heavy-duty equipment.
- Diesel engines have a better fuel economy than petrol engines because diesel has a higher energy efficiency and higher energy per litre.
- Diesel engines typically produce 10–20% less carbon dioxide emissions than petrol engines.
- Diesel fuel can be separated from crude oil by fractional distillation (petrodiesel) or synthesised from the triglycerides in plants or animals (biodiesel).
- Petrodiesel is a non-renewable fuel, whereas biodiesel is a renewable fuel.
- Petrodiesel is composed of about 75% alkanes containing 10–15 carbon atoms (see Figure 1.3.13) and 25% aromatic compounds.

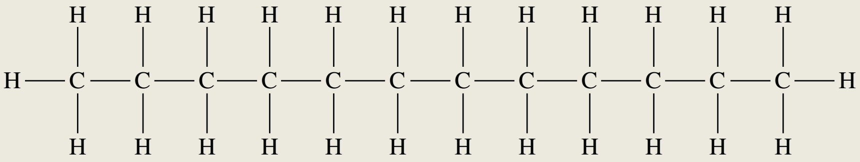


FIGURE 1.3.13 Structure of dodecane—a typical alkane in petrodiesel.

- Biodiesel is produced from triglycerides in animal fats or plant oils. The triglycerides react with methanol in a transesterification reaction to form biodiesel (see Figure 1.3.14).

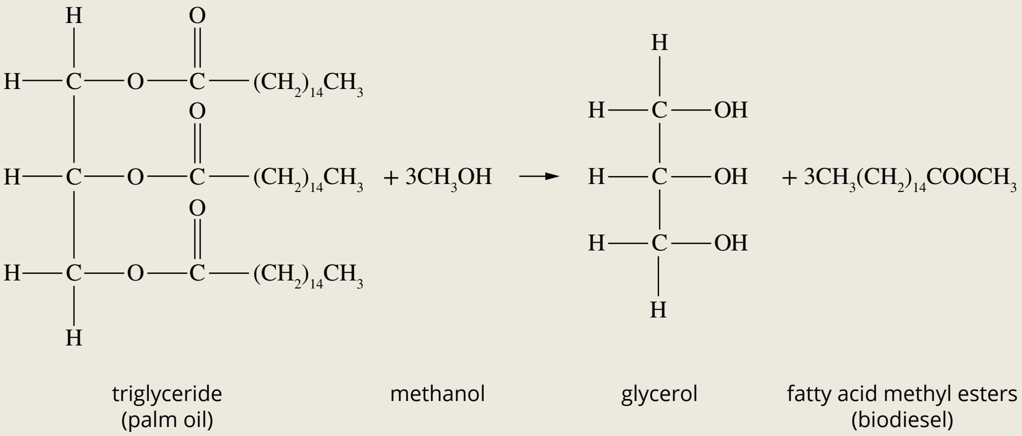


FIGURE 1.3.14 Production of biodiesel.

- Biodiesel molecules can be described as fatty acid esters.

- Table 1.3.3 compares petrodiesel with biodiesel.

TABLE 1.3.3 A comparison of petrodiesel and biodiesel

Property	Petrodiesel	Biodiesel
Renewability	Non-renewable	Renewable
Energy content	Marginally higher	Marginally lower
Viscosity	Lower	Higher
Cold flow	Can be used without additives at lower temperatures than biodiesel.	More likely to need antifreeze additives when used in cold climates.
Emissions	Produces CO_2, particulates and other pollutants.	Produces CO_2 but CO_2 is consumed in production of the triglycerides used to make the fuel. Produces fewer particulates. Produces other pollutants.
Environmental impact of production	Oil fields are prone to spills and damage to local habitats. Oil refineries produce emissions that have a negative impact on local regions.	Biodiesel produced from farm crops can add to land degradation and might lead to higher food prices. Biodiesel made from waste products such as used cooking oil has a positive impact on the environment.

KEY QUESTIONS

1 Select the correct statement about petrodiesel.
- **A** Petrodiesel is a renewable fuel as it is formed from plants.
- **B** Petrodiesel is purified to ensure all molecules include the same number of carbon atoms.
- **C** Petrodiesel is a mixture of substances including LPG and petrol.
- **D** Petrodiesel contains 75% alkanes with 10–15 carbon atoms.

2 What is the name of the reaction in which a triglyceride is broken down to form biodiesel molecules?

3 Determine if the following statements about biodiesel are true or false.
- **a** Biodiesel can contain several different compounds.
- **b** Biodiesel molecules contain ester groups.
- **c** Biodiesel is an alkane.
- **d** Three molecules of biodiesel can be obtained from each molecule of a triglyceride.
- **e** All hydrocarbon chains in biodiesel molecules are saturated.
- **f** Biodiesel is formed in a transesterification reaction.

4 Why are the CO_2 emissions from the use of biodiesel not considered as problematic as those produced from the use of petrodiesel?

Chapter review

01

KEY TERMS

acid rain
alkane
anaerobic
aromatic hydrocarbon
biodegradation
biodiesel
bioethanol
biofuel
biogas
carbon neutral
catalyst
cloud point
coal seam gas
combustion
dipole–dipole bond
dispersion force
electronegative
energy content
energy efficiency
energy transformation
enhanced greenhouse effect
enzyme
fatty acid
fatty acid ester
fermentation
fossil fuel
fracking
fractional distillation
fuel
greenhouse effect
greenhouse gas
homologous series
hydrocarbon
hygroscopic
liquefied petroleum gas
natural gas
non-renewable
petrodiesel
photosynthesis
renewable
saturated ester
shale gas
sustainable
transesterification
triglyceride
unsaturated ester
viscosity

Types of fuels

1 The world has become very dependent on the products of the petrochemical industry, but the raw materials of crude oil and natural gas are likely to be virtually exhausted by 2100. Assuming that current production remains unchanged and no alternative sources are available, suggest the impact of the lack of raw materials on our lifestyle.

2 Refer to Figure 1.1.4 on page 3 to answer the following questions.

- **a** In the year 2000, what type of fuel provided the most energy on a global scale?
- **b** Rank the different fuels in order from most to least amount of energy expected to be produced in 2020.

3 Why are fossil fuels considered to be non-renewable?

4 Refer to Figure 1.1.5 on page 4 to answer the following questions.

- **a** What type of coal takes the longest amount of time to form?
- **b** Of peat, brown coal and black coal, which releases the least amount of heat energy?
- **c** Which type of coal is a better quality fuel?

5 Refer to Table 1.1.1 on page 9, which lists the typical composition of biogas.

- **a** What two gases form the largest percentage of a typical biogas sample?
- **b** Why are there variations in the percentage of gases making up different samples of biogas?

6 What types of vegetable oils is biodiesel commonly sourced from?

7 When coal contains a greater amount of water (as it does in peat and brown coal), why is less heat released when the coal is burnt?

Fossil fuels and biofuels

8 The following energy sources are used across the world: coal, bioethanol, biodiesel, natural gas. Which one is likely to run out the fastest?

9 Explain the term ‘energy efficiency’.

10 What are some of the ways in which energy is lost, leading to a reduced efficiency in a coal-fired power station?

11 Biogas, petrol and bioethanol are used to power vehicles.

- **a** List the fuels in order of their energy content per gram (from highest to lowest). You may need to refer to Table 1.2.1 on page 17.
- **b** The emissions of carbon dioxide per gram from the combustion of bioethanol are less than that from octane (petrol). However, a car using bioethanol produces more carbon dioxide when driving the same distance as a car using octane. Which one of the follow could be the best explanation for this difference?
  - **A** Bioethanol is more efficient than octane.
  - **B** The energy content of bioethanol is less than that of octane.
  - **C** The temperature of the engine favours the combustion of octane.
  - **D** More energy transformations are required in the combustion of bioethanol.

12 Explain why bioethanol is sometimes described as a ‘carbon neutral’ fuel. Use chemical equations for photosynthesis, fermentation and combustion to support your answer.

13 Use the terms ‘methane’, ‘oxygen’, ‘bacteria’ and ‘carbon dioxide’ to explain the formation and composition of biogas.

14 **a** Explain what 'E10 petrol' means.

b How does the introduction of E10 help with the potential shortage of crude oil?

15 The fact that global warming is taking place is now generally accepted. Conduct some research using the internet to discover some of the consequences of global warming. Give one example each of the effect on:

a the polar ice caps

b changing weather patterns

c crop production

d extinction of plant or animal species.

Petrodiesel and biodiesel

16 Which one of the following is the most likely component of petrodiesel?

A Propene

B C_3H_8

C $C_{11}H_{24}$

D $C_{16}H_{24}O_2$

17 Trials are being conducted to source biodiesel from algae grown in the warm water of a power station cooling pond. The water is warm and carbon dioxide emitted from the power station can be trapped and bubbled through the water to enhance the growth of the algae. Classify the following as advantages or disadvantages of large-scale production of biodiesel from algae.

a Fewer particulate emissions than petrodiesel

b Renewable

c Less reliance on fossil fuels

d Distribution outlets required

e Fewer net CO_2 emissions than petrodiesel

f Oil can be 'harvested' many times per year

g Reduction of CO_2 emissions from coal-fired power stations

h More additives need to be added to the fuel in cold climates

18 For each of the following scenarios, decide if it is more likely to refer to petrodiesel or biodiesel.

a A sample of diesel has gone cloudy after being stored a long time.

b The exhaust from this engine contains significant particulates.

c The car will not start on a cold morning.

d The water content of the fuel has reached a high level.

Connecting the main ideas

19 Ethanol is produced industrially by reacting ethene with water using a phosphoric acid catalyst at 300°C:

$C_2H_4(g) + H_2O(g) \rightarrow CH_3CH_2OH(g)$

a Explain whether ethanol produced by this method is a biochemical fuel.

b Describe how ethanol, which is classified as a biochemical fuel, could be produced.

20 Conduct some research on the internet to find out which nations are the top ten consumers of energy.

21 The 2015 Paris Agreement was an international response to global warming in which all nations were asked to commit to keeping the global average temperature rise to below 2°C, through reductions in greenhouse gas emissions.

a What impact would adoption of the Paris Agreement have on Australia?

b Discuss the role that biofuels could play in helping Australia meet its target for reducing greenhouse gas emissions.

CHAPTER 02

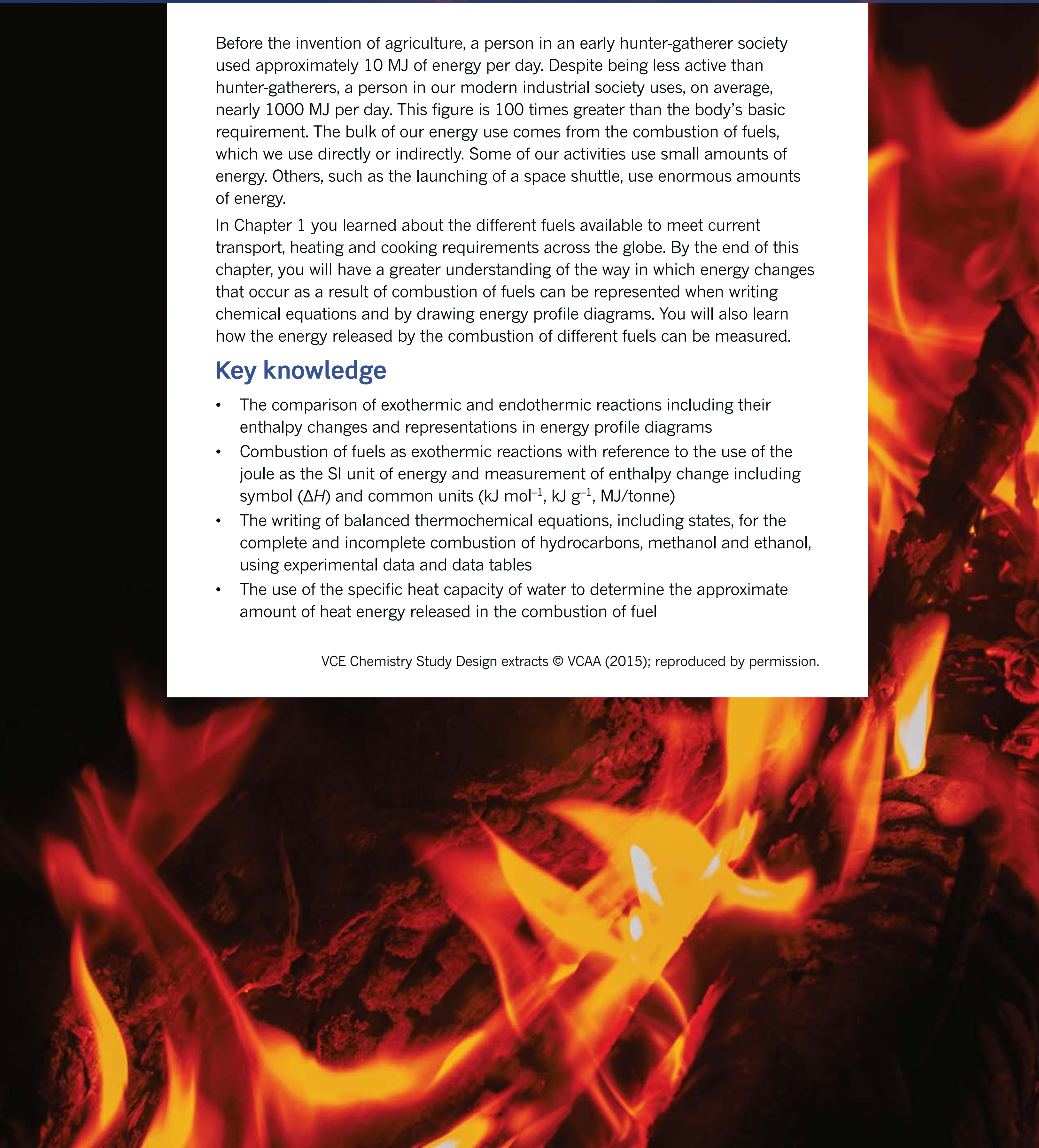
Energy from fuels

Before the invention of agriculture, a person in an early hunter-gatherer society used approximately 10 MJ of energy per day. Despite being less active than hunter-gatherers, a person in our modern industrial society uses, on average, nearly 1000 MJ per day. This figure is 100 times greater than the body's basic requirement. The bulk of our energy use comes from the combustion of fuels, which we use directly or indirectly. Some of our activities use small amounts of energy. Others, such as the launching of a space shuttle, use enormous amounts of energy.

In Chapter 1 you learned about the different fuels available to meet current transport, heating and cooking requirements across the globe. By the end of this chapter, you will have a greater understanding of the way in which energy changes that occur as a result of combustion of fuels can be represented when writing chemical equations and by drawing energy profile diagrams. You will also learn how the energy released by the combustion of different fuels can be measured.

Key knowledge

- The comparison of exothermic and endothermic reactions including their enthalpy changes and representations in energy profile diagrams
- Combustion of fuels as exothermic reactions with reference to the use of the joule as the SI unit of energy and measurement of enthalpy change including symbol (ΔH) and common units (kJ mol^{-1}, kJ g^{-1}, MJ/tonne)
- The writing of balanced thermochemical equations, including states, for the complete and incomplete combustion of hydrocarbons, methanol and ethanol, using experimental data and data tables
- The use of the specific heat capacity of water to determine the approximate amount of heat energy released in the combustion of fuel



2.1 Exothermic and endothermic reactions

FIGURE 2.1.1 The energy released by the combustion of wood in a fire is easily seen and felt.

Chemical reactions occur when particles (atoms, molecules or ions) collide and are rearranged to form new particles. Chemical reactions involve energy changes. As the reactant particles are rearranged, the **chemical energy** of the reactants is also 'rearranged', although not in quite the same way.

In some chemical reactions, including the **combustion** of fuels, the rearrangement of atoms causes energy to be released to the surroundings. For example, the amount of energy released in the combustion of wood is large enough to be easily seen or felt (Figure 2.1.1).

In other chemical reactions, energy is absorbed from the surroundings as the chemical reaction takes place. The energy change in some reactions is very small and can only be determined with specialised equipment.

In this section, you will learn about the energy changes that occur during chemical reactions. You will also learn how to classify chemical reactions based on their energy changes.

CHEMICAL ENERGY

There are many different forms of energy. You will be more familiar with some than others. For example, you are in contact with forms of heat (thermal energy), light (radiant energy), sound energy and electrical energy every day. You can probably see, hear or feel some of them as you are reading these pages.

All substances have a form of energy called chemical energy. It is stored in the bonds between atoms and molecules. This energy results from:

- attractions between electrons and protons in atoms
- repulsions between nuclei
- repulsions between electrons
- movement of electrons
- vibrations and rotations around bonds.

When you eat a meal, the bonds between the food molecules have stored energy that you can access to provide energy for other chemical and physical activities that take place in your body (Figure 2.1.2).

FIGURE 2.1.2 When you eat food, you access the chemical energy stored in the food. This energy powers all of the chemical reactions and physical activities that take place in your body.

As you learned in Chapter 1, the SI unit for energy is the joule, J. Other units also used for quantifying energy are kilojoules, kJ, and megajoules, MJ.

The relationship between joules and megajoules is:

$$1\ \text{J} = 10^{-3}\ \text{kJ} = 10^{-6}\ \text{MJ}$$

This can also be expressed as:

$$1\ \text{MJ} = 1000\ \text{kJ} = 1\,000\,000\ \text{J}$$

Figure 2.1.3 shows how you can convert between different units of energy.

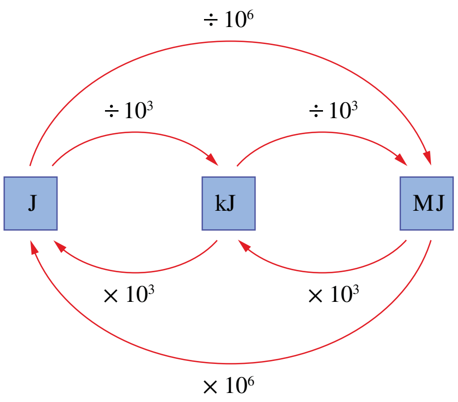


FIGURE 2.1.3 Converting between different energy units.

ENERGY CONSERVATION

According to the **law of conservation of energy**, energy cannot be created or destroyed. However, it can change forms. When energy is transformed from one form to another, the total amount of energy remains the same.

Systems and surroundings

When we talk about energy changes in chemical reactions, we often refer to a **system** and its **surroundings**.

In chemistry, the system is usually the chemical reaction. When we say that energy is released or absorbed by a system, we are referring to energy changes that occur as bonds are broken and formed between the atoms of the elements involved in the reaction.

The surroundings are usually regarded as everything else. For example, the walls of a container in which a reaction takes place in the gas phase, or the water in a solution in which a reaction takes place in the aqueous phase, can be regarded as the surroundings for the reaction. Energy leaves the system (the reaction) and enters the surroundings, or leaves the surroundings and enters the system.

Energy changes during chemical reactions

The reactants in a chemical reaction have a certain amount of chemical energy stored in their bonds. The products that form as a result of the rearrangement of particles during the chemical reaction have different bonds and so have a different amount of chemical energy. Energy will be released or absorbed during the reaction depending on the relative energies of the bonds within the reactants and products. When fuels undergo combustion, they are able to release energy that can be used. This is what makes them fuels.

Often the energy released to or absorbed from the surroundings is in the form of heat (thermal energy). However, heat can be converted into other types of energy, including light, electricity and movement (kinetic energy).

CHEMISTRY IN ACTION

Glow-in-the-dark light sticks

You might have seen glow-in-the-dark hoops, necklaces and bracelets similar to those shown in Figure 2.1.4 at festivals or concerts, especially those held at night.

Glow-in-the-dark bracelets contain chemicals held in separate containers. When these bracelets are bent, the containers break and the chemicals combine. Light is produced through a process called **chemiluminescence**.

The chemistry of a glow stick is fairly straightforward. When the aqueous reactants (hydrogen peroxide in one area and diphenyl oxalate in another area) mix, energy is released from the reaction that occurs. This reaction is shown in Figure 2.1.5.

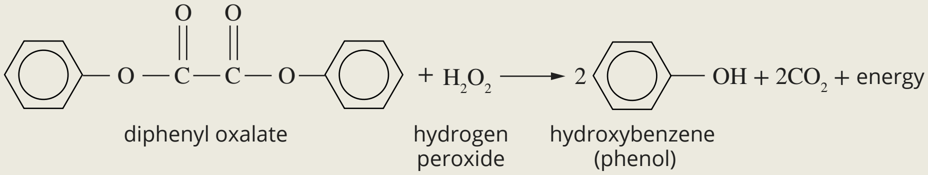


FIGURE 2.1.5 This reaction occurs in a glow stick.

Instead of the energy from this reaction being released to the surroundings solely as heat, a carrier molecule transfers the energy to a **chemiluminescent** dye in the glow stick. The electrons in the dye are excited to higher energy levels. Light is emitted as these electrons return to their original lower energy levels. The light from the glow stick is simply the emission spectrum of the dye molecule.

FIGURE 2.1.4 Glow-in-the-dark bracelets give off light that is the result of chemiluminescence.

CHEMFILE

Glow-worms

Glow-worms (Figure 2.1.6) apply similar chemical principles to chemiluminescence for their glow-in-the-dark **bioluminescence**. Three chemicals within the worm combine. However, they require oxygen to produce light. When the worm breathes, oxygen acts as the oxidising agent in the chemical reaction between the three reactants producing the bioluminescence. Worms are able to control the amount of 'glow' by breathing in more or less oxygen.

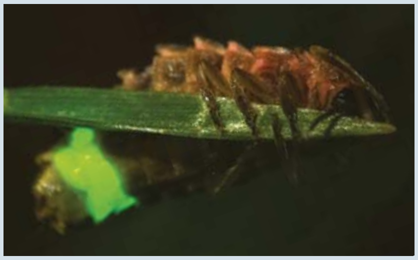


FIGURE 2.1.6 A female glow-worm. The luminescent abdominal organs are visible.

EXOTHERMIC AND ENDOTHERMIC SYSTEMS

When the total chemical energy of the products of a chemical reaction is less than the total chemical energy of the reactants, the excess energy is released to the surroundings. Energy 'exits' the reaction system and the chemical reaction is called an **exothermic** reaction.

The released energy can be shown in a chemical equation by writing 'energy' on the product side of the arrow.

For example, the production of water from the reaction between hydrogen and oxygen gas is an exothermic reaction. This can be represented by the equation:

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(l) + \text{energy}$$

Another example of an exothermic reaction is the combustion of methane gas:

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g) + \text{energy}$$

Heat is given off to the surroundings. All combustion reactions give off heat (energy) to the surroundings and are therefore exothermic reactions.

When the total chemical energy of the products of a chemical reaction is greater than the total chemical energy of the reactants, energy is absorbed from the surrounding environment. Energy 'enters' the reaction system and the chemical reaction is called an **endothermic** reaction.

If an endothermic reaction takes place in a container, the container may feel cold to the touch. This is because the reaction system is absorbing heat from the surroundings, leaving the environment cooler.

In a chemical equation of an endothermic reaction, the energy that is required can be written on the reactant side of the equation arrow.

For example, the **decomposition** of calcium carbonate is an endothermic process. This can be represented by the equation:

$$CaCO_3(s) + \text{energy} \rightarrow CaO(s) + CO_2(g)$$

Endothermic reactions require the constant input of energy.

If the total chemical energy of the products is *less* than the total energy of the reactants, energy will be released from the system into the surroundings. This is called an exothermic reaction.

If the total chemical energy of the products is *greater* than the total energy of the reactants, energy will be absorbed from the surroundings. This is called an endothermic reaction.

Changes of state

Changes of state, such as a solid melting to form a liquid, are a type of physical change, rather than a chemical change. These changes also involve energy being absorbed or released.

For example, the melting of ice into water requires the absorption of energy, making it an endothermic process. The boiling of water to produce water vapour is also endothermic.

Conversely, condensing a gas to a liquid and freezing a liquid to form a solid both release heat to the surroundings and so are exothermic processes.

CHEMFILE

Instant cold packs

Instant cold packs are often carried in first aid kits at sporting events (Figure 2.1.7). One type of cold pack contains a sealed bag of water surrounded by solid ammonium nitrate. When the cold pack is squeezed, the water bag is broken and ammonium nitrate dissolves in the water. The process is endothermic, absorbing heat from the surroundings and quickly lowering the pack's temperature.

FIGURE 2.1.7 An endothermic reaction produces an instant cold pack.

2.1 Review

SUMMARY

- Energy is measured in J, kJ or MJ:
  1 J = 10^{-3} kJ = 10^{-6} MJ
- Chemical energy is stored in the bonds between atoms and molecules.
- Energy is conserved during a chemical reaction; energy cannot be created or destroyed.
- Chemical reactions and changes of state involve energy changes.
- A chemical reaction that releases energy to the surroundings is called an exothermic reaction.
- A chemical reaction in which energy is absorbed from the surroundings is called an endothermic reaction.
- All combustion reactions are exothermic reactions.

KEY QUESTIONS

1 Which of the following statements about combustion reactions is correct?

A Combustion reactions are usually exothermic, meaning energy is absorbed during the reaction.

B Combustion reactions are always exothermic, meaning energy is absorbed during the reaction.

C Combustion reactions are usually endothermic, meaning energy is absorbed by the system.

D Combustion reactions are always exothermic, meaning energy is released during the reaction.

2 Convert the following energy values to kJ.

a 0.180 MJ

b 1.5×10^6 J

c 10.0 J

d 2.0×10^{-3} J

3 Explain the difference between the terms 'system' and 'surroundings' in relation to a chemical reaction.

4 Explain the term 'endothermic' in relation to the total amount of chemical energy of the reactants and products.

2.2 Thermochemical equations and energy profile diagrams

When fuels undergo combustion, energy is released in the form of heat. As you saw in the previous section, the word ‘energy’ can be included in a combustion equation to show that energy is released. However, it is generally more useful for a chemist to be precise about the magnitude (size) of the energy change that takes place.

Thermochemical equations achieve this by including a sign and numerical value for the energy change that occurs in the reaction.

It is also useful for chemists to be able to show the energy changes that occur as a reaction proceeds. All reactions absorb some energy before they can proceed, even if energy is released overall. An **energy profile diagram** represents the energy changes that occur during the course of a reaction.

In this section, you will learn how to write and interpret thermochemical equations and draw energy profile diagrams. Although the focus for this section is on the combustion of fuels (which are exothermic reactions), you will also learn about writing and representing other equations, including endothermic reactions. These reactions are important for your understanding of some of the concepts that will be covered in later chapters.

REPRESENTING ENERGY CHANGE IN A CHEMICAL EQUATION

Enthalpy change

Enthalpy change is a measure of the amount of energy absorbed or released during chemical reactions. It is given the symbol ΔH and is determined by subtracting the enthalpy of the reactants (H_r) from the enthalpy of the products (H_p).

The chemical energy of a substance is sometimes called its **heat content** or **enthalpy**. It is given the symbol H. The enthalpy of the reactants in a chemical reaction is given the symbol H_r and the enthalpy of the products is given the symbol H_p.

Most chemical processes take place in open systems under a constant pressure (usually atmospheric). The exchange of heat energy between the system and its surroundings under constant pressure is referred to as the **enthalpy change**, or **heat of reaction**, and is given the symbol ΔH. The capital delta symbol (Δ) is commonly used in chemistry to represent ‘change in’. For example, ΔT is the symbol for change in temperature.

Fuels provide you with energy by undergoing exothermic combustion reactions. Knowing the precise enthalpy change per mole or gram that occurs during combustion of different fuels helps you to decide which fuel might be most suitable for a particular purpose.

For the general reaction:

$$\text{reactants} \rightarrow \text{products}$$

the enthalpy change (ΔH) is calculated by:

$$\Delta H = H_p - H_r$$

Enthalpy change in exothermic reactions

When H_p is less than H_r, energy is released from the system into the surroundings, so the reaction is exothermic. The system has lost energy, so ΔH has a negative value.

Therefore, for combustion reactions (which are exothermic reactions), $\Delta H < 0$ (see Figure 2.2.1).

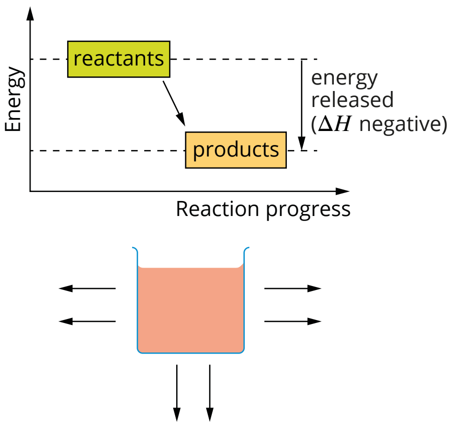


FIGURE 2.2.1 In the combustion of a fuel, the enthalpy of the reactants is greater than the enthalpy of the products, so energy is released to the surroundings during the reaction.

Enthalpy change in endothermic reactions

When H_p is greater than H_r, energy must be absorbed from the surroundings, so the reaction is endothermic. The system has gained energy, so ΔH has a positive value, i.e. $\Delta H > 0$ (see Figure 2.2.2).

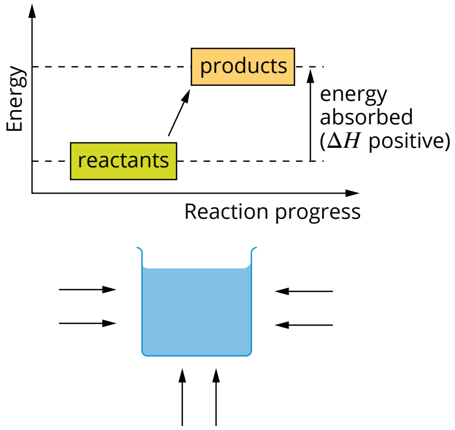


FIGURE 2.2.2 For an endothermic reaction, the enthalpy of the reactants is less than the enthalpy of the products so energy is absorbed during the reaction.

Thermochemical equations

The enthalpy change can be shown by writing the ΔH value to the right of the chemical equation. Such an equation is called a thermochemical equation. The ΔH value in a thermochemical equation usually has the units kJ mol^{-1}. This means that the amount of energy (in kJ) signified by the ΔH value corresponds to the mole amounts specified by the coefficients in the equation.

For example, respiration in most living things can be considered as a type of combustion reaction of glucose. Therefore, respiration is an exothermic reaction:

$$C_6H_{12}O_6(aq) + 6O_2(g) \rightarrow 6CO_2(g) + 6H_2O(l) \quad \Delta H = -2803 \text{ kJ mol}^{-1}$$

This thermochemical equation tells you that when 1 mole of glucose reacts with 6 moles of oxygen to produce 6 moles of carbon dioxide and 6 moles of water, 2803 kJ of energy is released.

Enthalpy changes also occur during physical changes, so thermochemical equations can be written for physical changes. Melting ice is an example of a physical change. It is an endothermic process, because heat must be applied to solid ice in order to convert it into liquid water. The thermochemical equation for this reaction is:

$$H_2O(s) \rightarrow H_2O(l) \quad \Delta H = +6 \text{ kJ mol}^{-1}$$

The ΔH value is positive because this is an endothermic reaction.

CHEMISTRY IN ACTION

Explosives—a blast of chemical energy

Humans have been using chemicals to make explosions since 919 BCE. Chinese people first mixed saltpetre (potassium nitrate), sulfur and charcoal with explosive results. They quickly realised that there were many uses for this mixture, which later became known as gunpowder. It was put to military use and eventually led to the development of bombs, cannons and guns.

Today, explosives are an essential tool for mining and other engineering works, such as road construction, tunnelling, building and demolition (see Figure 2.2.3).

Explosives transform chemical energy into large quantities of thermal energy very quickly. Although thermal energy is also released when fuels such as petrol and natural gas burn, the rate of combustion in these reactions is limited by the availability of oxygen gas to the fuel. In contrast, the compounds making up an explosive contain sufficient oxygen for a complete (or almost complete) reaction to occur very quickly.

FIGURE 2.2.3 An old bridge is demolished with the help of explosives.

CHEMISTRY IN ACTION

The chemistry behind an explosion

When chemical explosives, such as ammonium nitrate, trinitrotoluene (TNT) and nitroglycerine decompose, they release large amounts of energy and gaseous products very quickly.

This is the thermochemical equation for the decomposition of nitroglycerine:

$$4C_3H_5N_3O_9(l) \rightarrow 12CO_2(g) + 10H_2O(g) + 6N_2(g) + O_2(g) \quad \Delta H = -1456 \text{ kJ mol}^{-1}$$

Notice that 29 moles of gas (the total number of moles of all products) are produced from 4 moles of nitroglycerine. The negative ΔH value indicates that this is an exothermic reaction. At atmospheric pressure, the reactant products would expand to fill a volume more than 10 000 times larger than the volume of the nitroglycerine! During a blast, this gas is usually produced within a small hole into which the explosive has been placed, creating huge pressures that shatter the surrounding rock or structure.

THERMOCHEMICAL EQUATIONS AND MOLE RATIOS

The ΔH value in a thermochemical equation corresponds to the mole amounts specified by the equation. If the coefficients in the equation are changed, the ΔH value will also change.

For example, the thermochemical equation for the combustion of methanol can be written as:

$$CH_3OH(l) + \frac{3}{2}O_2(g) \rightarrow CO_2(g) + 2H_2O(l) \qquad \Delta H = -726 \text{ kJ mol}^{-1}$$

This means that 726 kJ of energy is released when 1 mole of methanol reacts with 1.5 moles of oxygen gas, to produce 1 mole of carbon dioxide and 2 moles of water.

If twice as much methanol were to react, then twice as much energy would be released. So, if the coefficients of the equation are doubled, the ΔH value is also doubled:

$$2CH_3OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 4H_2O(l) \qquad \Delta H = -1452 \text{ kJ mol}^{-1}$$

If the mole amounts are tripled, the ΔH value is also tripled:

$$3CH_3OH(l) + 4\frac{1}{2}O_2(g) \rightarrow 3CO_2(g) + 6H_2O(l) \qquad \Delta H = -2178 \text{ kJ mol}^{-1}$$

The importance of states

It is very important to always include state symbols in thermochemical equations. Physical changes involve an enthalpy change, so the state of the species in a chemical reaction affects the enthalpy change of the reaction.

For example, both of the following equations represent physical changes involving water. They have different ΔH values because the states are different.

$$H_2O(s) \rightarrow H_2O(l) \qquad \Delta H = +6.00 \text{ kJ mol}^{-1}$$

$$H_2O(l) \rightarrow H_2O(g) \qquad \Delta H = +40.7 \text{ kJ mol}^{-1}$$

You can see that it requires more energy to boil water than it does to melt ice.

Effect on ΔH of reversing a chemical reaction

Reversing a chemical equation changes the sign but not the magnitude of ΔH.

For example, methane (CH_4) reacts with oxygen gas to produce carbon dioxide gas and water in an exothermic reaction:

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

If this reaction is reversed, the magnitude of ΔH remains the same because the enthalpies of the individual chemicals have not changed, but the sign changes to indicate that energy must be absorbed for this reaction to proceed.

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

Worked example 2.2.1

CALCULATING Δ*H* FOR ANOTHER EQUATION

Iron reacts with oxygen according to the equation:

$3Fe(s) + 2O_2(g) \rightarrow Fe_3O_4(s) \quad \Delta H = -1121\ kJ\ mol^{-1}$

Calculate Δ*H* for the reaction represented by the equation:

$2Fe_3O_4(s) \rightarrow 6Fe(s) + 4O_2(g)$

Thinking	**Working**
The reaction has been reversed in the second equation, so the sign for Δ*H* is changed to the opposite sign.	Δ*H* for the second equation is positive.
Identify how the mole amounts in the equation have changed.	The mole amount of Fe_3O_4 has changed from 1 to 2, O_2 has changed from 2 to 4 and Fe has changed from 3 to 6. They have all doubled.
Identify how the magnitude of Δ*H* will have changed for the second equation.	The mole amounts of the chemicals have all doubled, so Δ*H* will also have doubled.
Calculate the new *magnitude* of Δ*H*. (You will write the sign of Δ*H* in the next step.)	2 × 1121 = 2242
Write Δ*H* for the second equation, including the sign.	$\Delta H = +2242\ kJ\ mol^{-1}$

Worked example: Try yourself 2.2.1

CALCULATING Δ*H* FOR ANOTHER EQUATION

Carbon reacts with hydrogen according to the equation:

$6C(s) + 3H_2(g) \rightarrow C_6H_6(g) \quad \Delta H = +49\ kJ\ mol^{-1}$

Calculate Δ*H* for the reaction represented by the equation:

$3C_6H_6(g) \rightarrow 18C(s) + 9H_2(g)$

Activation energy

The energy required to break the bonds of reactants so that a reaction can proceed is called the **activation energy**. The activation energy is an energy barrier that must be overcome before a reaction can get started. (The concept of activation energy is discussed in more detail in Chapter 7.)

A reaction cannot proceed unless the bonds in the reactants are broken.

An activation energy barrier exists for both exothermic and endothermic reactions. If the activation energy for a reaction is very low, the chemical reaction can be initiated as soon as the reactants come into contact because the reactants already have sufficient energy for a reaction to take place. Special conditions are not always required for reactions to occur. An example of this can be seen in the reaction between zinc and hydrochloric acid on page 44.

The reaction between zinc and hydrochloric acid produces hydrogen gas:

$$Zn(s) + 2HCl(aq) \rightarrow ZnCl_2(aq) + H_2(g)$$

As you can see in Figure 2.2.4, bubbles of hydrogen gas are vigorously produced as soon as zinc is added to the acid.

FIGURE 2.2.4 When zinc comes into contact with hydrochloric acid, it reacts almost immediately. The reactants have sufficient energy to 'overcome' the activation energy barrier.

ENERGY PROFILE DIAGRAMS

The energy changes that occur during the course of a chemical reaction can be shown on an energy profile diagram.

The energy profile diagram for an exothermic combustion reaction like the one shown in Figure 2.2.5 indicates that the enthalpy of the products is always less than the enthalpy of the reactants. Overall, energy is released and so the ΔH value is negative. The energy profile also shows that, even in exothermic reactions, the activation energy must first be absorbed to start the reaction.

The energy profile diagram for an endothermic reaction (Figure 2.2.6) shows that the enthalpy of the products is greater than the enthalpy of the reactants. Overall, energy is absorbed and so the ΔH value is positive. The energy profile also shows the absorption of the activation energy before the release of energy as bonds form in the products.

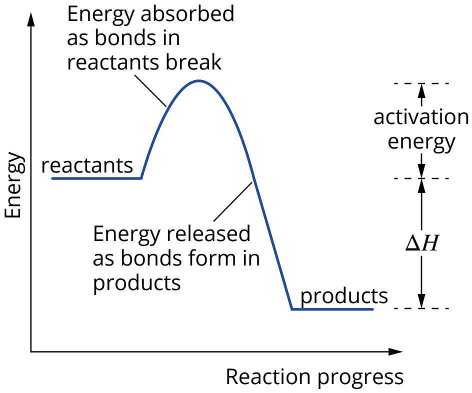


FIGURE 2.2.5 The characteristic shape of an energy profile diagram for an exothermic reaction.

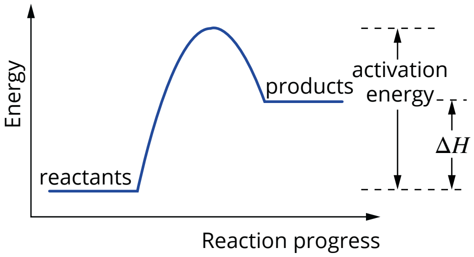


FIGURE 2.2.6 The characteristic shape of an energy profile diagram for an endothermic reaction.

2.2 Review

SUMMARY

- Thermochemical equations include a Δ*H* value for a chemical reaction. The unit of Δ*H* is usually kJ mol^{-1}.
- The value of Δ*H* indicates the magnitude of the energy change and whether the energy is absorbed (a positive value) or released (a negative value).
- Reversing an equation causes the sign of Δ*H* to change, as the reaction changes from exothermic to endothermic, or vice versa.
- Doubling the coefficients in a chemical reaction causes the Δ*H* value to also double, as twice as many reactants react to produce or absorb twice as much energy.
- States of matter must be included in thermochemical equations because changes of state involve enthalpy changes.
- Activation energy is the energy that must be absorbed to break the bonds in the reactants so that a chemical reaction can proceed. Both endothermic and exothermic reactions require activation energy.
- Energy profile diagrams show energy changes over the course of a reaction. They show the relative enthalpies of reactants and products and the activation energy.
- Combustion reactions are always exothermic and so always have a negative Δ*H* value.

KEY QUESTIONS

1 Explain what a negative Δ*H* value indicates about a chemical reaction, in terms of the relative enthalpies of the reactants and products.

2 When 1 mole of methane gas undergoes combustion in oxygen to produce carbon dioxide and water, 890 kJ of energy is released. Write a balanced thermochemical equation for this reaction.

3 The combustion of octane to form carbon dioxide and liquid water can be written as:

$$C_8H_{18}(g) + 12\frac{1}{2}O_2(g) \rightarrow 8CO_2(g) + 9H_2O(l) \quad \Delta H = -5450 \text{ kJ mol}^{-1}$$

The combustion of octane to form carbon dioxide and steam can be written as:

$$C_8H_{18}(g) + 12\frac{1}{2}O_2(g) \rightarrow 8CO_2(g) + 9H_2O(g)$$

How would the energy released by the combustion of 1 mole of octane to form steam compare with the energy released by 1 mole of octane to form liquid water?

4 The energy profile diagram in Figure 2.2.7 shows the energy changes during the reaction of hydrogen and iodine to form hydrogen iodide:

$$H_2(g) + I_2(g) \rightarrow 2HI(g)$$

a Is the reaction exothermic or endothermic?

b Describe the relative enthalpies of the reactants and products.

c Comment on the size of the activation energy compared with Δ*H*.

5 The reaction for photosynthesis is the opposite to the reaction for respiration shown on page 41. Write a thermochemical equation for photosynthesis.

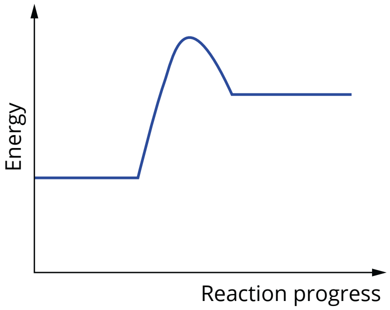


FIGURE 2.2.7 Energy profile of the reaction between hydrogen and iodine to form hydrogen iodide.

2.3 Energy from combustion

Review

The mole

The **mole** is a unit used by chemists for counting particles. One mole of any type of particle is a standard **amount** of substance, which contains the same number of specified particles as there are atoms in exactly 12 g of carbon-12.

The symbol for the amount of substance is *n*. The unit is **mole**, which is abbreviated to mol.

Because atoms are very small, chemists have defined the mole so that it represents a very large number. There are 6.02×10^{23} particles in 1 mole. This number is called **Avogadro's number** and has the symbol N_A.

A useful relationship links the amount of a substance (*n*), in mol, Avogadro's number (N_A) and the number of particles in a substance (*N*):

$$n = \frac{N}{N_A}$$

Where needed, this relationship can be rearranged to:

$$N = n \times N_A$$

Mass

Chemists often use mass, measured in grams, to measure an exact number of mole of an element or compound.

The **molar mass** of an element or compound is the mass of 1 mole of the element or compound. Molar mass is derived from the relative atomic mass, relative molecular mass or relative formula mass. A useful relationship links the amount of a substance (*n*), in mol, its molar mass (*M*), in g mol^{-1}, and the given mass of the substance (*m*), in g:

$$n = \frac{m}{M}$$

Where needed, this relationship can be rearranged to:

$$m = n \times M \quad \text{or} \quad M = \frac{m}{n}$$

Fire heats our homes, powers our cars and entertains us with firework displays. Bushfires can destroy homes and lives, devastating huge areas of bush and damaging the habitat of many animals. However, a bushfire can also be an agent of regrowth and renewal in land management.

Ancient cultures, such as the Ancient Greeks and Ancient Japanese, described fire as one of the fundamental elements, along with air, earth and water (see Figure 2.3.1).

FIGURE 2.3.1 According to the Ancient Greeks, the classical four elements were fire, earth, air and water.

Fire results from the combustion of substances. Combustion reactions need three things:

- fuel to burn
- oxygen for the fuel to burn in
- energy to get the process started.

Fire can be understood and controlled by applying your knowledge of chemistry. In this section, you will look at combustion reactions and their importance to the world in more detail.

COMBUSTION AS A CHEMICAL PROCESS

Combustion reactions are exothermic reactions in which the reactant combines with oxygen to produce oxides. This type of reaction is often referred to as an **oxidation** reaction. The combustion of a hydrocarbon produces carbon dioxide and water, provided there is enough oxygen present. An example is the combustion of propane (C_3H_8), a major component of LPG (liquefied petroleum gas), shown in the following equation:

$$C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(l) \qquad \Delta H = -2220 \text{ kJ mol}^{-1}$$

Note the following important features of this thermochemical equation.

- No atoms are created or destroyed in the reaction, so the numbers of atoms of each element are balanced on the two sides of the equation.

- The balanced equation tells you the number of molecules of oxygen that are required for the combustion of each molecule of propane.
- The enthalpy change for the reaction is negative, indicating that this is an exothermic reaction.
- The enthalpy change is given in kJ mol^{-1}. It tells you the energy released, in kJ, according to the coefficients given in the equation.
- State symbols show the state of each reactant and product. (Although in a combustion reaction, water is released as water vapour, the enthalpy change of this thermochemical equation shows the energy change if liquid water is formed.)

In redox reactions that involve oxygen as a reactant, oxidation can be defined as the addition of oxygen to form oxides, such as in a combustion reaction.

Complete and incomplete combustion

Combustion reactions can be described as complete or incomplete. The difference between the two is due to the amount of oxygen available to react with the fuel.

Complete combustion occurs when oxygen is plentiful. The only products are carbon dioxide and water.

An example is the complete combustion of methane:

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$$

When the oxygen supply is limited, **incomplete combustion** occurs. As less oxygen is available, not all of the carbon can be converted into carbon dioxide. Carbon monoxide and/or carbon are produced instead. The hydrocarbon burns with a yellow, smoky or sooty flame, due to the presence of glowing carbon particles. Figure 2.3.2 shows the appearance of the different flames of a Bunsen burner due to incomplete and complete combustion.

FIGURE 2.3.2 The yellow flame of a Bunsen burner is due to incomplete combustion and produces carbon as a product. The blue flame is a hotter flame that occurs when the collar hole is open and more oxygen is allowed into the reaction. Complete combustion can then occur.

The equation for the incomplete combustion of methane to form carbon monoxide is:

$$2CH_4(g) + 3O_2(g) \rightarrow 2CO(g) + 4H_2O(l)$$

CHEMFILE

Carbon monoxide poisoning

Carbon monoxide is a highly poisonous gas. It combines readily with haemoglobin, the oxygen carrier in blood. When attached to carbon monoxide, haemoglobin cannot transport oxygen around the body, which leads to oxygen starvation of tissues. (You can read more about the chemistry of carbon monoxide poisoning in Chapter 8, page 219.)

Even at concentrations as low as 10 parts per million (ppm), carbon monoxide can cause drowsiness, dizziness and headaches. At about 200 ppm, carbon monoxide can lead to death. The average carbon monoxide concentration in large cities, mostly due to incomplete combustion of fuels in cars (Figure 2.3.3), is now 7 ppm, but it can be as high as 120 ppm at busy intersections in heavy traffic.

FIGURE 2.3.3 Car exhaust gases can contain high levels of carbon monoxide as a result of incomplete combustion of fuels.

The complete combustion of hydrocarbons occurs when there is sufficient oxygen for the fuel to burn. The products of complete combustion are carbon dioxide and water. When oxygen is not plentiful, incomplete combustion occurs. The products of incomplete combustion are carbon monoxide and/or carbon and water.

WRITING EQUATIONS FOR COMPLETE COMBUSTION OF FUELS

It is important to write chemical equations correctly because they tell you a lot about chemical reactions. Writing equations for the complete combustion reactions of fuels containing carbon and hydrogen is relatively straightforward, because the products are always carbon dioxide and water.

Perhaps the most important of all combustion reactions involving fuels are those that occur when petrol is burnt. Petrol is a mixture of hydrocarbons, including octane.

The combustion reactions of octane (C_8H_{18}) and the other hydrocarbons in petrol power the internal combustion engines in most of Australia's 17.6 million motor vehicles.

Worked example 2.3.1

WRITING EQUATIONS FOR COMPLETE COMBUSTION OF HYDROCARBON FUELS

Write the equation, including state symbols, for the complete combustion of butane (C_4H_{10}).

Thinking	Working
Add oxygen as a reactant and carbon dioxide and water as the products.	$C_4H_{10} + O_2 \rightarrow CO_2 + H_2O$
Balance carbon and hydrogen atoms, based on the formula of the hydrocarbon.	$C_4H_{10} + O_2 \rightarrow 4CO_2 + 5H_2O$
Find the total number of oxygen atoms on the product side.	Total O $= (4 \times 2) + 5$ $= 13$
If this is an odd number, multiply all of the coefficients in the equation by two, except for the coefficient of oxygen.	$2C_4H_{10} + O_2 \rightarrow 8CO_2 + 10H_2O$
Balance oxygen by adding the appropriate coefficient to the reactant side of the equation.	$2C_4H_{10} + 13O_2 \rightarrow 8CO_2 + 10H_2O$
Add state symbols.	$2C_4H_{10}(g) + 13O_2(g) \rightarrow 8CO_2(g) + 10H_2O(l)$

Worked example: Try yourself 2.3.1

WRITING EQUATIONS FOR COMPLETE COMBUSTION OF HYDROCARBON FUELS

Write the equation, including state symbols, for the complete combustion of hexane (C_6H_{14}).

A similar series of steps can also be used to write the combustion equations for other carbon-based fuels that contain oxygen; for example, alcohols.

Worked example 2.3.2

WRITING EQUATIONS FOR COMBUSTION REACTIONS OF ALCOHOLS

Write the equation, including state symbols, for the complete combustion of liquid ethanol (C_2H_5OH).

Thinking	Working
Add oxygen as a reactant and carbon dioxide and water as the products.	$C_2H_5OH + O_2 \rightarrow CO_2 + H_2O$
Balance carbon and hydrogen atoms, based on the formula of the alcohol.	$C_2H_5OH + O_2 \rightarrow 2CO_2 + 3H_2O$
Find the total number of oxygen atoms on the product side. Then subtract the one oxygen atom in the alcohol molecule from the total number of oxygen atoms on the product side.	Total O on product side $= (2 \times 2) + 3$ $= 7$ Total O on product side – 1 in alcohol $= 7 - 1 = 6$
If this is an odd number, multiply all the coefficients in the equation by two, except for the coefficient of oxygen.	$C_2H_5OH + O_2 \rightarrow 2CO_2 + 3H_2O$
Balance oxygen by adding the appropriate coefficient to the reactant side of the equation.	$C_2H_5OH + 3O_2 \rightarrow 2CO_2 + 3H_2O$
Add state symbols.	$C_2H_5OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(g)$

Worked example: Try yourself 2.3.2

WRITING EQUATIONS FOR COMBUSTION REACTIONS OF ALCOHOLS

Write the equation, including state symbols, for the complete combustion of liquid methanol (CH_3OH).

WRITING EQUATIONS FOR INCOMPLETE COMBUSTION OF FUELS

When the supply of oxygen is insufficient, incomplete combustion of fuels occurs. Equations can also be written to represent this. In general, for the incomplete combustion of hydrocarbons, as well as carbon-based fuels that contain oxygen, the products are carbon monoxide and/or carbon and water.

Worked example 2.3.3

WRITING EQUATIONS FOR INCOMPLETE COMBUSTION OF FUELS

Write an equation, including state symbols, for the incomplete combustion of ethane gas (C_2H_6) to form carbon monoxide and water vapour.

Thinking	Working
Add oxygen as a reactant and carbon monoxide and water as the products.	$C_2H_6 + O_2 \rightarrow CO + H_2O$
Balance the carbon and hydrogen atoms, based on the formula of the hydrocarbon.	$C_2H_6 + O_2 \rightarrow 2CO + 3H_2O$
Balance oxygen by adding the appropriate coefficient to the reactant side of the equation.	$C_2H_6 + \frac{5}{2}O_2 \rightarrow 2CO + 3H_2O$
If oxygen gas has a coefficient that is half of a whole number, multiply all of the coefficients in the equation by two.	$2C_2H_6 + 5O_2 \rightarrow 4CO + 6H_2O$
Add state symbols.	$2C_2H_6(g) + 5O_2(g) \rightarrow 4CO(g) + 6H_2O(g)$

Worked example: Try yourself 2.3.3

WRITING EQUATIONS FOR INCOMPLETE COMBUSTION OF FUELS

Write an equation, including state symbols, for the incomplete combustion of liquid methanol (CH_3OH) to form carbon monoxide and water vapour.

HEAT OF COMBUSTION

The **heat of combustion** of a fuel is defined as the enthalpy change that occurs when a specified amount (e.g. 1 g, 1 L, 1 mol) of the fuel burns completely in oxygen. It is usually measured at conditions of 298 K and 100 kPa, which means that the water produced should be shown in the liquid state. The heat of combustion can be given the symbol ΔH_c.

ℹ The heat of combustion is usually measured at conditions of 298 K and 100 kPa. This means that the water produced should be shown in the liquid state.

Many fuels, including wood, coal and kerosene, are mixtures of chemicals and do not have a specific chemical formula or molar mass. This means their heat of combustion cannot be expressed in kJ mol^{-1}. Therefore, it is measured only as kJ g^{-1}, kJ L^{-1} or MJ/tonne.

ℹ Only fuels that exist as pure substances can have their heat of combustion measured in kJ mol^{-1}.

The heats of combustion for some common elements and compounds present in fuels are listed in Table 2.3.1. Heat energy is released during combustion, so ΔH_c always has a negative value.

TABLE 2.3.1 Heats of combustion for some common elements and compounds

Substance	Heat of combustion, ΔH_c (kJ mol^{-1})
Methane	–890
Ethane	–1560
Propane	–2220
Butane	–2886
Octane	–5450
Methanol	–725
Ethanol	–1367
Hydrogen	–286
Carbon (graphite)	–394

As you learned in Chapter 1, when these fuels are burnt, not all the energy is released as heat energy, and not all of the heat energy liberated can be harnessed for a particular purpose, such as powering a vehicle or producing electricity. However, even if the energy transformation process is not 100% efficient, you can still use these values to compare the energy released from combustion of different compounds.

As Worked Example 2.3.4 shows, you can use the data in Table 2.3.1 to calculate the energy released on combustion of a specified mass of one of the fuels. The energy released when *n* mol of a fuel burns is given by the equation:

$$\text{Energy} = n \times \Delta H_c$$

Worked example 2.3.4

CALCULATING ENERGY RELEASED BY A SPECIFIED MASS OF A PURE FUEL

Calculate the amount of energy released when 3.60 kg of butane (C_4H_{10}) is burnt in an unlimited supply of oxygen.

Thinking	Working
Calculate the number of moles of the compound using: $n = \frac{m \text{ (in grams)}}{M}$	$n(C_4H_{10}) = \frac{m}{M}$ $= \frac{3.60 \times 10^3}{58.0}$ $= 62.1$ mol
Multiply the number of moles by the heat of combustion.	Energy $= n \times \Delta H_c$ $= 62.1 \times 2886$ $= 1.79 \times 10^5$ kJ

Worked example: Try yourself 2.3.4

CALCULATING ENERGY RELEASED BY A SPECIFIED MASS OF A PURE FUEL

Calculate the amount of energy released when 5.40 kg of propane (C_3H_8) is burnt in an unlimited supply of oxygen.

Energy content per gram

The energy content of a a fuel is often expressed in units of kilojoules per gram.

For a pure substance, the heat of combustion per gram can be calculated by simply dividing the heat of combustion per mole (kJ mol^{-1}) by the molar mass of the substance.

For example, for ethanol (which is being burnt in a spirit burner in Figure 2.3.4):

$$\text{Heat of combustion per mole} = -1367 \text{ kJ mol}^{-1}$$

$$\text{Molar mass} = 46.0 \text{ g mol}^{-1}$$

$$\text{Heat of combustion per gram} = \frac{-1367}{46.0} = -29.7 \text{ kJ g}^{-1}$$

For fuels that are mixtures, approximate values for the heat of combustion per gram are shown in Table 2.3.2.

FIGURE 2.3.4 Ethanol burning in a spirit burner. Combustion of 1 gram of ethanol releases almost 30 kJ of energy.

TABLE 2.3.2 Approximate heat of combustion values for some fuel mixtures

Substance	Heat of combustion (kJ g^{-1}) (approx.)
Wood, dried	–18
Peat, dried	–25
Brown coal, dried	–30
Black coal, dried	–35

Energy content per tonne

The quantities of fuel consumed and the amount of energy produced are often so large that the unit megajoules per tonnes, MJ/tonne, is a more useful way of expressing the heat of combustion. For example, the Hazelwood power station consumes about 13 million tonnes of coal in 1 year. It is more useful to consider the energy released per tonne, rather than per gram of coal.

$$1 \text{ kJ} = 10^{-3} \text{ MJ}$$

$$1 \text{ g} = 10^{-6} \text{ tonne}$$

Therefore, 1 kJ $g^{-1} = 10^{-3}$ MJ/10^{-6} t.

This can be simplified to 1 kJ $g^{-1} = 10^{3}$ MJ/tonne.

EXTENSION

Energy density

Liquid fuels, such as petrol, are normally sold by **volume** rather than by mass. For these fuels, it is often convenient to refer to the heat of combustion per litre. Table 2.3.3 shows some heats of combustion per litre for common liquid fuels. The energy released per litre of fuel is often called the fuel's **energy density**.

TABLE 2.3.3 Energy densities for some common liquid fuels

Substance	Energy density (kJ L^{-1})
Petrol (unleaded 91)	–34 200
Kerosene	–36 500
Diesel fuel	–38 000
Heating oil	–38 500
Ethanol	–23 400

2.3 Review

SUMMARY

- Combustion reactions are exothermic reactions that can be represented by balanced thermochemical equations.
- The products of the complete combustion of hydrocarbons and carbon-based fuels containing oxygen are carbon dioxide and water.
- Incomplete combustion, resulting in the production of carbon monoxide and/or carbon, occurs when hydrocarbons and carbon-based fuels containing oxygen undergo combustion in a limited supply of oxygen.
- Heats of combustion, ΔH_c, indicate the maximum amount of energy that can be released when a specified amount of fuel undergoes complete combustion. Common units are kJ mol^{-1}, kJ g^{-1} and MJ/tonne.
- The amount of energy released by different fuels can be compared by referring to heats of combustion.
- For a pure fuel with a heat of combustion, ΔH_c, measured in kJ mol^{-1}, the energy released when n mol of the fuel burns is given by the equation: Energy = $n \times \Delta H_c$

KEY QUESTIONS

1 Write a balanced equation for the complete combustion of liquid benzene (C_6H_6).

2 Information about two hydrocarbon fuels, propane and octane, is given in Table 2.3.4.

TABLE 2.3.4

Characteristic	Propane (C_3H_8)	Octane (C_8H_{18})
Heat of combustion (kJ mol^{-1})	–2220	–5450
Molar mass (g mol^{-1})	44.0	114.0

Calculate the heat of combustion of each fuel in kJ g^{-1} and use your answer to state which fuel produces more energy per kilogram.

3 Write a balanced equation for the incomplete combustion of ethanol (C_2H_5OH) when carbon monoxide is formed.

4 Using the information in Tables 2.3.1 and 2.3.2, calculate the amount of energy released when the following amounts of each fuel undergo complete combustion.

a 250 g of methane
b 9.64 kg of propane
c 403 kg of ethanol
d 573 t of dried brown coal

2.4 Determining the heat of combustion of fuels

Knowing the energy released by similar quantities of different fuels helps you to compare fuels and determine their suitability for specific purposes. For example, the fuel used to power an aeroplane (Figure 2.4.1) is different from the fuel used to power a car or bus.

FIGURE 2.4.1 F15 jets being refuelled by a Boeing 707. The type of fuel suitable for use in aircraft is different from the type of fuel suitable for use in cars or buses.

In previous sections, you learned two ways of representing the energy change for fuels involved in combustion reactions.

- The heat of combustion of a fuel gives the amount of energy released when a specified amount of the fuel burns in oxygen.
- A thermochemical equation includes a ΔH value, which shows the amount of heat released when a fuel undergoes combustion. The value of ΔH is based on the stoichiometric ratios in the equation.

In this section, you will learn how knowledge of the specific heat capacity of water can be used to obtain an experimental estimate of the energy released in the combustion of a fuel.

SPECIFIC HEAT CAPACITY OF WATER

The **specific heat capacity** of a substance is a measure of the amount of energy (usually in joules) needed to increase the temperature of a specific quantity of that substance (usually 1 gram) by 1°C.

Specific heat capacity is given the symbol C and is usually expressed in joules per gram per degrees Celsius, i.e. $\text{J g}^{-1}\ {}^{\circ}\text{C}^{-1}$. It can also be expressed in joules per grams per kelvin, i.e. $\text{J g}^{-1}\ \text{K}^{-1}$ (an increase of 1°C is the same as an increase of 1 K).

The specific heat capacities of some common substances are listed in Table 2.4.1. You can see that the value for water is relatively high.

TABLE 2.4.1 Specific heat capacities of common substances

Substance	Specific heat capacity ($J\ g^{-1}\ °C^{-1}$)
Water	4.18
Glycerine	2.43
Ethanol	2.46
Sand	0.48
Copper	0.39
Lead	0.16

The specific heat capacity of a substance is a reflection of the types of bonds holding the molecules, ions or atoms together in the substance.

Water has a specific heat capacity of 4.18 $J\ g^{-1}\ °C^{-1}$. This means that 4.18 joules of heat energy are needed to increase the temperature of 1 gram of water by 1°C. This relatively high value is due to the hydrogen bonds between the water molecules. The higher the specific heat capacity, the more effectively a material stores heat energy.

When a substance is being heated, its temperature rises. The temperature of 1 g of water increases by 1°C when it is supplied with 4.18 J of heat energy. In comparison, 2.43 J of heat energy is required to increase the temperature of 1 g of glycerine by 1°C. The effect of the different specific heat capacities of water and glycerine on their temperatures when heated can be seen in Figure 2.4.2.

The specific heat capacity of a substance is the amount of energy required to increase the temperature of 1 g of the substance by 1°C . Specific heat capacity is frequently written using the units $J\ g^{-1}\ °C^{-1}$.

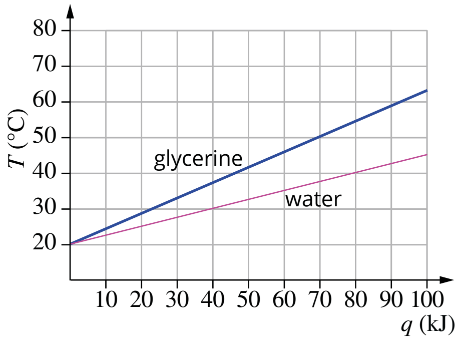


FIGURE 2.4.2 A comparison of the effect of the different specific heat capacities of water and glycerine on the increase in temperature (*T*). Water has a very high heat capacity so it requires more heat energy (*q*) to increase its temperature by 1°C.

Water is distinguished by its very high heat capacity, which is a consequence of the hydrogen bonding between its molecules. The special properties of water are described in *Heinemann Chemistry 1*.

Calculations using specific heat capacity

The specific heat capacity of water can be used to calculate the heat energy in joules needed to increase the temperature of a given mass of water by a particular amount. Heat energy is given the symbol *q*.

A useful equation can be written:

Heat energy = specific heat capacity × mass × temperature change

Using symbols, the equation can be written as:

$$q = C \times m \times \Delta T$$

where q is the amount of heat energy (in J), C is the specific heat capacity (in $J\ g^{-1}\ °C^{-1}$), m is the mass (in g) and ΔT is the temperature change (in °C).

The heat energy required to increase the temperature of a given mass of water by a particular amount can be calculated using the equation:

$$q = C \times m \times \Delta T$$

where q is the amount of heat energy (in J), C is the specific heat capacity (in $J\ g^{-1}\ °C^{-1}$), m is the mass (in g) and ΔT is the temperature change (in °C).

Worked example 2.4.1

CALCULATING THE AMOUNT OF ENERGY REQUIRED TO HEAT A SPECIFIED MASS OF WATER USING SPECIFIC HEAT CAPACITY

Calculate the heat energy, in kJ, needed to increase the temperature of 500 mL of water by 15°C.

Thinking	**Working**
Change the volume of water, in mL, to mass of water, in g. Remember that 1 mL of water has a mass of 1 g.	1 mL of water has a mass of 1 g, so 500 mL of water has a mass of 500 g.
Find the specific heat capacity of water from the data in Table 2.4.1.	The specific heat capacity of water is 4.18 J g^{-1} $°C^{-1}$.
To calculate the quantity of heat energy in joules, use the formula: $q = C$ (J g^{-1} $°C^{-1}$) × m (g) × ΔT (°C)	$q = 4.18 \times 500 \times 15$ $= 3.14 \times 10^4$ J
Express the quantity of energy in kJ. Remember that to convert from J to kJ, you multiply by 10^{-3}.	$q = 3.14 \times 10^4 \times 10^{-3}$ $= 31.4$ kJ

Worked example: Try yourself 2.4.1

CALCULATING THE AMOUNT OF ENERGY REQUIRED TO HEAT A SPECIFIED MASS OF WATER USING SPECIFIC HEAT CAPACITY

Calculate the heat energy, in kJ, needed to increase the temperature of 375 mL of water by 45°C.

EXPERIMENTAL DETERMINATION OF HEAT OF COMBUSTION

When a combustion reaction takes place, chemical energy is converted to thermal energy. You can use the thermal energy released by a specific quantity of fuel as it undergoes combustion to heat a measured volume of water. If you measure the temperature change of the water, it can be used to determine the approximate amount of energy released by the fuel.

An experimental arrangement for estimating the heat of combustion of a liquid fuel, such as ethanol, is shown in Figure 2.4.3.

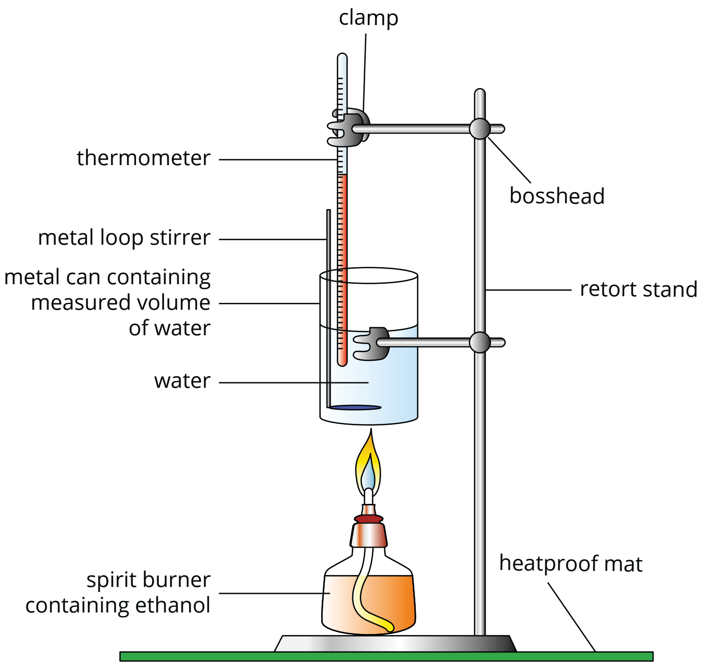


FIGURE 2.4.3 Apparatus for measuring heat of combustion of a fuel (for example, ethanol). A metal can containing a measured volume of water is held above the wick of a spirit burner.

Figure 2.4.4 summarises the steps followed in this experiment.

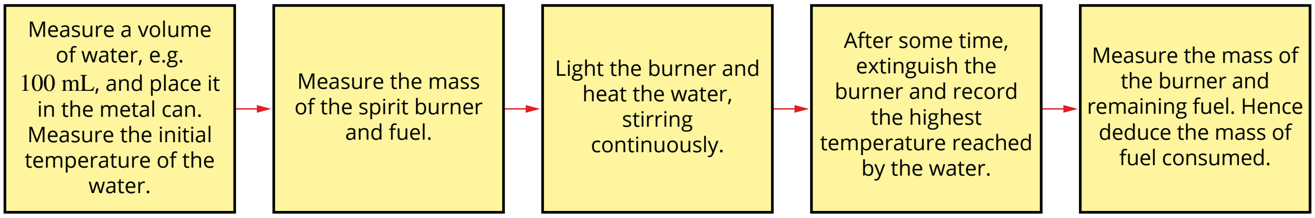


FIGURE 2.4.4 Flowchart of the steps followed when using the specific heat capacity of water to determine the heat of combustion of a fuel.

Three key pieces of information collected from this procedure are the:

- mass of water (because the density of water is 1.00 g mL^{-1}, the volume of water, measured in mL, is equal to its mass, in g)
- change in temperature of the water, ΔT
- mass of fuel consumed, m.

This data can be used to determine the heat of combustion of the fuel, as shown in Worked Example 2.4.2.

Note that when performing these calculations, it is assumed that all of the energy released by the combustion of the fuel is used to heat the water. In reality, some of the energy heats the metal can as well as being lost to the surroundings.

For this reason, measurements of heats of combustion from these experiments only give approximate values. More accurate measurements are obtained using bomb calorimetry, which is discussed in Chapter 17.

Worked example 2.4.2

CALCULATING THE HEAT OF COMBUSTION OF A FUEL FROM EXPERIMENTAL DATA

0.355 g of methanol (CH_3OH) undergoes complete combustion in a spirit burner. The heat energy released is used to heat 100 mL of water. The temperature of the water rose from 20.24°C to 37.65°C. Calculate the heat of combustion of methanol in kJ mol^{-1}.

Thinking	**Working**
Calculate the temperature change of the water.	$\Delta T = 37.65 - 20.24$ $= 17.41°C$
Use the specific heat capacity of water to determine the energy used to heat the water. Use the formula: $q = C \times m \times \Delta T$ (m in this formula is the mass of water.)	$q = 4.18 \times 100 \times 17.41$ $= 7277$ J
Express the quantity of energy in kJ. Remember that to convert from J to kJ, you multiply by 10^{-3}.	$q = 7277 \times 10^{-3}$ $= 7.277$ kJ
Calculate the amount, in moles, of methanol using the formula: $n = \frac{m}{M}$	$n = \frac{0.355}{32.0}$ $= 0.0111$ mol
Determine the heat of combustion of methanol, in kJ mol^{-1}. Heat of combustion = $\frac{\text{heat energy released by sample}}{\text{amount of sample (in mol)}}$	Heat of combustion = $\frac{-7.277}{0.0111}$ $= -656$ kJ mol^{-1} (Note: The negative sign indicates the reaction released energy, causing the temperature to rise.)

Worked example: Try yourself 2.4.2

CALCULATING THE HEAT OF COMBUSTION OF A FUEL FROM EXPERIMENTAL DATA

0.295 g of ethanol (C_2H_5OH) undergoes complete combustion in a spirit burner. The heat energy released is used to heat 100 mL of water. The temperature of the water rose from 19.56°C to 38.85°C. Calculate the heat of combustion of ethanol in kJ mol^{-1}.

DETERMINING THE Δ*H* VALUE FOR THERMOCHEMICAL EQUATIONS

Experimentally determined heats of combustion for different elements and compounds used as fuels can be listed in a data table, such as that shown in Table 2.4.2.

TABLE 2.4.2 Experimentally determined heats of combustion of various fuels

Fuel	Heat of combustion, ΔH_c (kJ mol^{-1})
Octane	–5450
Butane	–2886
Propane	–2220
Ethane	–1560
Ethanol	–1367
Methane	–890
Methanol	–725
Carbon (graphite)	–394
Hydrogen	–286

This data can be used to write thermochemical equations for the combustion of these fuels. For example, the equation for the complete combustion of propane is:

$C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(l) \qquad \Delta H = -2220 \text{ kJ mol}^{-1}$

In this equation, the coefficient of propane is 1 so the ΔH value is the same as the heat of combustion.

If the coefficient of the fuel in the combustion equation is 2 or more, the heat of combustion must be multiplied by this number to determine ΔH. For example, the thermochemical equation for the complete combustion of butane is written as:

$2C_4H_{10}(g) + 13O_2(g) \rightarrow 8CO_2(g) + 10H_2O(l) \qquad \Delta H = -5772 \text{ kJ mol}^{-1}$

ΔH in this case is twice the heat of combustion, $2 \times -2886 = -5772 \text{ kJ mol}^{-1}$.

Note that heats of combustion measured in kJ g^{-1} should be converted to units of kJ mol^{-1} for use in thermochemical equations. Combustion reactions are always exothermic, so the enthalpy change always has a negative sign.

Worked example 2.4.3

WRITING A THERMOCHEMICAL EQUATION USING HEAT OF COMBUSTION DATA

Write a thermochemical equation for the complete combustion of octane (C_8H_{18}).

Thinking	**Working**
Add oxygen as a reactant and carbon dioxide and water as the products in the equation.	$C_8H_{18} + O_2 \rightarrow CO_2 + H_2O$
Balance the carbon, hydrogen then oxygen atoms. Add states.	$2C_8H_{18}(g) + 25O_2(g) \rightarrow 16CO_2(g) + 18H_2O(l)$
Obtain the heat of combustion, in kJ mol^{-1}, from Table 2.4.2.	The heat of combustion of octane is -5450 kJ mol^{-1}.
Determine ΔH for the thermochemical equation by multiplying the heat of combustion by the coefficient of the fuel in the balanced equation.	$\Delta H = 2 \times -5450 = -10\,900 \text{ kJ mol}^{-1}$
Write the thermochemical equation.	$2C_8H_{18}(g) + 25O_2(g) \rightarrow 16CO_2(g) + 18H_2O(l)$ $\Delta H = -10\,900 \text{ kJ mol}^{-1}$

Worked example: Try yourself 2.4.3

WRITING A THERMOCHEMICAL EQUATION USING HEAT OF COMBUSTION DATA

Write a thermochemical equation for the complete combustion of ethane (C_2H_6).

2.4 Review

SUMMARY

- The specific heat capacity of a substance measures the quantity of energy (usually in joules) needed to increase the temperature of a specified quantity of that substance (usually 1 gram) by 1°C.
- The specific heat capacity of water is 4.18 J g^{-1} $°C^{-1}$.
- The heat energy required to increase the temperature of a given mass of water by a particular amount can be calculated using the equation:

  $q = C \times m \times \Delta T$

  where q is heat energy (in J), C is the specific heat capacity (in J g^{-1} $°C^{-1}$), m is mass (in g) and ΔT is the temperature change (in °C).
- Heat of combustion is the energy released when a specified quantity of a substance (usually 1 mole, 1 gram or 1 litre) is burnt.
- The specific heat capacity of water can be used in the experimental determination of the approximate amount of heat energy released in the combustion of a fuel.
- Heat of combustion data can be used to determine the enthalpy change, ΔH, in a thermochemical equation.

KEY QUESTIONS

1 Calculate the heat energy, in kJ, needed to increase the temperature of 1.00 kg of water by 25.0°C.

2 What assumptions are made when making calculations relating to the heat of combustion of fuels using experimental data obtained from the apparatus shown in Figure 2.4.3 (on page 57)?

3 A temperature rise of 1.78°C was observed when 1.00×10^{-3} mol of propane gas was burnt and used to heat 300 mL of water. Calculate the heat of combustion for propane in kJ mol^{-1}, assuming all the heat released was used to heat the water.

4 A temperature rise of 11.5°C was observed when 0.500 g of butane gas (C_4H_{10}) was burnt and used to heat 500 mL of water. Calculate the heat of combustion, in kJ g^{-1}, for butane, assuming all the heat released is used to heat the water.

5 The heat of combustion of methane is –890 kJ mol^{-1}.

  a Write a thermochemical equation for the complete combustion of methane.

  b Determine the mass of methane, in g, which has to be burnt in order to heat 500 mL of water from 20.0°C to boiling. Assume all the heat released was used to heat the water.

Chapter review

KEY TERMS

activation energy
bioluminescence
chemical energy
chemiluminescence
chemiluminescent
complete combustion
decomposition
endothermic
energy density
energy profile diagram
enthalpy
enthalpy change
exothermic
heat content
heat of combustion
incomplete combustion
law of conservation of energy
oxidation
SI units
specific heat capacity
surroundings
system
thermochemical equation
volume

Exothermic and endothermic reactions

1 Convert the following units of energy to the unit given (to 3 significant figures).

- **a** 2205 J to kJ
- **b** 0.152 kJ to J
- **c** 1 890 000 J to MJ
- **d** 0.0125 MJ to kJ

2 Decide whether the following processes are exothermic or endothermic. Give reasons for your answers.

- **a** burning of wood
- **b** melting of ice
- **c** recharging of a car battery
- **d** decomposition of plants in a compost heap

3 What is the difference between 'bioluminescence' and 'chemiluminescence'? Give an example in your answer.

Thermochemical equations and energy profile diagrams

4 Which one of the following is correct about the energy profile diagrams of both endothermic and exothermic reactions?

- **A** There is always less energy absorbed than released.
- **B** The enthalpy of the products is always less than the energy of the reactants.
- **C** Some energy is always absorbed to break bonds in the reactants.
- **D** The ΔH value is the difference between the enthalpy of the reactants and the highest energy point reached on the energy profile.

5 Identify whether each of the following statements related to activation energy is true or false.

- **a** Activation energy is the energy required to break bonds in the reactants.
- **b** Reactions that start immediately do not have an activation energy.
- **c** Reactions that release energy overall do not need to absorb activation energy.
- **d** The match used to light a fire is providing activation energy.

6 The combustion reaction of ethyne gas that occurs in a welding machine can be represented by the thermochemical equation:

$2C_2H_2(g) + 5O_2(g) \rightarrow 4CO_2(g) + 2H_2O(l)$
$\Delta H = -2619 \text{ kJ mol}^{-1}$

- **a** Is this reaction endothermic or exothermic?
- **b** What would be the new value of ΔH if the equation was now written as follows?
  $4C_2H_2(g) + 10O_2(g) \rightarrow 8CO_2(g) + 4H_2O(l)$

7 Explain why reversing a chemical reaction reverses the sign of ΔH.

8 The combustion of butane gas in portable stoves can be represented by the thermochemical equation:

$2C_4H_{10}(g) + 13O_2(g) \rightarrow 8CO_2(g) + 10H_2O(l)$
$\Delta H = -5772 \text{ kJ mol}^{-1}$

- **a** How does the overall energy of the bonds in the reactants compare with the overall energy of the bonds in the products?
- **b** Draw an energy profile diagram for the reaction, labelling ΔH and activation energy.

Energy from combustion

9 Write a balanced equation for the complete combustion of butanol (C_4H_9OH), a commonly used biofuel.

10 Write a balanced equation for the incomplete combustion of butane (C_4H_{10}) where carbon monoxide is formed.

11 Calculate the energy released when 5.00 kg of methane (CH_4) is burnt in an unlimited supply of oxygen. The heat of combustion of methane is -890 kJ mol^{-1}. (Give your answer in megajoules, MJ.)

12 **a** Use the data from Table 2.3.1 on page 51 to calculate the energy available from 1 kg of each of the following fuels.

- **i** Octane
- **ii** Butane
- **iii** Hydrogen

b Use the results of your calculations in part **a** to list octane, butane and hydrogen in order of most energy produced per kilogram to least energy produced per kilogram.

Determining the heat of combustion of fuels

13 Calculate the energy needed to heat:

- **a** 100 mL of water from 20.0°C to 80.0°C
- **b** 250 mL of water from 25.0°C to 100.0°C
- **c** 1.5 kg of water from 20.0°C to 30.0°C
- **d** 2300 g of water from 18.0°C to 100.0°C
- **e** 300 g of cooking oil from 18.0°C to 100.0°C (C(cooking oil) = 2.2 J g^{-1} $°C^{-1}$).

14 A 200 mL beaker of water at a temperature of 21.0°C is heated with 10.0 kJ of energy. Calculate the temperature reached by the beaker of water.

15 0.254 g of black coal was burnt and used to heat 300 mL of water. The temperature of the water rose from 18.25°C to 24.92°C. Calculate the heat of combustion, in kJ g^{-1}, of the coal. Assume all of the heat released during combustion was used to heat the water.

16 The heat of combustion of hydrogen is –286 kJ mol^{-1}. Write a thermochemical equation for the complete combustion of hydrogen.

Connecting the main ideas

17 In a steelworks, carbon monoxide present in the exhaust gases of the blast furnace can be used as a fuel elsewhere in the plant. It reacts according to the equation:

$$CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(g) \quad \Delta H = -283 \text{ kJ mol}^{-1}$$

a Which has the greater total enthalpy: 1 mol of CO(g) and 0.5 mol of O_2(g) or 1 mol of CO_2(g)?

b Write the value of ΔH for the following equations:

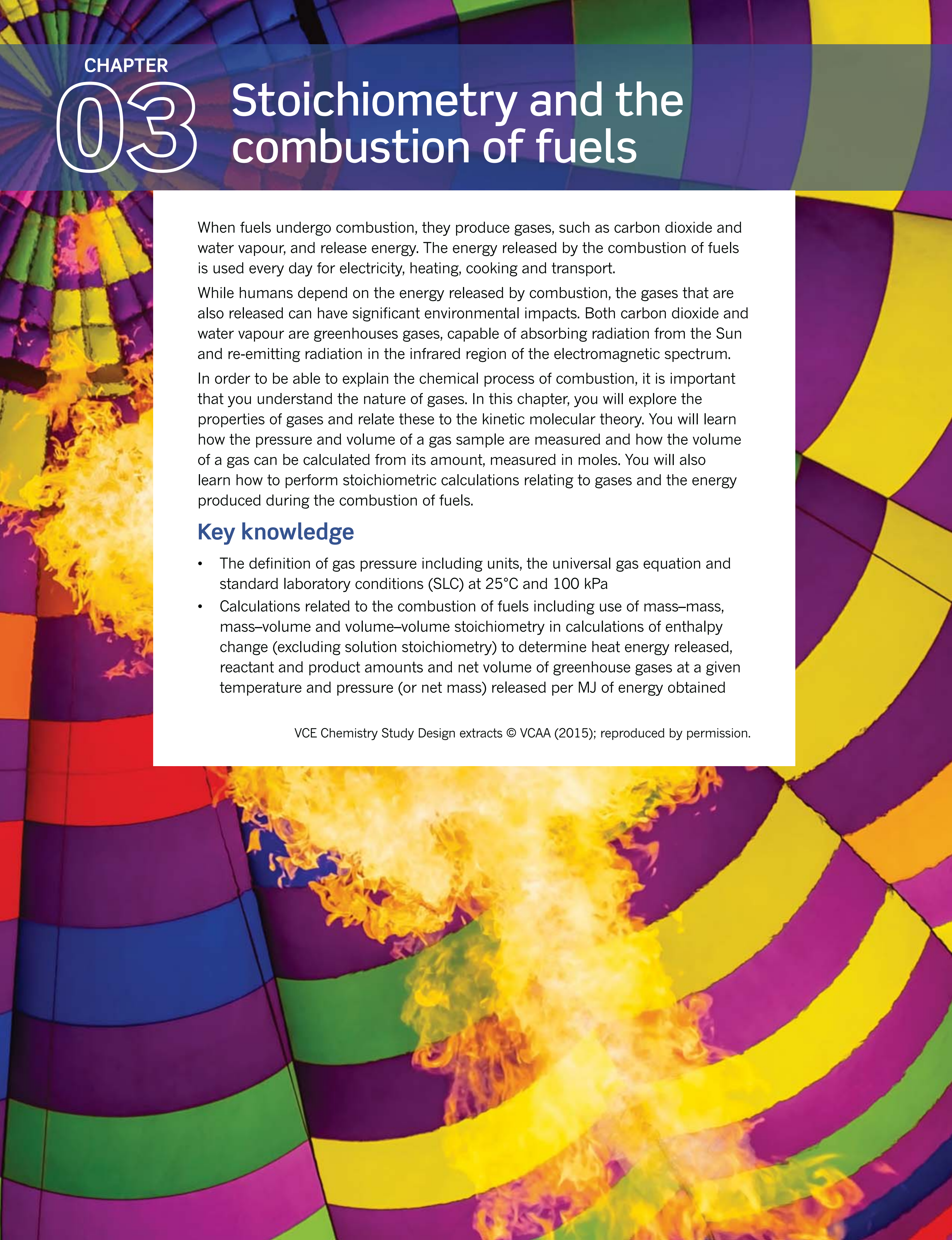
- **i** $2CO(g) + O_2(g) \rightarrow 2CO_2(g)$
- **ii** $2CO_2(g) \rightarrow 2CO(g) + O_2(g)$

18 A temperature rise of 5.52°C was observed when 0.0450 g of ethane (C_2H_6) was burnt and used to heat 100.0 mL of water. Use this information to write a balanced thermochemical equation for the complete combustion of ethane.

19 A 500 mL volume of water in a beaker was heated using the energy released by the combustion of a 3.00 g piece of wood. The observed temperature rise was 22.9°C.

a Calculate the heat of combustion of wood in kJ g^{-1} and in MJ/tonne.

b Would the heat of combustion you calculated in part **a** be higher or lower than the actual heat of combustion of the wood. Give reasons for your answer.



CHAPTER 03

Stoichiometry and the combustion of fuels

When fuels undergo combustion, they produce gases, such as carbon dioxide and water vapour, and release energy. The energy released by the combustion of fuels is used every day for electricity, heating, cooking and transport.

While humans depend on the energy released by combustion, the gases that are also released can have significant environmental impacts. Both carbon dioxide and water vapour are greenhouses gases, capable of absorbing radiation from the Sun and re-emitting radiation in the infrared region of the electromagnetic spectrum.

In order to be able to explain the chemical process of combustion, it is important that you understand the nature of gases. In this chapter, you will explore the properties of gases and relate these to the kinetic molecular theory. You will learn how the pressure and volume of a gas sample are measured and how the volume of a gas can be calculated from its amount, measured in moles. You will also learn how to perform stoichiometric calculations relating to gases and the energy produced during the combustion of fuels.

Key knowledge

- The definition of gas pressure including units, the universal gas equation and standard laboratory conditions (SLC) at 25°C and 100 kPa
- Calculations related to the combustion of fuels including use of mass–mass, mass–volume and volume–volume stoichiometry in calculations of enthalpy change (excluding solution stoichiometry) to determine heat energy released, reactant and product amounts and net volume of greenhouse gases at a given temperature and pressure (or net mass) released per MJ of energy obtained

3.1 Introducing gases

Whenever fuels undergo combustion, one or more gases are produced. Therefore, it is essential that you understand the nature of gases and their properties to gain a full appreciation of the process of combustion.

Every day you observe the behaviour of gases. Examples are shown in Figure 3.1.1. Such examples tell you a great deal about the physical properties of gases—those properties that can be observed and measured without changing the nature of the gas itself.

In this section, you will learn about the properties and behaviour of gases.

FIGURE 3.1.1 (a) Air is used to inflate vehicle tyres. Air is a mixture of gases and is easily compressed. When the car goes over a bump in the road, the air compresses slightly and absorbs the impact of the bump. (b) The gases that cause the smell of a freshly brewed cup of coffee rapidly fill an entire room. Gases mix readily and, unlike solids and liquids, occupy all available space. (c) This weather balloon is only partially inflated when released. Its volume increases because of pressure changes as it ascends into the atmosphere where it will collect data.

PROPERTIES OF GASES

Each of the examples shown in Figure 3.1.1 can be explained in terms of the properties of gases. Table 3.1.1 summarises some of the properties of gases and compares them with the properties of solids and liquids. These observations can be used to develop a particle model of gas behaviour.

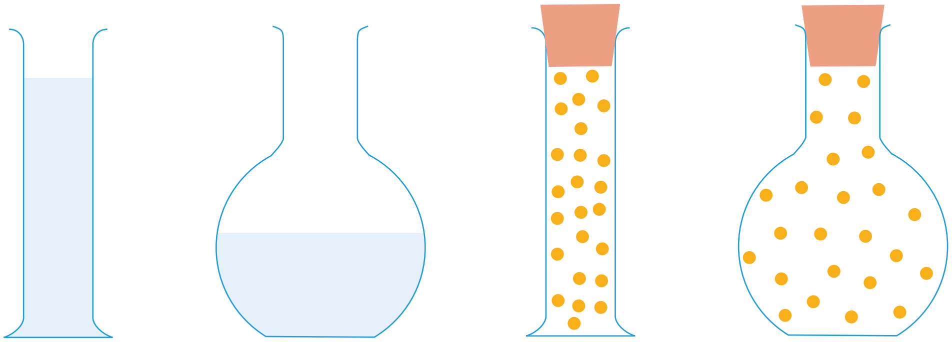
TABLE 3.1.1 Some properties of the three states of matter

	Gases	Liquids	Solids
Density	Low	High	High
Volume and shape	Fill the space available, because particles move independently of one another	Fixed volume, adopt shape of container, because particles are affected by attractive forces	Fixed volume and shape, because particles are affected by attractive forces
Compressibility	Compress easily	Almost incompressible	Almost incompressible
Ability to mix	Gases mix together rapidly	Liquids mix together slowly unless stirred	Solids do not mix unless finely divided

The low density of gases, relative to that of liquids and solids, suggests that the particles in a gas are much more widely spaced apart. The mass of any gas in a given **volume** is less than the mass of a liquid or solid in the same volume. The observation that gases are easily compressed can also be explained if gas particles are widely spaced.

The fact that gases spread to fill the space available, as shown in Figure 3.1.2, suggests that the particles of a gas move independently of each other.

The wide spacing and independent movement of particles explains why different gases mix rapidly.



Water takes the shape of a container, but its volume remains constant.

A gas takes up the shape and volume of a container.

FIGURE 3.1.2 Both liquids and gases take the shape of the container they are in. However, a liquid has a fixed volume, whereas the volume of a gas expands to fill all available space in a container.

KINETIC MOLECULAR THEORY

Scientists have developed a model to explain gas behaviour based on the behaviour of the particles of a gas. This model is known as the **kinetic molecular theory** of gases. According to this theory:

- gases are composed of small particles, either atoms or molecules
- the volume of the particles in a gas is very small compared with the volume they occupy. Consequently, most of the volume occupied by a gas is empty space
- gas particles move rapidly in random, straight-line motion
- particles collide with each other and with the walls of the container
- the forces between particles are extremely weak
- **kinetic energy** (KE) is the energy of motion. The kinetic energy of a particle is calculated from the formula:

  $$\text{KE} = \frac{1}{2}mv^2$$

  where KE is in joules, mass (m) is in grams, and **velocity** (v) is in metres per second.

  In a gas, when particles collide, the kinetic energy of the gas particles can be transferred from one particle to another, but the total kinetic energy remains constant. Therefore, collisions between gas particles are described as **elastic collisions**—kinetic energy is conserved.
- The average kinetic energy of the particles increases as the temperature of the gas increases.

THE NATURE OF PRESSURE AND VOLUME

When you blow up a balloon, the balloon expands because you put more air into it and the rubber of the balloon stretches. If you then plunge that balloon into liquid nitrogen, as shown in Figure 3.1.3, the balloon shrinks dramatically. The temperature of the gas decreases, causing the volume to decrease. Pumping more air into a tyre, as shown in Figure 3.1.4, increases the pressure inside the tyre. In section 3.2, you will examine the mathematical relationship between amount (number of moles), volume, pressure and temperature of a gas. This requires an understanding of the nature of volume and pressure.

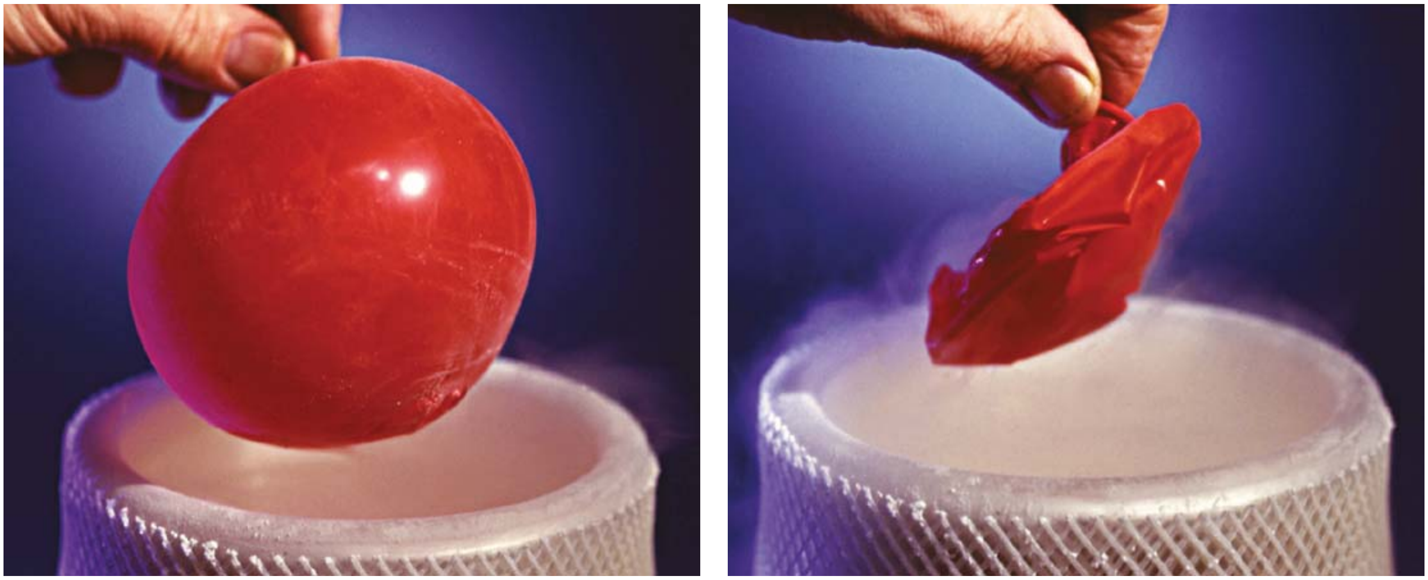


FIGURE 3.1.3 A balloon filled with air at room temperature is dipped into liquid nitrogen at –196°C. The volume of the air inside the balloon decreases dramatically.

FIGURE 3.1.4 Pumping more air into a tyre increases the pressure in the tyre because more particles are being pumped into a nearly fixed volume.

Volume

Volume is the quantity used to describe the space that a substance occupies. Because a gas occupies the whole container that it is in, the volume of a gas is equal to the volume of its container.

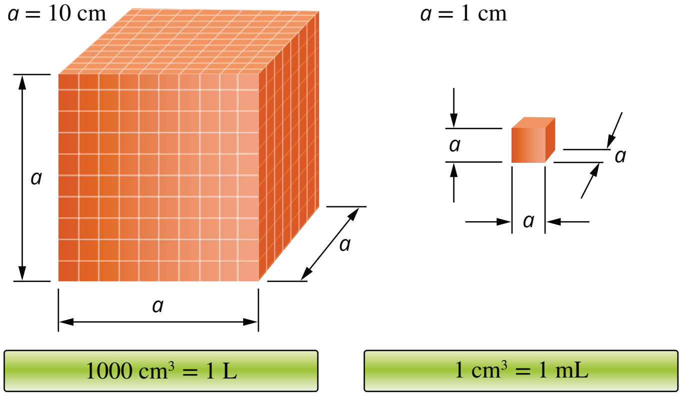


FIGURE 3.1.5 Cubic centimetres, millilitres and litres are the most commonly used units of volume.

There are several different units used for volume, some of which are represented in Figure 3.1.5. The common units are litre (L), millilitre (mL), cubic metre (m^3) and cubic centimetre (cm^3). Small volumes of gas are usually measured in millilitres (mL) or litres (L). Very large samples are measured in cubic metres (m^3).

- $1\ mL = 1\ cm \times 1\ cm \times 1\ cm = 1\ cm^3$
- $1\ L = 1 \times 10^3\ mL$ or $1000\ mL$
- $1\ m^3 = 1\ m \times 1\ m \times 1\ m = 100\ cm \times 100\ cm \times 100\ cm = 1 \times 10^6\ cm^3$
- $1\ m^3 = 1 \times 10^6\ cm^3 = 1 \times 10^6\ mL = 1000\ L$

Worked example 3.1.1

CONVERTING VOLUME UNITS

A gas has a volume of 255 mL.

What is its volume in:

a cubic centimetres (cm^3)?

b litres (L)?

c cubic metres (m^3)?

Thinking	Working
Recall the conversion factors for each of the units of volume. Apply the correct conversion to each situation.	**a** The units of mL and cm^3 are equivalent. $1\ mL = 1\ cm^3$ $255\ mL = 255\ cm^3$ **b** $1000\ mL = 1\ L$ Divide volume in mL by 1000 to convert to L. $255\ mL = \frac{255}{1000}$ $= 0.255\ L$ **c** $1 \times 10^6\ mL = 1\ m^3$ Divide volume in mL by 1×10^6 to convert to m^3. $255\ mL = \frac{255}{1 \times 10^6}$ $= 2.55 \times 10^{-4}\ m^3$

Worked example: Try yourself 3.1.1

CONVERTING VOLUME UNITS

A gas has a volume of 700 mL.

What is its volume in:

a cubic centimetres (cm^3)?

b litres (L)?

c cubic metres (m^3)?

Pressure

People often talk about exerting pressure on something as if it is some kind of force. In terms of the kinetic theory of gases, **pressure** is defined as the force exerted on a unit area of a surface by the particles of a gas as they collide with the surface.

The more a gas is compressed, the more frequently the gas particles collide with each other and the walls of their container. The increased frequency of collisions with the walls of the container increases the force on the walls of the container, such as the inside of a tyre. The force per unit area is described as pressure.

Air is a mixture of gases including nitrogen, oxygen, carbon dioxide and argon. In air, the nitrogen molecules collide with the walls of a container, exerting a pressure. In a similar way, the oxygen molecules exert a pressure, as do molecules of each gas present in the mixture. In the gaseous mixture of nitrogen and oxygen shown in Figure 3.1.6, the measured pressure is the sum of the **partial pressure** of oxygen and the partial pressure of nitrogen.

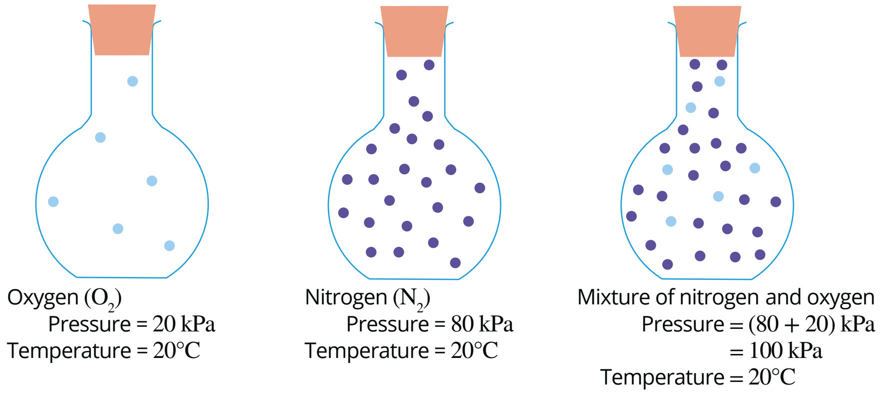


FIGURE 3.1.6 The total pressure of a mixture of gases is the sum of the partial pressures (individual pressures) of each of the gases in the mixture.

Units of pressure

Because pressure is the force exerted on a unit area of a surface, the relationship can be written as:

$$\text{Pressure} = \frac{\text{force}}{\text{area}}$$

$$P = \frac{F}{A}$$

The units of pressure depend on the units used to measure force and area. Over the years, scientists in different countries have used different units to measure force and area, so there are a number of different units of pressure.

The SI unit for force is the newton (N) and the SI unit for area is the square metre (m^2). Therefore, the SI units of pressure are newtons per square metre ($N\ m^{-2}$). One newton per square metre is equivalent to a pressure of one **pascal** (Pa).

In 1982, the International Union of Pure and Applied Chemistry (IUPAC), the organisation responsible for naming chemicals and setting standards, adopted a standard for pressure equivalent to 100 000 Pa or 100 kPa. This gave rise to a new pressure unit, the **bar**, where 1 bar equals 100 kPa.

The use of mercury barometers resulted in pressure often being measured in millimetres of mercury, or mmHg.

Another unit for pressure is the **standard atmosphere** (atm). One standard atmosphere (1 atm) is the pressure required to support 760 millimetres of mercury (760 mmHg) in a mercury barometer at 25°C. This is the average atmospheric pressure at sea level. One atmosphere equals 101.3 kPa.

Summary of pressure units

There are four common units of gas pressure: pascal, bar, millimetres of mercury and atmosphere (Table 3.1.2).

TABLE 3.1.2 Common units of gas pressure

Name of unit	Symbol for unit	Conversion to $N\ m^{-2}$
newtons per square metre	$N\ m^{-2}$	
pascal	Pa	$1\ Pa = 1\ N\ m^{-2}$
kilopascal	kPa	$1\ kPa = 1 \times 10^3\ Pa = 1 \times 10^3\ N\ m^{-2}$
atmosphere	atm	$1\ atm = 101.3\ kPa = 1.013 \times 10^5\ N\ m^{-2}$
bar	bar	$1\ bar = 100\ kPa = 1.00 \times 10^5\ N\ m^{-2}$
millimetres of mercury	mmHg	$760\ mmHg = 1\ atm = 1.013 \times 10^5\ N\ m^{-2}$

$1\ bar = 100\ kPa = 1.00 \times 10^5\ N\ m^{-2}$

$1\ atm = 101.3\ kPa = 1.013 \times 10^5\ N\ m^{-2}$

These relationships can be used to convert pressure from one unit to another.

CHEMFILE

Torricelli's barometer

In the 17th century, the Italian physicist Evangelista Torricelli invented the earliest barometer, an instrument used to measure atmospheric pressure. It was a straight glass tube, closed at one end, containing mercury. The tube was inverted so that the open end was below the surface of mercury in a bowl as seen in Figure 3.1.7.

The column of mercury in Torricelli's barometer was supported by the pressure of the gas particles in the atmosphere colliding with the surface of the mercury in the open bowl.

At sea level, the top of the column of mercury was about 760 mm above the surface of the mercury in the bowl. Torricelli found that the height of the mercury column decreased when he took his barometer to higher altitudes in the mountains.

At higher altitudes, there are fewer air particles and therefore less frequent collisions on the surface area of mercury. The reduced pressure supports a shorter column of mercury.

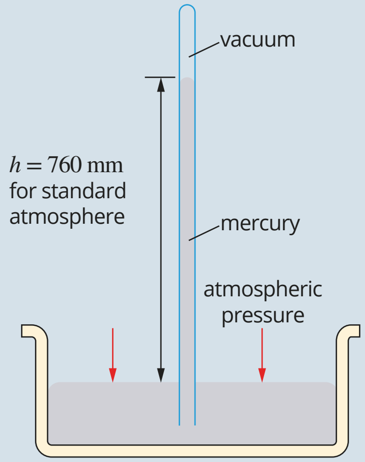


FIGURE 3.1.7 A simple Torricelli barometer.

Worked example 3.1.2

CONVERTING PRESSURE UNITS

Mount Everest is the highest mountain on Earth.

- **a** The atmospheric pressure at the top of Mount Everest is 0.337 bar. What is the pressure in kilopascals (kPa)?
- **b** The atmospheric pressure at the top of Mount Everest is 253 mmHg. What is the pressure in atmospheres (atm)?
- **c** The atmospheric pressure at the top of Mount Everest is 0.333 atm. What is the pressure in kilopascals (kPa)?
- **d** The atmospheric pressure at the top of Mount Everest is 253 mmHg. What is the pressure in bars?

Thinking	Working
a To convert bars to kilopascals, use the conversion relationship: 1 bar = 100 kPa To change bar to kPa, multiply the value by 100.	0.337 bar = 0.337×100 = 33.7 kPa
b To convert millimetres of mercury to atmospheres, use the relationship: 1 atm = 760 mmHg To change mmHg to atm, divide the value by 760.	253 mmHg = $\frac{253}{760}$ = 0.333 atm
c To convert atmospheres to kilopascals, use the conversion relationship: 1 atm = 101.3 kPa To change atm to kPa, multiply the value by 101.3.	0.333 atm = 0.333×101.3 = 33.7 kPa
d This can be done in two steps. First, convert millimetres of mercury to atmospheres. Use the conversion relationship: 760 mmHg = 1 atm To change mmHg to atm, divide the value by 760. Keep the answer in your calculator and proceed to the next step. Next, convert atmospheres to bar. Use the conversion relationship: 1 atm = 1.013 bar To change atm to bar, multiply the quotient from the previous step by 1.013.	253 mmHg = $\frac{253}{760}$ 253 mmHg = $\frac{253}{760} \times 1.013$ = 0.337 bar

Worked example: Try yourself 3.1.2

CONVERTING PRESSURE UNITS

Cyclone Yasi was one of the biggest cyclones in Australian history.

- **a** The atmospheric pressure in the eye of Cyclone Yasi was measured as 0.902 bar. What was the pressure in kilopascals (kPa)?
- **b** What was the pressure in the eye of Cyclone Yasi in atmospheres (atm) if it is known to be 677 mmHg?
- **c** If the atmospheric pressure in the eye of Cyclone Yasi was 0.891 atm, what was the pressure in kilopascals (kPa)?
- **d** The atmospheric pressure in the eye of Cyclone Yasi was 677 mmHg. What was the pressure in bars?

3.1 Review

SUMMARY

- One or more gases are produced whenever a fuel undergoes combustion.
- Gas properties can be explained by the kinetic molecular theory.
- According to the kinetic molecular theory:
  - the volume of the particles in a gas is very small compared with the distance between the particles
  - the average kinetic energy of the particles in a gas is proportional to its temperature
  - gas particles are in rapid random motion, colliding with each other and the container wall
  - the forces between particles in a sample of gas are negligible.
- To convert between different volume units, use these relationships:

  $1 \text{ L} = 1000 \text{ mL} = 1000 \text{ cm}^3$

  $1 \text{ m}^3 = 1 \times 10^6 \text{ cm}^3 = 1 \times 10^6 \text{ mL} = 1000 \text{ L}$
- Pressure is defined as the force per unit area.
- The pressure exerted by a gas depends on the collisions of gas particles against the wall of the container.
- To convert between different pressure units, use these relationships:

  $1 \text{ bar} = 100 \text{ kPa} = 1.00 \times 10^5 \text{ Pa}$

  $1 \text{ atm} = 760 \text{ mmHg} = 1.013 \times 10^5 \text{ Pa}$
  $= 101.3 \text{ kPa} = 1.013 \text{ bar}$

KEY QUESTIONS

1 Use the kinetic molecular theory to explain the following observed properties of gases.

a Gases occupy all the available space in a container.

b Gases can be easily compressed compared with their corresponding liquid forms.

c A given volume of a gaseous substance weighs less than the same volume of the substance in the liquid state.

d Gases readily mix together.

e The total pressure of a mixture of gases is equal to the sum of the pressures exerted by each of the gases in the mixture.

2 Use the ideas of the kinetic molecular theory of gases to explain the following observations.

a Tyre manufacturers recommend a maximum pressure for tyres.

b The pressure in a car's tyres will increase if a long distance is travelled on a hot day.

c You can smell dinner cooking as you enter your house.

d A balloon will burst if you blow it up too much.

3 In the kinetic molecular theory, pressure is described as the force per unit area of surface. Explain what happens to the pressure in each of the following situations.

a The temperature of a filled aerosol can is increased.

b A gas in a syringe is compressed.

4 Convert each of the following pressures to the units specified.

a 140 kPa to Pa

b 92 000 Pa to kPa

c 4.24 atm to mmHg and Pa

d 120 kPa to mmHg, atm and bar

e 1400 mmHg to atm, Pa and bar

f 80 000 Pa to atm, mmHg and bar

5 Convert the following volumes to the unit specified.

a 2 L to mL

b 4.5 L to m^3

c 2250 mL to L

d 120 mL to L

e 5.6 mL to L

f 3.7 m^3 to L

g 285 mL to m^3

h 4.70×10^{-3} m^3 to L and cm^3

3.2 Universal gas equation

Combustion reactions produce gases. Because the gaseous products may be harmful to people or to the environment, it is very useful for scientists to be able to quantify the amount of gas produced by different fuels.

The behaviour of gases has been described qualitatively in section 3.1. In this section, you will learn about the mathematical relationships that link volume, pressure, temperature and the number of particles of a gas, and in particular how to use these relationships to calculate the volumes of gases.

These mathematical relationships were developed over a period of several hundred years by different scientists who performed experiments on gases. Robert Boyle, pictured in Figure 3.2.1, experimentally determined the relationship between the pressure and volume of a gas. Figure 3.2.2 shows Jacques Charles, who identified the relationship between the volume and temperature of a gas. In 1787, Charles determined that the volume of a fixed amount of gas is directly proportional to the absolute temperature, provided the pressure remains constant. The relationship between gas volume and temperature is known as Charles' law.

FIGURE 3.2.1 Robert Boyle (1627–91). In 1662, Boyle showed by experiment that for a given amount of gas at constant temperature, the volume of a gas is inversely proportional to its pressure. The relationship between gas volume and pressure is known as Boyle's law.

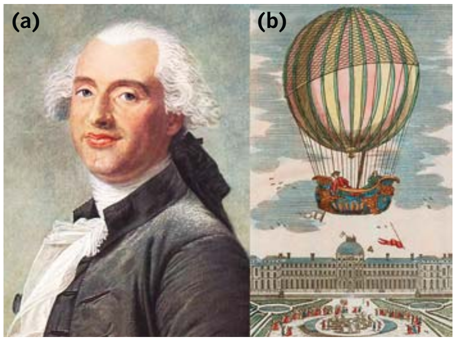


FIGURE 3.2.2 (a) Jacques Charles (1746–1823) was a French chemist, physicist and aeronaut. (b) Charles was famous for making the first flight in a hydrogen balloon on 1 December 1783.

These relationships have become known as the gas laws. The gas laws are used to describe the behaviour of all gases, regardless of their chemical composition.

VOLUME AND PRESSURE

Changing the volume of a fixed amount of gas at constant temperature causes a change in the pressure of the gas. The pressure of the gas in the syringe shown in Figure 3.2.3 increases as the plunger is pushed in and decreases as the plunger is pulled out.

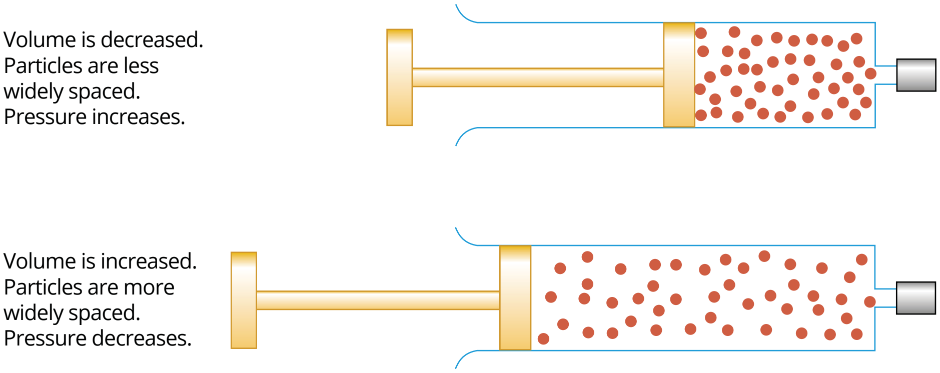


FIGURE 3.2.3 The pressure of the gas in the syringe is affected by a change in volume.

For a given amount of gas at constant temperature, the volume of the gas is inversely proportional to its pressure. This relationship is seen in the changing volume of a weather balloon as it rises to altitudes with much lower pressure than at ground level. A weather balloon filled with helium gas to a volume of 40 L at a pressure of 1 atm increases in volume to 200 L by the time it reaches an altitude with a pressure of 0.2 atm.

The mathematical relationship between the pressure, P, exerted by a gas and the volume, V, it occupies can be written as:

$$P \propto \frac{1}{V}$$

This relationship can also be expressed as $PV = k$, where k is a constant at a given temperature.

VOLUME AND TEMPERATURE

The kinetic molecular theory states that increasing the temperature of a gas increases the average kinetic energy of the molecules. The molecules move more rapidly and collide with the walls of the container more frequently and with greater force. This can cause the:

- volume of gas to increase, if the pressure on the gas remains the same, such as a gas in a syringe or balloon
- pressure to increase, if the volume of the gas container is fixed, such as in a sealed flask or a gas cylinder.

Table 3.2.1 shows the results of an experiment that investigates the relationship between temperature and the volume of a given amount of gas. In this experiment, the gas in a syringe is heated slowly in an oven. The pressure on the plunger of the syringe is held constant.

TABLE 3.2.1 Variation of volume with temperature

Temperature (°C)	20	40	60	80	100	120	140
Volume (mL)	60.0	64.1	68.2	72.3	76.4	80.5	84.6

The graph of these results is linear, as shown in Figure 3.2.4. When the graph is extrapolated to a volume of 0 L, it crosses the temperature axis at –273°C. If the origin is reset at –273°C, this graph passes through the origin. This has led scientists to develop a new temperature scale, known as the **kelvin scale** or **absolute temperature scale**. On the kelvin scale, each temperature increment is equal to one temperature increment on the Celsius scale, and 0°C is equal to 273 K.

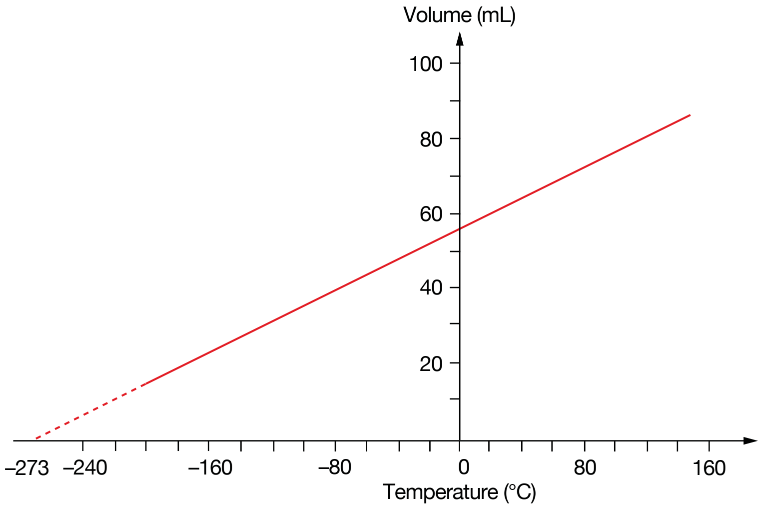


FIGURE 3.2.4 The variation of volume with temperature for fixed amount of gas at constant pressure.

The relationship between temperature on the Celsius scale and temperature on the kelvin scale is given by the equation:

$$T \text{ (in K)} = T \text{ (in °C)} + 273$$

The temperature 0 K (–273°C) is the lowest temperature theoretically possible. For this reason, 0 K is known as **absolute zero**. At this temperature, all molecules and atoms have minimum kinetic energy. Therefore, a temperature in degrees Celsius is converted to absolute temperature in kelvin by adding 273. For example, the boiling point of water at sea level is converted to absolute temperature by adding 273, so 100°C is equivalent to 373 K (Figure 3.2.5).

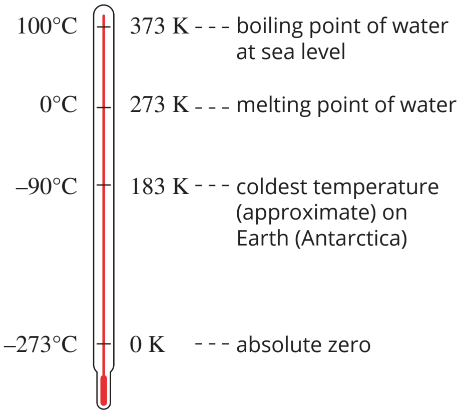


FIGURE 3.2.5 The Celsius and kelvin temperature scales.

To convert degrees Celsius to kelvin:

$$T \text{ (in K)} = T \text{ (in °C)} + 273$$

Extremely low temperatures, within 1×10^{-10} K of absolute zero, have been reached in the laboratory. Note that the kelvin scale has no degrees sign—it is written as just K.

CHEMFILE

FIGURE 3.2.6 Lord Kelvin (1824–1907) proposed the absolute temperature scale.

William Thomson

The kelvin scale is named after Irish mathematical physicist and engineer William Thomson (1824–1907), also known as Lord Kelvin (shown in Figure 3.2.6).

Born in Belfast, Thomson attended Glasgow University from the age of ten and Cambridge University from 1841 to 1845. In 1846, he returned to Glasgow to become Professor of Natural Philosophy, remaining in this position for 53 years. He is most famous for formulating the second law of thermodynamics, working to install telegraph cables under the Atlantic Ocean and proposing the absolute temperature scale. He correctly determined the value of absolute zero to be –273°C.

A marine engineering enthusiast, Thomson invented several marine instruments to improve navigation and safety, including a mariner's compass and a deep-sea sounding apparatus. In 1892, Thomson became the first scientist to join the House of Lords in England. By the time of his death in 1907, he was an international celebrity, having been the head of an international commission deciding upon the design of the Niagara Falls power station and lecturing at John Hopkins University in Baltimore, USA. On his death, he was buried beside Sir Isaac Newton in Westminster Abbey.

The ascending hot-air balloon in Figure 3.2.7 demonstrates the relationship between volume and temperature. Heating the air causes the balloon to expand, which reduces the density of the air inside, and allows the balloon to rise.

ℹ As the temperature, T, of a gas increases, the volume, V, of the gas increases. Therefore, V and T are directly proportional:

$$V \propto T$$

This relationship can also be expressed as $\frac{V}{T} = k$, where k is a constant at a given pressure. Note that the value of T must be expressed in kelvin, not degrees Celsius.

FIGURE 3.2.7 Hot-air balloonists take advantage of the relationship between the volume of a gas and temperature.

Worked example 3.2.1

CONVERTING TEMPERATURES FROM CELSIUS TO KELVIN

What is 300°C on the kelvin temperature scale?

Thinking	Working
T (in K) = T (in °C) + 273	T (in K) = T (in °C) + 273 = 300 + 273 = 573 K

Worked example: Try yourself 3.2.1

CONVERTING TEMPERATURES FROM CELSIUS TO KELVIN

What is 100°C on the kelvin temperature scale?

VOLUME AND AMOUNT OF GAS

The volume, V, occupied by a gas also depends directly on the amount of gas, n, in moles.

This relationship is shown in Figure 3.2.8. Both syringes show a gas at a constant temperature and pressure. The volume doubles with twice the number of molecules of gas in the syringe.

The mathematical relationship between the volume, V, occupied by a gas and the amount of gas, n, at constant temperature and pressure can be written as:

$$V \propto n$$

This relationship can also be expressed as $\frac{V}{n} = k$, where k is a constant at a given temperature and pressure.

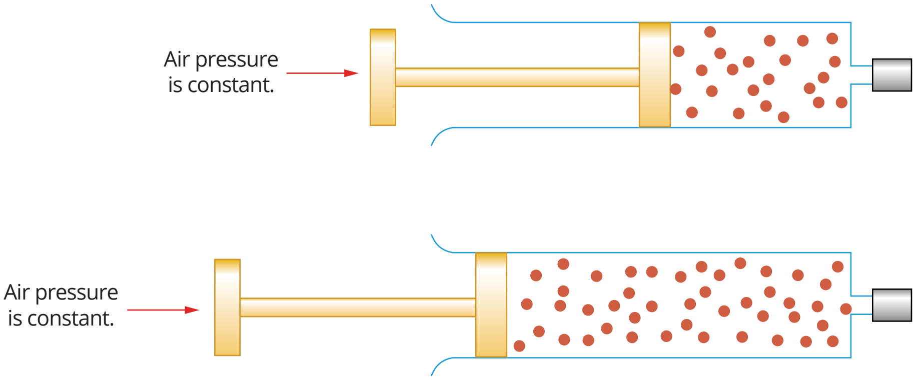
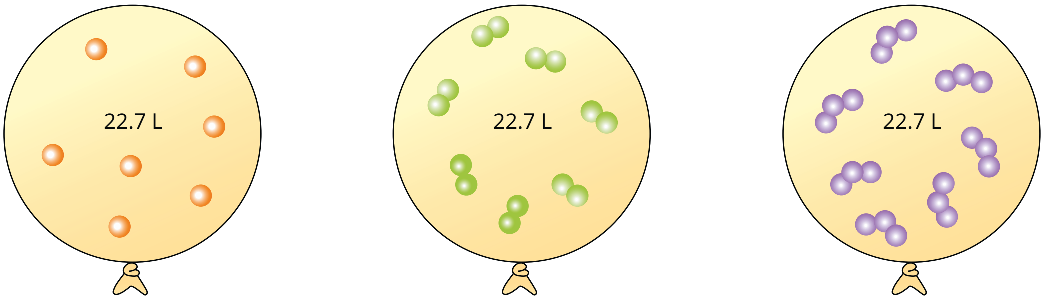


FIGURE 3.2.8 When the amount of gas in the syringe is doubled, the volume doubles, provided the pressure on the plunger and the temperature of the gas remain constant.

MOLAR VOLUME OF A GAS

If the amount of gas is fixed at 1 mole as shown in Figure 3.2.9, the volume it occupies depends almost entirely on its temperature and pressure. We define this volume as the **molar volume**, V_m, of a gas. Molar volume is the amount of space, or volume, occupied by 1 mole of any gas at a particular pressure and temperature.



1 mole of neon, Ne
P = 100 kPa
T = 0°C
V = 22.7 L
number of molecules = 6.02×10^{23}
mass = 20.2 g

1 mole of nitrogen, N_2
P = 100 kPa
T = 0°C
V = 22.7 L
number of molecules = 6.02×10^{23}
mass = 28.0 g

1 mole of ozone, O_3
P = 100 kPa
T = 0°C
V = 22.7 L
number of molecules = 6.02×10^{23}
mass = 48.0 g

FIGURE 3.2.9 One mole of any gas occupies the same volume given the same temperature and pressure. In this example, 1 mole of each gas occupies 22.7 L at 100 kPa and 0°C (273 K).

The volume of 1 mole of gas, V_m, is equal to its total volume, V, divided by the number of moles, n, of gas present. This can be represented by the relationship:

$$V_m = \frac{V}{n} \text{ (at a given temperature and pressure)}$$

Or, by rearranging this expression:

ℹ $n = \frac{V}{V_m}$ (at a given temperature and pressure)

The molar volume of a gas varies with temperature and pressure. However, molar volume does not vary with the identity of the gas. For example, 1 mole of hydrogen gas occupies the same volume as 1 mole of oxygen gas at the same temperature and pressure.

Standard conditions

A temperature of 25°C (298 K) and a pressure of 100 kPa is typical of the conditions you will encounter when you are working in a laboratory. These conditions are known as **standard laboratory conditions (SLC)**.

Table 3.2.2 shows the molar volume of an **ideal gas** and of helium at SLC. An ideal gas is a theoretical gas composed of particles that do not interact except during elastic collisions. At SLC, most gases behave very like an ideal gas and, therefore, have a molar volume very close to that of an ideal gas.

TABLE 3.2.2 Molar volume at SLC

Gas	Formula	Molar volume at SLC (L mol^{-1})
Ideal gas	–	24.79
Helium	He	24.83

It is usual to assume that the molar volume of a gas is 24.8 L mol^{-1} at SLC. From this value, you can calculate the amount, in moles, of a gas given its volume at SLC.

Another set of commonly used standard conditions is **standard temperature and pressure (STP)**. STP refers to a temperature of 0°C (273 K) and a pressure of 100 kPa. The molar volume of an ideal gas at STP is 22.7 L mol^{-1}.

ℹ V_m = 24.8 L mol^{-1} at SLC (25°C or 298 K and 100 kPa)
V_m = 22.7 L mol^{-1} at STP (0°C or 273 K and 100 kPa)

In section 3.4, you will see that when comparing the combustion of different fuels, the concept of molar volume is often used to determine the volume of oxygen gas required and the volume of gases produced.

Worked example 3.2.2

CALCULATING THE VOLUME OF A GAS FROM ITS AMOUNT (IN MOL)

Calculate the volume, in L, occupied by 0.24 mol of nitrogen gas at SLC. Assume that nitrogen behaves like an ideal gas.

Thinking	Working
Rearrange $n = \frac{V}{V_m}$ to make volume the subject.	$n = \frac{V}{V_m}$ $V = n \times V_m$
Substitute in the known values where V_m = 24.8 L mol^{-1} (at SLC) and solve.	$V = n \times V_m$ $= 0.24 \times 24.8$ $= 5.952$ L
Consider the units and significant figures. The answer should be given to the smallest number of significant figures in the measurement.	$V = 6.0$ L

Worked example: Try yourself 3.2.2

CALCULATING THE VOLUME OF A GAS FROM ITS AMOUNT (IN MOL)

Calculate the volume, in L, occupied by 3.5 mol of oxygen gas at SLC. Assume that oxygen behaves like an ideal gas.

THE UNIVERSAL GAS EQUATION

The following three laws describe the behaviour of gases under different conditions:

- $V \propto \frac{1}{P}$ (for constant T and n)
- $V \propto T$ (for constant P and n)
- $V \propto n$ (for constant P and T)

We can combine all three laws by writing:

$$V \propto \frac{nT}{P}$$

This relationship can be expressed as $V = \frac{RnT}{P}$, where R is a proportionality constant.

The equation is known as the **universal gas equation** and is more usually written in the form:

$$PV = nRT$$

where R is called the universal gas constant, or simply, the **gas constant**.

This constant can be determined experimentally by measuring the volume occupied by a known amount of gas at a known temperature and pressure.

The value of R depends on the units of pressure and volume used. It has a value of 8.31 J K^{-1} mol^{-1} when:

- P is measured in kilopascals, kPa
- V is measured in litres, L
- n is measured in moles, mol
- T is measured on the kelvin scale, K.

You will use the universal gas equation in section 3.4 to calculate the volume of oxygen gas consumed and the volume of gases produced during the combustion of different fuels.

Worked example 3.2.3

CALCULATING THE VOLUME OF A GAS USING THE UNIVERSAL GAS EQUATION

Calculate the volume, in L, occupied by 2.24 mol of oxygen gas (O_2) if the pressure is 200 kPa at 50°C.

Thinking	**Working**
Convert units, if necessary. Pressure is in kPa and temperature in K.	P = 200 kPa (no conversion required) $T = 50 + 273$ $= 323$ K
Rearrange the universal gas equation so that volume, V, is the subject.	$PV = nRT$ $V = \frac{nRT}{P}$
Substitute values for pressure, amount, temperature and the gas constant, R, then solve for V. Express the answer to the correct number of significant figures.	$V = \frac{2.24 \times 8.31 \times 323}{200}$ $= 30.1$ L

Worked example: Try yourself 3.2.3

CALCULATING THE VOLUME OF A GAS USING THE UNIVERSAL GAS EQUATION

Calculate the volume, in L, occupied by 13.0 mol of carbon dioxide gas (CO_2) if the pressure is 250 kPa at 75.0°C.

CHEMISTRY IN ACTION

Decompression chambers

Scuba diving and water pressure

If you swim at the water's surface, your body experiences a pressure, due to the surrounding air, of about 1 atm. Below the surface, your body experiences an additional pressure due to the water. This additional pressure amounts to about 1 atm for every 10 m of depth. Therefore, at 20 m the pressure on your body is about 3 atm.

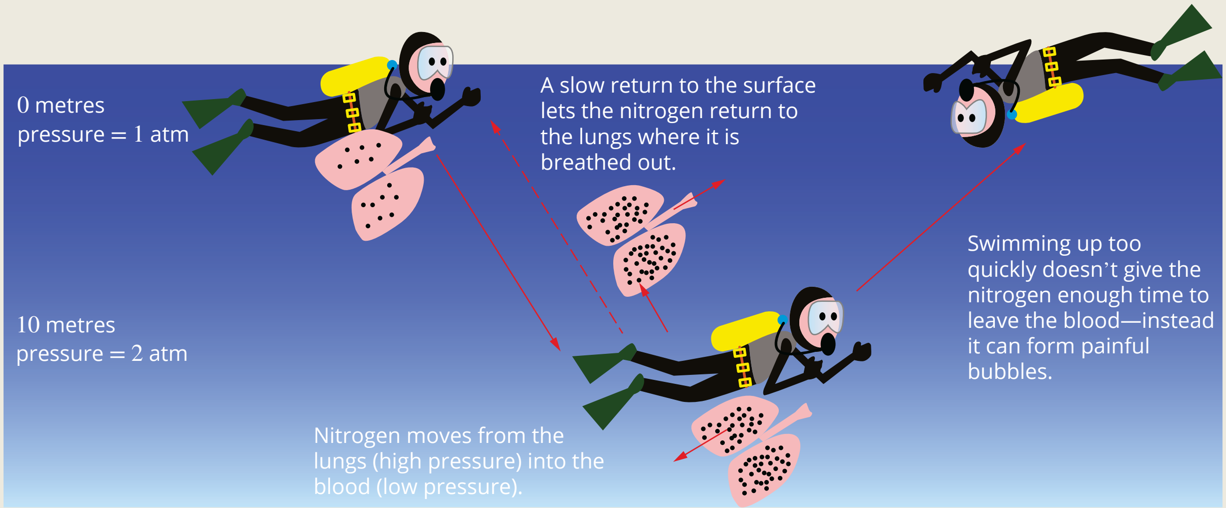
As the pressure on your body increases, the volume of your body cavities such as your lungs and inner ears decreases. This squeezing effect makes diving well below the water's surface without scuba equipment very uncomfortable. Scuba equipment overcomes this problem by supplying air from tanks to the mouth at the same pressure as that produced by the underwater environment.

Scuba diving and gas solubility

As the pressure in a diver's lungs increases during a dive, more gas dissolves in the blood. Nitrogen (N_2) is one of these gases. When a diver ascends, the pressure drops, the nitrogen becomes less soluble in the blood and so comes out of solution. If a diver ascends too quickly, the rapid pressure drop causes the nitrogen to come out of the blood as tiny bubbles (see Figure 3.2.10a). This is similar to the bubbles of carbon dioxide you observe when you open a bottle of soft drink.

These bubbles cause pain in joints and muscles. If they form in the spinal cord, brain or lungs, they can cause paralysis or death. Treatment for divers suffering from this effect (the bends) involves time in a decompression chamber similar to the one shown in Figure 3.2.10b.

(a)



(b)

FIGURE 3.2.10 (a) Scuba diving and the bends. (b) A decompression chamber used to treat divers with the bends.

The chamber increases the pressure surrounding the diver's body, forcing any nitrogen bubbles to dissolve in the blood, and then slowly reduces the pressure back to 1 atm. The duration of treatment depends on the severity of the symptoms, the dive history and the patient's response to treatment.

Hyperbaric oxygen therapy (HBOT) is a medical treatment in which patients breathe pure oxygen while inside a decompression chamber at a pressure higher than 1 atm. Its medical uses include improved wound healing by reduction of swelling, infection control and the stimulation of new blood vessel growth. The hyperbaric unit at the Alfred Hospital in Melbourne is equipped with three pressurisable hyperbaric rooms used for treating the bends, ulcers, soft tissue infections, carbon monoxide poisoning and wounds that won't heal such as those resulting from diabetes or radiotherapy.

HBOT is also used by athletes for faster recovery from soft tissue injuries, to produce sharper performance and to maintain more intense training schedules. Tennis star Novak Djokovic uses a hyperbaric chamber to assist with recovery from long, exhausting matches. AFL clubs are interested in the use of hyperbaric oxygen therapy for treating soft tissue injuries. One of the earliest cases of hyperbaric oxygen treatment in football was for an ankle injury sustained by Carlton midfielder Fraser Brown in the 1995 preliminary final against North Melbourne. Every morning, in the week leading up to the Grand Final, he spent an hour in a chamber in the hyperbaric unit at the Alfred Hospital. Eventually selected to play in the Grand Final, Brown made it through the game with the help of strapping and pain-killing injections, helping Carlton win the premiership.

3.2 Review

SUMMARY

- The following three laws describe the behaviour of gases under different conditions:
  - $V \propto \frac{1}{P}$ (for constant T and n)
  - $V \propto T$ (for constant P and n)
  - $V \propto n$ (for constant P and T)
- Absolute zero is a temperature of –273°C or 0 K. Molecules and atoms have minimum kinetic energy at this temperature.
- Standard laboratory conditions (SLC) refers to a temperature of 25°C (298 K) and a pressure of 100 kPa.
- Standard temperature and pressure (STP) refers to a temperature of 0°C (273 K) and a pressure of 100 kPa.
- The molar volume, V_m, of a gas is the volume occupied by 1 mol of gas at a given temperature and pressure:

$$n = \frac{V}{V_m}$$

- The value of V_m is 24.8 L mol^{-1} at SLC.
- The value of V_m is 22.7 L mol^{-1} at STP.
- $PV = nRT$ is the universal gas equation. It can be used to calculate one variable (P, V, n or T) when the other three variables are known.
- R is the universal gas constant and its value is 8.31 J K^{-1} mol^{-1} when pressure is in kPa, volume is in L, amount is in mol and temperature is in K.

KEY QUESTIONS

1 Convert the following Celsius temperatures to absolute temperatures.
   a 100°C
   b 175°C
   c −145°C

2 Calculate the volume of the following gases at SLC.
   a 1.4 mol of chlorine (Cl_2)
   b 1.0×10^{-3} mol of hydrogen (H_2)
   c 1.4 g of nitrogen (N_2)

3 Calculate the mass of the following gas samples. All volumes are measured at SLC.
   a 2.80 L of neon (Ne)
   b 50.0 L of oxygen (O_2)
   c 140 mL of carbon dioxide (CO_2)

4 0.25 mol of nitrogen is placed in a flask of volume 5.0 L at a temperature of 5°C. What is the pressure in the flask?

5 What volume of gas, in litres, is occupied by:
   a 0.20 mol of hydrogen at 115 kPa and 40°C?
   b 12.5 mol of carbon dioxide at 5 atm and 150°C?
   c 8.50 g of hydrogen sulfide (H_2S) at 100 kPa and 27°C?

6 Calculate the mass of helium in a balloon if the volume is 100 L at a pressure of 95 000 Pa and a temperature of 0°C.

7 At a given temperature, a sample of nitrogen, of mass 11.3 g, exerts a pressure of 102 kPa in a gas cylinder of volume 10.0 L. Calculate the temperature of the gas.

8 Which sample of gas contains the greater amount, in mol, of gas: 3.2 L of nitrogen at 25°C and a pressure of 1.2 bar or 2.5 L of helium at 23°C and a pressure of 1.2 atm?

3.3 Calculations involving combustion of fuels—Part 1

Measuring and predicting quantities is a very important part of chemistry. Scientists compare fuels by calculating the quantities of chemicals involved in reactions. The ethanol produced in the plant shown in Figure 3.3.1 can be compared to petroleum by calculating how much oxygen is required for complete combustion. How much atmospheric pollution a fuel will produce can be determined by calculating the mass of carbon emissions.

In this section you will learn about these types of calculations.

FIGURE 3.3.1 A corn ethanol processing plant. Ethanol is a biochemical fuel that is used as an alternative to petroleum. The concepts taught in this section allow you to calculate the mass of oxygen required to combust a given mass of ethanol or the mass of carbon dioxide (a greenhouse gas) produced.

STOICHIOMETRY AND REACTIONS OF FUELS

Calculations that involve the use of the mole concept, combined with an understanding of chemical equations, are called stoichiometric calculations. In this section and section 3.4, you will use these calculations for reactions involving fuels, but stoichiometry is important in all areas of chemistry.

Stoichiometry is the study of ratios of moles of substances. Stoichiometric calculations are based on the law of conservation of mass.

ℹ In a chemical reaction, the total mass of all products is equal to the total mass of all reactants.

Another way of expressing this is that, in a chemical reaction, atoms are neither created nor destroyed. Consequently, given the amount of one substance involved in a chemical reaction and a balanced equation for the reaction, you can calculate the amounts of all other substances involved.

Equations and reacting amounts

Consider the equation for the reaction that occurs when methane (CH_4) burns in oxygen:

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$$

The coefficients used to balance the equations show the ratios between the reactants and products involved in the reaction. The equation indicates that 1 mole of $CH_4(g)$ reacts with 2 moles of $O_2(g)$ to form 1 mole of $CO_2(g)$ and 2 moles of $H_2O(g)$. In more general terms, the amount of oxygen used will always be double the amount of methane used, double the amount of carbon dioxide produced and the same as the amount of water vapour produced.

$$\frac{n(O_2)}{n(CH_4)} = \frac{2}{1}, \frac{n(CO_2)}{n(O_2)} = \frac{1}{2} \text{ and } \frac{n(H_2O)}{n(O_2)} = \frac{2}{2} = 1$$

In general, for stoichiometric calculations you will be told, or you will be able to work out, the number of moles of one chemical in the reaction (the 'known'). You will then need to calculate the number of moles of another chemical (the 'unknown').

You can write the relationship between the known and unknown chemicals using ratios:

ℹ $$\frac{n(\text{unknown chemical})}{n(\text{known chemical})} = \frac{\text{coefficient of unknown chemical}}{\text{coefficient of known chemical}}$$

Worked example 3.3.1

USING MOLE RATIOS

How many moles of carbon dioxide are generated when 24 moles of propane (C_3H_8) are burned completely in oxygen?

Thinking	**Working**
Write a balanced equation for the reaction.	$C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(g)$
Note the number of moles of the known substance.	$n(C_3H_8) = 24$ mol
Write a mole ratio for: $\frac{\text{coefficient of unknown}}{\text{coefficient of known}}$	$\frac{n(CO_2)}{n(C_3H_8)} = \frac{3}{1}$
Calculate the number of moles of the unknown substance using: $n(\text{unknown}) = \text{mole ratio} \times n(\text{known})$	$n(CO_2) = \frac{3}{1} \times 24$ $= 72$ mol

Worked example 3.3.1: Try yourself

USING MOLE RATIOS

How many moles of carbon dioxide are generated when 0.50 moles of butane (C_4H_{10}) are burned completely in oxygen?

When carrying out any stoichiometric calculations, you must always clearly state the mole ratio for the reaction you are working with.

Mass–mass stoichiometry

Calculations can require you to start and finish with masses rather than moles, as this is how quantities of chemicals are often measured. To calculate the number of moles from the mass of a substance, use this relationship:

$$\text{moles } (n) = \frac{\text{mass in g } (m)}{\text{molar mass } (M)}$$

and to calculate a mass, rearrange this relationship as:

$$\text{mass in g } (m) = \text{number of moles } (n) \times \text{molar mass } (M)$$

Stoichiometric calculations generally follow the same pattern. The number of moles of a 'known' substance is calculated from data that is given to you, the mole ratios in the equation are used to find the number of moles of the 'unknown' substance, and the desired quantity of the unknown substance is then calculated.

These steps and details of formulas used when performing stoichiometric calculations involving the combustion of fuels are summarised in Figure 3.3.2.

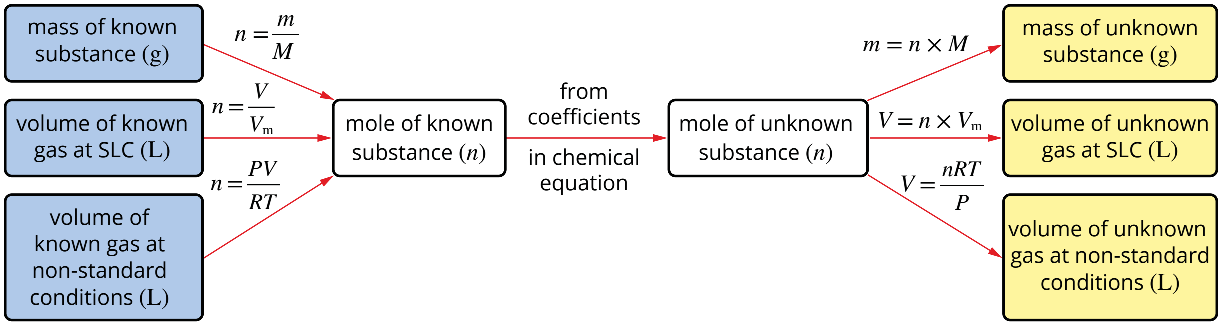


FIGURE 3.3.2 Most stoichiometric calculations follow the steps shown in the flowchart. Calculating the number of moles and using a mole ratio from a balanced chemical equation are always central to any stoichiometric calculation.

When carrying out stoichiometric calculations, always keep the answer in your calculator and proceed to the next step. Only round to the correct number of significant figures when finished.

Worked example 3.3.2

SOLVING MASS–MASS STOICHIOMETRIC PROBLEMS

Calculate the mass of carbon dioxide, in kg, produced when 540 g of propane (C_3H_8) are burned completely in oxygen.

Thinking	Working
Write a balanced equation for the reaction.	$C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(g)$
Calculate the number of moles of the known substance using: $n = \frac{m}{M}$	$n(C_3H_8) = \frac{540}{44.0}$ $= 12.3$ mol
Find the mole ratio: $\frac{\text{coefficient of unknown}}{\text{coefficient of known}}$	$\frac{n(CO_2)}{n(C_3H_8)} = \frac{3}{1}$
Calculate the number of moles of the unknown substance using: n(unknown) = mole ratio × n(known)	$n(CO_2) = \frac{3}{1} \times 12.3$ $= 36.8$ mol
Calculate the mass of the unknown substance using: $m = n \times M$	$m(CO_2) = 36.8 \times 44.0$ $= 1620$ g $= 1.62$ kg

Worked example: Try yourself 3.3.2

SOLVING MASS–MASS STOICHIOMETRIC PROBLEMS

Calculate the mass of carbon dioxide produced when 3.60 kg of butane (C_4H_{10}) is burned completely in oxygen.

3.3 Review

SUMMARY

- A balanced equation shows the ratio of the amount, in moles, of reactants and products in the reaction.
- Mass–mass stoichiometric calculations follow the general steps:
  1. Calculate the amount, in moles, of a known substance from the mass provided using:
  $$n = \frac{m}{M}$$
  2. Use the mole ratio from a balanced chemical equation to determine the amount, in moles, of the unknown substance.
  $$\frac{n(\text{unknown chemical})}{n(\text{known chemical})} = \frac{\text{coefficient of unknown chemical}}{\text{coefficient of known chemical}}$$
  3. Find the mass of the unknown substance from its amount, in moles, using $m = n \times M$.
- Stoichiometric calculations can be used to calculate the mass of carbon dioxide and water released during the combustion of a carbon-based fuel and the mass of oxygen required for complete combustion.

KEY QUESTIONS

1 Methanol burns in air according to the equation:

$2CH_3OH(g) + 3O_2(g) \rightarrow 2CO_2(g) + 4H_2O(g)$

Complete the following mathematical relationships:

a $\frac{n(CH_3OH)}{n(O_2)} =$ **b** $\frac{n(O_2)}{n(H_2O)} =$ **c** $\frac{n(CH_3OH)}{n(CO_2)} =$

2 Create a flowchart for completing mass–mass stoichiometric calculations by placing the steps in the correct order.

- Identify the known and unknown substances in the question.
- Use mole ratios from the equation to calculate the amount of the unknown substance.
- Calculate the mass of the unknown substance using $m = n \times M$.
- Write a balanced equation for the reaction.
- Calculate the amount, in mol, of the known substance using $n = \frac{m}{M}$.

3 Octane (C_8H_{18}) is a component of petrol. It burns in oxygen to produce carbon dioxide and water. Energy is released during this reaction.

The equation for this reaction is:

$2C_8H_{18}(g) + 25O_2(g) \rightarrow 16CO_2(g) + 18H_2O(g)$

a Calculate the mass of oxygen required to react with 200 g of octane.

b Calculate the mass of carbon dioxide produced in part **a**.

4 Propane burns in oxygen according to the equation:

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

6.70 g of propane was burned in excess oxygen.

a What mass of carbon dioxide would be produced?

b What mass of oxygen would be consumed in the reaction?

c What mass of water would be produced?

5 A combustion reaction occurred in which 1.00 kg of butane (C_4H_{10}) reacted with excess oxygen gas.

a Calculate the mass of oxygen, in kg, required for the complete combustion of this amount of butane.

b Calculate the mass of carbon dioxide, in kg, produced in this reaction.

3.4 Calculations involving combustion of fuels—Part 2

In section 3.3 you learned how to use stoichiometric calculations to find the mass of chemicals consumed or produced when fuels are burned. In this section, you will use stoichiometry to calculate the volumes of oxygen required to burn fuels and the volumes of gases produced by the reactions. Carbon dioxide emissions from power plants such as the one shown in Figure 3.4.1 can be calculated using stoichiometry.

FIGURE 3.4.1 It is useful to be able to calculate the volume of carbon dioxide emissions produced by the combustion of a particular fuel.

MASS–VOLUME STOICHIOMETRY

Some stoichiometric calculations require you to determine the volume of a gas that reacts with, or is produced from, a given mass of a fuel during combustion. For these calculations, you need to determine the number of moles of the fuel from its mass, and use the mole ratio from the balanced chemical equation.

The volume of the gas, in litres, is determined from its amount, in moles, using one of the following formulas.

1 At standard laboratory conditions of 25°C and 100 kPa (SLC), the molar volume equation is used:

$$n = \frac{V}{V_m}$$

This formula can be rearranged to make volume the subject:

$$V = n \times V_m$$

Remember that at SLC, the accepted volume of one mole of any gas is 24.8 L mol^{-1}.

2 At non-standard conditions, the universal gas equation is used:

$$PV = nRT$$

The universal gas equation can also be rearranged to make volume the subject:

$$V = \frac{nRT}{P}$$

Remember that for use in the universal gas equation, pressure must be in kPa, temperature must be in K and the gas constant is equal to 8.31 J K^{-1} mol^{-1}.

Worked Examples 3.4.1 and 3.4.2 show how to calculate the volume of carbon dioxide that is produced from a known mass of fuel at SLC and at non-standard conditions.

Worked example 3.4.1

MASS–VOLUME STOICHIOMETRIC CALCULATIONS AT STANDARD LABORATORY CONDITIONS

Calculate the volume of carbon dioxide, in L, produced when 2.00 kg of propane is burned completely in oxygen. The gas volume is measured at SLC.

Thinking	**Working**
Write a balanced equation for the reaction.	$C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(l)$
Calculate the number of moles of the known substance using: $n = \frac{m}{M}$	$n(C_3H_8) = \frac{2000}{44.0}$ $= 45.5$ mol
Find the mole ratio: $\frac{\text{coefficient of unknown}}{\text{coefficient of known}}$	$\frac{n(CO_2)}{n(C_3H_8)} = \frac{3}{1}$
Calculate the number of moles of the unknown substance using: $n(\text{unknown}) = \text{mole ratio} \times n(\text{known})$	$n(CO_2) = \frac{3}{1} \times 45.5$ $= 136$ mol
Calculate the volume of the unknown substance using: $V = n \times V_m$	$V(CO_2) = 136 \times 24.8$ $= 3382$ L $= 3.38 \times 10^3$ L

Worked example 3.4.1: Try yourself

MASS–VOLUME STOICHIOMETRIC CALCULATIONS AT STANDARD LABORATORY CONDITIONS

Calculate the volume of carbon dioxide, in L, produced when 300 g of butane is burned completely in oxygen. The gas volume is measured at SLC.

Worked example 3.4.2

MASS–VOLUME STOICHIOMETRIC CALCULATIONS AT NON-STANDARD CONDITIONS

Calculate the volume of carbon dioxide, in L, produced when 800 g of propane is burned completely in oxygen. The gas volume is measured at 60°C and 200 kPa.

Thinking	**Working**
Write a balanced equation for the reaction.	$C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(l)$
Calculate the number of moles of the known substance using: $n = \frac{m}{M}$	$n(C_3H_8) = \frac{800}{44.0}$ $= 18.2$ mol
Find the mole ratio: $\frac{\text{coefficient of unknown}}{\text{coefficient of known}}$	$\frac{n(CO_2)}{n(C_3H_8)} = \frac{3}{1}$

Calculate the number of moles of the unknown substance using: $n(\text{unknown}) = \text{mole ratio} \times n(\text{known})$	$n(CO_2) = \frac{3}{1} \times 18.2$ $= 54.5$ mol
Express the pressure and temperature in required units.	$P = 200$ kPa $T = 60 + 273$ $= 333$ K
Calculate the volume of the unknown substance using: $V = \frac{nRT}{P}$	$V(CO_2) = \frac{54.5 \times 8.31 \times 333}{200}$ $= 755$ L

Worked example: Try yourself 3.4.2

MASS–VOLUME STOICHIOMETRIC CALCULATIONS AT NON-STANDARD CONDITIONS

Calculate the volume of carbon dioxide, in L, produced when 5.00 kg of butane is burned completely in oxygen. The gas volume is measured at 40°C and 400 kPa.

GAS VOLUME–VOLUME CALCULATIONS

For chemical reactions where both the reactants and products are in the gaseous state, it is often convenient to measure volumes, rather than masses. This is the case for the combustion of a number of fuels.

For example, the reaction between propane gas and oxygen can be represented by the equation:

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

This equation tells us that when 1 mole of propane reacts with 5 moles of oxygen gas, 3 moles of carbon dioxide and 4 moles of water vapour are produced.

You saw in section 3.2 that equal amounts, in moles, of all gases occupy equal volumes measured at the same temperature and pressure.

Therefore, the mole ratios in the balanced equation become volume ratios at the same temperature and pressure. In the above reaction, this means that when 1 litre of propane gas reacts with 5 litres of oxygen gas, 3 litres of carbon dioxide and 4 litres of water vapour are produced.

Worked example 3.4.3

GAS VOLUME–VOLUME CALCULATIONS

Methane gas (CH_4) is burned in a gas stove according to the following equation:

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$$

If 50 mL of methane is burned, calculate the volume of O_2 gas required for complete combustion of the methane under constant temperature and pressure conditions.

Thinking	**Working**
Use the balanced equation to find the mole ratio of the two gases involved.	1 mol of CH_4 gas reacts with 2 mol of O_2 gas.
The temperature and pressure are constant, so volume ratios are the same as mole ratios.	1 volume of CH_4 reacts with 2 volumes of O_2 gas, so 50 mL of CH_4 reacts with 100 mL of O_2.

Worked example: Try yourself 3.4.3

GAS VOLUME–VOLUME CALCULATIONS

Methane gas (CH_4) is burned in a gas stove according to the following equation:

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$$

If 50 mL of methane is burned in air, calculate the volume of CO_2 gas produced under constant temperature and pressure conditions.

Always use the number of moles of the limiting reactant to determine the amount of product that will be formed.

EXTENSION

Calculations involving excess reactants

As you learned in Unit 2 Chemistry, stoichiometry calculations become more complex if the reactants are not present in their stoichiometric ratio. In these cases, you must determine which reactant is completely consumed in the reaction, the limiting reactant, and which one is present in excess. The amount of limiting reactant determines how much product is formed.

Worked Example 3.4.4 introduces a strategy that can be used to determine the limiting reactant in a reaction.

Worked example 3.4.4

EXCESS REACTANT CALCULATIONS

A gaseous mixture of 25.0 g of hydrogen gas and 100.0 g of oxygen gas are mixed and ignited. The water produced is collected and weighed. What is the expected mass of water produced? The equation for the reaction is:

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

a Which reactant is the limiting reactant?

b What is the mass of water vapour formed?

Thinking	Working
a Calculate the number of moles of each reactant using $n = \frac{m}{M}$ or $n = \frac{V}{V_m}$ or $n = \frac{PV}{RT}$ as appropriate.	$n(H_2) = \frac{m}{M}$ $= \frac{25.0}{2.0}$ $= 12.5$ mol $n(O_2) = \frac{m}{M}$ $= \frac{100.0}{32.0}$ $= 3.13$ mol

Use the coefficients of the equation to find the limiting reactant.	The equation shows 2 mol of H_2 reacts with 1 mol of O_2. So to react all of the O_2 will require $2 \times n(O_2)$ of H_2 $= 2 \times 3.13$ $= 6.26$ mol As there is 12.5 mol of H_2, the H_2 is in excess. The O_2 is the limiting reactant (it will be completely consumed).
b Find the mole ratio using: $\frac{\text{coefficient of unknown}}{\text{coefficient of known}}$ The limiting reactant is the known substance.	$\frac{n(H_2O)}{n(O_2)} = \frac{2}{1}$
Calculate the number of moles of the unknown substance using: $n(\text{unknown}) = \text{mole ratio} \times n(\text{known})$	$n(H_2O) = 2 \times 3.13$ $= 6.25$ mol
Calculate the required quantity of the unknown using $m = n \times M$ or $n = \frac{V}{V_m}$ or $PV = nRT$ as appropriate.	$m(H_2O) = 6.25 \times 18.0$ $= 113$ g

Worked example: Try yourself 3.4.4

EXCESS REACTANT CALCULATIONS

Calculate the volume of carbon dioxide, in L, produced when 65.0 g of butane is burned completely in 200 L of oxygen. The gas volume is measured at SLC. The equation for the reaction is:

$$2C_4H_{10}(g) + 13O_2(g) \rightarrow 8CO_2(g) + 10H_2O(l)$$

a Which reactant is the limiting reactant?

b What is the volume of carbon dioxide formed?

3.4 Review

SUMMARY

- A balanced equation shows the ratio of the amount, in moles, of reactants and products in the reaction.
- Stoichiometric calculations follow the general steps:
  1. Calculate the amount, in moles, of a known substance from the data given. Use $n = \frac{m}{M}$, $n = \frac{V}{V_m}$ or $n = \frac{PV}{RT}$
  2. Use the mole ratio from a balanced chemical equation to determine the amount, in moles, of the unknown substance.

$$\frac{n(\text{unknown chemical})}{n(\text{known chemical})} = \frac{\text{coefficient of unknown chemical}}{\text{coefficient of known chemical}}$$

  3. Find the desired quantity of the unknown substance from its amount, in moles, using $m = n \times M$, $V = n \times V_m$ or $PV = nRT$
- The mole ratio in a balanced equation is also a volume ratio if all reactants and products are in the gaseous state and the temperature and pressure are kept constant.
- Stoichiometric calculations can be used to calculate the volume of carbon dioxide and water released during the combustion of a carbon-based fuel and the volume of oxygen required for complete combustion.

KEY QUESTIONS

1 Propane (C_3H_8) burns in oxygen according to the equation:

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

When the following masses of propane react completely with excess oxygen, calculate the volume of:

i oxygen used at SLC

ii carbon dioxide produced at SLC.

a 22 g

b 16.5 g

c 3.40 kg

2 Octane is one of the main constituents of petrol. It burns according to the equation:

$$2C_8H_{18}(g) + 25O_2(g) \rightarrow 16CO_2(g) + 18H_2O(g)$$

What mass of octane must have been used if 50.0 L of carbon dioxide, measured at 120°C and 1.10 atm, was produced?

3 Hydrogen peroxide decomposes according to the equation:

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

Calculate the volume of oxygen, collected at 30.0°C and 91.0 kPa, that is produced when 10.0 g of hydrogen peroxide decomposes.

4 What volume of NO_2 is produced when 0.5 L of nitrogen(II) oxide (NO) reacts with excess oxygen? (All volumes are measured at 25°C and 100 kPa.) The equation for the reaction is:

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

5 Calculate the volume of oxygen needed to completely react with 150 mL of carbon monoxide according to the following equation. Assume all volumes are measured at the same temperature and pressure.

$$2CO(g) + O_2(g) \rightarrow 2CO_2(g)$$

3.5 Calculations involving energy changes

The combustion of fuels provides us with energy for daily use, including heat for warmth and cooking, and a source of power for transport.

The amount of energy released when a fuel burns is directly proportional to the amount of fuel consumed. The bonfire shown in Figure 3.5.1 contains more fuel than the match, so it releases more energy. Doubling the quantity of petrol in a car allows you to travel twice as far.

FIGURE 3.5.1 The amount of energy released by a bonfire is far greater than the amount of energy released by the burning of a single match. In general, the energy released or absorbed by a reaction is directly proportional to the amounts of reactants consumed.

In Chapter 2 you learned that **thermochemical equations** show the energy released or absorbed during a chemical reaction by including a sign and numerical value for the heat change that occurs in the reaction represented by the equation. You can use thermochemical equations to calculate the energy released by the combustion of specified quantities of fuel. You will learn how to do these types of calculations in this section.

COMBUSTION AND ENERGY

The amount of energy released by the combustion of fuels depends on:

- the type of fuel burned
- the amount of fuel burned
- whether **complete combustion** or **incomplete combustion** is involved.

Consider the thermochemical equations for the complete combustion of methane and pentane:

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

$$C_5H_{12}(g) + 8O_2(g) \rightarrow 5CO_2(g) + 6H_2O(l) \qquad \Delta H = -3509 \text{ kJ mol}^{-1}$$

The equations show us that the combustion of one mole of pentane (C_5H_{12}) releases much more energy than the combustion of one mole of methane (CH_4). Complete combustion occurs when there is a plentiful oxygen supply. Incomplete combustion occurs when the oxygen supply is limited, and carbon monoxide is formed rather than carbon dioxide. The complete combustion of a fuel releases more energy than incomplete combustion of the same amount. For example, for ethane:

$$2C_2H_6(g) + 7O_2(g) \rightarrow 4CO_2(g) + 6H_2O(l) \qquad \Delta H = -3120 \text{ kJ mol}^{-1}$$

$$2C_2H_6(g) + 5O_2(g) \rightarrow 4CO(g) + 6H_2O(l) \qquad \Delta H = -1989 \text{ kJ mol}^{-1}$$

Calculating energy change from thermochemical equations

ℹ The coefficients of the reactants in a thermochemical equation indicate the amounts, in moles, of each substance that react to give the specified **enthalpy** change.

For example, the thermochemical equation for the complete combustion of ethane indicates that 3120 kJ of energy is released by the reaction of 2 moles of ethane with 7 moles of oxygen.

Worked Examples 3.5.1 and 3.5.2 show you how to use a thermochemical equation to calculate the energy released by the combustion of different amounts of fuels or the amount of fuel required to produce a specified amount of energy.

Worked example 3.5.1

CALCULATING ENERGY RELEASED BY THE COMBUSTION OF A PARTICULAR AMOUNT OF A FUEL

Calculate the heat energy released, in MJ, when 10.0 kg of octane undergoes complete combustion.

$$2C_8H_{18}(l) + 25O_2(g) \rightarrow 16CO_2(g) + 18H_2O(l) \quad \Delta H = -10\,900 \text{ kJ mol}^{-1}$$

Thinking	Working
Calculate the amount, in moles, of the fuel using: $n = \frac{m}{M}$	$n(C_8H_{18}) = \frac{10\,000}{114.0}$ $= 87.7$ mol
Using the thermochemical equation, write a relationship between the number of moles of fuel burned and energy released.	2 moles of C_8H_{18} release 10 900 kJ. Let 87.7 moles of C_8H_{18} release x kJ.
Calculate the energy released by the fuel in kilojoules.	By proportion: $\frac{87.7}{2} = \frac{x}{10\,900}$ $x = \frac{87.7}{2} \times 10\,900$ $= 477\,965$ kJ
Convert the energy released to MJ. 1 MJ = 10^3 kJ	477 965 kJ = 478 MJ

Worked example: Try yourself 3.5.1

CALCULATING ENERGY RELEASED BY THE COMBUSTION OF A PARTICULAR AMOUNT OF A FUEL

Calculate the heat energy released, in MJ, when 10.0 kg of ethane undergoes complete combustion.

$$2C_2H_6(g) + 7O_2(g) \rightarrow 4CO_2(g) + 6H_2O(l) \quad \Delta H = -3120 \text{ kJ mol}^{-1}$$

Worked example 3.5.2

CALCULATING THE AMOUNT OF FUEL THAT MUST BE BURNED TO PRODUCE A PARTICULAR AMOUNT OF ENERGY

What volume of methane, measured at SLC, burns completely to provide 4.00×10^4 kJ?

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

Thinking	Working
Using the thermochemical equation, write a relationship between the number of moles of fuel burned and energy released.	1 mole of CH_4 releases 890 kJ. Let x moles release 4.00×10^4 kJ.
Calculate the amount of the fuel that was burned to produce the energy.	By proportion: $\frac{1}{x} = \frac{890}{4.00 \times 10^4}$ $x = \frac{4.00 \times 10^4}{890}$ $= 44.9$ mol
Calculate the volume of the fuel, at SLC.	$n = \frac{V}{V_m}$ $V(CH_4) = n \times V_m$ $= 44.9 \times 24.8$ $= 1115$ L $= 1.12 \times 10^3$ L

Worked example: Try yourself 3.5.2

CALCULATING THE AMOUNT OF FUEL THAT MUST BE BURNED TO PRODUCE A PARTICULAR AMOUNT OF ENERGY

What volume of methane, measured at SLC, burns completely to provide 5.00×10^3 kJ.

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

COMPARING FUELS USING STOICHIOMETRIC CALCULATIONS

Octane (C_8H_{18}) and ethanol (C_2H_5OH) are used as fuels for transport. Octane is derived from a fossil fuel whereas ethanol is a biofuel. You can use your knowledge of stoichiometry and thermochemical equations to compare the benefits of the use of the two fuels by calculating quantities such as the:

- energy released by the same mass of each fuel
- volumes of carbon dioxide and water vapour released by the same mass of each fuel
- volume of carbon dioxide released per MJ of energy produced for each fuel
- total (net) volume of greenhouse gases released per MJ of energy produced for each fuel.

Both carbon dioxide and water vapour are **greenhouse gases**, which absorb and emit infrared or heat radiation, thus trapping heat in the lower atmosphere.

The thermochemical equations for the complete combustion of the fuels to form carbon dioxide and water vapour are given below:

Octane: $2C_8H_{18}(l) + 25O_2(g) \rightarrow 16CO_2(g) + 18H_2O(g) \quad \Delta H = -10\,108 \text{ kJ mol}^{-1}$

Ethanol: $C_2H_5OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(g) \quad \Delta H = -1235 \text{ kJ mol}^{-1}$

Calculations for octane are shown below. A comparison of each of these quantities for octane and ethanol is given in Table 3.5.1 on page 95.

Energy released per kilogram

For 1.00 kg of octane:

$$\begin{aligned} n(C_8H_{18}) &= \frac{m}{M} \\ &= \frac{1000}{114.0} \\ &= 8.77 \text{ mol} \end{aligned}$$

From the equation:

2 moles of C_8H_{18} release 10 108 kJ

Let 8.77 moles of C_8H_{18} release x kJ.

$$\begin{aligned} \frac{8.77}{2} &= \frac{x}{10\,108} \\ x &= \frac{8.77}{2} \times 10\,108 \\ &= 44\,333 \text{ kJ} \\ &= 44.3 \text{ MJ} \end{aligned}$$

The energy content of octane is 44.3 MJ kg^{-1}.

Volume of CO_2 produced per kilogram at SLC conditions

For 1.00 kg of octane:

From the equation:

$$\begin{aligned} \frac{n(CO_2)}{n(C_8H_{18})} &= \frac{16}{2} \\ \text{So } n(CO_2) &= \frac{16}{2} \times 8.77 \\ &= 70.2 \text{ mol} \end{aligned}$$

$$n = \frac{V}{V_m}$$

$$\text{So } V = n \times V_m$$

$$\begin{aligned} \text{At SLC, } V(CO_2) &= 70.2 \times 24.8 \\ &= 1.74 \times 10^3 \text{ L} \end{aligned}$$

Complete combustion of octane produces 1.74×10^3 L kg^{-1}.

Volume of CO_2 (a greenhouse gas) released at SLC per MJ of energy obtained

From the equation:

16 mol of CO_2 is released when 10 108 kJ of energy is released.

Calculate the volume occupied by 16 mol of CO_2 at SLC:

$$n = \frac{V}{V_m}$$

$$\text{So } V = n \times V_m$$

$$\begin{aligned} \text{At SLC, } V(CO_2) &= 16 \times 24.8 \\ &= 397 \text{ L} \end{aligned}$$

So, production of 397 L of CO_2 releases 10 108 kJ (10.108 MJ).

Let the production of x L of CO_2 release 1 MJ of energy.

By proportion:

$$\begin{aligned} \frac{x}{397} &= \frac{1}{10.108} \\ x &= \frac{397}{10.108} \\ &= 39.3 \text{ L} \end{aligned}$$

Complete combustion of octane to produce 1 MJ of energy produces 39.3 L of CO_2, measured at SLC.

Total volume of greenhouse gases (CO_2 and H_2O) per MJ of energy in car exhaust gases at 500 K and 1 atm

Under these conditions, water will be in the gaseous state.

From the equation:

16 mol of CO_2 and 18 mol of H_2O (a total of 34 mol of gases) are released when 10 108 kJ of energy is released.

Calculate the volume occupied by 34 moles of gases at 500 K and 1 atm (101.3 kPa):

$$PV = nRT$$

$$\text{So, } V = \frac{nRT}{P}$$

$$V(\text{greenhouse gases}) = \frac{34 \times 8.31 \times 500}{101.3}$$

$$= 1395 \text{ L}$$

So, production of 1395 L of gases releases 10 108 kJ (10.108 MJ).

Let the production of *x* L of gases release 1 MJ of energy.

By proportion:

$$\frac{x}{1395} = \frac{1}{10.108}$$

$$x = \frac{1395}{10.108}$$

$$= 138 \text{ L}$$

Complete combustion of octane to produce 1 MJ of energy produces 138 L of greenhouse gases, measured at 500 K and 1 atm.

A comparison of octane and ethanol

TABLE 3.5.1 Quantities calculated for the complete combustion of octane and ethanol

Fuel	Complete combustion of octane	Complete combustion of ethanol
Energy content (MJ kg^{-1})	44.3	26.8
Volume of CO_2 per kg produced at SLC (L kg^{-1})	1.74×10^3	1.08×10^3
Volume of CO_2 produced per MJ of energy (L MJ^{-1})	39.2	40.2
Total volume of greenhouse gases (CO_2 and H_2O) produced per MJ of energy at 500 K and 1 atm (L MJ^{-1})	138	166

The calculations show that octane has a greater energy content than ethanol. On the other hand, ethanol releases less carbon dioxide per kilogram. Their carbon dioxide emissions per megajoule of energy produced are similar. However, octane produces less greenhouse gases overall.

Comparisons such as these assist scientists and engineers to decide on the best fuel for a particular purpose.

CHEMFILE

Choosing a fuel

Octane and ethanol are two of a wide range of fuels that could suit many different purposes. As discussed in this section, two of the factors that need to be considered when selecting a fuel for a particular purpose are:

- energy released per unit mass or unit volume
- mass of greenhouse gases produced per energy released.

Other factors include:

- availability and cost of fuel
- ease of transport
- hazards to people and the environment associated with its use and its waste products
- social, economic, cultural and political values that can affect the choice of a fuel.

You can find many examples of these factors influencing fuel choice. The Saturn V rocket shown in Figure 3.5.2 was used by NASA between 1966 and 1973. Liquid hydrogen was chosen for the Saturn rockets used in the American space program because liquid hydrogen produces large quantities of energy per gram. Because space rockets need to carry their own fuel, the mass of the propellant was a crucial factor.

Liquid hydrogen is considered to be unsuitable for use in the internal combustion engine in cars because it is very costly and highly flammable. Safe storage of hydrogen is a major difficulty when considering the use of hydrogen as a fuel. Petrol, diesel and LPG are preferred over coal for cars because they can be transported and handled more easily and produce less pollution when burned. Biofuels are promoted as fuels for cars because they are a renewable energy source and have the potential to reduce greenhouse gas emissions.

FIGURE 3.5.2 The Saturn V rocket used in the Apollo program was the most powerful rocket ever built and used liquid hydrogen as the propellant. The combustion of hydrogen releases a very large quantity of energy per gram.

3.5 Review

SUMMARY

- Stoichiometric calculations based on thermochemical equations can be used to calculate the amount of heat energy released during the combustion of a carbon-based fuel.
- Thermochemical equations can be used to calculate the volume or mass of greenhouse gases released per MJ of energy obtained.
- Fuels can be compared quantitatively in terms of the amount of energy released and the amount of carbon emissions released to the environment.

KEY QUESTIONS

1 Which one of the following equations represents the incomplete combustion of methane?

A $2CH_4(g) + 3O_2(g) \rightarrow 2CO(g) + 4H_2O(l)$

B $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$

C $C_2H_6(g) + 2O_2(g) \rightarrow CO(g) + C(s) + 3H_2O(l)$

D $2C_2H_6(g) + 7O_2(g) \rightarrow 4CO_2(g) + 6H_2O(l)$

2 When petrol is burned in a car engine, the major products of the combustion reaction are carbon dioxide and water.

- **a** Taking octane (C_8H_{18}) as one of the constituents of petrol, write a balanced equation to represent its combustion to carbon dioxide and water. Under the conditions in a car engine, octane is a gas and the water produced is also a gas.
- **b** Sometimes petrol does not burn completely, for example in an engine that has not been properly tuned. This is because the oxygen supply is limited and is not sufficient to completely convert the octane to carbon dioxide and water. Under these conditions, one of the products of combustion will be carbon monoxide. Write a balanced equation to show the production of carbon monoxide when octane burns in a limited supply of oxygen. Assume that carbon monoxide is the only carbon-containing compound produced.

3 Calculate the energy released when the following quantities of ethane gas burn according to the equation:

$2C_2H_6(g) + 7O_2(g) \rightarrow 4CO_2(g) + 6H_2O(l) \quad \Delta H = -3120 \text{ kJ mol}^{-1}$

- **a** 3.00 mol
- **b** 100 g
- **c** 10.0 L at SLC

4 What volume of ethane, measured at SLC, must be burnt according to the equation in Question **3** in order to yield 100 kJ of heat energy?

5 Calculate the energy released when 250.0 g of petrol burns completely in a car engine. Assume petrol is mainly octane (C_8H_{18}) and burns according to the equation:

$2C_8H_{18}(l) + 25O_2(g) \rightarrow 16CO_2(g) + 18H_2O(l) \quad \Delta H = -10\,900 \text{ kJ mol}^{-1}$

6 Butane is used as the fuel in some portable camping stoves. It is a liquid when stored under pressure in a butane cylinder, but vaporises when the valve is opened. Combustion of butane is represented by the equation:

$2C_4H_{10}(g) + 13O_2(g) \rightarrow 8CO_2(g) + 10H_2O(l) \quad \Delta H = -5772 \text{ kJ mol}^{-1}$

- **a** How much energy is produced when 10.0 g of butane burns completely?
- **b** How much energy is produced when 0.100 L of butane, measured at SLC, burns completely?
- **c** Calculate the volume of butane, measured at 15°C and 108 kPa, that must be burnt to produce 1.00 kJ of energy.

7 Methane and methanol both burn in air according to the thermochemical equations:

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

$2CH_3OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 4H_2O(l) \quad \Delta H = -1450 \text{ kJ mol}^{-1}$

- **a** If 1 mole of methane and 1 mole of methanol are completely burned in separate experiments, which experiment will release the most energy?
- **b** If each of the above reactions is used to produce 2000 kJ of energy, which fuel will release the most carbon dioxide?

Chapter review

03

KEY TERMS

absolute temperature scale
absolute zero
bar
complete combustion
elastic collision
enthalpy
gas constant
greenhouse gas
ideal gas
incomplete combustion
kelvin scale
kinetic energy
kinetic molecular theory
molar volume
partial pressure
pascal
pressure
standard atmosphere
standard laboratory conditions (SLC)
standard temperature and pressure (STP)
stoichiometry
thermochemical equation
universal gas equation
velocity
volume

Introducing gases

1 Which one of the following volumes is equal to 4.5 L?

A 4.5×10^2 mL
B 4.5×10^3 mL
C 4.5×10^{-3} mL
D 4.5×10 mL

2 Which one of the following best describes the effect of an increase in temperature on gas particles?

A Both the average kinetic energy and the average speed of the particles increase.
B Both the average kinetic energy and the average speed of the particles decrease.
C The average kinetic energy of the particles increases and the average speed of the particles decreases.
D The average kinetic energy of the particles decreases and the average speed of the particles increases.

3 Select the correct answers from the pairs of words to complete the paragraph about gases.

The volume occupied by the atoms or molecules in a gas is much **smaller/larger** than the total volume occupied by the gas. The particles move in rapid, **straight-line/curved** paths and collide with each other and with the walls of the container. The forces between particles are extremely **weak/strong**. The collisions between particles are **elastic/rigid**. The average kinetic energy of the particles is **directly/inversely** proportional to the temperature of the gas, in units of **K/°C**.

4 Use the kinetic theory of gases to explain why:

a the pressure of a gas increases if its volume is reduced at constant temperature
b the pressure of a gas decreases if its temperature is lowered at a constant volume
c in a mixture of gases, the total pressure is the sum of the partial pressure of each gas
d the pressure of a gas, held at constant volume and temperature, will increase if more gas is added to the container.

5 **a** If a container of gas is opened and some of the gas escapes, what happens to the pressure of the remaining gas in the container?
b Use the kinetic molecular theory to explain what happens to the gas pressure in part **a**.

Universal gas equation

6 Calculate the mass of oxygen (O_2) present in a 50.0 L container of oxygen at SLC.

7 Use the molar volume of a gas at SLC to find the:

a volume occupied by 8.0 g of oxygen at SLC
b mass of nitrogen dioxide present in 10 L at SLC.

8 If 64.0 g of oxygen gas occupies a volume of 25.0 L when the temperature is 30.0°C, then the pressure of the gas, in kPa, is closest to:

A 20.0
B 200
C 400
D 6.40×10^3

9 Calculate the volume, in litres, occupied by 10.0 g of carbon dioxide at 25°C and 101.3 kPa.

10 What is the mass of oxygen present in a 10.0 L container of oxygen at a pressure of 105 kPa and at 20°C?

11 At what temperature will 0.2 g of helium exert a pressure of 80 kPa in a container with a fixed volume of 4.0 L?

12 Carbon dioxide gas is a product of the complete combustion of fuels.

a Calculate the mass of 1.00 mol of carbon dioxide.
b What is the volume occupied by 1.00 mol of carbon dioxide at SLC?
c Given that density is defined as mass/volume, calculate the density of carbon dioxide at SLC in g L^{-1}.
d Would you expect the density of carbon dioxide at STP to be less than, equal to or greater than its density at SLC? Justify your answer.

13 A sample of gas of mass 10.0 g occupies a volume of 5.4 L at 27°C and 100 × 10^3 Pa.

- **a** Calculate the amount, in mol, of gas in the sample.
- **b** Determine the molar mass of the gas.

14 Which container holds more molecules of oxygen gas: container A of volume 40.0 L at 25°C and 770 mmHg or container B of volume 0.10 L at 45°C and 390 mmHg?

15 A room has a volume of 220 m^3.

- **a** Calculate the amount, in moles, of air particles in the room at 23°C and a pressure of 100 kPa.
- **b** Assume that 20% of the molecules in the air are oxygen molecules and the remaining molecules are nitrogen. Calculate the mass of air in the room.

Calculations involving combustion of fuels

16 Propane (C_3H_8) burns in oxygen according to the equation:

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

6.70 g of propane was burned in excess oxygen.

- **a** What mass of carbon dioxide would be produced?
- **b** What mass of oxygen would be consumed in the reaction?
- **c** What mass of water would be produced?

17 The ethanol produced by the fermentation of glucose is used as a biochemical fuel or biofuel. Fermentation of glucose produces ethanol and carbon dioxide according to the following equation:

$$C_6H_{12}O_6(aq) \xrightarrow{\text{yeast}} 2C_2H_5OH(aq) + 2CO_2(g)$$

Calculate the mass of ethanol produced by the fermentation of 80.0 g of glucose.

18 Large quantities of coal are burned in Australia to generate electricity, in the process generating significant amounts of the greenhouse gas carbon dioxide. The equation for this combustion reaction is:

$$C(s) + O_2(g) \rightarrow CO_2(g)$$

Determine the mass of carbon dioxide produced by the combustion of 1.0 tonne (10^6 g) of coal, assuming that the coal is pure carbon.

19 Propane (C_3H_8) burns in oxygen according to the equation:

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

Calculate the volume of:

- **i** oxygen at SLC used
- **ii** carbon dioxide at SLC produced

when the following masses of propane react completely with excess oxygen.

- **a** 22 g
- **b** 5.0 g
- **c** 0.145 g
- **d** 16.5 g
- **e** 3.4 kg

20 Octane is one of the main constituents of petrol. It burns according to the equation:

$$2C_8H_{18}(g) + 25O_2(g) \rightarrow 16CO_2(g) + 18H_2O(g)$$

Calculate the mass of octane used if 50.0 L of carbon dioxide, measured at 120°C and 1.10 atm, was produced.

21 What volume of oxygen gas (in L) is required for the complete combustion of 10.0 L of ethane gas at constant pressure and a temperature of 150°C?

22 Methane burns in excess oxygen according to the equation:

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$$

This reaction produces 5 L of carbon dioxide at 200°C and 100 kPa. Assuming all volumes are measured at the same temperature and pressure, calculate the:

- **a** volume of methane used
- **b** volume of oxygen used
- **c** mass of water vapour produced.

23 Propane undergoes complete combustion as follows:

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

All volumes are measured at 120°C and 102 kPa. When 80 mL of propane and 500 mL of oxygen are reacted:

- **a** one of the gases does not react completely. Which gas is it and what volume of it is unreacted?
- **b** what volumes of carbon dioxide and water are produced in the reaction?
- **c** what change in the total volume of all the gases has occurred as a result of the reaction?

24 There are many scientists investigating possible fuels to replace fossil fuels. A group of Japanese chemists is investigating the following reaction as a source of methane:

$$CaCO_3(s) + 4H_2(g) \rightarrow CH_4(g) + Ca(OH)_2(s) + H_2O(g)$$

At 400°C, 100 kPa and under suitable reaction conditions what:

- **a** volume of methane is produced if 100 L of hydrogen is completely reacted?
- **b** mass of calcium carbonate is used in part **a**?

25 An indoor gas heater burns propane (C_3H_8) at a rate of 12.7 g per minute. Calculate the minimum mass of oxygen per minute, in g, that needs to be available for the complete combustion of propane.

26 The Hazelwood power station in the Latrobe Valley consumes about 13.0 million tonnes (1 tonne = 10^6 g) of coal in 1 year. The coal used in the power station is composed of approximately 25% carbon. Calculate the volume of the greenhouse gas carbon dioxide released each year by the power station at SLC.

Calculations involving energy changes

27 Calculate the amount of energy released when 806 g of butan-1-ol reacts with excess air according to the equation:

$C_4H_9OH(g) + 6O_2(g) \rightarrow 4CO_2(g) + 5H_2O(l)$ $\Delta H = -2677$ kJ mol^{-1}

28 Octane, the principal component of petrol, undergoes combustion with a plentiful supply of oxygen according to the equation:

$2C_8H_{18}(l) + 25O_2(g) \rightarrow 16CO_2(g) + 18H_2O(l)$ $\Delta H = -10\,900$ kJ mol^{-1}

- **a** What mass of octane must be burnt in order to yield 100 kJ of energy?
- **b** Given the density of octane is 0.698 g mL^{-1}, calculate the energy released when 50.0 L of octane undergoes complete combustion.

29 The complete combustion of propane is represented by the thermochemical equation:

$C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(l)$ $\Delta H = -2220$ kJ mol^{-1}

Calculate the energy released per tonne of carbon dioxide produced when propane undergoes complete combustion. (1 tonne = 10^6 g)

30 The equation for the complete combustion of ethane is:

$2C_2H_6(g) + 7O_2(g) \rightarrow 4CO_2(g) + 6H_2O(l)$ $\Delta H = -3120$ kJ mol^{-1}

Calculate the volume of carbon dioxide released at SLC per MJ of energy generated.

31 Methane and propane are used as alternative transport fuels. The heats of combustion of methane and propane are 890 kJ mol^{-1} and –2220 kJ mol^{-1}, respectively.

- **a** Calculate the mass, in kg, of each gas required to release 100 MJ of energy.
- **b** Calculate the mass of carbon dioxide produced by each fuel during the production of 100 MJ of energy.
- **c** Calculate the energy produced per tonne of carbon dioxide released for each fuel.
- **d** Compare methane and propane as transport fuels based on the values you calculated in parts **a–c**.

Connecting the main ideas

32 Consider two containers of equal size. One contains oxygen and the other carbon dioxide. Both containers are at 23°C and at a pressure of 1.0 atm. Answer each of the following questions about the two gases and give a reason for your answers.

- **a** Which of the two samples of gas contains more molecules?
- **b** Which of the two samples of gas contains the greater number of atoms?
- **c** Which of the two gases has the greater density?

33 Propane burns completely in oxygen according to the equation:

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

The amount of energy released per tonne of carbon dioxide produced is determined to be 1.68×10^4 MJ t^{-1}. Determine the ΔH value, in kJ mol^{-1}, for the thermochemical equation. (1 tonne = 10^6 g)

34 Ethanol can be used as an alternative fuel for cars. When ethanol (C_2H_5OH) undergoes complete combustion, it forms carbon dioxide (CO_2) and water (H_2O).

- **a** Write a balanced equation that represents the complete combustion of ethanol.
- **b** **i** What mass of carbon dioxide would be formed if 1.00 kg of ethanol reacts?
  - **ii** What volume of carbon dioxide would be formed from 1.00 kg of ethanol at SLC?
- **c** **i** If the density of ethanol is 0.785 g mL^{-1}, calculate the mass of ethanol in a 50.0 L tank of the fuel.
  - **ii** The heat of combustion of ethanol is –1367 kJ mol^{-1}. Calculate the energy that can be obtained from the complete combustion of 50.0 L of ethanol.
- **d** Calculate the mass of carbon dioxide formed when 1.00 kJ of energy is released.

CHAPTER

04 Redox reactions

Some of the most colourful and exothermic reactions are classified as redox reactions. This group of reactions includes some that are vitally important for the functioning of the human body and that provide the energy for our modern lifestyle.

In this chapter, you will learn how redox reactions can be defined in terms of electron transfer, and how this definition can be extended by using the concept of oxidation number. You will find out how to write balanced half-equations that describe the transfer of electrons, and then how to combine these half-equations to create an overall equation for the reaction.

Key knowledge

- Redox reactions with reference to electron transfer, reduction and oxidation reactions, reducing and oxidising agents, and use of oxidation numbers to identify conjugate reducing and oxidising agents
- The writing of balanced half-equations for oxidation and reduction reactions and balanced ionic equations, including states, for overall redox reactions

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4.1 Oxidation and reduction

The highly exothermic reaction between glycerol and potassium permanganate shown in Figure 4.1.1 is just one example of a redox reaction. Many reactions that occur in our daily lives are redox reactions. The bleaching of hair, corrosion of metals, extraction of metals from their ores, combustion of fuels, and reactions in batteries that produce electrical energy, as well as respiration and photosynthesis, are all redox reactions.

FIGURE 4.1.1 When glycerol is added to potassium permanganate, a vigorous reaction occurs in which the glycerol is oxidised by the potassium permanganate.

In this section, you will revise and extend the definitions of oxidation and reduction that were covered in Unit 2 Chemistry, and learn how they may be applied.

REDOX REACTIONS

Transfer of electrons

In your study of Unit 2 Chemistry you learned that **redox reactions** (*red*uction and *ox*idation) involve the transfer of electrons from one chemical species to another. Redox reactions can be considered as occurring in two parts.

In these reactions:

- one of the reactants *loses* electrons in a process called **oxidation**
- one of the reactants *gains* electrons in a process called **reduction**.

Oxidation and reduction occur simultaneously as electrons are transferred between the reactants.

The mnemonic OIL RIG is a way to remember the difference between oxidation and reduction processes in terms of electron movement (see Figure 4.1.2).

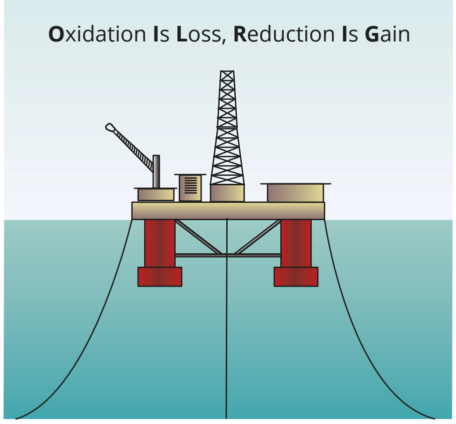

FIGURE 4.1.2 The mnemonic OIL RIG is a useful way to remember that Oxidation Is the Loss of electrons and Reduction Is the Gain of electrons.

The mnemonic 'OIL RIG' reminds you that:

- oxidation is defined as the loss of electrons
- reduction is defined as the gain of electrons.

Reduction and oxidation reactions

You will recall from Unit 1 Chemistry that metals generally have low electronegativities and their atoms contain 1, 2 or 3 electrons in their valence shells. When a metal atom loses the electrons in its valence shell, the atom becomes a stable positive ion with the electronic configuration of the nearest noble gas. In comparison, non-metals have relatively high electronegativities and their atoms generally need to gain 1, 2 or 3 electrons to achieve the stability of a noble gas electronic configuration. When non-metal atoms gain electrons, the atoms become negative ions.

Consider the reaction shown in Figure 4.1.3 between aluminium and iodine. Aluminium is in group 13 and each atom has 3 electrons in its valence shell, while iodine is in group 17, so each atom has 7 electrons in its valence shell. When these two elements react together, each aluminium atom loses 3 electrons and becomes an Al^{3+} ion. The aluminium is **oxidised**. At the same time, each iodine atom gains 1 electron and becomes an I^- ion. The iodine is **reduced**. These two ions form the ionic compound aluminium iodide.

FIGURE 4.1.3 In a vigorously exothermic reaction, aluminium is oxidised by iodine upon the addition of a few drops of water, to form aluminium iodide. The heat that is released during the reaction causes iodine to sublime from a solid to a purple gas.

This reaction can be represented by the equation:

$$2Al(s) + 3I_2(s) \rightarrow 2AlI_3(s)$$

The oxidation and reduction processes can be clearly seen when you break the equation into two **half-equations**. One half-equation describes the oxidation (loss of electrons) of the aluminium atoms:

$$Al(s) \rightarrow Al^{3+}(s) + 3e^-$$

The other half-equation describes the reduction (gain of electrons) of the iodine atoms:

$$I_2(s) + 2e^- \rightarrow 2I^-(s)$$

The electrons that are gained by the iodine atoms have been lost by the aluminium atoms.

When you write the overall redox equation, the number of electrons produced during the oxidation process must be the same as the number of electrons consumed in the reduction process. You will learn how to write overall redox equations later in this section.

WRITING REDOX EQUATIONS

Writing simple half-equations

Half-equations show what is happening as electrons are transferred in a redox reaction. Like other chemical equations, half-equations must be balanced so there is the same number of atoms of each element on each side of the arrow. Similarly, charge must also be balanced. Half- and overall equations should also indicate states.

The half-equation for the oxidation of $Fe^{2+}(aq)$ to $Fe^{3+}(aq)$ is written as:

$$Fe^{2+}(aq) \rightarrow Fe^{3+}(aq) + e^-$$

Charge is balanced by the addition of an electron to the right-hand side of the equation.

In an oxidation half-equation, the electrons are 'lost' or produced so they are always written on the right-hand side of the equation.

The half-equation for the reduction of Cl_2(g) to Cl^-(aq) is written as:

$$Cl_2(g) + 2e^- \rightarrow 2Cl^-(aq)$$

Charge is balanced by the addition of two electrons to the left-hand side of the equation.

For a reduction process, electrons are 'gained' by the reactant. For this to happen, the electrons must appear on the left-hand side of the equation. Checking which side of the equation the electrons appear on allows you to determine whether a process is oxidation or reduction.

Writing an overall redox equation

When writing equations for redox reactions, the two half-equations are normally written first and then added together to obtain an overall, or full, equation.

The overall equation does not show any electrons transferred; that is, no electrons appear in a properly balanced full equation. All the electrons lost in the oxidation reaction are gained in the reduction reaction. You may need to multiply one, or perhaps both, of the half-equations by a factor to ensure that the electrons balance and can be cancelled out in the overall equation.

States must be included in both redox half-equations and full equations for each species. Electrons do not have a state and should always cancel in the overall equation.

FIGURE 4.1.4 The reaction between chlorine and iron is a redox reaction. It is so exothermic that the iron burns as it reacts.

Consider the reaction of iron and chlorine shown in Figure 4.1.4.

In this reaction, each Fe atom is oxidised and loses three electrons. Each Cl_2 molecule is reduced and gains two electrons.

$$Fe(s) \rightarrow Fe^{3+}(s) + 3e^-$$

$$Cl_2(g) + 2e^- \rightarrow 2Cl^-(s)$$

To write an overall equation for this reaction, the number of electrons lost during oxidation must equal the number of electrons gained during reduction. Three electrons are produced by the oxidation of an iron atom but only two electrons are required to reduce a chlorine molecule. The lowest common multiple of 3 and 2 is 6, so this is the number of electrons that are transferred from iron to chlorine.

The half-equation involving the oxidation of Fe is multiplied by a factor of 2 to bring the total number of electrons to 6 and the half-equation involving the reduction of Cl_2 is multiplied by a factor of 3 to also bring the total number of electrons to 6.

$$2Fe(s) \rightarrow 2Fe^{3+}(s) + 6e^-$$

$$3Cl_2(g) + 6e^- \rightarrow 6Cl^-(s)$$

When multiplying half-equations, it is essential to multiply the coefficients of all of the species in the equation by the same factor.

The two half-equations are then added to find the overall equation:

$$2Fe(s) + 3Cl_2(g) \rightarrow 2FeCl_3(s)$$

You can see that the electrons have been cancelled from each side of the equation to give the overall equation with no electrons.

Oxidising agents and reducing agents

Substances that cause oxidation to occur are called **oxidising agents** or oxidants. In the reaction between aluminium and iodine:

$$2Al(s) + 3I_2(s) \rightarrow 2AlI_3(s)$$

the iodine is the oxidising agent. An oxidising agent *causes* oxidation but is always reduced itself.

Substances that cause reduction are called **reducing agents** or reductants. Aluminium is the reducing agent in our example. A reducing agent *causes* reduction but is always oxidised itself.

Figure 4.1.5 shows you how to identify the oxidising and reducing agents for the overall reaction between aluminium and iodine.

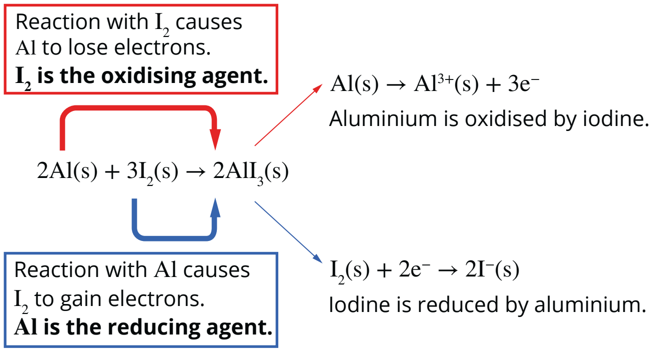

FIGURE 4.1.5 In the reaction between aluminium and iodine, aluminium is the reducing agent and iodine is the oxidising agent.

Metals, such as zinc and magnesium, and negatively charged non-metal ions, such as Br^- and I^-, can lose electrons, so they tend to act as reducing agents:

$$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$$
$$2Br^-(aq) \rightarrow Br_2(aq) + 2e^-$$

Species that can lose electrons will act as reducing agents.

Non-metals, such as fluorine and chlorine, and positively charged metal ions, such as Cu^{2+} and Ag^+ can gain electrons, so they tend to act as oxidising agents, for example:

$$Cl_2(g) + 2e^- \rightarrow 2Cl^-(aq)$$
$$Ag^+(aq) + e^- \rightarrow Ag(s)$$

Species that can gain electrons will act as oxidising agents.

4.1 Review

SUMMARY

- Redox (reduction–oxidation) reactions involve the transfer of electrons from one species to another.
- Oxidation and reduction always occur at the same time.
- Half-equations are used to represent oxidation and reduction.
- Oxidation is defined as the loss of electrons, e.g. $Mg(s) \rightarrow Mg^{2+}(aq) + 2e^-$.
- Reduction is defined as the gain of electrons, e.g. $Cl_2(g) + 2e^- \rightarrow 2Cl^-(aq)$.
- The reducing agent donates electrons to another substance, causing that substance to be reduced.
- The oxidising agent accepts electrons from another substance, causing that substance to be oxidised.
- Half-equations are added together to obtain the overall equation. Before adding the half-equations, it may be necessary to multiply them by a factor to balance the electrons.
- State symbols should always be included in half-equations and balanced equations for overall redox reactions.

KEY QUESTIONS

1 Complete the summary about redox reactions by using the following terms: gains, loses, I_2, I^-, reduced, oxidised.

When a reducing agent, such as Fe, reacts with an oxidising agent, such as ________, an ionic compound is formed. The reducing agent _________ electrons (is ________) and at the same time the oxidising agent _________ electrons (is ________). In this case, the products are Fe^{2+} and __________, which form FeI_2.

2 Classify each of the following half-equations as oxidation or reduction.

a $2Br^-(aq) \rightarrow Br_2(aq) + 2e^-$

b $Fe^{2+}(aq) \rightarrow Fe^{3+}(aq) + e^-$

c $Cl_2(g) + 2e^- \rightarrow 2Cl^-(aq)$

d $Li(s) \rightarrow Li^+(aq) + e^-$

e $Sn^{4+}(aq) + 2e^- \rightarrow Sn^{2+}(aq)$

f $Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$

3 When nickel metal reacts with copper(II) ions in an aqueous solution, nickel(II) ions are formed. Write the oxidation half-equation for the reaction.

4 The overall equation for the reaction between aluminium metal and liquid sulfur is:

$$2Al(s) + 3S(l) \rightarrow Al_2S_3(l)$$

From the overall equation, write the half-equations for the redox process and label each one as either reduction or oxidation.

5 Name the chemicals that undergo oxidation in the following reactions.

a $2Zn(s) + O_2(g) \rightarrow 2ZnO(s)$

b $Ca(s) + Cl_2(g) \rightarrow CaCl_2(s)$

c $2AgBr(s) \rightarrow 2Ag(s) + Br_2(g)$

6 Identify each oxidising and reducing agent in Question **5**.

7 Metal M is found to react with oxygen to form the compound M_2O_3.

In a separate reaction, metal M reacted with an aqueous solution of silver nitrate ($AgNO_3$). The unbalanced and incomplete equations for the reaction between metal M and $AgNO_3$ are given below.

$Ag^+(aq)$ + _____ → Ag(s)

M(s) → ______(aq) + ___e^-

M(s) + _____(aq) → _____(aq) + ____Ag(s)

a Complete the half-equations and the overall equation for the reaction between metal M and silver ions, $Ag^+(aq)$.

b Identify each half-equation as either reduction or oxidation.

c Identify the oxidising and reducing agents for the reaction.

4.2 Oxidation numbers

In this section, you will learn the set of rules that chemists have devised to allow a wider range of reactions to be classified as redox reactions. This involves assigning **oxidation numbers** to the atoms in a reaction.

You will see how oxidation numbers can be used to determine whether a reaction that does not involve the formation of ions could be classified as a redox reaction and which substances in a redox reaction have been oxidised or reduced.

You will also discover that many transition metals have multiple oxidation states and that many of these compounds can be coloured, such as in the reaction shown in Figure 4.2.1

FIGURE 4.2.1 Many redox reactions involve colour changes. It is convenient to assign individual oxidation numbers to the atoms involved in redox reactions such as this.

OXIDATION NUMBERS

In section 4.1 you looked at redox reactions that involved the production of ionic compounds from their elements. In these cases, it was relatively easy to deduce which element gained or lost electrons by considering the charge on the ions produced in the reaction. A species that was reduced gained electrons, becoming less positive, whereas the oxidised species lost electrons, becoming more positive.

For some redox reactions, it is harder to identify the species that are oxidised and reduced. For example, the reaction that occurs during the wet corrosion of iron metal can be represented by the half-equations:

$$Fe(s) \rightarrow Fe^{2+}(aq) + 2e^-$$

$$O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq)$$

The first half-equation shows that the iron loses electrons and is oxidised. The second half-equation represents a reduction reaction because electrons have been gained. However, it is not obvious if oxygen or hydrogen has gained these electrons.

It is possible to determine which element has been oxidised and which has been reduced in this reaction by looking at oxidation numbers. Oxidation numbers are also called oxidation states.

Oxidation numbers have no physical meaning—they do not indicate a formal charge or the physical or chemical properties of the substance. However, they are a useful tool for identifying which atoms have been oxidised and which atoms have been reduced.

Oxidation number rules

Oxidation numbers are assigned to elements involved in a reaction by following a specific set of rules. In applying these rules, we regard all compounds and polyatomic ions as though they are composed of individual ions.

Table 4.2.1 (on page 108) describes the rules for determining oxidation numbers. In the examples, the oxidation number of an element is placed above its symbol. The plus or minus sign precedes the number and so distinguishes the oxidation number from the charge on an ion where the sign is generally placed after the number. For example, the oxide ion (O^{2-}) has a charge of 2– and an oxidation number of –2. While the values are the same in this instance, it is important to remember that oxidation states do not always indicate a charge on the species.

TABLE 4.2.1 Rules for determining oxidation numbers of elements in compounds

Rule	Examples
1 The oxidation number of a free element is zero.	$\overset{0}{Na}$, $\overset{0}{C}$, $\overset{0}{Cl_2}$, $\overset{0}{P_4}$
2 The oxidation number of a simple ion is equal to the charge on the ion.	$\overset{+1}{Na^+}$, $\overset{-1}{Cl^-}$, $\overset{+2}{Mg^{2+}}$, $\overset{-2}{O^{2-}}$, $\overset{+3}{Al^{3+}}$, $\overset{-3}{N^{3-}}$
3 In compounds, some elements have oxidation numbers that are regarded as fixed, except in a few exceptional circumstances. (a) **Main group metals** have an oxidation number equal to the charge on their ions. (b) Hydrogen has an oxidation number of +1 when it forms compounds with non-metals. Exception: In metal hydrides the oxidation number of hydrogen is –1. (c) Oxygen usually has an oxidation number of –2. Exceptions: In compounds with fluorine, oxygen has a positive oxidation number. In peroxides, oxygen has an oxidation number of –1.	Ionic compounds: $\overset{+1}{K}Cl$, $\overset{+2}{Mg}SO_4$ Compounds of H: $\overset{+1}{H_2}O$ Metal hydrides: $Na\overset{-1}{H}$, $Ca\overset{-1}{H_2}$ Compounds of O: $H_2\overset{-2}{O}$ Peroxides: $H_2\overset{-1}{O_2}$, $Ba\overset{-1}{O_2}$
4 The sum of the oxidation numbers in a neutral compound is zero.	$\overset{+4}{C}\overset{-2}{O_2}$ Note that in CO_2, the oxidation number of each oxygen atom is written as –2. It is not written as –4 for two O atoms.
5 The sum of the oxidation numbers in a polyatomic ion is equal to the charge on the ion.	$\overset{+6}{S}\overset{-2}{O_4}{}^{2-}$, $\overset{-3}{N}\overset{+1}{H_4}{}^{+}$
6 The most electronegative element is assigned the negative oxidation number.	$\overset{+2}{O}\overset{-1}{F_2}$

Common oxidation states of the first 36 elements in their compounds are shown in the periodic table in Figure 4.2.2. Transition metals and some non-metals can have a range of oxidation states, these are usually calculated after applying the rules for all other elements in the compound.

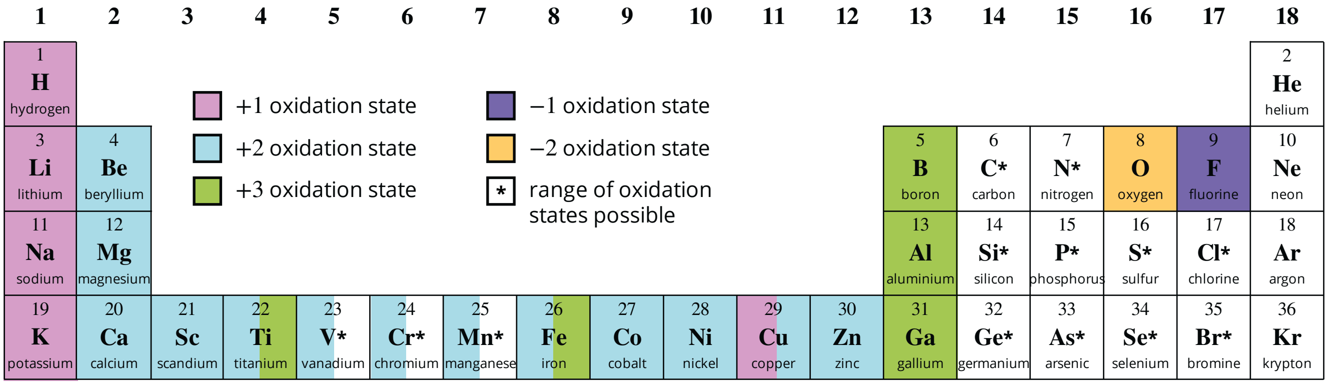

FIGURE 4.2.2 Part of the periodic table showing the most common oxidation states of some elements.

Calculating oxidation numbers

For a compound containing several elements, you can use algebra and the rules given in Table 4.2.1 to calculate the oxidation number of an element.

For example, to find the oxidation number of sulfur in H_2SO_4, there is a rule for hydrogen and for oxygen, which leaves sulfur as the only unknown. If you let the oxidation number of S equal x, the following expression can be written to solve for x:

$$\begin{aligned}(2 \times +1) + x + (4 \times -2) &= 0\\ 2 + x - 8 &= 0\\ x - 6 &= 0\\ x &= +6\end{aligned}$$

You will learn later on in this section how to use oxidation numbers to determine if a substance has been oxidised or reduced.

Worked example 4.2.1

CALCULATING OXIDATION NUMBERS

Use the rules in Table 4.2.1 to determine the oxidation number of each element in $KClO_4$.

Thinking	**Working**
Identify an element that has a set value.	K is a main group metal in group 1. Applying rule 3a, the oxidation number of potassium is +1.
Identify any other elements that have set values.	According to rule 3c, oxygen has an oxidation number of −2 unless attached to fluorine or in a peroxide.
Use algebra to work out the oxidation number of other elements.	Let the oxidation number of chlorine in $KClO_4$ be x. Solve the sum of the oxidation numbers for x: $+1 + x + (4 \times -2) = 0$ $+1 + x - 8 = 0$ $x - 7 = 0$ $x = +7$
Write oxidation numbers above the elements in the formula.	$\overset{+1}{K}\overset{+7}{Cl}\overset{-2}{O}_4$ Note that the oxidation number of oxygen is written as −2 (not as −8), even though there are four oxygen atoms in the formula.

Worked example: Try yourself 4.2.1

CALCULATING OXIDATION NUMBERS

Use the rules in Table 4.2.1 to determine the oxidation number of each element in $NaNO_3$.

USING OXIDATION NUMBERS

Using oxidation numbers to name chemicals

You may recall from Unit 1 Chemistry that **transition elements** can form ions with a number of different charges. This means that many transition metals have variable oxidation numbers. For example, there are two compounds that can be called iron chloride: $FeCl_2$ and $FeCl_3$.

Using the rules in Table 4.2.1 (on page 108), you can see that the chloride ion has an oxidation number of –1. In $FeCl_2$ this means the oxidation number of iron is +2, whereas in $FeCl_3$ the oxidation number is +3.

To distinguish between the two iron chlorides, insert Roman numerals representing the appropriate oxidation number in the name.

- $FeCl_2$ is named iron(II) chloride.
- $FeCl_3$ is named iron(III) chloride.

When naming non-metal compounds, you can also use Roman numerals to show the oxidation number of an element such as nitrogen that has several possible oxidation states. Nitrogen dioxide (NO_2) is called nitrogen(IV) oxide, while nitric oxide (NO) is nitrogen(II) oxide. This method of naming makes it much easier to determine the formula from the name of the oxide.

For elements that can have variable oxidation states, the use of a Roman numeral in the name indicates the specific oxidation state of the element.

FIGURE 4.2.3 These colourful solutions have been made by adding a reducing agent (mercury–zinc amalgam) to a yellow solution containing vanadium(V) ions. The amalgam reduces the oxidation state of the vanadium by one each time it is shaken, producing, in order: blue (+4), green (+3) and magenta (+2) solutions.

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Colourful oxidation states

A characteristic property of the transition elements is that they form brightly coloured compounds. Different oxidation states can result in different colours for the same transition metal.

Vanadium is a very colourful transition element that has a wide variety of colours depending on its oxidation state. You can see this in Figure 4.2.3. When its oxidation state is +5, vanadium is yellow; when its oxidation state is +4, it is light blue; when its oxidation state is +3, it is green; and when its oxidation state is +2, it is magenta.

Using oxidation numbers to identify oxidation and reduction

You can use the concept of oxidation numbers to extend the definition of oxidation and reduction.

In this new definition, a change in oxidation numbers indicates that a redox reaction has taken place. This can be used as an alternative definition of oxidation and reduction instead of our earlier definition involving loss and gain of electrons. It is particularly useful for non-ionic compounds when it is difficult to determine whether electrons have been transferred.

It can now be stated that:

- oxidation involves an increase in oxidation number
- reduction involves a decrease in oxidation number.

Remember that oxidation and reduction always occur together in a redox reaction. One process cannot happen without the other.

If there is no change of oxidation number for all elements in a reaction, then the reaction is not a redox reaction.

Oxidation numbers can be used to analyse the equation of a reaction and determine whether it represents a redox process.

At the beginning of this chapter, you were alerted to a number of everyday processes that are redox reactions. Combustion reactions, where fuel is burned in order to produce heat while giving off CO_2 and water, are examples of redox reactions that are very important in our society. The equation for the burning of carbon in excess oxygen is:

$$C(s) + O_2(g) \rightarrow CO_2(g)$$

At first glance, the reaction may not seem like a redox reaction because none of the species are ionic compounds so it is not clear which reactant is losing or gaining electrons. Using oxidation numbers though, you can identify both an oxidation process and a reduction process for the reaction.

$$\overset{0}{C}(s) + \overset{0}{O}_2(g) \rightarrow \overset{+4}{C}\overset{-2}{O}_2(g)$$

The carbon is oxidised because its oxidation number increases from 0 to +4 and the oxygen is reduced because its oxidation number decreases from 0 to –2.

The use of oxidation numbers allows you to look at a chemical reaction and determine whether it is a redox process.

An increase in oxidation number indicates the element was oxidised. A decrease in oxidation number indicates the element was reduced.

Worked example 4.2.2

USING OXIDATION NUMBERS TO IDENTIFY OXIDATION AND REDUCTION IN AN EQUATION

Use oxidation numbers to determine which element has been oxidised and which has been reduced in the following equation:

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$$

Thinking	**Working**
Determine the oxidation numbers of one of the elements on each side of the equation.	Choose C as the first element. $\overset{-4}{C}H_4(g) + 2O_2(g) \rightarrow \overset{+4}{C}O_2(g) + 2H_2O(l)$
Assess if the oxidation number has changed. If so, identify if it has increased (oxidation) or decreased (reduction).	The oxidation number of C has increased from –4 to +4, so carbon in CH_4 has been oxidised.
Determine the oxidation numbers of a second element on the left-hand and the right-hand side of the equation.	Choose oxygen as the second element. $CH_4(g) + 2\overset{0}{O}_2(g) \rightarrow C\overset{-2}{O}_2(g) + 2H_2\overset{-2}{O}(l)$
Assess if the oxidation number has changed. If so, identify if it has increased (oxidation) or decreased (reduction).	The oxidation number of O has decreased from 0 to –2, so O_2 has been reduced.
Continue this process until the oxidation numbers of all elements have been determined.	Determine the oxidation numbers of hydrogen. $C\overset{+1}{H}_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2\overset{+1}{H}_2O(l)$ The oxidation number of H has not changed.

Worked example: Try yourself 4.2.2

USING OXIDATION NUMBERS TO IDENTIFY OXIDATION AND REDUCTION IN AN EQUATION

Use oxidation numbers to determine which element has been oxidised and which has been reduced in the following equation:

$$CuO(s) + H_2(g) \rightarrow Cu(s) + H_2O(l)$$

Using oxidation numbers to identify conjugate redox pairs

When a half-equation is written for an oxidation reaction, the reactant, a reducing agent, loses electrons. The product is an oxidising agent. We refer to the reactant and the product that it forms as a **conjugate redox pair**.

For example, in the half-equation for the oxidation of zinc:

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

zinc metal (Zn) is a reducing agent and it forms $Zn^{2+}(aq)$, an oxidising agent. Zn(s) and $Zn^{2+}(aq)$ form a conjugate redox pair $Zn(s)/Zn^{2+}(aq)$.

When listing conjugate redox pairs, it is best to include the states of both the oxidising and reducing agent.

In the $Zn(s)/Zn^{2+}(aq)$ conjugate redox pair, the oxidation number of zinc increases from 0 to +2. The increase in the oxidation number of zinc indicates that it is an oxidation half-reaction.

For the reduction half-equation, the reactant is an oxidising agent and will gain electrons. The product formed is a reducing agent. Therefore, another conjugate redox pair is present in the redox reaction.

For example, consider the half-equation for the reduction of $Ag^+(aq)$:

$$Ag^+(aq) + e^- \rightarrow Ag(s)$$

$Ag^+(aq)$ is an oxidising agent and forms Ag(s), which is a reducing agent. $Ag^+(aq)$ and Ag(s) are also a conjugate redox pair. In this case, the oxidation number of silver decreases from +1 to 0, indicating that this is a reduction half-equation.

The relationship between changes in oxidation numbers and conjugate redox pairs can be seen by following the colour-coding in the equation in Figure 4.2.4. One conjugate redox pair is red and the other one is blue.

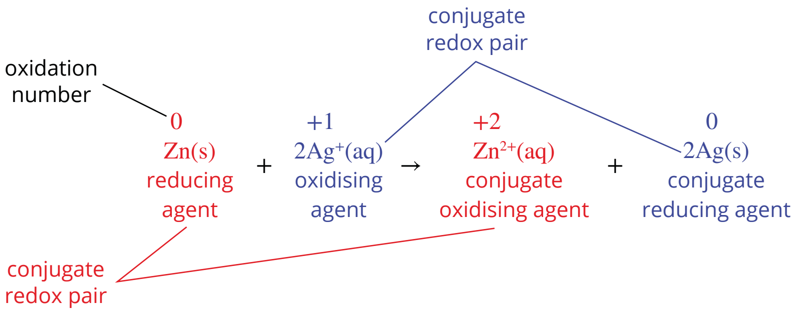


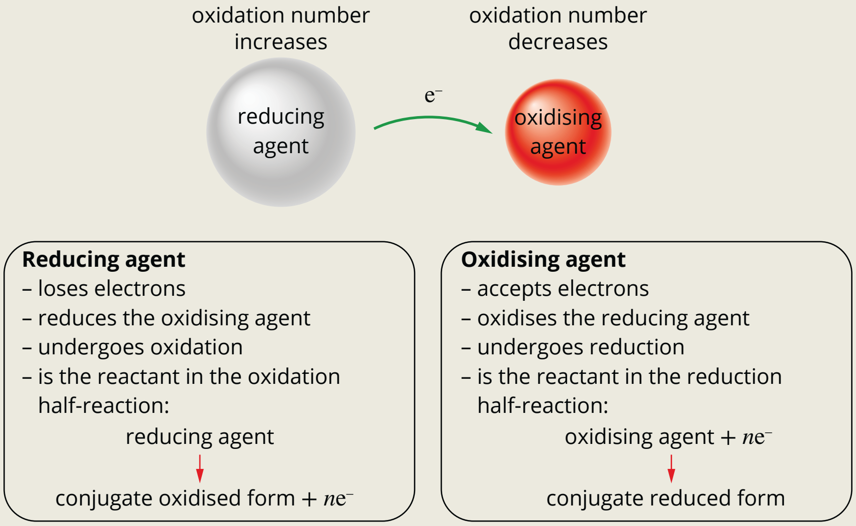
FIGURE 4.2.4 The change in oxidation numbers seen in conjugate redox pairs. For each redox reaction, there are two conjugate redox pairs.

4.2 Review

SUMMARY

- Oxidation numbers are calculated according to a set of rules.
    - Free elements have an oxidation number of 0.
    - In ionic compounds composed of simple ions, the oxidation number is equal to the charge on the ion.
    - Oxygen in a compound usually has an oxidation number of –2.
    - Hydrogen in a compound usually has an oxidation number of +1.
    - The sum of the oxidation numbers in a neutral compound is 0.
    - The sum of the oxidation numbers in a polyatomic ion is equal to the charge on the ion.
- Transition metals and some non-metals have variable oxidation numbers that can be calculated using the rules above.
- An increase in the oxidation number of an element in a reaction indicates oxidation has occurred.
- A decrease in the oxidation number of an element in a reaction indicates reduction has occurred.
- For oxidation to occur, there must be a corresponding reduction.
- If there is no change in the oxidation number of all elements in the equation for a reaction, then the reaction is not a redox reaction.
- A conjugate redox pair consists of an oxidising agent (a reactant) and the reducing agent (a product) that is formed when the oxidising agent gains electrons. In this case, the oxidation number of the oxidising agent decreases.

  The other conjugate redox pair in a redox reaction is made up of a reducing agent (a reactant) and the oxidising agent (a product) that is formed when the reducing agent loses electrons. In this case, the oxidation number of the reducing agent increases.
- Figure 4.2.5 summarises the redox terms that you need to understand from this section. This information is built up from the basic principles of redox that were introduced in *Heinemann Chemistry 1*, Chapter 16.



Reducing agent
- loses electrons
- reduces the oxidising agent
- undergoes oxidation
- is the reactant in the oxidation half-reaction:

$$\text{reducing agent} \rightarrow \text{conjugate oxidised form} + ne^-$$

Oxidising agent
- accepts electrons
- oxidises the reducing agent
- undergoes reduction
- is the reactant in the reduction half-reaction:

$$\text{oxidising agent} + ne^- \rightarrow \text{conjugate reduced form}$$

FIGURE 4.2.5 Summary of redox reaction terms.

KEY QUESTIONS

1 State the oxidation number of carbon in:

- **a** CO
- **b** CO_2
- **c** CH_4
- **d** C (graphite)
- **e** HCO_3^-

2 Which one or more of the following substances contain manganese in the +6 oxidation state: $MnCl_2$, $MnCl_3$, MnO_2, K_2MnO_4, $KMnO_4$?

3 Find the oxidation numbers of each element in the following compounds or ions. Hint: For ionic compounds, use the charge on each ion to help you.

- **a** CaO
- **b** $CaCl_2$
- **c** HSO_4^-
- **d** MnO_4^-
- **e** F_2
- **f** SO_3^{2-}
- **g** $NaNO_3$
- **h** $K_2Cr_2O_7$

4 Assign oxidation numbers to each element in these equations, and hence identify the oxidising agents and reducing agents.

- **a** $Mg(s) + Cl_2(g) \rightarrow MgCl_2(s)$
- **b** $2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$
- **c** $Fe_2O_3(s) + 3CO(g) \rightarrow 2Fe(s) + 3CO_2(g)$
- **d** $2Fe^{2+}(aq) + H_2O_2(aq) + 2H^+(aq) \rightarrow 2Fe^{3+}(aq) + 2H_2O(l)$

5 For each of the following redox reactions, complete the table to show the conjugate redox pairs.

Redox reaction	Conjugate redox pair (oxidation process)	Conjugate redox pair (reduction process)
$Na(s) + Ag^+(aq) \rightarrow Na^+(aq) + Ag(s)$		
$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$		
$2K(s) + Cl_2(g) \rightarrow 2K^+(s) + 2Cl^-(s)$		

4.3 Writing complex redox equations

Not all oxidation and reduction half-equations involve simple ions and their elements. Many interesting redox reactions, such as the iodine clock reaction shown in Figure 4.3.1, involve reactants and products that have oxygen and hydrogen in their formulas. In this section, you will learn how to balance more complex half-equations in a few simple steps.

FIGURE 4.3.1 This redox reaction involving colour changes is known as a clock reaction. The black compound is a starch–iodine complex.

BALANCING OXYGEN AND HYDROGEN IN HALF-EQUATIONS

Half-equations that involve atoms or simple ions can be written quite easily. For example, knowing that magnesium metal is oxidised to form Mg^{2+} ions in solution, you can readily write the half-equation as:

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

However, half-equations involving polyatomic ions are usually less obvious. The anaesthetic nitrous oxide or laughing gas (N_2O) can be prepared by the reduction of nitrate ions in an acidic solution:

$$2NO_3^-(aq) + 10H^+(aq) + 8e^- \rightarrow N_2O(g) + 5H_2O(l)$$

Such equations can be deduced from the following steps. The reduction of nitrate ions will be used to illustrate this process.

1. Balance all elements except hydrogen and oxygen in the half-equation.
$$2NO_3^- \rightarrow N_2O$$
2. Balance the oxygen atoms by adding water molecules.
$$2NO_3^- \rightarrow N_2O + 5H_2O$$
3. Balance the hydrogen atoms by adding H^+ ions (which are present in acidic solution).
$$2NO_3^- + 10H^+ \rightarrow N_2O + 5H_2O$$
4. Balance the charge in the equation by adding electrons.
In this case, the total charge on the left-hand side is $(2 \times -1) + (10 \times +1) = +8$. The total charge on the right-hand side is 0. Make the charges equal by adding 8 electrons to the left-hand side.
$$2NO_3^- + 10H^+ + 8e^- \rightarrow N_2O + 5H_2O$$
5. Add states to complete the half-equation.
$$2NO_3^-(aq) + 10H^+(aq) + 8e^- \rightarrow N_2O(g) + 5H_2O(l)$$

The steps outlined are for balancing redox half-equations in acidic solution only.

When writing half- and overall equations, it is important that they are fully balanced (Figure 4.3.2). The number of each element must be equal on each side, just as with any other chemical equation. The charge for each side of the equation must also be equal. It is important to remember that the charges being equal does not mean they must be zero.

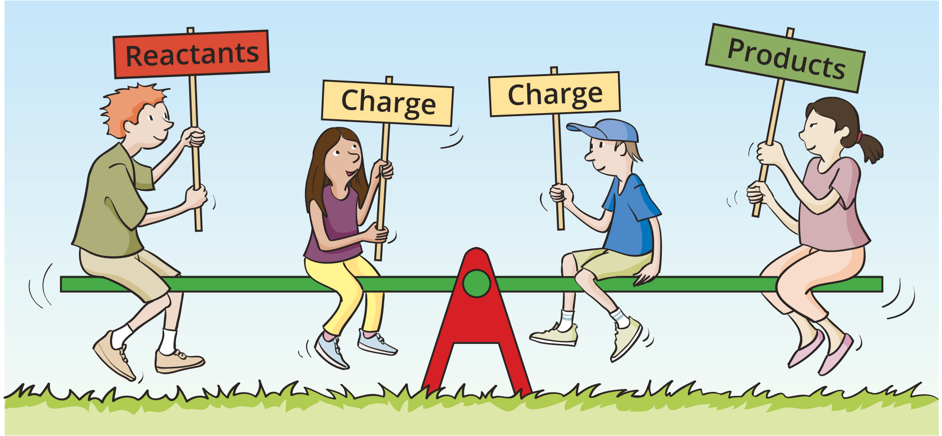


FIGURE 4.3.2 In balanced half- and overall equations, the number of atoms of each element is equal on both sides and the total charge on each side is equal.

The steps for balancing complex redox half-equations must be carried out in sequence for the process to work.

Worked Example 4.3.1 shows how to balance a complex redox half-equation. The final equation in this example has an overall charge of +6 for each side.

Worked example 4.3.1

BALANCING A HALF-EQUATION IN ACIDIC SOLUTION

Write the half-equation for the reduction of an acidified solution of $Cr_2O_7^{2-}$ to aqueous Cr^{3+}.

Thinking	Working
Balance all elements except hydrogen and oxygen in the half-equation.	There are 2 Cr atoms in $Cr_2O_7^{2-}$, so 2 Cr atoms are needed on the right-hand side (RHS). $Cr_2O_7^{2-} \rightarrow 2Cr^{3+}$
Balance the oxygen atoms by adding water.	There are 7 O atoms in $Cr_2O_7^{2-}$, so 7 H_2O molecules are added to the RHS. $Cr_2O_7^{2-} \rightarrow 2Cr^{3+} + 7H_2O$
Balance the hydrogen atoms by adding H^+ ions. Acids provide a source of H^+ ions.	There are now 14 H atoms on the RHS and none on the left-hand side (LHS), so 14 H^+ ions are added to the LHS. $Cr_2O_7^{2-} + 14H^+ \rightarrow 2Cr^{3+} + 7H_2O$
Balance the charge in the equation by adding electrons.	The charge on the LHS is (–2) + (+14) = +12 and on the RHS is 2 × +3 = +6, so 6 electrons are added to the LHS to make the charges equal. $Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$
Add states to complete the half-equation.	All states are (aq) except for water, which is (l). $Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$

Worked example 4.3.1: Try yourself

BALANCING A HALF-EQUATION IN ACIDIC SOLUTION

Write the half-equation for the reduction of an acidified solution of MnO_4^- to solid MnO_2.

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Vinegary wine or winey vinegar?

The oxidation of ethanol forms ethanoic acid. Ethanoic acid is the main ingredient of vinegar and is responsible for its sourness. If a bottle of wine is left open to the atmosphere for a few days, it becomes 'vinegary' and undrinkable.

This reaction is put to good use when specialist vinegars such as apple cider vinegar, red wine vinegar and even beer vinegar (Figure 4.3.3) are made by deliberately oxidising the appropriate alcoholic beverage under the right conditions.

The oxidation half-equation for the production of ethanoic acid from ethanol is given by:

$$C_2H_5OH(aq) + H_2O(l) \rightarrow CH_3COOH(aq) + 4H^+(aq) + 4e^-$$

FIGURE 4.3.3 A selection of vinegars. From left to right: distilled malt vinegar, cider vinegar, white wine vinegar and malt vinegar.

EXTENSION

Balancing half-equations under alkaline conditions

If a redox reaction occurs in an alkaline environment, OH^- rather than H^+ can be used to balance the equation. The steps are very similar to balancing redox processes under acidic conditions as outlined below.

Consider the oxidation of cadmium, Cd(s), to $Cd(OH)_2(s)$ in alkaline solution.

1 Balance all elements except hydrogen and oxygen in the half-equation.

$Cd(s) \rightarrow Cd(OH)_2(s)$

2 Balance the hydroxide ions by adding $OH^-(aq)$ on the left-hand side of the equation.

$Cd(s) + 2OH^-(aq) \rightarrow Cd(OH)_2(s)$

3 Balance the charge by adding electrons on the right-hand side of the equation.

$Cd(s) + 2OH^-(aq) \rightarrow Cd(OH)_2(s) + 2e^-$

Sometimes it is not obvious where the hydroxide ions should be placed; for example, in the reduction of oxygen to form water. In this case, you can balance the half-equation as though it occurs in acidic solution, then add hydroxide ions later. Follow the steps below to see how this is done.

1 Balance the oxygen atoms by adding water.

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

2 Balance the hydrogen atoms by adding H^+ ions.

$O_2(g) + 4H^+(aq) \rightarrow 2H_2O(l)$

3 Balance the charge by adding electrons.

$O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$

4 Add enough hydroxide ions to both sides of the equation to neutralise the H^+ ions on the left-hand side of the equation.

$O_2(g) + 4H^+(aq) + 4OH^-(aq) + 4e^- \rightarrow 2H_2O(l) + 4OH^-(aq)$

5 The neutralisation reaction between $H^+(aq)$ and $OH^-(aq)$ produces water, so cancel out the water molecules on the side where there are less water molecules.

$O_2(g) + \overset{2}{\cancel{4}}H_2O(l) + 4e^- \rightarrow \cancel{2H_2O(l)} + 4OH^-(aq)$

$O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq)$

While you will not see many examples of balancing under alkaline conditions during your study of Units 3 and 4 Chemistry, you will probably have made use of these reactions many times in your daily life. For example, the redox process that generates electricity in a common alkaline battery is maintained through alkaline conditions rather than acidic conditions.

OVERALL REDOX EQUATIONS UNDER ACIDIC CONDITIONS

To write an overall redox equation, you add the oxidation half-equation to the reduction half-equation, making sure that the number of electrons used in reduction equals the number of electrons released during oxidation. In addition, for redox reactions under acidic conditions, H^+ ions and H_2O molecules are also present as reactants and products, which will need to be cancelled down.

Worked example 4.3.2

COMBINING HALF-EQUATIONS TO WRITE OVERALL REDOX EQUATIONS UNDER ACIDIC CONDITIONS

Write balanced oxidation and reduction half-equations for the reaction in which $C_2H_5OH(aq)$ and $Cr_2O_7^{2-}(aq)$ react to form $CH_3COOH(aq)$ and $Cr^{3+}(aq)$. Then write the overall redox equation for the reaction.

Thinking	Working
Identify one reactant and the product it forms, and write the balanced half-equation.	$C_2H_5OH(aq) + H_2O(l) \rightarrow CH_3COOH(aq) + 4H^+(aq) + 4e^-$
Identify the second reactant and the product it forms, and write the balanced half-equation.	$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$
Multiply one or both equation(s) by a suitable factor to ensure that the number of electrons on both sides of the arrow is equal.	Lowest common multiple = 12 $3 \times [C_2H_5OH(aq) + H_2O(l) \rightarrow CH_3COOH(aq) + 4H^+(aq) + 4e^-]$ $2 \times [Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)]$ $3C_2H_5OH(aq) + 3H_2O(l) \rightarrow 3CH_3COOH(aq) + 12H^+(aq) + 12e^-$ $2Cr_2O_7^{2-}(aq) + 28H^+(aq) + 12e^- \rightarrow 4Cr^{3+}(aq) + 14H_2O(l)$
Add the oxidation and the reduction half-equations together, cancelling electrons so that none appear in the final equation. Also cancel H_2O and H^+ if these occur on both sides of the arrow.	$3C_2H_5OH(aq) + \cancel{3H_2O(l)} \rightarrow 3CH_3COOH(aq) + \cancel{12H^+(aq)} + \cancel{12e^-}$ $2Cr_2O_7^{2-}(aq) + \overset{16H^+}{\cancel{28H^+(aq)}} + \cancel{12e^-} \rightarrow 4Cr^{3+}(aq) + \overset{11H_2O}{\cancel{14H_2O(l)}}$ $3C_2H_5OH(aq) + 2Cr_2O_7^{2-}(aq) + 16H^+(aq) \rightarrow$ $3CH_3COOH(aq) + 4Cr^{3+}(aq) + 11H_2O(l)$

FIGURE 4.3.4 The oxidation of ethanol, described in Worked Example 4.3.2, was the basis of an older form of the breathalyser. The presence of alcohol in a motorist's breath was identified by a colour change in the oxidising agent, potassium dichromate. During the reaction, the yellow-orange colour of dichromate ions changed to the green colour of chromium(III) ions as the alcohol was oxidised.

Worked example 4.3.2: Try yourself

COMBINING HALF-EQUATIONS TO WRITE OVERALL REDOX EQUATIONS UNDER ACIDIC CONDITIONS

Write balanced oxidation and reduction half-equations for the reaction in which $SO_3^{2-}(aq)$ and $ClO^-(aq)$ react to form $H_2S(g)$ and $ClO_3^-(aq)$. Then write the overall equation for the reaction.

Some strong oxidising agents such as potassium dichromate are highly coloured. The change in colour that occurs as the redox process proceeds can be used for a number of chemical analyses.

The reaction of an alcohol with acidified dichromate as seen in Worked Example 4.3.2 can be followed by the colour change of the solution from orange to green (Figure 4.3.4). This colour change was the basis for older form of handheld breathalysers used for testing the blood alcohol level of drivers.

CHEMISTRY IN ACTION

Alcohol and the road toll

Drinks such as wine, beer, vodka and bourbon contain ethanol (CH_3CH_2OH). Ethanol acts as a depressant, slowing the functioning of the brain. When alcoholic drinks are consumed in excess, their intoxicating qualities can lead to antisocial behaviour and can damage a person's health.

The ethanol content of alcoholic drinks varies, as shown in Table 4.3.1.

TABLE 4.3.1 Typical ethanol contents of selected alcoholic beverages

Drink	Ethanol content (%v/v)
Spirits (brandy, bourbon, gin, rum, vodka whiskey etc.)	37
Port, sherry	18
Wines (including sparkling wines)	12
Alcoholic cider	10
Beer	5.0
'Light' beer	2.5
Pre-mixed vodka-based drinks	9

Regulations require that the ethanol content of alcoholic drinks be specified on their labels, since the content determines how much drink can be consumed without adverse effects.

Because ethanol slows down reaction time, it seriously affects a person's driving skills. It is estimated that alcohol has contributed to nearly 40% of all road accidents. Governments have responded by introducing penalties, such as fines and licence disqualification, for drivers whose blood alcohol concentration exceeds a certain level—typically 0.05%(m/v). Probationary or P-plate drivers are required to have a zero blood alcohol level.

The introduction of penalties, a policy of randomly testing motorists for blood alcohol level, and various advertising campaigns have all helped to increase public awareness of the link between alcohol consumption and road accidents. Figure 4.3.5 shows how the road toll in Victoria changed during the period when these various measures designed to discourage drink driving were introduced.

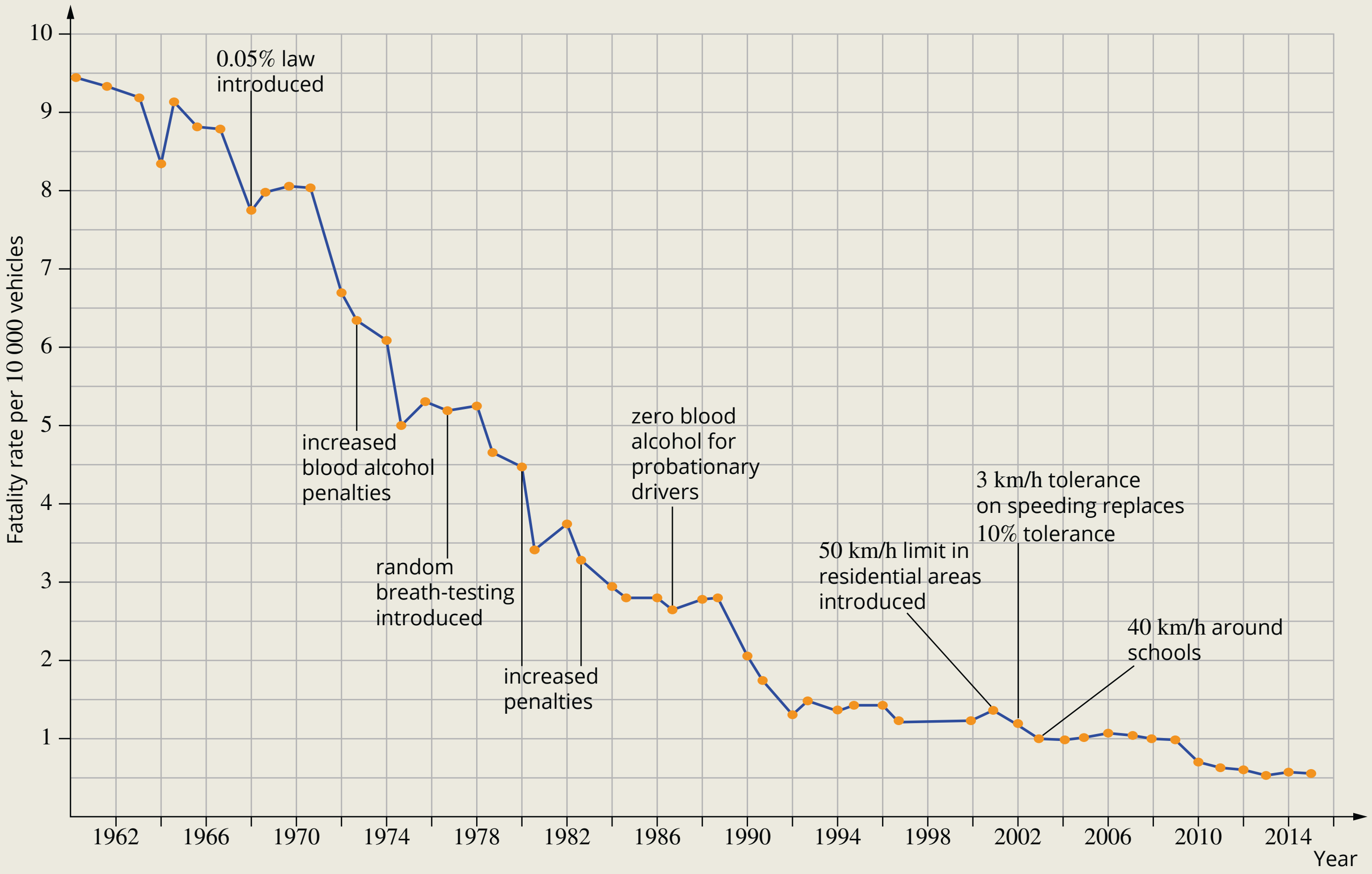


FIGURE 4.3.5 Deaths on Victorian roads 1960–2015. Continual improvements and action on road safety, including crackdowns on drink-driving, has seen the road toll continue to decrease.

FIGURE 4.3.6 Breathalysers are used to analyse the blood alcohol content of motorists. The sensor detects the change in colour as the ethanol is oxidised to ethanoic acid in the presence of acidified potassium dichromate.

Chemists were involved in the invention of the breathalyser, an instrument designed for police to use to estimate blood alcohol content (Figure 4.3.6). Rather than analysing samples of blood, this instrument measures the concentration of alcohol in a person's breath, which is closely related to the concentration of alcohol in their blood.

If this screening test indicates that a driver's blood is over 0.05%(m/v), more accurate measurements are taken either in a 'booze bus' or at a police station. The blood alcohol content may then be confirmed by instrumental techniques such as infrared spectroscopy or gas–liquid chromatography. Some police departments also use alcohol fuel cell sensors.

The first breathalysers operated by detecting the colour change that occurs when ethanol reacts with an acidified solution of potassium dichromate ($K_2Cr_2O_7$), forming Cr^{3+} ions and ethanoic acid. The redox reaction can be represented by the equation:

$$\underset{\text{orange}}{2Cr_2O_7^{2-}(aq)} + 3CH_3CH_2OH(g) + 16H^+(aq) \rightarrow \underset{\text{green}}{4Cr^{3+}(aq)} + 3CH_3COOH(aq) + 11H_2O(l)$$

CHEMFILE

Elephant's toothpaste

Hydrogen peroxide is such a strong oxidising agent that it can even oxidise itself, decomposing to form water and oxygen gas:

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

In this reaction the two half-equations are:

$$H_2O_2(aq) + 2H^+(aq) + 2e^- \rightarrow 2H_2O(l)$$

$$H_2O_2(aq) \rightarrow O_2(g) + 2H^+(aq) + 2e^-$$

The decomposition reaction of hydrogen peroxide is the basis for the impressive 'foam column' or 'elephant's toothpaste' demonstration that is commonly shown by chemistry teachers to their classes.

When detergent and a catalyst are added to concentrated hydrogen peroxide solution, a column of foam is formed (Figure 4.3.7).

FIGURE 4.3.7 The 'elephant's toothpaste' demonstration involves a redox reaction in which hydrogen peroxide reacts with itself to form water and oxygen gas. In this reaction, the hydrogen peroxide is both the reducing agent and the oxidising agent. In this image, solid potassium iodide catalyst is added to hydrogen peroxide solution. Red colouring has also been added for effect.

4.3 Review

SUMMARY

- To balance redox half-equations under acidic conditions:
  1. Balance all atoms except hydrogen and oxygen.
  2. Balance the oxygen atoms by adding water molecules.
  3. Balance the hydrogen atoms by adding H^+ ions.
  4. Balance the charge by adding electrons.
  5. Add states.
- To write an overall equation, add the oxidation half-equation and the reduction half-equation, making sure that the number of electrons used in reduction equals the number of electrons released during oxidation.
- When combining oxidation and reduction half-equations under acidic conditions, any $H^+(aq)$ and $H_2O(l)$ that appear on both sides of the arrow should be cancelled down.

KEY QUESTIONS

1 Write half-equations for the:

a reduction of MnO_2 to Mn^{2+}

b reduction of MnO_4^- to MnO_2

c reduction of SO_4^{2-} to H_2S

d oxidation of SO_2 to SO_4^{2-}

e oxidation of H_2S to S

f oxidation of SO_3^{2-} to SO_4^{2-}.

2 When zinc powder is sprinkled into an acidified solution of potassium dichromate, a reaction occurs that produces zinc ions and chromium(III) ions in solution.

a Write the oxidation half-equation for the reaction.

b Write the reduction half-equation for the reaction.

c Use your answers to parts **a** and **b** to write a balanced equation for the overall reaction.

3 Write the half-equations and the balanced overall equation for the reaction in which:

a a solution containing iron(II) ions is oxidised by an acidified solution containing dichromate ions ($Cr_2O_7^{2-}$). The products include iron(III) and chromium(III) ions

b a solution containing sulfite ions (SO_3^{2-}) reacts with an acidified solution of permanganate ions (MnO_4^-) to produce a colourless solution containing sulfate ions and manganese(II) ions

c manganese dioxide (MnO_2) reacts with concentrated hydrochloric acid to form chlorine gas and a solution containing manganese(II) ions.

4 The following equations are not balanced.

i Identify the species that has been reduced and the species that has been oxidised.

ii Write balanced half-equations for the oxidation and reduction reactions.

iii Combine the half-equations to write a balanced overall equation.

a $Ce^{4+}(aq) + H_2S(g) \rightarrow Ce^{3+}(aq) + S(s) + H^+(aq)$

b $NO_3^-(aq) + H^+(aq) + Cu(s) \rightarrow NO(g) + H_2O(l) + Cu^{2+}(aq)$

c $H_2O_2(aq) + Br^-(aq) + H^+(aq) \rightarrow Br_2(l) + H_2O(l)$

d $MnO_2(s) + H^+(aq) + S(s) \rightarrow Mn^{2+}(aq) + H_2O(l) + SO_2(g)$

Chapter review

04

KEY TERMS

conjugate redox pair
half-equation
main group metal
oxidation
oxidation number
oxidised
oxidising agent
redox reaction
reduced
reducing agent
reduction
transition element

Oxidation and reduction

1 State whether each of the statements are true or false.
  a Group 1 and 2 metal ions, such as Na^+, are reducing agents because they tend to lose electrons.
  b Group 17 molecules, such as I_2, can be oxidising agents or reducing agents.
  c Non-metal ions, such as Cl^-, can be reducing agents because they can lose electrons.
  d Metals, such as Cu, can be oxidising agents because they can gain electrons.

2 Complete the following sentences, which describe oxidation and reduction.
Oxidation and reduction occur together. Oxidation occurs when an atom ____________ electrons to form a ____________ ion, such as happens when a calcium atom, with an electronic configuration of 2,8,8,2 ______________ electrons to form a Ca^{2+} ion. Reduction occurs when an atom ______________ electrons to form a ____________ ion or a cation __________ electrons to become a neutral atom. An example is when a bromine atom, with ___________ electrons in its valence shell, __________ an electron to form a ___________ ion.

3 Lead metal is oxidised to form Pb^{2+} ions by reaction with silver ions in solution. Write half-equations for the reaction and then write the balanced overall equation.

4 Classify each of the following half-equations as either oxidation or reduction half-equations.
  a $Mg(s) \rightarrow Mg^{2+}(aq) + 2e^-$
  b $2Br^-(aq) \rightarrow Br_2(aq) + 2e^-$
  c $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$
  d $K(s) \rightarrow K^+(aq) + e^-$
  e $Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq)$
  f $I_2(aq) + 2e^- \rightarrow 2I^-(aq)$

5 Each of the following half-equations have a mistake in them. For each half-equation state what the error is and then write the correct half-equation.
  a $Ag(s) + e^- \rightarrow Ag^+(aq)$
  b $Cu(s) + e^- \rightarrow Cu^{2+}(aq) + 3e^-$
  c $Zn(aq) \rightarrow Zn^{2+}(s) + 2e^-$
  d $I_2(aq) + e^- \rightarrow I^-(aq)$
  e $Na^+(aq) - e^- \rightarrow Na(s)$

6 Identify the reducing agent in each of these redox reactions.
  a $2Cu(s) + O_2(g) \rightarrow 2CuO(s)$
  b $Mg(s) + Cl_2(g) \rightarrow MgCl_2(s)$
  c $2Fe^{3+}(aq) + Zn(s) \rightarrow Zn^{2+}(aq) + 2Fe^{2+}(aq)$
  d $2Ag^+(aq) + Ni(s) \rightarrow Ni^{2+}(aq) + 2Ag(s)$

Oxidation numbers

7 What is the oxidation number of sulfur in each of the following compounds?
  a SO_2
  b H_2S
  c H_2SO_4
  d SO_3
  e Na_2SO_3
  f $Na_2S_2O_3$

8 Complete the following table.

Compound	Element	Oxidation number
$CaCO_3$	Ca	
HNO_3	O	
H_2O_2		–1
HCO_3^-		+4
HNO_3	N	
$KMnO_4^-$	Mn	
H_2S	S	
Cr_2O_3	Cr	
N_2O_4	N	

9 Place the following substances in order of increasing oxidation states of nitrogen.
$NO, K_3N, N_2O_4, N_2O, Ca(NO_3)_2, N_2O_3, N_2$

10 Which of the following reactions are redox reactions? Give reasons for each of your answers.
  a $BaCl_2 + H_2SO_4 \rightarrow BaSO_4 + 2HCl$
  b $2Ag + Cl_2 \rightarrow 2AgCl$
  c $2FeCl_3 + SnCl_2 \rightarrow 2FeCl_2 + SnCl_4$
  d $ZnCO_3 \rightarrow ZnO + CO_2$
  e $HPO_3^{2-} + I_2 + OH^- \rightarrow H_2PO_4^- + 2I^-$
  f $2Cu^+ \rightarrow Cu^{2+} + Cu$
  g $CaF_2 \rightarrow Ca^{2+} + 2F^-$
  h $P_4 + 6H_2 \rightarrow 4PH_3$

11 Complete the table by determining the oxidation number of the underlined atom in the compound or ion.

	Species	Oxidation number of the underlined atom
a	$\underline{Cu}O$	
b	$\underline{Fe}(OH)_3$	
c	$H\underline{Cl}O_2$	
d	$\underline{Mn}O_4^-$	
e	$\underline{Cr}_2O_7^{2-}$	

12 Copper bowls and trays can be decorated by etching patterns on them using concentrated nitric acid. The overall reaction is:

$$Cu(s) + 4HNO_3\,(aq) \rightarrow Cu(NO_3)_2(aq) + 2NO_2(g) + 2H_2O(l)$$

a What is the oxidation number of copper:
  i before the reaction?
  ii after the reaction?

b What is the oxidation number of nitrogen:
  i before the reaction?
  ii after the reaction?

c Name the oxidising agent and reducing agent in this process.

13 Complete the following table, giving the conjugate redox pairs for each of the reactions.

Equation	Conjugate redox pair (oxidation)	Conjugate redox pair (reduction)
$Fe(s) + I_2(aq) \rightarrow FeI_2(aq)$		
$Mg(s) + FeCl_2(aq) \rightarrow MgCl_2(aq) + Fe(s)$		
$10Br^-(aq) + 2MnO_4^-(aq) + 16H^+(aq) \rightarrow 2Mn^{2+}(aq) + 8H_2O(l) + 5Br_2(aq)$		
$Cu(s) + 2NO_3^-(aq) + 4H^+(aq) \rightarrow Cu^{2+}(aq) + 2NO_2(g) + 2H_2O(l)$		

Writing complex redox equations

14 Complete the summary below as you balance the half-equation for the reduction of NO_3^- to NO_2 in acidic solution.

$NO_3^-(aq) \rightarrow NO_2(g)$

Step	Task	How it's done	Half-equation
1	Balance nitrogens.		$NO_3^-(aq) \rightarrow NO_2(g)$
2	Balance oxygens by adding _______.	Add _____ H_2O molecule(s) to right-hand side of the equation.	
3	Balance hydrogens by adding _____.	Add ______ H^+ ion(s) to _________ of the equation.	
4	Balance charge by adding _______.	Charge on left-hand side = ______ Charge on right-hand side = ______ Add ______ e^- to the _______ of the equation.	
5	Add state symbols to give the final half equation.	Give the appropriate states for each reactant and product in the equation.	

15 The unbalanced half-equation for the reduction of the iodate ion (IO_3^-) is:

$$2IO_3^-(aq) + xH^+(aq) + ye^- \rightarrow I_2(aq) + zH_2O(l)$$

Complete the equation by inserting the correct coefficients for *x*, *y* and *z*.

16 When sulfur dioxide is bubbled through an acidified solution of sodium dichromate, sulfate ions and green chromium(III) ions are formed. Write the half-equations for this reaction and then deduce the balanced overall equation.

17 During each of the following analyses, redox reactions occurred. Write half-equations for the oxidation and reduction reactions. Use these half-equations to write an overall equation for each reaction.

a Zinc was analysed by reacting it with a solution of Pb^{2+} ions. Lead metal was precipitated and Zn^{2+} ions were formed.

b The amount of Fe^{2+} ions in iron tablets was determined by oxidising them to Fe^{3+} ions, using an acidified solution of MnO_4^- ions. The MnO_4^- ions were reduced to Mn^{2+} ions during the reaction.

c Sulfur(IV) dioxide (SO_2), a preservative in dried fruit, was determined by oxidation to SO_4^{2-} using a solution of I_2. Iodide (I^-) ions were produced.

d An acidified solution of bleach, which contains OCl^- ions, was titrated against a solution of I^- ions. The reaction products included Cl^- and I_2.

18 In dry cells commonly used in torches, an electric current is produced from the reaction of zinc metal with solid MnO_2. During this reaction, Zn^{2+} ions and solid Mn_2O_3 are formed. Write half-equations, and hence an overall equation, for the reaction.

19 Vitamin C is an essential vitamin to maintain good health. The amount of vitamin C present in food can be determined by titration against a solution of iodine, using starch as an indicator. The reaction is a redox process and can be represented by the following overall equation:

$C_6H_8O_6(aq) + I_2(aq) \rightarrow C_6H_6O_6(aq) + 2H^+(aq) + 2I^-(aq)$

a Write the two half-equations for the reaction.

b Identify each reaction as either oxidation or reduction.

20 Answer the following questions about the reaction of $H_3AsO_4(aq)$ with $I^-(aq)$. The unbalanced equation for the reaction is:

$H_3AsO_4(aq) + I^-(aq) \rightarrow As_2O_3(s) + IO_3^-(aq) + H_2O(l)$

a Write the two half-equations for the reaction.

b Write a balanced overall equation using your two half-equations from part **a**.

Connecting the main ideas

21 As a result of a traffic accident, residents in a Melbourne suburb had to be evacuated when toxic fumes leaked from a container of sodium dithionite ($Na_2S_2O_4$). The dithionite ion reacts with water according to the equation:

$2S_2O_4^{2-}(aq) + H_2O(l) \rightarrow S_2O_3^{2-}(aq) + 2HSO_3^-(aq)$

a State the oxidation number of the sulfur in the following ions.

- **i** $S_2O_4^{2-}$
- **ii** $S_2O_3^{2-}$
- **iii** HSO_3^-

b Write half-equations for the oxidation and reduction reactions that occur when sodium dithionite is mixed with water.

22 Solid ammonium dichromate decomposes to form chromium(III) oxide, nitrogen gas and steam.

a Calculate the oxidation numbers of chromium and nitrogen in the reactant ammonium dichromate ($(NH_4)_2Cr_2O_7$) and the products Cr_2O_3 and N_2. Identify which reactants have been reduced and oxidised.

b Complete and balance the following half-equations.

- **i** $NH_4^+(s) \rightarrow N_2(g)$
- **ii** $Cr_2O_7^{2-}(s) \rightarrow Cr_2O_3(s)$

c Identify each of the half-equations in part **b** as either reduction or oxidation processes and explain your answer in terms of oxidation numbers.

d Write the balanced overall equation for the reaction that occurs.

e Identify the conjugate redox pairs for the reaction.

23 The thermite process can be used to weld lengths of railway track together. A mould placed over the ends of the two rails to be joined is filled with a charge of aluminium powder and iron(III) oxide. When the mixture is ignited, a redox reaction occurs to form molten iron, which joins the rails together, and aluminium oxide.

a Write a half-equation for the conversion of iron(III) oxide to metallic iron and oxide ions.

b Is the half-equation you wrote for part **a**, an oxidation or a reduction process?

c Write the overall equation for the thermite process.

d What mass of iron(III) oxide must be present in the charge if each joint requires 3.70 g of iron to weld it together?

CHAPTER

05

Galvanic cells as a source of energy

By the end of this chapter, you will know how galvanic cells generate electricity from chemical reactions. You will see how experimental data from galvanic cells can be used to compare the relative strengths of oxidising and reducing agents.

You will compare an exothermic redox reaction in a test tube with the same redox reaction where the reactants are in separate half-cells and electron transfer is used to produce a portable energy source.

The relative strengths of oxidising and reducing agents are conveniently summarised in a table known as the electrochemical series. You can use the electrochemical series to predict the likelihood of individual redox reactions occurring, and to calculate the potential differences of different galvanic cells.

Finally, you will investigate how different types of galvanic cells are used as a source of power for a range of uses.

Key knowledge

- Redox reactions with reference to electron transfer, reduction and oxidation reactions, reducing and oxidising agents
- The writing of balanced half-equations for oxidation and reduction reactions and balanced ionic equations, including states, for overall redox reactions
- Galvanic cells as primary cells and as portable or fixed chemical energy storage devices that can produce electricity (details of specific cells not required) including common design features (anode, cathode, electrolytes, salt bridge and separation of half-cells) and chemical processes (electron and ion flows, half-equations and overall equations)
- The comparison of the energy transformations occurring in spontaneous exothermic redox reactions involving direct contact between reactants (transformation of chemical energy to heat energy) compared with those occurring when the reactants are separated in galvanic cells (transformation of chemical energy to electrical energy)
- The use of the electrochemical series in designing and constructing galvanic cells and as a tool for predicting the products of redox reactions, deducing overall equations from redox half-equations and determining maximum cell voltage under standard conditions
- The operation of rechargeable batteries (secondary cells) with reference to discharging as a galvanic cell and recharging as an electrolytic cell, including the redox principles (redox reactions and polarity of electrodes) and the factors affecting battery life with reference to components and temperature (no specific battery is required)

5.1 Galvanic cells

FIGURE 5.1.1 Your way of life depends on cells and batteries.

Electronic devices such as mobile phones, notebook computers, cameras and hearing aids all depend on small portable sources of electricity: cells and batteries (see Figure 5.1.1). Portable energy in the form of cells and batteries enables you to operate electrical equipment without the restrictions of a power cord.

The demand for electronic devices has stimulated the production of a variety of cells, from tiny button cells for watches and calculators, to the huge batteries used to operate lighthouses. The energy provided by cells and batteries may be more expensive than energy from other sources, such as fossil fuels, but this cost is offset by their convenience.

In this section, you will find out how cells are constructed, and how they provide you with a source of electrical energy.

FIGURE 5.1.2 An original voltaic pile. The pile is 15 cm high and contains alternating copper and zinc discs separated by cardboard.

CHEMISTRY IN ACTION

A technological leap beginning with a frog's leap

The history of electrochemistry began in 1791 when Italian biologist Luigi Galvani and his assistant were experimenting with dissected frogs. They were startled to see a frog's leg hanging on a copper hook twitch when it touched an iron rail. The muscles of the frog were stimulated by an electric shock. Galvani had just discovered how to generate a current. His 'error' was in thinking that the current was some sort of life force, a perfectly reasonable idea for the time.

Other scientists set out to investigate the possibility that metals were involved in this phenomenon. After several years' work, in 1800, Alessandro Volta developed a device that used a chemical reaction to produce an electric current. Figure 5.1.2 shows the device, now called a 'voltaic pile'. It consisted of a stack of alternating copper and zinc discs separated by cardboard soaked in salt water.

INTRODUCING GALVANIC CELLS

An **electrochemical cell** is a device in which chemical energy is converted into electrical energy, or vice versa. A **galvanic cell** (which is also known as a **voltaic cell**) is a type of electrochemical cell in which chemical energy is converted into electrical energy. The cells in your mobile phone and laptop are galvanic cells.

If we connect several cells in series to obtain a higher potential difference or 'voltage', the combination of cells is called a **battery**. The term 'battery' strictly only applies to a combination of cells, but it is in everyday use to describe cells as well.

Figure 5.1.3 shows how you can produce a galvanic cell from simple laboratory equipment.

In Figure 5.1.4, you can see a diagram of a cell called the Daniell cell, named after the scientist who invented it in 1836, John Daniell. The cell produces an electric current that flows through the wire and light globe. This part of the cell is called the **external circuit**. The globe converts the electrical energy of the current into light and heat.

FIGURE 5.1.3 Construction of a galvanic cell from simple laboratory equipment.

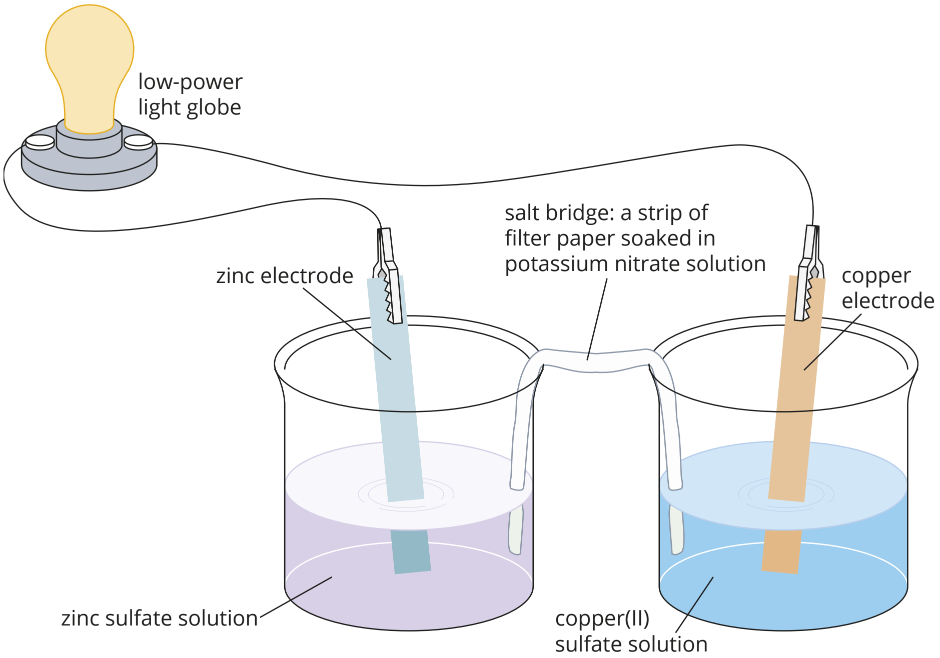


FIGURE 5.1.4 The Daniell cell is a type of galvanic cell.

The current flows because a chemical reaction is taking place in the cell. If you leave the cell with a light globe connected for several hours, you will see evidence of this reaction occurring: the zinc metal corrodes, the copper metal becomes covered with a furry dark brown deposit and the blue copper(II) sulfate solution loses some of its colour.

CHEMFILE

The Daniell cell

In 1836, English chemist John Daniell invented a device that could supply a useful electric current. The device, which became known as the Daniell cell, was used almost exclusively to power the early English and US telegraph systems because of its reliable output.

If you replace the light globe with a **galvanometer** (an instrument for detecting electric current), the galvanometer will indicate that electrons flow from the zinc **electrode** through the wire to the copper electrode. Current flows only if the two halves of the cell are connected by a **salt bridge**. A salt bridge is often made from filter paper soaked in a relatively unreactive **electrolyte**, such as a solution of potassium nitrate.

These observations lead to the following explanations about what is occurring in a galvanic cell.

- The reaction in the cell is a **redox reaction**, because electrons are being transferred.
- The zinc electrode corrodes because the zinc metal forms zinc ions in solution:

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

- The oxidation of the zinc metal releases electrons, which flow through the wire to the copper electrode.
- Electrons are accepted by copper(II) ions in the solution when the ions collide with the copper electrode:

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

- The copper metal that is formed deposits on the electrode as a dark brown coating.

In this cell, there is a transformation of chemical energy to electrical energy. Figure 5.1.5 shows the processes that occur during the operation of the cell. The equation for the overall reaction is found by adding the two half-equations:

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

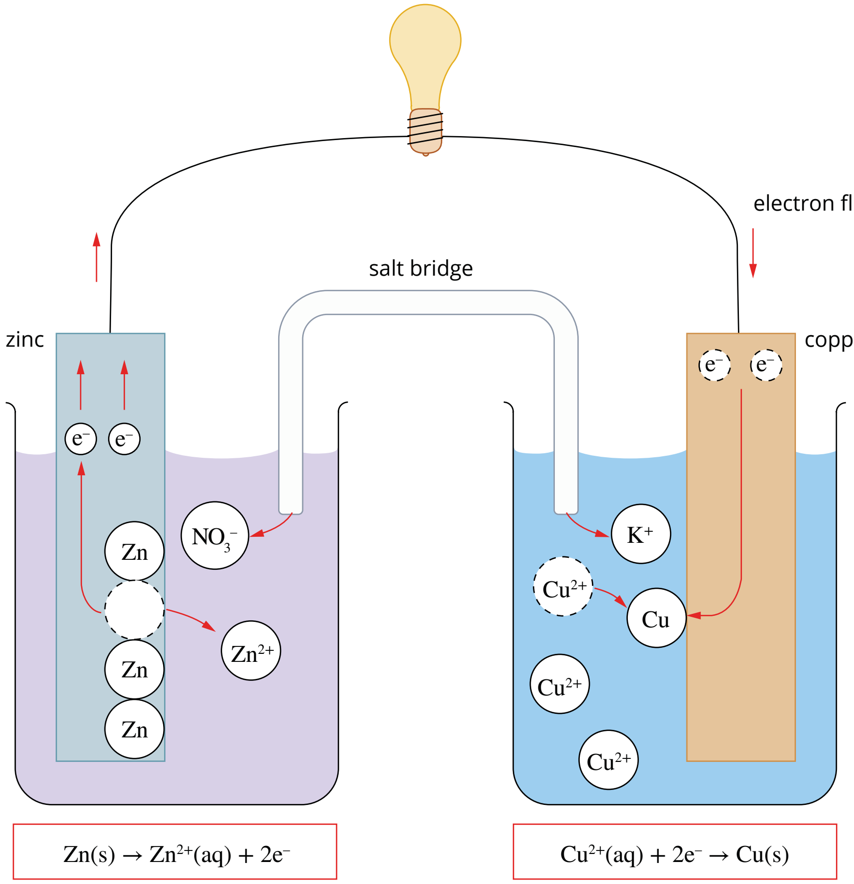


FIGURE 5.1.5 A representation of the electrode reactions in a Daniell cell. The salt bridge contains potassium nitrate solution.

This redox reaction is described as a **spontaneous reaction** because it occurs naturally.

Copper(II) ions act as the **oxidising agent**, or **oxidant**, and zinc metal acts as the **reducing agent**, or **reductant**.

A chemical that causes another substance to be oxidised is called an oxidising agent and is itself reduced in the redox reaction. Similarly, a chemical that causes another substance to be reduced is called a reducing agent. Reducing agents are oxidised in redox reactions.

ENERGY TRANSFORMATIONS IN DIRECT REACTIONS

You may have seen a similar reaction to the one that occurs in a Daniell cell if you have copper-plated a piece of metal, such as zinc. When zinc is immersed in an aqueous solution containing $Cu^{2+}(aq)$ ions, the metal becomes coated in dark brown copper (Figure 5.1.6). At the same time, thermal energy is produced, which escapes into the surrounding environment as heat.

The overall equation for this metal displacement reaction is:

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

FIGURE 5.1.6 $Cu^{2+}(aq)$ ions in blue-coloured copper(II) sulfate solution reacting directly with a strip of zinc metal.

This reaction is an example of a spontaneous exothermic reaction. If the reactants are allowed to come into direct contact with each other, their chemical energy is transformed directly to thermal energy. However, in a galvanic cell, the half-reactions occur in separate containers, and the electrons are transferred by the external circuit so that chemical energy is transformed into electrical energy.

The energy changes that occur in galvanic cells and when reactants undergo direct reaction are summarised in Figure 5.1.7.

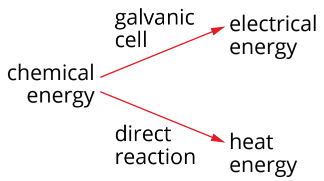


FIGURE 5.1.7 Energy transformations that occur when reactants are separated in a galvanic cell and when the reactants react directly.

HOW A GALVANIC CELL OPERATES

A galvanic cell is designed so that half-reactions occur in two separate compartments of the cell. Because the oxidising agent and reducing agent do not come into direct contact with each other, electrons can only be transferred through an external circuit connecting the negative and positive electrodes.

This flow of electrons creates an electric current. Therefore, the chemical energy of the reactants is transformed into electrical energy.

Half-cells

A galvanic cell can be regarded as consisting of two **half-cells**. Each half-cell contains an electrode in contact with a solution (see Figure 5.1.8). In the Daniell cell, one half-cell contains Cu(s) and Cu^{2+}(aq); the other contains Zn(s) and Zn^{2+}(aq). The species present in each half-cell forms a **conjugate redox pair** (an oxidising agent and its corresponding reduced form).

If one member of the conjugate pair in a half-cell is a metal, it is usually used as the electrode. Some redox pairs, such as Br_2(aq)/Br^-(aq) and Fe^{3+}(aq)/Fe^{2+}(aq), do not involve solid metals. If no metal is present, an inert (unreactive) electrode, such as platinum or graphite, is used, as shown in Figure 5.1.8.

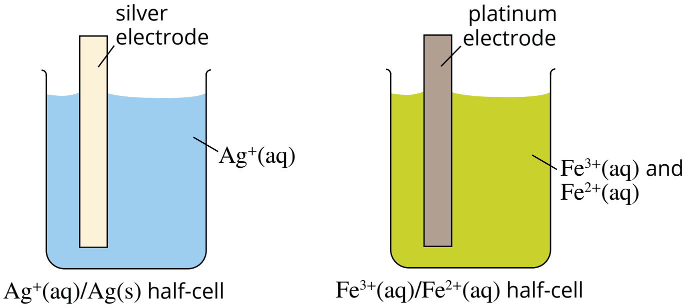


FIGURE 5.1.8 Typical half-cells. The Fe^{3+}(aq)/Fe^{2+}(aq) half-cell on the right does not contain a solid metal to act as an electrode, so an inert platinum electrode has to be added.

In some half-cells, one of the conjugate pairs may be a gas. In such cases, the special 'gas electrode' like the one shown in Figure 5.1.9 for the H^+(aq)/H_2(g) half-cell is used. Note that half-cells usually contain other species not involved in the reaction, such as spectator ions and the solvent.

The electrode at which oxidation occurs is called the **anode**. In a galvanic cell, the anode, where electrons are released, is described as the negative terminal. The electrode at which reduction occurs is called the **cathode**. The cathode, where electrons are gained, is the positive terminal in a galvanic cell.

The purpose of the salt bridge

The salt bridge contains ions that are free to move so that they can balance charges formed in the two compartments. *Cat*ions move towards the *cat*hode and *an*ions move towards the *an*ode.

Without a salt bridge, the solution in one compartment in the galvanic cell would accumulate negative charge and the solution in the other compartment would accumulate positive charge as the reaction proceeded. Such accumulation of charge would stop the reaction very quickly and, hence, prevent further reaction.

The salt bridge is also called the **internal circuit**.

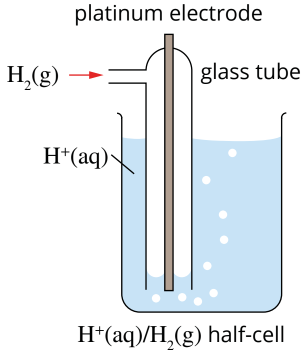


FIGURE 5.1.9 A H^+(aq)/H_2(g) half-cell consists of a platinum rod in a solution of H^+(aq) with H_2 gas bubbling through the solution.

Cations in the salt bridge move towards the cathode and anions in the salt bridge move towards the anode.

WRITING HALF-CELL EQUATIONS

If a conjugate redox pair consists of an element and its corresponding ion, then the half-equation is relatively easy to write. For instance, knowing that a reduction reaction involves the conjugate redox pair of Zn^{2+} ions and Zn, you can quickly write the half-cell equation as:

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

Half-cell equations involving polyatomic ions may be more complex to write. The equation for the reduction reaction in a half-cell containing the dichromate ion ($Cr_2O_7^{2-}$) and Cr^{3+} ion redox pair is:

$$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$$

You learned to write half-equations such as these in Chapter 4.

In balanced half- and overall equations, the:

- number of atoms of each element is equal on both sides
- total charge on each side is equal.

Writing an overall equation for a cell reaction

The half-equations for the oxidation and reduction reactions that occur in a cell can be added together to obtain an overall, or full, equation. An overall equation does not show any electrons; all the electrons lost in the oxidation reaction are gained in the reduction reaction. You may need to multiply one or both half-equations by a factor to ensure that the electrons balance and can be cancelled out in the overall equation.

The number of electrons lost in the oxidation reaction must equal the number of electrons gained in the reduction reaction.

DRAWING AND LABELLING A DIAGRAM OF A GALVANIC CELL

If you know the reaction occurring in a galvanic cell, then you can draw a diagram of the cell identifying key features, such as the anode, cathode, electrode polarity, direction of electron flow and direction of the flow of ions.

For example, consider a cell with the cell reaction:

$$Cu(s) + Cl_2(g) \rightarrow Cu^{2+}(aq) + 2Cl^-(aq)$$

From this reaction, you can see that:

- copper metal is at the anode (because copper is oxidised and oxidation occurs at the anode)
- chlorine gas is present at the cathode (because chlorine is reduced and reduction occurs at the cathode).

As in all galvanic cells:

- electrons flow through the external circuit from the anode (negative) to the cathode (positive)
- anions flow in the internal circuit to the anode and cations flow towards the cathode.

This information is used to draw and label the diagram of the cell as shown in Figure 5.1.10.

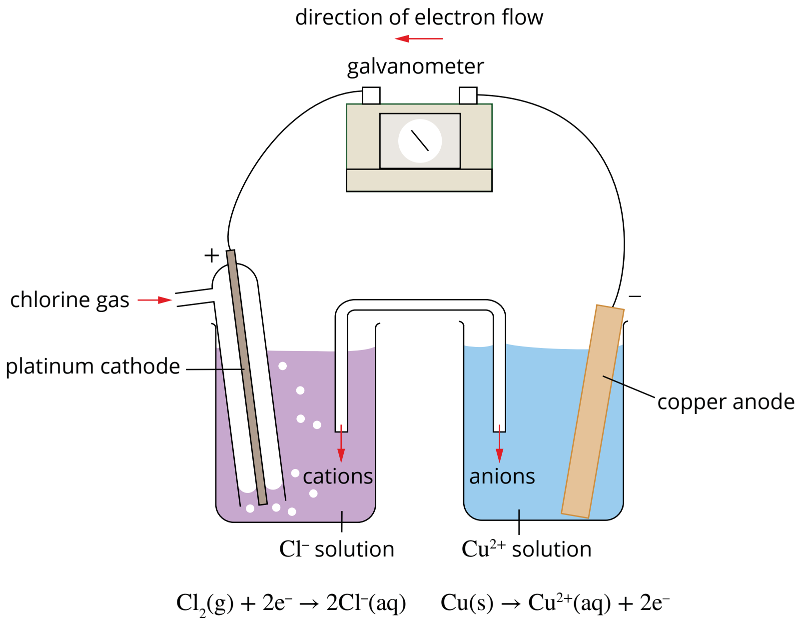


FIGURE 5.1.10 A diagram of the cell containing $Cl_2(g)/Cl^-(aq)$ and $Cu^{2+}(aq)/Cu(s)$ half-cells.

5.1 Review

SUMMARY

- The reactions that occur in galvanic cells are spontaneous and exothermic.
- In a galvanic cell, chemical energy is converted directly into electrical energy in a redox reaction.
- A cell is made from two half-cells.
- Each half-cell contains a conjugate redox pair.
- An oxidation reaction occurs in one half-cell and a reduction reaction occurs in the other half-cell.
- The electrode in the half-cell in which oxidation occurs is called the anode; the electrode in the half-cell in which reduction occurs is called the cathode.
- In galvanic cells, the anode is negative and the cathode is positive.
- Electrons flow through the external circuit from the anode to the cathode.
- A salt bridge allows a cell to produce electricity by preventing the accumulation of charge. Cations in the salt bridge move towards the cathode and anions move towards the anode.
- If the reactants in a galvanic cell reaction are allowed to come into direct contact, chemical energy is converted into heat energy rather than electrical energy.
- These key concepts about a galvanic cell are summarised in Figure 5.1.11.

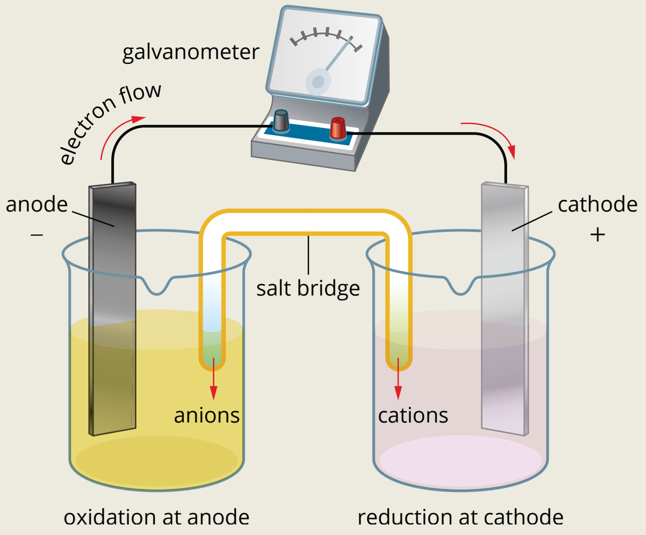


FIGURE 5.1.11 Key concepts about how a galvanic cell works.

KEY QUESTIONS

1 Which one of the following statements about a galvanic cell is correct?

A The electrode where oxidation occurs is the cathode.
B Electrons flow towards the electrode where oxidation occurs.
C Anions flow into the half-cell containing the electrode where reduction occurs.
D The electrode where oxidation occurs has a positive polarity.

2 Draw labelled diagrams of the following half-cells.

a $Ni^{2+}(aq)/Ni(s)$
b $Sn^{4+}(aq)/Sn^{2+}(aq)$
c $H^{+}(aq)/H_2(g)$

3 The overall equation for the reaction that occurs in a cell made up of $Al^{3+}(aq)/Al(s)$ and $Sn^{2+}(aq)/Sn(s)$ half-cells is:

$$2Al(s) + 3Sn^{2+}(aq) \rightarrow 2Al^{3+}(aq) + 3Sn(s)$$

Write half-equations for the reaction occurring at the:

a cathode
b anode.

4 Draw a diagram of the cell from Question **3** and label the:

- half-equation for the reaction occurring in each half-cell
- anode and cathode
- direction of electron flow
- electrode polarities (which electrode is positive and which is negative)
- direction of anion and cation flow from the salt bridge.

5 In the spaces provided, label the galvanic cell in Figure 5.1.12 with:

- anode
- cathode
- positive electrode
- negative electrode
- reduction
- oxidation
- salt bridge.

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

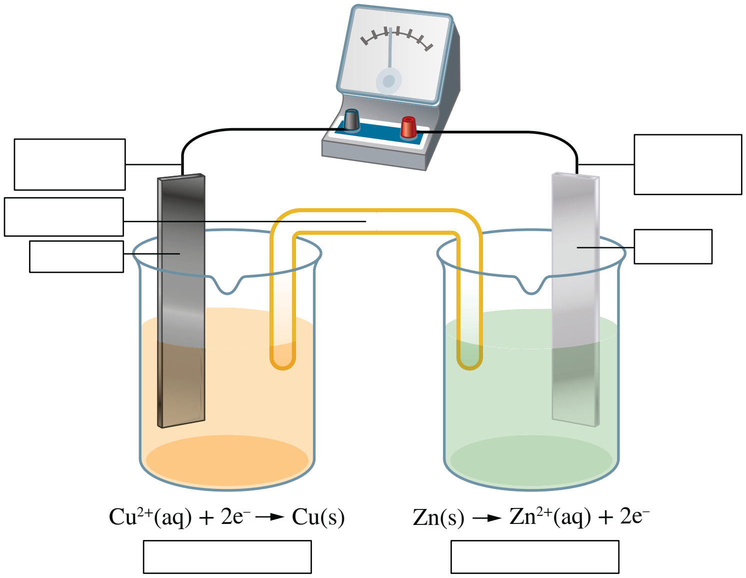


FIGURE 5.1.12 A galvanic cell.

5.2 The electrochemical series

As you saw in Chapter 4, metals vary in their reactivity. Platinum and gold are unreactive and widely used for jewellery. Other metals are very reactive. For example, sodium reacts so readily with oxygen and water (Figure 5.2.1) that it must be stored in paraffin oil.

FIGURE 5.2.1 Water dropped onto sodium metal. Sodium is highly reactive; the products are sodium hydroxide and hydrogen gas.

Galvanic cells can help you compare the relative reactivity of metals. Galvanic cells can be constructed from various combinations of half-cells. The experimental data collected from these combinations allows chemists to determine the oxidising and reducing strengths of many different substances. This information is very useful, because it allows you to predict the products of various reactions, calculate the voltages of cells and develop more powerful and longer-lasting batteries.

RELATIVE OXIDISING AND REDUCING STRENGTHS

A half-cell contains a conjugate redox pair. The reactions that can occur in a half-cell can be written as reversible reactions, showing the relationship between the two chemicals in the redox pair. For example, the reaction in a:

- half-cell containing the $H^+(aq)/H_2(g)$ redox pair may be written as:

$$2H^+(aq) + 2e^- \rightleftharpoons H_2(g)$$

- half-cell containing the $Zn^{2+}(aq)/Zn(s)$ redox pair may be written as:

$$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s)$$

Figure 5.2.2 shows a diagram of a cell constructed from $H^+(aq)/H_2(g)$ and $Zn^{2+}(aq)/Zn(s)$ half-cells.

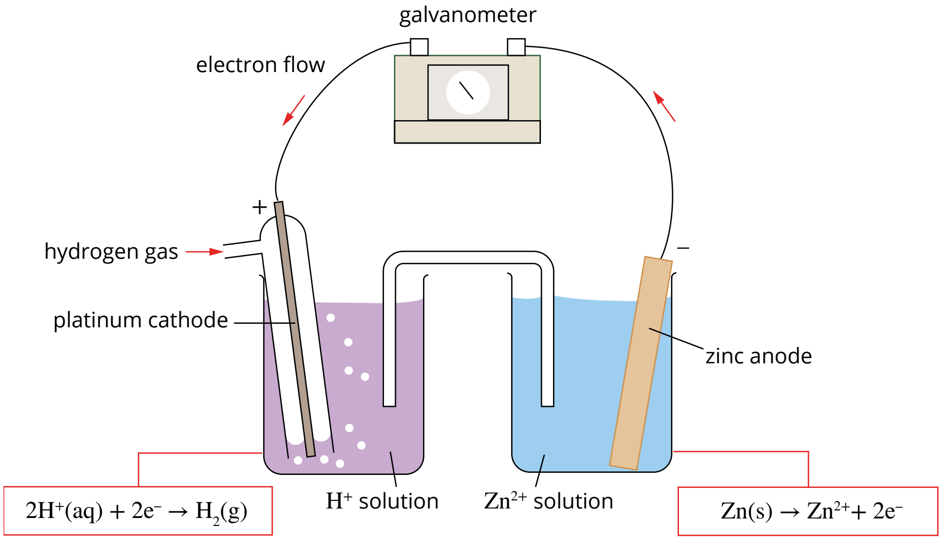


FIGURE 5.2.2 A diagram of a cell constructed from $H^+(aq)/H_2(g)$ and $Zn^{2+}(aq)/Zn(s)$ half-cells.

Notice that in this cell the zinc electrode is negative. The reactions that are occurring are:

$$2H^+(aq) + 2e^- \rightarrow H_2(g)$$
$$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$$

Zn is oxidised to Zn^{2+} and H^+ is reduced to H_2. Zinc can be described as a reducing agent or reductant because it causes the reduction of H^+ to occur. The H^+ is described as an oxidising agent or oxidant because it causes the Zn to be oxidised to Zn^{2+}.

Because electrons flow from the Zn^{2+}/Zn half-cell to the H^+/H_2 half-cell, we can infer that:

- zinc is a stronger reducing agent than H_2
- H^+ is a stronger oxidising agent than Zn^{2+} ions.

ℹ In a galvanic cell, the stronger reducing agent is in the half-cell with the negative electrode (anode). The stronger oxidising agent is in the half-cell with the positive electrode (cathode).

POTENTIAL DIFFERENCE

A current flows in a galvanic cell because one half-cell has a greater tendency to push electrons into the external circuit than the other half-cell. Chemists say that a **potential difference** exists between the two half-cells. The potential difference of a cell is sometimes also called the **electromotive force**, or emf, and is commonly referred to as the voltage.

The potential difference of a cell, symbol E, has the unit of a **volt** (V) and is measured with a **voltmeter**.

Potential differences of cells are usually measured under the **standard conditions** of:

- a pressure of 1 bar (100 kPa)
- 1 M concentration of solutions.

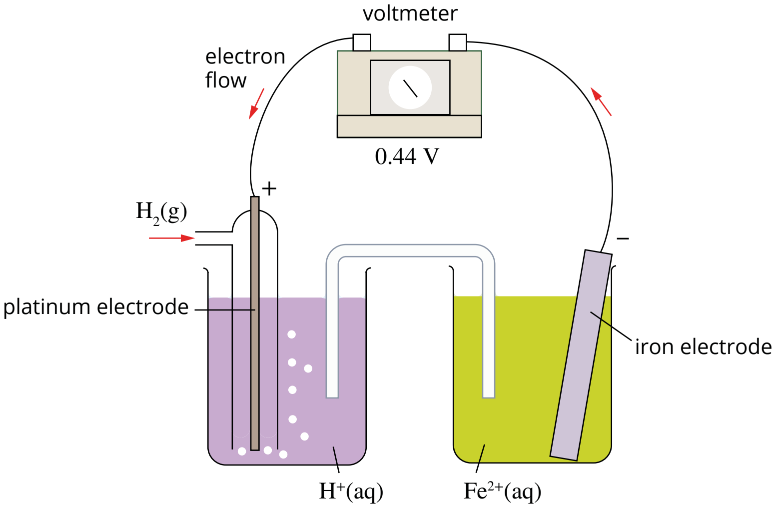
The potential difference of a cell under standard conditions is given the symbol $E°$. Potential differences are usually measured at 25°C.

Standard electrode potentials

It is impossible to measure the potential difference of an isolated half-cell because both oxidation and reduction must take place for a potential difference to exist. However, you can assign a standard half-cell potential ($E°$) to each half-cell by connecting the cells to a standard reference half-cell and measuring the voltage produced.

A hydrogen half-cell, $H^+(aq)/H_2(g)$, under standard conditions, is used for this purpose and its $E°$ value is arbitrarily assigned as zero. This half-cell is known as the **standard hydrogen half-cell** or standard hydrogen electrode.

The **standard electrode potential** of other cells may then be measured by connecting them to the standard hydrogen half-cell, as shown in Figure 5.2.3 for the $Fe^{2+}(aq)/Fe(s)$ half-cell.



Both cells are under standard conditions.

FIGURE 5.2.3 Measuring the standard half-cell potential of a $Fe^{2+}(aq)/Fe(s)$ half-cell. From the voltmeter reading and negative polarity of the iron electrode, the $E°$ of this half-cell is –0.44 V.

We can summarise the information obtained from this measurement shown in Figure 5.2.3 as follows:

$$Fe^{2+}(aq) + 2e^- \rightleftharpoons Fe(s) \quad E° = -0.44\,V$$

The negative sign indicates that the electrode in the half-cell was negative when connected to the hydrogen half-cell. Oxidation is occurring in the $Fe^{2+}(aq)/Fe(s)$ half-cell and the electrons that are produced from the iron electrode move towards the hydrogen half-cell. The value of –0.44 V is known as both the standard electrode potential and the **standard reduction potential**. The standard electrode potential gives a numerical measure of the tendency of a half-cell reaction to occur as a reduction reaction.

THE ELECTROCHEMICAL SERIES

By connecting the standard hydrogen electrode to different half-cells and measuring their standard reduction potentials, chemists have developed a table called the **electrochemical series** (Table 5.2.1).

TABLE 5.2.1 The electrochemical series. The strongest oxidising agents are at the top left of the table and the strongest reducing agents are at the bottom right of the table

	Oxidising agents		Reducing agents		$E°$ (V)
Increasing oxidising strength ↑	$F_2(g) + 2e^-$	$\rightleftharpoons$	$2F^-(aq)$	Increasing reducing strength ↓	+2.87
	$H_2O_2(aq) + 2H^+(aq) + 2e^-$	$\rightleftharpoons$	$2H_2O(l)$		+1.77
	$Au^+(aq) + e^-$	$\rightleftharpoons$	$Au(s)$		+1.68
	$Cl_2(g) + 2e^-$	$\rightleftharpoons$	$2Cl^-(aq)$		+1.36
	$O_2(g) + 4H^+(aq) + 4e^-$	$\rightleftharpoons$	$2H_2O(l)$		+1.23
	$Br_2(l) + 2e^-$	$\rightleftharpoons$	$2Br^-(aq)$		+1.09
	$Ag^+(aq) + e^-$	$\rightleftharpoons$	$Ag(s)$		+0.80
	$Fe^{3+}(aq) + e^-$	$\rightleftharpoons$	$Fe^{2+}(aq)$		+0.77
	$O_2(g) + 2H^+(aq) + 2e^-$	$\rightleftharpoons$	$H_2O_2(aq)$		+0.68
	$I_2(s) + 2e^-$	$\rightleftharpoons$	$2I^-(aq)$		+0.54
	$O_2(g) + 2H_2O(l) + 4e^-$	$\rightleftharpoons$	$4OH^-(aq)$		+0.40
	$Cu^{2+}(aq) + 2e^-$	$\rightleftharpoons$	$Cu(s)$		+0.34
	$Sn^{4+}(aq) + 2e^-$	$\rightleftharpoons$	$Sn^{2+}(aq)$		+0.15
	$S(s) + 2H^+(aq) + 2e^-$	$\rightleftharpoons$	$H_2S(g)$		+0.14
	$2H^+(aq) + 2e^-$	$\rightleftharpoons$	$H_2(g)$		0.00
	$Pb^{2+}(aq) + 2e^-$	$\rightleftharpoons$	$Pb(s)$		–0.13
	$Sn^{2+}(aq) + 2e^-$	$\rightleftharpoons$	$Sn(s)$		–0.14
	$Ni^{2+}(aq) + 2e^-$	$\rightleftharpoons$	$Ni(s)$		–0.23
	$Co^{2+}(aq) + 2e^-$	$\rightleftharpoons$	$Co(s)$		–0.28
	$Fe^{2+}(aq) + 2e^-$	$\rightleftharpoons$	$Fe(s)$		–0.44
	$Zn^{2+}(aq) + 2e^-$	$\rightleftharpoons$	$Zn(s)$		–0.76
	$2H_2O(l) + 2e^-$	$\rightleftharpoons$	$H_2(g) + 2OH^-(aq)$		–0.83
	$Mn^{2+}(aq) + 2e^-$	$\rightleftharpoons$	$Mn(s)$		–1.03
	$Al^{3+}(aq) + 3e^-$	$\rightleftharpoons$	$Al(s)$		–1.67
	$Mg^{2+}(aq) + 2e^-$	$\rightleftharpoons$	$Mg(s)$		–2.34
	$Na^+(aq) + e^-$	$\rightleftharpoons$	$Na(s)$		–2.71
	$Ca^{2+}(aq) + 2e^-$	$\rightleftharpoons$	$Ca(s)$		–2.87
	$K^+(aq) + e^-$	$\rightleftharpoons$	$K(s)$		–2.93
	$Li^+(aq) + e^-$	$\rightleftharpoons$	$Li(s)$		–3.02

Under non-standard conditions, the order of the half-cells may change.

Notice the value of 0.00 V given for the $H^+(aq)/H_2(g)$ half-equation. All other $E°$ values are relative to this arbitrary standard. The strongest oxidising agent, F_2, is at the top left of the table and the strongest reducing agent, Li, is at the bottom right of the table.

In a galvanic cell, the stronger reducing agent is oxidised so it is in the half-cell with the negative electrode (anode). The stronger oxidising agent is reduced so it is in the half-cell with the positive electrode (cathode).

Strong reducing agents donate electrons more readily than weak ones.

Strong oxidising agents accept electrons more readily than weak ones.

Strong reducing agents have weak conjugate oxidising agents.

Strong oxidising agents have weak conjugate reducing agents.

USING THE ELECTROCHEMICAL SERIES

Predicting cell reactions

You can use the electrochemical series to predict what will happen when two specific half-cells are combined to form a cell. The strongest oxidising agent in the cell will react with the strongest reducing agent.

Another way to predict the electrode reactions is to remember that the half-reaction that is higher in the electrochemical series goes forward and the lower one is reversed. As a consequence:

- a reduction reaction will occur in the half-cell with the higher $E°$ value, whereas an oxidation reaction will occur in the half-cell with the lower $E°$ value
- the positive electrode will be in the half-cell with the higher $E°$ value, whereas the negative electrode will be in the other half-cell.

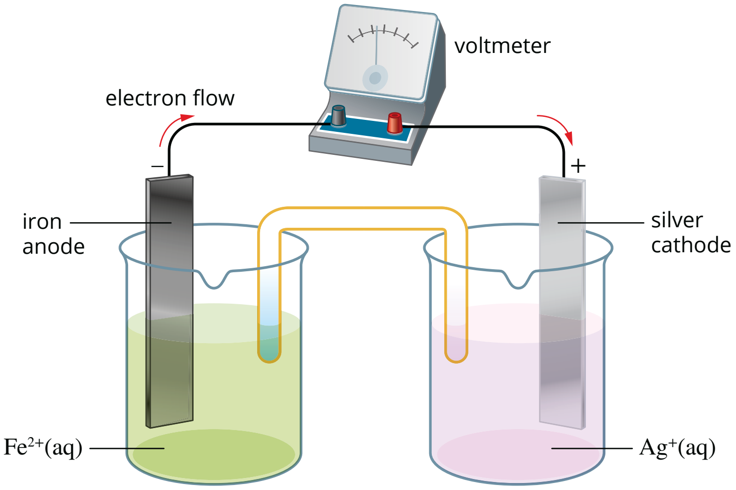
The equation for the overall cell reaction is found by adding the two half-equations. Worked Example 5.2.1 shows you how to use the electrochemical series to predict a cell reaction.

Worked example 5.2.1

PREDICTING THE OPERATION OF A GALVANIC CELL

A cell is made from $Ag^+(aq)/Ag(s)$ and $Fe^{2+}(aq)/Fe(s)$ half-cells under standard conditions and 25°C. Use the electrochemical series to predict the overall cell reaction, identify the anode and cathode, and determine the direction of electron flow.

Thinking	Working
Identify the two relevant half-equations in the electrochemical series.	$Ag^+(aq) + e^- \rightleftharpoons Ag(s) \quad E° = 0.80\ V$ $Fe^{2+}(aq) + 2e^- \rightleftharpoons Fe(s) \quad E° = -0.44\ V$
Identify the strongest oxidising agent (the species on the left of the series with the most positive $E°$ value) and the strongest reducing agent (bottom right).	Because Ag^+ is higher on the left side of the table than Fe^{2+}, it is the stronger oxidising agent. Fe, being lower on the right side of the table than Ag, is a stronger reducing agent.
Write the two half-equations that will occur. The strongest oxidising agent will react with the strongest reducing agent. (Hint: The reduction equation has the most positive $E°$ value and the oxidation equation has the most negative $E°$ value.)	Reduction: $Ag^+(aq) + e^- \rightarrow Ag(s)$ Oxidation: $Fe(s) \rightarrow Fe^{2+}(aq) + 2e^-$ Because this is the oxidation reaction, the equation should be written in reverse.
Write the overall cell equation.	Multiply the Ag^+/Ag half-cell equation by two so that the number of electrons in each half-equation is equal, and then add the two equations together: $[Ag^+(aq) + e^- \rightarrow Ag(s)] \times 2$ $Fe(s) \rightarrow Fe^{2+}(aq) + 2e^-$ $2Ag^+(aq) + Fe(s) \rightarrow 2Ag(s) + Fe^{2+}(aq)$
Identify the anode and the cathode in this cell. The anode is the electrode at which oxidation occurs. The cathode is the electrode at which reduction occurs.	The silver electrode will be the cathode and the iron electrode will be the anode.

Determine the polarities of the electrodes and the direction of electron flow in the cell. The anode is negative; the cathode is positive.	Electrons flow from the negative electrode (anode) to the positive electrode (cathode) as shown in Figure 5.2.4.  **FIGURE 5.2.4** A diagram of the cell containing Fe^{2+}/Fe and Ag^{+}/Ag half-cells.

Worked example: Try yourself 5.2.1

PREDICTING THE OPERATION OF A GALVANIC CELL

A cell is made from $Sn^{2+}(aq)/Sn(s)$ and $Ni^{2+}(aq)/Ni(s)$ half-cells under standard conditions and at 25°C. Use the electrochemical series to predict the overall cell reaction, identify the anode and cathode, and determine the direction of electron flow.

Calculating the voltage of a cell

The maximum potential difference of a cell under standard conditions is the difference between the $E°$ values of its two half-cells. It is defined as follows:

$$\begin{array}{c} \text{cell potential} \\ \text{difference} \end{array} = \begin{array}{l} E° \text{ of half-cell containing} \\ \text{the oxidising agent} \end{array} - \begin{array}{l} E° \text{ of half-cell containing} \\ \text{the reducing agent} \end{array}$$

An easy way to remember this for galvanic cells is:

$$\text{cell potential difference} = \text{higher half-cell } E° - \text{lower half-cell } E°$$

For example, the maximum cell voltage of a cell constructed from $Ag^{+}(aq)/Ag(s)$ and $Fe^{2+}(aq)/Fe(s)$ half-cells under standard conditions can be calculated as follows:

$$\begin{aligned} \text{cell potential difference} &= \text{higher half-cell } E° - \text{lower half-cell } E° \\ &= E°(Ag^{+}(aq)/Ag(s)) - E°(Fe^{2+}(aq)/Fe(s)) \\ &= 0.80 - (-0.44) \\ &= 1.24\text{ V} \end{aligned}$$

Different values for the cell voltage are obtained under non-standard conditions.

As a galvanic cell discharges, the cell voltage eventually drops to zero and the cell is referred to as ‘flat’. Equilibrium has then been reached.

The easiest way to calculate the cell potential difference is to remember:
cell potential difference = higher half-cell $E°$ – lower half-cell $E°$

5.2 Review

SUMMARY

- The standard hydrogen half-cell is used as the standard reference half-cell; its value is arbitrarily assigned as zero.
- The standard electrode potential or standard reduction potential (E°) of a half-cell is measured by connecting the half-cell to a standard hydrogen half-cell and measuring the voltage produced.
- The standard electrode potential gives a numerical measure of the tendency of a half-cell reaction to occur as a reduction reaction.
- Standard electrode potentials are used as the basis of the electrochemical series.
- In the electrochemical series, half-reactions are listed in order so that the strongest oxidising agent is at the top left of the series (with the most positive E° value) and the strongest reducing agent is at the bottom right (with the most negative E° value).
- The electrochemical series is valid for standard conditions; that is, gas pressures of 1 bar and solution concentrations of 1 M. Standard electrode potentials are usually measured at 25°C.
- The relative strengths of oxidising and reducing agents can be determined by comparing standard electrode potentials, and these can be used to predict half-cell and overall cell reactions.
- The maximum potential difference of a cell under standard conditions can be calculated from standard electrode potentials:

  $$\text{cell potential difference} = \begin{array}{l}E^\circ \text{ of half-cell}\\ \text{containing the}\\ \text{oxidising agent}\end{array} - \begin{array}{l}E^\circ \text{ of half-cell}\\ \text{containing the}\\ \text{reducing agent}\end{array}$$

  A simple way of remembering this is:

  $$\text{cell potential difference} = \text{higher half-cell } E^\circ - \text{lower half-cell } E^\circ$$

- For a spontaneous reaction to occur, an oxidising agent (on the left of the electrochemical series) must react with a reducing agent (on the right) that is lower in the series.

KEY QUESTIONS

1 A galvanic cell was constructed from $Al^{3+}(aq)/Al(s)$ and $Pb^{2+}(aq)/Pb(s)$ half-cells. Use the electrochemical series to predict the:

- **a** oxidation and reduction half-equations
- **b** overall cell reaction
- **c** identity of the anode and cathode.

2 Draw a labelled diagram of a cell formed from $Cl_2(g)/Cl^-(aq)$ and $Sn^{2+}(aq)/Sn(s)$ half-cells. Use the electrochemical series to indicate the:

- **a** half-cell reactions
- **b** anode and cathode
- **c** direction of electron flow
- **d** electrode polarities (which electrode is positive and which is negative)
- **e** directions of flow of the anions and cations in the salt bridge
- **f** overall reaction.

3 Repeat Question **2** for the cells formed from the following half-cells.

- **a** $Fe^{3+}(aq)/Fe^{2+}(aq)$ and $H^+(aq)/H_2(g)$
- **b** $Cl_2(g)/Cl^-(aq)$ and $Pb^{2+}(aq)/Pb(s)$

4 Calculate the cell potential difference for each of the cells in Questions **1–3**.

5.3 Predicting direct redox reactions

The electrochemical series provides us with a ranking of the relative strengths of oxidising and reducing agents.

In this section, you will see that you can apply your understanding of the electrochemical series to predict the likelihood of a redox reaction taking place when different chemicals are combined.

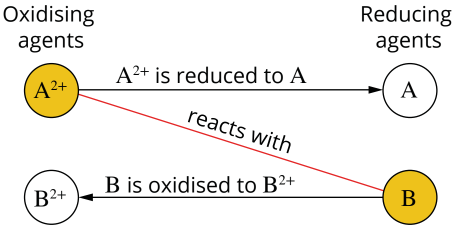
PREDICTING REACTIONS

If the contents of the half-cells of a galvanic cell were mixed, the reactants would react directly. Energy would be released as heat rather than as electrical energy. Reactions that occur in galvanic cells or when chemicals are directly mixed are described as naturally occurring reactions, or spontaneous reactions.

In the last section, you saw that in a galvanic cell the strongest oxidising agent in the cell reacts with the strongest reducing agent. In other words, the higher half-reaction (the one with the most positive $E°$ value) in the electrochemical series occurs in the forward direction (as reduction) and the lower reaction (the one with the most negative $E°$ value) occurs in the reverse direction (as oxidation).

This principle applies equally to redox reactions that occur when reactants are mixed directly.

As shown in Figure 5.3.1, for a spontaneous reaction to occur, an oxidising agent (on the left of the electrochemical series) must react with a reducing agent (on the right) that is lower in the electrochemical series.



A^{2+} reacts with B.
No reaction occurs for the other combinations: A and B, A^{2+} and B^{2+}, A^{2+} and A, A and A^{2+}, A^{2+} and B.

FIGURE 5.3.1 Oxidising agents only react significantly with reducing agents that are lower in the electrochemical series.

With half-equations arranged in order of increasing reducing agent strength, you can predict that a spontaneous reaction will occur by looking for substances that are arranged in a top-left/bottom-right position.

Worked example 5.3.1

PREDICTING DIRECT REDOX REACTIONS

Consider the following equations that appear in the order shown in the electrochemical series.

$Br_2(aq) + 2e^- \rightleftharpoons 2Br^-(aq) \quad E° = +1.09\ V$

$Ni^{2+}(aq) + 2e^- \rightleftharpoons Ni(s) \quad E° = -0.23\ V$

$Mg^{2+}(aq) + 2e^- \rightleftharpoons Mg(s) \quad E° = -2.34\ V$

Use the electrochemical series to predict the effect of mixing:

a $Br_2(aq)$ and $Mg^{2+}(aq)$ **b** $Mg^{2+}(aq)$ and Ni(s) **c** $Ni^{2+}(aq)$ and Mg(s).

Thinking	Working
Identify the two relevant half-equations in the electrochemical series.	**a** $Br_2(aq) + 2e^- \rightleftharpoons 2Br^-(aq) \quad E° = +1.09\ V$ $Mg^{2+}(aq) + 2e^- \rightleftharpoons Mg(s) \quad E° = -2.34\ V$ No reaction occurs because both $Br_2(aq)$ and $Mg^{2+}(aq)$ are oxidising agents. **b** $Ni^{2+}(aq) + 2e^- \rightleftharpoons Ni(s) \quad E° = -0.23\ V$ $Mg^{2+}(aq) + 2e^- \rightleftharpoons Mg(s) \quad E° = -2.34\ V$ No reaction occurs because the oxidising agent, Mg^{2+}, is below the reducing agent, Ni, in the electrochemical series.
Predict whether or not a reaction occurs. A chemical species on the left (an oxidising agent) of the electrochemical series reacts with a chemical species on the right (a reducing agent) that is lower in the series.	**c** $Ni^{2+}(aq) + 2e^- \rightleftharpoons Ni(s) \quad E° = -0.23\ V$ $Mg^{2+}(aq) + 2e^- \rightleftharpoons Mg(s) \quad E° = -2.34\ V$ A reaction occurs because the oxidising agent, Ni^{2+}, is above the reducing agent, Mg, in the electrochemical series.
Write the overall equation.	The higher half-equation occurs in the forward direction: $Ni^{2+}(aq) + 2e^- \rightarrow Ni(s)$ The lower half-equation occurs in the reverse direction: $Mg(s) \rightarrow Mg^{2+}(aq) + 2e^-$ The overall reaction equation is found by adding the half-equations: $Ni^{2+}(aq) + Mg(s) \rightarrow Ni(s) + Mg^{2+}(aq)$

Worked example: Try yourself 5.3.1

PREDICTING DIRECT REDOX REACTIONS

Consider the following equations that appear in the order shown in the electrochemical series:

$Cl_2(g) + 2e^- \rightleftharpoons 2Cl^-(aq) \quad E° = +1.36\ V$

$I_2(s) + 2e^- \rightleftharpoons 2I^-(aq) \quad E° = +0.54\ V$

$Pb^{2+}(aq) + 2e^- \rightleftharpoons Pb(s) \quad E° = -0.13\ V$

Use the electrochemical series to predict the effect of mixing:

a $I_2(s)$ and $Pb^{2+}(aq)$

b $Cl^-(aq)$ and $I_2(s)$

c $Cl^-(aq)$ and $Pb(s)$.

CHEMFILE

The thermite reaction

The thermite reaction is a highly exothermic reaction between powdered aluminium and iron(III) oxide.

The two relevant half-equations for this reaction, listed in order in the electrochemical series are:

$Fe^{3+} + 3e^- \rightleftharpoons Fe \quad E° = -0.036\ V$

$Al^{3+} + 3e^- \rightleftharpoons Al \quad E° = -1.67\ V$

A spontaneous reaction is predicted to occur because the oxidising agent, Fe^{3+}, is above the reducing agent, Al, in the series

The thermite reaction releases so much heat that it is enough to melt the iron that is produced. One use for the thermite reaction is for welding together railway tracks (Figure 5.3.2).

FIGURE 5.3.2 Thermite welding of railway tracks.

LIMITATIONS OF PREDICTIONS

The standard half-cell potentials given in the electrochemical series are measured under standard conditions. As you would expect, half-cell potentials can vary under other conditions.

When conditions are very different from standard conditions, the order of half-reactions in the electrochemical series may also be different, and predictions of reactions based on the standard half-cell potentials may not be reliable.

It is also important to remember that the electrochemical series gives no information about the rate at which reactions occur.

5.3 Review

SUMMARY

- The relative strength of oxidising and reducing agents can be determined by comparing standard electrode potentials, and these can be used to predict the tendency of a reaction to occur, both in galvanic cells and in direct reactions.
- For a spontaneous reaction to occur, an oxidising agent (on the left of the electrochemical series) must react with a reducing agent (on the right) that is lower in the series.
- Overall equations for redox reactions can be obtained by adding half-equations.
- When reactants react in a galvanic cell, chemical energy is transformed into electrical energy. However, when they react directly, their chemical energy is transformed into heat energy.
- The standard half-cell potentials in the electrochemical series are measured under standard conditions. Under other conditions, the order of half-reactions may be different, and predictions based on the electrochemical series may not be reliable.

KEY QUESTIONS

1 Which one of the following metals would you expect to be coated with lead when immersed in a solution of lead(II) nitrate?

A Copper
B Cobalt
C Silver
D Gold

2 Which one of the following species would react with $H_2S(g)$ but not with $H_2O(l)$ under standard conditions?

A $Cl_2(g)$
B Mg(s)
C $Ag^+(aq)$
D Cu(s)

3 Using the electrochemical series, predict whether a reaction will occur in the following situations. If a reaction does occur, write the overall equation for the reaction.

a Chlorine gas is bubbled into a solution containing bromide ions.
b Chlorine gas is bubbled into a solution containing iodide ions.
c A bromine solution is added to a solution containing chloride ions.
d A bromine solution is added to a solution containing iodide ions.

4 A reaction occurs when a strip of zinc metal is placed in a silver nitrate solution.

a Write the overall equation for the reaction.
b Describe the energy change that takes place in this reaction.

5 Iron nails are placed into 1 M solutions of $CuSO_4$, $MgCl_2$, $Pb(NO_3)_2$ and $ZnCl_2$. Use the electrochemical series to identify in which solution(s) you would expect a coating of a metal other than iron to appear on the nail.

5.4 Everyday sources of power

The battery was invented by Alessandro Volta in 1800. More than two centuries later, cells and batteries are a common power source for many household and industrial applications. Cells and batteries can be used as fixed energy storage systems, such as in solar energy systems, burglar alarms and smoke detectors. They are also used extensively in portable applications, including mobile phones, watches, digital cameras and laptop computers. The portability of these devices relies on these sources of electrical energy.

Cells and batteries use spontaneous redox reactions as the source of energy. In this section, you will look at the two main types of cells in use and how chemical reactions in these cells are used to produce electricity for everyday applications.

The two basic types of cells are:

- **primary cells**, which are disposable and designed not to be recharged
- **secondary cells**, which are rechargeable and designed to be reused many times.

Both primary cells and secondary cells are types of galvanic cells.

FIGURE 5.4.1 Non-rechargeable alkaline cells are used to power many devices, including torches, smoke detectors and calculators. They are discarded once they go flat.

PRIMARY CELLS

Common commercial **alkaline cells**, such as those you would usually use in a torch or a remote control, are **non-rechargeable cells** (Figure 5.4.1). They 'go flat' when the cell reaction reaches equilibrium, and you have to buy a replacement.

Cells that cannot be recharged are called primary cells. In primary cells, the products slowly migrate away from the electrodes or are consumed by side reactions occurring in the cell, preventing the cells from being recharged.

EXTENSION

Primary cells—alkaline cells

Following World War II, an expanding range of electrical appliances became available that required small, high-capacity power sources. With earlier types of cells unable to meet these demands, the alkaline cell was developed in the late 1960s.

Figure 5.4.2 shows the construction of an alkaline cell. This cell is similar to the simple galvanic cells looked at earlier in this chapter, but has been designed so the two half-reactions occur in separate places within the one container. A potassium hydroxide electrolyte performs the same function as a salt bridge in the simple cells.

An alkaline cell needs less electrolyte than a dry cell, which it has largely replaced for household use. The smaller quantity of electrolyte allows more reactant to be included. A typical D size alkaline cell contains about 40 g of manganese dioxide, compared with 25 g in a dry cell of equivalent size.

The following reactions occur in an alkaline cell.

- At the anode (–), zinc powder around the central metal rod is oxidised and reacts with hydroxide ions, forming zinc hydroxide:

  $Zn(s) + 2OH^-(aq) \rightarrow Zn(OH)_2(s) + 2e^-$

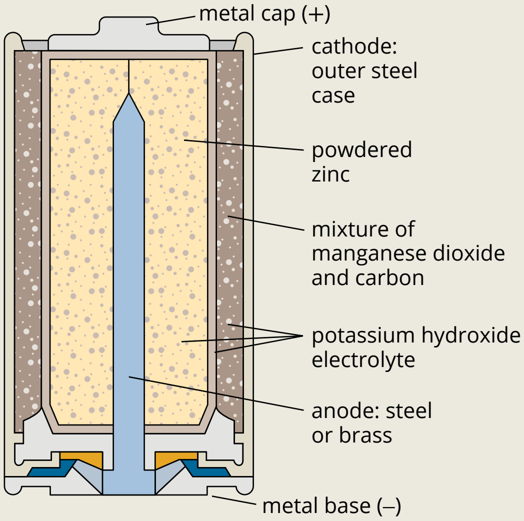


FIGURE 5.4.2 Construction of an alkaline cell.

- At the cathode (+), manganese dioxide is reduced:

  $2MnO_2(s) + H_2O(l) + 2e^- \rightarrow Mn_2O_3(s) + 2OH^-(aq)$

Alkaline cells are especially cost-effective in torches, flashguns and motorised toys, where high currents are needed intermittently. The cell produces about 1.5 V. Once the reaction in the cell reaches equilibrium, the cell is 'flat', and cannot be used again.

CHEMFILE

Powering the Overland Telegraph

One of the first primary cells in widespread use in the 19th century was called the Leclanché cell. It had a similar overall cell reaction to the reaction in alkaline cells.

Leclanché cells were one of the sources of power for the Australian Overland Telegraph Line, one of the great engineering feats of 19th-century Australia. The 3200 km telegraph line was completed in 1872 and connected Darwin in the Northern Territory with Port Augusta in South Australia, allowing fast communication between Australia and the rest of the world. An additional section to Western Australia was added in 1877.

FIGURE 5.4.3 The Alice Springs telegraph station, built in 1872.

RECHARGEABLE CELLS AND BATTERIES

Rechargeable cells such as **lithium-ion cells** and **nickel–metal hydride cells**, are known as secondary cells or **accumulators**.

Rechargeable cells and batteries have become very popular and are found in mobile phones, laptop computers, cameras and portable power tools. They are also fundamental to the operation of electric vehicles and solar power energy storage systems.

Most types of rechargeable cells can undergo many hundreds of recharges. To recharge a cell, the cell reaction must occur in reverse: the products of the reaction must be converted back into the original reactants. This is done by connecting the cell to a 'charger', a source of electrical energy, which has a potential difference a little greater than the potential difference of the cell. The positive terminal of the charger is connected to the cell's positive electrode and the negative electrode of the charger to the cell's negative electrode (see Figure 5.4.4).

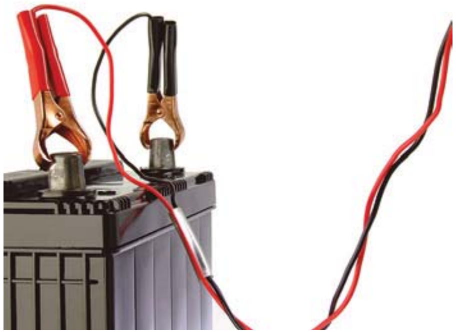


FIGURE 5.4.4 Charging a secondary battery involves connecting the positive terminal of a charger to the battery's positive electrode and the negative electrode of the charger to the battery's negative electrode.

Electrical energy supplied by the charger is converted into chemical energy in the cell. In order for it to be possible to regenerate the reactants, the products formed in the cell during discharge must remain in contact with the electrodes in a convertible form.

The energy transformations in a secondary cell can be summarised as follows.

- When a secondary cell discharges, it acts as a galvanic cell, converting chemical energy into electrical energy.
- When the cell is recharged, it acts as a type of cell called an **electrolytic cell**. Electrical energy is transformed into chemical energy in an electrolytic cell. You will learn more about the operation of electrolytic cells in Chapter 9.

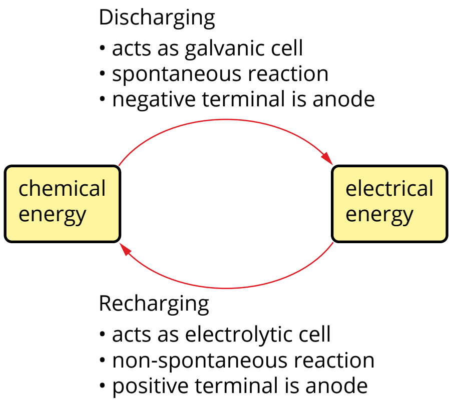


FIGURE 5.4.5 Energy transformations in secondary cells.

During the discharging process in a secondary cell:

- oxidation occurs at the negative terminal (the anode)
- reduction occurs at the positive terminal (the cathode).

However, when the cell is recharging, the cell reaction is reversed:

- oxidation occurs at the positive terminal (the anode)
- reduction occurs at the negative terminal (the cathode).

The energy transformations and redox processes that occur during the discharging and recharging of a secondary cell are summarised in Figure 5.4.5.

When a secondary cell is recharged, the reactions are reversed at each electrode:

- oxidation occurs at the positive terminal, which is now the anode
- reduction occurs at the negative terminal, which is now the cathode.

EXTENSION

Secondary batteries—car batteries

Lead–acid batteries are the most widely used type of secondary cell. They are relatively cheap and reliable, provide high currents, and have a long lifetime.

Most people know the lead–acid battery simply as a car battery (Figure 5.4.6). It is used to start the car's engine and to operate the car's electrical accessories when the engine is not running. Once the engine starts, an alternator, which is run by the engine, provides electrical energy to operate the car's electrical system and recharge the battery.

FIGURE 5.4.6 Lead–acid batteries are used to start cars, trucks and motorcycles.

Lead–acid batteries are also used for emergency light and power systems, for small-scale energy storage and to power some electric vehicles such as golf buggies and small fork lifts.

As shown in the diagram in Figure 5.4.7, a modern lead–acid battery is actually six separate cells connected together in series. The positive electrodes consist of a lead grid packed with lead(IV) oxide (PbO_2) while the negative electrodes consist of a lead grid packed with powdered lead. A solution of sulfuric acid, of about 4 M concentration, acts as the electrolyte.

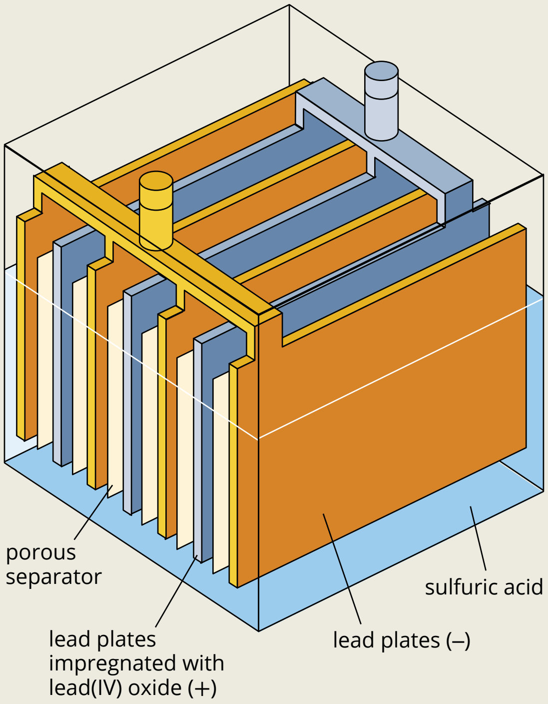


FIGURE 5.4.7 Construction of a lead–acid battery.

Each cell has a potential difference of just over 2 V. A car battery has six of these cells connected in series, giving a total potential difference of about 12 V.

The following reactions occur in a lead–acid battery as it produces electricity.

- At the anodes (–), lead is oxidised to Pb^{2+} ions:
  $Pb(s) + SO_4^{2-}(aq) \rightarrow PbSO_4(s) + 2e^-$
- At the cathodes (+), lead(IV) oxide is reduced to Pb^{2+} ions:
  $PbO_2(s) + SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \rightarrow PbSO_4(s) + 2H_2O(l)$

The two half-equations can be combined as an overall equation:

$$Pb(s) + PbO_2(s) + 2SO_4^{2-}(aq) + 4H^+(aq) \rightarrow 2PbSO_4(s) + 2H_2O(l)$$

The product of both electrode reactions, lead(II) sulfate, forms as a solid on the surface of the electrodes. This enables the battery to be recharged.

To recharge the battery, the electrode reactions are reversed. The alternator, with a potential difference of about 14 V, is used to force electrons into the battery's negative terminal and draw them out at the positive terminal, in effect driving the spontaneous reaction backwards. The recharging process converts electrical energy into chemical energy.

The overall equation for the reaction as the battery recharges is:

$$2PbSO_4(s) + 2H_2O(l) \rightarrow Pb(s) + PbO_2(s) + 2SO_4^{2-}(aq) + 4H^+(aq)$$

Battery life

The term **battery life** is used in several ways to describe the performance of a cell or battery. You might use the term to simply describe the time the battery operates in your phone following a full charge, but in technical specifications battery life normally refers to the number of charge–discharge cycles before a battery becomes unusable.

Batteries have a limited life because unwanted physical and chemical changes occur within them. A battery's performance deteriorates at each charge–discharge cycle. Modern batteries have lifetimes of 500–1200 cycles, but may continue to be useful for up to 2000 cycles, although the **battery capacity** (amount of charge available) may drop to 80% of the original value.

Many factors influence how the performance of a battery decreases over time. These include:

- loss of **active materials** (reactants and products of the cell reaction). Active material may become detached from the electrode on each cycle or be slowly converted into inactive forms by side reactions
- progressive conversion of small crystals of active material at the electrodes into larger crystals at each cycle, which increases resistance to current flow
- formation of other chemicals in side reactions that impede the efficient functioning of the cell
- impurities in cell materials, including the electrodes, which can react with active materials
- decrease in contact of electrolyte with electrodes, either through leakage of electrolyte or its transformation into a non-conductive material
- corrosion or failure of internal components.

The graph in Figure 5.4.8 (on page 146) summarises the effect of temperature on both battery life and battery capacity.

The rate of deterioration of a battery depends on temperature: the higher the temperature, the faster the deterioration occurs. Batteries release heat energy under normal operation. As the battery operating temperature rises, the rate of the side reactions increases and the battery life becomes shorter. Nickel–metal hydride batteries are particularly sensitive to the effect of heat.

Conversely, because the rates of reactions fall as temperature decreases, batteries can deliver less electric charge at a specific discharge rate under cold conditions and battery capacity decreases. In summary, cold conditions are not good for the performance of a battery; warmer conditions are not good for battery life.

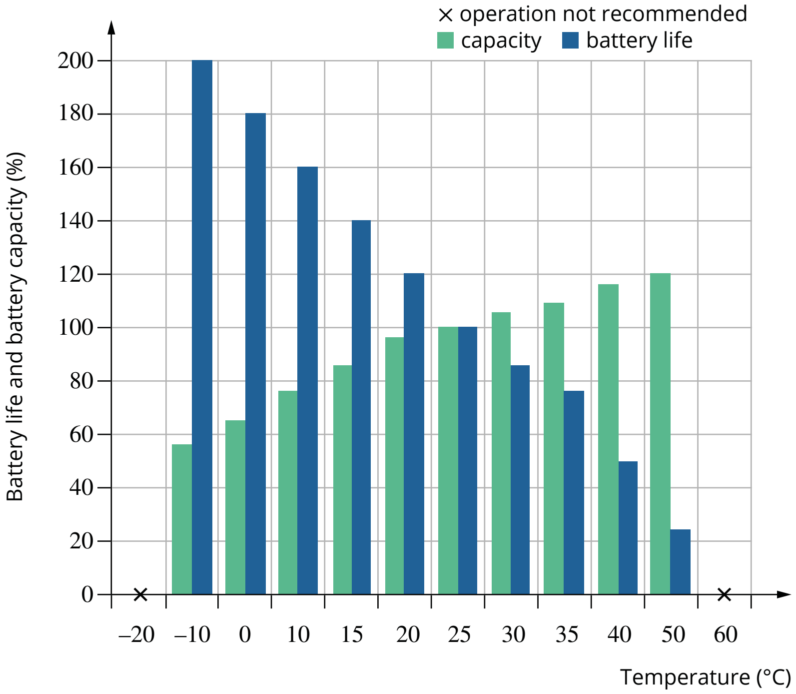


FIGURE 5.4.8 Battery life and battery capacity at different temperatures. Operation of the battery is not recommended at very low or very high temperatures.

Side reactions and deterioration continue even when batteries are not in use, in a process called **self-discharge**. The life of a battery that is not in use can be extended by storing it at a low temperature in a refrigerator, which slows the side reactions.

5.4 Review

SUMMARY

- Primary and secondary cells are examples of galvanic cells.
- Primary cells cannot be recharged.
- Secondary cells can be recharged by connecting them to an external source of electricity.
- For a cell to be rechargeable, the products of the discharge reaction have to remain in contact with the electrodes.
- During the recharging of a secondary cell, the cell reaction is reversed and the products of the cell reaction are converted back into the original reactants. Therefore, the equation for the reaction that occurs during the recharging of a secondary cell is the reverse of the equation for the cell discharging.
- For a secondary cell, the anode, where oxidation occurs, is the negative terminal during discharging but the positive terminal during recharging.
- When a secondary cell discharges and produces electrical energy, it acts as a galvanic cell; when it is recharged, it acts as an electrolytic cell.
- Battery life decreases over time, due in part to side reactions that reduce the amount of active material in a battery.
- The rate of deterioration of a battery increases as temperature increases.

KEY QUESTIONS

1 Describe the key difference between a primary cell and a secondary cell.

2 Which one of the following statements is correct about a secondary cell as it recharges?

A Oxidation occurs at the cathode, which acts as the negative terminal.
B Oxidation occurs at the cathode, which acts as the positive terminal.
C Oxidation occurs at the anode, which acts as the negative terminal.
D Oxidation occurs at the anode, which acts as the positive terminal.

3 Most modern mobile phones contain lithium-ion cells. Select the correct statement about the process that occurs when a phone battery is recharged.

A A non-spontaneous reaction occurs and the lithium-ion cell acts as an electrolytic cell.
B A non-spontaneous reaction occurs and the lithium-ion cell acts as a galvanic cell.
C A spontaneous reaction occurs and the lithium-ion cell acts as an electrolytic cell.
D A spontaneous reaction occurs and the lithium-ion cell acts as a galvanic cell.

4 Decide whether each of the following statements about cells and batteries is true or false.

a The rate of deterioration of a battery decreases as temperature decreases.
b Primary cells cannot be recharged effectively because their reaction products are not in contact with the electrodes.
c Batteries only deteriorate as they undergo charge–discharge cycles.
d Side reactions in a battery can decrease battery life.
e In a secondary cell, all of the reactants and products of the cell reaction remain in contact with the electrodes throughout the cell's life.
f The life of a modern battery is not affected by the recharging process.

5 In a silver–zinc button cell, the cell reaction is:

$$Zn(s) + Ag_2O(s) + H_2O(l) \rightarrow Zn(OH)_2(s) + 2Ag(s)$$

The zinc acts as the anode and the cell contains a potassium hydroxide electrolyte. Write a half-equation for the reaction occurring at the:

a anode
b cathode.

Chapter review

05

KEY TERMS

accumulator
active material
alkaline cell
anode
battery
battery capacity
battery life
cathode
conjugate redox pair
electrochemical cell
electrochemical series
electrode
electrolyte
electrolytic cell
electromotive force
external circuit
galvanic cell
galvanometer
half-cell
internal circuit
lead–acid battery
lithium-ion cell
nickel–metal hydride cell
non-rechargeable cell
oxidant
oxidising agent
potential difference
primary cell
rechargeable cell
redox reaction
reducing agent
reductant
salt bridge
secondary cell
self-discharge
spontaneous reaction
standard conditions
standard electrode potential
standard hydrogen half-cell
standard reduction potential
volt
voltaic cell
voltmeter

Galvanic cells

1 Which one of the following statements best describes the role of the salt bridge in a galvanic cell?

A It allows positive charges to accumulate in one half-cell and negative charges to accumulate in the other.

B It provides a pathway for electrons to move between the half-cells.

C It allows reactants from one half-cell to mix with reactants from the other half-cell.

D It allows movement of ions to balance charges formed at the electrodes.

2 Which one of the following materials would be least suitable for use as an electrode in a $Cl_2(g)/Cl^-(aq)$ half-cell?

A Iron **B** Platinum

C Graphite **D** Gold

3 Explain the difference between:

a oxidising agent and reducing agent

b anode and cathode

c conjugate redox pair and conjugate acid–base pair

d external circuit and internal circuit.

4 The overall reaction for a galvanic cell constructed from the $Cl_2(g)/Cl^-(aq)$ and $Pb^{2+}(aq)/Pb(s)$ half-cells is:

$$Cl_2(g) + Pb(s) \rightarrow 2Cl^-(g) + Pb^{2+}(aq)$$

Draw a diagram of the galvanic cell and on your diagram show:

a the direction of electron flow in the external circuit

b a half-equation for the reaction at each electrode

c which electrode is the anode

d which electrode is positive

e which way cations flow in the salt bridge.

5 Two half-cells are set up. One contains a solution of magnesium nitrate with a strip of magnesium as the electrode. The other contains lead nitrate with a strip of lead as the electrode. The solutions in the two half-cells are connected by a piece of filter paper soaked in potassium nitrate solution. When the electrodes are connected by wires to a galvanometer, the magnesium electrode is shown to be negatively charged.

a Sketch the galvanic cell described. Label the positive and negative electrodes. Mark the direction of the electron flow.

b Write the half-equations for the reactions that occur in each half-cell and an equation for the overall reaction.

c Label the anode and cathode.

d Indicate the direction in which ions in the salt bridge migrate.

The electrochemical series

6 Show that under standard conditions, according to the electrochemical series, the Daniell cell (Figure 5.1.4, page 127) should have a cell potential difference of 1.10 V.

7 The two galvanic cells shown in Figure 5.5.1 were constructed under standard conditions.

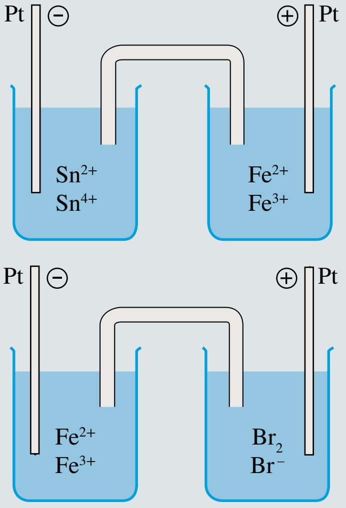


FIGURE 5.5.1 Two galvanic cells constructed under standard conditions.

On the basis of the electrode polarities, determine the order of reducing agent strength from strongest to weakest.

8 Consider the four galvanic cells made from half-cells as listed below. Use the electrochemical series to rank the galvanic cells in order of the maximum voltage they could generate under standard conditions.

- $Fe^{2+}(aq)/Fe(s)$ and $Fe^{3+}(aq)/Fe^{2+}(aq)$
- $Ni^{2+}(aq)/Ni(s)$ and $Fe^{2+}(aq)/Fe(s)$
- $Ni^{2+}(aq)/Ni(s)$ and $Br_2(l)/Br^-(aq)$
- $Ni^{2+}(aq)/Ni(s)$ and $Fe^{3+}(aq)/Fe^{2+}(aq)$

9 Each of these pairs of half-cells combines to form a galvanic cell.

i $Ag^+(aq)/Ag(s)$ and $Zn^{2+}(aq)/Zn(s)$
ii $Fe^{2+}(aq)/Fe(s)$ and $Pb^{2+}(aq)/Pb(s)$
iii $Ni^{2+}(aq)/Ni(s)$ and $Cu^{2+}(aq)/Cu(s)$

Draw a diagram of each galvanic cell and on your diagrams show:

a the direction of electron flow in the external circuit
b a half-equation for the reaction at each electrode
c an equation for the overall reaction in the galvanic cell
d which electrode is the anode
e which electrode is positive
f which way negative ions flow in the salt bridge.

10 Four half-cells $A^{2+}(aq)/A(s)$, $B^{2+}(aq)/B(s)$, $C^{2+}(aq)/C(s)$ and $D^{2+}(aq)/D(s)$ are used to make the cells shown in Figure 5.5.2.

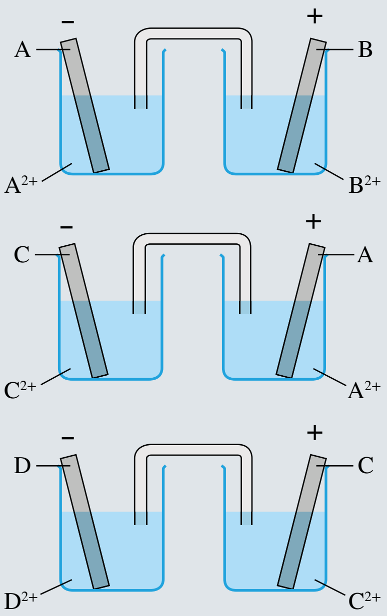


FIGURE 5.5.2 Four half-cells.

Rank the half-cells in order of their reduction half-cell potentials, from highest to lowest.

Predicting direct redox reactions

11 The following equations appear in the order shown in the electrochemical series:

$Cl_2(g) + 2e^- \rightleftharpoons 2Cl^-(aq)$
$Ag^+(aq) + e^- \rightleftharpoons Ag(s)$
$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s)$

i Predict whether a redox reaction would occur in the following mixtures. Assume concentrations of 1 M and gas pressures of 1 bar.

For mixtures where you predict a reaction will occur, write:

ii separate half-equations for the oxidation and reduction reactions
iii an overall equation.

a $Cl_2(g)$ and $Zn(s)$
b $Ag^+(aq)$ and $Ag(s)$
c $Ag^+(aq)$ and $Zn(s)$
d $Zn^{2+}(aq)$ and $Cl^-(aq)$

12 Use the electrochemical series to predict whether a reaction will occur in each of the following situations. Write an equation for each reaction that you predict will occur.

a Copper(II) sulfate solution is stored in an aluminium container.
b Sodium chloride solution is stored in a copper container.
c Silver nitrate solution is stored in a zinc container.
d An iron nail is placed in 1 M hydrochloric acid solution.
e A plumber uses hydrochloric acid to clean copper pipes.

13 The following equations form part of the electrochemical series. They are ranked in the order shown.

$Ag^+(aq) + e^- \rightleftharpoons Ag(s)$
$Pb^{2+}(aq) + 2e^- \rightleftharpoons Pb(s)$
$Fe^{2+}(aq) + 2e^- \rightleftharpoons Fe(s)$
$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s)$
$Mg^{2+}(aq) + 2e^- \rightleftharpoons Mg(s)$

a Which species is the strongest oxidising agent and which species is the weakest oxidising agent?
b Which species is the strongest reducing agent and which species is the weakest reducing agent?
c Lead rods are placed in solutions of silver nitrate, iron(II) sulfate and magnesium chloride. In which solutions would you expect to see a coating of another metal form on the lead rod? Explain.
d Which of the metals silver, zinc or magnesium might be coated with lead when immersed in a solution of lead(II) nitrate?

14 Use the electrochemical series to determine whether:

a elemental iodine is an oxidising agent or a reducing agent
b calcium metal is a strong or weak reducing agent

c nickel is a better reducing agent than silver

d $Cu^{2+}(aq)$ is a better oxidising agent than $Ag^{+}(aq)$

e $Fe^{2+}(aq)$ can act as an oxidising agent and a reducing agent.

15 **a** Use the electrochemical series to predict what might be expected to occur if hydrogen gas were bubbled through a solution containing Fe^{3+} ions.

b Write an equation for the predicted reaction.

c When the reactants were mixed in an experiment, no reaction was observed. Suggest possible reasons for this.

Everyday sources of power

16 Match the following terms with their correct definition.

Term	Definition
Galvanic cell	A rechargeable galvanic cell
Primary cell	A device that converts chemical energy into electrical energy
Secondary cell	A non-rechargeable galvanic cell

17 Explain the difference between:

a anode and cathode

b cell and battery

c discharge and recharge.

18 What feature enables secondary cells such as lithium-ion cells to be recharged?

19 Explain what happens to the oxidising agent, reducing agent, anode and cathode when a secondary cell is switched from discharge to recharge.

20 Mains electricity costs about 5 cents per MJ of energy, or less, depending on the tariff. The cost of the same amount of electrical energy produced by a cell is far more—about $1300 for a dry cell and even more for a button cell. Why are people prepared to use cells and pay such relatively high prices for electricity?

Connecting the main ideas

21 Fill in the blanks in the following passage about galvanic cells.

The redox reaction occurring in a galvanic cell takes place in two ______________. The electrode at which oxidation occurs is called the ______________, whereas the other electrode where reduction occurs is the ______________. The polarity of the anode is ______________ and the polarity of the cathode is ______________.

Galvanic cells can be classified as either primary cells, which ______________ be recharged, or secondary cells, which ______________ be recharged.

The life of commercial cells and batteries decreases as temperature ______________ and the extent of ______________ reactions increases.

22 A student was told that the redox pair $Mn^{2+}(aq)/Mn(s)$ is lower in the electrochemical series than the $Fe^{2+}(aq)/Fe(s)$ pair and higher than $Al^{3+}(aq)/Al(s)$. Explain how the student could experimentally determine the relative positions of the three pairs in the series.

23 Account for the following observations.

a Bromine reacts with iodide ions in solution but does not react with chloride ions.

b Hydrogen peroxide (H_2O_2) solution can spontaneously decompose to form water and oxygen.

c Tin metal is added to solutions of tin(II) chloride to prevent oxidation of the tin(II) ions by oxygen in air.

d Blocks of zinc are attached to the iron hulls of ships to reduce corrosion.

24 A student working in the laboratory spilled an iodine solution over the bench, causing a dark brown stain to form. Suggest how the student could remove the iodine stain.

25 What are the limitations that need to be considered when using the electrochemical series to predict whether or not a certain reaction will occur?

26 Many of the 'alkaline cells' on the market contain zinc electrodes in contact with an electrolyte containing hydroxide ions. The half-cell reaction might be represented as:

$$Zn(s) + 4OH^{-}(aq) \rightarrow Zn(OH)_4^{2-}(aq) + 2e^{-}$$

To investigate if the standard electrode potential ($E°$) of these half-cells is the same as that of a half-cell reaction using a zinc electrode in contact with a zinc nitrate electrolyte (for which the electrode reaction would be $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^{-}$), a student was provided with the two half-cells shown in Figure 5.5.3, as well as a $Cu^{2+}(aq)/Cu(s)$ half-cell.

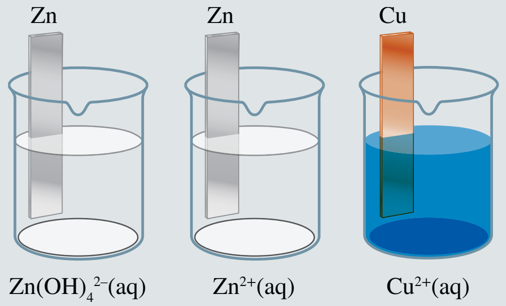
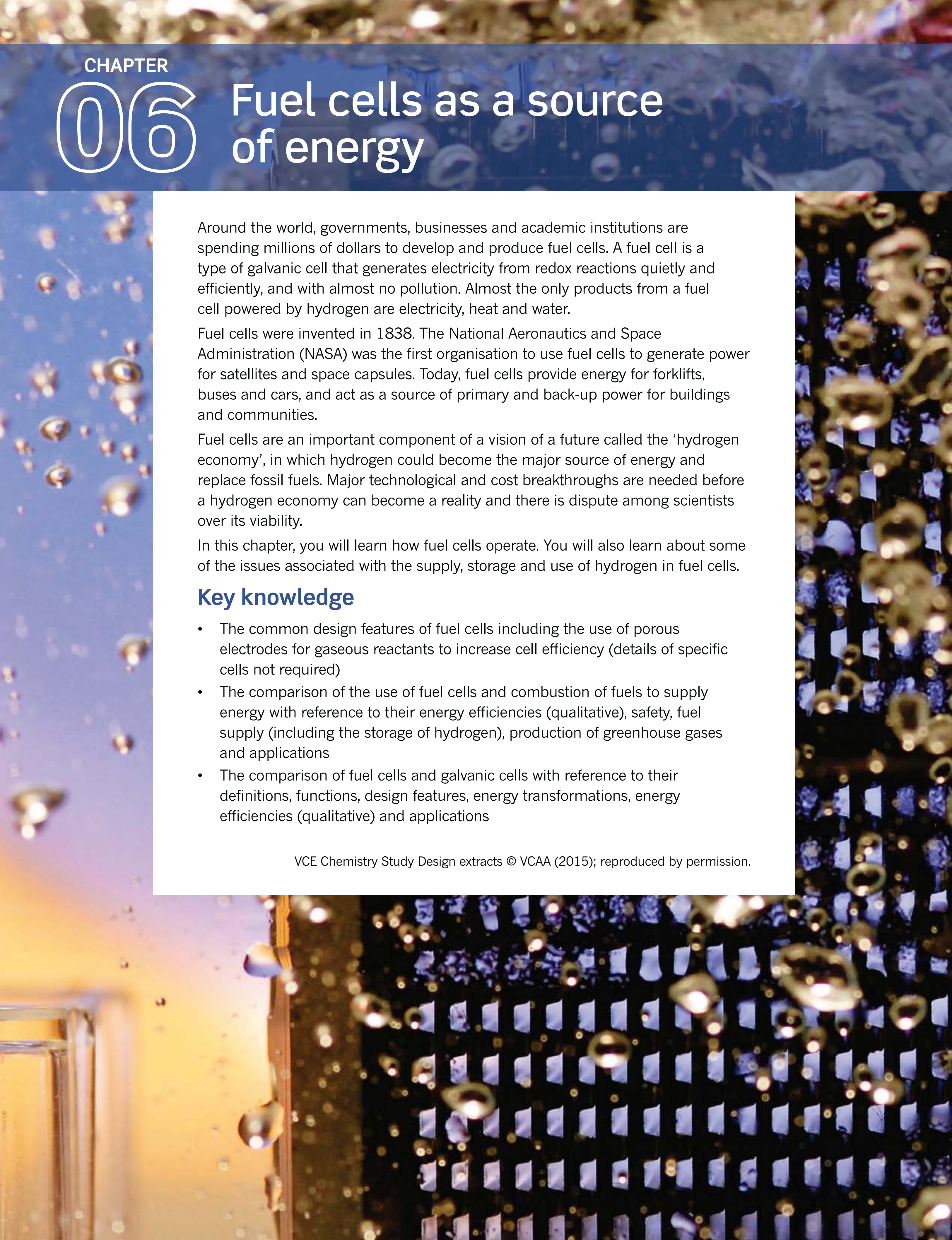


FIGURE 5.5.3 The two zinc electrode half-cells in question and the $Cu^{2+}(aq)/Cu(s)$ half-cell.

a Write a net equation for the reaction in a galvanic cell in which the 'alkaline zinc half-cell' is connected to the Cu^{2+}/Cu half-cell.

b Carefully explain how the student could use the half-cells that were provided to determine whether the two different half-cells containing zinc had the same $E°$ value. Include fully labelled diagrams with your answer and explain how the results could be interpreted.



CHAPTER

06 Fuel cells as a source of energy

Around the world, governments, businesses and academic institutions are spending millions of dollars to develop and produce fuel cells. A fuel cell is a type of galvanic cell that generates electricity from redox reactions quietly and efficiently, and with almost no pollution. Almost the only products from a fuel cell powered by hydrogen are electricity, heat and water.

Fuel cells were invented in 1838. The National Aeronautics and Space Administration (NASA) was the first organisation to use fuel cells to generate power for satellites and space capsules. Today, fuel cells provide energy for forklifts, buses and cars, and act as a source of primary and back-up power for buildings and communities.

Fuel cells are an important component of a vision of a future called the ‘hydrogen economy’, in which hydrogen could become the major source of energy and replace fossil fuels. Major technological and cost breakthroughs are needed before a hydrogen economy can become a reality and there is dispute among scientists over its viability.

In this chapter, you will learn how fuel cells operate. You will also learn about some of the issues associated with the supply, storage and use of hydrogen in fuel cells.

Key knowledge

- The common design features of fuel cells including the use of porous electrodes for gaseous reactants to increase cell efficiency (details of specific cells not required)
- The comparison of the use of fuel cells and combustion of fuels to supply energy with reference to their energy efficiencies (qualitative), safety, fuel supply (including the storage of hydrogen), production of greenhouse gases and applications
- The comparison of fuel cells and galvanic cells with reference to their definitions, functions, design features, energy transformations, energy efficiencies (qualitative) and applications

6.1 Continuous sources of electrical energy

FIGURE 6.1.1 A hydrogen fuel cell for an electric bicycle. The hydrogen bicycle operates like a standard electric bicycle, but the battery lasts three times longer.

Fuel cells use the chemical energy of hydrogen or other fuels to cleanly and efficiently generate electricity. Even though fuel cell technology is still being developed, fuel cells can be used in numerous applications. These uses include as a source of power for transport (see Figure 6.1.1) and for emergency back-up power applications.

A fuel cell is a type of **galvanic cell** but, unlike the cells you studied in Chapter 5, fuel cells do not run down or need recharging. Electricity is available for as long as fuel is supplied to them.

In this section, you will learn about how fuel cells operate, their advantages, and some of the challenges scientists face in bringing the potential of their use to reality.

FUEL CELLS

The major limitation of the cells that have been examined so far is that they contain relatively small amounts of reactants. Furthermore, when the reaction reaches equilibrium, the cell must be discarded or recharged.

Cells can be constructed in which the reactants are supplied continuously, allowing constant production of electrical energy. These devices are called fuel cells.

A key difference between a fuel cell and a primary or secondary cell is that the reactants are not stored in the fuel cell. They must be continuously supplied from an external source.

Efficiency of fuel cells

Fuel cells transform chemical energy directly into electrical energy, enabling efficient use of the energy released by spontaneous redox reactions. They are a useful source of continuous electricity and could be used to provide energy for vehicles, buildings and even cities. Energy losses such as those that occur in coal-fired power stations and combustion engines are avoided, with a consequential reduction in the volume of greenhouse gases produced.

Fuel cells are generally quoted as being 40–60% efficient, compared with efficiencies of 30–40% for thermal power stations and 25–30% for car engines, which involve a series of different energy transformations.

In addition, modern fuel cells use the waste heat that they produce to make steam. This steam can be used for heating or to operate a turbine, thus raising the efficiency of the cells to up to 85%.

Fuel cells have a much higher efficiency than thermal power stations because chemical energy is directly converted into electrical energy.

The hydrogen economy

Some scientists predict that, in the future, hydrocarbons will be replaced by hydrogen as the principal source of energy for transport and other purposes (the **hydrogen economy**). This would mean a drastic reduction in the production of greenhouse gases and other pollutants without affecting your quality of life. In the hydrogen economy, fuel cells are seen as a replacement for the internal combustion engine.

A fuel cell using hydrogen as a fuel produces electricity, water, heat and very small amounts of nitrogen dioxide and other emissions.

Although the basic principles behind the operation of a fuel cell were discovered in 1838, it was not until the 1950s that fuel cells were used for small-scale power production. Fuel cells, such as the one shown in Figure 6.1.2, were the main on-board power supply units and source of water during the Apollo space program that put humans on the Moon. An explosion in a fuel cell was responsible for the failure of the Apollo 13 mission.

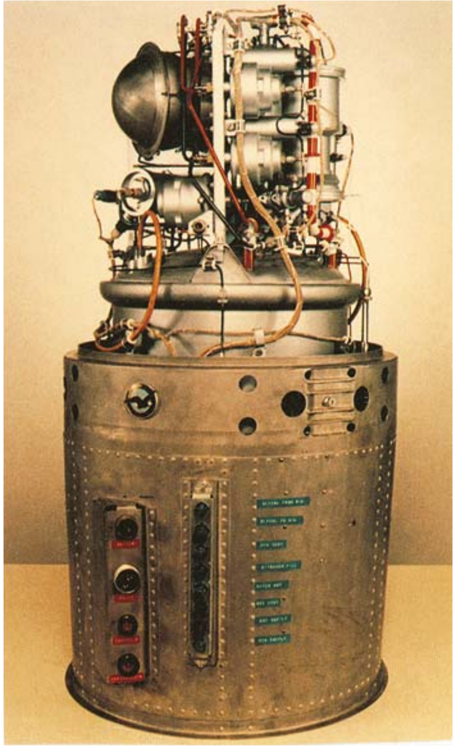


FIGURE 6.1.2 Fuel cells like this were used to supply electricity for the Apollo space program (1969–1972). Fuel cells were also used in the later space shuttles.

Fuel cell design

Figure 6.1.3 shows a simplified diagram of the key parts of a hydrogen–oxygen fuel cell. The fuel cell has two compartments: one for the hydrogen gas and the other for the oxygen gas. The gas compartments are separated from each other by two porous **electrodes** and an **electrolyte** solution. The electrode at the hydrogen compartment is the **anode**; the electrode at the oxygen compartment is the **cathode**.

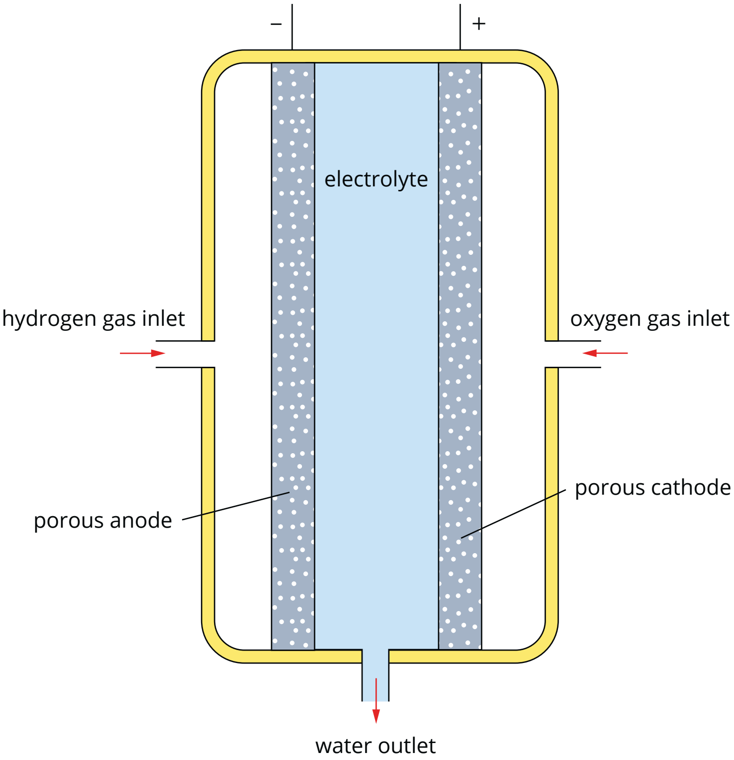


FIGURE 6.1.3 A simplified diagram showing the key parts of a hydrogen–oxygen fuel cell.

The type of fuel cell used in the Apollo program used potassium hydroxide solution as the electrolyte and the cell operated at about 250°C. Because the fuel cell uses potassium hydroxide for the electrolyte, it is commonly referred to as an alkaline fuel cell. Alkaline fuel cells are still used in the space program today.

- At the anode (–), hydrogen gas (the 'fuel') is oxidised by reacting with hydroxide ions from the electrolyte:

  $H_2(g) + 2OH^-(aq) \rightarrow 2H_2O(l) + 2e^-$
- At the cathode (+), oxygen gas is reduced:

  $O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq)$

  The overall equation for the reaction is:

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

  Each cell produces about 1 volt. Higher voltages are obtained by connecting a number of fuel cells in series to form a battery or fuel cell stack. The only by-products are water and heat.

A range of different fuel cells has been developed, using different electrolytes, electrodes and operating temperatures, as shown in Table 6.1.1.

TABLE 6.1.1 A comparison of different types of fuel cells

Fuel cell	Electrolyte	Efficiency (%)	Operating temperature (°C)	Application	Typical half-equations
Alkaline fuel cell	Potassium hydroxide	60	90–100	Space vehicles	Anode: $H_2(g) + 2OH^-(aq) \rightarrow 2H_2O(l) + 2e^-$ Cathode: $O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq)$
Methanol fuel cell	Polymer membrane	40	50–100	Mobile phones Laptop computers	Anode: $CH_3OH(l) + H_2O(l) \rightarrow CO_2(g) + 6H^+(aq) + 6e^-$ Cathode: $4H^+(aq) + O_2(g) + 4e^- \rightarrow 2H_2O(l)$
Molten carbonate fuel cell	Molten lithium, sodium or potassium carbonates	50–60	600–1000	Electricity utility	Anode: $H_2(g) + CO_3^{2-}(l) \rightarrow H_2O(l) + CO_2(g) + 2e^-$ Cathode: $O_2(g) + 2CO_2(g) + 4e^- \rightarrow 2CO_3^{2-}(l)$
Phosphoric acid fuel cell	Liquid phosphoric acid	40–45	175–200	Electricity utility Transportation	Anode: $H_2(g) \rightarrow 2H^+(aq) + 2e^-$ Cathode: $O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$
Proton exchange membrane fuel cell	Solid polyperfluoro sulfonic acid	60	60–100	Portable power Transportation	Anode: $H_2(g) \rightarrow 2H^+(aq) + 2e^-$ Cathode: $O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$
Solid oxide fuel cell	Solid zirconium oxide	50–60	600–1000	Electricity utility	Anode: $H_2(g) + O^{2-}(s) \rightarrow H_2O(l) + 2e^-$ Cathode: $O_2(g) + 4e^- \rightarrow 2O^{2-}(s)$

The nature of the electrodes is crucial to the efficiency of a fuel cell. The electrodes must be both conducting and porous to allow the hydrogen and oxygen to come into contact with the ions in the electrolyte and to allow the redox half-reactions to occur at their surface. The size of the current that can be drawn from a fuel cell depends on the surface area of the electrodes.

Catalysts are employed to enhance the rate of reaction and the current that can be produced from a cell. The catalyst incorporated in the anode increases the rate of oxidation of the fuel gas. Platinum metal is commonly used as a catalyst at this electrode. The cathode catalyst, which increases the rate of the reduction half-reaction, can be made from a different material, such as nickel powder or a nano-material.

Fuels cells contain porous electrodes that allow reactants to diffuse through them to react with ions in the electrolyte. They often contain catalysts to increase the rate of reaction.

The electrolyte in a fuel cell carries ions from one electrode to the other. Different electrolytes have been employed in fuel cells, including:

- aqueous alkaline solutions, usually KOH
- liquids such as phosphoric acid (H_3PO_4)
- molten carbonate salts, such as Na_2CO_3 or $MgCO_3$
- permeable polymer membranes, which only allow the passage of positive ions
- ceramics, made from oxides of metals such as calcium and zirconium.

CHEMFILE

Fuel cells around us

Some types of breathalysers use fuel cell technology to measure blood alcohol levels. In this fuel cell, ethanol is oxidised and the electricity generated indicates the blood alcohol level (Figure 6.1.4).

Fuel cells are also found in nature. The electric eel, which grows to more than 1 metre in length, has a natural battery made of specialised fuel cells within its body (Figure 6.1.5). The fuel for each cell is the food consumed by the eel and the oxidising agent is oxygen. Each cell generates about 1.5 V, yielding a total voltage from the head of the eel to its tail of more than 300 V.

FIGRUE 6.1.4 Hand-held breathalysers are a type of fuel cell.

FIGURE 6.1.5 Electric eels use electricity for several reasons. Low pulses of electrical discharge are emitted by the eel and then bounce back from passing objects to be detected by special electroreceptors on the skin. In this way, the eel navigates and locates its prey. High-intensity electrical discharges can also be used to stun or kill prey or as a form of defence.

HYDROGEN—A FUEL FOR FUEL CELLS

Although fuel cells can be designed to use a range of different fuels, most are designed to use hydrogen. The widespread use of hydrogen as a source of energy presents special challenges and issues, in terms of its production, distribution, storage and safety.

Hydrogen production

A fuel cell using hydrogen can be described as a 'zero-emission' device because water is almost the only product apart from electricity and heat. However, unless the hydrogen fuel is produced using renewable energy, the production of hydrogen can result in significant levels of greenhouse gases and other pollutants. To some extent, this negates the benefits of the use of fuel cells.

At present, almost 95% of hydrogen is produced from fossil fuels, such as natural gas, oil and coal through the process of **steam reforming**. In this process, steam reacts with the fossil fuel at high temperature in the presence of a nickel catalyst. The reaction for methane is represented by:

$$CH_4(g) + H_2O(g) \xrightarrow{Ni} CO(g) + 3H_2(g)$$

The carbon monoxide generated can be used to generate further hydrogen, using a copper or iron catalyst:

$$CO(g) + H_2O(g) \xrightarrow{\text{Cu or Fe}} CO_2(g) + H_2(g)$$

The hydrogen produced by steam reforming has a lower energy content than the original fuel, as some of the original chemical energy is lost as waste heat during production. Furthermore, steam reforming leads to carbon dioxide emissions, in the same way as the use of the fossil fuel in a power station or car engine would do. It is argued that hydrogen generated in this way would still be cleaner overall than fossil fuels due to the higher efficiency of fuel cells.

Advocates of the use of steam reforming for generating hydrogen for fuel cells also suggest that, because the carbon dioxide is produced at the site of the steam-reforming process, it could be possible to capture the greenhouse gas at its source and store it, preventing its release to the atmosphere.

At present, there are only two practical methods of generating hydrogen without producing carbon dioxide.

- Using electrical energy to convert water to hydrogen. Electricity can be generated from renewable sources such as solar-power farms and wind farms. (You will look at the chemical principles involved in the process of converting electrical energy to chemical energy in Chapter 9.)
- Collecting **biogas** from landfill sites and converting the methane in the gas to hydrogen by steam reforming.

Hydrogen storage

Widespread adoption of hydrogen as the primary fuel (for powering vehicles and providing electricity for industrial and domestic applications) would require massive expenditure on infrastructure. Changes to pipelines and filling stations, as well as improvements in hydrogen storage methods, would be required. Figure 6.1.6 shows a vision for the future use of hydrogen.

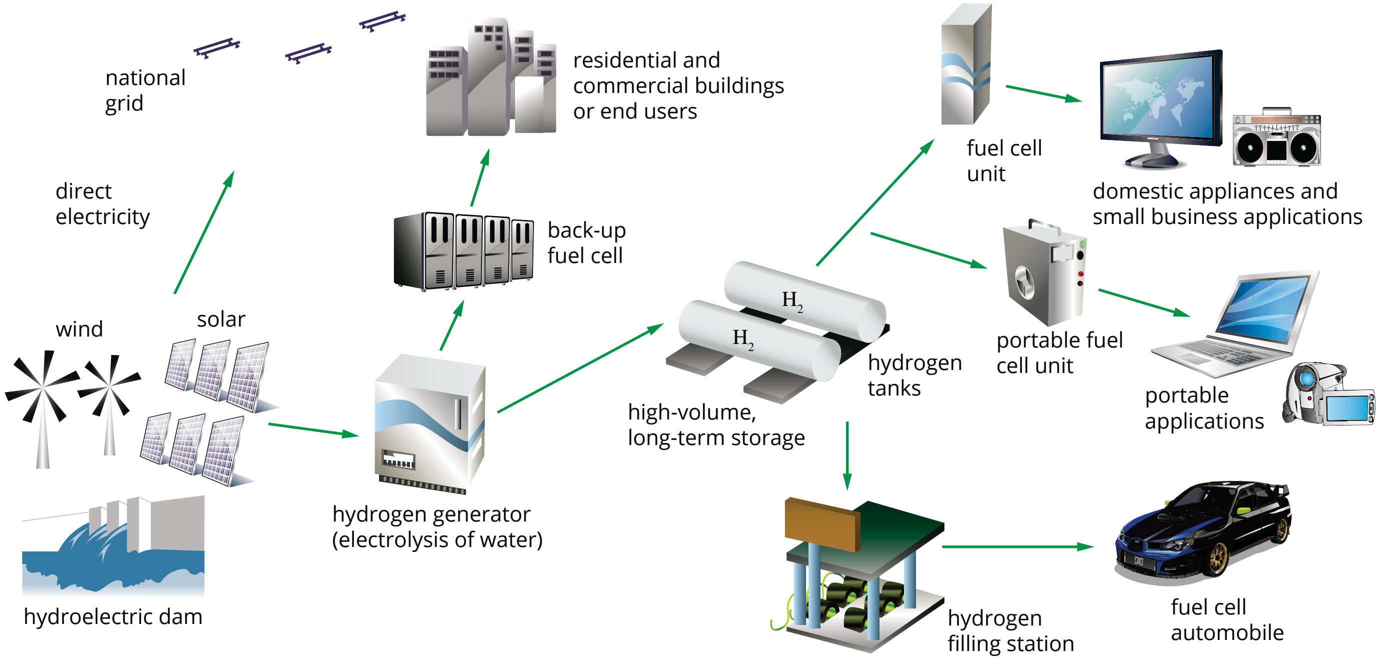


FIGURE 6.1.6 A view of future energy production based on the use of hydrogen.

Although hydrogen has a very high energy content by mass (143 kJ g^{-1}) compared with fuels such as petrol (44 kJ g^{-1}), there are issues with storage, particularly within vehicles. This is because hydrogen is a gas at room temperature.

The established methods of hydrogen storage in cars, trucks and buses are as liquid hydrogen or compressed hydrogen.

- *Liquid hydrogen*. Liquid hydrogen boils at the extremely low temperature of –252°C and a considerable quantity of energy is needed to liquefy it. The tanks used to store liquid hydrogen must be well insulated. The energy available per litre of liquid hydrogen (8 MJ L^{-1}) is about four times less than for a liquid hydrocarbon fuel such as petrol (32 MJ L^{-1}), so a vehicle using liquid hydrogen requires a much larger fuel tank to achieve the same driving range.
- *Compressed hydrogen*. Hydrogen can be stored in high-pressure tanks (up to 700 bar pressure). A high-pressure hydrogen storage tank needs to be larger to store the same amount of energy as a liquid hydrogen tank. In fact, using currently available high-pressure technology, a high-pressure tank would need to be larger than the boot of a typical car to effectively replace a standard hydrocarbon fuel tank.

Scientists are investigating alternative methods of storing hydrogen, known generally as **materials-based storage** (see Figure 6.1.7), which offer considerable promise but require further development.

- Hydrogen can **adsorb** to the surface of materials such as metal hydrides, either as hydrogen molecules or as hydrogen atoms.
- Hydrogen can also dissociate and be **absorbed** into the lattice structure of some solid materials.
- Hydrogen can react reversibly with a range of different chemicals.

By these means, it may be possible to store hydrogen in smaller volumes at low pressure and at temperatures close to room temperature.

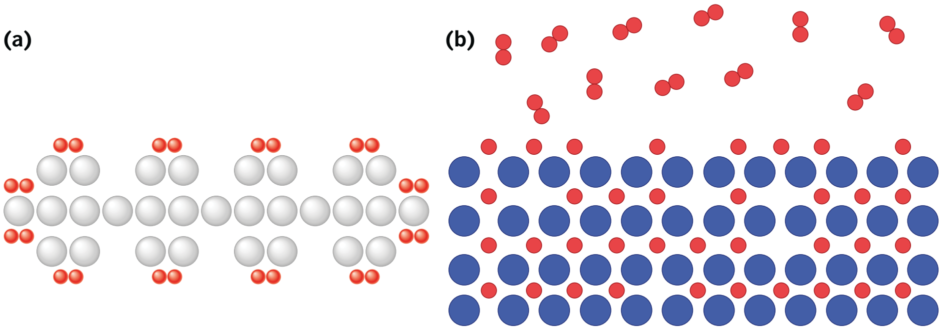


FIGURE 6.1.7 Two materials-based methods of storing hydrogen: (a) surface adsorption of hydrogen molecules and (b) absorption into a solid lattice as hydrogen atoms.

Safety issues

Hydrogen is generally regarded as a more dangerous fuel than hydrocarbon fuels such as petrol. Hydrogen burns readily and a flame or spark will ignite almost any combination of hydrogen and air. An explosion, rather than merely a flame, is the likely outcome.

On the other hand, the low density of hydrogen means that, if a leak occurs, hydrogen rises rapidly and quickly disperses in ventilated areas, often without ignition. In fact, a fire in a hydrogen-powered vehicle can be less damaging than a fire in a petrol-powered vehicle.

The use of hydrogen poses unique safety challenges. Strict codes and standards will be required for its use, including the need for hydrogen sensors to detect leaks. A number of studies have concluded that, while there are different safety concerns, hydrogen is no more dangerous than petrol. Experts predict that, in the future, hydrogen will be used as a fuel with at least the same level of safety and convenience as today's hydrocarbon fuels.

FIGURE 6.1.8 Technicians with a prototype aircraft powered by a combination of solar cells, which power the on-board electronics, and a hydrogen fuel cell, which powers the electric engine.

APPLICATIONS OF FUEL CELLS

Most major vehicle manufacturers are investigating the use of fuel cells as an alternative to the internal combustion engine, given that fuel cells have better fuel efficiency and lower emissions of greenhouse gases and other pollutants. Also, fuel cells do not rely on oil (Figure 6.1.8).

Aside from their use in transport, the use of fuel cells is small at present but growing rapidly.

- A 1.3 MW power plant in Italy is a phosphoric acid fuel cell that uses hydrogen from steam reforming of natural gas as its fuel source (Figure 6.1.9).
- A 59 MW power plant began operation in South Korea in 2014, providing power and heat for local homes.
- One supermarket chain in the United States has ordered fuel cells to power its fleet of 1700 forklifts.
- Silicon Valley technology companies in California, USA, are installing fuel cells as a stable, sustainable source of power.

FIGURE 6.1.9 Interior of the PRODE fuel cell power station in Milan, Italy, which began operating in 1992. The cells use hydrogen as the fuel and phosphoric acid as the electrolyte. The fuel cells can produce up to 1.3 MW of electricity.

EXTENSION

Redox flow batteries

An interesting type of fuel cell under development is the redox flow battery, which has the potential of cheaper energy storage than devices such as lead–acid batteries.

As shown in Figure 6.1.10, a redox flow battery has two separate compartments of solutions containing the reactants. A wide range of different reactants has been used in experimental cells. The solutions are pumped into the cell from storage tanks. A membrane between the compartments allows exchange of ions while preventing contact between the two solutions.

A redox flow battery can be recharged by applying an opposite voltage to the cell, which causes the reverse cell reaction to occur. Alternatively, for a rapid recharge, the spent solutions can be replaced with a new batch of solutions.

Although these batteries could provide cheaper energy storage, their storage tanks, pumps and flow control units add to their weight and make their operation complicated.

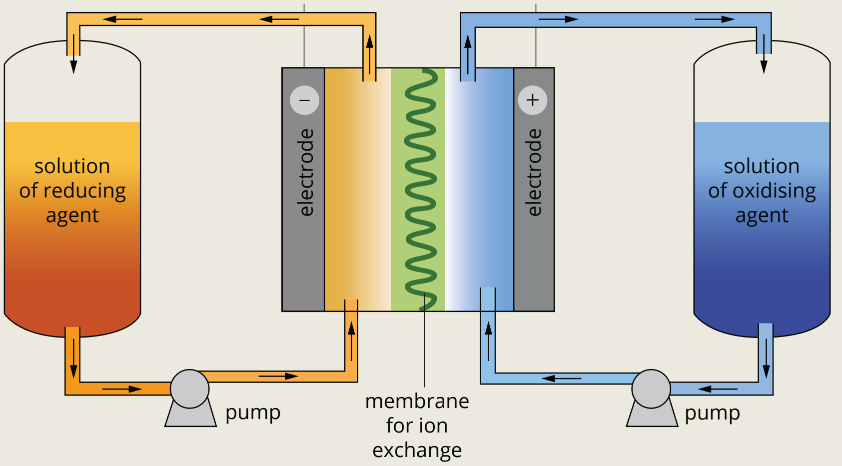


FIGURE 6.1.10 A representation of a redox flow battery.

ADVANTAGES AND DISADVANTAGES OF FUEL CELLS

Scientists are striving to reduce the overall costs of fuel cells and to improve the electric current that can be drawn from them by increasing the rate of reaction at the electrodes. As described above, various types of fuel cells have been developed and tested, using a number of different fuels, electrolytes and catalysts.

Table 6.1.2 lists some of the advantages and disadvantages of fuel cells.

TABLE 6.1.2 Advantages and disadvantages of fuel cells

Advantages	Disadvantages
• Fuel cells convert chemical energy directly to electrical energy. This is more efficient than the series of energy conversions that takes place in power stations that burn fossil fuels: chemical energy → heat energy → mechanical energy → electrical energy. • Hydrogen fuel cells produce water and heat as by-products. No greenhouse gases, such as carbon dioxide, are released. • Fuel cells will generate electricity as long as the fuel is supplied. Conventional batteries need to be recharged or replaced. • Fuel cells can use a variety of fuels. • Electricity can be generated on-site and users are not reliant on connection to an electricity grid. Waste heat can be used to heat water for a hot water system or provide heating for a home during winter.	• Fuel cells require a constant fuel supply. • Fuel cells are expensive. They are still a developing technology, and are not being made in large numbers so there are no economies of scale as there are in other industries. • Some types of fuel cell use expensive electrolytes and catalysts. • The use of fuel cells in transport will require an extensive network of hydrogen filling stations before it can become widespread. • Fuel cells generate a direct current (DC); electrical appliances used in the home and in industry rely on an alternating current (AC). An inverter is required to change DC to AC at the appropriate voltage. • At present, the hydrogen used in many fuel cells is mainly sourced from fossil fuels. This process involves energy losses and generates greenhouse gases. • There are significant issues associated with the storage and safety of hydrogen fuel.

COMPARING FUEL CELLS AND PRIMARY AND SECONDARY CELLS

A fuel cell is a type of galvanic cell in which the reactants are supplied continuously.

Unlike the **primary cells** and **secondary cells** described in Chapter 5, which can produce power for only a limited time until their reactants are depleted, in a fuel cell the reactants (a combustible fuel and oxygen or air) are constantly entering the cell and products are being removed.

Primary and secondary cells and fuel cells are compared in Table 6.1.3.

TABLE 6.1.3 A comparison of galvanic cells and fuel cells

	Primary and secondary cells	Fuel cells
Definition	A primary or secondary cell is a type of galvanic cell, or **voltaic cell**. These galvanic cells are **electrochemical cells** that convert chemical energy from spontaneous redox reactions in the cell into electrical energy. The reactants in primary and secondary cells are contained within the galvanic cell. As a consequence, primary and secondary cells can produce power for only a limited time until their reactants are depleted.	A fuel cell is a galvanic cell that converts the chemical energy of a fuel into electrical energy. The fuel and air or oxygen are supplied continuously.
Function	To produce electrical energy; they are particularly useful as a source of portable electrical energy.	To produce electrical energy; they are particularly useful as a continuous source of high electric current for both portable and fixed applications.
Design features	• Oxidation occurs in one part of the cell and reduction in another. • An oxidation half-reaction occurs at the negatively charged anode. • A reduction half-reaction occurs at the positively charged cathode. • A salt bridge composed of an electrolyte carries charge between the electrodes.	• Two separate compartments are present: one for inflow of a combustible gaseous fuel (at the negatively charged anode) and the other for oxygen or air (at the positively charged cathode). • An oxidation half-reaction occurs at the negatively charged anode. • A reduction half-reaction occurs at the positively charged cathode. • Electrodes are porous to allow contact between reactant gases and the electrolyte. • Catalysts are used to increase cell efficiency. • An electrolyte carries charge between the electrodes.
Energy transformations	Chemical to electrical	Chemical to electrical
Energy efficiencies	60–90% (high compared with energy efficiency of power stations and hydrocarbon-powered cars).	40–60% efficient; up to 85% if heat produced by the cell is also used to generate electricity.
Typical applications	Primary cells: energy for watches, remote controls, portable radios, cameras, heart pacemakers and hearing aids Secondary cells: cars, mobile phones, cameras, computers, power tools	Cars, buses, commercial electricity generation, emergency back-up power supplies

6.1 Review

SUMMARY

- Fuel cells are a type of galvanic cell, converting chemical energy directly into electrical energy.
- Fuel cells are devices in which the reactants (usually gases) are supplied continuously, allowing constant production of electrical energy.
- The electrodes used in fuel cells allow direct contact between the gases and electrolyte. They have a high surface area and are porous to ensure high cell efficiency. Catalysts are often part of an electrode to increase the rate of reaction.
- Electricity generation using fuel cells is more efficient than if the electricity were generated by the combustion of the same fuel.
- The emissions of greenhouse gases from a fuel cell are much less than if the fuel were burnt in a power station or internal combustion engine.
- Some scientists predict that fuel cells will play a key role in the transition from a dependence on fossil fuels for energy to a hydrogen economy.
- The widespread use of hydrogen as a source of energy presents special challenges and issues, in terms of its production, distribution, storage and safety.

KEY QUESTIONS

1 Which one of the following is a correct statement about what happens in a hydrogen–oxygen fuel cell.

A Hydrogen gas is oxidised at the anode.
B Electrons flow through the external circuit from cathode to anode.
C Solid, impermeable electrodes are required to prevent contact between reactants and the electrolyte.
D Oxygen gas is oxidised at the anode.

2 Which one or more of the following features do secondary cells and fuel cells have in common as they produce electricity?

A A catalyst is used to increase reaction rate.
B Cations in the electrolyte move towards the cathode.
C The anode is negative.
D The cathode is constructed from a porous material.
E Oxidation occurs at the cathode.
F The oxidising agent is a gas.
G Chemical energy is converted into electrical energy.

3 Hydrogen gas and oxygen gas are reacted in a phosphoric acid fuel cell, which is a type of fuel cell that uses liquid phosphoric acid as an electrolyte.

a Write equations for the half-reactions that occur at the anode and cathode.
b Based on the two half-equations from part **a**, determine the overall cell equation for this reaction.

4 An experimental fuel cell that uses methanol as the fuel has the half-equations:

$CH_3OH(g) + 6OH^-(aq) \rightarrow CO_2(g) + 5H_2O(l) + 6e^-$

$O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq)$

a Write the equation for the overall cell reaction.
b Which reaction occurs at the positive electrode of the cell?
c Suggest a suitable electrolyte for the cell.
d When the cell begins to produce electricity, the pH of the electrolyte near the cathode increases and eventually reaches a constant value. Explain why this occurs.
e Electricity could be obtained from thermal energy produced by combustion of methanol. What is the main advantage of using a fuel cell to produce electricity?

5 Why is large-scale production of electricity using fuel cells suggested as part of a solution to the greenhouse problem?

Chapter review

06

KEY TERMS

absorb
adsorb
anode
biogas
cathode
electrochemical cell
electrode
electrolyte
fuel cell
galvanic cell
hydrogen economy
materials-based storage
primary cell
secondary cell
steam reforming
voltaic cell

Continuous sources of electrical energy

1 Which one of the following reactions might be used as the basis for an experimental fuel cell?

A $2CO(g) + O_2(g) \rightarrow 2CO_2(g)$
B $2NO_2(g) \rightarrow N_2O_4(g)$
C $HCl(g) + NH_3(g) \rightarrow NH_4Cl(s)$
D $CO_2(g) + H_2O(l) \rightarrow H_2CO_3(aq)$

2 Which one of the following statements best describes the role of the electrolyte in a fuel cell?

A It allows positive charges to accumulate in one half-cell and negative charges to accumulate in the other.
B It allows direct contact of the fuel from the anode to mix with the oxidising agent from the cathode.
C It allows movement of ions to balance charges formed at the electrodes.
D It provides a pathway for electrons to move between the half-cells.

3 Which one of the following substances is least likely to be found as a reactant at the anode of a fuel cell?

A CH_3OH
B CO_2
C H_2
D CH_4

4 Which one of the following is not being considered as a means of storing hydrogen for use in fuel cells?

A Adsorbed to the surface of metal hydrides
B As pure solid hydrogen
C As pure compressed hydrogen
D As pure liquid hydrogen

5 Indicate whether the following statements about the generation, storage and safety of hydrogen are true or false.

a Most of the hydrogen produced in the world is generated from fossil fuels.
b Hydrogen is regarded by scientists as almost twice as dangerous a fuel for vehicles as petrol.
c Hydrogen can be stored by adsorption onto metal hydrides.
d Fuel cell vehicles fitted with a tank of liquid hydrogen can travel up to four times further than fuel cell vehicles fitted with petrol tanks of the same size.
e Hydrogen stored under pressure can provide the same energy per litre as hydrocarbon fuels.

6 Select the correct answer from the options given in bold to complete the following paragraphs, which summarise information about fuel cells.

Fuel cells convert **chemical/electrical** energy to **chemical/electrical** energy and are a type of galvanic cell. At the anode, the **fuel/oxidising agent** undergoes **oxidation/reduction** whereas at the cathode the **fuel/oxidising agent** is **oxidised/reduced**. Energy is supplied constantly if **reactants/products** are available.

The nature of the electrodes is critical to the operation of the fuel cell. Electrodes must conduct electricity, catalyse the reaction and allow contact between the **electrolyte/oxidising agent** and the fuel and the **electrolyte/fuel** and the oxidising agent. There must be **controlled contact / no direct contact** between the fuel and the oxidising agent.

Electricity generation using fuel cells is **more/less** efficient than if the electricity were generated by the combustion of the same fuel. The emissions of greenhouse gases from a fuel cell are **much less/ significantly greater** than if the fuel were burnt in a power station or internal combustion energy.

While hydrogen–oxygen fuel cells are a clean energy source producing only **energy and water /oxygen**, the production, storage, distribution and safety of **hydrogen/water** are challenging issues.

7 Label the diagram of a hydrogen–oxygen fuel cell in Figure 6.2.1.

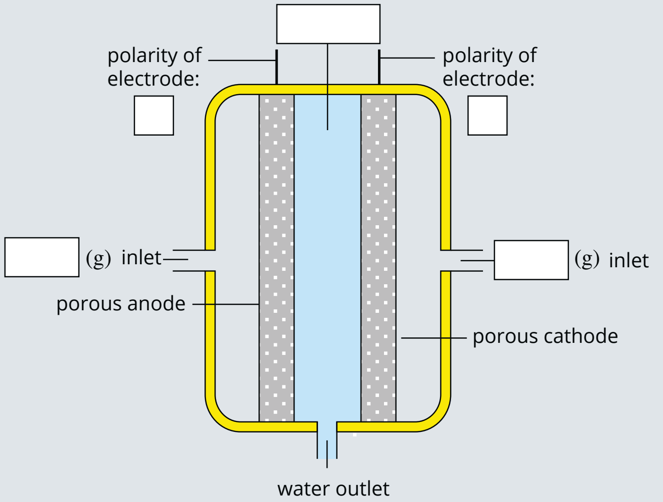


FIGURE 6.2.1 A hydrogen–oxygen fuel cell.

8 Decide whether the following statements apply to fuel cells, primary cells or secondary cells. Some statements apply to all types of cells.

- **a** Convert chemical to electrical energy.
- **b** Oxidation occurs at the anode and reduction occurs at the cathode.
- **c** The anode is the negative electrode as the cell generates electricity.
- **d** Recharged by connecting to a power supply.
- **e** Electrode reactions occur in separate compartments.
- **f** Chemical energy is stored within the cell.
- **g** Reactant is supplied constantly.

9 A fuel cell is used as a breathalyser to detect the presence of alcohol in a motorist's breath.

The equation for the cell reaction is:

$CH_3CH_2OH(g) + O_2(g) \rightarrow CH_3COOH(aq) + H_2O(l)$

In this reaction, ethanol (CH_3CH_2OH) is oxidised to ethanoic acid (CH_3COOH) and oxygen is reduced to water.

- **a** Write an equation for the half-reaction that occurs at the anode.
- **b** Write an equation for the half-reaction that occurs at the cathode.
- **c** As the cell operates, will cations in the electrolyte move towards the anode or the cathode?
- **d** Explain whether the fuel cell will generate a voltage if natural gas, which contains mostly methane, is blown into the breath inlet.

10 An experimental fuel cell uses methane as the source of energy. The relevant half-equations in the electrochemical series are:

$CO_2(g) + 8H^+(aq) + 8e^- \rightleftharpoons CH_4(g) + 2H_2O(l)$

$E^\circ = +0.17$ V

$O_2(g) + 4H^+(aq) + 4e^- \rightleftharpoons 2H_2O(l)$

$E^\circ = +1.23$ V

- **a** Write a half-equation for the reaction that occurs at the negative electrode of the fuel cell.
- **b** If the fuel cell operates under standard conditions, what is the maximum voltage that could be generated?

11 A fuel cell uses methanal gas (HCHO) as a fuel and oxygen gas as the oxidising agent. It uses an alkaline electrolyte and operates at 70°C.

- **a** Write the equation for the overall cell reaction.
- **b** What is the half-equation for the cathode reaction?

Connecting the main ideas

12 An Australian company developed a ceramic fuel cell. Instead of a liquid electrolyte, the cell uses a ceramic electrolyte through which oxide ions (O^{2-}) can move. The fuel cells are designed so that the fuel and air are directed separately onto the appropriate electrode. The diagram in Figure 6.2.2 represents a ceramic fuel cell that uses methane gas (CH_4) as the energy source. The electrode reactions are:

$O_2(g) + 4e^- \rightarrow 2O^{2-}(s)$

$CH_4(g) + 4O^{2-}(s) \rightarrow CO_2(g) + 2H_2O(g) + 8e^-$

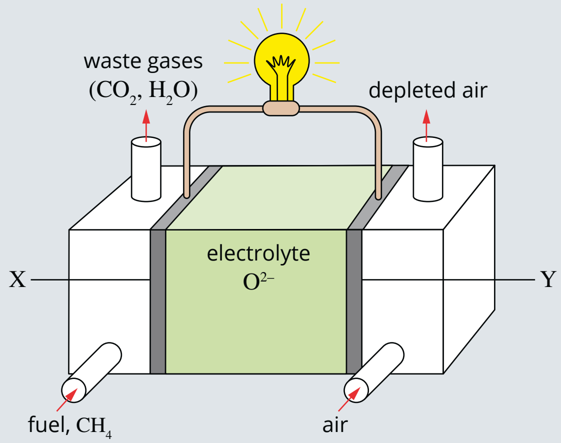


FIGURE 6.2.2 A ceramic fuel cell.

- **a** Write an overall equation for the reaction that occurs in this ceramic fuel cell.
- **b** Identify electrodes X and Y as the cathode or the anode.
- **c** Explain the claim that this method of generating electricity will reduce carbon dioxide emissions, by comparison with a power plant that burns natural gas (containing methane) and uses the heat released to boil water and then generate electricity.

13 Consider the similarities and differences between a primary cell and a fuel cell.

- **a** List the design features that the two types of cells have in common.
- **b** List the design features that are different in the two types of cells.

14 'Hydrogen–oxygen fuel cells are the energy source of the future.' Discuss the advantages and disadvantages of an energy supply based on these fuel cells.

UNIT 3 • Area of Study 1

REVIEW QUESTIONS

What are the options for energy production?

Multiple-choice questions

1 Which of the following is **not** an example of using the energy obtained from a fuel to produce electrical energy?

A Production of electricity in a methanol fuel cell
B Production of electricity in a wind turbine
D Production of electricity in a coal-fired power plant
D Production of electricity in a nuclear power plant

2 Which of the following is **not** characteristic of a reaction in which energy is obtained from a fuel?

A It is exothermic.
B Chemical energy (enthalpy) is converted into other forms of energy.
C The combined enthalpy of the products is higher than that of the reactants.
D The enthalpy change (ΔH) is negative.

3 Which of the following equations correctly represents the complete combustion of ethanol?

A $CH_3CH_2OH(l) + O_2(g) \rightarrow 2C(s) + 3H_2O(g)$
B $CH_3CH_2OH(l) + 2O_2(g) \rightarrow 2CO(g) + 3H_2O(g)$
C $CH_3CH_2OH(l) + O_2(g) \rightarrow CH_3COOH(l) + H_2O(g)$
D $CH_3CH_2OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(g)$

4 Two gaseous fuels that have been investigated as possible alternative energy sources are hydrogen gas, (H_2) and biogas, which comprises mostly methane (CH_4). The table below shows the energy released by the combustion of 1 mol of hydrogen and 1 mol of methane.

Fuel	**Equation for combustion reaction**	**Energy released per mole of fuel (kJ mol⁻¹)**
Hydrogen	$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(g)$	242
Methane	$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$	802

Consider the following situations that may apply to the use of the fuels.

I Limiting greenhouse gas emissions is very important.
II Equal masses of the two gases are to be stored.
III Equal volumes of the gases are to be stored (at the same temperature and pressure).

Hydrogen gas would be the preferred fuel in which situation(s)?

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

The following information relates to Questions 5–7.

Biodiesel manufactured from plant oils is an increasingly important alternative to the petrodiesel isolated from crude oil. One issue with the use of biodiesel is that it has a higher affinity for water than petrodiesel, and consequently has a higher water content. However, the potential reduction in net greenhouse emissions of switching to biodiesel makes it very attractive.

5 The reason for the higher affinity of biodiesel for water is that:

A molecules in biodiesel possess polar functional groups that enable bonding to water molecules
B biodiesel is 'natural' and natural things always have an affinity for water
C the water is removed from petrodiesel in the refining process
D the larger molecules in biodiesel are able to form more bonds to water molecules.

6 The use of biodiesel in cold climates can be problematic because:

A at low temperatures the molecules in biodiesel undergo decomposition
B unburnt fuel can clog the exhaust systems of motor vehicles
C combustion of biodiesel at low temperatures increases greenhouse gas emissions
D its higher viscosity can cause fuel line blockages.

7 The difference in the amount of carbon dioxide generated by the combustion of petrodiesel and biodiesel is very small, yet it is argued that switching to biodiesel will reduce net greenhouse emissions. This is mainly because:

A growing plant feedstocks for biodiesel production removes carbon dioxide from the air through photosynthesis
B the carbon dioxide produced by burning fossil fuels is a stronger greenhouse gas than the carbon dioxide produced by burning biofuels
C combustion of biodiesel produces fewer other greenhouse gases, such as methane
D biodiesel combustion produces significantly more energy so less needs to be burnt for the same energy output.

Refer to the following equation for the reaction between hydrochloric acid and ammonia solution when answering Questions 8 and 9.

$HCl(aq) + NH_3(aq) \rightarrow NH_4Cl(aq) \quad \Delta H = -52 \text{ kJ mol}^{-1}$

8 The reaction is:

A endothermic, because the energy involved in bond forming is more than that involved in bond breaking

B endothermic, because the energy involved in bond forming is less than that involved in bond breaking

C exothermic, because the energy involved in bond forming is more than that involved in bond breaking

D exothermic, because the energy involved in bond forming is less than that involved in bond breaking.

9 Which of the following happens when hydrochloric acid and ammonia solutions are allowed to react in a perfectly insulated container?

A The total energy inside the container decreases.

B The total energy inside the container increases.

C The total energy inside the container is unchanged but there is less enthalpy (chemical energy) after the reaction.

D The total energy inside the container is unchanged but there is more enthalpy (chemical energy) after the reaction.

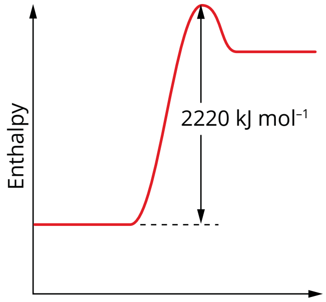
The following information relates to Questions 10–12.

As a response to rising petrol prices, the Australian Government in 2006 offered car owners a $2000 incentive to convert their cars from petrol to LPG. Propane is one of the gases in the mixture sold as LPG. The thermochemical equation for the complete combustion of propane is:

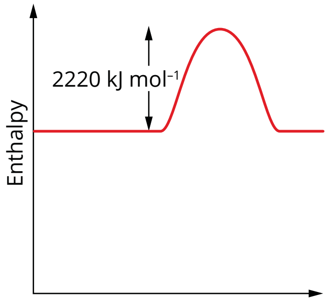
$$C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(l) \qquad \Delta H = -2220 \text{ kJ mol}^{-1}$$

10 Which energy profile diagram best represents the energy changes that take place during this reaction?

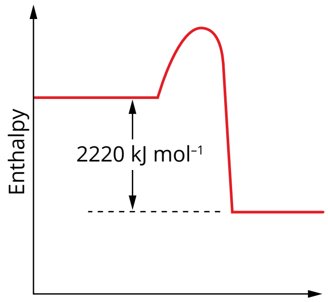
A



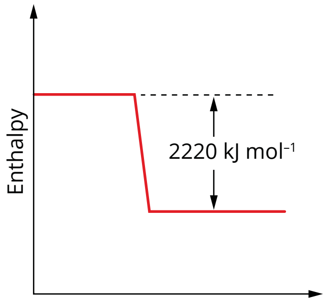
B



C



D



11 When 10.0 g of propane undergoes complete combustion:

A 5.05×10^3 kJ of energy is absorbed

B 5.05×10^3 kJ of energy is released

C 3.92×10^1 kJ of energy is absorbed

D 3.92×10^1 kJ of energy is released.

12 When 1 MJ of energy is released in this reaction, the volume of $CO_2(g)$ produced, at standard laboratory conditions (SLC), is:

A 3.35×10^4 L

B 33.5 L

C 1.12×10^4 L

D 11.2 L

13 Given that the density, d, of a substance is given by the formula $d = \frac{m}{V}$ and that M represents molar mass, then the density of any gas is given by which formula?

A $d = \dfrac{R \times T}{p \times M}$

B $d = \dfrac{p}{R \times T \times M}$

C $d = \dfrac{R \times T \times M}{p}$

D $d = \dfrac{p \times M}{R \times T}$

14 Which of the following lists species arranged with the nitrogen atoms in order of increasing oxidation number?

A NH_4^+, N_2, NO, NO_3^-

B NO_3^-, NO, NH_3, N_2

C NO_2, N_2, NO, HNO_3

D NO_3^-, NO, N_2, NH_3

15 Use the electrochemical series to determine which one of the following would **not** be expected to occur to an appreciable extent.

A $2H^+(aq) + Fe(s) \rightarrow Fe^{2+}(aq) + H_2(g)$

B $2Ag^+(aq) + Ni(s) \rightarrow 2Ag(s) + Ni^{2+}(aq)$

C $Br_2(aq) + 2Fe^{2+}(aq) \rightarrow 2Br^-(aq) + 2Fe^{3+}(aq)$

D $2I^-(aq) + Pb^{2+}(aq) \rightarrow I_2(s) + Pb(s)$

16 Hydrogen gas (H_2) is bubbled through a solution of $Sn^{4+}(aq)$. Which of the following observations is most likely?

A No reaction will occur.

B A precipitate of SnH_4 will form.

C The pH of the solution will decrease.

D Oxygen gas will form.

17 The following equations involve ions of the transition metal vanadium. The half-cell potential $E°$ (V) is shown for each equation.

$V^{3+}(aq) + e^- \rightarrow V^{2+}(aq) \quad E° = -0.25$ V

$VO^{2+}(aq) + 2H^+(aq) + e^- \rightarrow V^{3+}(aq) + H_2O(l) \quad E° = +0.36$ V

$VO_2^+(aq) + 2H^+(aq) + e^- \rightarrow VO^{2+}(aq) + H_2O(l) \quad E° = +1.00$ V

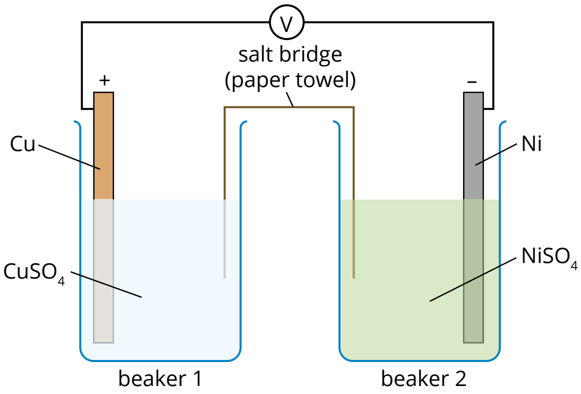
Of the ions listed, which are the strongest oxidant and the strongest reductant?

	Strongest oxidant	Strongest reductant
A	VO_2^+	V^{2+}
B	VO_2^+	VO^{2+}
C	V^{3+}	VO^{2+}
D	V^{2+}	VO_2^+

18 Which of the following best describes the features of an anode in a galvanic cell?

	Polarity	Electrode reaction
A	Positive	Oxidation
B	Positive	Reduction
C	Negative	Oxidation
D	Negative	Reduction

19 An electrochemical cell was made by dipping a copper rod into a solution of 1 M $CuSO_4$ in one beaker and dipping a nickel rod into a solution of 1 M $NiSO_4$ in another beaker. The metals were connected with wire and the two solutions were connected by a piece of paper towel that had been soaked in a potassium nitrate solution. The cell is shown in the following diagram.



The solution in beaker 1 was initially coloured blue, owing to the presence of Cu^{2+} ions. The solution in beaker 2 was initially coloured green because of the presence of Ni^{2+} ions. Which of the following changes might it be possible to detect after the galvanic cell has been discharging for a period of time?

A The green colour in beaker 2 has faded and the mass of the copper electrode has increased.

B The blue colour in beaker 1 has faded and the mass of the nickel electrode has increased.

C The green colour in beaker 2 has faded and the mass of the copper electrode has decreased.

D The blue colour in beaker 1 has faded and the mass of the nickel electrode has decreased.

20 Fuel cells provide an alternative method, often more efficient than direct combustion, of extracting energy from the reaction between a fuel and oxygen. Which of the following are the main energy transformations occurring when a fuel is directly combusted, and when reacted with oxygen in a fuel cell?

	Direct combustion	Fuel cell
A	enthalpy → heat	electricity → enthalpy
B	heat → enthalpy	electricity → enthalpy
C	heat → enthalpy	enthalpy → electricity
D	enthalpy → heat	enthalpy → electricity

21 Much of the research advancing fuel cell technology aims at improving the catalytic effect of the electrode materials. This is crucial because:

A a key limitation of fuel cells is their power output, which relates to the rate at which the reactions can occur

B it increases the total energy available from a given quantity of reactants

C it reduces the output of greenhouse gases and other wastes from the cell

D it allows the fuel cell reactions to be reversed, making it rechargeable.

Short-answer questions

22 **a** Explain what is meant by the term ‘fuel’.

b Methane is a useful fuel that is the major component both of natural gas and of many forms of biogas. Compare these two forms of methane with respect to:

i the processes that lead to their formation

ii their renewability

iii their impact on carbon dioxide levels when used as energy sources.

23 Consider the following table of values of energy available from the combustion of a range of liquid fuels. Note that because many of these fuels are mixtures whose composition can vary, the values provided are representative only.

Liquid fuel	Typical formula	Typical energy available	
		kJ g^{-1}	kJ mL^{-1}
Methanol	CH_3OH	20	16
Ethanol	CH_3CH_2OH	27	21
Petrol	C_8H_{18}	46	33
Petrodiesel	$C_{14}H_{30}$	48	40
Biodiesel	$C_{19}H_{38}O_2$	38	34
Liquefied natural gas (LNG)	CH_4 and C_2H_6	45	27
Liquefied petroleum gas (LPG)	C_3H_8 and C_4H_{10}	49	26

a Identify the fossil fuels present in the table.

b Identify the renewable fuels present in the table.

c What is the general relationship between the energy available from each fuel and the proportion of oxygen in its formula?

d Given the relatively low energy contents of methanol and ethanol, suggest reasons why their use as fuels is becoming more common.

e Suggest one application where a fuel with a high energy/mass ratio would be preferred.

f Suggest one application where a fuel with a high energy/volume ratio would be preferred.

24 One of the boilers at a power station burns 75.6 kg of brown coal every second. Each kilogram of brown coal produces 9.82 MJ of energy. The electrical output of the generator connected to this boiler is 300 MJ s^{-1}.

a Calculate the amount of energy produced each second by burning 75.6 kg of coal.

b Give two reasons why the answer to part **a** is much greater than the output of the generator.

c Over three-quarters of the electricity generated in Victoria comes from brown coal, a non-renewable energy source. Explain what is meant by the term ‘non-renewable energy source’.

d Many sewage treatment plants incorporate digesters that generate biogas, which can be burnt to produce electricity in power plants similar to Victoria’s coal-fired ones. List some of the benefits this might provide.

25 Consider the following thermochemical equations involving the formation of nitrogen oxides.

$N_2(g) + O_2(g) \rightarrow 2NO(g) \quad \Delta H = +181 \text{ kJ mol}^{-1}$

$2NO(g) + O_2(g) \rightarrow 2NO_2(g) \quad \Delta H = -114 \text{ kJ mol}^{-1}$

Use this information to calculate Δ*H* for each of the following equations.

a $2N_2(g) + 2O_2(g) \rightarrow 4NO(g)$

b $2NO(g) \rightarrow N_2(g) + O_2(g)$

c $NO_2(g) \rightarrow NO(g) + \frac{1}{2}O_2(g)$

d $N_2(g) + 2O_2(g) \rightarrow 2NO_2(g)$

26 Lighter fluid is mainly butane (molar enthalpy of combustion is –2876 kJ mol^{-1}), which undergoes combustion according to the following equation:

$$2C_4H_{10}(g) + 13O_2(g) \rightarrow 8CO_2(g) + 10H_2O(g)$$

a What is the value of Δ*H* for the equation?

b Sketch and label an energy-level diagram (showing the relative enthalpies of reactants and products) illustrating the energy changes that occur during this reaction.

c Use your diagram from part **b** to explain why butane does not spontaneously ignite when exposed to air; that is, why a spark is necessary to begin combustion.

d Calculate the heat of combustion of butane in kJ g^{-1}.

e An inexperienced hiker wishes to use his lighter, which contains 3.00 g of butane, to heat the water in his mug. If his mug contains 150 mL of water initially at 20.0°C, and 70.0% of the heat generated by the lighter is lost to the surroundings, what will be the temperature of the water when the fuel in the lighter is exhausted?

27 Many transport vehicles are fuelled by compressed natural gas (CNG) rather than petrol. CNG is largely methane. The thermochemical equation for the complete combustion of methane is:

$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$ $\Delta H = -802$ kJ mol^{-1}

- **a** How much energy, in MJ, is released by the complete combustion of 1.00 kg of methane?
- **b** What volume of carbon dioxide is formed, at standard laboratory conditions (SLC), for each MJ of energy produced?
- **c** If vehicles are not properly tuned, incomplete combustion of methane can lead to the formation of carbon monoxide (CO). For every gram of carbon monoxide produced, 18.6 kJ of energy is released. Write a balanced thermochemical equation (including ΔH) for the reaction of methane with oxygen to produce carbon monoxide and water vapour.
- **d** How much energy (in kJ) is released by combustion of one mole of methane if the percentage converted to carbon monoxide (with the balance converted to carbon dioxide) is:
  - **i** 0%?
  - **ii** 20%?
  - **iii** 100%?

28 A 224 L domestic hot water system running on natural gas is filled with water at 14°C and requires combustion of 1.25 kg of fuel to heat the water to the storage temperature of 70°C (density of water is 1.00 g mL^{-1}).

- **a** Assuming 100% conversion, how much energy is available, in MJ kg^{-1}, from combustion of the natural gas?
- **b** A typical energy value for natural gas is around 54 MJ kg^{-1}. Account for any discrepancy with your answer to part **a**.

29 A helium cylinder for the inflation of party balloons holds 25.0 L of gas, and is filled to a pressure of 16 500 kPa at 15°C.

- **a** Express the pressure of helium gas inside the cylinder in units of:
  - **i** atm
  - **ii** mmHg.
- **b** What mass of helium does the cylinder contain when full?
- **c** What volume would the helium occupy at standard laboratory conditions (SLC)?
- **d** How many balloons can be inflated from a single cylinder at 30°C if the volume of one balloon is 6.5 L and each needs to be inflated to a pressure of 10^8 kPa?

30 Hydrogen seems likely to be among the most prominent of the next generation of fuels, with many potential applications.

- **a** It is a promising replacement for traditional fossil fuels in combustion engines for transport. List two advantages and two disadvantages of hydrogen as a transport fuel in combustion engines, relative to conventional fossil fuels.
- **b** Hydrogen fuel cells are also strong candidates to power electric cars in the future. List two advantages and two disadvantages of hydrogen fuel cells, relative to rechargeable battery technologies (such as lead–acid cells), for use in electric cars.
- **c** List one advantage and one disadvantage of hydrogen fuel-cell powered electric motors relative to hydrogen combustion engines for transport.

31 One manufacturer of direct methanol fuel cells (DMFCs) quotes a methanol consumption rate of 900 mL kWh (1 kWh (kilowatt hour) = 3600 kJ). The equation for the reaction in these fuel cells is identical to that for the direct combustion of methanol (with liquid water as a product):

$2CH_3OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 4H_2O(l)$ $\Delta H = -1453$ kJ mol^{-1}

- **a** Given that the fuel cell contains an acidic electrolyte, write balanced half-equations for the reactions occurring at the anode and cathode respectively.
- **b** Use the thermochemical equation given above to calculate the maximum energy (in kJ) available from the reaction of 1.00 g of methanol with oxygen.
- **c** Use the fuel consumption figure provided to calculate the amount of electrical energy obtained from the reaction of 1.00 g of methanol in the fuel cell (density of liquid methanol is 0.79 g mL^{-1}).
- **d** What is the percentage efficiency of conversion of available energy to electrical energy in the fuel cell?
- **e** List some possible losses that might occur in the fuel cell to lower the efficiency of electricity production.

32 For each of the following reactions:

- identify them as redox or non-redox reactions
- for each redox reaction, list the changes in oxidation number occurring
- for each redox reaction, identify the oxidant and the reductant.

a $HIO_3(aq) + 3SO_2(g) \rightarrow 3SO_3(aq) + HI(aq)$

b $SO_3(g) + Ca(OH)_2(aq) \rightarrow CaSO_4(s) + H_2O(l)$

c $4Fe(OH)_2(s) + 2H_2O(l) + O_2(g) \rightarrow 4Fe(OH)_3(aq)$

d $NaH(s) + H_2O(l) \rightarrow H_2(g) + NaOH(aq)$

33 For each of the following unbalanced redox reactions (all occurring in acidic aqueous solution)

- write separate balanced ionic equations for the oxidation and reduction half-reactions
- write a balanced ionic equation for the overall reaction.

a $Al(s) + Br_2(aq) \rightarrow Al^{3+}(aq) + Br^-(aq)$

b $ClO^-(aq) + S_2O_3^{2-}(aq) \rightarrow SO_4^{2-}(aq) + Cl^-(aq)$

c $H_2O_2(aq) + MnO_4^-(aq) \rightarrow O_2(aq) + MnO_2(s)$

34 When a Ni–Cad cell is converting chemical energy to electrical energy (discharge), the electrode reactions are best described as follows.

- positive electrode:
  $NiOOH(s) + H_2O(l) + e^- \rightarrow Ni(OH)_2(s) + OH^-(aq)$
- negative electrode:
  $Cd(s) + 2OH^-(aq) \rightarrow Cd(OH)_2(s) + 2e^-$

a Which metal, nickel or cadmium, is at the anode of this cell as it is discharging?

b Give the formula of an ionic compound that might be expected to be found in the electrolyte paste of a Ni–Cad cell.

Ni–Cad cells are superior to alkaline cells because they can be recharged.

c Explain why cells such as the Ni–Cad can be recharged.

d Write equations for the half-reactions and the overall cell reaction occurring when a Ni–Cad cell is recharged.

e Describe the energy transformation that occurs when a Ni–Cad cell is discharging.

35 Referring to an electrochemical series and for each of the half-cell combinations listed below, predict:

i the maximum cell voltage expected at standard conditions

ii which of the half-cells will contain the negative electrode

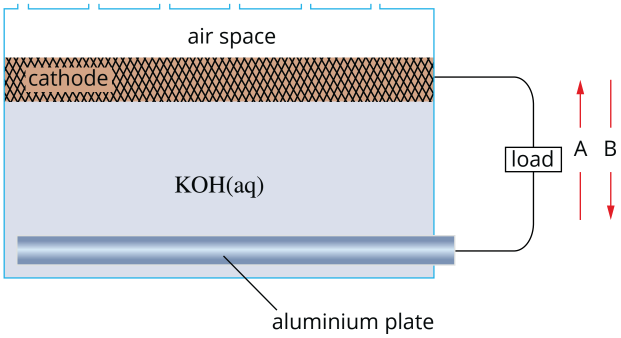
iii the ionic equation for the overall reaction occurring when the cell is discharging.

a $Sn^{2+}(aq)/Sn(s)$ and $Fe^{2+}(aq)/Fe(s)$

b $Fe^{3+}(aq)/Fe^{2+}(aq)$ and $Al^{3+}(aq)/Al(s)$

c $H^+(aq)/H_2(g)$ and $I_2(aq)/I^-(aq)$

36 The diagram below shows a version of an alkaline aluminium–air fuel cell being used to power a load, such as an electric motor.



The half-reactions occurring are:

$Al(s) \rightarrow Al^{3+}(aq) + 3e^-$

$O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq)$

a Which arrow, A or B, shows the direction of electron flow through the load?

b What is the oxidant in this cell?

c Write a balanced equation for the overall cell reaction.

d Explain why it is important for the cathode to be porous.

Using a zinc (Zn) plate in place of the aluminium plate gave a cell that still functioned. However, when a silver (Ag) plate was used instead, the cell did not function.

e Account for this difference by referring to the relative strengths of the oxidants and reductants involved.

f Would the cell potential (voltage) produced by the cell with the zinc plate be larger or smaller than that with the original aluminium plate? Explain your answer.

g When the potassium hydroxide electrolyte was replaced with a sulfuric acid solution, the cell with the silver plate began to deliver current. Explain why changing the electrolyte made this difference.

CHAPTER

07

Rate of chemical reactions

Chemical reactions occur at many different rates. The explosion of gunpowder and the combustion of petrol in a car's engine occur very quickly. On the other hand, the weathering of buildings, the ripening of fruit and the rusting of iron all occur quite slowly.

During chemical reactions, particles such as atoms, molecules and ions collide with each other and undergo a rearrangement to produce new substances. It is important to appreciate that collisions between reactant particles do not always result in a chemical reaction. For example, while a car's fuel tank is being filled with petrol, the hydrocarbon molecules in the fuel are colliding with oxygen molecules in the air without a reaction occurring.

By the end of this chapter, you will understand how rates of chemical reactions can be measured. You will also be able to describe how varying the conditions of chemical reactions can affect the rate of a reaction.

Using collision theory, you will learn to predict the effects of concentration of solutions, temperature, surface area, gas pressure and the presence of a catalyst on the rate of chemical reactions, and explain these effects.

The role of catalysts in changing the rate of chemical reactions will be considered in relation to reaction pathways and the energy changes that occur during reactions.

Key knowledge

- Chemical reactions with reference to collision theory, including qualitative interpretation of Maxwell–Boltzmann distribution curves
- Factors affecting the rate of a chemical reaction, including temperature, surface area, concentration of solutions, gas pressures and presence of a catalyst
- The role of catalysts in changing the rate of chemical reactions with reference to alternative reaction pathways and their representation in energy profile diagrams

7.1 Investigating the rate of chemical reactions

FIGURE 7.1.1 How quickly do the chemical reactions involved in baking occur?

The time it takes for a batch of chocolate brownies to cook in the oven (Figure 7.1.1) and the time taken for a fibreglass patch on a surfboard to set are processes related to the rate of chemical reactions.

In this section, you will learn how changes to reaction conditions affect reaction rates. You will also learn how chemists measure the rate at which a chemical reaction occurs.

FAST AND SLOW REACTIONS

Chemical reactions are taking place all around us:

- in the soil and rocks beneath our feet
- in the air around and above us
- inside every plant and animal
- in our homes, schools and workplaces.

Some of these reactions are over in a flash. In a car accident when a car's airbag needs to be inflated, the chemical reactions producing the gas that expands the airbag need to happen extremely quickly. On the other hand, if the car's painted surface is scratched to expose the metal beneath, the rusting reactions take place at a very slow rate.

CHEMISTRY IN ACTION

Saved by a very fast chemical reaction

Imagine the scene. An 18-year-old borrows his parent's car to take his girlfriend for a drive to celebrate gaining his driver's licence. Roof down, enjoying the beautiful afternoon and the countryside, the driver rounds a corner to find the road wet. The car begins to slide on the wet surface. In his inexperience the driver brakes; the car starts to spin. Suddenly, the car is leaving the road and heading straight for a large tree. Then, bang!

Later, the car was estimated to have been travelling at 60 km/h when it hit the tree. The collision was a 'head-on', with the front and passenger side taking most of the impact. Yet the girl in the passenger seat suffered just a chipped tooth, and her boyfriend sustained only minor bruising.

This is the true story of a lucky escape, thanks to a very rapid chemical reaction. As the collision took place, airbags were inflating and then deflating as the travellers were slammed forward towards the windscreen. The driver described it as being 'all over in a flash' and had no clear recollection of the airbags going off.

Hidden in the car's steering wheel, dashboard and windscreen pillars, special nylon bags fill with gas within 30 milliseconds of impact (see Figure 7.1.2). As a consequence, the car occupants are prevented from smashing their heads against the steering wheel, dashboard, windscreen or front pillars, all within the blink of an eye. As the head and body strike the airbags, the cushion of gas is forced out of the bag through tiny vents, and within 100 milliseconds the bag has completely deflated.

FIGURE 7.1.2 Airbags are deployed within 30 milliseconds of an impact.

Air bags contain a mixture of crystalline solids—sodium azide (NaN_3), potassium nitrate (KNO_3) and silica (SiO_2)—stored in a canister. Sensors in the front of the car detect the difference between a bump and life-threatening impact. When a response is required, an electronic impulse 'ignites' the sodium azide. Sodium metal and hot nitrogen gas are the products of this energy-releasing redox reaction:

$$2NaN_3(s) \rightarrow 2Na(l) + 3N_2(g)$$

The pulse of hot nitrogen gas released from this reaction starts to inflate the nylon bag. The molten sodium metal immediately reduces the potassium nitrate, generating more nitrogen gas, as well as sodium oxide and potassium oxide, which are white powdery solids.

The equation for this reaction is:

$$10Na(l) + 2KNO_3(s) \rightarrow K_2O(s) + 5Na_2O(s) + N_2(g)$$

A filtration system prevents any of the oxides from entering the nylon bag, while a third reaction 'captures' them to produce a harmless glassy solid.

In this reaction they combine with silica:

$$K_2O(s) + 5Na_2O(s) + SiO_2(s) \rightarrow \text{alkaline silicate ('glass')}$$

Chemical reactions do save lives!

FACTORS THAT AFFECT REACTION RATES

Experimental investigations have shown that five main factors can change the rate of a chemical reaction:

- surface area of solid reactants
- concentration of reactants in a solution
- gas pressure
- temperature
- the presence of **catalysts**.

You can probably think of some examples of situations where one or more of these conditions is changed and a reaction becomes noticeably faster or slower.

Surface area

The surface area of solid reactants can have a significant effect on reaction rate. Smaller particles have a much larger surface area than the same mass of large particles. As a result, the smaller particles react much faster.

Manufacturers of fireworks modify the surface area of solid reactants to control the rate at which fuels in the fireworks burn and create different effects (Figure 7.1.3). For example, very small pieces of aluminium confined in a shell explode violently. If larger pieces of aluminium are used, the reaction is slower and sparks are seen as pieces of burning metal being ejected.

FIGURE 7.1.3 Particle size can be used to control the rate of reaction and create different effects during fireworks displays.

FIGURE 7.1.4 This limestone statue has become pitted in recent years. Limestone (calcium carbonate) reacts more rapidly with the increased concentration of hydrogen ions in rainwater.

FIGURE 7.1.5 Food is stored at low temperatures in a refrigerator to slow down the rate of reactions that cause food spoilage.

Concentration

The concentration of solutes dissolved in a solution can influence the rate of their reactions: higher concentrations usually lead to increased reaction rates.

Pollutants such as sulfur dioxide and nitrogen dioxide are released by cars and many industrial processes. When these compounds react with rainwater, acids such as sulfurous acid and nitric acid are formed. This causes the rainwater's hydrogen ion concentration to increase significantly and it is called **acid rain**. The increasing acidity of rain over the past 200 years has caused many famous marble buildings and statues to deteriorate much more rapidly due to the reaction between marble and the acids (see Figure 7.1.4).

Pressure

In reactions involving gases, increasing the pressure on a reaction increases the rate at which the reaction takes place. Increasing the pressure at constant temperature will result (on average) in the reactant particles becoming closer together.

This will increase the chance of the gas molecules colliding, and therefore increase the rate of reaction. Increasing the pressure of a reacting gas is the same as increasing the concentration because you have the same mass in a smaller volume.

For this reason, engineers often employ high gas pressures in their design of chemical processes that use gas-phase reactions. An example is the production of ammonia gas by reacting hydrogen gas and nitrogen gas. Increasing the pressure ensures a faster rate of reaction.

Temperature

As every cook knows, the temperature of an oven affects the rate of the chemical reactions during baking. The higher the temperature, the more rapidly the reactions occur.

On the other hand, in hot weather it is wise to store fruit and vegetables in the refrigerator so that the chemical reactions that cause them to over-ripen and then spoil will be slowed down at the lower temperatures (Figure 7.1.5).

CHEMFILE

Fireworks and nanoparticles

Studies have shown that the fireworks (see Figure 7.1.6) associated with celebrations such as New Year's Eve and the Lantern Festival in China can significantly increase air pollution levels. Sulfur dioxide and particles of metals are released when fireworks explode. These can cause breathing problems and lung disease.

Recent research aimed at lowering the environmental impact of fireworks has focused on reducing the particle size of chemicals used as fuels in the fireworks. By using smaller nanoparticles, reaction rates are increased and smaller amounts of chemicals are needed for the same performance. Thus, fewer pollutants are released into the atmosphere.

However, this new approach carries increased risks because fireworks made of such small particles could be even more explosive.

FIGURE 7.1.6 Fireworks on New Year's Eve, Sydney.

Catalysts

Some chemical reactions occur much more rapidly if another substance is added to the reaction mixture. Such substances are called catalysts. Catalysts allow the reaction to follow a more energetically favourable pathway.

For example, if you chew a piece of dry biscuit or bread for several minutes, you may notice it tasting much sweeter. This happens because there is a catalyst present in your saliva that speeds up the breakdown of starch into sweet-tasting sugars.

In the following sections, you will learn how each of these factors can cause these changes in reaction rate.

MEASURING RATES OF REACTION EXPERIMENTALLY

The **rate of reaction** is defined as the change in concentration of a reactant or product per unit time. The usual unit for a rate of reaction is M s^{-1}.

The rate of reaction is defined as the change in concentration of a reactant or product per unit time.

To experimentally determine the rate of reaction, either directly or indirectly, you need to measure how much of a reactant is being used up or how much of a product is being formed in a given time period.

When a reaction involves gaseous products, this might involve measuring changes in mass or gas volume with time.

The graphs shown in Figure 7.1.7 were obtained by measuring the mass of carbon dioxide produced in the reaction between marble chips and hydrochloric acid. The experiment was performed twice, first with large marble chips, then with small marble chips.

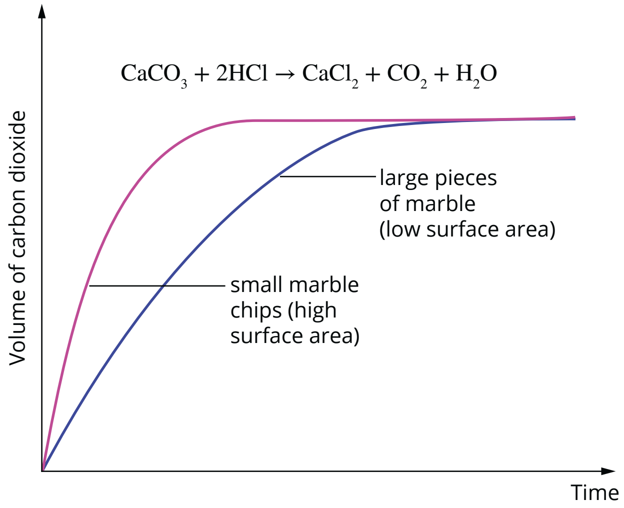


FIGURE 7.1.7 As carbon dioxide is produced from the reaction between marble chips and hydrochloric acid, it is collected in a gas syringe and its volume is recorded.

The steeper initial gradient of the graph with small marble chips indicates that the rate of production of carbon dioxide gas is faster with the marble chips that have a higher surface area.

Colour changes and pH changes can also be used to follow the rate of some reactions, depending on the colour and acidity of reactants and products.

7.1 Review

SUMMARY

- The rate of a reaction is the change in concentration of reactants or products over time.
- The rate of a reaction may be increased by:
  - increasing surface area
  - increasing the concentration of a reactant in solution
  - increasing the pressure of a gaseous reactant
  - increasing temperature
  - adding a catalyst.
- A range of experimental methods can be used to measure the rate of a reaction, including measuring the following during specific time intervals:
  - mass loss
  - volume of gas produced
  - colour change
  - concentration changes
  - pH change.

KEY QUESTIONS

1 Which one of the following changes would decrease the rate of the reaction between zinc metal and dilute hydrochloric acid?

A Increasing the temperature of the hydrochloric acid
B Decreasing the size of the pieces of zinc
C Decreasing the concentration of the hydrochloric acid
D Decreasing the volume of hydrochloric acid used

2 Select the correct response in the statements about the five main ways in which reaction rates can be increased.

a **Increasing/decreasing** surface area of solid reactants
b **Increasing/decreasing** the temperature of a reaction mixture
c **Increasing/decreasing** the concentration of a reactant in solution
d **Increasing/decreasing** the pressure of gaseous reactants
e **Adding/removing** a catalyst

3 The graph in Figure 7.1.8 shows the mass of carbon dioxide gas produced during a 4-minute period of a reaction between marble chips (calcium carbonate) and 1.0 M nitric acid.

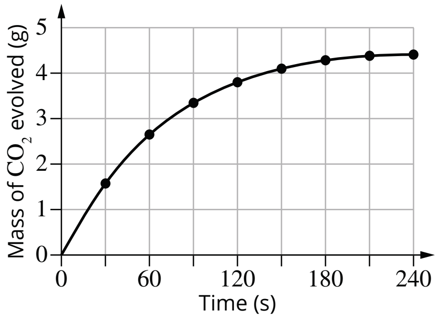


FIGURE 7.1.8 The mass of carbon dioxide produced in a reaction between nitric acid and marble chips.

a Write a full chemical equation for this reaction.
b Explain whether the rate of this chemical reaction is increasing or decreasing over time.

4 Describe one way of increasing the rate of each of the following reactions.

a Wood burning on a camp fire
b Removing excess mortar from between bricks using brick cleaner
c Baking a cake in the oven

7.2 Collision theory

The chemical equation for a reaction indicates the nature of the reactants and products, but provides no information about the way in which the reaction proceeds.

Look at the equation for the decomposition of hydrogen peroxide:

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

This equation gives no indication about whether the reaction proceeds quickly or slowly; nor can you tell how the products have been formed.

In fact, this reaction normally occurs very slowly, but when a catalyst, such as crystals of potassium permanganate, are added to the hydrogen peroxide solution, the reaction occurs rapidly, producing so much oxygen gas and heat that the reaction mixture foams and that some of the liquid water vaporises (see Figure 7.2.1).

Chemical reactions occur as a result of collisions between the reacting particles. This idea is part of the **collision theory** of reaction rates, which will be discussed in this section.

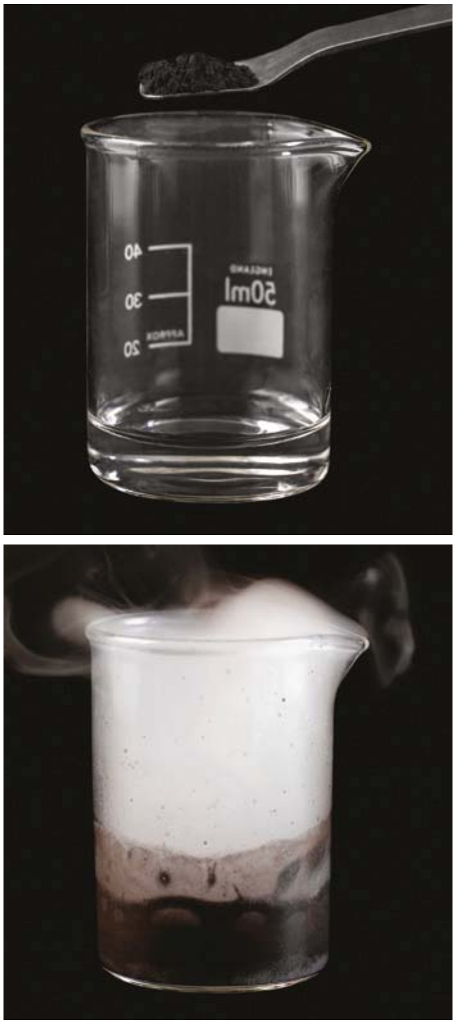


FIGURE 7.2.1 The decomposition of hydrogen peroxide is usually very slow, but the addition of crystals of potassium permanganate results in the rapid evolution of oxygen gas and water vapour.

COLLISION THEORY AND ACTIVATION ENERGY

During chemical reactions, particles (atoms, molecules or ions) collide and are rearranged to produce new particles. Consider the decomposition reaction of hydrogen peroxide:

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

The collision that forms the first step of the reaction occurs between the two hydrogen peroxide molecules. If this collision is to result in the formation of molecules of water and oxygen, the collision must occur in such a way that the covalent bonds in the hydrogen peroxide break. To break bonds, energy is required.

The collision theory of reactions explains why some collisions result in reactions and others do not. According to collision theory, for a reaction to occur, the reactant particles must:

- collide with each other
- collide with sufficient energy to break the bonds within the reactants
- collide with the correct orientation to break the bonds within the reactants and so allow the formation of new products.

If a collision does not meet all of these requirements, then no reaction occurs. In fact, most collisions do not result in a chemical reaction. Collision theory explains why this is the case.

Activation energy

For a reaction to occur between reactant molecules, the molecules must collide with a certain minimum amount of energy. Unless this minimum amount of energy is met or exceeded, the colliding molecules will rebound and simply move away from each other without reacting.

The minimum energy that a collision must possess for a reaction to occur is called the **activation energy**, E_a. (You learned about activation energy in Chapter 2.) When the energy of a collision is equal to or greater than the activation energy, a reaction can occur.

Activation energy can be represented on an **energy profile diagram**. Energy profile diagrams for both **endothermic** and **exothermic** reactions were looked at in Chapter 2, page 44. An energy profile diagram represents the potential energies of the reactants and the products over the course of the reaction.

Energy profile diagrams for both exothermic and endothermic reactions have a peak that represents the activation energy. This is sometimes referred to as the activation energy barrier, and represents the minimum energy that must be absorbed in order to break the bonds of reactants so that a chemical reaction can progress. The activation energy is measured from the energy of the reactants to the top of the peak.

Reactant particles must have energy equal to or greater than the activation energy before a reaction can occur.

You will recall that an exothermic reaction releases more heat energy during the reaction than it absorbs. An endothermic reaction absorbs more heat energy during the reaction than it releases. This is represented on the diagram as ΔH and is the difference in energy between the reactants and the products.

Transition state

When the activation energy is absorbed, a new arrangement of the atoms known as the **transition state** occurs. The transition state occurs at the stage of maximum potential energy in the reaction: the activation energy (see Figure 7.2.2). Bond breaking and bond forming are both occurring at this stage, and the arrangement of atoms is unstable. The atoms in the transition state rearrange into the products as the reaction progresses.

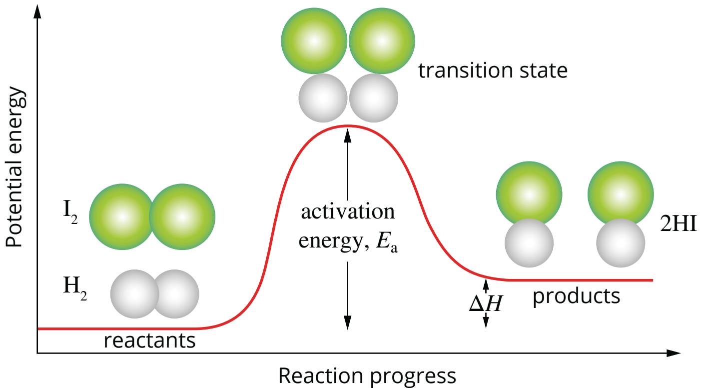


FIGURE 7.2.2 Energy profile diagram for the endothermic reaction $H_2(g) + I_2(g) \rightarrow 2HI(g)$.

Activation energy and reaction rate

The size of the activation energy determines how easy it is for a reaction to occur and therefore what proportion of collisions results in a successful reaction. For this reason, the reaction rate is dependent upon the activation energy.

The existence of an activation energy for a reaction means that collisions between reactants do not always result in a chemical change. For example, nitrogen (N_2) and oxygen (O_2) molecules collide frequently in the air around us at room temperature. However, it is only when energy is provided by a spark, such as in car engines or during a lightning strike, that the energy of the collisions is increased enough to overcome the activation energy barrier. This allows nitrogen monoxide to be produced. The nitrogen monoxide formed in this process can then react to form brown nitrogen dioxide (NO_2), a poisonous gas that is a major contributor to the formation of the **photochemical smog** seen in Figure 7.2.3.

FIGURE 7.2.3 Photochemical smog, such as seen here over Barcelona, Spain, in December 2013, is caused by NO_2, a poisonous gas.

Orientation of colliding molecules

For a reaction to occur, reactants need to collide with enough energy to provide the activation energy. Reacting molecules must also collide with each other in the correct orientation in such a way that particular bonds in the reactants are broken and new bonds are formed in the products.

Figure 7.2.4 shows the importance of collision orientation. In the decomposition of hydrogen iodide gas into hydrogen gas and iodine gas, two hydrogen iodide molecules must collide with hydrogen and iodine atoms orientated towards each other, for a reaction to possibly occur. If the collision orientation is incorrect, the particles simply bounce off each other, and no reaction occurs.

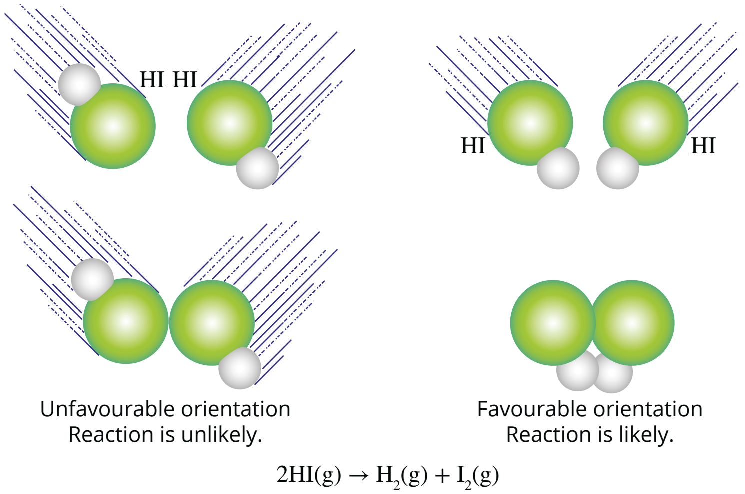


FIGURE 7.2.4 A reaction between colliding molecules is more likely to occur if the orientation of the collision is favourable.

CHEMFILE

A little too reactive!

In 1846, the Italian chemist Ascanio Sobrero reacted glycerol with a mixture of sulfuric and nitric acids to make the explosive liquid nitroglycerin. Nitroglycerin is so unstable that even a small bump can cause it to explode. It decomposes according to the equation:

$4C_3H_5N_3O_9(l) \rightarrow 12CO_2(g) + 10H_2O(g) + 6N_2(g) + O_2(g)$

Despite being many times more powerful than conventional gunpowder, it was far too dangerous to be practical. Some years later, the Swedish scientist Alfred Nobel learned how to manage nitroglycerin more safely through his invention of dynamite.

The reason for nitroglycerin's instability is the very small activation energy for its decomposition reaction (see Figure 7.2.5).

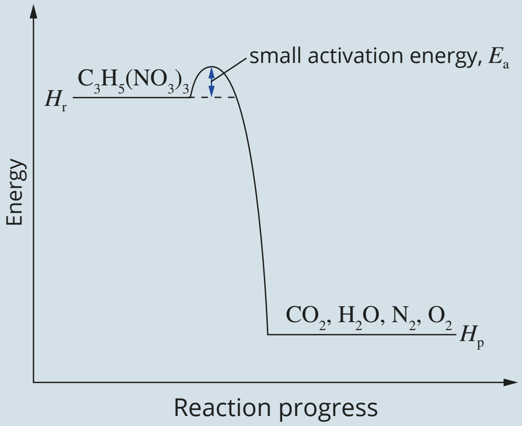


FIGURE 7.2.5 Nitroglycerin has a very low activation energy, making its rate of reaction very large.

7.2 Review

SUMMARY

- The activation energy of a reaction is the minimum amount of energy required to break reactant bonds to allow a reaction to proceed. It is the minimum amount of energy that a collision between reactant particles must possess for a reaction to occur.
- The transition state is an arrangement of atoms that occurs when the activation energy is absorbed. The transition state is an unstable state in which bonds in the reactants are being broken and bonds in the products are starting to form.
- An energy profile diagram shows the activation energy as a peak of highest potential energy between the energy of the reactants and the energy of the products.
- Collision theory is a theoretical model that accounts for the rates of chemical reactions in terms of collisions between particles during a chemical reaction.
- According to collision theory, for a reaction to occur, the reactant particles must:
  - collide with each other
  - collide with sufficient energy to break the bonds within the reactants
  - collide with the correct orientation to break the bonds within the reactants and so allow the formation of new products.

KEY QUESTIONS

1 According to the collision theory, which one of the following is *not* essential for a reaction to occur?

A Molecules must collide to react.
B The reactant particles should collide with the correct orientation.
C The reactant particles should collide with enough energy to overcome the activation energy barrier.
D The reactant particles should collide with double the energy of the activation energy.

2 Which one of the following is the energy required to produce the transition state in a reaction?

A Activation energy
B Difference in energy between the products and reactants
C Difference in energy between the products and the activation energy
D Transition state energy

3 When 1 mol of methane gas burns completely in oxygen, the process of bond breaking uses 3380 kJ of energy and 4270 kJ of energy is released as new bonds form.

a Write a balanced chemical equation for the reaction.
b Calculate the value of the heat of reaction, Δ*H*, for the reaction.
c Draw and label a diagram to show the changes in energy during the course of the reaction.

4 The formation of hydrogen iodide from its elements is represented by the equation:

$$H_2(g) + I_2(g) \rightarrow 2HI(g)$$

This reaction has an activation energy of 167 kJ mol^{-1} and the heat of reaction, ΔH, is +28 kJ mol^{-1}. What is the activation energy for the reverse reaction, the decomposition of 2 mol of hydrogen iodide?

7.3 Effect of temperature on rate of reaction

Earlier in this chapter you saw that the rate of a reaction can be changed by the:

- surface area of a solid reactant
- concentration of reactants in a solution
- pressure of any gaseous reactants
- temperature of the reaction
- presence of a catalyst.

In any given reaction mixture, only a certain proportion of the collisions are successful. To increase a reaction rate, you can increase the proportion of successful collisions by:

- increasing the frequency of successful collisions by increasing the number of collisions that can occur in a given time
- increasing the proportion of collisions that have energy that is equal to or greater than the activation energy (i.e. overcome the activation energy barrier).

In this section, you will consider how various changes to conditions can affect the proportion of successful collisions that occur between reactant particles and hence change the rate of reaction.

INCREASING THE FREQUENCY OF COLLISIONS

The rate of a reaction increases as the frequency of collisions increases. The frequency of collisions between reactants can be increased by:

- increasing the concentration of the reactants. Collisions occur more frequently when particles are closer together
- increasing the surface area of a solid reactant.

Changing concentration or pressure

In section 7.1, you learned that the rate of a reaction can be increased by increasing the concentration of a reacting solution or the pressure of a reacting gas. This can be explained by collision theory.

The rate of a reaction increases when the frequency of collisions between reactants increases. When the concentration of a solution increases, there are more reactant particles moving randomly in a given volume of solution (see Figure 7.3.1). The frequency of collisions consequently increases and so more successful collisions occur in a given time.

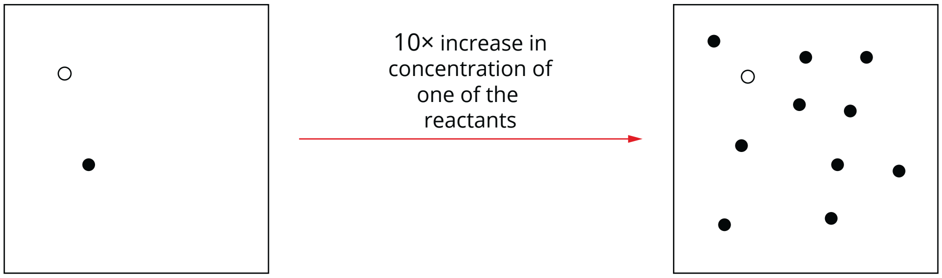


FIGURE 7.3.1 On the left, the concentration of both reactants is low. On the right, the concentration of one of the reactants has been increased 10-fold, resulting in an increase in collision frequency.

For a reaction in the gas phase, the pressure of the gases can be increased either by adding more gas to a fixed volume container or by decreasing the volume of a container with a variable volume, such as a gas syringe. Increasing the pressure increases the concentration of gas molecules, causing more frequent collisions and increasing the number of successful collisions in a given time.

Changing surface area

When a solid is involved in a reaction, only the particles at the surface of the solid are involved in the reaction. The number of particles at the surface depends on the **surface area** of the substance. As you can see in Figure 7.3.2, breaking a solid into smaller parts means that more particles are present at the surface and available to react. The surface area has increased.

As a consequence of the greater number of exposed particles, the frequency of collisions between these particles and the other reactant particles increases, and so the reaction occurs more rapidly.

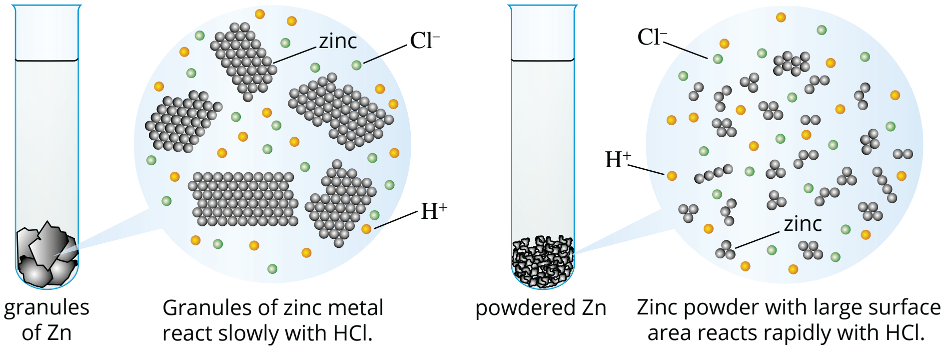


FIGURE 7.3.2 The reaction of hydrochloric acid and zinc. As the surface area of zinc increases, the rate of reaction with hydrochloric acid increases. (The H_3O^+ ion is represented as H^+ in the diagrams.)

When using collision theory to explain the effect of concentration, pressure and surface area on the rate of a chemical reaction, you must discuss the effect on either collision frequency or the number of successful collisions per unit time.

The effect of increasing surface area can be seen when setting up an open fire at home or on a camp. It is best to first light a pile of kindling rather than trying to directly light large logs. The kindling has a larger surface area than the logs, so it catches fire more easily and will then burn rapidly, providing enough sustained heat energy to make the logs catch fire as well.

Worked example 7.3.1

USING COLLISION THEORY TO EXPLAIN CHANGES IN RATES OF REACTIONS

There have been many explosions in underground coal mines due to the presence of coal dust. Explain this observation in terms of collision theory.

Thinking	Working
Consider the state of the reactants.	Coal is a solid. In the mine, there would be lumps of coal and also powdered coal.
Relate the state of the reactant to the factor that affects the reaction rate and explain in terms of collision theory.	The surface area of powdered coal is greater than that of solid coal. When the surface area increases, the frequency of collisions increases and so the rate of reaction increases.
Return to the question to complete your answer.	An explosion is a very fast reaction. The very large surface area of the coal dust allows for an increase in the frequency of collisions with reacting particles, which increases the reaction rate so much that explosions occur.

Worked example: Try yourself 7.3.1

USING COLLISION THEORY TO EXPLAIN CHANGES IN RATES OF REACTIONS

Iron anchors recovered from shipwrecks at considerable depths can show little corrosion after years in the sea, whereas anchors recovered from shallow water are badly corroded. Explain this observation in terms of collision theory.

INCREASING THE ENERGY OF COLLISIONS

As you have seen, a reaction can be made to occur more rapidly by increasing the concentration of the reactants or, for solids, increasing the surface area. A change in temperature can also have a major effect on the rate of a reaction. An increase in temperature not only increases the frequency of collisions, it also increases the kinetic energy of the particles and hence the energy of their collisions.

Maxwell–Boltzmann distribution

At any particular temperature, the particles in a substance have a range of kinetic energies. Although most of the particles have similar kinetic energies, there are always some particles with a high energy or a low energy. This range of energies is shown on a graph called a **Maxwell–Boltzmann distribution curve**, also known as a **kinetic energy distribution diagram**. Figure 7.3.3 shows how the distribution of energies is represented in a Maxwell–Boltzmann distribution curve.

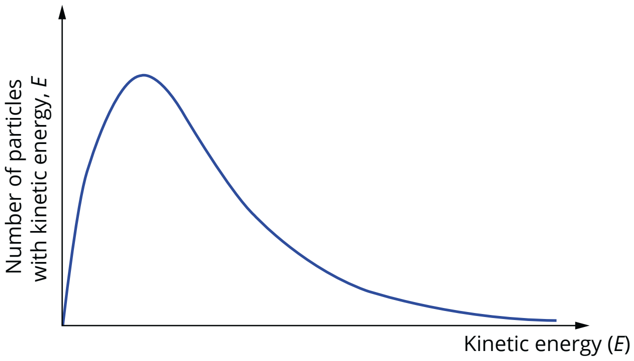


FIGURE 7.3.3 This Maxwell–Boltzmann curve shows the distribution of energies of particles in a sample at a particular temperature. The peak of the graph corresponds to the energy of the greatest number of particles.

During a reaction at a given temperature, only a small proportion of the reactant particles have kinetic energy that is equal to or greater than the activation energy and so are able to react. You can see this in Figure 7.3.4 as a small shaded area to the right of the activation energy, E_a.

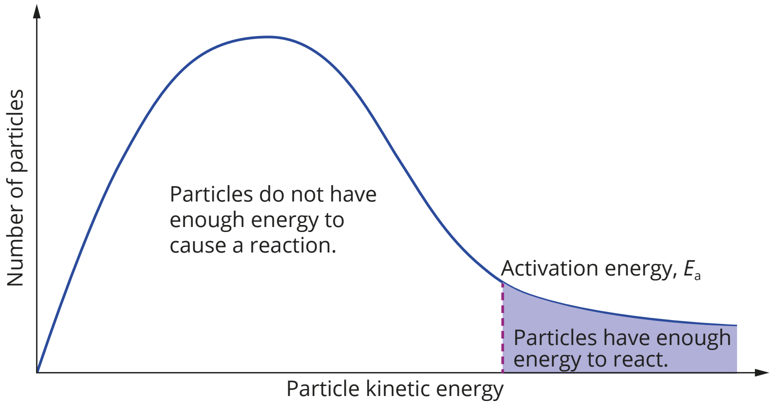


FIGURE 7.3.4 Only a small number of higher energy particles (represented by the shaded area) have sufficient energy to overcome the activation energy barrier.

Effect of temperature and rate of reaction

The relationship between **kinetic energy** and velocity is given by the formula $KE = \frac{1}{2}mv^2$. As the temperature of a reaction system increases, the average kinetic energy of the particles increases and the average speed of the particles in the system increases as well.

This is illustrated in Figure 7.3.5 in which the range of kinetic energies for a gas at three different temperatures is shown. Note that the area under the curve, which is equal to the total number of particles in the sample, stays constant when the temperature is changed. As the temperature increases, the increasing average kinetic energy of the particles can be seen by the movement to the right of the peak in the Maxwell–Boltzmann curve.

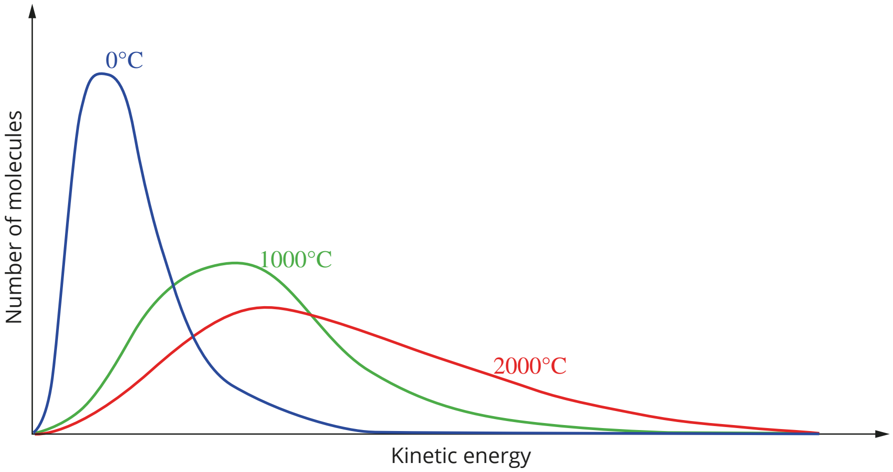


FIGURE 7.3.5 Kinetic energy distribution for a gas at a range of temperatures.

As the temperature of a reaction increases, the increased speed of particles causes more collisions, increasing the frequency of successful collisions and the rate of reaction.

The increased kinetic energy of the particles also means that collisions occurring at higher temperatures have greater energy than those at lower temperatures. More particles will have energies that are greater than or equal to the activation energy and so the proportion of successful collisions also increases.

When the temperature increases, the increase in reaction rate due to the increased energy of the collisions significantly outweighs the increase in reaction rate due to the increased frequency of collisions.

A temperature increase of just 10°C causes the rate of many reactions to double (an increase of 100%), but it can be shown that this is not due to the increased frequency of collisions. The frequency of collisions only increases by about 3% when the temperature increases by 10°C. The main reason why the reaction rate increases is that more particles have sufficient energy to overcome the activation energy barrier of the reaction.

The effect of increasing temperature on the rate of reaction is mainly through increasing the proportion of reacting particles that have energies equal to or greater than the activation energy for the reaction. This increases the proportion of successful collisions.

CHEMFILE

Ötzi the Iceman

In September 1991, Erika and Helmut Simon were walking in the Ötztal Alps near the border between Austria and Italy when they discovered the body of what they thought was a dead mountaineer (see Figure 7.3.6). It was known that, in this region, bodies decompose very slowly because they are enclosed in ice. Closer examination of the body, and the Bronze Age items with it, eventually established that he had died approximately 5300 years ago.

FIGURE 7.3.6 Ötzi the Iceman was so well preserved for 5300 years in the ice that his stomach contents could be identified and pollen of a spring plant was found on his clothes.

7.3 Review

SUMMARY

- Collision theory can be used to explain the increase in rate of reaction by an increase in:
  - concentration of a reactant solution
  - pressure of a gaseous reactant
  - surface area of a solid reactant
  - temperature.
- Increase in concentration, pressure or surface area results in an increase in the:
  - frequency of collisions between reactants
  - number of successful collisions in a given time.
- Increase in temperature results in an increase in the:
  - frequency of collisions between reactants
  - number of successful collisions in a given time
  - most importantly, energy of collisions, so an increased proportion of collisions has an energy larger than the activation energy for the reaction.

KEY QUESTIONS

1 Which one of the following alternatives correctly explains why a sample of magnesium reacts more rapidly with 1 M HCl than with 0.1 M HCl?

A The energy of collisions between reactant particles is greater for the reaction containing 1 M HCl.

B The rate of collisions between reactant particles is greater for the reaction containing 0.1 M HCl.

C There are more collisions between the magnesium and 1 M hydrochloric acid.

D The frequency of collisions between reactant particles is greater than for the reaction containing 1 M HCl.

2 Which one or more of the following may be true if a reaction is observed to proceed very slowly?

A The activation energy may be very large.

B The temperature may be low.

C Few collisions may be occurring with the correct orientation.

3 A number of experiments involving the reaction between 100 mL of hydrochloric acid and 5 g of calcium carbonate were carried out. Rearrange experiments A–F to place them in increasing order of rate of reaction (slowest to fastest).

A Powdered $CaCO_3$ and 1 M HCl are mixed at 40°C.

B Small pieces of $CaCO_3$ and 1 M HCl are mixed at 15°C.

C Powdered $CaCO_3$ and 1 M HCl are mixed at 25°C.

D Large pieces of $CaCO_3$ and 0.5 M HCl are mixed at 15°C.

E Powdered $CaCO_3$ and 1 M HCl are mixed at 15°C.

F Small pieces of $CaCO_3$ and 0.5 M HCl are mixed at 15°C.

4 Account for the following observations with reference to the collision model of particle behaviour.

a Surfboard manufacturers find that fibreglass plastics set within hours in summer but may remain tacky for days in winter.

b A bottle of fine aluminium powder has a caution sticker warning ‘Highly flammable, dust explosion possible’.

c A potato cooks much more slowly in a pot of boiling water on a trekking holiday in Nepal than a potato boiled in a similar way in the Australian bush.

7.4 Catalysts

In this section, you will learn how catalysts increase the rate of reaction.

The change in reaction rate when a catalyst is present is often very substantial. The action of a catalyst can be understood using collision theory and the changes in energy that occur during a chemical reaction. Catalysts play an important role in industrial chemistry, in limiting air pollution and in controlling biochemical processes, as shown in the examples in Figure 7.4.1.

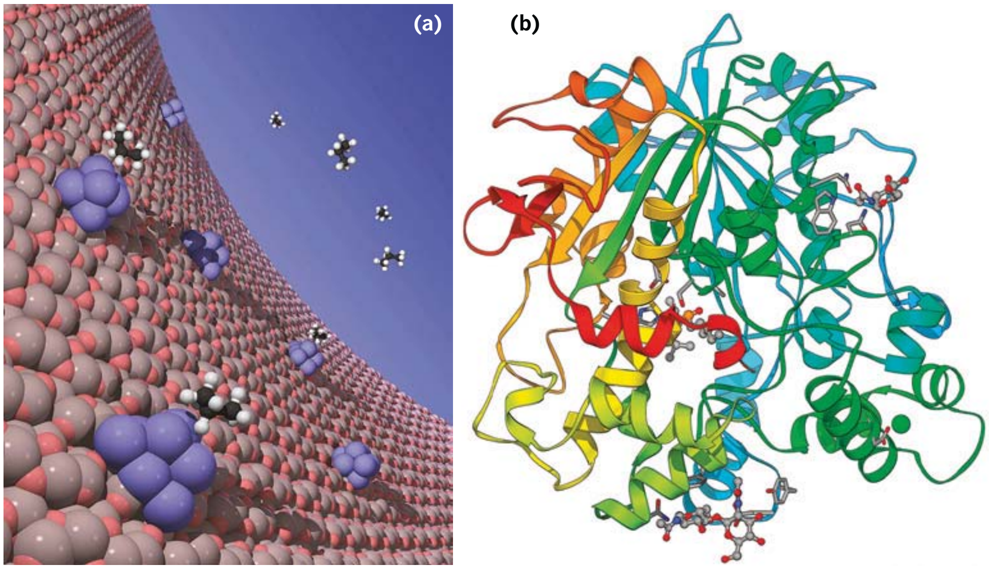


FIGURE 7.4.1 (a) A representation of the structure of a synthetic zeolite catalyst that is widely used in petroleum refineries to break down large hydrocarbon molecules into smaller, more useful molecules. Zeolite is a silica–alumina mineral. (b) A model of a lipase enzyme. Lipase is a catalyst that breaks down fats in the digestive system of the human body.

CATALYSTS AND ACTIVATION ENERGY

You have already learned that the potential energy changes associated with a reaction can be represented as an energy profile diagram of the reaction. An energy profile diagram for an exothermic reaction is shown in Figure 7.4.2.

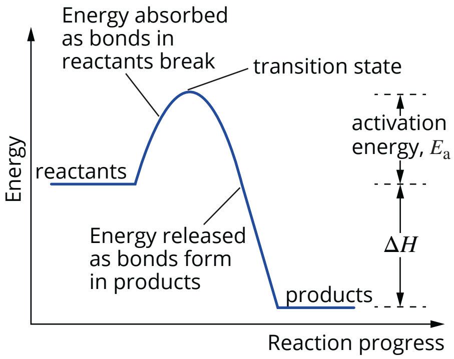


FIGURE 7.4.2 Energy profile diagram of an exothermic reaction such as burning natural gas.

The activation energy is the minimum amount of energy required for a reaction to take place. On the energy profile diagram, the activation energy is measured from the energy of the reactants to the peak of the energy profile diagram.

The enthalpy change, ΔH, can also be represented on an energy profile diagram and is equal to the difference in energy between the products and the reactants.

Some reactions occur very readily because they have very small activation energies, E_a. These reactions need only a small amount of energy to be absorbed for bonds in the reactants to be broken.

Many reactions occur much more rapidly in the presence of a particular element or compound. These substances are known as catalysts. Catalysts are not consumed during the reactions they speed up, and so do not appear as either reactants or products in reaction equations.

Catalysts are able to cause a reaction to occur more quickly because they provide a new **reaction pathway**, which causes the activation energy barrier of the overall reaction to be dramatically reduced, as seen in the energy profile diagram in Figure 7.4.3.

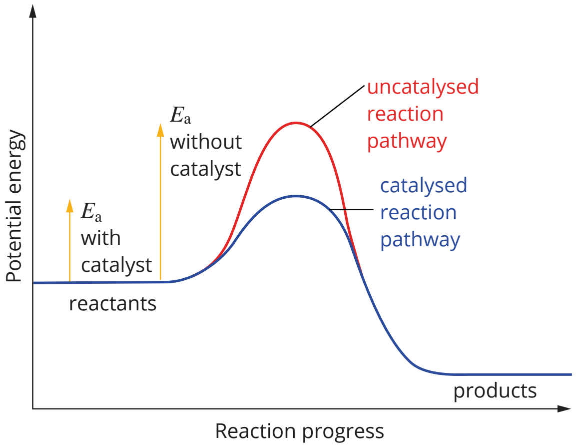


FIGURE 7.4.3 Energy profile diagrams of a catalysed and uncatalysed reaction.

With the catalyst present and a lower activation energy, the colliding particles are more likely to have energies that exceed this lower barrier, causing the bonds in the reactants to be broken more frequently. As a result, a greater proportion of collisions are 'successful'; that is, they lead to the formation of products. Thus, the reaction rate is increased.

The Maxwell–Boltzmann curve in Figure 7.4.4 shows the smaller number of particles with energies that exceed the activation energy in an uncatalysed reaction (shaded in red) compared with the number of particles with energies that exceed the activation energy in a catalysed reaction (regions shaded in red and blue).

Catalysts only lower the activation energy for a reaction. There is no change to ΔH for the reaction.

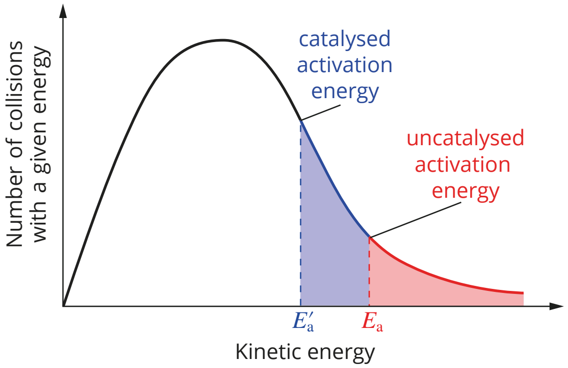


FIGURE 7.4.4 A catalyst provides a reaction pathway with a lower activation energy, increasing the proportion of collisions that exceed the activation energy and lead to a reaction.

Catalysts lower the activation energy by providing an alternative reaction pathway for the reaction. This increases the proportion of reactant particles with energies equal to or greater than the lower activation energy. This increases the proportion of successful collisions.

CHEMFILE

Routes from Melbourne to Canberra

Figure 7.4.5 shows two groups of tourists travelling from Melbourne to Canberra by two different routes. The slower route can be likened to the progress of an uncatalysed reaction; the faster route can be likened to the progress of a catalysed reaction.

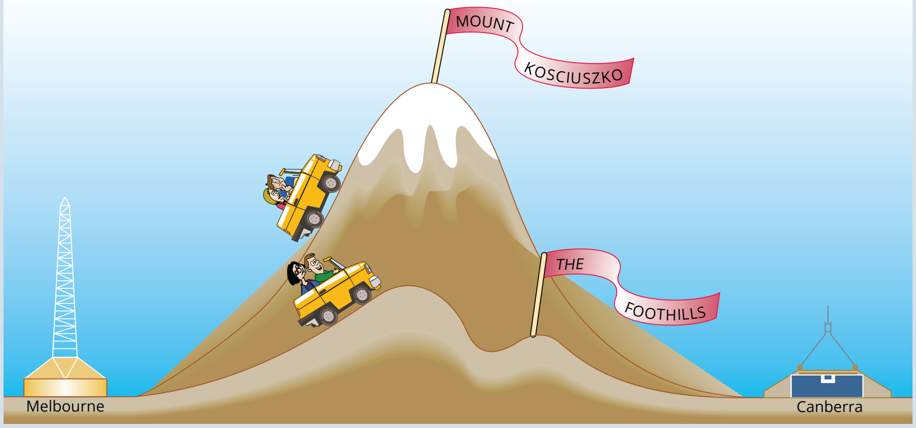


FIGURE 7.4.5 An analogy for the role of a catalyst in a chemical reaction.

TYPES OF CATALYSTS

Depending on the physical state of the chemicals involved in the reaction and the catalyst, catalysts can be divided into two groups.

- **Homogeneous catalysts** are in the same physical state as the reactants and products of the reaction.
- **Heterogeneous catalysts** are in a different physical state from the reactants and products of the reaction.

An example of homogeneous **catalysis** occurs in the upper atmosphere and has contributed to the depletion of the ozone layer. Chlorine atoms in the gaseous state act as catalysts in the decomposition of ozone gas into oxygen gas. The chlorine atoms may have come from chlorofluorocarbons (CFCs) released into the atmosphere from refrigerators or air conditioners.

You may be familiar with the catalysed decomposition of a hydrogen peroxide solution using the black powder manganese(IV) oxide (MnO_2). This is an example of the use of a heterogeneous catalyst.

CATALYSTS IN INDUSTRY

The chemical industry uses catalysts extensively. Chemists prefer to use heterogeneous catalysts for industrial processes because they are:

- more easily separated from the products of a reaction
- much easier to reuse
- able to be used at high temperatures.

Particles at the surface of some solids of high surface area tend to adsorb (form a bond with) gas molecules that strike the surface. **Adsorption** distorts bonds in the gas molecules or may even break them completely. This allows a reaction to proceed more easily than it would if the solid were absent.

These solid surfaces provide a new way for the reaction to occur (a new reaction pathway) that has a significantly lower activation energy.

A powdered or sponge-like form of a solid catalyst is often used to provide the greatest possible surface area. With a larger surface area, more reactant molecules can be adsorbed and the reaction is even faster.

EXTENSION

Heterogeneous catalysis and the Haber process

The Haber process is a very important commercial reaction that produces ammonia gas, which is used to make fertilisers, nylon, explosives and some pharmaceuticals. In the Haber process, hydrogen and nitrogen gas are converted to ammonia (NH_3), using a catalyst of powdered iron.

The reaction is represented by the equation:

$$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g) \qquad \Delta H = -91 \text{ kJ mol}^{-1}$$

Hydrogen and nitrogen molecules both adsorb onto the iron surface (see Figure 7.4.6a). As they attach themselves to the surface, the covalent bonds within their molecules break (Figure 7.4.6b).

The hydrogen and nitrogen atoms now readily combine to form ammonia molecules and move away from the iron surface (Figure 7.4.6c). The catalyst remains unaltered by the reaction.

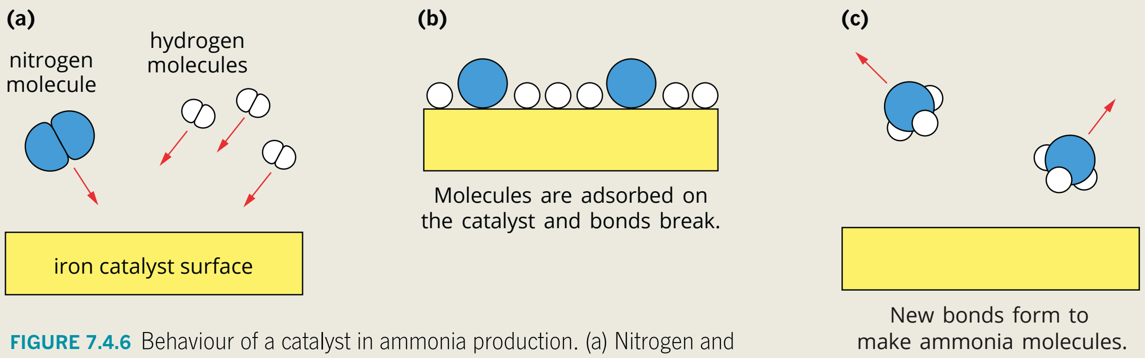


FIGURE 7.4.6 Behaviour of a catalyst in ammonia production. (a) Nitrogen and hydrogen molecules approach the iron catalyst surface. (b) The nitrogen and hydrogen molecules adsorb on the surface of the catalyst and their covalent bonds are broken. (c) The hydrogen and nitrogen atoms readily combine to form ammonia molecules. The molecules then leave the catalyst surface, and the catalyst remains unaltered by the reaction.

Without a catalyst, temperatures over 3000°C are needed for a significant reaction to occur. The catalyst allows the manufacture of ammonia to proceed at an economical rate using a temperature of about 500°C.

The iron catalyst provides an alternative reaction pathway that dramatically reduces the activation energy 'barrier'—the energy needed to break the covalent bonds in the nitrogen and hydrogen molecules. Even though collisions are less frequent at 500°C than at 3000°C, a greater proportion of colliding particles have sufficient energy to successfully react.

CHEMFILE

Catalytic converters in cars

All new cars sold in Australia have a catalyst fitted between the engine and the exhaust pipe. The purpose of the catalyst is to clean the exhaust gases from the engine and reduce the air pollution that could be caused if these gases entered the atmosphere.

Catalysts in cars convert carbon monoxide and nitrogen oxide, formed in the engine, to the non-toxic gases carbon dioxide and nitrogen. Several reactions are involved in this process, including:

$2NO(g) \rightarrow N_2(g) + O_2(g)$

$2CO(g) + O_2(g) \rightarrow 2CO_2(g)$

Unburnt hydrocarbons are also converted by the catalyst to carbon dioxide and water:

$2C_8H_{18}(g) + 25O_2(g) \rightarrow 16CO_2(g) + 18H_2O(g)$

The catalyst is usually a mixture of platinum, palladium and rhodium metals and aluminium oxide, and it is mounted on a honeycomb-shaped support (see Figure 7.4.7). Millions of tiny pores in the metals provide a large surface area.

Exhaust gases enter the catalyst chamber, pass quickly over the metals, and leave the exhaust pipe in a purified condition. The catalyst is unchanged by the reaction and can be used without replacement for many years.

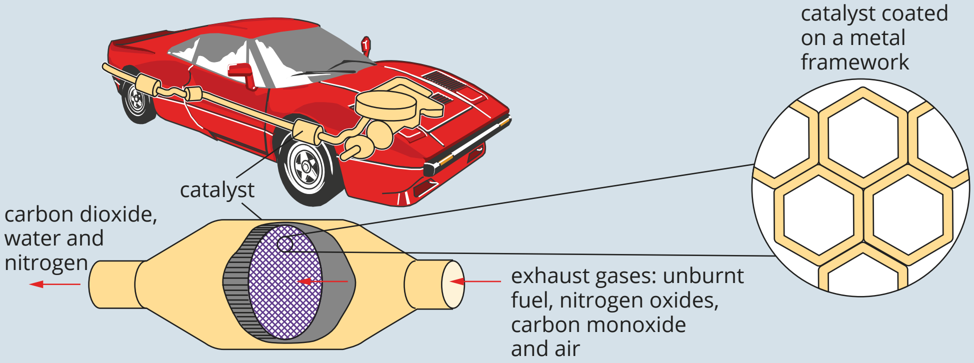


FIGURE 7.4.7 A catalyst fitted in the exhaust system of a car reduces air pollution.

7.4 Review

SUMMARY

- The rate of a reaction can be increased by using a catalyst.
- A catalyst provides an alternative reaction pathway that has a lower activation energy.
- Energy profile diagrams (see Figure 7.4.8), which can include catalysed and uncatalysed pathways, may be used to represent the enthalpy changes and activation energy associated with a chemical reaction.
- A catalyst provides a new reaction pathway and it is not used up in the reaction.
- When a catalyst is present, a greater proportion of the collisions between particles exceed the activation energy barrier of the reaction and therefore lead to a chemical change.

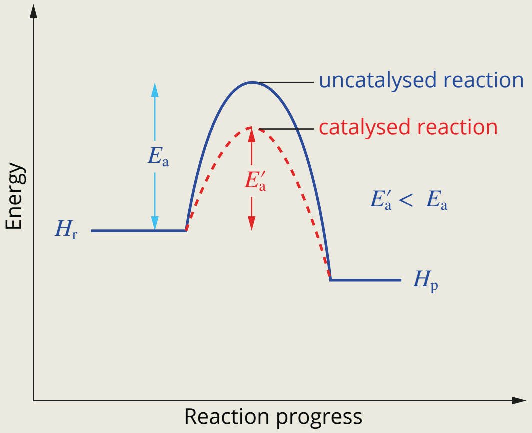


FIGURE 7.4.8 Energy profile diagram of a reaction showing the effect of a catalyst.

KEY QUESTIONS

1 Consider the reaction between solutions V and W that produces X and Z according to the equation:

$V(aq) + W(aq) \rightarrow X(aq) + Z(aq)$

The energy profile diagram for this process is shown in Figure 7.4.9.

Which one of the following alternatives describes the change that a catalyst produces to increase the reaction rate?

A B only is decreased.
B A only is decreased.
C A, B and C are decreased.
D A and C only are decreased.

2 Explain the meaning of:

a catalyst
b activation energy.

3 If a sugar cube is held in the flame of a candle, the sugar melts and browns but does not burn. However, the cube burns if salt is first rubbed into it, even though the salt does not react. Explain the effect of the salt on the activation energy of this combustion reaction.

4 **a** Explain why surface properties are important to the operation of catalysts.
b Many industrial catalysts are made into porous pellets. What is the reason for this?

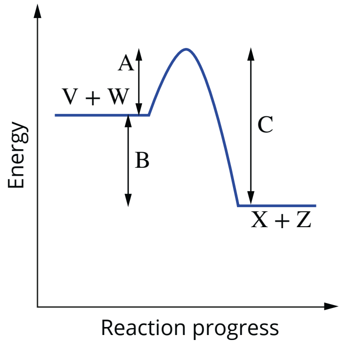


FIGURE 7.4.9 The energy profile diagram for the reaction between V(aq) and W(aq).

Chapter review

07

KEY TERMS

acid rain
activation energy
adsorption
catalysis
catalyst
collision theory
endothermic
energy profile diagram
exothermic
heterogeneous catalyst
homogeneous catalyst
kinetic energy
kinetic energy distribution diagram
Maxwell–Boltzmann distribution curve
photochemical smog
rate of reaction
reaction pathway
surface area
transition state

Investigating the rate of chemical reactions

1 Which one of the following is the correct definition of rate of reaction?
- **A** The time it takes for all of a reactant to be used up
- **B** How fast a reaction is going at the end of 1 minute
- **C** How much a reaction is bubbling
- **D** The change in concentration of reactants or products over time

2 Which of the following combinations of reactants will produce the greatest initial reaction rate?

$2HCl(aq) + CaCO_3(s) \rightarrow CaCl_2(aq) + H_2O(l) + CO_2(g)$
- **A** $CaCO_3$ chips and 1 M HCl
- **B** $CaCO_3$ chips and 2 M HCl
- **C** $CaCO_3$ powder and 2 M HCl
- **D** $CaCO_3$ powder and 1 M HCl

3 The following changes are made to a reaction mixture. Which change will lead to a decrease in reaction rate?
- **A** Smaller solid particles are used.
- **B** The temperature is decreased.
- **C** A catalyst is added.
- **D** The concentration of an aqueous reactant is increased.

4 Which of the following is the correct unit for measuring the rate of a reaction?
- **A** $mol^{-1}\ L\ s^{-1}$
- **B** $mol\ L^{-1}\ s^{-1}$
- **C** $mol^{-1}\ L^{-1}\ s$
- **D** $mol\ L\ s^{-1}$

5 A 5.00 g piece of copper was dissolved in a beaker containing 500 mL of 2.00 M nitric acid. The equation for the reaction that occurred is:

$$3Cu(s) + 8HNO_3(aq) \rightarrow 3Cu(NO_3)_2(aq) + 2NO(g) + 4H_2O(l)$$

The changing mass of the mixture was observed for a period of time, and the graph in Figure 7.5.1 was obtained.

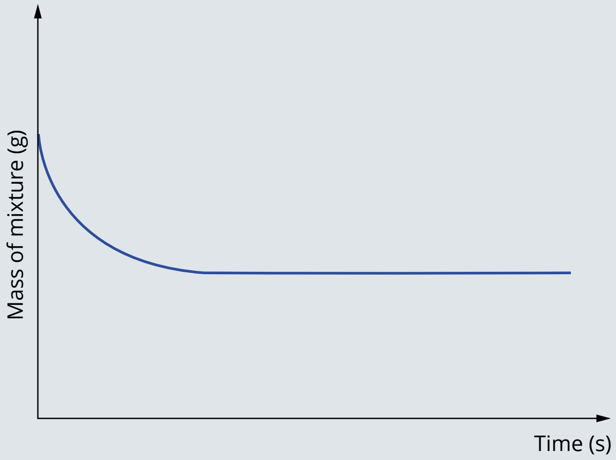


FIGURE 7.5.1 Mass of reaction mixture over time.

- **a** Explain why the mass of the mixture initially decreases with increasing time.
- **b** Based on the information provided, determine which reactant is limiting.
- **c** Redraw Figure 7.5.1, then sketch in the expected curve if 500 mL of 1.00 M nitric acid had been used instead. Label your new graph line. Explain the difference in shape.
- **d** Redraw Figure 7.5.1, then sketch in the expected curve if 5.00 g of powdered copper was used instead. Label this new graph line. Explain the difference in shape.

Collision theory

6 According to collision theory, what must happen for a reaction to occur?

7 Figure 7.5.2 shows the substitution reaction between chloromethane and a hydroxide ion.
Using collision theory, explain why collision 1 might be successful while collisions 2–4 will not be successful.

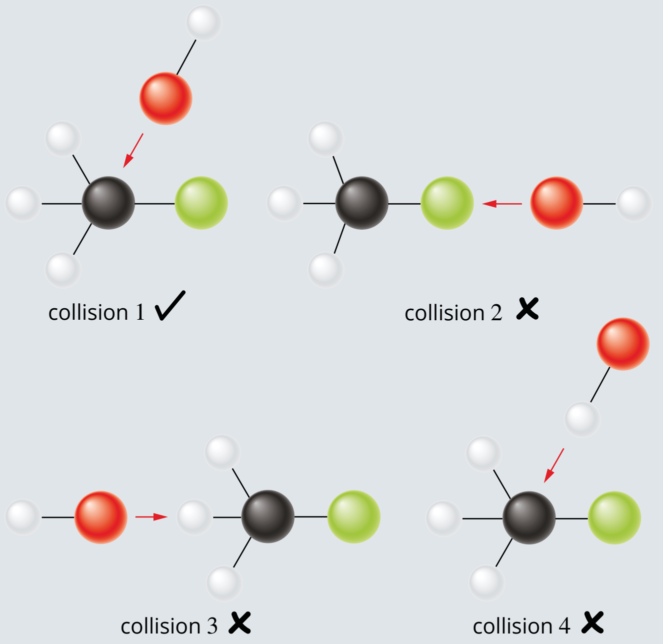


FIGURE 7.5.2 Possible collision orientations in the substitution reaction between chloromethane and hydroxide ion.

8 Figure 7.5.3 is an energy profile diagram for the substitution reaction between chloromethane and hydroxide ion.

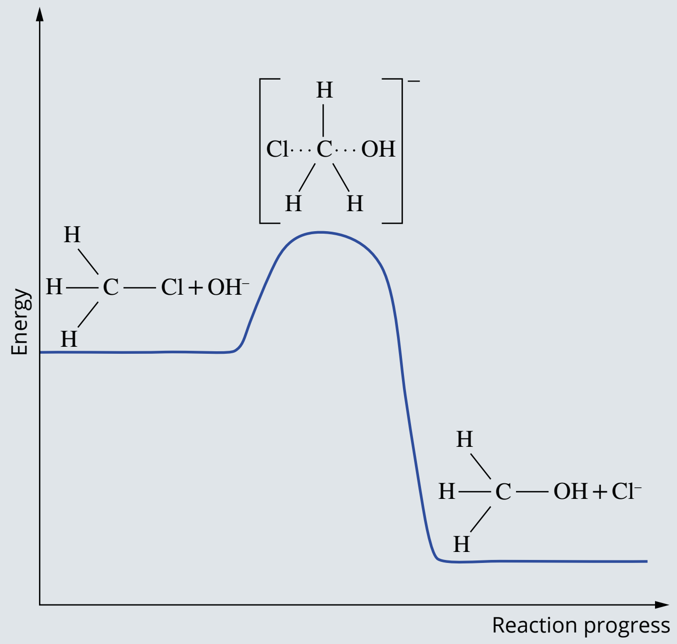


FIGURE 7.5.3 Energy profile diagram for the substitution reaction between chloromethane and the hydroxide ion.

a Copy this diagram and label Δ*H* and activation energy.

b Explain what is meant by the term ‘activation energy’.

c Is the reaction endothermic or exothermic?

d Label the transition state in this reaction on your diagram.

e What bonds are beginning to be broken and formed to produce the transition state?

9 Hydrogen reacts explosively with oxygen to form water.

a What chemical bonds are broken in the reaction?

b What chemical bonds are formed?

c Explain how the energy changes during bond-breaking and bond-forming affect the overall energy change for the reaction.

d Why is there no reaction until the reaction mixture is ignited?

Effect of temperature on rate of reaction

10 Which one of the following alternatives correctly explains why the rate of reaction between 1 M $CuSO_4$ and powdered zinc is greater than with an equal amount of large zinc pieces.

A The energy of collisions between the $Cu^{2+}(aq)$ ions and powdered zinc is greater than with the large zinc pieces.

B The frequency of collisions between the $Cu^{2+}(aq)$ ions and powdered zinc is greater than with the large zinc pieces.

C The energy of collisions between the $Cu^{2+}(aq)$ ions and large zinc pieces is greater than with the powdered zinc.

D The frequency of collisions between the $Cu^{2+}(aq)$ ions and large zinc pieces is greater than with the powdered zinc.

11 Which one of the following statements correctly describes what must occur when reactant particles collide and react?

A Colliding particles must have an equal amount of kinetic energy.

B Colliding particles must have different amounts of kinetic energy.

C Colliding particles must have kinetic energy equal to or greater than the average kinetic energy.

D Colliding particles must have kinetic energy equal to or greater than the activation energy of the reaction.

12 Account for the following observations with reference to the collision model of particle behaviour.

a Refrigeration slows down the browning of sliced apples.

b Hydrogen gas burns in air to produce water vapour. Using pure oxygen gas instead of air increases the rate of this reaction.

Catalysts

13 Which one of the following factors would *not* increase the rate of decomposition of hydrogen peroxide?

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

A Increasing the pressure of oxygen gas
B Increasing the concentration of hydrogen peroxide
C Increasing the temperature of hydrogen peroxide
D Adding a potassium iodide catalyst

14 Which statement is correct for the effects of catalyst and concentration on the rate of reaction?

	Adding a catalyst	**Increasing the concentration**
A	Collision frequency increases	Collision frequency increases
B	Activation energy decreases	Activation energy decreases
C	Activation energy decreases	Collision frequency increases
D	Collision frequency increases	Activation energy decreases

15 **a** What are the five factors that influence the rate of a reaction?

b Classify the five factors from part **a** according to whether they increase the proportion of successful collisions by:

- **i** increasing collision frequency
- **ii** increasing the proportion of collisions that have energy equal to or greater than the activation energy.

16 The Haber process involves the reaction of nitrogen gas and hydrogen gas to make ammonia gas. Describe two ways the rate of this reaction could be increased, at constant temperature. Using collision theory, explain why rate is increased.

17 Many major car makers have plans for hydrogen-powered cars. In the fuel cells of these cars, hydrogen reacts with oxygen from the air to produce water.

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

Energy changes for the reaction are shown in the graph in Figure 7.5.4.

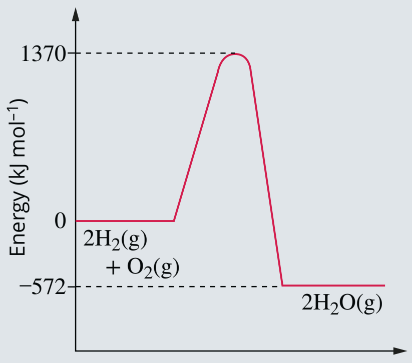


FIGURE 7.5.4 Energy changes for the reaction of hydrogen and oxygen.

a What is the magnitude of the activation energy of this reaction?

b What is ΔH for this reaction?

Several groups of scientists have claimed to have split water into hydrogen and oxygen using a molybdenum catalyst:

$$2H_2O(g) \xrightarrow{Mo} 2H_2(g) + O_2(g)$$

c Sketch energy change graphs for this reaction with and without the presence of a catalyst.

d What is the value of ΔH for this water-splitting equation?

Connecting the main ideas

18 **a** Figure 7.5.5 shows the distribution of energies of particles in a substance at two different temperatures, 40°C and 60°C. Indicate the temperatures represented by graphs A and B.

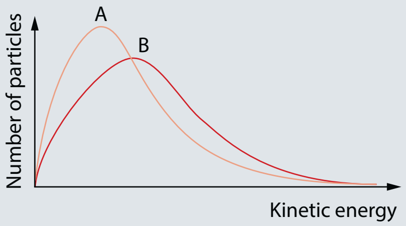


FIGURE 7.5.5 Energy profiles at 40°C and 60°C.

b Copy this diagram for temperature B and use the diagram to show the effect of a catalyst on a reaction.

c Use the diagram you have drawn in part **b** to explain in terms of collision theory how a catalyst increases the rate of a reaction.

19 Lumps of limestone, calcium carbonate, react readily with dilute hydrochloric acid. Four large lumps of limestone, mass 10.0 g, were reacted with 100 mL 0.100 M acid.

a Write a balanced equation to describe the reaction.

b Which reactant is in excess? Use a calculation to support your answer.

c Describe a technique that you could use in a school laboratory to measure the rate of the reaction.

d 10.0 g of small lumps of limestone will react at a different rate from four large lumps. Will the rate of reaction with the smaller lumps be faster or slower? Explain your answer in terms of collision theory.

e List two other ways in which the rate of this reaction can be altered. Explain your answer in terms of collision theory.

20 Figure 7.5.6 shows the energy profile diagram for the reaction of hydrogen and iodine to form hydrogen iodide:

$H_2(g) + I_2(s) \rightleftharpoons 2HI(g)$

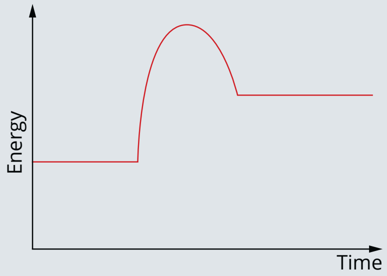


FIGURE 7.5.6 Energy profile diagram for the production of hydrogen iodide.

- **a** Copy the diagram and label the following: $H_2(g)$ and $I_2(s)$; $HI(g)$; ΔH; activation energy.
- **b** Is the reaction endothermic or exothermic?
- **c** On the diagram draw the energy profile that would result if a catalyst was used in the reaction.

21 Read the article and answer the questions that follow.

Exploding iron

In 1996, while the Turkish ship MV *B. Onal* was riding at anchor in Delaware Bay, near Philadelphia in the USA, a 2-tonne hatch cover suddenly blew off. As the ship was carrying a cargo of iron, the surprised crew asked themselves, 'Can iron explode?'

As you may be aware, traditionally iron oxide (Fe_2O_3) is reduced to molten iron in a blast furnace

A new process that uses less energy has been developed. Iron oxide is converted directly to solid iron without having to heat the reactants to the melting point of iron. Iron oxide is heated to 550°C in the presence of carbon monoxide and hydrogen gas. The iron oxide is reduced to iron by both gases with the formation of carbon dioxide or water.

$$Fe_2O_3(s) + 3CO(g) \rightarrow 2Fe(s) + 3CO_2(g) \qquad (1)$$

$$Fe_2O_3(s) + 3H_2(g) \rightarrow 2Fe(s) + 3H_2O\,(g) \qquad (2)$$

The pellets of pure iron that are formed are extremely porous and full of many tiny holes, in contrast to the solid formed when the molten iron from a blast furnace cools. Under the right conditions the iron pellets can be oxidised back to iron oxide.

In most cases, iron is oxidised slowly by oxygen back to iron oxide and the resulting heat can readily escape. If the pellets are more than 1 metre deep, as in the hold of a ship, the heat cannot escape quickly enough and the temperature rises. This speeds up the reaction rate. If the temperature increases sufficiently and water is present, another reaction occurs and the oxidation rate is speeded up 100-fold, with the release of more heat:

$$Fe(s) + H_2O(g) \rightarrow FeO(s) + H_2(g) \qquad (3)$$

Any spark or fire will set off an explosion of hydrogen gas, and that is what happened on the MV *B. Onal*.

- **a** What is the main reason the new reduction process uses less energy than the old process?
- **b** Write equations showing the oxidation of iron by oxygen to form iron(II) oxide and iron(III) oxide.
- **c** If water is present the oxidation reaction speeds up 100-fold. Is water acting as a catalyst? Explain your answer.
- **d** Is the reaction shown in equation 3 endothermic or exothermic?
- **e** List the factors that increased the rate of reaction in equation 3.
- **f** Firefighters were not able to use water to put out the fire in the cargo hold. Why not? Suggest how they could put out the fire.

22 Chemical reactions in the body normally take place at 37°C. Explain how the rate of chemical reactions in the body can account for the following facts.

- **a** The body often responds to illness by an increase in temperature, accompanied by a higher pulse rate and faster breathing.
- **b** People rescued from drowning after 20–30 minutes in freezing water can sometimes survive and recover with no brain damage.

23 The first step in most toffee recipes is to dissolve about 3 cups of sugar in 1 cup of water. Although sugar is quite soluble in water, this step could be time-consuming. Use your knowledge of reaction rates to suggest at least three things you could do to increase the rate of dissolution without ruining the toffee.

CHAPTER

08 Extent of chemical reactions

In this chapter, you will investigate the ideas of reversibility and irreversibility of chemical systems. This study of reversible reactions will introduce the concept of chemical equilibrium.

Various factors can change the position of a chemical equilibrium. Le Châtelier's principle enables us to understand the effects of changes in concentrations in solutions, pressures of gases and temperature on an equilibrium.

The fact that many reactions do not proceed to completion has serious consequences on the efficiency of chemical manufacturing industries. You will learn how the reaction conditions chosen for an industrial process can be adjusted to ensure optimum efficiency, taking into account considerations of rate and equilibrium yield.

You will also learn how to write a mathematical relationship, known as an equilibrium law, for an equilibrium system. This law can be used to calculate the relative amounts of reactants and products present when a reaction is at equilibrium.

Key knowledge

- The distinction between reversible and irreversible reactions, and between rate and extent of a reaction
- Homogenous equilibria involving aqueous solutions or gases with reference to collision theory and representation by balanced chemical or thermochemical equations (including states) and by concentration–time graphs
- Calculations involving equilibrium expressions and equilibrium constants (K_c only) for a closed homogeneous equilibrium system including dependence of value of equilibrium constant, and its units, on the equation used to represent the reaction and on the temperature
- Le Châtelier's principle: identification of factors that favour the yield of a chemical reaction, representation of equilibrium system changes using concentration–time graphs and applications, including competing equilibria involved in the occurrence and treatment of carbon monoxide poisoning resulting from incomplete combustion of fuels

8.1 Dynamic equilibrium

In this section, you will learn that some reactions can occur in both the forward and reverse directions. These reactions are called 'reversible reactions'.

Reversible chemical systems are encountered in many everyday situations, including chemical manufacturing processes, the reactions of ions within individual cells in your body and the reactions carbon dioxide undergoes in the environment.

This section also describes how some reversible reactions can reach a point where they appear to 'stop'. At this point, the concentrations of the reactants and products remain constant, even though there are still reactants remaining.

The fact that many reactions do not proceed to completion has serious consequences for the production of chemicals by industry. The presence of large amounts of unreacted starting materials in reaction mixtures is wasteful and costly. The profitability of an industry depends on the yield—the extent of conversion of reactants into products.

Although these reactions appear to stop, they actually continue to proceed. If you could see what was occurring at the atomic scale, you would notice that as rapidly as the reactants are forming products, the products are re-forming reactants. This situation can be likened to the queue shown in Figure 8.1.1. Although the length of the queue may seem constant, people at the front are continually leaving the queue and others are joining it at the back at the same rate.

FIGURE 8.1.1 A queue of constant length can be likened to a reaction that appears to have stopped, with people leaving the queue at one end at the same rate as others join it at the other end.

OPEN AND CLOSED SYSTEMS

In previous chapters, you learned that a chemical reaction can be regarded as a **system**, with everything else around it (the rest of the universe) being the **surroundings**. In an **endothermic** reaction, the system absorbs energy from the surroundings, whereas in an **exothermic** reaction, energy is released to the surroundings.

Figure 8.1.2 illustrates how you can distinguish between two different types of systems:

- **open systems**
- **closed systems**.

The most common situation in everyday life is an open system. In an open system, matter and energy can be exchanged with the surroundings. In contrast, a closed system only exchanges energy with the surroundings.

Some everyday examples of open and closed systems are illustrated in Figure 8.1.3.

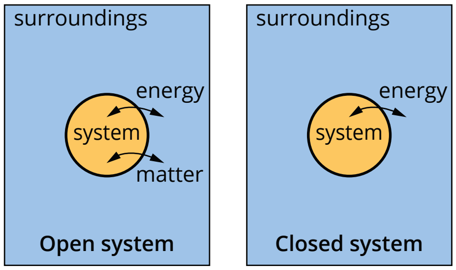


FIGURE 8.1.2 Open systems exchange energy and matter with the surroundings. Closed systems only exchange energy with the surroundings.

In a closed system, only energy can be exchanged with the surroundings.

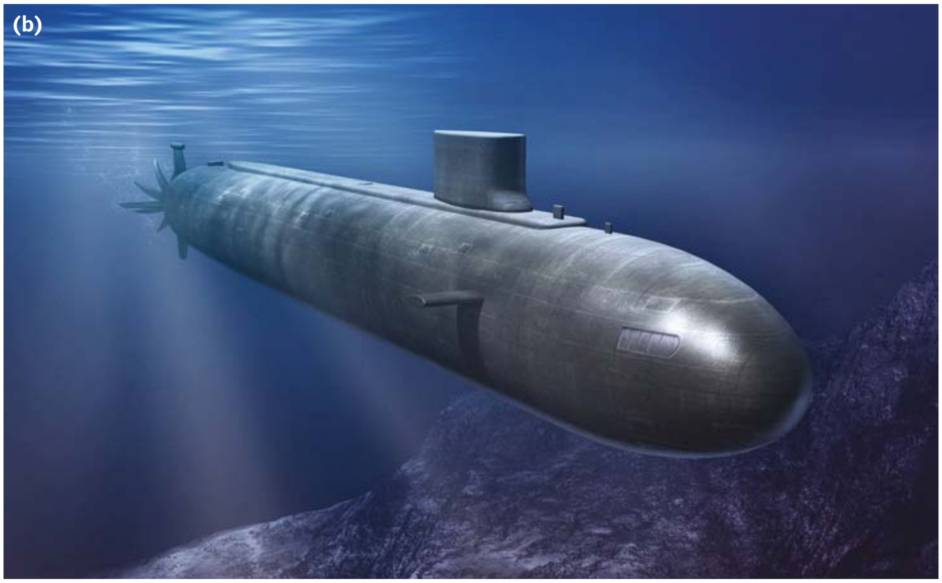


FIGURE 8.1.3 Everyday examples of open and closed systems. (a) A bushfire burning through a forest on 3 February 2014 in Banjip, Western Australia. This is an example of an open system. Carbon dioxide and water vapour produced by the burning trees are released into the atmosphere. (b) A nuclear submarine in operation under water—the carefully monitored environment of the submarine can be regarded as a closed system.

IRREVERSIBLE AND REVERSIBLE SYSTEMS

You may have thought, as a younger student, that when chemical reactions occur, the reactants form products and these products cannot be converted back to the reactants. Such reactions, which occur only in one direction, are called non-reversible or **irreversible reactions**.

Baking a cake, like the one shown in Figure 8.1.4, involves several irreversible reactions. Combustion reactions such as the burning of methane are also irreversible:

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$$

Once a fuel has burnt, the products, carbon dioxide and water, do not react with each other under normal conditions.

FIGURE 8.1.4 Baking a cake involves a series of irreversible chemical reactions.

As you will see, other reactions are **reversible reactions** where the products, once formed, can react again, re-forming the reactants.

You are familiar with the idea that a physical change, such as a state change, can be reversed. The evaporation of water from lakes and rivers leading to cloud formation and eventually rain is an example of a physical change. Water can cycle between the different phases of solid, liquid and gas because each process is reversible.

In chemistry, a double arrow (⇌) is used when writing a chemical equation to show a reversible process. In this way, you can show the phase changes associated with water using the following equation:

$$H_2O(l) \rightleftharpoons H_2O(g)$$

Many reversible reactions are essential to our society; for example, the reactions that power rechargeable batteries.

In reversible reactions, the formation of products as a result of collisions between reactant particles is not the end of the process. Once some products are formed, collisions between product particles can result in the reactants being re-formed.

Consider the production of ammonia from hydrogen gas and nitrogen gas, known as the Haber process.

The equation for the reaction can be written as:

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

Suppose you mix 1 mol of nitrogen gas and 3 mol of hydrogen gas in a sealed container. From the equation, you might expect that 2 mol of ammonia would eventually be formed. However, no matter how long you wait, the reaction seems to 'stop' when much less than 2 mol of ammonia is present, as shown in Figure 8.1.5.

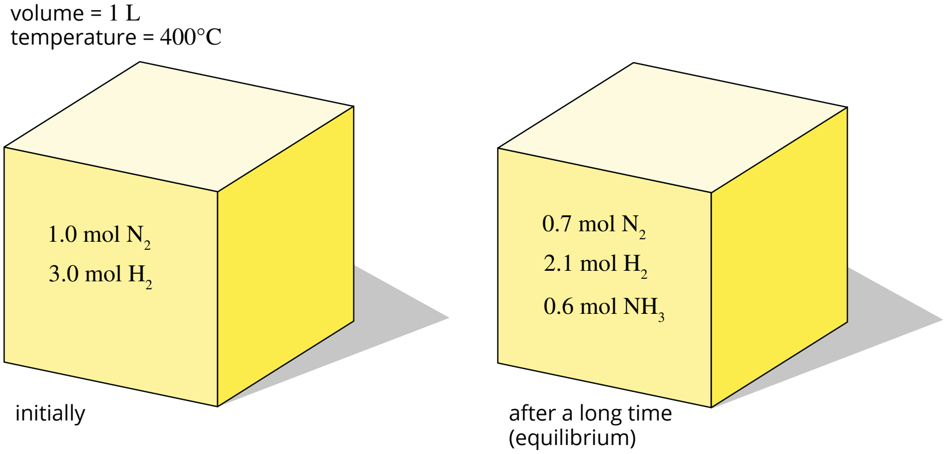


FIGURE 8.1.5 When 1 mol of nitrogen and 3 mol of hydrogen are mixed, the reaction to form ammonia appears to stop before all the reactants are consumed.

The reaction vessel this process occurs in can be thought of as a closed system from which the reactants and products cannot escape. Reversible reactions in a closed system eventually reach a situation where the rate of the forward reaction and the rate of the reverse reaction are equal.

At this point, there appears to be no further change to the observer. In the case of a chemical reaction, when the reaction appears to have 'stopped', the system is described as having reached **equilibrium**. At equilibrium, there still may be significant amounts of reactants in the system.

Reversible reactions can reach a state of equilibrium where the overall concentrations of reactants and products do not change over time.

CHEMFILE

Limestone caves

An example of reversibility in nature is the formation of stalactites and stalagmites in limestone caves (Figure 8.1.6).

The main mineral in limestone is calcite ($CaCO_3$). Water saturated with carbon dioxide from the atmosphere drips through the roof of the cave, resulting in the following reaction:

$$CO_2(g) + H_2O(l) + CaCO_3(s) \rightarrow Ca^{2+}(aq) + 2HCO_3^-(aq)$$

As the water seeps through the rocks, it becomes saturated with Ca^{2+} ions and HCO_3^- ions. The water then evaporates and the reverse reaction produces stalactites from the ceiling of the cave:

$$Ca^{2+}(aq) + 2HCO_3^-(aq) \rightarrow CO_2(g) + H_2O(l) + CaCO_3(s)$$

Some of the solution drips onto the floor of the cave, where more deposits of $CaCO_3$ are produced, forming stalagmites. Stalactites and stalagmites grow in pairs and can produce beautiful columns like the ones seen in the Buchan cave system shown in Figure 8.1.6.

FIGURE 8.1.6 Stalactites and stalagmites in the Buchan Caves in Victoria. They are made of the mineral calcite.

EXPLAINING REVERSIBILITY

The reason why reversible reactions can occur can be understood by referring to an energy profile diagram like the ones you saw in section 2.2.

When particles collide, the energy associated with collisions can break bonds in the reacting particles, allowing them to rearrange to form new products. The energy required to break the bonds of the reactants is known as the **activation energy** of the reaction.

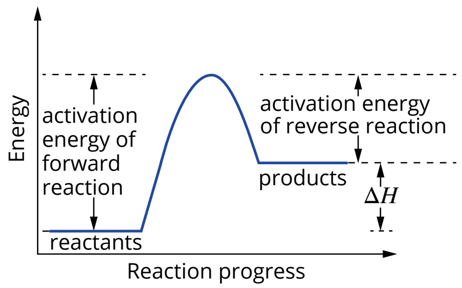


FIGURE 8.1.7 An energy profile diagram for an endothermic reaction showing the activation energy required for both the forward (formation of products) and reverse (re-formation of reactants) reactions.

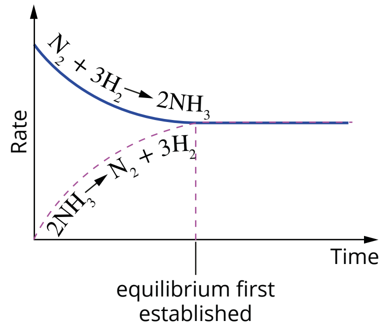


FIGURE 8.1.8 The variation of the rates of the forward and reverse reactions with time when nitrogen and hydrogen are mixed.

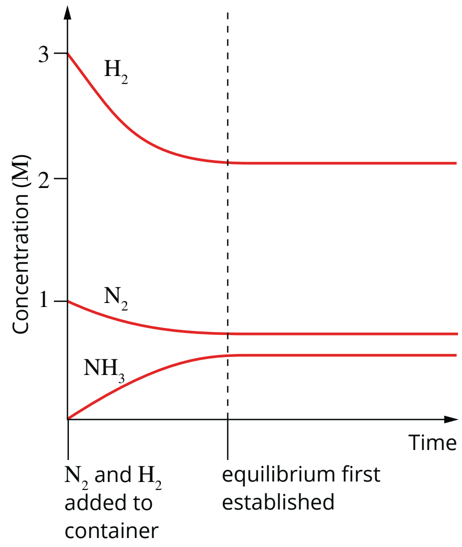


FIGURE 8.1.9 Changes in the concentrations of N_2, H_2 and NH_3 as a mixture of nitrogen and hydrogen gas reacts. As indicated by the coefficients of the equation for the reaction, for every mole of N_2 that reacts, three times as much H_2 reacts and twice as much NH_3 is produced.

You can see from the energy profile diagram shown in Figure 8.1.7 that once the products form, it is possible for the reverse process to occur. If the newly formed product particles collide with enough energy to break their bonds (equal to the activation energy of the reverse reaction), then it is possible to re-form the original reactants.

If the forward reaction is endothermic, the reverse reaction is exothermic, and vice versa.

EXPLAINING EQUILIBRIUM

Because the reaction between nitrogen and hydrogen to form ammonia is a reversible reaction, it is best written using an equilibrium arrow:

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

Equilibrium arrows indicate that the reaction can occur in both the forward and reverse directions. These arrows should not be used where the reaction can only proceed one way.

The idea that processes can be reversed can be used to understand why this reaction reaches equilibrium. When nitrogen gas and hydrogen gas are added to a sealed container at a constant temperature, a sequence of events occurs that can be illustrated by a plot of reaction rate versus time like the one shown in Figure 8.1.8.

If you consider the graph in Figure 8.1.8, you can understand the following.

- Nitrogen and hydrogen gas molecules collide with each other and form ammonia. As the forward reaction, $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$, proceeds, the concentrations of nitrogen and hydrogen decrease, so the frequency of collisions between molecules decreases and the rate of the production of ammonia decreases.
- At the same time as ammonia is being formed, some ammonia molecules collide and decompose to re-form nitrogen and hydrogen: $2NH_3(g) \rightarrow N_2(g) + 3H_2(g)$.
- Eventually the forward and reverse reactions proceed at the same rate. When this situation is reached, ammonia is formed at exactly the same rate as it is breaking down. The concentrations of ammonia, nitrogen and hydrogen then remain constant. To an observer, the reaction now appears to have stopped with no observable change.

In a closed system at constant pressure and temperature, no further change will take place. The reaction has reached a point of balance—an equilibrium.

The concentration versus time graph in Figure 8.1.9 shows the changes in concentrations of the chemicals with time. Equilibrium is established when there is no longer any change in any of the concentrations.

When considering graphs involving equilibrium systems, always check if the data is presented as a plot of concentration versus time or plot of reaction rate versus time.

DYNAMIC STATE OF EQUILIBRIUM

Chemical equilibrium can be described as being in a dynamic state because the forward and reverse reactions have not ceased. Instead, they occur simultaneously at the same rate.

During **dynamic equilibrium**:

- the reaction is ‘incomplete’ and *all* of the substances (that is, the reactants and products) are present in the equilibrium mixture
- at the molecular level, bonds are constantly being broken and new bonds are being formed as the reactants and products continue to be converted from one to another.

The decomposition of dinitrogen tetroxide (N_2O_4) to nitrogen dioxide (NO_2) is an example of a reversible reaction that reaches a dynamic equilibrium. The progression of this reaction from pure N_2O_4 to the equilibrium mixture containing both N_2O_4 and NO_2 can be monitored through the changing colour of the gases in the reaction vessel. N_2O_4 is colourless and NO_2 is dark brown.

The reaction occurs according to the following equation:

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

Figure 8.1.10 illustrates the observations made of a reaction vessel that is injected with some pure N_2O_4. As the forward reaction proceeds, the formation of a dark brown gas is observed. The depth of colour increases until equilibrium is reached at which point there is no further change in the colour.

Dynamic equilibrium is reached by reversible physical or chemical reactions taking place in a closed system.

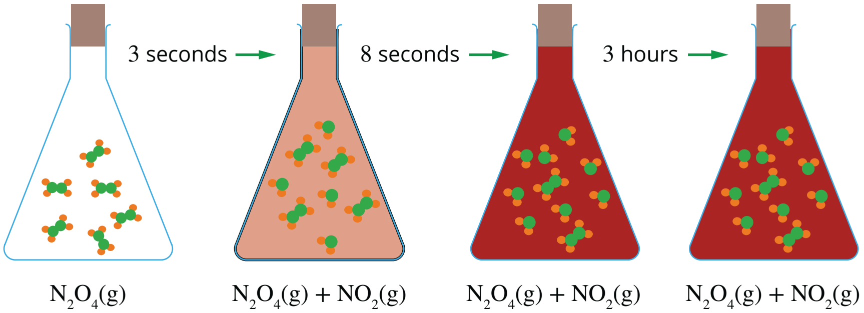


FIGURE 8.1.10 The decomposition of dinitrogen tetroxide produces the brown gas nitrogen dioxide. As the concentration of nitrogen dioxide increases, the colour deepens until equilibrium is reached. At equilibrium (after 8 seconds), there is no further change in colour regardless of how long the reaction is allowed to proceed.

EXTENSION

Investigating dynamic equilibrium

Chemists can use radioactive **isotopes** to investigate systems in dynamic equilibrium. Radioactive isotopes behave chemically in the same way as non-radioactive atoms of the same element, but their presence and location can be easily determined by a radiation detector.

When solid sodium iodide (NaI) is added to water, it dissolves readily at first. As the concentration of dissolved sodium iodide increases, a **saturated solution** forms and no further solid dissolves. The concentrations of the Na^+ ions and I^- ions in solution remain constant and some solid NaI is always present on the bottom of the test tube.

When solid sodium iodide containing radioactive iodide ions is added to a saturated solution, the subsequent movement of these ‘labelled’ ions can be traced. Figure 8.1.11 shows that although solid sodium iodide is still observed in the bottom of the flask, the solution quickly becomes radioactive.

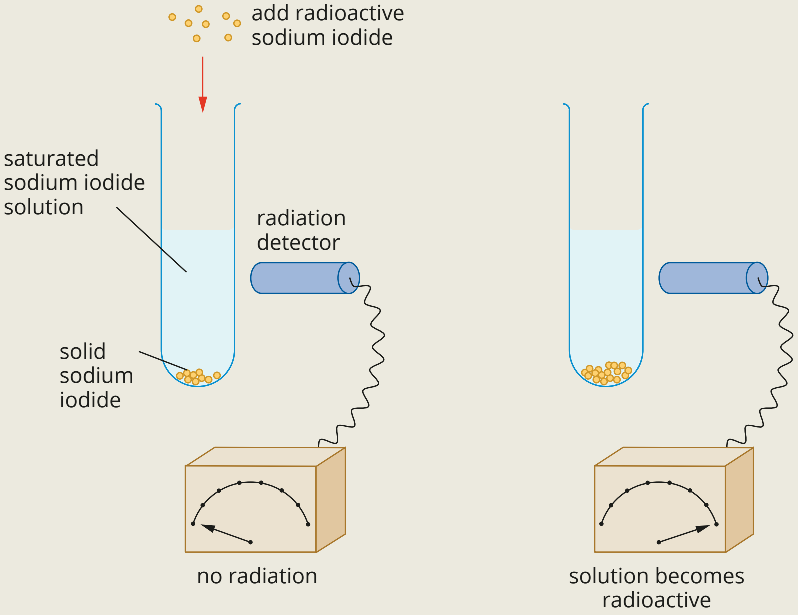


FIGURE 8.1.11 This experiment shows that a dynamic equilibrium between the solid substrate and dissolved ions is present in a saturated solution.

The radioactivity of the solution shows that some of the radioactive sodium iodide has dissolved. The concentration of sodium iodide remains constant, so particles that were not radioactive must have crystallised from the solution at the same rate as the radioactive solid was dissolving (Figure 8.1.12).

Even though we see nothing happening, there must be continual activity at the surface of the solid. The process is a dynamic equilibrium:

$$NaI(s) \rightleftharpoons NaI(aq)$$

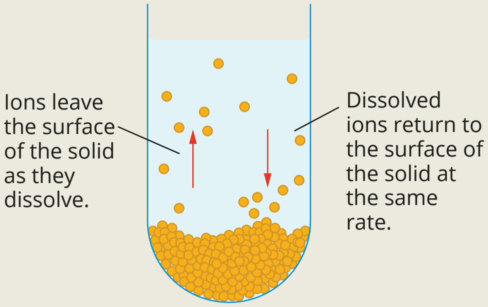


FIGURE 8.1.12 The cyclic dissolving and redepositing of ions in a saturated solution is an example of dynamic equilibrium.

EXTENT OF REACTION

You have seen that reactions are reversible, but do all reactions proceed to the same extent before they reach equilibrium? This can be answered with a simple experiment.

Both hydrogen chloride (HCl) and ethanoic acid (CH_3COOH) react with water to form ions, according to the equations:

$HCl(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + Cl^-(aq)$

$CH_3COOH(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3COO^-(aq)$

Solutions of both chemicals conduct electricity because they contain mobile ions. The relative conductivity of the solutions is proportional to the number of free ions in the solution. By measuring the electrical conductivity of solutions of the same concentration, you can compare how much each compound ionises in water.

Figure 8.1.13 shows the results obtained from such an experiment. You can see that the solution formed when hydrogen chloride dissolves in water (called hydrochloric acid) is a much better conductor than the ethanoic acid solution. Both solutions were formed by adding the same number of moles of acid molecules to identical volumes of water.

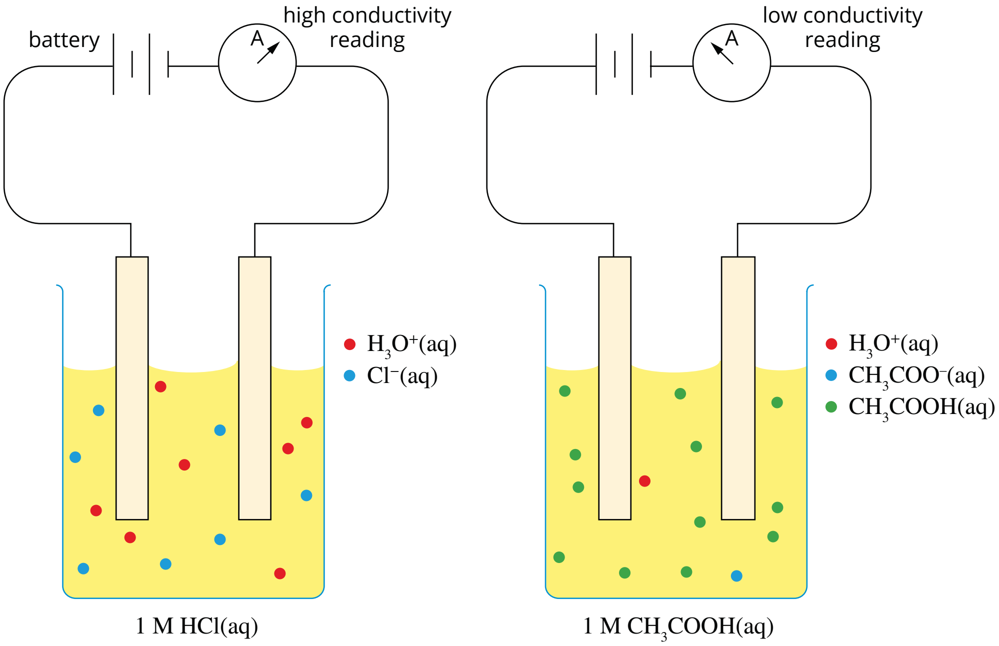


FIGURE 8.1.13 This experiment compares the electrical conductivity of 1 M solutions of hydrogen chloride and ethanoic acid.

As you will remember from Unit 2, ethanoic acid is a weak acid and will therefore only partially ionise in an aqueous solution. Hydrochloric acid is a strong acid that almost completely ionises in aqueous solution. The concept of equilibrium allows us to better explain the idea of strong and weak acids by looking at the extent of the ionisation reaction.

The difference in conductivity observed in the experiment arises because these reactions occur to remarkably different extents. At equilibrium in a 1 M solution, at 25°C, almost all the HCl molecules are ionised, whereas only approximately 1% of the CH_3COOH molecules are ionised.

We can conclude that different reactions proceed to different extents. The ratios of reactants to products are different for different equilibrium systems.

It is important to note that the **extent of reaction** describes how much product is formed when the system reaches equilibrium. However, the **rate of reaction** is a measure of the change in concentration of the reactants and products with time and is not directly related to the extent of reaction. The rates of reversible reactions range from very slow to very fast and determine how long the reaction takes to reach equilibrium.

The extent of a reaction does not give any information about how fast a reaction will proceed. It only indicates how much product is formed once the system is at equilibrium.

8.1 Review

SUMMARY

- In a closed system, only energy, not matter, is exchanged with the surroundings.
- In an open system, both matter and energy are exchanged between the system and the surroundings.
- A reversible reaction is a reaction in which the products can be converted back to the reactants.
- An irreversible reaction is a reaction in which the products cannot be converted back to the reactants.
- Reversible reactions can reach a point where the rate of the forward reaction and the rate of the reverse reaction are equal. At this point, a dynamic equilibrium has been achieved.
- Equilibrium can be achieved in closed systems but not in open systems.
- Different reactions proceed to different extents.
- The relative ratios of reactants to products when equilibrium is reached are different for different reactions.
- The extent of reaction indicates how much product is formed at equilibrium, whereas the rate of reaction is a measure of the change in concentration of the reactants and products with time.

KEY QUESTIONS

1 Which one of the following statements about the extent of reaction is true?

A The extent of reaction indicates the rate of the reaction, and indicates the time taken to reach equilibrium.

B The extent of reaction is the point when there are equal amounts of reactants and products.

C The extent of reaction indicates how far the reaction has proceeded in the forward direction when equilibrium is achieved.

D The extent of reaction indicates the rate of reaction and is the point when the rate of the forward reaction is equal to the rate of the reverse reaction.

2 Hydrogen gas is mixed with iodine gas in a sealed container. A reaction occurs according to the equation:

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

On the rate–time graph for this system (Figure 8.1.14), label the lines for the forward and reverse reactions with the appropriate chemical equation. Also label the point when equilibrium is first established.

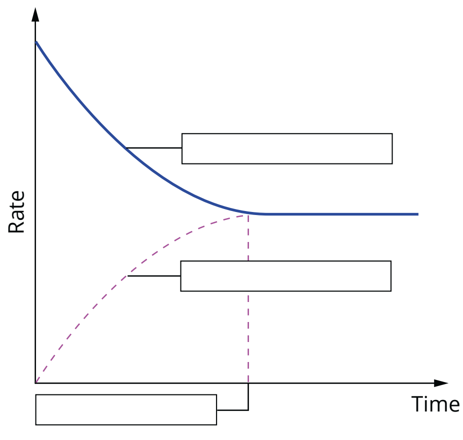


FIGURE 8.1.14 Rate–time graph.

3 Fill in the blanks to complete the sentences about dynamic equilibrium.

In a ____________ system, as the concentrations of the reactants decreases, the rate of the forward reaction also _______________. The collisions between these reactant molecules occur ___________ frequently. Once some product starts to form, the __________ reaction occurs and the frequency of collisions between product molecules ____________. At equilibrium, the rates of the forward and backward reactions are ____________ and the concentrations of all species do not change.

4 The graph in Figure 8.1.15 shows the concentration versus time plot for the decomposition of dinitrogen tetroxide: $N_2O_4(g) \rightleftharpoons 2NO_2(g)$ at 100°C in a 1 L reaction vessel. N_2O_4 is a colourless gas and NO_2 is brown. Use the graph to answer the following questions.

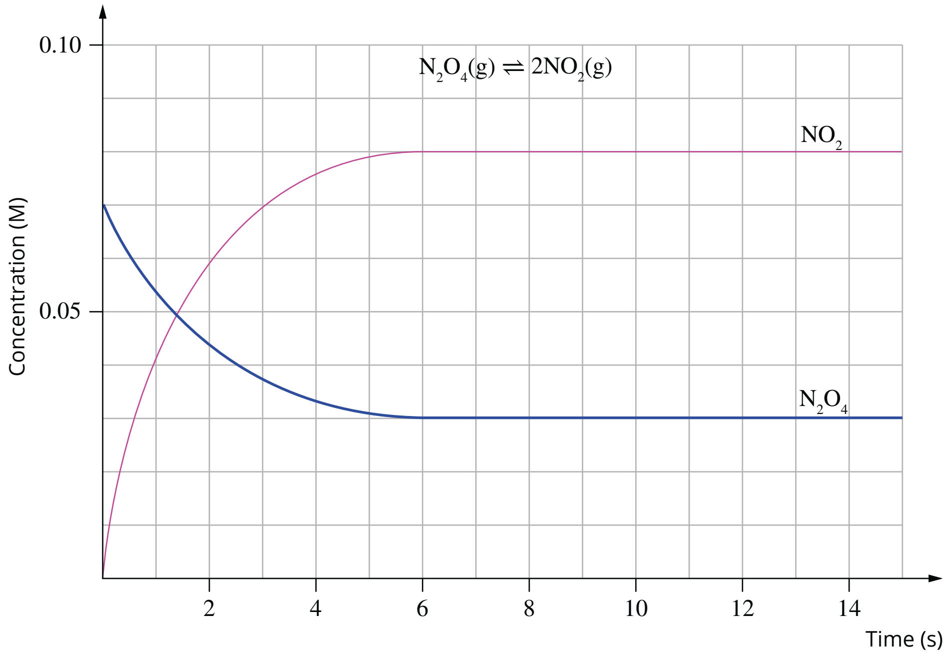


FIGURE 8.1.15 Graph showing the reaction progress for the reversible decomposition of dinitrogen tetroxide.

a What is the initial concentration of N_2O_4 in the flask?

b What is the initial concentration of NO_2 in the flask?

c What is the concentration of N_2O_4 at equilibrium?

d What is the concentration of NO_2 at equilibrium?

e Over the course of the reaction, how many moles of N_2O_4 decompose?

f What do the horizontal regions of the graph indicate?

g How long does it take for equilibrium to be reached?

h A student studying this reaction records her observations over time. What will she observe as the reaction proceeds?

8.2 The equilibrium law

In this section, you will investigate the relationship between the quantities of reactants and the quantities of products present when a system reaches equilibrium.

This relationship allows you to qualitatively predict the relative amounts of reactants and products in individual equilibrium systems.

THE REACTION QUOTIENT

Consider the equilibrium system you were introduced to in section 8.1:

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

An unlimited number of different equilibrium mixtures of the three gases, nitrogen, hydrogen and ammonia, can be prepared. Table 8.2.1 shows the concentrations of each of these gases in four different equilibrium mixtures at a constant temperature of 400°C. The values of the fraction $\frac{[NH_3]^2}{[N_2][H_2]^3}$ for each mixture are also given.

The fraction $\frac{[NH_3]^2}{[N_2][H_2]^3}$ is called the **reaction quotient** (Q_c) or **concentration fraction** of the mixture.

TABLE 8.2.1 Concentrations of reactants and products present in equilibrium mixtures

Equilibrium mixture	$[N_2]$ (M)	$[H_2]$ (M)	$[NH_3]$ (M)	$\frac{[NH_3]^2}{[N_2][H_2]^3}$
1	0.25	0.75	0.074	0.052
2	0.25	0.65	0.089	0.052
3	0.0025	0.0055	4.6×10^{-6}	0.051
4	0.0011	0.0011	2.7×10^{-7}	0.051

As you can see in Table 8.2.1, the reaction quotient $\frac{[NH_3]^2}{[N_2][H_2]^3}$ has an almost constant value of 0.052 for each equilibrium mixture regardless of the concentration of each component. Note that the coefficients of the reactants and products in the chemical equation above form the indices of the respective reactant and product concentrations used in the reaction quotient.

While the reaction quotient can be calculated for any mixture of reactants and products at any time during a reaction, it is only when the mixture is at equilibrium that it gives a constant value. At equilibrium, the value of the reaction quotient is equal to the **equilibrium constant**, K_c.

In general, for chemical reactions at equilibrium:

- different chemical reactions have different values of K_c
- the size of K_c indicates the proportions (relative amounts) of reactants and products in the equilibrium mixture
- for a particular reaction, K_c is constant for all equilibrium mixtures at a fixed temperature.

ℹ K_c is the equilibrium constant for a reaction. The value of K_c is different for different reactions.

THE EXPRESSION FOR THE EQUILIBRIUM LAW

By studying a large number of reversible systems such as the one between nitrogen, hydrogen and ammonia in the previous example, chemists have been able to develop the concept of the **equilibrium law**.

The equilibrium law states that the:

- equilibrium constant, K_c, is the concentrations of products divided by the concentrations of reactants at equilibrium
- index of each component concentration is the same as the coefficient for the substances in the balanced chemical equation.

For the general equation $a\text{W} + b\text{X} \rightleftharpoons c\text{Y} + d\text{Z}$ at equilibrium at a particular temperature, the equilibrium expression can be written as:

$$K_c = \frac{[\text{Y}]^c[\text{Z}]^d}{[\text{W}]^a[\text{X}]^b}$$

where K_c is the equilibrium constant.

A useful way of remembering the equilibrium law is that:

K_c can be represented as $\frac{[\text{products}]^{\text{coefficients}}}{[\text{reactants}]^{\text{coefficients}}}$. Remember that if there is more than one product or reactant, you must multiply the terms.

When you write an equilibrium expression, the concentrations of the products are always on the top of the expression.

Units for equilibrium constants

Units for equilibrium constants depend on the expression used to represent the chemical reaction. They can be determined by substituting M or mol L^{-1}, for each concentration into the concentration fraction expression. In the case of the equilibrium between nitrogen, hydrogen and ammonia above, since:

$$K_c = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3}$$

the unit is given by:

$$\frac{\text{M}^2}{\text{M} \times \text{M}^3} = \text{M}^{-2} \text{ (or mol}^{-2}\text{ L}^2\text{)}$$

The units of K_c depend on the reaction equation and can vary.

Worked example 8.2.1

DETERMINING THE UNITS FOR AN EQUILIBRIUM EXPRESSION

The decomposition of N_2O_4 is a reversible reaction that occurs according to the equation:

$$\text{N}_2\text{O}_4(g) \rightleftharpoons 2\text{NO}_2(g)$$

Write the expression for the equilibrium constant K_c and determine its units.

Thinking	Working
Write the expression for K_c. $\frac{[\text{products}]^{\text{coefficients}}}{[\text{reactants}]^{\text{coefficients}}}$	$K_c = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]}$
Substitute the units of concentration into the expression for K_c . Solve to find the units of K_c.	$\frac{\text{M}^2}{\text{M}} = \text{M} = \text{mol L}^{-1}$

Worked example 8.2.1: Try yourself

DETERMINING THE UNITS FOR AN EQUILIBRIUM EXPRESSION

Write the equilibrium expression and determine the units for K_c for the reversible reaction:

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

The reaction quotient and the equilibrium law

An expression for the equilibrium constant, K_c, can be written for any system at equilibrium. As you learned earlier, a similar expression can be written, called a reaction quotient, Q_c (or concentration fraction), for systems that are not necessarily at equilibrium. For:

$$aA + bB \rightleftharpoons cC + dD$$

$$Q_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

A reaction quotient can be calculated for any mixture of reactants and products at any time during a reaction. However, it is only when the mixture is at equilibrium that the reaction quotient is a constant value. At equilibrium, the value of the reaction quotient is equal to the equilibrium constant, K_c.

If the reaction quotient is:

- greater than K_c, the system 'shifts to the left' to achieve equilibrium and more reactants are formed
- smaller than K_c, the system 'shifts to the right' to achieve equilibrium and more products are formed
- equal to K_c, the system is at equilibrium.

The relationship between Q_c and K_c is illustrated in Figure 8.2.1. By comparing the value of Q_c for a reaction to K_c at a given temperature, it is possible to predict the direction a reaction will proceed in order to reach equilibrium.

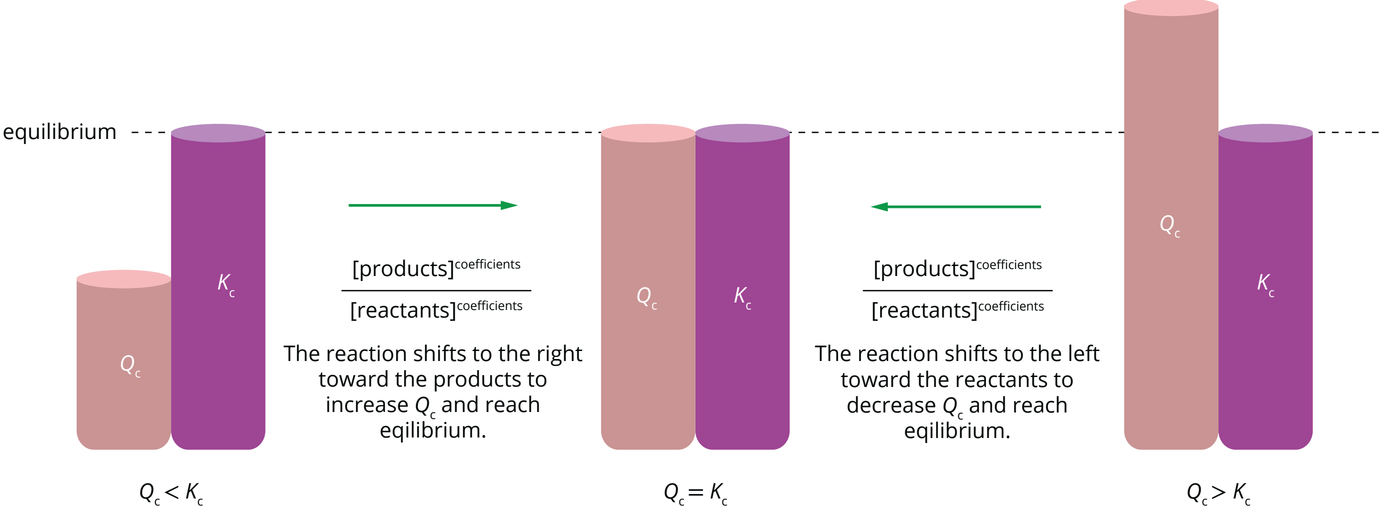


FIGURE 8.2.1 For any reversible reaction at equilibrium $K_c = Q_c$, so comparing these two values for a reaction can indicate which way a reaction must progress to reach equilibrium.

CHEMFILE

Equilibrium in the theatre

A yellow solution containing Fe^{3+} ions reacts with a colourless solution containing SCN^- ions to form a blood-red coloured solution containing $FeSCN^{2+}$ ions, according to the equilibrium reaction:

$Fe^{3+}(aq) + SCN^-(aq) \rightleftharpoons FeSCN^{2+}(aq) \quad K_c = 9 \times 10^2\ M^{-1}$ at 25°C

An appreciable amount of the product $FeSCN^{2+}$ is present in an equilibrium mixture, so the mixture appears blood red (Figure 8.2.2).

This equilibrium reaction is used in theatrical productions to make fake blood. A layer of colourless SCN^- solution can be painted onto an actor's hand prior to the scene. If a plastic knife that has been previously dipped in pale yellow Fe^{3+} solution is used to make a fake cut across the hand, a blood-red 'cut' appears due to the production of red $FeSCN^{2+}$.

FIGURE 8.2.2 Chemicals needed to make fake blood. From left to right: a solution containing Fe^{3+}, a solution containing SCN^-, and an equilibrium mixture of Fe^{3+}, SCN^- and $FeSCN^{2+}$.

Homogeneous and heterogeneous equilibria

The chemical reactions discussed so far have involved **homogeneous reactions**, in which all reactants and products are in the same state or phase. Homogeneous equilibria are the focus of this chemistry course. However, some equilibria involve **heterogeneous reactions**, in which reactants and products are in different states or phases. The following extension section describes how to write an equilibrium law for a heterogeneous equilibrium.

EXTENSION

Equilibria in heterogeneous reactions

The important feature of the equilibrium law for heterogeneous reactions is that the concentration of a pure solid or a pure liquid is assigned as 1. This is because these concentrations do not depend on how much of the pure substance is present.

Because the concentration of the solid in the heterogeneous system is considered a constant, it is removed from the equilibrium expression. As a result, the expression for the equilibrium of a heterogeneous system is often much simpler.

For example, for the equation:

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

the expression for the equilibrium constant is $K_c = [CO_2]$. CaO and $CaCO_3$ are both solids and do not appear in the equilibrium law.

The dissolution of a solid into an aqueous solution is another example of a heterogeneous equilibrium system.

Consider the dissociation of lead chloride ($PbCl_2$) into lead and chloride ions in solution:

$$PbCl_2(s) \rightleftharpoons Pb^{2+}(aq) + 2Cl^-(aq)$$

Because the concentration of the lead chloride is constant, it can be said to be equal to 1 and simply removed from the expression for the equilibrium law. This results in the expression:

$$K_c = [Pb^{2+}][Cl^-]^2$$

8.2 Review

SUMMARY

- The equilibrium constant, K_c, is a constant for a particular chemical reaction at a particular temperature.
- The equilibrium law for the equation:

  $$aW + bX \rightleftharpoons cY + dZ$$

  is:

  $$K_c = \frac{[Y]^c[Z]^d}{[W]^a[X]^b}$$

- A reaction quotient (concentration fraction) can be calculated for any stage of a chemical reaction. The reaction quotient, Q_c, has the same mathematical expression as the equilibrium law.
- When a reaction system at a particular temperature has reached equilibrium, the reaction quotient is equal to the equilibrium constant.
- The unit for an equilibrium constant depends on the equation for the equilibrium. The unit can be determined by substituting M (mol L^{-1}), for each concentration into the reaction quotient.

KEY QUESTIONS

1 Write an expression for the reaction quotient for the reaction of hydrogen and chlorine with the equation:

$$H_2(g) + Cl_2(g) \rightleftharpoons 2HCl(g)$$

2 At a particular temperature, the equilibrium constant for the reaction represented by the following equation is 0.667 M^{-2}:

$$CO(g) + 3H_2(g) \rightleftharpoons CH_4(g) + H_2O(g)$$

At a specific point in the reaction, the reaction quotient is found to be 0.234 M^{-2}. With reference to the concentration of the products, predict which way the reaction will shift in order to reach equilibrium.

3 Define:

a homogenous system

b reaction quotient

c equilibrium constant.

4 Consider the reaction represented by the equation:

$$Cu^{2+}(aq) + 4NH_3(aq) \rightleftharpoons [Cu(NH_3)_4]^{2+}(aq)$$

At 25°C the equilibrium constant is determined to be $K_c = 0.46\ M^{-4}$.
At a particular time during the reaction, the reaction quotient is 1.2 M^{-4}.
Write an expression for the reaction quotient for this reaction and predict what will happen to the system as it moves to equilibrium.

8.3 Working with equilibrium constants

In section 8.2, you learned that an equilibrium law can be written for a chemical reaction at equilibrium. The mathematical expression for the equilibrium law is a fraction involving the concentrations of the reactants and products, which has a value equal to K_c, the equilibrium constant for the reaction at equilibrium.

The value of an equilibrium constant indicates the extent of a reaction or how far a reaction will proceed towards the products. In this section, you will learn how to interpret these values in terms of the relative amounts of reactants and products present at equilibrium.

You will also discover how temperature affects an equilibrium constant and what happens to the value of an equilibrium constant when an equation is reversed or the coefficients of the equation are changed.

DEPENDENCY OF AN EQUILIBRIUM CONSTANT ON THE EQUATION

The equilibrium law depends upon the chemical equation used for a particular reaction.

For example, the equilibrium between the gases N_2O_4 and NO_2 can be represented by several equations. For each equation provided below, the expression for the equilibrium constant, K_c, is also given.

$$N_2O_4(g) \rightleftharpoons 2NO_2(g) \qquad K_c = \frac{[NO_2]^2}{[N_2O_4]}$$

$$2NO_2(g) \rightleftharpoons N_2O_4(g) \qquad K_c = \frac{[N_2O_4]}{[NO_2]^2}$$

$$2N_2O_4(g) \rightleftharpoons 4NO_2(g) \qquad K_c = \frac{[NO_2]^4}{[N_2O_4]^2}$$

$$\frac{1}{2}N_2O_4(g) \rightleftharpoons NO_2(g) \qquad K_c = \frac{[NO_2]}{[N_2O_4]^{\frac{1}{2}}}$$

You can see from these expressions that if:

- one equation is the reverse of another, the equilibrium constants are the inverse (or reciprocal) of each other
- the coefficients of an equation are doubled, the value of K_c is squared
- the coefficients of an equation are halved, the value of K_c is the square root of the original value of K_c.

Therefore, it is important to specify the equation when quoting an equilibrium constant.

When comparing values of K_c, it is important to know the equation associated with the equilibrium constant.

THE MEANING OF THE VALUE OF AN EQUILIBRIUM CONSTANT

The value of an equilibrium constant is based on the equilibrium concentrations of the products divided by the equilibrium concentrations of the reactants. Therefore, it indicates the extent of reaction at equilibrium (how far the forward reaction proceeds before equilibrium is established) and the **equilibrium yield** (the amount of products present at equilibrium).

The concentrations used to determine K_c must be the concentration of each component of the mixture at equilibrium.

The relationship between the value of K_c and the relative proportions of reactants and products at equilibrium is shown in Table 8.3.1.

TABLE 8.3.1 The relationship between the value of K_c and the extent of a reaction provides information on the relative amounts of reactants and products in the reaction mixture at equilibrium

Value of K_c	Extent of reaction
Between about 10^{-4} and 10^4	The extent of reaction is significant. Appreciable concentrations of both reactants and products are present at equilibrium. e.g. $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ $K_c = 0.52\ M^{-2}$ at 400°C
Very large; $>10^4$	Almost complete reaction occurs. The concentrations of products are much higher than the concentrations of the reactants at equilibrium. e.g. $HCl(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + Cl^-(aq)$ $K_c = 10^7\ M$ at 25°C
Very small; $<10^{-4}$	Negligible reaction occurs. The concentrations of reactants are considerably higher than the concentrations of products at equilibrium. e.g. $CH_3COOH(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3COO^-(aq)$ $K_c = 1.8 \times 10^{-5}\ M$ at 25°C

When K_c is very large, the numerator of the equilibrium expression must be large compared to the denominator, which means there is a large amount of products relative to the amount of reactants.

When K_c is very small, the numerator of the equilibrium expression must be very small compared to the denominator, which means there must be a large amount of reactants relative to the amount of products.

Effect of temperature on an equilibrium constant

It has been shown experimentally that the value of the equilibrium constant, K_c, for a particular reaction depends only upon temperature. It is not affected by the addition of reactants or products, changes in pressure, or the use of catalysts.

The effect of a change in temperature on an equilibrium constant depends on whether the reaction is exothermic or endothermic. As temperature increases, for:

- exothermic reactions, the value of K_c decreases and so the amount of products present at equilibrium decreases
- endothermic reactions, the value of K_c increases and so the amount of products present at equilibrium increases.

Only a change in temperature will change the value of K_c for a given reaction.

Table 8.3.2 summarises the effect on K_c when temperature increases. The opposite is true when temperature decreases.

TABLE 8.3.2 The effect on the value of K_c when the temperature of the system increases

ΔH	T	K_c
Exothermic (–)	Increases	Decreases
Endothermic (+)	Increases	Increases

Because the value of K_c depends on temperature, it is essential to specify the temperature at which an equilibrium constant has been measured.

8.3 Review

SUMMARY

- The equilibrium constant, K_c, is specific for an equation.
- The value of K_c provides a measure of the extent of reaction and the relative concentrations of reactants and products at equilibrium.

Value of K_c	Extent of reaction
Between about 10^{-4} and 10^4	Indicates significant reaction occurs
$>10^4$	Indicates an almost complete reaction occurs
$<10^{-4}$	Indicates negligible reaction occurs

- When an equation is reversed, the new equilibrium constant is the reciprocal, or inverse, of the original K_c.
- When coefficients are doubled, K_c is squared.
- As temperature increases, the value of K_c increases for endothermic reactions and decreases for exothermic reactions.

KEY QUESTIONS

1 The equilibrium constant for the decomposition of ammonia is 100 M^2 at 255°C for the equation:

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

a Write an expression for the equilibrium constant for the equation:

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

b Calculate the equilibrium constant for the equation given in part **a**.

c Write an expression for the equilibrium constant for the equation:

$$NH_3(g) \rightleftharpoons \frac{1}{2}N_2(g) + \frac{3}{2}H_2(g)$$

d Calculate the equilibrium constant for the equation in part **c**.

e Use your answers to parts **a–d** to state the effect on the value of an equilibrium constant when the:

i equation is reversed

ii coefficients of the equation are halved.

2 Water reacts with chlorine according to the equation:

$$2H_2O(g) + 2Cl_2(g) \rightleftharpoons 4HCl(g) + O_2(g)$$

At a particular temperature the value of the equilibrium constant for this reaction is determined to be 4.0×10^{-4} M. Assuming no change in temperature, calculate the value for the equilibrium constant for the reaction:

a $H_2O(g) + Cl_2(g) \rightleftharpoons 2HCl(g) + \frac{1}{2}O_2(g)$

b $2HCl(g) + \frac{1}{2}O_2(g) \rightleftharpoons H_2O(g) + Cl_2(g)$

3 For the chemical reaction: $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$ the equilibrium constant is 1.70 M at 250°C.

For each equation, calculate the value of K_c at the same temperature.

a $4PCl_5(g) \rightleftharpoons 4PCl_3(g) + 4Cl_2(g)$

b $\frac{1}{2}PCl_3(g) + \frac{1}{2}Cl_2(g) \rightleftharpoons \frac{1}{2}PCl_5(g)$

c $\frac{1}{2}PCl_5(g) \rightleftharpoons \frac{1}{2}PCl_3(g) + \frac{1}{2}Cl_2(g)$

d $2PCl_3(g) + 2Cl_2(g) \rightleftharpoons 2PCl_5(g)$

4 A chemist investigated three different reactions and determined the value of the equilibrium constant for each. In which of the reactions would there be substantially more products produced compared to reactants?

A Reaction 1: $K_c = 0.0057$

B Reaction 2: $K_c = 2.5 \times 10^9$

C Reaction 3: $K_c = 3.1 \times 10^{-3}$

5 State whether the equilibrium constants for each of the following would be increased, decreased or unchanged by an increase in temperature:

a $2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g)$ $\Delta H = +91$ kJ mol^{-1}

b $4HCl(g) + O_2(g) \rightleftharpoons 2H_2O(g) + 2Cl_2(g)$ $\Delta H = -113$ kJ mol^{-1}

c $H_2(g) + CO_2(g) \rightleftharpoons H_2O(g) + CO(g)$ $\Delta H = +42$ kJ mol^{-1}

d $2CO(g) + O_2(g) \rightleftharpoons 2CO_2(g)$ $\Delta H = -564$ kJ mol^{-1}

8.4 Calculations involving equilibrium

In section 8.3, you saw that for a reversible reaction, an expression for an equilibrium constant, K_c, can be written as a ratio of the molar concentrations of the products to the molar concentrations of the reactants. In this section, you will learn to determine equilibrium constants given molar concentrations. You will also learn to calculate the concentration of a reactant or product using the equilibrium constant at a specified temperature.

Although the calculations in this section will be restricted to chemical equilibria, the same principles can be applied to other systems in our surroundings. For example, on the African plains of Tanzania, there is a delicate balance of herbivores such as zebras and wildebeest, and carnivores such as lions (Figure 8.4.1). If the populations change through drought or disease, the relative numbers change and a new balance is established. This new balance can be predicted in much the same way as occurs for chemical equilibrium.

FIGURE 8.4.1 The populations of zebras and lions in Africa can be understood using the principles of equilibrium.

CALCULATIONS INVOLVING THE EQUILIBRIUM CONSTANT AND CONCENTRATIONS

Calculating an equilibrium constant

An equilibrium constant can be calculated from the molar concentrations of reactants and products at equilibrium, as shown in Worked Example 8.4.1.

Worked example 8.4.1

CALCULATING THE EQUILIBRIUM CONSTANT

A 2.00 L vessel contains a mixture of 0.0860 mol of H_2, 0.124 mol of I_2 and 0.716 mol of HI in equilibrium at 460°C according to the equation:

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

Calculate the value of the equilibrium constant, K_c, at 460°C.

Thinking	Working
Find the molar concentrations for all species at equilibrium. Convert mol to mol L^{-1} using $c = \frac{n}{V}$.	The volume of the vessel = 2.00 L $[H_2] = \frac{n(H_2)}{V}$ $= \frac{0.0860}{2.00} = 0.0430$ M $[I_2] = \frac{n(I_2)}{V}$ $= \frac{0.124}{2.00} = 0.0620$ M $[HI] = \frac{n(HI)}{V}$ $= \frac{0.716}{2.00} = 0.358$ M
Write the expression for K_c.	$K_c = \frac{[HI]^2}{[H_2][I_2]}$
Substitute into the expression for K_c to determine the value of K_c.	$K_c = \frac{0.358^2}{0.0430 \times 0.0620}$ $= 48.1$
Determine the units of K_c.	$\frac{M^2}{M \times M} = \frac{M^2}{M^2}$ Units cancel so K_c has no unit.

Worked example: Try yourself 8.4.1

CALCULATING THE EQUILIBRIUM CONSTANT

A 3.00 L vessel contains a mixture of 0.120 mol of N_2O_4 and 0.500 mol of NO_2 in equilibrium at 460°C according to the equation:

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

Calculate the value of the equilibrium constant, K_c, for the reaction at that temperature.

Calculating equilibrium concentrations

Another type of calculation involves 'working backwards'. In this situation, you use the equilibrium constant to determine the molar equilibrium concentration of one of the species in the reaction.

Worked example 8.4.2

CALCULATING AN EQUILIBRIUM CONCENTRATION

Consider the following equilibrium with an equilibrium constant of 0.400 M at 250°C.

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$

An equilibrium mixture contains 0.0020 M PCl_5 and 0.0010 M PCl_3 at 250°C. What is the equilibrium concentration of Cl_2 in this mixture?

Thinking	**Working**
Write the expression for K_c.	$K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]}$
Substitute the known values into the expression for K_c.	$0.400 = \frac{0.0010 \times [Cl_2]}{0.0020}$
Reorganise the expression to make the unknown the subject and calculate the concentration of this species.	$[Cl_2] = \frac{0.400 \times 0.0020}{0.0010}$ $= 0.80$ M

Worked example: Try yourself 8.4.2

CALCULATING AN EQUILIBRIUM CONCENTRATION

Consider the following equilibrium with an equilibrium constant of 0.72 M at 250°C.

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

An equilibrium mixture contains 0.040 M N_2O_4 at 250°C. What is the equilibrium concentration of NO_2 in this mixture?

Calculating an equilibrium constant using stoichiometry

For some calculations, stoichiometry is used to calculate the molar equilibrium concentrations of the reactants and products from the data provided. Once these are known, the equilibrium constant can then be calculated as you saw in Worked Example 8.4.1.

A popular way to set out calculations of this type is with the use of a **reaction table** (also known as an ICE table). The reaction table shows the initial amounts of reactants and products, the changes that occur as the system reaches equilibrium and the final values at equilibrium, as Worked Example 8.4.3 illustrates.

ℹ An ICE table (reaction table) sets up the steps for working out equilibrium calculations where the equilibrium concentration of one or more species is unknown. The first letter of each word corresponds to the information that is recorded in each row of the table: **I**nitial, **C**hange, **E**quilibrium.

Worked example 8.4.3

USING STOICHIOMETRY TO CALCULATE AN EQUILIBRIUM CONSTANT

An equilibrium is established between A and B at a specified temperature according to the following equation:

$$A(g) \rightleftharpoons 2B(g)$$

0.540 mol of A was placed in a 2.00 L vessel. When equilibrium was achieved, 0.280 mol of B was present. Calculate the value of the equilibrium constant at this temperature.

<table>
<tr><th>Thinking</th><th>Working</th></tr>
<tr>
<td>Construct a reaction table using each species in the balanced equation as the headings for the columns in the table. Insert three rows in the table labelled ‘I’ (Initial), ‘C’ (Change) and ‘E’ (Equilibrium):
<table>
<tr><th></th><th colspan="2">Reactants ⇌ Products</th></tr>
<tr><td>I</td><td></td><td></td></tr>
<tr><td>C</td><td></td><td></td></tr>
<tr><td>E</td><td></td><td></td></tr>
</table>
Enter the data provided in the table.
When a species is consumed, the change is negative; when a species is produced, the change is positive.</td>
<td>Initially, there is:
0.540 mol of A(g)
0 mol of the product B(g).
Let x mol of A react; $2x$ mol of B is produced.
At equilibrium, there is 0.280 mol of B(g).
<table>
<tr><th></th><th>A(g) ⇌</th><th>2B(g)</th></tr>
<tr><td>I</td><td>0.540 mol</td><td>0 mol</td></tr>
<tr><td>C</td><td>$-x$</td><td>$+2x$</td></tr>
<tr><td>E</td><td>$0.540 - x$</td><td>$2x = 0.280$ mol</td></tr>
</table>
</td>
</tr>
<tr>
<td>Using the coefficients from the equation, calculate the moles of all species at equilibrium.</td>
<td>Initially no B was present, so because 0.280 mol of B has been produced at equilibrium:
$2x = 0.280$ mol
$x = 0.140$ mol
We can enter these values in the table:
<table>
<tr><th></th><th>A(g) ⇌</th><th>2B(g)</th></tr>
<tr><td>I</td><td>0.540</td><td>0</td></tr>
<tr><td>C</td><td>$-x = -0.140$</td><td>$+2x = 0.280$</td></tr>
<tr><td>E</td><td>$0.540 - x$
$= 0.540 - 0.140$
$= 0.400$</td><td>0.280</td></tr>
</table>
</td>
</tr>
</table>

Using the volume of the vessel, calculate the equilibrium concentrations for all species at equilibrium. Use the formula $c = \frac{n}{V}$.	The volume of the vessel is 2.00 L. $[A] = \frac{n}{V}$ $= \frac{0.400}{2.00}$ $= 0.200\ M$ $[B] = \frac{n}{V}$ $= \frac{0.280}{2.00}$ $= 0.140\ M$
Write the expression for K_c and substitute the equilibrium concentrations. Calculate the equilibrium constant, K_c, and include the units for the equilibrium constant.	$K_c = \frac{[B]^2}{[A]}$ $= \frac{0.140^2}{0.200}$ $= 0.0980\ M$

Worked example: Try yourself 8.4.3

USING STOICHIOMETRY TO CALCULATE AN EQUILIBRIUM CONSTANT

At one step during the synthesis of nitric acid, nitrogen dioxide (NO_2) is in equilibrium with dinitrogen tetroxide (N_2O_4) at 60°C:

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

0.350 mol of N_2O_4 was placed in a 2.0 L vessel. When equilibrium was achieved, 0.120 mol of NO_2 was present. Calculate the value of the equilibrium constant at this temperature.

8.4 Review

SUMMARY

- An equilibrium constant for a particular temperature can be calculated from the concentrations of the reactants and products at equilibrium and the expression for the equilibrium constant.
- The concentration of a reactant or product can be calculated if the concentrations of the other reactants and products and the equilibrium constant are known.
- Stoichiometry may be used to calculate equilibrium concentrations of reactants and products and hence the value of the equilibrium constant using a reaction (ICE) table.

KEY QUESTIONS

1 Calculate the equilibrium constant for the reaction represented by the equation:

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

if an equilibrium mixture in a 2.0 L container was found to consist of 0.80 mol of N_2O_4 and 0.40 mol of NO_2.

2 Phosgene is a poisonous gas that was used during World War I. It can be formed by the reaction of carbon monoxide with chlorine gas in the equilibrium reaction:

$$CO(g) + Cl_2(g) \rightleftharpoons COCl_2(g)$$

The reaction was allowed to proceed at 74°C until equilibrium was reached. The equilibrium concentrations of each species was determined and recorded as follows: [CO] = 2.4×10^{-2} M, [Cl_2] = 0.108 M and [$COCl_2$] = 0.28 M. Calculate the equilibrium constant for the reaction at this temperature.

3 The following reaction was allowed to reach equilibrium at a temperature of 230°C:

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

The value of the equilibrium constant was determined to be 6.44×10^5 M^{-1}. If the equilibrium concentration of [NO_2] = 15.5 M and [NO] = 0.0542 M, determine the concentration of O_2 in the equilibrium mixture.

4 4.45 mol of PCl_3 and 5.50 mol of Cl_2 were mixed in a 2.00 L vessel. They reacted according to the equation:

$$PCl_3(g) + Cl_2(g) \rightleftharpoons PCl_5(g)$$

When equilibrium was reached, it was found that 0.35 mol of PCl_5 had been formed. Calculate the value of the equilibrium constant and give the units.

5 5.89 mol of N_2 and 8.23 mol of H_2 were mixed in a 5.00 L vessel. They reacted according to the equation:

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

When equilibrium was reached, it was found that 0.48 mol of NH_3 had been formed. Calculate the value of the equilibrium constant and give the units.

6 The equilibrium constant for the following reaction is 48.8 at 455°C.

$$2HI(g) \rightleftharpoons H_2(g) + I_2(g)$$

An equilibrium mixture in a 2.0 L vessel at this temperature contains 0.220 mol of H_2 and 0.110 mol of I_2.

a Calculate the concentration of HI in this mixture.

b Another mixture was prepared by placing 4.00 mol of HI in a 2.0 L vessel at 330°C. At equilibrium, 0.44 mol of H_2 and 0.44 mol of I_2 were present. Calculate the value of the equilibrium constant at this temperature.

c A third mixture consisted of 1.0 mol of HI, 0.24 mol of H_2 and 0.32 mol of I_2 in a 2.0 L container at 330°C. Decide if the mixture is at equilibrium and, if not, predict the direction the reaction will shift to reach equilibrium.

7 A mixture of 0.100 mol NO, 0.051 mol H_2 and 0.100 mol of H_2O were added to a reaction vessel with a volume of 1.0 L at 300°C. The reaction at equilibrium is given by the equation:

$$2NO(g) + 2H_2(g) \rightleftharpoons N_2(g) + 2H_2O(g)$$

After equilibrium was established, the concentration of NO was found to be 0.062 M. Determine the equilibrium constant, K_c, including units for the reaction at 300°C.

8.5 Le Châtelier's principle

In this section, you will learn about some of the effects of changes on chemical systems at equilibrium.

Your understanding of the underlying principles of chemical equilibrium will enable you to predict the impact of changes when a reactant or product is added or removed from an equilibrium system, as seen in the cobalt system described in Figure 8.5.1.

The effect of changes on a chemical equilibrium is very important to the chemical industry. Conditions must be carefully selected to ensure that optimum yields of products are obtained within a reasonable timeframe.

FIGURE 8.5.1 The effect of changes on the equilibrium:
$Co(H_2O)_6^{2+}(aq) + 4Cl^-(aq) \rightleftharpoons CoCl_4^{2-}(aq) + 6H_2O(l)$
The addition of excess Cl^- ions causes a net forward reaction and the solution turns blue as more $CoCl_4^{2-}$ is formed. The addition of excess water causes a net reverse reaction and the solution returns to the original pink colour as more $[Co(H_2O)_6]^{2+}$ is formed.

The position of equilibrium should not be confused with K_c. The value of K_c is only ever changed by a change in temperature.

CHANGES TO AN EQUILIBRIUM SYSTEM

You have seen that different reactions proceed to different extents. As a consequence, the relative amounts of reactants and products differ from one reaction to another at equilibrium. The relative amounts of reactants and products at equilibrium is called the **position of equilibrium**.

The relative amounts of substances present in equilibrium mixtures depend upon reaction conditions. For any equilibrium system, the position of equilibrium may be changed by:

- adding or removing a reactant or product
- changing the pressure by changing the volume (for equilibria involving gases)
- dilution (for equilibria in solution)
- changing the temperature.

Careful control of the reaction conditions allows chemists to maximise the equilibrium yield of a desired product by moving the position of equilibrium 'to the right' (and therefore increasing the amount of products formed).

LE CHÂTELIER'S PRINCIPLE

The effect of a change in conditions on an equilibrium system is summarised in a useful generalisation called **Le Châtelier's principle**.

Le Châtelier's principle states that if an equilibrium system is subjected to a change, the system will adjust itself to partially oppose the effect of the change.

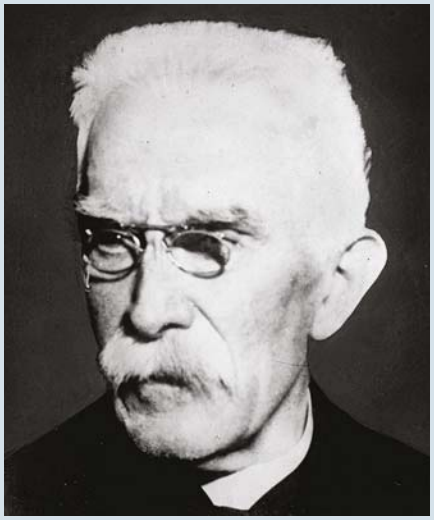


FIGURE 8.5.2 Henri Le Châtelier.

CHEMFILE

Henri Le Châtelier

Henri Le Châtelier (1850–1936), seen in Figure 8.5.2, was a French chemist and engineer. He is best known for developing the principle of chemical equilibrium, which is now named after him.

Le Châtelier made an early attempt at synthesising ammonia from nitrogen and hydrogen, but an error in the design of the experiment resulted in an explosion that nearly killed one of his laboratory assistants. Le Châtelier also developed the oxyacetylene welding torch and the thermocouple for accurate temperature measurement.

When a change occurs to an equilibrium system so that it is momentarily no longer at equilibrium, a net reaction occurs that partially counteracts the effect of the change. The system will establish a new equilibrium.

As a result, the position of equilibrium will change. There may be an increase in the amount of either products or reactants, depending on the nature of the change. By understanding Le Châtelier's principle, you can predict the effect of a change to an equilibrium system.

You will now consider the effect of different changes on equilibrium systems.

Adding extra reactant or product

A sealed reaction vessel of hydrogen and nitrogen gases at a particular temperature will establish an equilibrium according to the equation:

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

If extra nitrogen gas were added to the container without changing the volume or temperature, the mixture would momentarily not be in equilibrium.

The events outlined in the rate–time graph in Figure 8.5.3 occur as the composition of the mixture adjusts to return to a new equilibrium.

ℹ Remember, dynamic equilibrium is a state where the rate of formation of products is equal to the rate of formation of reactants.

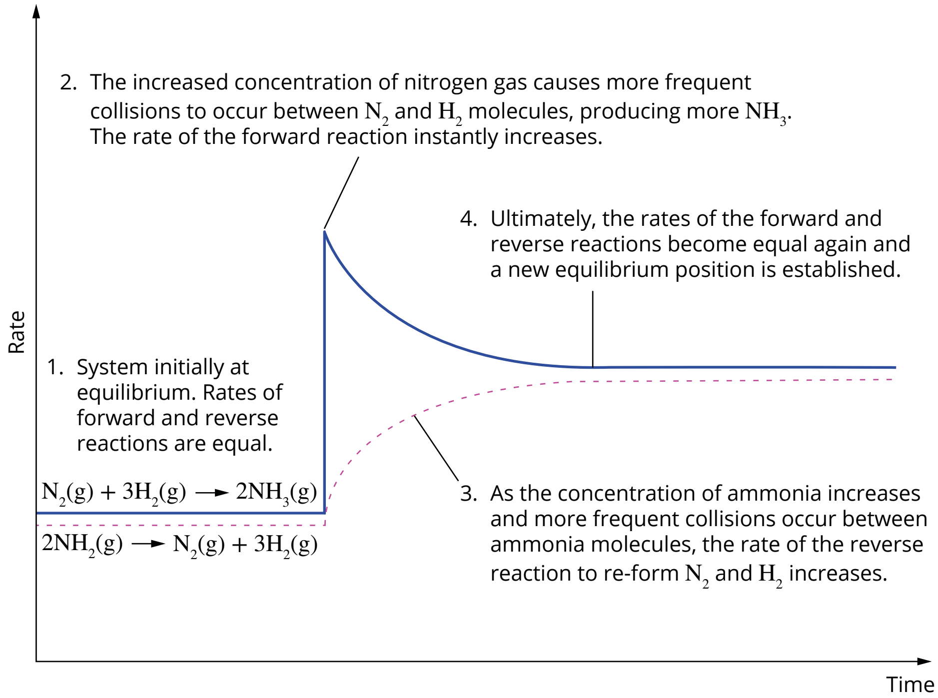


FIGURE 8.5.3 This rate–time graph shows the events that occur as a mixture of nitrogen and hydrogen gas returns to equilibrium after the addition of extra nitrogen gas.

Once the system has re-established equilibrium, the rates of the forward and reverse reactions will again be equal. Overall though, a net forward reaction has occurred with an increase in the concentration of ammonia at equilibrium. The equilibrium position is said to have shifted 'to the right'.

It is important to note that, even though the concentration of N_2 gas decreases as the system moves to establish the new equilibrium, its final concentration is still higher than in the original equilibrium. Le Châtelier's principle states that the change is *partially* opposed. The system does not return to the initial equilibrium position following the change in conditions.

The changes occurring to the system can also be shown on a concentration–time graph. Figure 8.5.4 illustrates the effect on the system when N_2 gas is added as described.

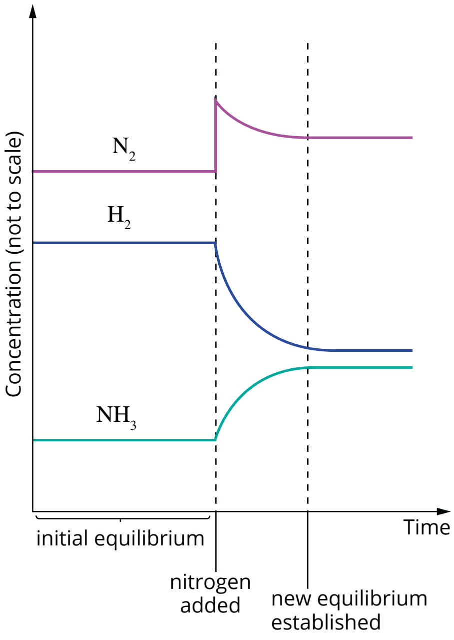


FIGURE 8.5.4 A representation of changes in concentrations that occur when additional nitrogen gas is added to the equilibrium:

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

Note that the *y* axis shows the concentration, not rate of reaction.

The value of K_c for the equilibrium reaction remains unchanged as the temperature has not changed.

ℹ Only temperature changes the value of K_c for an equilibrium system.

If you follow the same reasoning as for N_2, you can see that adding extra amounts of the other reactant, H_2, to the system will also increase the concentration of ammonia produced. However, the addition of more product, NH_3, would result in a net reverse reaction and the equilibrium position shifting to the left, reducing the overall concentration of ammonia as seen in Figure 8.5.5.

While knowledge of collision theory and reaction rates can be used to determine the overall effect of changes on an equilibrium as was done above, applying Le Châtelier's principle is a simpler way of predicting these effects.

Table 8.5.1 shows how an equilibrium system acts to oppose the addition or removal of reactants and products.

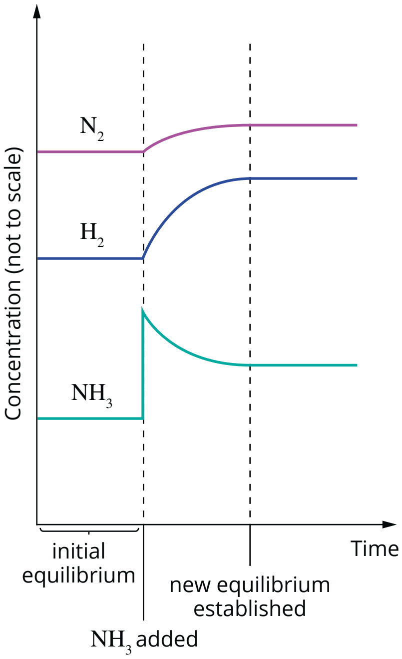


FIGURE 8.5.5 A representation of changes in concentrations that occur when additional ammonia gas is added to the equilibrium:

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

The reaction shifts to the left, forming more N_2 and H_2.

TABLE 8.5.1 The general effects of a change to a system at equilibrium as predicted by Le Châtelier's principle

Change to equilibrium	Effect
Adding a reactant	Formation of more products—a net forward reaction Equilibrium position shifts to the right
Adding a product	Formation of more reactants—a net reverse reaction Equilibrium position shifts to the left
Removing a product	Formation of more products—a net forward reaction Equilibrium position shifts to the right

Predicting the effect of a change using the equilibrium law

The effect of adding more reactants or products can also be predicted using the equilibrium law.

If you again consider the equilibrium formed between nitrogen and hydrogen as an example:

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

The expression for the equilibrium law for this reaction can then be written as:

$$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3}$$

If extra nitrogen is added, the concentration of N_2 is increased so the reaction quotient (Q_c) is momentarily less than the equilibrium constant K_c. The mixture is no longer at equilibrium. As you saw in section 8.2, when $Q_c < K_c$, the reaction favours the formation of products (a net forward reaction). This increases the amount of products and decreases the amount of reactants, until the reaction quotient again becomes equal to K_c.

Making predictions using the mathematical expression for the equilibrium law gives the same result as using the qualitative reasoning of Le Châtelier's principle.

CHEMFILE

Soft drink and equilibrium

In a sealed bottle of soft drink, $CO_2(g)$ and $CO_2(aq)$ are in equilibrium according to the equation:

$$CO_2(g) \rightleftharpoons CO_2(aq)$$

When the cap is removed from the bottle, pressure is reduced and carbon dioxide escapes to the atmosphere. According to Le Châtelier's principle, a net reverse reaction occurs and carbon dioxide comes out of solution.

This normally happens slowly, but when Mentos® mints are added to the bottle of soft drink, the drink erupts violently as you can see in Figure 8.5.6. The high surface area of the mints provides many sites for bubbles to form, increasing the rate of the reaction, and quickly producing an eruption of soft drink from the bottle.

FIGURE 8.5.6 Erupting soft drink when mints have been added.

COMPETING EQUILIBRIA—CARBON MONOXIDE POISONING

Haemoglobin is a large protein molecule that is the pigment in red blood cells. It is responsible for the transport of oxygen from your lungs to the cells in your body. The haemoglobin complex combines with oxygen to form an equilibrium system with oxyhaemoglobin:

$$\text{haemoglobin} + \text{oxygen} \rightleftharpoons \text{oxyhaemoglobin}$$

When you inhale, oxygen from the air combines with haemoglobin in the small blood vessels in the lining of your lungs. According to Le Châtelier's principle, this increase in concentration of oxygen in this environment will cause a net forward reaction, producing greater amounts of oxyhaemoglobin. In your lungs, most haemoglobin is converted to oxyhaemoglobin as a result of the continual addition of oxygen from each breath you take.

Carbon monoxide is a colourless, odourless and tasteless gas that is formed as a product in the incomplete combustion of fuels. Carbon monoxide is present in cigarette smoke and in the exhaust gases from car engines (Figure 8.5.7).

FIGURE 8.5.7 Carbon monoxide gas is formed when hydrocarbon fuels, such as petrol, are burnt in limited supplies of oxygen.

The high toxicity of carbon monoxide is a result of its reaction with haemoglobin:

$$\text{haemoglobin} + \text{carbon monoxide} \rightleftharpoons \text{carboxyhaemoglobin}$$

The equilibrium constant for the reaction between carbon monoxide and haemoglobin is nearly 20 000 times greater than for the reaction between oxygen and haemoglobin. The larger equilibrium constant means that the forward reaction is much more likely to occur. Even small concentrations of carbon monoxide shift the position of equilibrium well to the right.

The formation of carboxyhaemoglobin reduces the concentration of haemoglobin, causing the reverse reaction of oxyhaemoglobin formation to occur. In extreme cases, almost no oxyhaemoglobin is left in the blood and carbon monoxide poisoning occurs.

Symptoms of carbon monoxide poisoning include drowsiness, dizziness, headaches, shortness of breath and loss of intellectual skills. Loss of consciousness and even death can result from carbon monoxide concentrations as low as 200 ppm.

The reactions of oxygen and carbon monoxide with haemoglobin are described as **competing equilibria**, because both oxygen and carbon monoxide 'compete' for the same substance, haemoglobin. The equilibrium reaction with the larger equilibrium constant has a significant effect on the extent of reaction of the other reaction.

A common treatment for carbon monoxide poisoning is to give the person pure oxygen. This is an attempt to shift the equilibria between oxyhaemoglobin and haemoglobin. Addition of oxygen in this equilibrium:

$$\text{haemoglobin} + \text{oxygen} \rightleftharpoons \text{oxyhaemoglobin}$$

should shift the reaction in the net forward direction.

However, the large value of the carboxyhaemoglobin equilibrium constant and the relatively slow rate of release of carbon monoxide means that this treatment is not always successful.

CHEMFILE

Chickens lay eggs with thinner shells in the summer

Chickens, like dogs, do not perspire. Therefore, in hot weather they must resort to panting to try to maintain a healthy temperature. This means that they exhale more carbon dioxide gas than when they are breathing normally.

This affects the following series of competing equilibria, which produces eggshells made from calcium carbonate:

$$CO_2(g) \rightleftharpoons CO_2(aq)$$
$$CO_2(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq)$$
$$H_2CO_3(aq) \rightleftharpoons H^+(aq) + HCO_3^-(aq)$$
$$HCO_3^-(aq) \rightleftharpoons H^+(aq) + CO_3^{2-}(aq)$$
$$CO_3^{2-}(aq) + Ca^{2+}(aq) \rightleftharpoons CaCO_3(s)\ \text{(eggshell)}$$

Removing CO_2 gas shifts each equilibrium, in turn, to the left. This ultimately results in less $CaCO_3$ being made. So, in summer, chickens lay eggs with thinner shells (Figure 8.5.8). This means eggs are more easily broken, at great economic cost to farmers and supermarkets.

Scientists solved the problem by giving the chickens carbonated water to drink. This increases the concentration of aqueous carbon dioxide and pushes the equilibria to the right, increasing the amount of calcium carbonate.

Apparently the chickens like the carbonated water and they produce eggs with thicker, stronger shells. Another victory for chemistry and Le Châtelier!

FIGURE 8.5.8 The eggshell dilemma is solved with the aid of Le Châtelier's principle.

8.5 Review

SUMMARY

- Le Châtelier's principle states that if an equilibrium system is subjected to change, the system will adjust itself to partially oppose the change.
- The effect of a change on an equilibrium can be predicted from Le Châtelier's principle. The effects of changes can also be explained by the use of collision theory and the equilibrium law.

Change to system in equilibrium	Effect of change on equilibrium position
Adding extra reactant	Shifts to the right (net forward reaction)
Adding product	Shifts to the left (net reverse reaction)

- Inhaling carbon monoxide creates competing equilibria in the blood because both oxygen and carbon monoxide react with haemoglobin.
- In competing equilibria, the reaction with the larger equilibrium constant reduces the extent of reaction of the other equilibrium.

KEY QUESTIONS

1 Use Le Châtelier's principle to predict the effect of adding more hydrogen gas to the following equilibria.

   a $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$

   b $2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g)$

   c $H_2(g) + CO_2(g) \rightleftharpoons H_2O(g) + CO(g)$

2 Predict the effect of the following changes on the position of each equilibrium.

   a Addition of SO_3 to the equilibrium:
   $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$

   b Removal of CH_3COO^- from the equilibrium:
   $CH_3COOH(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3COO^-(aq)$

3 For each of the equilibrium systems in Question **2**, explain your answer by referring to the mathematical expression for the equilibrium law for the system.

4 Carbon monoxide is a poisonous gas, even at low concentrations. Which one of the following statements explains this fact?

   A Carbon monoxide forms carbon dioxide gas when it reacts with oxygen gas in the blood.

   B Carbon monoxide reacts with the Fe^{3+} ions in the blood to form Fe metal deposits.

   C Carbon monoxide reacts with haemoglobin in the blood, reducing the formation of oxyhaemoglobin.

   D Carbon monoxide reacts with water in the blood, producing an acidic solution.

5 Fill in the gaps to complete the paragraph about carbon monoxide poisoning.

   Carbon monoxide gas is a product of the ____________ combustion of fuels. Competing equilibria are established between carbon monoxide and oxygen for ____________ in the blood of a person suffering from carbon monoxide poisoning. The transport of ____________ to the cells in the body is prevented. The equilibrium constant for the ____________ reaction is 20000 times greater than that of the ____________reaction. A person suffering from carbon monoxide poisoning is likely to be treated with ____________. This treatment aims to shift the position of the ________–haemoglobin equilibrium so more ____________ is formed.

8.6 Further applications of Le Châtelier's principle

Le Châtelier's principle can be used to understand how changes to chemical equilibria can affect numerous natural systems, as well as to optimise yields of reactions occurring in industrial processes.

For example, in the oceans, carbon dioxide gas is involved in equilibria that provide the carbonate ions needed for the growth of seashells, coral reefs and other marine organisms.

Using Le Châtelier's principle, scientists predict that increasing levels of carbon dioxide in the atmosphere will affect the pH of the Earth's oceans. This will put marine ecosystems and organisms at risk, including the cuttlefish in Figure 8.6.1, whose shells are made of calcium carbonate.

FIGURE 8.6.1 Cuttlefish have an internal shell made of calcium carbonate. Cuttlefish and other marine animals could be affected by the decreasing pH of oceans.

In this section, you will continue your study of the effects of changes on chemical systems at equilibrium. Your understanding of chemical equilibrium will enable you to predict the impact of changes in gas pressure, solution concentration and temperature, and the addition of a catalyst on an equilibrium system.

The impacts of such changes are significant in industrial processes. In the next section, you will learn how the principles of equilibrium can be applied to predict the optimum conditions for the production of chemicals, by considering both rate and yield as well as costs and energy requirements.

CHANGING PRESSURE BY CHANGING VOLUME

The pressure of a gas is inversely proportional to the volume of its container. So the pressure of gases in an equilibrium mixture can be changed by increasing or decreasing the volume of the container while keeping the temperature constant.

Consider the effect of increasing the pressure on the equilibrium between sulfur dioxide gas, oxygen and sulfur trioxide gas for the following reaction:

$$\underbrace{2SO_2(g) + O_2(g)}_{\text{3 gas particles}} \rightleftharpoons \underbrace{2SO_3(g)}_{\text{2 gas particles}}$$

You can see that the forward reaction involves a reduction in the number of particles of gas from three to two. The formation of products would cause an overall reduction in pressure of the system. The reverse reaction involves an increase in the number of gas particles from two to three. So a net reverse reaction causes an overall increase in pressure of the system.

You can predict the change in the position of this equilibrium by either applying Le Châtelier's principle or analysing the equilibrium law for the reaction.

Remember that pressure is a measure of the force per unit area, which is proportional to the number and frequency of collisions with the sides of the container. A change in the number of particles will change the pressure.

Applying Le Châtelier's principle

Le Châtelier's principle tells you that an equilibrium system will respond to an increase in pressure by adjusting to reduce the pressure. The position of equilibrium will therefore move in the direction of the fewest gas particles.

In the example:

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

an increase in pressure will cause a net forward reaction to occur in order to reduce the overall pressure (three gaseous reactant particles become two gaseous product particles). The amount of SO_3 present at equilibrium will increase, as represented in Figure 8.6.2.

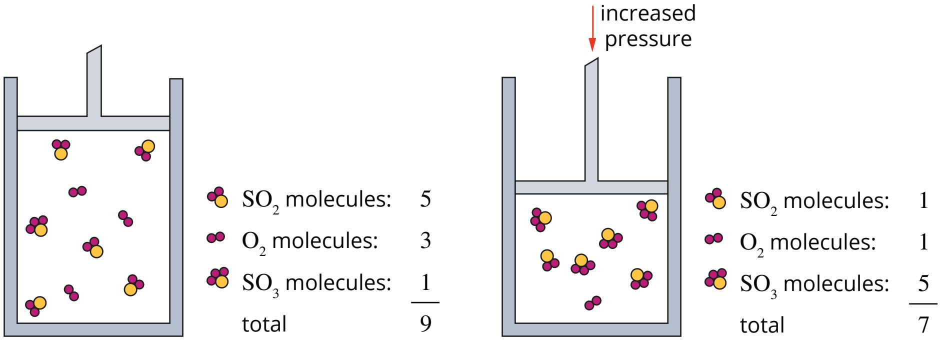


FIGURE 8.6.2 A representation of the effect of increased pressure on the equilibrium: $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$

The effect of the change can also be illustrated graphically (Figure 8.6.3). When the system is initially at equilibrium and there is an increase in pressure, the **partial pressures** of all gases increase simultaneously, as do the concentrations.

As the system adjusts, there is a gradual change in concentration of each of the species until the new equilibrium is established. At the new equilibrium position, the individual partial pressures and concentrations are different from at the first equilibrium. However, the equilibrium constant, K_c, has not changed. The ratio of products to reactants in the equilibrium law still equals K_c at the new equilibrium position.

An increase in pressure will favour the side of the reaction with the least number of particles.

Applying the equilibrium law

You can also predict and explain the effect of a change of pressure on the equilibrium system above in terms of the equilibrium law.

For the equilibrium system:

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

the expression for the equilibrium constant is:

$$K_c = \frac{[SO_3]^2}{[SO_2]^2[O_2]}$$

Suppose the volume of the closed system is halved. The partial pressures of all reactant and product gases double, as does their concentrations.

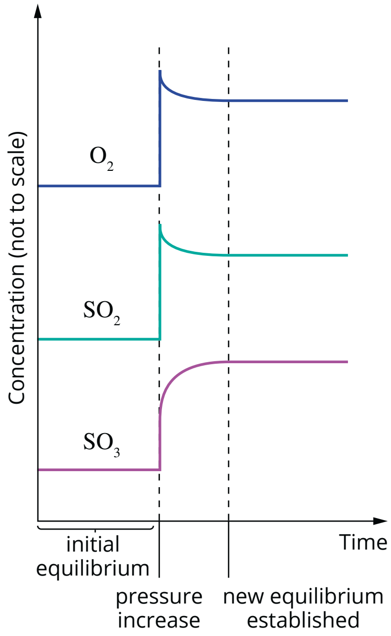


FIGURE 8.6.3 The effect of increased pressure on the equilibrium $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$.

Momentarily, the reaction quotient, Q_c, becomes:

$$\frac{(2[SO_3])^2}{(2[SO_2])^2(2[O_2])} = \frac{2^2}{2^2 \times 2} \times \frac{[SO_3]^2}{[SO_2]^2[O_2]} = \frac{1}{2}K_c$$

The reaction quotient is now lower than K_c. Accordingly, there will be a net forward reaction to increase the value of the reaction quotient until it becomes equal to K_c, just as was predicted earlier using Le Châtelier's principle.

Pressure changes do not affect the equilibrium position of systems in the liquid or solid phases. Particles in these systems are too tightly packed for an increase in pressure to have a noticeable effect on volume. This means that there is negligible change in the concentration of the species involved and no effect on the concentration fraction.

Further examples

The effect of a change of pressure or concentration, by changing the container volume, depends on the relative number of particles on both sides of the equation.

When there are equal numbers of reactant and product particles, a change in pressure will not shift the position of equilibrium. This is the case for the reaction between hydrogen and iodine in the following equilibrium:

$$\underset{\text{2 gas particles}}{H_2(g) + I_2(g)} \rightleftharpoons \underset{\text{2 gas particles}}{2HI(g)}$$

It does not matter which way the system shifts; the number of particles in the container will remain constant. The system is unable to oppose the change applied.

Worked example 8.6.1

USING LE CHÂTELIER'S PRINCIPLE TO DETERMINE THE SHIFT IN EQUILIBRIUM POSITION FOR A VOLUME DECREASE

Consider the equilibrium:

$$CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g)$$

Predict the shift in equilibrium position and the effect on the amount of CO when the volume is halved at constant temperature.

Thinking	Working
Determine the immediate effect of the change of volume on the pressure.	Halving the volume will double the pressure of all species at equilibrium.
The system will try to partially oppose the change in pressure by reducing or increasing the pressure of the system. (For a volume decrease, the system will shift in the direction of the fewest particles, and vice versa for a volume increase.) Decide how the equilibrium will respond.	There are 2 molecules of gas on the reactant side and 4 molecules of gas on the product side, so the system will shift to the left. This decreases the amounts of the products, including CO. (Note that the CO concentration will still be higher than it was at the initial equilibrium. The shift in equilibrium position only partially compensates for the change.)

Worked example: Try yourself 8.6.1

USING LE CHÂTELIER'S PRINCIPLE TO DETERMINE THE SHIFT IN EQUILIBRIUM POSITION FOR A VOLUME INCREASE

Consider the equilibrium:

$$PCl_3(g) + Cl_2(g) \rightleftharpoons PCl_5(g)$$

Predict the shift in equilibrium position and the effect on the amount of Cl_2 when the volume is doubled at constant temperature.

CHANGING PRESSURE BY ADDING AN INERT GAS

The total pressure of an equilibrium mixture of gases may also be changed, without changing the volume of the container, by adding a non-reacting gas such as helium, neon or argon (Figure 8.6.4).

System at equilibrium
Volume 1 L

[●] = 5 particles L^{-1}

[●] = 5 particles L^{-1}

System still in equilibrium but at
higher pressure. Volume 1 L

[●] = 5 particles L^{-1}

[●] = 5 particles L^{-1}

FIGURE 8.6.4 The equilibrium of a gaseous system is unaffected by the addition of an inert gas. The total pressure of the system increases without changes in concentrations of reactants or products, so there is no change to the concentration fraction according to the equilibrium law.

Because the presence of the additional gas does not change any of the concentrations of the reactants and products, there is no effect on the position of equilibrium or the equilibrium constant.

DILUTION

For equilibria in solution, the situation is similar to the one you saw with pressure and gases. The focus is on the number of particles per volume of solvent.

For an equilibrium occurring in solution, dilution by adding water reduces the number of particles per volume. This results in a shift in the position of equilibrium towards the side that produces the greater number of dissolved particles.

For example, consider the equilibrium system:

$$Fe^{3+}(aq) + SCN^{-}(aq) \rightleftharpoons FeSCN^{2+}(aq)$$

2 particles in solution   1 particle in solution

The addition of water momentarily lowers the concentration of each species. In terms of Le Châtelier's principle, a net reverse reaction will occur, increasing the total concentration of particles in solution.

Figure 8.6.5 shows the changes of concentrations that occur. Note that there is an instantaneous decrease in the concentration of all species at the time of dilution.

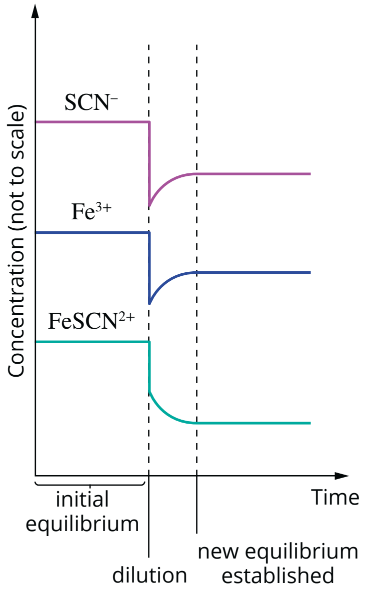


FIGURE 8.6.5 Effect of dilution on the equilibrium $Fe^{3+}(aq) + SCN^{-}(aq) \rightleftharpoons FeSCN^{2+}(aq)$. Although the equilibrium position shifts to the left, note that the concentrations of Fe^{3+} and SCN^- at the new equilibrium are lower than their concentrations prior to dilution, as the equilibrium shift only partially opposes the change.

i Dilution of an aqueous equilibrium system has no effect on the value of K_c for the reaction.

CHANGING TEMPERATURE

In section 8.3, you saw that the effect of a temperature change on an equilibrium reaction depends upon whether the reaction is exothermic or endothermic, as shown in Table 8.6.1.

TABLE 8.6.1 The effect on the value of K_c when the temperature of the system is increased

ΔH	T	K_c
Exothermic (–)	Increase	Decrease
Endothermic (+)	Increase	Increase

Changing the temperature of an equilibrium in a closed system affects both the equilibrium position and the value of the equilibrium constant.

The overall effect on equilibrium position due to temperature can also be predicted according to Le Châtelier's principle.

An example of this is the conversion of brown nitrogen dioxide gas (NO_2) to colourless dinitrogen tetroxide gas (N_2O_4). The reaction is exothermic, releasing energy to the environment. You could (but wouldn't usually) write an equation for the reaction that includes the energy released:

$$2NO_2(g) \rightleftharpoons N_2O_4(g) + \text{energy}$$

Increasing the temperature of the system increases the energy of the substances in the mixture. Applying Le Châtelier's principle, you can see that the reaction can 'oppose' an increase in energy by absorbing energy. As the reverse reaction is endothermic, this favours a net reverse reaction. This can be seen in Figure 8.6.6 where there is a gradual decrease in the concentration of N_2O_4 as the system moves to produce more reactants, NO_2. Note that with a change in temperature, there is no instantaneous change in concentration.

Because the reactants and products of the system are different colours, you can monitor the change in this equilibrium visually. When a new equilibrium is attained, there is less dinitrogen tetroxide and more nitrogen dioxide present so the mixture appears a darker brown (Figure 8.6.7).

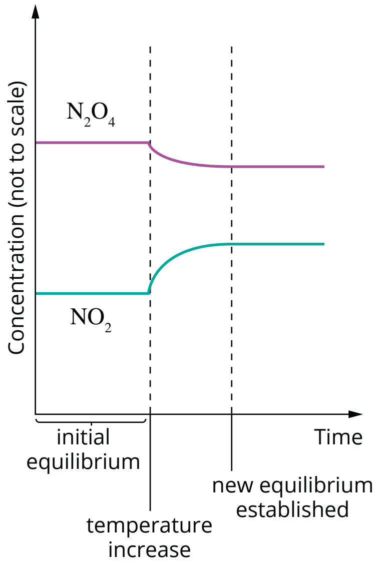


FIGURE 8.6.6 The effect of heating on the equilibrium $2NO_2(g) \rightleftharpoons N_2O_4(g)$.

FIGURE 8.6.7 Equilibrium mixtures of NO_2 and N_2O_4 in hot water and ice. Heating the mixture favours the formation of brown NO_2 gas.

Heating an endothermic reaction causes the opposite result to occur. Applying Le Châtelier's principle, you can see that the reaction opposes an increase in energy by absorbing energy, resulting in a net forward reaction.

In summary, increasing the temperature of an equilibrium mixture results in a:

- net reverse reaction (fewer products) for exothermic reactions, and a decrease in K_c
- net forward reaction (more products) for endothermic reactions, and an increase in K_c.

Decreasing the temperature has the opposite effect.

EFFECT OF A CATALYST ON EQUILIBRIUM

As you have seen in Chapter 7, a catalyst lowers the activation energy of the forward and reverse reactions by the same amount. This can be seen in the energy profile diagram shown in Figure 8.6.8.

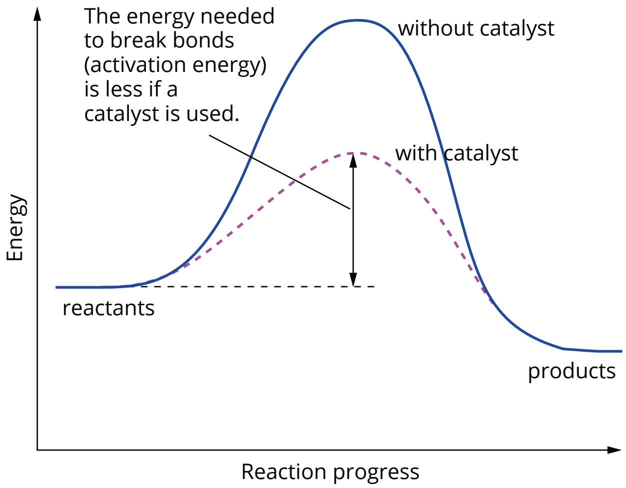


FIGURE 8.6.8 Energy changes in a catalysed and uncatalysed reaction.

The lower activation energy causes an increase in the number of effective collisions. As a result, there is an increase in the rate of both forward and reverse reactions. This occurs because more particles have energies greater than the activation energy barrier of the reaction.

A catalyst increases the rate of the forward and reverse reactions equally. Therefore, it will not change the relative concentrations of the reactants and products in the equilibrium law expression. Consequently the presence of a catalyst does not change the position of equilibrium or the value of the equilibrium constant, K_c. A catalyst will increase the rate at which an equilibrium is attained. It is for this reason that catalysts are used in many industrial and biological systems.

Addition of a catalyst does not change the position of equilibrium of a system, just how quickly equilibrium is attained.

CHEMISTRY IN ACTION

Equilibria in a swimming pool

The water in swimming pools is used again and again. Even though it is filtered, the water can quickly become contaminated with microscopic algae and bacteria. Some interesting chemistry involving chemical equilibria is involved in keeping swimming pools clean, clear and safe to swim in (Figure 8.6.9).

Swimming pools are 'chlorinated' to prevent the growth of harmful microorganisms. Chlorination produces hypochlorous acid (HOCl), which is a very efficient antibacterial agent and algicide.

Commercially available 'pool chlorine' powder (Figure 8.6.10, page 228) consists of calcium hypochlorite ($Ca(OCl)_2$), which dissolves in water to release hypochlorite ions (OCl^-). The hypochlorite ions then react with hydronium ions in the water to form hypochlorous acid:

$Ca(OCl)_2(s) \rightleftharpoons Ca^{2+}(aq) + 2OCl^-(aq)$

$OCl^-(aq) + H_3O^+(aq) \rightleftharpoons HOCl(aq) + H_2O(l)$

FIGURE 8.6.9 Chemical equilibria are responsible for keeping the water in backyard swimming pools hygienic and safe for swimmers.

FIGURE 8.6.10 Commercial 'pool chlorine' contains the hypochlorite ion (OCl^-), which forms an equilibrium with H_3O^+ ions in water.

The H_3O^+ is available from the self-ionisation of water, another equilibrium reaction, this time between water molecules, forming H_3O^+ and OH^- ions:

$H_2O(l) + H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$

The relative amounts of HOCl, OCl^- and H_3O^+ in a swimming pool need to be controlled carefully. This is done by monitoring the pH of the swimming pool and adding either more pool chlorine or more acid as needed to maintain a pH in the range 7.2–7.8. Figure 8.6.11 shows the relationship between the three substances. Remember, pH measures the concentration of H_3O^+ ions.

As pH increases, the concentration of $H_3O^+(aq)$ decreases. Le Châtelier's principle tells you that the position of equilibrium will move to the left, consuming some of the HOCl. If the pH rises above about 7.8, the concentration of HOCl will be insufficient to control the growth of bacteria and algae.

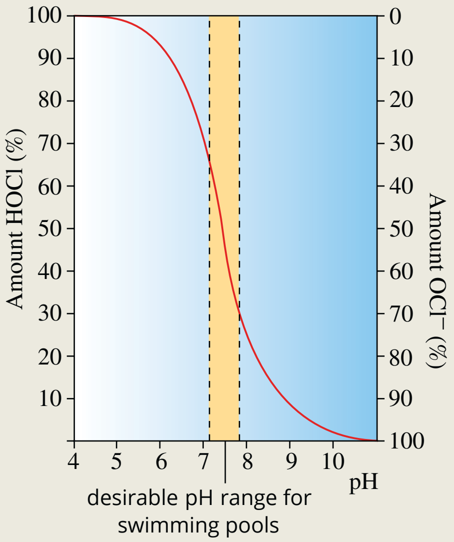


FIGURE 8.6.11 The effect of pH on the proportion of HOCl and OCl^- in water means that the position of the equilibrium can be monitored by changes in pH of the water.

On the other hand, as pH falls, the concentration of $H_3O^+(aq)$ increases.

Le Châtelier's principle tells you the position of equilibrium will move to the right and more HOCl will be formed. Although pH values below around 7.2 result in greater amounts of HOCl in the pool, if the pool is too acidic, the water can irritate eyes and skin.

Thus, maintaining a pool so that it is hygienic and comfortable for swimmers involves carefully maintaining an optimum equilibrium position in the reaction mixture.

8.6 Review

SUMMARY

- The effect of a change on an equilibrium can be predicted using Le Châtelier's principle. Alternatively, the effects of some changes can be predicted on the basis of collision theory and also the equilibrium law.

Change on equilibrium	Effect of change on equilibrium position
Decreasing pressure by increasing volume (for gases)	Shifts in the direction of the most particles
Adding a catalyst	No change
Adding an inert gas (container volume remains constant)	No change
Adding water (dilution of solutions)	Shifts in the direction of the most particles
Increasing the temperature for exothermic reactions	Shifts to the left
Increasing the temperature for endothermic reactions	Shifts to the right

KEY QUESTIONS

1 In which one the following systems will the position of equilibrium be unaffected by a change of volume at constant temperature?

A $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

B $Cl_2(g) + H_2(g) \rightleftharpoons 2HCl(g)$

C $2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$

D $2C_2H_6(g) + 7O_2(g) \rightleftharpoons 4CO_2(g) + 6H_2O(g)$

2 Predict the effect of the following changes on the position of each equilibrium.

a Halving the volume (doubling the pressure) of the equilibrium:
$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

b Increasing the pressure of the equilibrium:
$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$

c Increasing the temperature of the endothermic equilibrium:
$N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$

3 Consider the following equilibria.

i $H_2(g) + CO_2(g) \rightleftharpoons H_2O(g) + CO(g)$ $\Delta H = +42\ \text{kJ mol}^{-1}$

ii $N_2O_4(g) \rightleftharpoons 2NO_2(g)$ $\Delta H = +58\ \text{kJ mol}^{-1}$

iii $H_2(g) + F_2(g) \rightleftharpoons 2HF(g)$ $\Delta H = -536\ \text{kJ mol}^{-1}$

How would you alter the:

a temperature of each equilibrium mixture in order to produce a net forward reaction?

b volume of each equilibrium mixture in order to produce a net forward reaction?

4 An equilibrium mixture consists of the gases N_2O_4 and NO_2:

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

The volume of the container is increased at constant temperature and a new equilibrium is established. Predict how each of the following quantities would change at the new equilibrium compared with the initial equilibrium.

a Concentration of NO_2

b Mass of NO_2

5 The International Space Station uses waste hydrogen and the carbon dioxide released by astronauts during respiration to form water according to the reaction:

$$CO_2(g) + 4H_2(g) \rightleftharpoons CH_4(g) + 2H_2O(g) \quad \Delta H = -165\ \text{kJ mol}^{-1}$$

a How would you alter the temperature in order to produce a net forward reaction?

b How would you alter the volume in order to produce a net forward reaction?

8.7 Optimising the yield of industrial processes

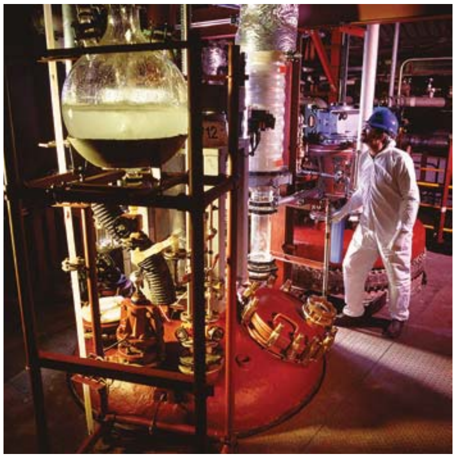


FIGURE 8.7.1 A chemical engineer at work. It is critical to select reaction conditions that carefully balance the demands of equilibrium yield, reaction rate and other factors, such as costs and safety.

The chemical industry is central to the world economy. The companies in this sector convert raw materials (oil, natural gas, air, water, metals and minerals) into tens of thousands of different products, including dyes and pigments, ammonia, chlorine, caustic soda, sulfuric and nitric acids, and organic chemicals.

The extent of the reactions in these industrial processes and the rate of conversion of reactants to products are influenced by reaction conditions such as temperature, pressure and concentration. In order to avoid waste and reduce costs, conditions are carefully selected to ensure that acceptable yields of product are obtained.

It is essential to select the optimum conditions for an efficient reaction process to make the production of useful chemicals economically viable (Figure 8.7.1).

In this section, you will learn how industrial chemists maximise the reaction rate and product yield of chemical reactions by manipulating the position of equilibrium and controlling reaction rate.

CONFLICTS IN CHEMICAL MANUFACTURING

A chemical process must operate efficiently if it is to be economically viable. At the same time, companies must operate in a responsible manner that minimises hazards to employees and damage to the environment. At times, the need to be efficient can conflict with the need to be environmentally responsible.

A similar conflict can occur when an industrial chemist tries to increase the reaction rate and also to convert a high proportion of reactants to products.

The dependence of the composition of equilibrium mixtures on reaction conditions is very important to chemical industry. As you learned in previous sections, Le Châtelier's principle predicts how changes that are made to a system at equilibrium affect the overall position of equilibrium. The conditions for a high reaction rate must also be optimised to ensure that a chemical plant is operating at full capacity.

A temperature increase will increase the reaction rate but decrease the product yield of an exothermic reaction because of the effect of temperature on the equilibrium of the system. In such a situation, a moderate temperature and a catalyst can be used to increase the rate to obtain satisfactory yields.

The selection of an appropriate pressure is also difficult for some processes that occur in the gas phase. High pressures that favour rapid reaction will sometimes give low equilibrium yields of product, depending on the equilibrium reaction.

Table 8.7.1 summarises the conditions that favour fast reaction rates and those that favour high equilibrium yields.

TABLE 8.7.1 Conditions for high rate of reaction versus high equilibrium yield

For fast rates	For high equilibrium yields
High concentrations/pressures	Pressures depend on the relative numbers of reactant and product particles
High temperatures	Low temperatures for exothermic reactions High temperatures for endothermic reactions
High surface area of solids	Addition of excess reactant
Use of a catalyst	Removal of product as it forms

By careful control of reaction conditions, chemists can maximise the equilibrium yield and reaction rate for a desired product.

PERCENTAGE YIELD

The mass of product that is expected to be formed if all reactants react fully according to the equation is known as the **theoretical yield** and it can be calculated using stoichiometry.

However, when reactants are mixed together, even in the correct mole ratio, the amount of products will not always be exactly as predicted from stoichiometric calculations. The **actual yield** obtained for industrial processes is often less than the theoretical yield because of:

- formation of an equilibrium
- a slow reaction rate
- loss of reactants and products during transfers between reaction vessels and in separation and purification stages.

The **percentage yield** compares the actual yield to the theoretical yield. It tells you how much product is formed in a particular reaction or process. The greater the value of the percentage yield, the greater is the degree of conversion from reactants to products. A high percentage yield is desirable in industry in order to reduce waste and maximise profits. Percentage yield can be calculated using the formula:

$$\text{percentage yield} = \frac{\text{actual yield}}{\text{theoretical yield}} \times \frac{100}{1}$$

The percentage yield compares the stoichiometric theoretical yield to the actual yield of a reaction.

CASE STUDY—OPTIMISING AMMONIA PRODUCTION

Ammonia (NH_3) is one of the most commonly produced industrial chemicals. Most of the ammonia produced by industry is used in agriculture as fertiliser. Ammonia is also used in the manufacture of plastics, explosives, textiles, pesticides, dyes and other chemicals.

Ammonia is produced in large industrial plants, such as the one north of Newcastle in New South Wales (Figure 8.7.2), where Orica produces 360 kilotonnes of ammonia annually.

FIGURE 8.7.2 Orica produces ammonia at its Kooragang Island plant in New South Wales. It also produces nitric acid and ammonium nitrate.

Ensuring a high yield gives the plant greater productivity and reduces waste and energy use. Maintaining a high reaction rate ensures the product is generated in a timely manner so that the plant can be economically viable.

Ammonia is manufactured from nitrogen gas (obtained from air) and hydrogen gas in the Haber process. The reaction is reversible and exothermic, and can be represented by the equation:

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \quad \Delta H = -92 \text{ kJ mol}^{-1}$$

Rate considerations

According to collision theory, the rate of reaction will be increased by increasing the frequency of collisions between reactant particles and by increasing the proportion of collisions that have energies equal to or greater than the required activation energy. This means that a higher reaction rate can be achieved when:

- the temperature is higher
- a catalyst is present
- the partial pressures of the gaseous reactants are higher (higher pressure overall).

Equilibrium considerations

Changing the temperature in the reactor will change the equilibrium constant of the reaction. Because the reaction in the Haber process is exothermic, lowering the temperature will increase the value of the equilibrium constant and increase the equilibrium yield of ammonia by favouring the net forward reaction.

The equilibrium yield of ammonia can also be increased by changing the pressure in the reactor. According to Le Châtelier's principle, increasing the pressure will cause the system to partially oppose this pressure change by shifting to the side of the equation with fewer gaseous particles to reduce the pressure.

Because the equation for the Haber process has four gaseous reactant particles and two gaseous product particles, increasing the pressure will cause a shift to the right and increase the amount of ammonia present at equilibrium.

The effects of changing temperature and pressure on the equilibrium yield are shown in Figure 8.7.3. As pressure is increased, the proportion of ammonia present at equilibrium increases. As the temperature is decreased, the proportion of ammonia present at equilibrium increases. Therefore, a high yield is obtained at a low temperature and high pressure.

Table 8.7.2 summarises the effects of changing conditions on the reaction rate and the equilibrium yield of the reaction.

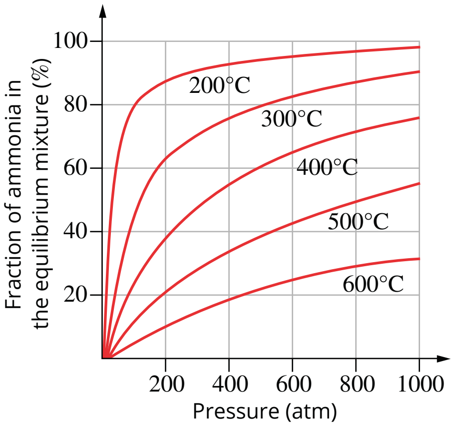


FIGURE 8.7.3 The percentage of ammonia present when a mixture of nitrogen and hydrogen has reached equilibrium.

TABLE 8.7.2 Effect of changing reaction conditions on the equilibrium yield and rate of reaction in the Haber process

Condition	Effect on equilibrium yield	Effect on reaction rate
Catalyst	No effect	Increases
Increasing temperature	Decreases	Increases
Increasing pressure	Increases	Increases

Increasing the pressure of a system, especially on an industrial scale, is a costly and potentially hazardous process. However, in the production of ammonia, a high pressure favours both a high yield and high reaction rate. In this process, the economic benefits from the increased rate and yield outweigh the cost of maintaining high pressures.

A conflict arises in the choice of temperature: a low temperature is desirable for a high equilibrium yield, whereas a high temperature gives higher reaction rates. The actual conditions used to overcome the conflict between rate and yield in the production of ammonia are:

- high pressures of 100–250 atm
- moderate temperatures of 350–550°C
- a porous iron/iron oxide (Fe_3O_4) catalyst.

ℹ In industry it is essential to balance the reaction conditions for high equilibrium yield and reaction rate for the best economic outcome.

CHEMFILE

Fritz Haber

Fritz Haber (1868–1934), seen in Figure 8.7.4, was a German chemist who invented the process for producing ammonia that now bears his name. The reaction produces ammonia from atmospheric nitrogen and hydrogen according to the equation:

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

The Haber process made it feasible to produce fertilisers with a high nitrogen content. This allowed for better crop yields in agriculture. Easy access to reasonably priced fertilisers has saved lives and reduced starvation in many areas across the world. This fact was acknowledged when Haber was awarded the Nobel Prize in Chemistry in 1918, following the end of the World War I.

However, Haber's involvement in the production and use of chemical weapons by the German army in World War I meant that the award of a Nobel Prize was seen as controversial by many scientists who considered him to be guilty of war crimes.

FIGURE 8.7.4 Fritz Haber (1868–1934) invented a process for producing ammonia from atmospheric nitrogen and hydrogen. He was awarded the Nobel Prize in Chemistry in 1918.

CHEMISTRY IN ACTION

Improving the catalyst for ammonia synthesis

The effectiveness of the catalyst in the converter in the Haber process is critical to its efficiency. Fritz Haber and his colleague Carl Bosch tested nearly 2000 different materials as catalysts when developing their process for ammonia synthesis. Haber used rare elements such as osmium and even suggested uranium as a potential catalyst in his earlier research.

By good fortune, the iron ore that they tested was from Sweden and contained traces of group 1 metal compounds that act as 'promoters', increasing the efficiency of the catalyst. A promoter creates many small pores in the catalyst, exposing iron crystals and providing a greater surface area and more sites for reaction. The catalyst widely used today is not very different—iron oxide with a potassium hydroxide promoter.

An alternative catalyst is ruthenium metal supported on high-surface-area carbon. This material began to attract considerable interest from industry in the 1990s. While this catalyst is much more expensive, it is 45 times more active per square metre of surface, allowing the use of a lower operating temperature of about 400°C and 40 atm pressure. It has been installed in a number of ammonia plants.

Even more recently, a Danish company has announced the discovery of a new catalyst based on metal nitrides such as $Fe_3Mo_3N_3$ and Co_3Mo_3N. This catalyst is two to three times as effective as commercial iron oxide catalysts but less expensive than the ruthenium-based ones.

A dream for many chemists has been to devise a catalyst with the efficiency of nitrogenase, the enzyme found in nitrogen-fixing bacteria in legumes such as broad beans (Figure 8.7.5). Nitrogenase enzymes convert atmospheric nitrogen to ammonia without the need for the high pressures and temperatures of the industrial process. Harnessing this process would allow for the efficient production of ammonia at ambient temperatures and atmospheric pressure.

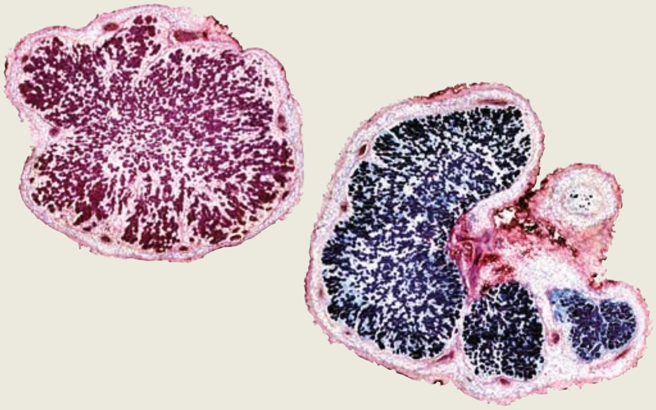


FIGURE 8.7.5 Sections through root nodules from broad beans, stained to show the presence of nitrogen-fixing bacteria. Chemists developing new catalysts for the production of ammonia at atmospheric temperature and pressure hope to mimic the pathways used by bacteria.

Nitrogenase contains clusters of iron, molybdenum and sulfur. Research is continuing to develop similar artificial clusters that could allow low-cost ammonia synthesis at normal temperatures and pressures. The area of catalysis for the production of ammonia remains an active field; recent research includes the use of photocatalysts developed from osmium–gold nanoparticles.

8.7 Review

SUMMARY

- The theoretical yield is the mass of product that would be formed if the limiting reagent reacted completely.
- To calculate the percentage yield, divide the actual yield obtained by the theoretical yield that would be obtained, if all the limiting reactant reacted completely:

$$\text{percentage yield} = \frac{\text{actual yield}}{\text{theoretical yield}} \times \frac{100}{1}$$

- Conditions for the reaction in any chemical process need to be selected carefully to ensure that both a reasonable yield and reaction rate are achieved.
- A compromise is often needed to resolve a conflict between rate and yield.

KEY QUESTIONS

1 In the industrial production of methanol, the conditions are adjusted to maximise the rate and the yield. The reaction is exothermic and represented by the equation:

$$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$$

Fill in the blanks in the following sentences to complete the description of the effects of conditions on this process.

In the production of methanol, both a higher reaction rate and a higher equilibrium yield could be achieved with a ________ pressure. However, a moderate ________ needs to be used to ensure that a reasonable reaction rate and equilibrium yield are achieved. A ________ is used to further increase the ________.

2 In the endothermic reaction below, specify what conditions for temperature and pressure will maximise the equilibrium yield of SO_2.

$$2SO_3(g) \rightleftharpoons 2SO_2(g) + O_2(g)$$

3 Consider the reaction:

$$H_2O(g) + Cl_2O(g) \rightleftharpoons 2HOCl(g)$$

If 2.85 g of Cl_2O is converted into 2.00 g of HOCl, what would be the percentage yield of this process?

4 A step during sulfuric acid production is the oxidation of sulfur dioxide to sulfur trioxide:

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) \quad \Delta H = -197 \text{ kJ mol}^{-1}$$

a Outline the conditions that would increase the equilibrium yield of sulfur trioxide.

b Outline the conditions that would increase the rate of production of sulfur trioxide.

c The actual conditions used for the production of sulfur trioxide are a temperature of 450°C and a pressure of 1 atm. Explain why this compromise is made for the production process.

5 At 200°C, nearly twice as much ammonia forms when a 3:1 hydrogen/nitrogen mixture under 250 atm pressure reaches equilibrium as is formed at 400°C. Why then are temperatures above 400°C used to manufacture ammonia?

6 During the Haber process described on page 196, as a gas passes through the catalyst in the converter its temperature increases.

a Why does the temperature of the gas rise?

b The gases leaving the converter are cooled and liquid ammonia is removed before unreacted nitrogen and hydrogen are pumped back into the converter. Why is this gas mixture cooled before re-entry into the reaction?

Chapter review

08

KEY TERMS

activation energy
actual yield
closed system
competing equilibria
concentration fraction
dynamic equilibrium
endothermic
equilibrium
equilibrium constant
equilibrium law
equilibrium yield
exothermic
extent of reaction
heterogeneous reaction
homogeneous reaction
irreversible reactions
isotope
Le Châtelier's principle
open system
partial pressure
percentage yield
position of equilibrium
rate of reaction
reaction quotient
reaction table
reversible reaction
saturated solution
surroundings
system
theoretical yield

Dynamic equilibrium

1 What are the characteristics of a homogeneous reaction system at equilibrium?

2 Consider the following equilibrium.

$$H_2O(l) \rightleftharpoons H_2O(g)$$

a Explain what is meant by the 'dynamic nature' of equilibrium and why wet clothes in a closed laundry bag do not dry.

b When the bag in part **a** is opened, the clothes begin to dry. Is this because of an equilibrium process? Explain your answer.

The equilibrium law

3 Write the expression for K_c for the following equilibrium system:

$$2Fe^{3+}(aq) + Sn^{2+}(aq) \rightleftharpoons 2Fe^{2+}(aq) + Sn^{4+}(aq)$$

4 Write balanced equations for the reactions with the following equilibrium laws.

a $K_c = \frac{[H_2]^2[CO]}{[CH_3OH]}$

b $K_c = \frac{[H_2S]^2}{[S_2][H_2]^2}$

c $K_c = \frac{[N_2O_4]^{\frac{1}{2}}}{[NO_2]}$

5 Explain the difference between the terms 'reaction quotient' (Q_c) and 'equilibrium constant' (K_c).

6 The value of K_c for the following reaction is equal to 4 at 25°C.

$$C_2H_5OH(l) + CH_3COOH(l) \rightleftharpoons CH_3COOC_2H_5(l) + H_2O(l)$$

At time *t*, the reaction quotient, Q_c, for a mixture of ethanol, water, ethyl ethanoate ($CH_3COOC_2H_5$) and ethanoic acid is equal to 6. Assuming that the mixture is also at 25°C, and referring to the values of K_c and Q_c, describe what will happen to the concentration of ethyl ethanoate as the system reaches equilibrium.

Working with equilibrium constants

7 Complete the following statements about the equilibrium constant K_c.

a If $K_c = 0.0001$ for a particular reaction, at equilibrium the concentrations of products will be __________ the concentrations of reactants.

b For the reaction with the equation:

$$2H_2(g) + 2NO(g) \rightleftharpoons 2H_2O(g) + N_2(g)$$

the expression for the equilibrium constant, K_c, is ________________.

c When the reaction quotient is smaller than K_c, the reaction _________ to establish equilibrium.

8 The equilibrium constant for the following reaction at 25°C is 10^{-10}.

$$2Fe^{2+}(aq) + Sn^{4+}(aq) \rightleftharpoons 2Fe^{3+}(aq) + Sn^{2+}(aq)$$

a Explain whether a significant reaction would occur when solutions of tin(IV) chloride and iron(II) chloride are mixed.

b Determine the value of the equilibrium constant for the reaction:

$$2Fe^{3+}(aq) + Sn^{2+}(aq) \rightleftharpoons 2Fe^{2+}(aq) + Sn^{4+}(aq)$$

c Explain whether a significant reaction would occur when solutions of tin(II) chloride and iron(III) chloride are mixed.

9 Consider the following equilibrium at 227°C:

$$2BrCl(g) \rightleftharpoons Br_2(g) + Cl_2(g)$$

a Write the expression for K_c for the equilibrium system.

b Given that the value of K_c at 227°C for the expression in part **a**, is 32. Deduce the equilibrium constant for each of the following.

i $BrCl(g) \rightleftharpoons \frac{1}{2}Br_2(g) + \frac{1}{2}Cl_2(g)$

ii $Cl_2(g) + Br_2(g) \rightleftharpoons 2BrCl(g)$

iii $4BrCl(g) \rightleftharpoons 2Br_2(g) + 2Cl_2(g)$

iv $\frac{1}{2}Cl_2(g) + \frac{1}{2}Br_2(g) \rightleftharpoons BrCl(g)$

Calculations involving equilibrium

10 The reaction used to manufacture ammonia is represented by the equation:

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

The equilibrium constant for the reaction is 0.052 M^{-2} at 400°C.

A gas mixture contains 1.0 mol of N_2 gas, 1.0 mol of H_2 gas and 0.25 mol of NH_3 gas in a 1.0 L vessel at 400°C. Decide if the mixture is at equilibrium and, if not, predict the direction it will shift to reach equilibrium.

11 An equilibrium mixture contains 0.020 mol of H_2O gas, 0.030 mol H_2 gas, 0.040 mol CO gas and 0.050 mol of CO_2 gas in a 2.0 L container. The gases react according to the equation:

$$H_2(g) + CO_2(g) \rightleftharpoons H_2O(g) + CO(g)$$

Calculate the equilibrium constant at 900°C.

12 At a specified temperature the reaction between solutions of Sn^{2+} and Fe^{3+} reaches equilibrium according to the equation:

$$2Fe^{3+}(aq) + Sn^{2+}(aq) \rightleftharpoons 2Fe^{2+}(aq) + Sn^{4+}(aq)$$

The equilibrium concentrations are 0.30 M Fe^{3+}, 0.40 M Fe^{2+}, 0.20 M Sn^{4+} and 0.10 M Sn^{2+}.

Calculate the equilibrium constant at this temperature with the correct units.

13 Acetone (C_3H_6O) is used to remove nail polish. It can be prepared from propan-2-ol (C_3H_8O) using a copper–zinc catalyst, according to the equation:

$$C_3H_8O(g) \rightleftharpoons C_3H_6O(g) + H_2(g)$$

If an equilibrium mixture of these gases consists of 0.018 mol of propan-2-ol, 0.082 mol of acetone and 0.082 mol of hydrogen in a 20 L vessel, calculate the value of the equilibrium constant.

14 Consider the equilibrium:

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$

A 3.00 L vessel contained 6.00 mol of PCl_3, 4.50 mol of PCl_5 and 0.900 mol of Cl_2 at equilibrium at 250°C.

- **a** Write an expression for the equilibrium constant for this reaction.
- **b** Calculate the equilibrium constant for the reaction at 250°C.
- **c** Another equilibrium mixture contains 0.0020 M PCl_5 and 0.0010 M PCl_3 at 250°C. What is the concentration of Cl_2 in this mixture?
- **d** Determine the equilibrium constant at 250°C for the reaction:

$$PCl_3(g) + Cl_2(g) \rightleftharpoons PCl_5(g)$$

15 At one step during the synthesis of nitric acid, dinitrogen tetroxide is in equilibrium with nitrogen dioxide:

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

0.540 mol of N_2O_4 was placed in a 2.00 L vessel. When equilibrium was achieved, 0.280 mol of NO_2 was present. Calculate the value of the equilibrium constant at this temperature.

16 Consider the reaction:

$$A + 3B \rightleftharpoons 2C + D$$

Analysis of an equilibrium mixture in a 2.0 L container shows that 2.0 mol of A, 0.50 mol of B and 3.0 mol of D are present. If the equilibrium constant of the reaction is 0.024 M^{-1}, calculate the:

- **a** concentration of A, B and D at equilibrium
- **b** concentration of C in the equilibrium mixture
- **c** amount of C, in mol, in the equilibrium mixture.

Le Châtelier's principle

17 How will the concentration of hydrogen gas in each of the following equilibrium mixtures change when the mixtures are heated and kept at constant volume?

- **a** $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \quad \Delta H = -91$ kJ mol^{-1}
- **b** $CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g) \quad \Delta H = +208$ kJ mol^{-1}

18 The following equations represent reactions that are important in industrial processes. Predict the effect on the equilibrium position if each reaction mixture were compressed at constant temperature.

- **a** $C_3H_8O(g) \rightleftharpoons C_3H_6O(g) + H_2(g)$
- **b** $CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$
- **c** $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$

19 Elderly people, especially women, can become very susceptible to bone breakages. It is thought that as people age they absorb Ca^{2+} from food inefficiently, reducing the concentration of these ions in body fluids. An equilibrium exists between calcium phosphate in bone and calcium ions in body fluids:

$$Ca_3(PO_4)_2(s) \rightleftharpoons 3Ca^{2+}(aq) + 2PO_4^{3-}(aq)$$

Use your understanding of equilibrium to explain why inefficient absorption of Ca^{2+} ions could cause weakness in bones.

20 Carbon monoxide is used as a fuel in many industries. It reacts according to the equation:

$$2CO(g) + O_2(g) \rightleftharpoons 2CO_2(g)$$

In a study of this exothermic reaction, an equilibrium system is established in a closed vessel of constant volume at 1000°C.

- **a** Predict what will happen to the equilibrium position as a result of:
  - **i** a decrease in temperature
  - **ii** addition of a catalyst
  - **iii** addition of more oxygen.
- **b** What will happen to the equilibrium constant as a result of each of the changes in part **a**?
- **c** If carbon monoxide can be used as a fuel, comment on the magnitude of the equilibrium constant for the reaction.

21 A step during nitric acid production is the oxidation of nitrogen oxide to nitrogen dioxide:

$$2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g) \quad \Delta H = -114 \text{ kJ mol}^{-1}$$

Nitrogen dioxide is a brown gas and nitrogen oxide and oxygen are colourless. An equilibrium mixture was prepared in a 1 L container at 350°C. Copy the following table, and for each of the changes listed, indicate if the reaction mixture would become darker or lighter. Give a reason for your choice.

	Colour change (lighter or darker)	Explanation
a The temperature is increased to 450°C at constant volume.		
b The volume of the container is increased at constant temperature.		
c A catalyst is added at constant volume and temperature.		
d More oxygen is added at constant volume and temperature.		

22 Carbon monoxide (CO) is a colourless, odourless gas that can be toxic at concentrations above 35 ppm. Describe the treatment commonly used when a person experiences carbon monoxide poisoning. Explain the effect on the haemoglobin equilibrium that the treatment utilises.

23 Carbon monoxide and oxygen compete with each other when reacting with haemoglobin. Which of the following statements is true?

A CO displaces O_2 and the production of oxyhaemoglobin is increased.

B CO displaces O_2 and the production of carboxyhaemoglobin is increased.

C O_2 displaces CO and the production of carboxyhaemoglobin is increased.

D O_2 displaces CO and the production of oxyhaemoglobin is increased.

Optimising the yield of industrial processes

24 Ethene gas is produced from ethane gas in an endothermic reaction represented by the equation:

$$C_2H_6(g) \rightleftharpoons C_2H_4(g) + H_2(g) \quad \Delta H = +138 \text{ kJ mol}^{-1}$$

a State whether the following changes will result in the equilibrium percentage yield of ethene increasing, decreasing or not changing.

- **i** The volume is reduced at constant temperature.
- **ii** More hydrogen gas is added at constant temperature and volume.
- **iii** The temperature is increased at constant volume.
- **iv** A catalyst is added.
- **v** Argon gas is added at constant temperature and volume.

b How will each of the changes in part **a** affect the rate at which the reaction achieves equilibrium?

25 Methanol is manufactured for use as a fuel for racing cars. It can be made by reaction between carbon monoxide and hydrogen:

$$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g) \quad \Delta H = -103 \text{ kJ mol}^{-1}$$

a What conditions of temperature and pressure would be required for a:

- **i** fast reaction rate?
- **ii** high equilibrium yield of methanol?

b Will a compromise be needed in the choice of temperature or pressure?

c Suggest another method that could be employed at a manufacturing plant to increase the rate of methanol production.

d As part of an investigation of this process, the concentration of a mixture of CO, H_2 and CH_3OH was monitored continuously. The mixture was initially at equilibrium at 400°C and constant volume. After 10 minutes, additional CO was added to the mixture, as shown in Figure 8.8.1.

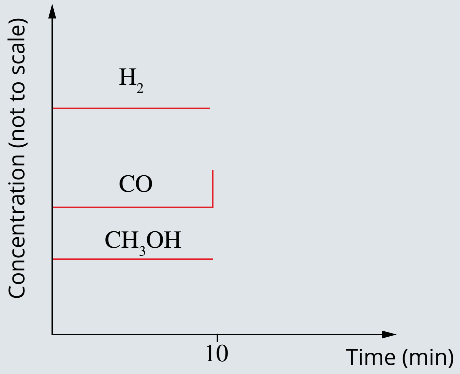


FIGURE 8.8.1 Concentration versus time graph for the production of methanol.

- **i** Sketch a graph to show how concentrations would change as a consequence of the addition of CO.
- **ii** Following the addition of the CO the mixture again reaches equilibrium. Sketch a second graph to show the effect on the concentrations if the temperature were then increased to 450°C.

26 During the process for sulfuric acid manufacture, sulfur dioxide is converted to sulfur trioxide at temperatures of 400–500°C:

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) \quad \Delta H = -197 \text{ kJ mol}^{-1}$$

a What would be the effect of increasing the pressure on:
  i reaction rate?
  ii equilibrium yield?

b In practice, this step is usually performed at atmospheric pressure. Suggest a reason why.

c During the process, sulfur trioxide is removed from the reaction mixture by converting it to sulfuric acid. The remaining gases are then recycled to the reaction vessel. Explain the reason for recycling the gases.

d What factors would have influenced the choice of the reaction temperature?

Connecting the main ideas

27 The reaction used to manufacture ammonia is represented by:

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

The equilibrium constant for the reaction is 0.052 M^{-2} at 400°C.

Each of the following gas mixtures is contained in a 1.0 L vessel at 400°C. Decide if each mixture is in equilibrium. If not, predict the direction the reaction will shift in order to reach equilibrium.

a 0.20 mol of N_2, 0.20 mol of H_2, 0.20 mol of NH_3

b 0.050 mol of N_2 and 0.50 mol of H_2 only

28 **a** The equilibrium constant is 0.67 M^{-2} at a particular temperature for the reaction:

$$CO(g) + 3H_2(g) \rightleftharpoons CH_4(g) + H_2O(g)$$

A mixture of 0.100 M CO, 0.200 M H_2, 0.300 M CH_4 and 0.400 M H_2O is heated to this temperature. Predict whether the concentration of the following would increase, decrease or not change.
  i CO
  ii H_2
  iii CH_4
  iv H_2O

b When the temperature of the reaction mixture is increased by 10°C, the equilibrium constant for the reaction becomes 0.71 M^{-2}. What conclusion can you make about the enthalpy change of this reaction?

29 Carbon disulfide gas (CS_2) is used in the manufacture of rayon. CS_2(g) can be made in an endothermic gas-phase reaction between sulfur trioxide gas (SO_3) and carbon dioxide. Oxygen gas is also produced in the reaction.

a Write a balanced chemical equation for the reaction.

b Write an expression for the equilibrium constant of the reaction.

c An equilibrium mixture of these gases was made by mixing sulfur trioxide and carbon dioxide. The equilibrium mixture consisted of 0.028 mol of CS_2, 0.022 mol of SO_3, 0.014 mol of CO_2 and an unknown amount of O_2 in a 20 L vessel. Calculate the:
  i amount of O_2, in mol, present in the equilibrium mixture
  ii value of the equilibrium constant at that temperature.

d Predict how each of the following changes to an equilibrium mixture would affect the yield of CS_2.
  i Removal of O_2 (at constant total volume)
  ii Increasing the temperature
  iii Adding a catalyst
  iv Increasing the pressure by decreasing the volume of the reaction vessel (at constant temperature)
  v Increasing the pressure by introducing argon gas into the reaction vessel (at constant volume)

30 Sulfur dioxide gas and oxygen gas were mixed at 600°C to produce a gaseous equilibrium mixture:

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

A number of changes were then made, including the addition of a catalyst, resulting in the formation of new equilibrium mixtures. Figure 8.8.2 shows how the concentrations of the three gases changed.

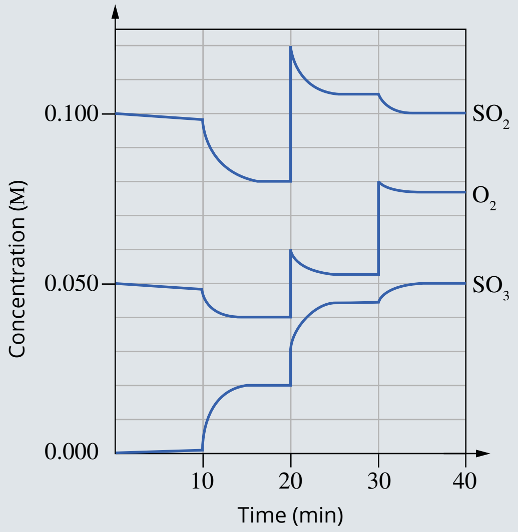


FIGURE 8.8.2 Graph of concentration versus time.

a Write an expression for the equilibrium constant, K_c, of the reaction.

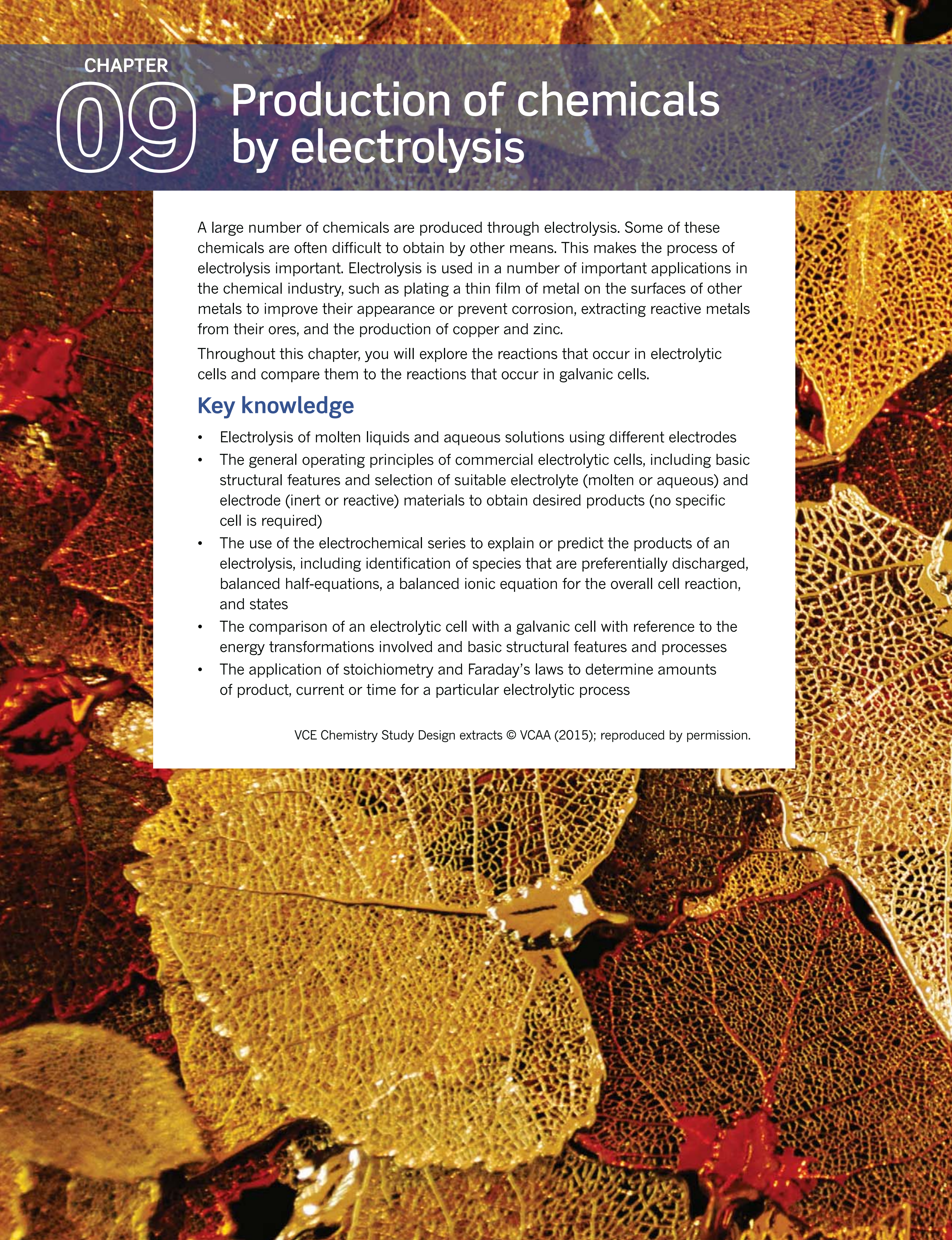
b During which time intervals was the reaction at equilibrium?

c Calculate the value of K_c at 18 minutes.

d At what time was the catalyst added? Explain your reasoning.

e Calculate the value of K_c at 25 minutes.

f What changes were made to the system at 20 minutes?



CHAPTER

09 Production of chemicals by electrolysis

A large number of chemicals are produced through electrolysis. Some of these chemicals are often difficult to obtain by other means. This makes the process of electrolysis important. Electrolysis is used in a number of important applications in the chemical industry, such as plating a thin film of metal on the surfaces of other metals to improve their appearance or prevent corrosion, extracting reactive metals from their ores, and the production of copper and zinc.

Throughout this chapter, you will explore the reactions that occur in electrolytic cells and compare them to the reactions that occur in galvanic cells.

Key knowledge

- Electrolysis of molten liquids and aqueous solutions using different electrodes
- The general operating principles of commercial electrolytic cells, including basic structural features and selection of suitable electrolyte (molten or aqueous) and electrode (inert or reactive) materials to obtain desired products (no specific cell is required)
- The use of the electrochemical series to explain or predict the products of an electrolysis, including identification of species that are preferentially discharged, balanced half-equations, a balanced ionic equation for the overall cell reaction, and states
- The comparison of an electrolytic cell with a galvanic cell with reference to the energy transformations involved and basic structural features and processes
- The application of stoichiometry and Faraday's laws to determine amounts of product, current or time for a particular electrolytic process

9.1 Electrolytic cells

Electrolysis involves the passage of electrical energy from a power supply, such as a battery, through a conducting liquid. The electrical energy causes redox reactions that are normally non-spontaneous to occur. An example of this is shown in Figure 9.1.1, where an electric current is being passed through a dilute sodium chloride solution, causing water to decompose into hydrogen gas and oxygen gas.

In this section, you will learn about the principles of electrolysis. You will also see that the electrochemical series that you used in Chapter 5 can enable you to identify the reactions that occur at the electrodes in electrolytic cells.

FIGURE 9.1.1 During electrolysis, electrical energy is used to make redox reactions occur. In this experiment, electricity passing through dilute sodium chloride solution creates bubbles of hydrogen gas at the left-hand electrode and bubbles of oxygen gas at the right-hand electrode. The gases are being collected in the test tubes.

ELECTROLYSIS OF MOLTEN SODIUM CHLORIDE

A diagram showing the process of **electrolysis** of molten sodium chloride in a simple **electrolytic cell** is shown in Figure 9.1.2.

Platinum metal or graphite is used for the electrodes because they allow the passage of electrons to and from the power supply. Because platinum and graphite are **inert** (unreactive), the electrodes do not react with the contents of the cell. The molten sodium chloride is described as the **electrolyte** because it is a conducting liquid.

Sodium chloride melts at 801°C, so this electrolysis reaction occurs at a high temperature. No water is present. The species present in the electrolyte in the cell are Na^+ ions and Cl^- ions.

During electrolysis, reactions occur at the surface of both electrodes. The electrical energy required for these reactions to occur is provided by the power supply. The power supply can be regarded as a type of 'electron pump', pushing electrons onto one electrode and withdrawing them from the other. The electrode connected to the negative terminal of the power supply is the negative electrode; the positive electrode is connected to the positive terminal of the power supply.

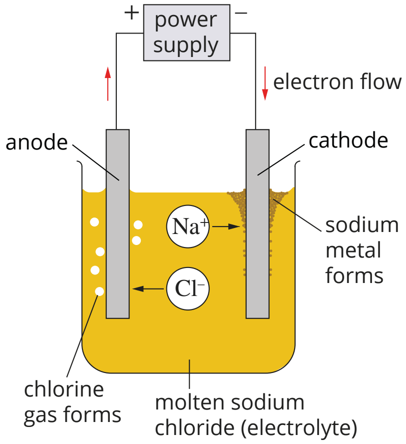


FIGURE 9.1.2 Electrolysis of molten sodium chloride.

At the negative electrode

The power supply pushes electrons towards the negative electrode. Na^+ ions in the electrolyte are attracted to the negative electrode, where they accept electrons and become sodium atoms:

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

Because this is a reduction reaction, by definition this electrode is known as the **cathode**.

Sodium is solid at normal temperatures, but it is liquid at the temperatures required to melt sodium chloride. It is less dense than molten sodium chloride and floats to the top of the cell.

At the positive electrode

Chloride ions in the electrolyte migrate towards the positive electrode to give up electrons and form chlorine atoms. These atoms quickly form molecules of Cl_2 and bubbles of chlorine gas appear at the electrode:

$$2Cl^-(l) \rightarrow Cl_2(g) + 2e^-$$

The electrons from the chloride ions move through the electrode towards the power supply. Because this is an oxidation reaction, by definition this electrode is known as the **anode**.

The overall reaction that takes place in the cell is:

$$2NaCl(l) \rightarrow 2Na(l) + Cl_2(g)$$

This is a **non-spontaneous reaction**—a reaction that would not occur naturally. In such reactions, the supply of electrical energy from a power supply is converted into chemical energy in the products of electrolysis. The reverse reaction, between sodium and chlorine, is a **spontaneous reaction**.

In galvanic cells, the chemical energy in the cells is converted to electrical energy. The opposite occurs in electrolytic cells, where electrical energy supplied from an external power source is converted to chemical energy.

In an electrolytic cell:

- oxidation occurs at the anode, which is the positive electrode
- reduction occurs at the cathode, which is the negative electrode.

The electrolytic process usually takes place in one container. Unlike galvanic cells, there is no need to locate the electrodes in separate containers because a non-spontaneous reaction is involved. However, the products do need to be kept apart as they are produced. Otherwise, they would spontaneously react with each other to re-form the original reactants.

COMPETITION AT ELECTRODES

Unlike the electrolysis of molten sodium chloride, in some electrolytic cells there may be several chemicals present at each electrode that might be able to react. Water is often a potential reactant. Even the material used for the electrodes may participate in the reaction.

In these cases, you can use the **electrochemical series** (Table 5.2.1, page 135) to predict which of the possible reactions would be most likely to occur.

Remember:

- an oxidation reaction occurs at the anode
- a reduction reaction occurs at the cathode.

During electrolysis the:

- strongest oxidising agent usually reacts at the cathode (i.e. the highest reaction in the electrochemical series that can occur in the forward direction is likely to occur at the cathode)
- strongest reducing agent usually reacts at the anode (i.e. the lowest reaction in the series that can occur in reverse is likely to occur at the anode).

Just as in a galvanic cell, the strongest reducing agent reacts at the anode and the strongest oxidising agent reacts at the cathode.

ELECTROLYSIS OF AQUEOUS SODIUM CHLORIDE

Consider the electrolysis of a 1.0 M solution of sodium chloride using **inert electrodes** (Figure 9.1.3). With water present in the cell as well as $Na^+(aq)$ and $Cl^-(aq)$, there are a number of species that might be able to react.

- $H_2O(l)$ could be oxidised or reduced.
- Na^+ ions could be reduced.
- Cl^- ions could be oxidised.

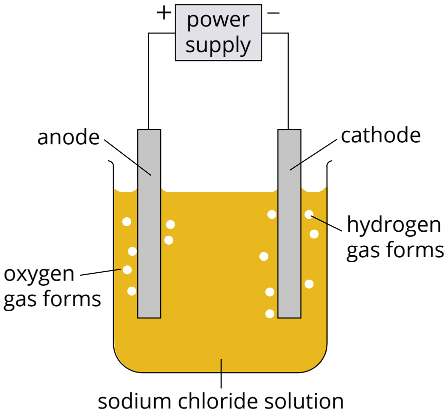


FIGURE 9.1.3 Electrolysis of aqueous sodium chloride solution.

At the cathode

The power supply pushes electrons towards the negative electrode and Na^+ ions are attracted to the negative electrode. If you look on the left-hand side of the electrochemical series (Table 5.2.1, page 135), you will see that there are two species in the cell that can act as oxidising agents and therefore could react at this electrode. These two species are H_2O and Na^+:

$$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq) \qquad E^\circ = -0.83\text{ V}$$
$$Na^+(aq) + e^- \rightarrow Na(s) \qquad E^\circ = -2.71\text{ V}$$

Reactions higher in the electrochemical series involve stronger oxidising agents and are more likely to occur as reduction reactions. Therefore, water will be reduced at the cathode and hydrogen gas will form:

$$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$$

The sodium ions will not react and will remain in solution as spectator ions.

At the anode

Electrons are withdrawn from this electrode by the power supply. On the right-hand side of the electrochemical series (Table 5.2.1) are two species in the cell that can act as reducing agents and could react at this electrode, Cl^- and H_2O:

$$Cl_2(g) + 2e^- \rightarrow 2Cl^-(l) \qquad E^\circ = -1.36\text{ V}$$
$$O_2(g) + 4H^+(aq) + 4e^- \rightarrow H_2O(l) \qquad E^\circ = -1.23\text{ V}$$

Reactions lower in the series involve stronger reducing agents and have a greater tendency to occur as oxidation reactions. While the two reactions are close together in the series, the predicted anode reaction is:

$$2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$$

The overall reaction is:

$$6H_2O(l) \rightarrow 2H_2(g) + O_2(g) + 4H^+(aq) + 4OH^-(aq)$$

If the $H^+(aq)$ ions formed at the anode are allowed to come in contact with the $OH^-(aq)$ formed at the cathode, they react to form water. The overall equation can then be written as:

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

Therefore, water is being broken up into its elements in this process.

In practice, it is possible for either of the anode reactions to occur when sodium chloride solution is electrolysed, depending on conditions such as the concentration of the solution. In some cases, O_2 and H^+ are formed and in others Cl_2 is produced.

Recall that the electrochemical series was determined for reactions under standard conditions (concentrations of 1 M, gas pressures of 1 bar and a temperature of 25°C). When the conditions are not standard and the concentration of sodium chloride is high, chlorine gas is produced at the anode.

Comparing molten and aqueous electrolytes

Table 9.1.1 summarises differences between the electrolysis of molten and aqueous sodium chloride.

TABLE 9.1.1 A comparison of the electrolysis of molten NaCl with aqueous NaCl

	Molten NaCl	Aqueous dilute NaCl
Temperature	High	Room temperature
Anode reaction	$2Cl^-(l) \rightarrow Cl_2(g) + 2e^-$	$2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$
Cathode reaction	$Na^+(l) + e^- \rightarrow Na(l)$	$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(l)$
Overall reaction	$2Na^+(l) + 2Cl^-(l) \rightarrow 2Na(l) + Cl_2(g)$	$2H_2O(l) \rightarrow 2H_2(g) + O_2(g)$

The products formed at each electrode depend on the state and, in the case of aqueous NaCl, the concentration of the electrolyte.

CHEMISTRY IN ACTION

Producing hydrogen for the hydrogen economy

As discussed in Chapter 6, scientists predict that one day our society will transition to a hydrogen economy, where the main source of energy for transport and other sources comes from hydrogen.

Currently, the major source of hydrogen is the steam reforming process, which requires fossil fuels. We need a greener process that does not rely on fossil fuels or produce greenhouse gases.

As discussed in this section, hydrogen is produced through the electrolysis of water with the addition of an electrolyte such as NaCl. The electrolytic process can be made greener by using renewable electricity sources. However, the efficiency of the process ranges from 50 to 70%. Efficiency can be increased by the use of electrodes with catalytic abilities, such as platinum, but this is prohibitively expensive. Scientists are currently working on developing cheap and effective catalytic electrodes from materials such as molybdenum sulfide, carbon nanotubes and nickel/nickel oxide.

Electrolysis is still an energy-intensive way of producing hydrogen. Another area of scientific research is ‘artificial photosynthesis’, which aims to replicate the process of splitting water molecules using light, just as green plants do. Titanium dioxide and other titanium-based compounds form a group of materials that can split water in the presence of light to produce hydrogen.

With these scientific developments, the prospect of a future hydrogen economy is looking much brighter.

ELECTROLYSIS INVOLVING REACTIVE ELECTRODES

In the examples of electrolysis that you have encountered so far, the electrodes do not take part in the reaction and are described as inert electrodes. However, in many electrolytic cells, the electrodes are consumed in the cell reaction. Such electrodes are called **reactive electrodes**.

Worked example 9.1.1

PREDICTING THE PRODUCTS OF ELECTROLYSIS

Use the electrochemical series to predict the products of the electrolysis of 1 M nickel(II) sulfate solution with copper electrodes at 25°C. A diagram of this electrolytic process is shown in Figure 9.1.4.

Thinking	Working
Identify which species are present in the solution.	$Ni^{2+}(aq)$, $SO_4^{2-}(aq)$ and $H_2O(l)$
Identify what the electrodes are made of.	Copper
Refer to the electrochemical series and identify the possible reactions. Write these half-equations in the order they appear in the series.	By referring to the electrochemical series, you can see that a number of reactions need to be considered because the cell contains two oxidising agents, Ni^{2+} and H_2O, and two reducing agents, Cu and H_2O. $O_2(g) + 4H^+(aq) + 4e^- \rightleftharpoons 2H_2O(l)$ 1.23 V $Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$ 0.34 V $Ni^{2+}(aq) + 2e^- \rightleftharpoons Ni(s)$ –0.24 V $2H_2O(l) + 2e^- \rightleftharpoons H_2(g) + 2OH^-(aq)$ –0.83 V The SO_4^{2-} ions are not involved in the reaction.
Determine the reactions that could occur at the anode.	At the anode (+), oxidation reactions that could occur are: $2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$ $Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$
Determine the most likely reaction at the anode.	The strongest reducing agent, Cu(s), will be oxidised: $Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$
Determine the reactions that could occur at the cathode.	At the cathode (–), reduction reactions that could occur are: $Ni^{2+}(aq) + 2e^- \rightarrow Ni(s)$ $2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$
Determine the most likely reaction at the cathode.	The strongest oxidising agent, $Ni^{2+}(aq)$, will be reduced. $Ni^{2+}(aq) + 2e^- \rightarrow Ni(s)$
Combine the two half-reactions to obtain the overall reaction in the electrolysis cell.	The overall equation is: $Ni^{2+}(aq) + Cu(s) \rightarrow Ni(s) + Cu^{2+}(aq)$

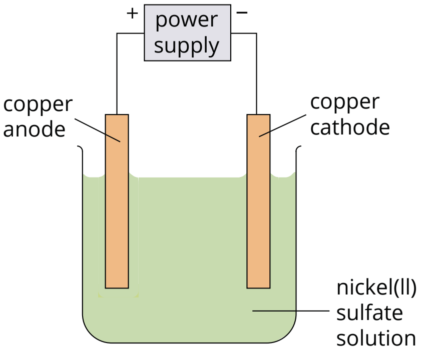


FIGURE 9.1.4 Electrolysis of nickel(II) sulfate solution using copper electrodes.

Worked example: Try yourself 9.1.1

PREDICTING THE PRODUCTS OF ELECTROLYSIS

Use the electrochemical series to predict the products of electrolysis of 1 M zinc sulfate solution with copper electrodes at 25°C.

The electrochemical series can be used in this way to make predictions. The series is based on standard conditions. However, most of the electrolysis reactions that occur in the laboratory and in industry are not at standard conditions. Experiments are the only sure way to find out what products form in a particular instance. In practice, reactions are affected by factors such as electrolyte concentration, gas pressures, current, voltage and the use of different electrodes.

COMPARISON OF ELECTROLYTIC AND GALVANIC CELLS

Galvanic cells and electrolytic cells are types of **electrochemical cells**. While both cells involve the conversion between electrical energy and chemical energy, there are important differences between them.

Table 9.1.2 and Figure 9.1.5 summarise the similarities and differences between galvanic and electrolytic cells.

TABLE 9.1.2 A summary of the similarities and differences between galvanic and electrolytic cells

Galvanic cells	Electrolytic cells
Produce electricity	Consume electricity
Have spontaneous reactions	Have non-spontaneous reactions
Convert chemical energy to electrical energy	Convert electrical energy to chemical energy
Oxidation occurs at the anode and reduction occurs at the cathode	Oxidation occurs at the anode and reduction occurs at the cathode
Anode is negative and cathode is positive	Anode is positive and cathode is negative

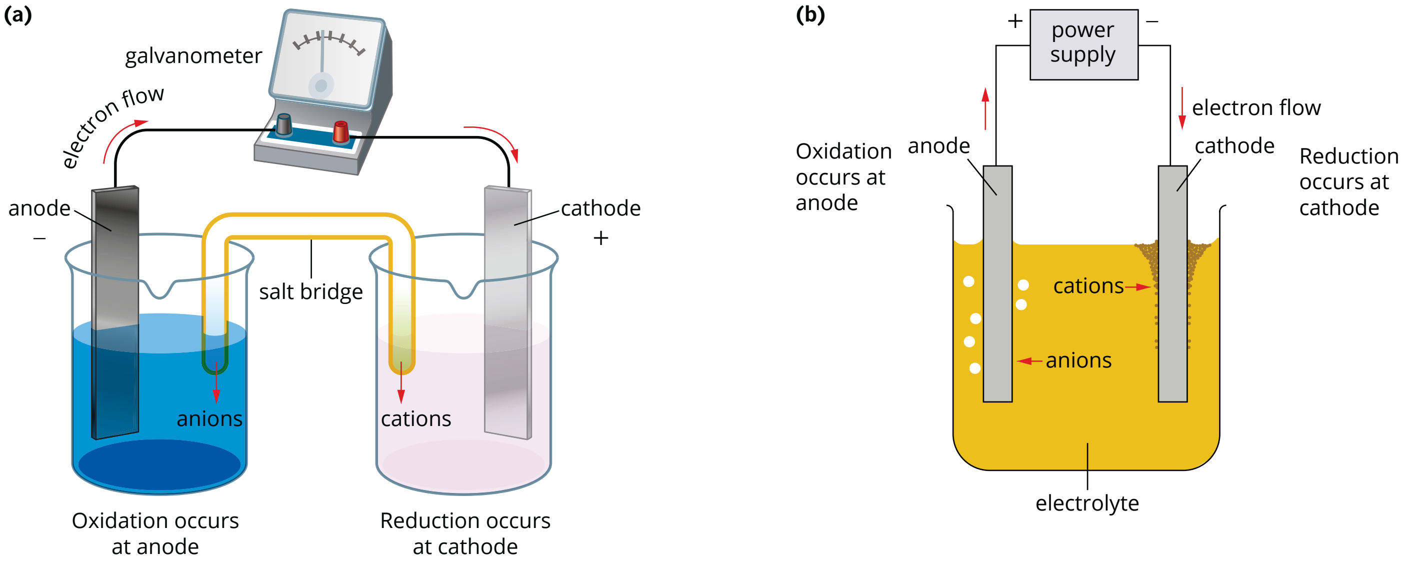


FIGURE 9.1.5 General construction of (a) a galvanic cell and (b) an electrolytic cell.

9.1 Review

SUMMARY

- Electrolytic cells convert electrical energy to chemical energy, whereas galvanic cells convert chemical energy to electrical energy.
- Non-spontaneous redox reactions occur in electrolytic cells.
- The anode is defined as the electrode at which oxidation occurs; the cathode is the electrode at which reduction occurs.
- In electrolytic cells, the anode is the positive electrode and the cathode is the negative electrode.
- While several reactions may be possible at the anode of a particular cell, generally the strongest reducing agent undergoes oxidation.
- While several reactions may be possible at the cathode of a particular cell, generally the strongest oxidising agent undergoes reduction.
- The electrochemical series can be used to predict the products of electrolysis.
- The electrodes used in electrolysis can be either inert or reactive.
- Both molten and aqueous electrolytes can be used in electrolysis.

KEY QUESTIONS

1 Which one of the following applies to both galvanic and electrolytic cells?

A Oxidation occurs at the anode and reduction occurs at the cathode.
B The anode is negative and cathode is positive.
C Both cells convert chemical energy to electrical energy.
D Both cells have non-spontaneous reactions.

2 What are the products of electrolysis of molten potassium iodide using inert electrodes?

A Potassium at the anode and iodine at the cathode
B Potassium at the cathode and iodine at the anode
C Iodine at the negative electrode and potassium at the positive electrode
D Iodine at the anode and hydrogen at the cathode

3 Select the correct words to complete the following statements.

In electrolytic cells:

- the reactions are **spontaneous/non-spontaneous**
- **chemical/electrical energy** is converted into **chemical/electrical energy**
- the anode is **negative/positive** and the cathode is **negative/positive**
- **oxidation/reduction** occurs at the anode and **oxidation/reduction** occurs at the cathode.

4 In an electrolysis experiment, a student is provided with an aqueous solution of nickel(II) nitrate ($Ni(NO_3)_2$). The student sets up an electrolytic cell using an unreactive carbon rod as the positive electrode and a nickel rod as the negative electrode.

a During operation of the cell, a nickel coating will appear on which rod?
b Write the half-equations for the reactions that occur at each electrode.
c Write an equation for the overall reaction.

5 A student sets up an electrolysis experiment using a cell made of a lead anode, an iron cathode and a magnesium nitrate solution as the electrolyte.

a Refer to the electrochemical series and identify the possible reactions that could occur. Write these half-equations in the order they appear in the series.
b Identify the correct equations for the reactions that occur at the anode and cathode.
c Write an equation for the overall reaction.

9.2 Commercial electrolytic cells

Although chemical industries tend to avoid using **electrolysis** for the manufacture of chemicals because of the relatively high cost of electrical energy, this process enables some chemicals to be produced that could not be readily produced any other way.

In an electrolytic cell, the transformation of electrical energy into chemical energy results in **non-spontaneous** reactions in which reactive chemicals are products, rather than reactants.

In this section, you will look at the use of molten and aqueous electrolytes in commercial electrolytic cells and the advantages and disadvantages of each type of electrolyte. You will also study the use of inert and reactive electrodes in these cells.

MOLTEN ELECTROLYTES

One of the best examples of the use of molten electrolytes in commercial electrolytic cells is in the Downs cell (Figure 9.2.1). This electrolytic cell is used to produce sodium and chlorine in commercial quantities.

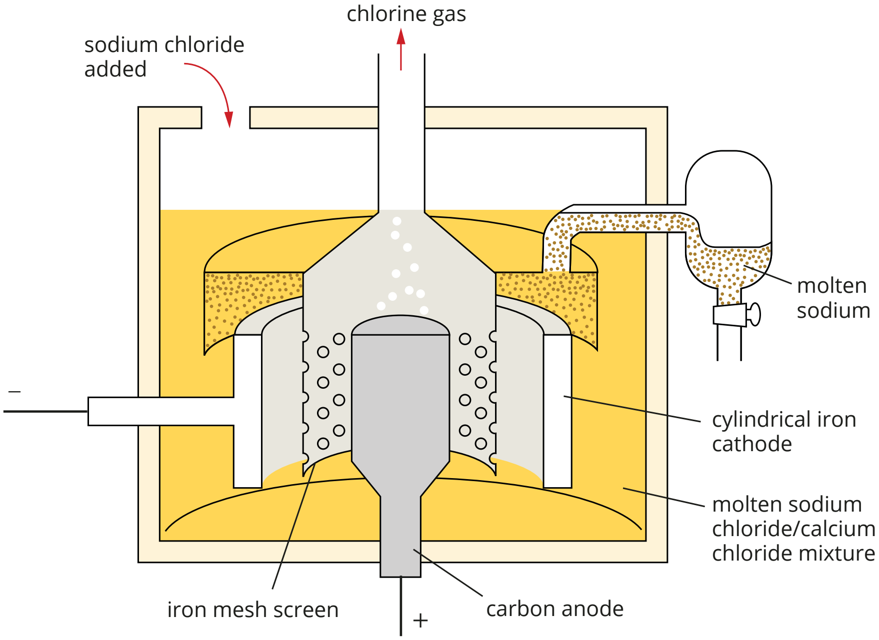


FIGURE 9.2.1 Diagram of a Downs cell, which produces chlorine gas and sodium.

The electrodes used in this cell are inert (unreactive). The anode is made of a conducting material, such as graphite or platinum, and is not consumed in the reaction. The cathode is made of iron, which is effectively inert because electrons are pumped onto this electrode, preventing the iron from reacting. The reactions occurring at each electrode were discussed in the previous section on page 240.

At the cathode (–):

$$\mathrm{Na}^+(l) + e^- \rightarrow \mathrm{Na}(l)$$

At the anode (+):

$$2\mathrm{Cl}^-(l) \rightarrow \mathrm{Cl}_2(g) + 2e^-$$

An overall equation may be written for the cell reaction by adding the half-equations:

$$\begin{array}{r} 2(\mathrm{Na}^+(l) + e^- \rightarrow \mathrm{Na}(l)) \\ 2\mathrm{Cl}^-(l) \rightarrow \mathrm{Cl}_2(g) + 2e^- \\ \hline 2\mathrm{Na}^+(l) + 2\mathrm{Cl}^-(l) \rightarrow \mathrm{Na}(l) + \mathrm{Cl}_2(g) \end{array}$$

The advantage of using a molten electrolyte in the Downs cell is that there is no water present to interfere with the desired reactions. Water is a stronger oxidising agent than Na^+ ions. If aqueous sodium chloride were used as the electrolyte instead of molten sodium chloride, water would react at the cathode and form hydrogen gas, according to the equation:

$$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$$

In general, the main disadvantage of using a molten electrolyte is that the process requires much more energy. Energy must be expended to maintain the electrolyte in a molten state and at the temperature needed for the electrolysis to proceed efficiently.

Heat energy is produced when an electric current passes through a resistor. In the Downs cell, the electrolyte provides a resistance and the flow of electricity keeps the electrolyte molten. A mixture of sodium chloride/calcium chloride in a 1:2 ratio is used as the electrolyte because the presence of the calcium chloride lowers the melting point of sodium chloride from 801°C to about 600°C. This saves on energy costs.

An iron mesh screen is used in the cell to keep the products at the anode and cathode apart. Since Cl_2 is a strong oxidising agent and Na is a strong reducing agent, there must be no contact between them. Otherwise, they will react to re-form sodium chloride and the products from the electrolysis will be lost. The construction of the Downs cell minimises contact between the two products.

In the electrolysis of a molten electrolyte:
- anions are oxidised at the anode (positive)
- cations are reduced at the cathode (negative)
- water is not present to interfere with the desired reactions.

AQUEOUS ELECTROLYTES

Where possible, aqueous electrolytes are used in preference to molten electrolytes. It takes energy to maintain an electrolyte in a molten state and so a cell that uses an aqueous electrolyte is more cost-effective. The membrane cell is an example of a modern industrial electrolytic cell that uses an aqueous electrolyte.

Membrane cells

Sodium hydroxide, chlorine and hydrogen are produced through the electrolysis of a concentrated sodium chloride solution, also known as a **brine**. This occurs in a membrane cell, so named because the two compartments are separated by a **semipermeable membrane** (Figure 9.2.3). The membrane helps to prevent contact between the reactive products.

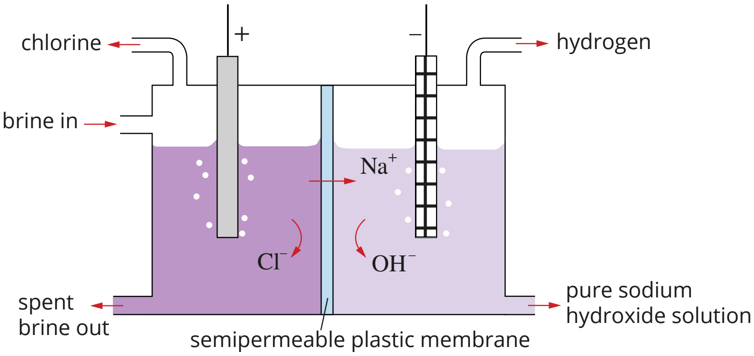


FIGURE 9.2.3 A membrane cell produces chlorine and hydrogen gas and aqueous sodium hydroxide.

CHEMFILE

Sodium first isolated by electrolysis

Sodium is one of the most reactive metals. Few substances are capable of reducing Na^+ ions to the metal, Na. Because of this, sodium was not isolated until 1807 when Humphry Davy (1778–1829), shown in Figure 9.2.2, electrolysed molten sodium hydroxide.

The following year, Davy discovered five elements—barium, magnesium, strontium, boron and calcium—and reported news of his discoveries in two entertaining public lectures in London. Davy was renowned for the flair of his lectures and demonstrations.

FIGURE 9.2.2 Humphry Davy used electrolysis to be the first person to isolate potassium, calcium, barium, magnesium, sodium and strontium.

In a membrane cell, water is not oxidised. Instead, because a concentrated sodium chloride solution is used, chloride ions are oxidised at the anode to produce chlorine gas.

The membrane is made from a polymer that only allows positive ions to pass through it. The polymer prevents the mixing of the products formed at the electrodes and allows only Na^+ ions to move from one electrode chamber to the other. Chloride and hydroxide ions are unable to move through the membrane. This results in a very pure sodium hydroxide product with very little chloride ion contamination.

At the cathode (–), water is reduced by electrons from the power supply to produce hydrogen gas and hydroxide ions:

$$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$$

At the anode (+), even though water is a stronger reducing agent, through the use of a concentrated sodium chloride solution, chloride ions are oxidised instead:

$$2Cl^-(aq) \rightarrow Cl_2(g) + 2e^-$$

The advantages of the membrane in this cell are that the:

- sodium hydroxide solution produced does not become contaminated with sodium chloride solution
- use of an aqueous electrolyte allows the process to occur between 80 and 90°C, so there is no need to heat the electrolyte and the cost of production is reduced.

REACTIVE ELECTRODES

The cells described so far use inert electrodes. Inert electrodes are used in many commercial electrolytic cells. Note that cathodes made of metals such as iron are always inert (they cannot be oxidised) because they are connected to the negative terminal of the power supply and receive a continual supply of electrons.

Reactive electrodes have benefits in certain situations. As you will see in the Extension on page 250, metals such as copper can be purified using an electrolytic cell in which the anode is made of the impure metal. The pure metal is then deposited on the other electrode.

You will now examine how aluminium metal is produced by electrolysis. This process involves the use of both an inert and a reactive electrode. The low density and high strength of aluminium make it particularly useful for many applications, including cooking foil, drink cans, car engines, gutters, caravans, aeroplanes, window frames and boats (Figure 9.2.4).

FIGURE 9.2.4 Boats made from aluminium are light, strong and resistant to corrosion.

Electrolytic production of aluminium

Aluminium metal is obtained from aluminium oxide (also known as alumina, Al_2O_3) by electrolysis. Pure alumina is extracted from the mineral bauxite, which is found in large deposits in the Darling Ranges in Western Australia, Weipa in northern Queensland and Gove in the Northern Territory.

Alumina melts at the very high temperature of 2050°C. However, it is soluble in molten cryolite (Na_3AlF_6). By dissolving alumina in cryolite, electrolysis can be performed at 950–1000°C, avoiding the much higher energy costs that would be involved if pure molten alumina were used as the electrolyte. Figure 9.2.5 shows a diagram of the Hall–Héroult cell, which was used in this electrolytic process.

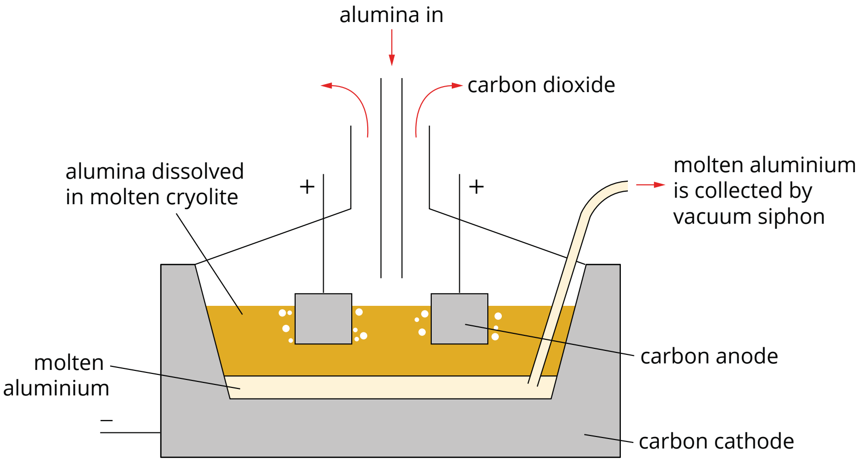


FIGURE 9.2.5 The Hall–Héroult cell used to extract aluminium from alumina.

At the cathode (–), Al^{3+} ions from the alumina are reduced by electrons from the power supply to produce aluminium metal:

$$Al^{3+}(\text{in cryolite}) + 3e^- \rightarrow Al(l)$$

The aluminium, which is molten at the temperatures used, sinks to the bottom of the cell and is periodically removed by siphoning.

At the anode (+), the oxide ions of the alumina are oxidised to oxygen gas:

$$2O^{2-}(\text{in cryolite}) \rightarrow O_2(g) + 4e^-$$

The oxide ions then react with the carbon anodes to produce carbon dioxide gas. The electrode reaction may therefore be written as:

$$C(s) + 2O^{2-}(\text{in cryolite}) \rightarrow CO_2(g) + 4e^-$$

The overall equation for the extraction of aluminium is:

$$2Al_2O_3(\text{in cryolite}) + 3C(s) \rightarrow 4Al(l) + 3CO_2(g)$$

Unlike in the other electrolytic cells described so far in this section, the carbon anodes take part in the reaction. Therefore, the carbon anodes need to be replaced regularly. Chemists are investigating alternative inert electrode materials to avoid the production of carbon dioxide and the cost of replacing the electrodes. Metals such as platinum and gold could be used as inert electrodes, but they are not economical on an industrial scale.

EXTENSION

Electrorefining of copper

Copper metal is extracted from its ores by **smelting**. The process involves several stages in which the copper ore is heated strongly in air to produce impure copper metal.

As hot gases escape, the copper surface becomes blistered and it is commonly known as 'blister copper'. It contains about 2% of impurities such as sulfur, iron, antimony, silver and gold.

Blister copper is purified by electrolysis. Sheets of blister copper are placed in a large tank of sulfuric acid and thin sheets of pure copper are positioned between them. An external power source is connected so that the blister copper acts as a positive electrode (anode) and the pure copper acts as a negative electrode (cathode), as shown in Figure 9.2.6.

At the anode (+) electrons are drawn away from the blister copper anode to the positive terminal of the power source. Copper and impurities such as nickel and zinc that are more reactive (stronger reducing agents) than copper are oxidised and enter the solution as ions:

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

Impurities less reactive than copper, such as silver, gold and platinum, are not oxidised and simply fall from the anode, collecting at the bottom of the tank. This anode residue is sometimes called 'anode mud'. The precious metals are later recovered from the valuable mud.

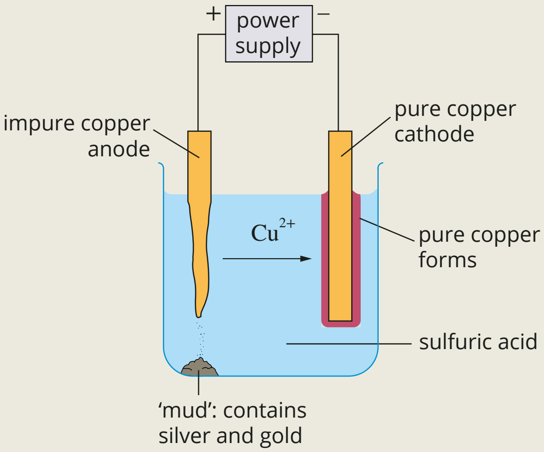


FIGURE 9.2.6 Electrorefining of copper metal by electrolysis.

At the pure copper cathode, copper metal is deposited as electrons from the power source are accepted by metal ions from solution. Since copper ions are the strongest oxidising agents present in solution, copper is the only metal formed:

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

9.2 Review

SUMMARY

- The design features of industrial electrolytic cells must consider the:
  - chemical nature of the reactants and products
  - physical conditions under which the electrolysis takes place
  - energy requirements of operating the cell.
- To obtain the desired products from electrolysis reactions, industrial cells may use:
  - aqueous or molten electrolytes
  - reactive or inert electrodes (the cathode is always inert).
- Cells that use molten electrolytes require a higher energy input than aqueous electrolytic cells because the electrolyte must be kept in a molten state.
- Cells are designed to keep the products at each electrode separate. They would spontaneously react if they came in contact with each other.
- The electrochemical series is useful for predicting the products and selecting the reactants for a particular industrial cell.

KEY QUESTIONS

1 Chemists are investigating the possibility of replacing the carbon anodes in the electrolytic cell used for aluminium extraction from alumina (Al_2O_3) in a molten electrolyte. The cell is normally constructed so that the electrodes take part in the reaction and form carbon dioxide.
Which one of the following would *not* be an advantage of changing to unreactive anodes?

A Carbon dioxide would not be produced.
B The frequent replacement of the anodes would be avoided.
C The gas produced at the anodes would not be a greenhouse gas.
D The cell could use an aqueous electrolyte.

2 Potassium can be produced in the cell represented in Figure 9.2.7 by using molten potassium bromide as the electrolyte. Complete the missing labels for this cell.

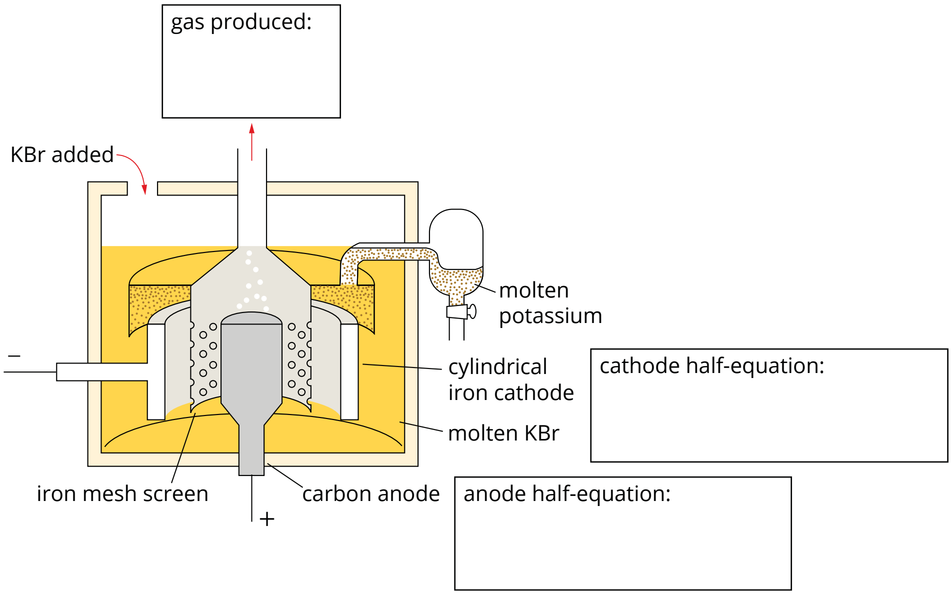


FIGURE 9.2.7 Electrolysis of molten potassium bromide.

3 Zinc can be extracted from its compounds by electrolysis at room temperature with the cell shown in Figure 9.2.8.

a Explain whether an inert or reactive electrode would be suitable for use as an anode.
b Explain why an aqueous solution of zinc nitrate, instead of molten zinc nitrate, is used as the electrolyte in this cell.
c Identify the gas formed at the anode.

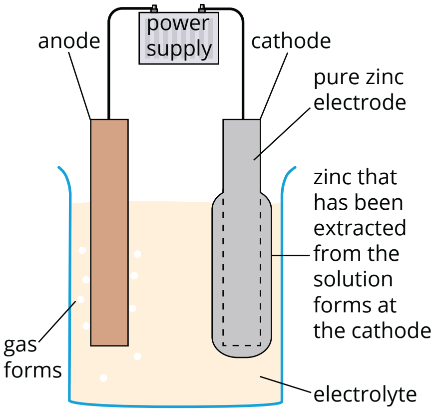


FIGURE 9.2.8 Electrolytic cell for extracting zinc.

4 Account for the fact that:

a most chlorine is produced by electrolysis of sodium chloride solution, rather than by electrolysis of the molten salt
b fluorine was first isolated from fluorine compounds by electrolysis
c although calcium chloride is present in the electrolyte in the Downs cell, calcium metal is not formed at the cathode.

9.3 Faraday's laws

Industrial chemists monitoring the operation of commercial electrolytic cells need to know the relationship between the amount of product produced by the cell, the size of the electric current and the operating time of the cell.

In this section, you will learn about the laws that Michael Faraday discovered in 1834 that allow chemists to understand relationships such as these. You will also learn how these laws can be applied to an electrolytic process called electroplating.

FIGURE 9.3.1 Tin cans are used as packaging for a wide range of products. The tin coating on the can prevents it from corroding.

ELECTROPLATING

One commercially important application of electrolysis is **electroplating**. During this process, a thin surface coating of metal, only a fraction of a millimetre thick, can be applied over another surface.

A common application of electroplating is the coating applied to 'tin' cans (Figure 9.3.1). Tin cans are used extensively for packaging food items as varied as soups, fruit and fish. Although they are commonly called 'tin' cans, they are mainly composed of steel, which is an alloy of iron and carbon. There is just a thin layer of tin plated over the surface of the steel can. Tin corrodes very slowly and prevents contact between the iron, moisture and air. Effectively, the tin prevents the iron from rusting.

Electroplating cells

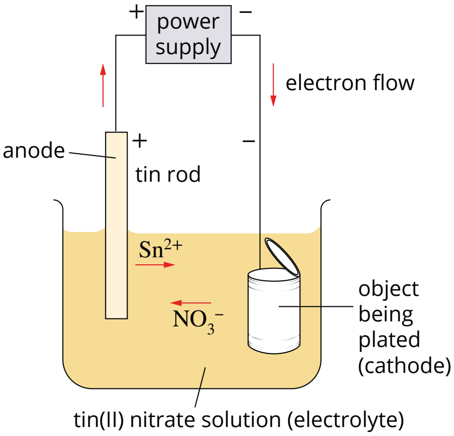


FIGURE 9.3.2 A cell used for electroplating tin.

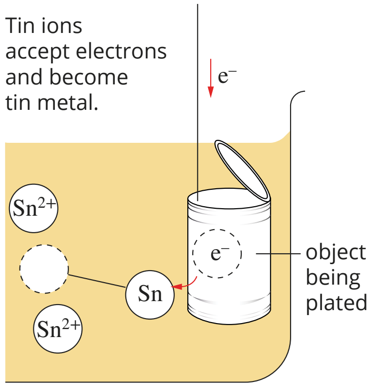
Electroplating is performed in electrolytic cells, such as the simplified one shown in Figure 9.3.2 for tin plating. The object to be plated is connected by a wire to the negative terminal of a power supply. This object becomes the negative electrode in the cell.

The object is immersed in an electrolyte solution, such as tin(II) nitrate solution, which contains ions of the metal to be plated. The Sn^{2+} ions in the solution move towards the negative electrode (the object to be plated) and NO_3^- ions move towards the positive electrode, allowing current to pass through the cell.

An electrode of tin metal is connected to the positive terminal of the power supply.

When the cell is in operation, the power supply acts as an 'electron pump', pushing electrons onto the negative electrode and removing electrons from the positive electrode.

At the negative electrode (cathode)



$Sn^{2+}(aq) + 2e^- \rightarrow Sn(s)$

FIGURE 9.3.3 A representation of the reaction at the cathode in the process of tin plating.

As shown in Figure 9.3.3, tin ions are attracted to the negative electrode, where they accept electrons and are converted to tin metal:

$$Sn^{2+}(aq) + 2e^- \rightarrow Sn(s)$$

A coating of tin is formed on the object. Because reduction of the tin ions (Sn^{2+}) occurs, the negative electrode is acting as a cathode.

At the positive electrode (anode)

As shown in Figure 9.3.4, the positive terminal of the power supply withdraws electrons from the tin electrode, causing an oxidation reaction to occur. Tin metal slowly dissolves as Sn^{2+} ions are formed:

$$Sn(s) \rightarrow Sn^{2+}(aq) + 2e^-$$

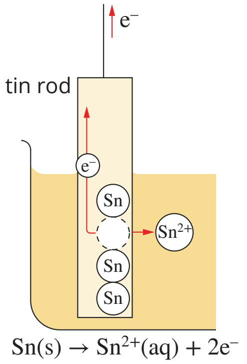
This reaction replaces Sn^{2+} ions in solution that were consumed by the reaction at the negative electrode. The overall concentration of tin ions in the electrolyte remains constant.

Because an oxidation reaction is involved, the positive electrode is acting as an anode.

Several key factors determine the amounts of products that will form in an electrolytic cell, such as an electroplating cell, including the:

- charge on the ion involved in the electrode reaction
- current flowing through the cell
- length of time that the current flows.

Faraday described the relationship between these factors. You will now apply your knowledge of electroplating cells to learn about Faraday's laws.



$Sn(s) \rightarrow Sn^{2+}(aq) + 2e^-$

FIGURE 9.3.4 A representation of the reaction at the anode in the process of tin plating.

The set-up of an electroplating cell can be summarised as follows.

- The object being plated is at the cathode (negative).
- An electrode of the metal is at the anode (positive).

FARADAY'S FIRST LAW OF ELECTROLYSIS

An electroplating cell can be constructed as shown in Figure 9.3.5.

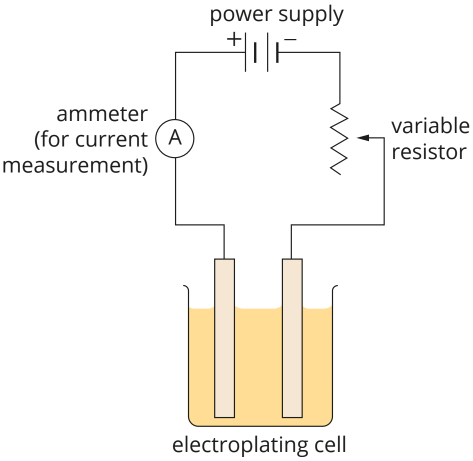


FIGURE 9.3.5 Experimental apparatus used to investigate electroplating. The variable resistor is used to keep the current constant.

This cell can be used to study the relationship between the mass of metal formed at the cathode and the quantity of charge that passes through the cell. While the mass of metal formed is easily measured by weighing the cathode, electric charge is determined indirectly.

Electric charge, symbol Q, is measured using the unit **coulomb**. The electric charge passing through a cell may be calculated from measurements of the current, I, through the cell and the time, t, for which the current flows.

The relationship is:

charge (coulombs) = current (amps) × time (seconds)

$$Q = I \times t$$

Experimental data from a silver-plating cell

An experiment was set up using the equipment shown in Figure 9.3.5 to determine the relationship between the amount of charge and the mass of silver formed in a silver-plating cell.

As Table 9.3.1 shows, the experimental data indicates that the more charge that passes through the cell, the more metal is formed at the cathode.

TABLE 9.3.1 The relationship between charge and the mass of silver in a silver-plating cell

Current (A)	Time (s)	Charge (C) $Q = I \times t$	Mass of silver formed (g)
2.0	200	400	0.45
2.0	400	800	0.91
2.0	600	1200	1.34
2.0	800	1600	1.79
2.0	1000	2000	2.24

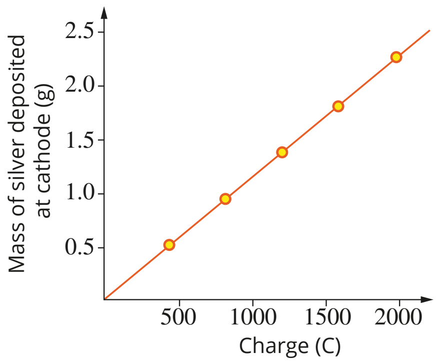


FIGURE 9.3.6 The variation with charge of mass of silver formed at the cathode in a silver-plating cell.

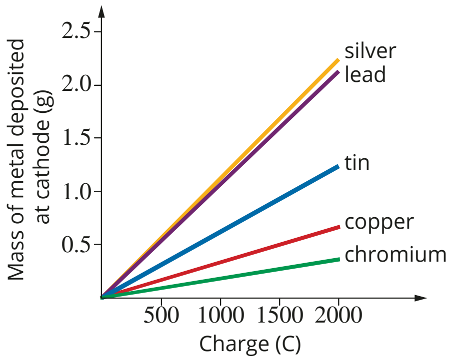


FIGURE 9.3.7 Variation with charge of the mass of metal formed at the cathode for different metal-plating cells.

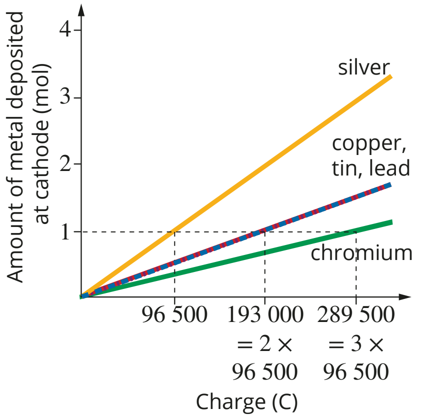


FIGURE 9.3.8 Variation with charge of amount of metal (in moles) formed at the cathode for different metal-plating cells.

The graph in Figure 9.3.6 shows the relationship between charge and the mass of metal formed. The mass of metal produced at the cathode is directly proportional to the electrical charge passed through the cell. This is **Faraday's first law of electrolysis**. It may be written symbolically as:

$$m \propto Q$$

FARADAY'S SECOND LAW OF ELECTROLYSIS

The previous experiment can be repeated using electroplating cells for metals other than silver. Results from experiments with cells using electrolytes containing Cu^{2+}, Sn^{2+}, Pb^{2+}, Cr^{3+} and Ag^{+} ions are shown in the graph in Figure 9.3.7.

While the data for each metal obeys Faraday's first law, at first inspection there seems little relationship between the graphs for each metal. However, if the amount of each metal, measured in moles, is graphed against charge, the results are more interesting (Figure 9.3.8). All the data lies along just three lines. One mole of silver is produced by about 96 500 coulombs of charge, whereas one mole of copper, tin or lead is produced by 193 000 (which is 2 × 96 500) coulombs.

An underlying pattern is now evident. In order to deposit 1 mole of silver from a solution of Ag^{+} ions, just 1 mole of electrons is required:

$$Ag^{+}(aq) + e^{-} \rightarrow Ag(s)$$

The charge on 1 mole of electrons must be 96 500 C.

The charge on 1 mole of electrons is known as a **faraday**, and has the symbol F. Therefore, 1 F = 96 500 C.

The charge on a given number of moles of electrons, $n(e^{-})$, can be readily calculated. For example, 2 moles of electrons has a charge of 193 000 C. We can express this mathematically by:

$$Q = n(e^{-}) \times F$$

$$\text{or } Q = n(e^{-}) \times 96\,500$$

where Q is charge (in coulombs), $n(e^{-})$ is number of moles of electrons and F is Faraday's constant (96 500 C mol^{-1}). The electrode reactions when copper, tin or lead are electroplated are:

$$Cu^{2+}(aq) + 2e^{-} \rightarrow Cu(s)$$
$$Sn^{2+}(aq) + 2e^{-} \rightarrow Sn(s)$$
$$Pb^{2+}(aq) + 2e^{-} \rightarrow Pb(s)$$

For 1 mole of each of these metals to be deposited, 2 moles of electrons are required. Therefore, 2 faradays of charge (193 000 C) must be passed through the cell.

To deposit 1 mole of chromium, 3 faradays of charge (289 500 C) are required, because the equation for the electrode reaction is:

$$Cr^{3+}(aq) + 3e^{-} \rightarrow Cr(s)$$

This is just what you can observe in the graph in Figure 9.3.8. Three different lines on the graph arise because of the different charges on the metal ions.

Faraday's second law of electrolysis states that in order to produce 1 mole of a metal, 1, 2, 3 or another whole number of moles of electrons must be consumed.

Although Faraday's laws were developed by studying the deposition of metal at the cathode in electroplating cells, the laws apply just as well to the production or consumption of any substance at the electrodes of either electrolytic cells or galvanic cells. Calculations are based on the two relationships:

- $Q = I \times t$
- $Q = n(e^{-}) \times F$

Faraday's laws can be restated more generally as follows.

- The mass of any substance deposited, evolved or dissolved at an electrode in an electrochemical process is directly proportional to the electrical charge passed through the cell.
- For 1 mole of a substance to be deposited, evolved, or dissolved at an electrode, the passage of 1, 2, 3 or another whole number of moles of electrons is required.

CHEMFILE

Michael Faraday's electrolysis experiments

Michael Faraday (1791–1867) was an English scientist who made great contributions to the fields of electromagnetism and electrochemistry (see Figure 9.3.9). His experiments on the decomposition of tin(II) chloride revealed that the amounts of tin and chlorine gas that were produced were always in proportion to the amount of electric charge that was passed through the cell. He also played a key role in popularising the use of the terms 'anode', 'cathode', 'electrode' and 'electrolyte'.

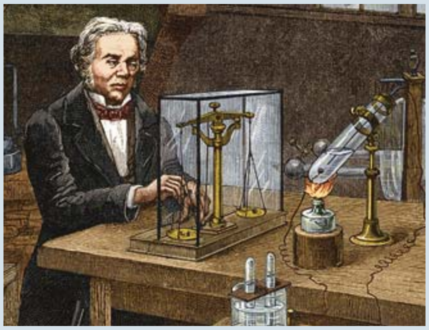


FIGURE 9.3.9 A painting of Michael Faraday working on an electrolysis experiment.

CALCULATIONS USING FARADAY'S LAWS

Worked Examples 9.3.1 and 9.3.2 show you how to calculate the mass of a chemical produced at an electrode of an electrolytic cell.

Worked example 9.3.1

CALCULATING MASS OF A PRODUCT AT AN ELECTRODE

A silver-plating cell operates with a steady current of 30.0 A for 20.0 minutes. What mass of silver is plated on the object at the cathode? The equation for the reaction is:

$$Ag^+(aq) + e^- \rightarrow Ag(s)$$

Thinking	Working
Calculate the quantity of charge passing through a cell using the formula: $Q = I \times t$. Remember that time must be expressed in seconds.	$Q = I \times t$ $= 30.0 \times (20.0 \times 60)$ $= 3.60 \times 10^4$ C
Calculate the number of moles of electrons that passed through the cell using the equation: $Q = n(e^-) \times F$	$n(e^-) = \frac{Q}{F}$ $= \frac{3.60 \times 10^4}{96\,500}$ $= 0.373$ mol
Use the mole ratio from the equation to determine the amount, in moles, of metal plated at the cathode.	The cathode reaction is: $Ag^+(aq) + e^- \rightarrow Ag(s)$ 1 mole of electrons will deposit 1 mole of silver metal. Mole ratio: $\frac{n(Ag)}{n(e^-)} = \frac{1}{1}$ $n(Ag) = n(e^-)$ $= 0.373$ mol
Calculate the mass of metal plated at the cathode.	The molar mass of Ag is 107.9 g mol^{-1}. $m(Ag) = n \times M$ $= 0.373 \times 107.9$ $= 40.3$ g

Worked example: Try yourself 9.3.1

CALCULATING MASS OF A PRODUCT AT AN ELECTRODE

A copper-plating cell operates with a steady current of 20.0 A for 15.0 minutes. What mass of copper is plated on the object at the cathode? The equation for the reaction is:

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

Faraday's laws can also be used to calculate the time it would take to produce a specific amount of product at an electrode.

Worked example 9.3.2

CALCULATING TIME TO PRODUCE A PRODUCT AT AN ELECTRODE

How long would it take, in hours, to deposit 50.0 g of copper at the cathode of a copper-plating cell operating at a current of 8.00 A? The half-equation for the reaction is:

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

Thinking	**Working**
Calculate the amount of substance that was deposited or consumed at the electrode using the formula: $n = \frac{m}{M}$	$n(Cu) = \frac{m}{M}$ $= \frac{50.0}{63.5}$ $= 0.787$ mol
Calculate the number of moles of electrons that passed through the cell using the mole ratio from the equation.	The cathode reaction is: $Cu^{2+}(aq) + 2e^{-} \rightarrow Cu(s)$ 2 mol of electrons will deposit 1 mol of copper metal. $\frac{n(e^{-})}{n(Cu)} = \frac{2}{1}$ so: $n(e^{-}) = 2 \times n(Cu)$ $= 2 \times 0.787$ $= 1.57$ mol
Calculate the quantity of charge which passed through the cell using the formula: $Q = n(e^{-}) \times F$	$Q = n(e^{-}) \times F$ $= 1.57 \times 96\,500$ $= 1.52 \times 10^{5}$ C
Calculate the time required using the formula: $t = \frac{Q}{I}$	$t = \frac{Q}{I}$ $= \frac{1.52 \times 10^{5}}{8.00}$ $= 1.90 \times 10^{4}$ s
Convert seconds to hours by dividing by (60 × 60).	$t = \frac{1.90 \times 10^{4}}{60 \times 60}$ $= 5.28$ h

Worked example: Try yourself 9.3.2

CALCULATING TIME TO PRODUCE A PRODUCT AT AN ELECTRODE

How long would it take, in hours, to deposit 20.0 g of silver at the cathode of a silver-plating cell operating at a current of 6.50 A? The half-equation for the reaction is:

$$Ag^{+}(aq) + e^{-} \rightarrow Ag(s)$$

9.3 Review

SUMMARY

- Electroplating is an application of electrolysis. It involves the deposition of a thin surface coating of metal over another surface to improve the appearance of an object, its resistance to corrosion, or both.
- The charge passing through an electrochemical cell can be calculated from the formula:

  charge (coulombs) = current (amps) × time (seconds)

  $Q = I \times t$
- Faraday's first law states that the mass of metal produced at the cathode is directly proportional to the electrical charge passed through the cell.
- Faraday's second law states that in order to produce 1 mole of a metal, 1, 2, 3 or another whole number of moles of electrons must be consumed.
- The charge on one mole of electrons is called a faraday (F), where 1 F = 96 500 C.
- The charge on an amount of electrons can be calculated from:

  charge (coulombs) = amount of electrons (moles) × 96 500

  $Q = n(e^-) \times F$
- Faraday's laws can be used to calculate the:
  - mass of a product formed in a cell, given the current and operating time
  - current passing through a cell, given the mass of product and the operating time
  - time required for a cell to operate, given the mass of product and the current through the cell.

KEY QUESTIONS

1 How many faradays of charge are required to produce:

a 1 mole of silver atoms from a silver nitrate solution?

b 1 mole of zinc atoms from a zinc nitrate solution?

c 1 mole of chlorine molecules (Cl_2) from molten potassium chloride?

d 1 mole of hydrogen molecules (H_2) from sodium chloride solution?

2 A nickel-plating cell with $NiSO_4(aq)$ electrolyte operates with a current of 10.0 A for 55.0 minutes. What mass of nickel is plated on the object at the cathode?

3 A car's lights are left on and the battery discharges at a current of 1.2 A. How long would it take, in hours, for 15.6 g of lead to be lost from the anode? The electrode reaction is represented by the half-equation:

$$Pb(s) + SO_4^{2-}(aq) \rightarrow PbSO_4(s) + 2e^-$$

4 Figure 9.3.10 shows an electroplating cell that was devised by a student to place a silver coating onto a key. An electric current is passed through a solution of 1.0 M silver nitrate ($AgNO_3$) using an inert carbon electrode as the anode.

a Write a half-equation for the reaction that occurs at the electrode connected to the negative terminal of the power source.

b What current is required if 0.055 g silver is deposited on the surface of the key when a current is passed through the cell for 7.0 minutes?

5 Electrolysis of a molten ionic compound with a current of 0.50 A for 30.0 minutes yielded 0.700 g of a metallic element at the cathode. If the element has a relative atomic mass of 150.0, calculate the charge on the metal ions.

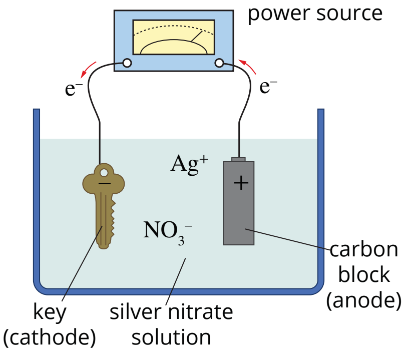


FIGURE 9.3.10 Electroplating a key with silver.

Chapter review

09

KEY TERMS

anode
brine
cathode
coulomb
electrochemical cell
electrochemical series
electrolysis
electrolyte
electrolytic cell
electroplating
faraday
Faraday's first law of electrolysis
Faraday's second law of electrolysis
galvanic cell
inert
inert electrode
non-spontaneous reaction
reactive electrode
semipermeable membrane
smelting
spontaneous reaction

Electrolytic cells

1 For electrolytic and galvanic cells, compare the:
  - a polarity of the anode and cathode
  - b direction of electron flow
  - c energy transformation occurring in the cells
  - d tendency of the cell reaction to occur spontaneously.

2 Write the electrode reactions and overall reaction for when molten $ZnCl_2$ is used as the electrolyte in an electrolytic cell with inert electrodes.

3 Two electrolytic cells were set up for the electrolysis of aqueous copper(II) sulfate. One cell contained copper electrodes and the other contained platinum electrodes. Determine the reactions that would occur at the electrodes of both cells.

4 An electrochemical cell (shown in Figure 9.4.1) is set up to produce potassium metal. Label the parts of the cell using the following options (options may be used more than once): Cl^-, molten potassium chloride, platinum, K^+.

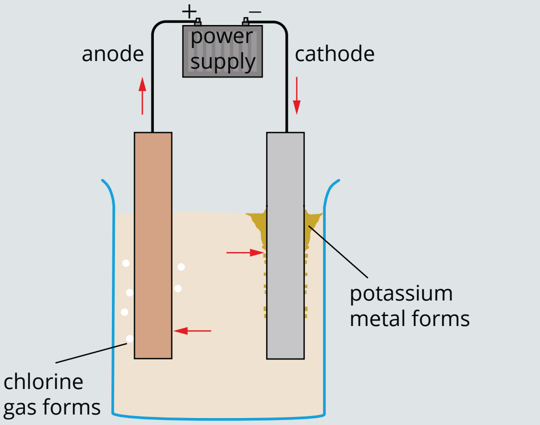


FIGURE 9.4.1 Electrochemical cell for producing potassium metal.

5 A student attempts to electroplate magnesium onto an iron electrode using a cell made of a magnesium anode, an iron cathode and a magnesium nitrate solution as electrolyte (see Figure 9.4.2). The student discovered that no magnesium has plated onto the cathode, despite careful checks of all the electrical connections in the electrolytic cell. Describe why the magnesium did not plate onto the cathode and what reaction occurred instead at the iron electrode.

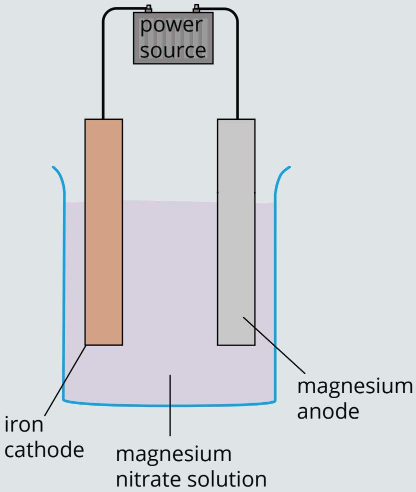


FIGURE 9.4.2 Electrolytic cell for plating an iron cathode with magnesium as constructed by a student.

6 An aqueous zinc sulfate solution was electrolysed using copper electrodes.
  - a Refer to the electrochemical series and identify the possible reactions that could occur. Write these half-equations in the order they appear in the series.
  - b Identify the correct half-equations for the reactions that occur at the anode and cathode.
  - c Write an equation for the overall reaction.

7 Using the electrochemical series, complete the table by predicting the initial products of each of the following electrolysis experiments.

Experiment	Electrolyte	Electrodes	Cathode reaction	Anode reaction
a	Molten potassium iodide	Platinum		
b	Copper(II) sulfate solution	Platinum		
c	Potassium bromide solution	Copper		
d	A mixture of copper(II) nitrate and nickel(II) nitrate solutions	Carbon		
e	Lithium fluoride solution	Platinum		

Commercial electrolytic cells

8 Sodium and chlorine are manufactured by passing direct current through molten sodium chloride. Why is it necessary for the electrolyte to be molten and not aqueous?

9 A membrane cell is used to produce sodium hydroxide through electrolysis of a concentrated sodium chloride solution (brine).

a Write half-equations for the reactions that occur at each electrode.

b What is the purpose of the semipermeable membrane in the cell?

10 Early attempts to produce aluminium by electrolysis of aqueous solutions of aluminium compounds were unsuccessful. Use the electrochemical series to explain why.

Faraday's laws

11 Zinc–air cells have been developed for a range of different uses, including electric vehicles, heart pacemakers and laptop computers. In the cells, zinc metal is oxidised at the negative electrode and oxygen gas is reduced to water at the positive electrode.

a Write a half-equation for the reaction occurring at the negative electrode of the cell.

b A zinc–air cell used for a pacemaker operates with a steady current of 3.5×10^{-5} A. If the cell will continue to operate until 1.5 g of zinc in the negative electrode has been used up, determine how many years the pacemaker will last before it needs replacing.

12 A copper-plating cell operates with a current of 5.0 A for 75.0 minutes. What mass of copper is plated on the object at the cathode?

13 Iron is plated with tin in an electrolytic cell containing $K_2Sn(OH)_6$ as the electrolyte. A cell operates for 5.00 h at a current of 25.0 A.

a What is the charge on the tin ions in the electrolyte?

b How many faradays of charge are required to produce 1.00 mole of tin?

c Calculate the mass of tin deposited during this period.

14 A charge of 0.400 faraday was passed through 1.00 L of 1.00 M copper(II) sulfate solution using carbon electrodes.

a Write half-equations for the reactions that occur at each electrode.

b Calculate the concentration of the copper(II) ions in solution after electrolysis.

15 Three electrolytic cells containing silver nitrate solution, copper(II) sulfate solution and chromium(III) sulfate solution, respectively, were connected in series so that the same amount of electric charge passed through each cell (see Figure 9.4.3). Metal was deposited at the cathode of each cell.

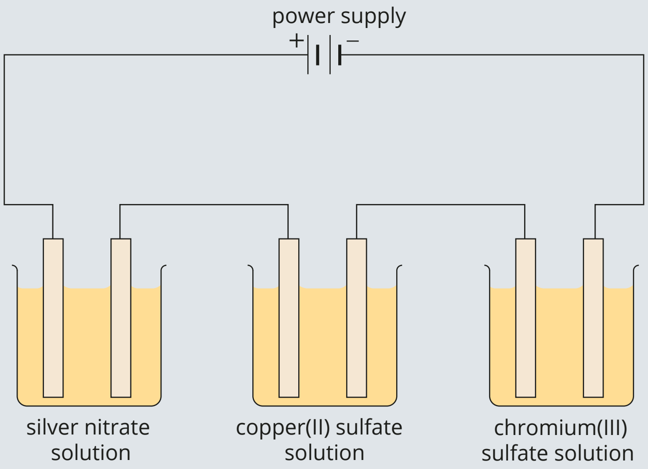


FIGURE 9.4.3 Three electrolytic cells in series.

a Write half-equations for the reduction reaction that occurs in each cell.

b If 10.0 g of silver was obtained from one cell, what mass of metal would be obtained from each of the other cells?

16 A nickel teapot, with a surface area of 0.0900 m^2, is to be silver plated.

a Which electrode should the teapot be connected to?

b What is the polarity of this electrode?

c If the plating is to be 0.00500 cm thick and the density of silver is 10.5 g cm^{-3}, how long should the pot be put in a silver-plating cell with a current of 0.500 A?

17 A student wishes to copper-plate a nickel medallion and sets up an electrolytic cell using 250 mL of 1.00 M copper(II) sulfate solution and a large copper anode. The student runs a current of 10.0 A through the cell for 20 minutes.

- **a** What mass of copper will be plated onto the medallion?
- **b** What will be the concentration of copper(II) sulfate remaining in solution?

The student replaces the copper anode with an inert graphite electrode and runs the same current through the cell for a further 20 minutes.

- **c** What gas will be produced at the anode?
- **d** What will be the concentration of copper(II) sulfate remaining in solution?

18 A number of important metals are produced by electrolysis of molten salts. In one such process a current of 25 000 A produces 272 kg of metal in 24 hours. If the cation in the salt has a 2+ charge, what is the identity of the metal?

19 Two electrolytic cells are connected in series as shown in Figure 9.4.4. A current of 5.00 A flows for 15.0 minutes.

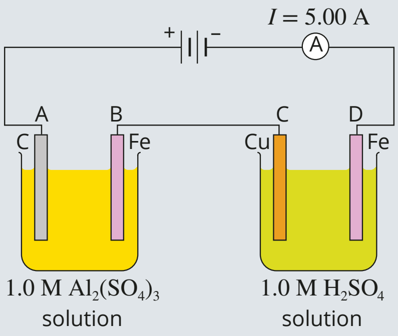


FIGURE 9.4.4 Electrolytic cells in series.

- **a** Calculate the charge flowing through each cell.
- **b** Write half-equations for the reactions occurring at each electrode (A–D) when the current commences to flow.
- **c** Calculate the change in mass of electrode C after 15 minutes.
- **d** Calculate the volume of gas, measured at STP, that is formed at electrode B after 15.0 minutes.
- **e** As the current flows through the cells, how does the reaction at electrode D change?

Connecting the main ideas

20 Sodium and chlorine are produced by electrolysis of molten sodium chloride in the Downs cell. A typical Downs cell runs at 600°C, 7 V and with a current of 30 kA. In a 24-hour period, what:

- **a** mass of sodium metal will be produced?
- **b** volume of chlorine gas (at STP) will be produced?

21 An electrolytic cell for the extraction of aluminium operates at a current of 150 000 A.

The electrode reactions are:

Al_3^+(in cryolite) + $3e^- \rightarrow Al(l)$

$C(s) + 2O_2^-$(in cryolite) $\rightarrow CO_2(g) + 4e^-$

In order to produce 1.00 tonne (10^6 g) of Al, calculate:

- **a** how long the cell must operate
- **b** the mass of carbon consumed at the anodes
- **c** the volume of carbon dioxide gas produced, measured at STP.

22 Commercial operation of an aluminium smelter depends upon the availability of cheap electric power.

- **a** Calculate the electric charge required to produce 1.00 tonne of aluminium from alumina (Al_2O_3) by electrolysis.
- **b** If the cell operates at 5.00 V, calculate the energy needed to make 1.00 tonne of aluminium. (1 volt = 1 joule per coulomb)
- **c** Calculate the cost of the electricity required to make 1.00 tonne of aluminium if the smelter purchased electricity at the domestic rate of 12 cents per kilowatt hour. (1 kilowatt hour = 3 600 000 J)

23 Construct a concept map that includes the terms electrolysis, electrolytic cell, chemical energy, electrical energy, anode, cathode, reducing agent, oxidising agent, reduction, oxidation, electrolyte and non-spontaneous reactions.

24 When constructing a galvanic cell in the laboratory, why are two half-cells usually used whereas the reactants of an electrolysis cell are often placed in a single container?

25 Rutile is a mineral composed of titanium and oxygen. In a trial electrolytic cell running at 100% efficiency, a potential difference of 4.0 V was applied and used 463.2 kJ of electricity to produce 14.37 g of titanium metal.

- **a** Calculate the amount of titanium produced, in mol.
- **b** Calculate the total charge of the electrons (*Q*) used to produce the titanium metal. (1 volt = 1 joule per coulomb)
- **c** Calculate the amount of electrons, in mol, needed to produce the titanium metal.
- **d** Calculate the charge of the titanium ion in rutile.
- **e** Determine the empirical formula of rutile.

REVIEW QUESTIONS

How can the yield of a chemical product be optimised?

Multiple-choice questions

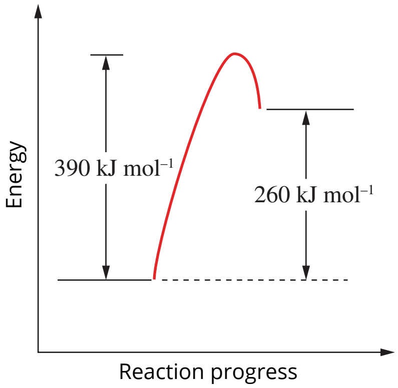
1 Which of the following requires involvement of a reversible chemical reaction?

A Combustion of a fuel to produce heat for cooking
B An electric car powered by a fuel cell
C The rechargeable battery in a mobile phone
D The setting of a two-part epoxy glue after the parts are mixed

Questions 2 and 3 refer to the following information.

The energy profile diagram shown below is for the following reaction.

$CO_2(g) + NO(g) \rightleftharpoons CO(g) + NO_2(g)$



2 The ΔH of the forward reaction, in kJ mol^{-1}, is:

A –170
B +130
C +230
D +260

3 The activation energy of the reverse reaction, in kJ mol^{-1}, is:

A 40
B 130
C 230
D 360

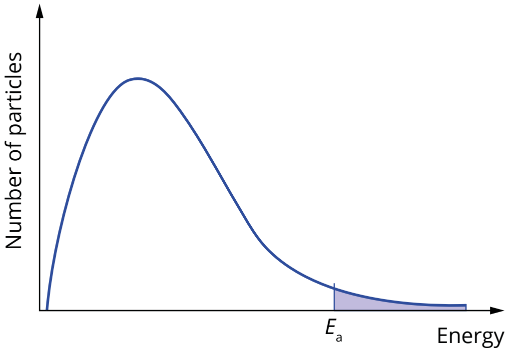
4 Consider the following reactions.

I $A(g) + B(g) \rightleftharpoons 2C(g) \quad \Delta H = +180$ kJ mol^{-1}
II $D(g) + 3E_2(g) \rightleftharpoons 2F(g) \quad \Delta H = -90$ kJ mol^{-1}
III $2G(g) \rightleftharpoons H(g) + I(g) \quad \Delta H = -180$ kJ mol^{-1}

From a comparison of the enthalpy changes, ΔH, which of the following is definitely true?

A Activation energy of equation I > activation energy of equation II
B Activation energy of equation I < activation energy of equation II
C Activation energy of equation I = activation energy of equation III
D No information about activation energy can be deduced.

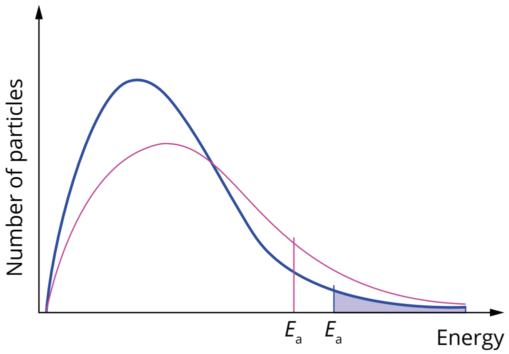
5 The diagram below shows the typical Maxwell–Boltzmann distribution of kinetic energies of the particles in a reaction mixture.



If E_a represents the activation energy for the reaction, then what does the shaded area represent?

A The total amount of energy that will be released when the reaction reaches equilibrium
B The proportion of reactant particles that are moving fast enough at a given instant for a collision to result in the formation of products
C The energy that must be added to the reactant mixture to initiate the reaction
D The proportion of reactant particles that will be converted to products when the reaction reaches equilibrium

6 Two changes are made to the reaction mixture from Question 5, affecting both the distribution curve and the activation energy, as shown in red in the diagram below.



Which of the following gives changes in conditions that are consistent with these effects?

	Change in distribution curve	Change in activation energy
A	Higher temperature	Catalyst added
B	Higher temperature	Lower pressure
C	Higher pressure	Lower temperature
D	Higher pressure	Catalyst added

7 Which of the following statements about a catalyst is **not** true?

A A catalyst is not consumed in the course of a reaction.
B A catalyst alters the reaction pathway between reactants and products.
C A catalyst reduces the energy released or absorbed by a reaction.
D The proportion of molecules with sufficient energy to react is increased by a catalyst.

8 Water vapour reacts with chlorine according to the following equation.

$$2H_2O(g) + 2Cl_2(g) \rightleftharpoons 4HCl(g) + O_2(g)$$

At a particular temperature, the value of the equilibrium constant, *K*, for this reaction is 4.0×10^{-4} M. At the same temperature, the value of the equilibrium constant for the reaction:

$$2HCl(g) + \frac{1}{2}O_2(g) \rightleftharpoons H_2O(g) + Cl_2(g)$$

is equal to:

A 2×10^{-4} $M^{-\frac{1}{2}}$
B 2×10^{-2} $M^{-\frac{1}{2}}$
C 2.5×10^{3} $M^{-\frac{1}{2}}$
D 50 $M^{-\frac{1}{2}}$

9 Consider the following equation.

$$A + 3B \rightleftharpoons 2C + 4D$$

The correct expression for the equilibrium constant is:

A $\frac{[A][3B]^3}{[2C]^2[4D]^4}$
B $\frac{[C]^2[D]^4}{[A][B]^3}$
C $\frac{[A][B]^3}{[C]^2[D]^4}$
D $\frac{[2C][4D]}{[A][3B]}$

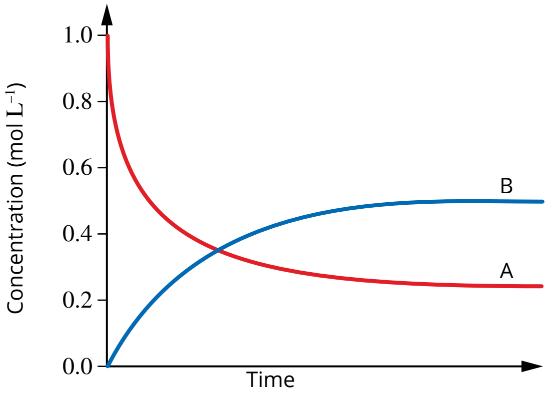
10 Consider the following equation:

$2W + 2X \rightleftharpoons 2Y + nZ$

which, at a particular temperature, has an equilibrium constant of $K = 5.0$ M^2. From this information we can conclude that the coefficient *n* in the equation is:

A 1
B 2
C 3
D 4

11 Examine the concentration–time diagram shown below.



This graph could represent the concentrations of A and B in the equation:

A A → B
B B → A
C 2A → B
D A → 2B

12 In a sealed vessel, nitrogen monoxide, oxygen and nitrogen dioxide form the following equilibrium:

$2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$; $\Delta H = -114$ kJ mol^{-1}

Which one of the following sets of conditions is likely to lead to the highest yield of nitrogen dioxide gas?

A 200°C and 1 atm pressure
B 200°C and 2 atm pressure
C 300°C and 1 atm pressure
D 300°C and 2 atm pressure

13 A sample of NOCl is allowed to come to equilibrium according to the following equation:

$2NOCl(g) \rightleftharpoons 2NO(g) + Cl_2(g)$

The volume of the mixture is halved and the mixture is allowed to come to a new equilibrium, the temperature remaining constant. At the new equilibrium the chlorine has:

A decreased in amount and decreased in concentration

B increased in amount and decreased in concentration

C decreased in amount and increased in concentration

D increased in amount and increased in concentration.

14 The reaction between nitrogen monoxide and ozone is:

$NO(g) + O_3(g) \rightleftharpoons NO_2(g) + O_2(g) \quad K = 6 \times 10^{34}$ at 25°C

Equal amounts of NO and O_3 are used. Which of the following statements cannot be inferred from the magnitude of the equilibrium constant?

A At equilibrium, $[NO_2][O_2] \rightarrow [NO][O_3]$.

B The equilibrium of the reaction lies well to the right.

C The reaction has a low activation energy.

D Very little ozone will remain at equilibrium.

15 Carbon dioxide gas dissolves to a small extent in water, forming carbonic acid in an exothermic reaction.

$CO_2(g) + H_2O(l) \rightleftharpoons H_2CO_3(aq)$; ΔH negative

$H_2CO_3(aq) + H_2O(l) \rightleftharpoons HCO_3^-(aq) + H_3O^+(aq)$

This is the reaction involved in forming fizzy drinks. Which of the following strategies would **not** be effective at increasing the amount of dissolved carbon dioxide?

A Decreasing the pH of the solution

B Decreasing the temperature of the solution

C Increasing the concentration of carbon dioxide in the gas

D Increasing the pressure of the carbon dioxide gas

16 The self-ionisation of water is affected by temperature as shown below.

$H_2O(l) + H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$

$K_w = [H_3O^+][OH^-]$

Temperature (°C)	Ionisation constant for water, K_w
5	1.85×10^{-15}
15	4.51×10^{-15}
25	1.00×10^{-14}
35	2.09×10^{-14}

From the data it can be inferred that:

A the pH of pure water at 35°C is greater than 7

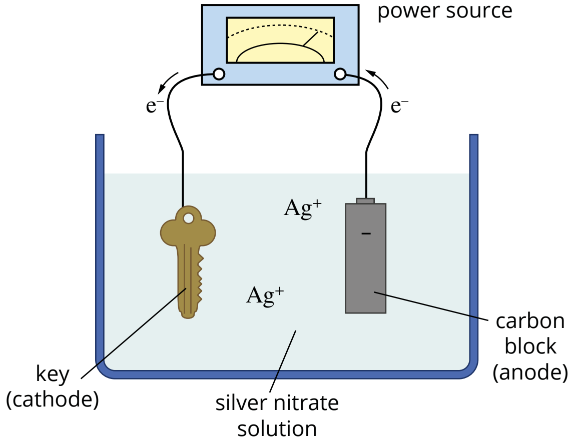
B self-ionisation of water is an exothermic reaction

C equilibrium for the reaction lies well to the left with mainly reactants present

D in pure water at 15°C, $[OH^-]$ is lower than $[H_3O^+]$.

The following information relates to Questions 17 and 18.

The diagram shows an electroplating cell that was devised by a student to place a silver coating onto a key. An electric current is passed through a solution of 1 M silver nitrate, $AgNO_3$, using an inert carbon electrode as the anode.



17 What reaction occurs at the electrode connected to the negative terminal of the external power supply?

A $Ag^+(aq) + e^- \rightarrow Ag(s)$

B $2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$

C $2Cl^-(aq) \rightarrow Cl_2(g) + 2e^-$

D $2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$

18 If 0.055 g silver is deposited on the surface of the key when a current is passed through the cell for 7.0 minutes, what current is required?

A 0.12 A

B 0.75 A

C 7.0 A

D 49 A

19 Three beakers contain solutions of 1.0 M chromium(III) nitrate, 1.0 M copper(II) nitrate and 1.0 M silver nitrate. Each solution has 0.60 F of electric charge passed through it, using carbon electrodes and a power pack. In each beaker a different metal is deposited onto the cathode. In decreasing order, the amount of metal (in moles) deposited onto the cathode in each beaker will be:

A Cr < Cu < Ag

B Ag < Cu < Cr

C Cr < Ag < Cu

D the same in all three beakers.

20 A series of experiments is described below.

I Adding zinc granules to a solution of tin(II) chloride

II Adding copper turnings to tin(II) chloride solution

III Electrolysis of molten tin(II) chloride

IV Electrolysis of an aqueous solution of tin(II) chloride

The experiments that would result in the production of metallic tin, Sn, are:

A all of them

B I, III and IV

C I and II

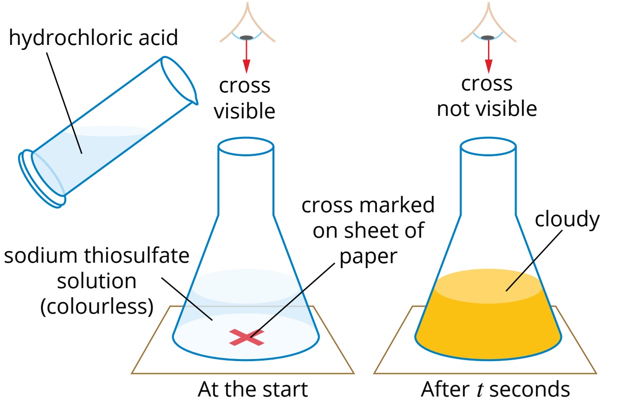
D only III.

Short-answer questions

21 A student investigated the factors affecting the rate of reaction between a solution of sodium thiosulfate and hydrochloric acid:

$$Na_2S_2O_3(aq) + 2HCl(aq) \rightarrow 2NaCl(aq) + SO_2(g) + S(s) + H_2O(l)$$

The reaction was carried out in a conical flask placed on top of a piece of white paper with a dark cross marked on it. The rate of reaction was determined by measuring the time taken for the cross to be masked by the suspension of sulfur formed during the reaction, as shown.



The rate was determined for different concentrations of sodium thiosulfate and for different temperatures. The volume of each solution and the concentration of hydrochloric acid was kept constant. The results are summarised in the table below.

Experiment number	$[Na_2S_2O_3(aq)]$ (M)	Temperature (°C)	Time taken for the cross to be masked (s)
1	0.1	20	36
2	0.2	20	20
3	0.1	25	28

a Explain, in terms of collision theory, why the rate in experiment 2 is higher than the rate in experiment 1.

b Explain, in terms of collision theory, why the rate in experiment 3 is higher than the rate in experiment 1.

c What factors, other than the two investigated in this experiment, may affect the rate of a reaction?

22 The activation energy for the decomposition of hydrogen peroxide to oxygen was measured under two different conditions.

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

I The activation energy for the decomposition reaction when an enzyme was added was found to be 36.4 kJ mol^{-1}. The temperature of the reaction mixture increased.

II When platinum was added to another sample of the hydrogen peroxide solution, the activation energy was 49.0 kJ mol^{-1}. The temperature of the reaction mixture increased.

a What is the function of the enzyme and platinum in each these reactions?

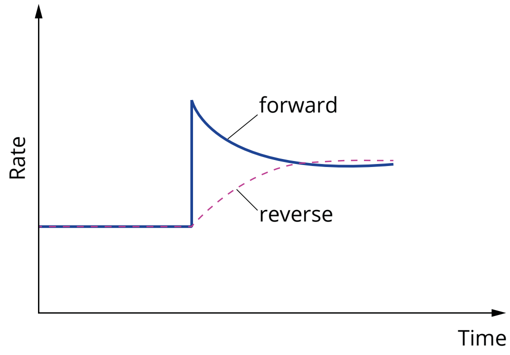
b Sketch, on the same set of axes, the energy profiles for the decomposition of hydrogen peroxide with the enzyme and the decomposition using the platinum.

c Which reaction system, I or II, would be faster? Explain your answer.

23 Consider the following readily reversible gas-phase reaction.

$$W(g) + 2X(g) \rightleftharpoons Y(g) + Z(g)$$

The graph below shows the changes to the rates of the forward and reverse reactions when some additional reactant, W, is added to an equilibrium mixture of these gases at time *T*.



a Explain how this graph shows that the mixture was at equilibrium before time *T*.

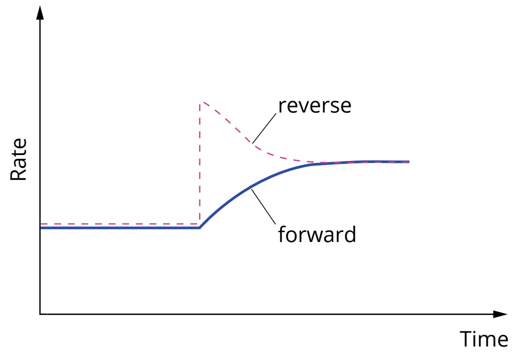
b Use collision theory to account for the changes in the rates of the forward and reverse reactions from time *T*.

The process was repeated several times, each time with a different change occurring at time *T*. Changes tested included:

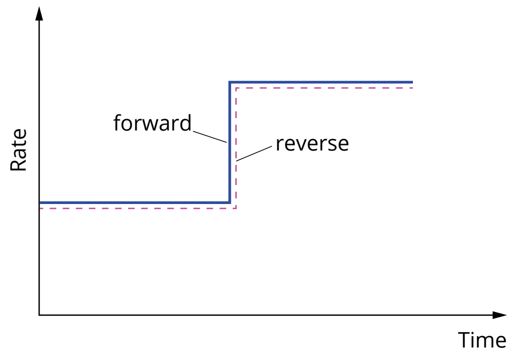
- removing W from the mixture
- removing Y
- adding Y
- adding an inert gas (argon)
- adding a catalyst
- increasing the volume of the container.

c For each of the graphs below, select a change from this list that is consistent with the rate changes depicted. In each case, briefly justify your choice.

i



ii



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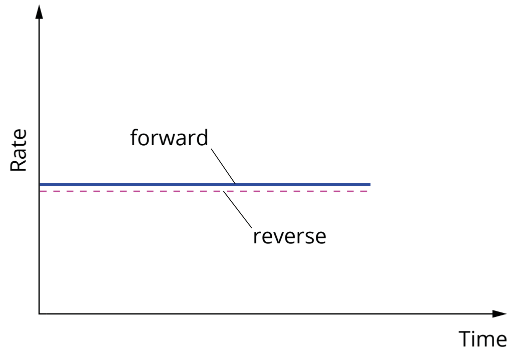
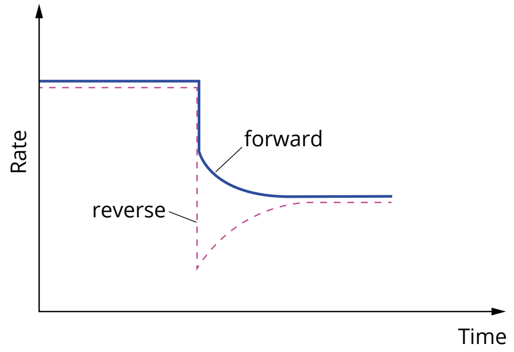


The graph below shows the rate changes after lowering the temperature at time *T*.



d Why does lowering the temperature cause an initial drop in both reaction rates?

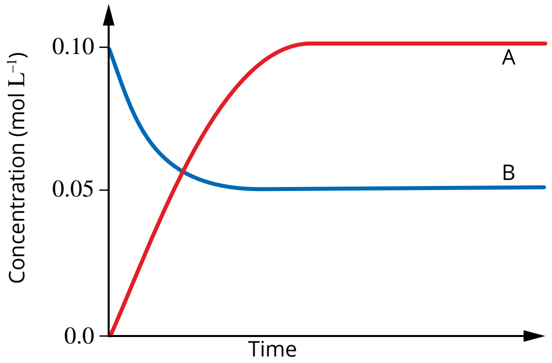
e Considering the period during which the rates are unequal, in which direction does the equilibrium shift?

f Is the reaction exothermic or endothermic? Explain.

24 The gases dinitrogen tetroxide, N_2O_4, and nitrogen(IV) oxide, NO_2, coexist according to the following equilibrium reaction.

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

A concentration–time graph for the system coming to equilibrium is shown below.



a Identify A and B.

b Write an expression for the equilibrium constant of the decomposition of N_2O_4.

c On the graph provided, sketch the line showing the effect on A if a catalyst had been present in the mixture from the beginning.

d Calculate *K* for the reaction at equilibrium according to this concentration graph.

25 Carbon monoxide and iodine pentoxide react to form iodine and carbon dioxide in the equilibrium reaction.

$5CO(g) + I_2O_5(s) \rightleftharpoons I_2(g) + 5CO_2(g) \qquad \Delta H = -1175 \text{ kJ}$

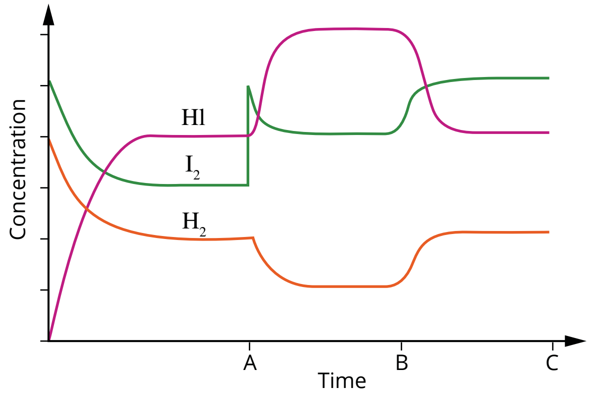
Use your knowledge of Le Châtelier's principle to predict the effect (*decrease, increase* or *no change*) of the change (column 1) on the designated quantity (column 2). Assume that the change listed is the only one taking place (e.g. if I_2 is added, the volume and the temperature are kept constant).

	Change	Quantity	Increase/decrease/ no change
a	Increase T	K	
b	Decrease T	Amount of $I_2O_5(s)$	
c	Add $I_2(g)$	K	
d	Add $CO_2(g)$	Amount of $I_2(g)$	
e	Double volume	Amount of CO_2	
f	Double volume	Concentration of CO_2	
g	Remove CO	Amount of CO_2	
h	Add catalyst	Amount of $I_2(g)$	
i	Add inert gas Ar	K	

26 The reaction between hydrogen and iodine in the gaseous phase to produce hydrogen iodide is described by the following equation:

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g) \quad \Delta H \text{ negative}$$

The following diagram shows the change in concentration of gaseous hydrogen, iodine and hydrogen iodide as the equilibrium is reached and disturbed.



a At point A, a sudden change occurs to the system. What has happened?

b At point B, another change has occurred. What has happened?

c On the graph provided, mark an X on the time axis to indicate a point when the system as at equilibrium.

d Extend the graph past point C, until equilibrium is re-established, to show what would happen to the concentration of the gases if the volume of the reaction vessel was doubled. Assume the temperature remains constant.

27 Methanol is used as a fuel for some racing cars. The synthesis of methanol from methane involves two reactions.

I A reaction of methane with steam to yield carbon monoxide and hydrogen

II An exothermic reaction between carbon monoxide and hydrogen to produce methanol

a Write equations for the two reactions that are described.

b The reaction of carbon monoxide with hydrogen is performed at about 250°C and 100 atm pressure. Copper, zinc oxide and alumina are also present.

- **i** What is the likely function of the copper, zinc oxide and alumina in the reactor?
- **ii** How would the yield be affected if the reaction were performed at a higher temperature?
- **iii** State two advantages of using such a high pressure.

c Any process involving carbon monoxide presents hazards because of its toxicity, which arises because of its ability to bind very strongly to haemoglobin in competition with oxygen.

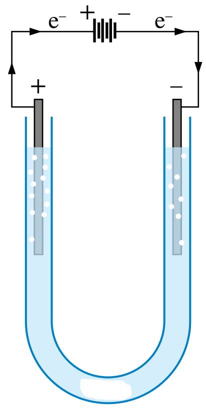
$Hb_4 + CO \rightleftharpoons Hb_4.CO$

$Hb_4 + O_2 \rightleftharpoons Hb_4.O_2$

- **i** Referring to these competing equilibria, explain why exposure to carbon monoxide leads to decreased levels of oxyhaemoglobin ($Hb_4.O_2$) in the blood.
- **ii** Treatment for carbon monoxide poisoning often includes hyperbaric oxygen (pure oxygen at a pressure well above 1 atm). Explain how this helps remove $Hb_4.CO$ from the blood.

d Another source of carbon monoxide is the incomplete combustion of many fuels. Write a balanced equation for the incomplete combustion of methanol to form carbon monoxide and water.

28 A series of electrolyses are carried out in a U-tube as shown in the diagram.

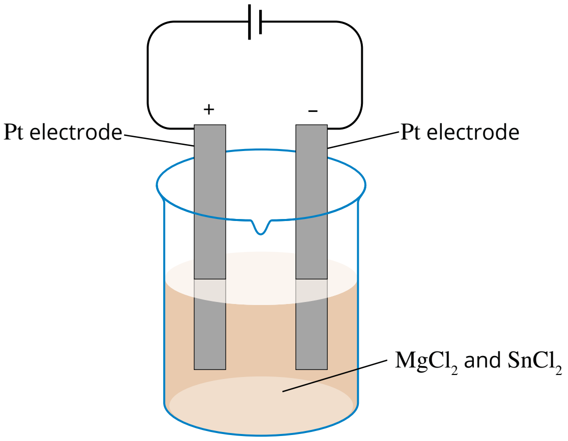


The electrolyte solution in each case, along with the electrode materials used, are listed below. Refer to an electrochemical series and for each of the electrolyses.

- **i** Write half-equations for the reactions predicted to occur at the positive and negative electrodes.
- **ii** State one visible change you could look for to confirm the formation of your predicted products.

	Solution	**Electrode materials**	
		Positive electrode	**Negative electrode**
a	KI(aq)	Carbon	Carbon
b	$PbCl_2$(aq)	Carbon	Carbon
c	$AlCl_3$(aq)	Copper	Copper

29 A 100 mL solution containing a mixture of magnesium chloride ($MgCl_2$) and tin(II) chloride ($SnCl_2$) is prepared by dissolving 0.025 mol of each salt in water. Platinum electrodes are placed in the solution and a small current is passed through it, as shown in the diagram below.



- **a** Write half-equations for the electrode reactions occurring just after the electrolysis is started at the:
  - **i** anode
  - **ii** cathode.
- **b** After electrolysis has been occurring for a considerable period of time, all of the metal that was first plated on the cathode will have been used up and a new electrode reaction will occur at the cathode. Write a half-equation for the next electrode reaction that occurs at the cathode.
- **c** What major difference would occur in the cell if the solution that was used had been a saturated solution of tin(II) chloride?

30 In an electrolysis experiment, a student is provided with a solution of nickel(II) nitrate ($Ni(NO_3)_2$). The electrodes to be used were a carbon rod as the positive electrode and a metal spatula as the negative electrode.

- **a** Will the nickel coating appear on the carbon rod or on the metal spatula during the experiment described?
- **b** Write equations for the half-reactions that occur at each electrode.
- **c** A current of 2.5 A was passed through this nickel-plating cell for 15 minutes. Calculate the mass of nickel that could be plated on the cathode.

31 Lithium metal is prepared by electrolysis of a molten mixture of lithium chloride and potassium chloride.

- **a** Write a half-equation for the reaction occurring at the cathode in this cell.
- **b** Write a half-equation for the reaction occurring at the anode in the cell.
- **c** Why is it not possible to produce lithium metal by the electrolysis of an aqueous solution of lithium chloride?
- **d** Suggest why a mixture of lithium chloride and potassium chloride is used, rather than pure lithium chloride, in this electrolytic process.
- **e** Assuming that lithium reacts in a similar way to sodium, describe two precautions that would need to be taken in this preparation.

32 This question requires you to compare galvanic cells with electrolytic cells.

- **a** List two structural features (components) that both types of cell possess.
- **b** Compare the energy transformations occurring in a galvanic cell with those occurring in an electrolytic cell.
- **c** Explain why the negative electrode of a galvanic cell is the site of oxidation, whereas the negative electrode of an electrolytic cell is the site of reduction.
- **d** Explain why a galvanic cell is always constructed to keep its reacting oxidant and reductant apart, while in an electrolytic cell they are usually combined in the same electrolyte mixture and instead steps are taken to keep the cell products apart.

33 Some industrially important chemicals are produced by the electrolysis of a molten electrolyte while others are produced by electrolysis of an aqueous solution.

- **a** Name one chemical produced by the electrolysis of:
  - **i** a molten electrolyte
  - **ii** an aqueous solution.
- **b** For each chemical that you have selected:
  - **i** write an equation for the reaction occurring at the anode
  - **ii** write an equation for the cathode reaction
  - **iii** describe one feature of the electrolytic cell used to manufacture of each selected chemical.
- **c** Explain why some chemicals can be produced by the electrolysis of a molten electrolyte but not from the electrolysis of an aqueous solution.
- **d** Suggest three properties of graphite that account for its frequent use as an electrode material in commercial electrolytic cells.
- **e** Steel cathodes are often used in commercial electrolytic cells but never steel anodes. Account for this.

34 Write equations to represent the anode and cathode reactions that occur when an electric current is passed through:

- **a** a dilute solution of sodium chloride
- **b** a concentrated solution of sodium chloride
- **c** molten sodium chloride.

35 The half-equations occurring in a nickel–zinc (NiZn) battery as it discharges are as follows.

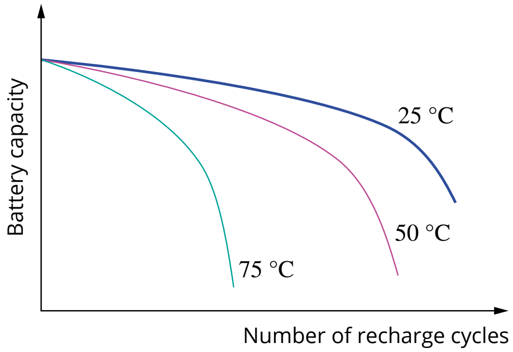
cathode (+): $2H_2O(l) + 2NiOOH(s) + 2e^- \rightarrow 2Ni(OH)_2(s) + 2OH^-(aq)$

anode (−): $2OH^-(aq) + Zn(s) \rightarrow Zn(OH)_2(s) + 2e^-$

The NiZn battery is rechargeable.

- **a** Write the half-equation for the reaction occurring at the negative and positive electrodes when the battery is being recharged.
- **b** Why is recharging a secondary cell such as this classed as a type of electrolysis?
- **c** One issue with this cell is that zinc hydroxide is slightly soluble, allowing small quantities to migrate away from the electrode during discharge. Explain how this will affect the performance of the cell.

In testing a new type of secondary cell, the capacity of the cell when fully charged was measured against the number of discharge–recharge cycles at different operating temperatures. The results are shown in the graph below.



- **d** Suggest a reason for the different battery life observed at different temperatures.
- **e** What other factors contribute to the fact that no rechargeable cell survives unlimited recharge–discharge cycles?

UNIT 4

How are organic compounds categorised, analysed and used?

AREA OF STUDY 1

How can the diversity of carbon compounds be explained and categorised?

Outcome 1: On completion of this unit the student should be able to compare the general structures and reactions of the major organic families of compounds, deduce structures of organic compounds using instrumental analysis data, and design reaction pathways for the synthesis of organic molecules.

AREA OF STUDY 2

What is the chemistry of food?

Outcome 2: On completion of this unit the student should be able to distinguish between the chemical structures of key food molecules, analyse the chemical reactions involved in the metabolism of the major components of food including the role of enzymes, and calculate the energy content of food using calorimetry.

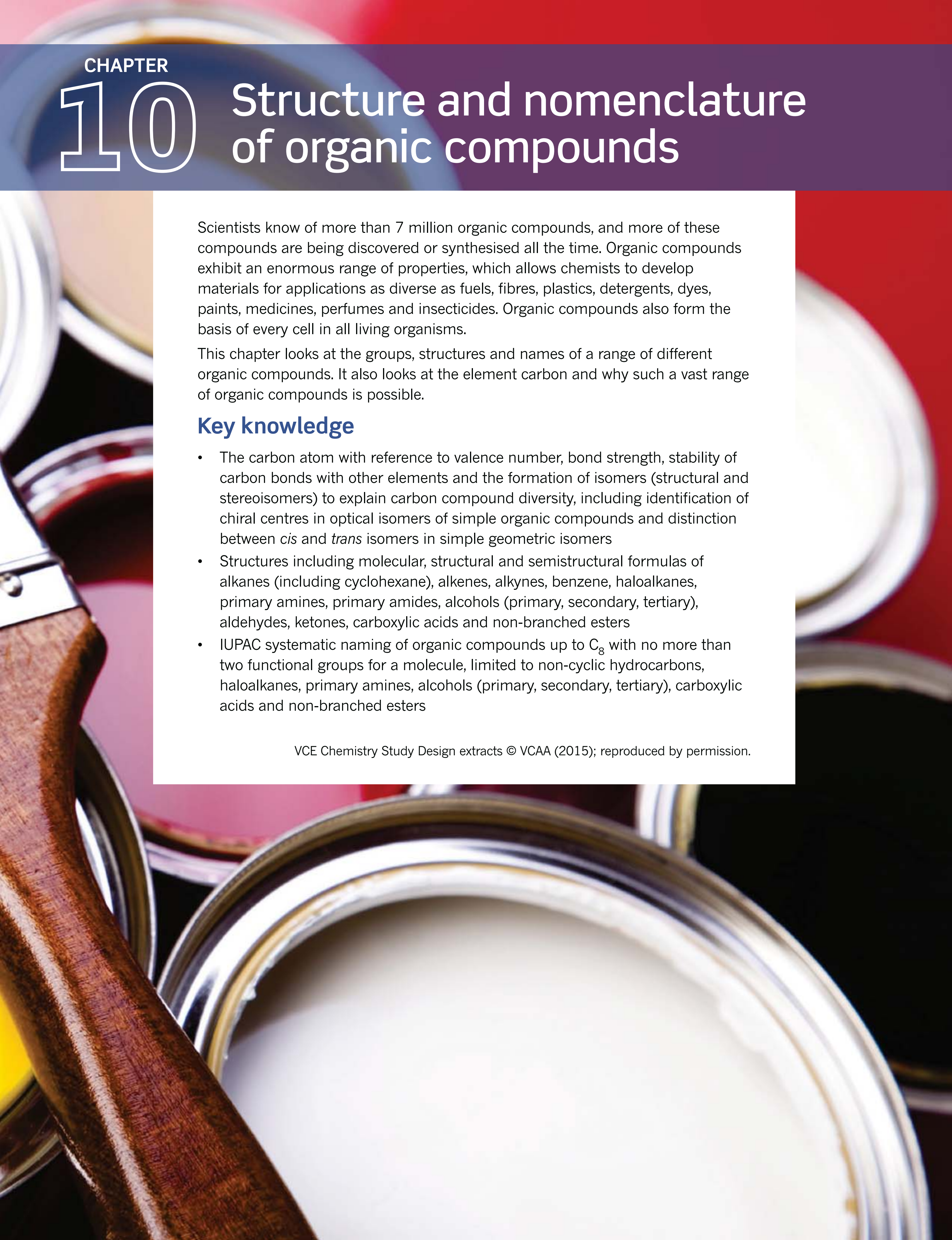
AREA OF STUDY 3

Practical investigation

Outcome 3: On the completion of this unit the student should be able to design and undertake a practical investigation related to energy and/or food, and present methodologies, findings and conclusions in a scientific poster.

To achieve this outcome the student will draw on the key knowledge outlined in Area of Study 3 and the related key skills.

The key skills to complete Area of Study 3 Practical investigation can be found in *Heinemann Chemistry 2 5th Edition ProductLink*.



CHAPTER

10

Structure and nomenclature of organic compounds

Scientists know of more than 7 million organic compounds, and more of these compounds are being discovered or synthesised all the time. Organic compounds exhibit an enormous range of properties, which allows chemists to develop materials for applications as diverse as fuels, fibres, plastics, detergents, dyes, paints, medicines, perfumes and insecticides. Organic compounds also form the basis of every cell in all living organisms.

This chapter looks at the groups, structures and names of a range of different organic compounds. It also looks at the element carbon and why such a vast range of organic compounds is possible.

Key knowledge

- The carbon atom with reference to valence number, bond strength, stability of carbon bonds with other elements and the formation of isomers (structural and stereoisomers) to explain carbon compound diversity, including identification of chiral centres in optical isomers of simple organic compounds and distinction between *cis* and *trans* isomers in simple geometric isomers
- Structures including molecular, structural and semistructural formulas of alkanes (including cyclohexane), alkenes, alkynes, benzene, haloalkanes, primary amines, primary amides, alcohols (primary, secondary, tertiary), aldehydes, ketones, carboxylic acids and non-branched esters
- IUPAC systematic naming of organic compounds up to C_8 with no more than two functional groups for a molecule, limited to non-cyclic hydrocarbons, haloalkanes, primary amines, alcohols (primary, secondary, tertiary), carboxylic acids and non-branched esters

10.1 Diversity of carbon compounds

Review

Homologous series

The study of organic chemistry is simplified by grouping the millions of different molecules that exist into families called **homologous series**. Members of the same homologous series have:

- a similar structure
- a pattern to their physical properties
- similar chemical properties
- the same general formula.

Each member of a homologous series differs by a $-CH_2-$ unit from the previous member.

Alkanes

Alkanes are a homologous series of molecules that consist entirely of carbon and hydrogen atoms. They have the general formula C_nH_{2n+2}. The other distinguishing feature of alkanes is that their molecules contain only single bonds.

Alkanes are **saturated** molecules. A saturated molecule is defined as one that contains only single bonds. The carbon atoms in alkanes are 'saturated' because they cannot bond with any more atoms. When a molecule contains one or more double or triple bonds, it is described as **unsaturated**. An unsaturated molecule has the potential to bond with more atoms.

Naming simple alkanes

In the systematic name of simple 'straight-chain' alkanes, the prefix, or first part, of the name refers to the number of carbon atoms in one molecule of the alkane. The prefixes used are listed in Table 10.1.1.

TABLE 10.1.1 Prefixes used to name molecules with between one and eight carbon atoms

Number of carbon atoms	Prefix (parent/stem)
1	Meth-
2	Eth-
3	Prop-
4	But-
5	Pent-
6	Hex-
7	Hept-
8	Oct-

The names of all alkanes have the suffix (ending) '-ane' to indicate that the carbon–carbon bonds are all single bonds. Combining the prefix and suffix, you can see that methane is a hydrocarbon that contains one carbon atom, ethane is a hydrocarbon that contains two carbon atoms and propane is a hydrocarbon that contains three carbon atoms, and each of the carbons have four bonds with different atoms. The structures are shown in Figure 10.1.1.

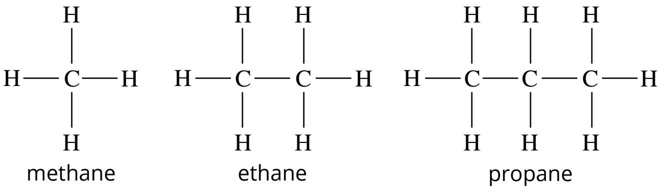


FIGURE 10.1.1 Structural formulas of methane, ethane and propane.

Isomers of alkanes

Methane, ethane and propane are the smallest alkanes. There is only one possible arrangement for the carbon and hydrogen atoms in these small molecules. Once alkane molecules are above a certain size, their carbon and hydrogen atoms can be arranged in different ways. These molecules are called **isomers**.

Butane (C_4H_{10}) has two structural isomers as shown in Figure 10.1.2. One isomer has the carbon atoms in a chain, while the other has a branched arrangement.

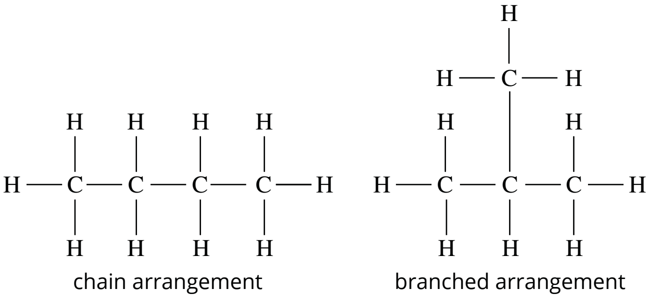


FIGURE 10.1.2 Structural isomers of butane (C_4H_{10}).

Naming simple structural isomers

Alkyl groups

Branched alkanes are named systematically to provide information about the number and size of branches on the molecule. Branches, also called **side chains**, can be thought of as alkane molecules that have lost a hydrogen atom. The side chain is called an **alkyl group**.

Alkyl groups are named in the following way.

- The prefix indicates the number of carbon atoms in the side chain.
- The suffix '-yl' is used.

Alkyl groups and the alkanes from which they are derived are shown in Table 10.1.2.

TABLE 10.1.2 Alkanes and their derivative alkyl groups

Alkane	Semistructural (condensed) formula	Alkyl group	Formula
Methane	CH_4	Methyl-	$-CH_3$
Ethane	CH_3CH_3	Ethyl-	$-CH_2CH_3$
Propane	$CH_3CH_2CH_3$	Propyl-	$-CH_2CH_2CH_3$
Butane	$CH_3(CH_2)_2CH_3$	Butyl-	$-CH_2(CH_2)_2CH_3$
Pentane	$CH_3(CH_2)_3CH_3$	Pentyl-	$-CH_2(CH_2)_3CH_3$
Hexane	$CH_3(CH_2)_4CH_3$	Hexyl-	$-CH_2(CH_2)_4CH_3$
Heptane	$CH_3(CH_2)_5CH_3$	Heptyl-	$-CH_2(CH_2)_5CH_3$
Octane	$CH_3(CH_2)_6CH_3$	Octyl-	$-CH_2(CH_2)_6CH_3$

Branched alkanes

The systematic naming of structural isomers of alkanes that contain branches requires the following steps.

1. Identify the parent name or **stem name** by finding the longest continuous chain of carbon atoms.
2. Identify any alkyl side chains by counting the number of carbon atoms in any branches.
3. Number the carbon atoms by starting from the end of the chain closest to a side chain.
4. Identify the number of the carbon atom to which an alkyl group is attached.
5. Name the isomer.

An example of the naming of a branched isomer of C_6H_{14} is shown in Figure 10.1.3.

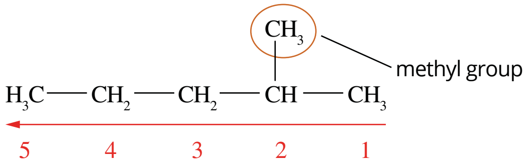


FIGURE 10.1.3 The name of this hydrocarbon is 2-methylpentane.

The steps in naming this molecule are as follows.

1. There are five carbon atoms in the longest chain so the parent name is pentane.
2. The only branch is a methyl group, $-CH_3$.
3. The methyl group is nearest to the right end.
4. The methyl group is attached to the second carbon.
5. The name of the molecule is therefore 2-methylpentane.

Functional groups

Alkanes are hydrocarbons. This means they are compounds in which carbon atoms are covalently bonded only to other carbon and hydrogen atoms. However, in other compounds carbon can form covalent bonds with other atoms or groups of atoms called **functional groups**.

A functional group is an atom or group of atoms that gives a characteristic set of chemical properties to a molecule containing those atoms.

For example, **alkenes** are molecules that contain a carbon–carbon double bond as their functional group. Alcohols contain a functional group that consists of an oxygen atom covalently bonded to a hydrogen atom.

Table 10.1.3 summarises the functional groups found in some different homologous series.

TABLE 10.1.3 Functional groups in some homologous series

Homologous series	Name of functional group	Semistructural (condensed) formula of the functional group
Aldehydes	Carbonyl (aldehyde)	$-CHO$
Alkenes	Carbon–carbon double bond	$-C=C-$
Alkynes	Carbon–carbon triple bond	$-C\equiv C-$
Alcohols	Hydroxyl	$-OH$
Amides (primary)	Amide	$-CONH_2$
Amines (primary)	Amino	$-NH_2$
Carboxylic acids	Carboxyl	$-COOH$
Esters	Ester	$-COOC-$
Haloalkanes	Halo	$-X$ (X = F, Cl, Br, I)
Ketones	Carbonyl	$-CO-$

FIGURE 10.1.4 Different types of organic molecules form the basis of all living systems, including the child, tomatoes, timber and plants in this photograph.

Carbon compounds make up more than 90% of all chemical compounds and form the basis of living systems. The association of carbon compounds with living systems led to the study of carbon compounds being called 'organic chemistry' and the molecules of carbon compounds being referred to as 'organic molecules' (Figure 10.1.4). **Organic molecules** can be defined as compounds containing carbon atoms linked to each other, and to other non-metallic atoms, by covalent bonds.

In its many millions of compounds, carbon is almost always associated with hydrogen, giving organic molecules a hydrocarbon skeleton. Organic molecules also commonly contain the elements oxygen, nitrogen, sulfur and chlorine.

In this section, you will learn about the diversity of carbon compounds and the factors that contribute to carbon being the element upon which all life forms are based.

BONDING IN CARBON COMPOUNDS

Carbon atoms contain six electrons—two electrons in the first shell and four in the second. The **electronic configuration** of a carbon atom can be written as 2,4 or $1s^22s^22p^2$. This means the following.

- Each carbon atom has four valence electrons, which gives it a **valence number** of four. The valence number of an element is equal to the number of valence electrons in an atom of the element. All four of carbon's valence electrons are available for bonding with other atoms.
- A carbon atom can form four covalent bonds with up to four other carbon atoms, each of which in turn can bond with up to four other carbon atoms, potentially forming long, branched chains and even rings.
- A carbon atom can form four covalent bonds with up to four other non-metal atoms.
- Single, double or triple bonds can be formed between two carbon atoms. A molecule that contains only single carbon–carbon bonds is described as a **saturated molecule**. A molecule that contains one or more double or triple bonds is described as an **unsaturated molecule**.

The wide variety of compounds formed by carbon is due to its ability to form strong covalent bonds with other carbon and hydrogen atoms and also by forming covalent bonds with atoms of other elements such as oxygen, nitrogen, sulfur, phosphorus and the halogens.

HYDROCARBONS

Carbon is a very versatile atom because it can form four covalent bonds in different ways, for example:

- four single bonds with four other atoms
- one double bond and two single bonds with three other atoms
- one triple bond and one single bond with two other atoms.

Hydrocarbons are formed solely from carbon and hydrogen. Despite consisting of only two types of atoms, there are an incredible number of hydrocarbon compounds with different structures. Look at Figures 10.1.5–10.1.10 to learn about some of the different types of hydrocarbon compounds encountered in everyday life.

FIGURE 10.1.5 (a) Methane (CH_4) contains one carbon atom with four single covalent bonds to four hydrogen atoms. (b) Methane is the gas used in most laboratory Bunsen burners and household gas stoves.

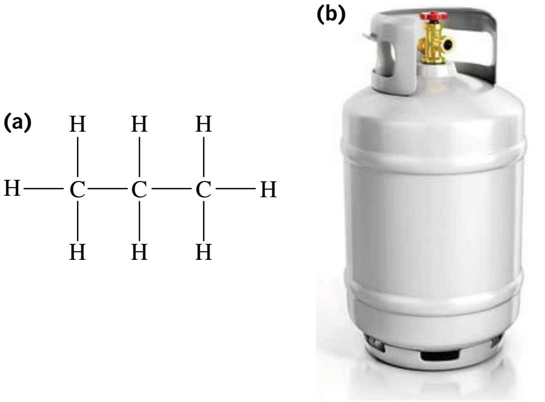


FIGURE 10.1.6 (a) Propane (C_3H_8) contains only single bonds. (b) Propane is the fuel contained in many portable gas bottles.

FIGURE 10.1.7 (a) Carbon can form compounds that contain carbon–carbon double bonds. These compounds include ethene (C_2H_4). (b) Among other uses, ethene is used to make the polymers in these food storage containers.

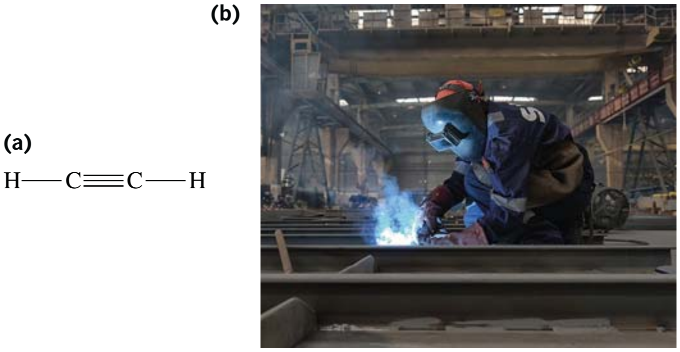


FIGURE 10.1.8 (a) Carbon can form hydrocarbons that contain carbon–carbon triple bonds, such as ethyne (C_2H_2). (b) Ethyne is commonly used as fuel for welding torches.

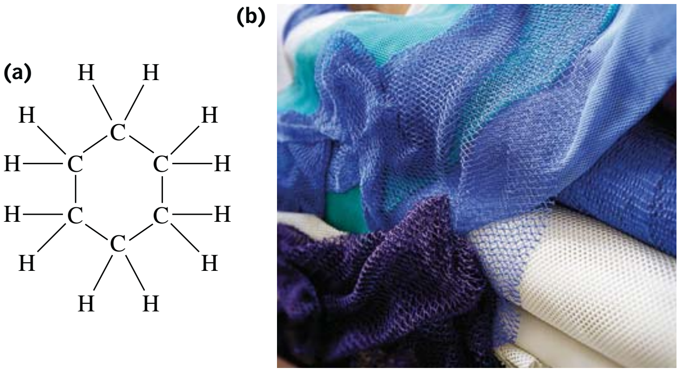


FIGURE 10.1.9 (a) Hydrocarbons can form ring structures with single bonds, such as cyclohexane (C_6H_{12}). (b) Cyclohexane is used by industry to make the starting materials for the manufacture of nylon.

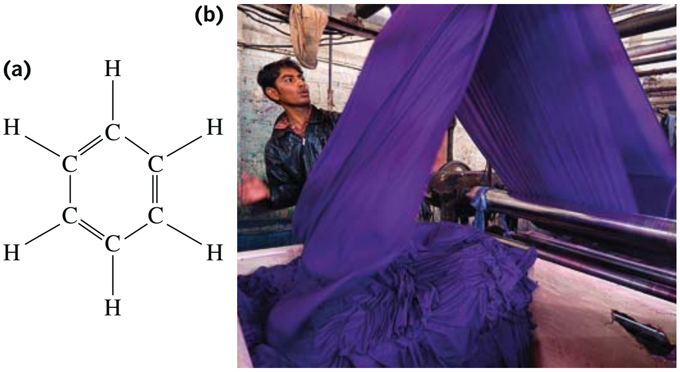


FIGURE 10.1.10 (a) Some molecules containing rings are unsaturated, such as benzene (C_6H_6), which is found in crude oil. (b) In this image, a textile is dyed using a dye based on benzene.

STABILITY OF CARBON BONDS WITH OTHER ELEMENTS

The covalent bonds between carbon and other atoms each have a **bond energy**. Bond energy is a measure of **bond strength** and is the amount of energy required to break the covalent bond. The higher the bond energy, the stronger the bond.

The bond energies of a number of covalent bonds are listed in Table 10.1.4. You can see that a carbon–carbon triple bond has a higher bond energy, and so is a stronger bond than a carbon–carbon single bond. You can also see that there is wide variation in the bond energies of single covalent bonds between carbon and other elements.

TABLE 10.1.4 Bond energies in common organic molecules

Covalent bond	Bond energy (kJ mol^{-1})
C≡C	839
C=C	614
C–C	348
C–F	488
C–H	413
C–O	360
C–Cl	330
C–N	308
C–S	272

A single covalent bond between two carbon atoms, C–C, is very strong, particularly compared to covalent bonds between other atoms of the same type; for example O–O, Si–Si and P–P. This is one of the reasons why only carbon tends to form chain-like structures at the temperatures and pressures found on Earth, and why it is carbon upon which life is built.

REPRESENTING ORGANIC MOLECULES

Before exploring organic molecules further, you should revise the different ways that the formulas of molecules can be represented. The formulas used in this course are:

- **molecular formulas**
- **structural formulas**
- condensed or **semistructural formulas**.

Molecular formulas

Molecular formulas such as C_2H_6O and $C_4H_8O_2$ indicate the number and type of atoms of each element present in a molecule. However, they do not indicate how the atoms are actually arranged.

Structural formulas

Structural formulas show the spatial location of atoms relative to one another in a molecule, as well as the number and location of covalent bonds. Non-bonding electrons (lone pairs) are often omitted for convenience.

When four single bonds are formed around a carbon atom, the pairs of electrons in each bond act as a negatively charged cloud. **Valence shell electron pair repulsion (VSEPR) theory** tells you that these electron pairs repel each other so the bonds are as far apart as possible, at an angle to each other of nearly 109.5°. The structure of methane, shown in Figure 10.1.11, is described as a **tetrahedral** shape because the four single bonds are pointing to the corners of a tetrahedron (shown in red).

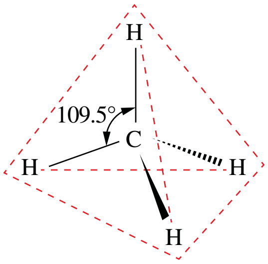


FIGURE 10.1.11 The structure of a molecule of methane (CH_4) showing the tetrahedral geometry. The solid wedge represents a bond coming out of the page, whereas the dashed wedge represents a bond going into the page.

Molecules consisting of long chains of carbon atoms joined by single bonds are often referred to as 'straight-chain' molecules. Because of the tetrahedral distribution of each carbon's bonds the chain actually has a zig-zag shape.

Structural formulas showing a tetrahedral arrangement of bonds around carbon atoms can become complicated and difficult to interpret. To make the structure of these molecules clearer, the bonds are often drawn at right angles. These two representations are shown in Figure 10.1.12.

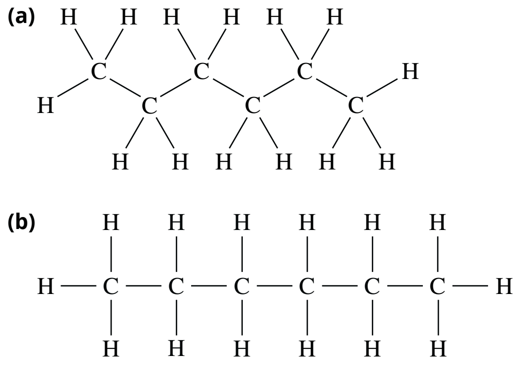


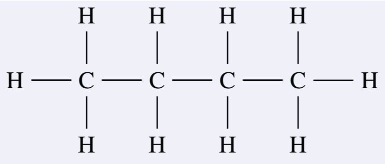
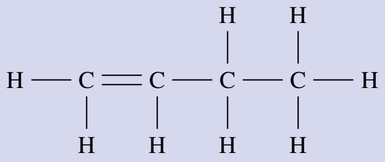
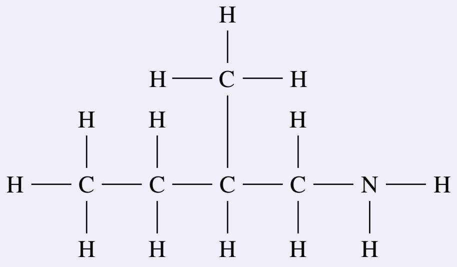
FIGURE 10.1.12 (a) The six carbon chain of hexane (C_6H_{14}). There is a tetrahedral arrangement of bonds around each carbon atom. (b) The chain can be drawn in a straight line for convenience.

Semistructural formulas

A semistructural formula is used to indicate the connections in the structure of a compound without showing the three-dimensional arrangement of atoms. The term 'condensed formula' is also used to describe this type of formula.

In a semistructural formula, the carbon chain is represented on one line of text. The carbon atoms in the chain, and all the atoms attached to each of them, are listed in the order that they appear in the structural formula. Single bonds are not shown but double and triple carbon–carbon bonds are often shown. Groups of atoms that form branches in a molecule are written in parentheses after the carbon atom to which they are attached. Some examples of structural, semistructural and molecular formulas are shown in Table 10.1.5.

TABLE 10.1.5 Examples of structural, semistructural and molecular formulas

Structural formula and name	Semistructural (condensed) formula	Molecular formula
 Butane	$CH_3CH_2CH_2CH_3$	C_4H_{10}
 But-1-ene	$CH_2{=}CHCH_2CH_3$	C_4H_8
 2-Methylbutan-1-amine	$CH_3CH_2CH(CH_3)CH_2NH_2$	$C_5H_{13}N$

ISOMERS

Isomers are molecules that contain the same number and type of atoms, arranged in different ways. The existence of isomers is a major reason why there are so many different carbon compounds. Isomers have the same molecular formula but they can have different physical and chemical properties and so behave differently.

There are two main types of isomers:

- **structural isomers**
- **stereoisomers**. (Stereoisomers are discussed in section 10.2, page 281.)

Structural isomers form when the atoms in molecules with the same molecular formula bond together in different arrangements. Two types of structural isomers are **chain isomers** and **positional isomers**.

Chain isomers

Chain isomers are a consequence of the branching that is possible in the carbon chains that form the backbone of any large organic molecule. Chain isomers of alkanes can contain more than one **alkyl group**; some molecules may also have more than one alkyl group attached to the same carbon atom.

Hexane is an example of an alkane with no branches. It has the molecular formula C_6H_{14} and its structure is shown in Figure 10.1.13.

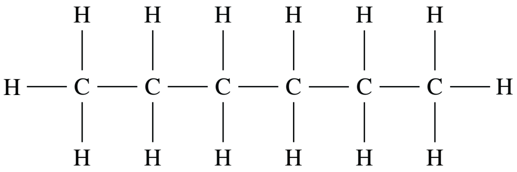
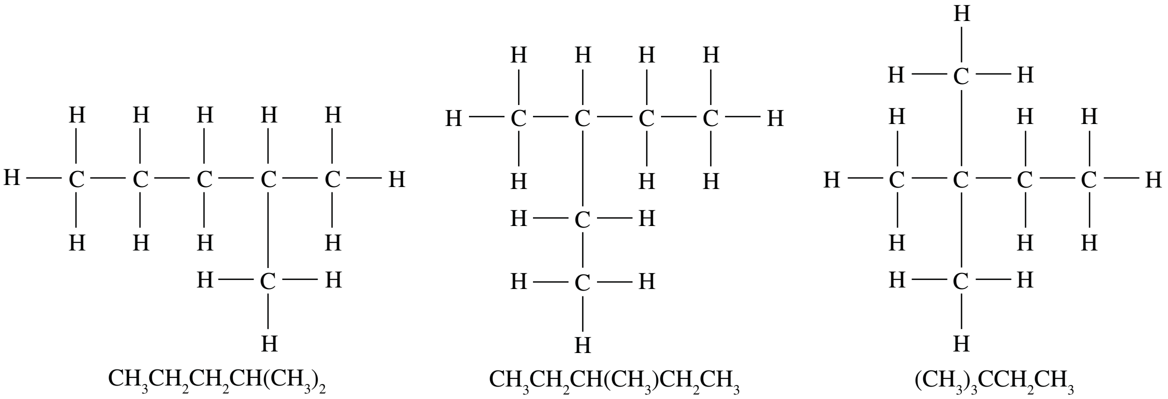


FIGURE 10.1.13 Hexane is a single-chain hydrocarbon with single bonds that contains six carbon atoms and fourteen hydrogen atoms.

Three of the chain isomers of hexane are shown in Figure 10.1.14. Each isomer has a different name that represents their exact molecular structure. The naming of chain isomers is described in the next section.



$CH_3CH_2CH_2CH(CH_3)_2$ $CH_3CH_2CH(CH_3)CH_2CH_3$ $(CH_3)_3CCH_2CH_3$

FIGURE 10.1.14 Three chain isomers of hexane.

Positional isomers

Positional isomers can occur for organic molecules that contain **functional groups**. Two molecules with the same carbon chain and functional group but with the functional group attached to a different location in the molecule are called positional isomers.

Alcohols are organic molecules that contain a **hydroxyl** (–OH) **functional group**. A number of positional isomers can be drawn for an alcohol with the molecular formula $C_4H_{10}O$. Like chain isomers, each positional isomer is given a different name. Figure 10.1.15 shows two positional isomers, butan-1-ol and butan-2-ol.

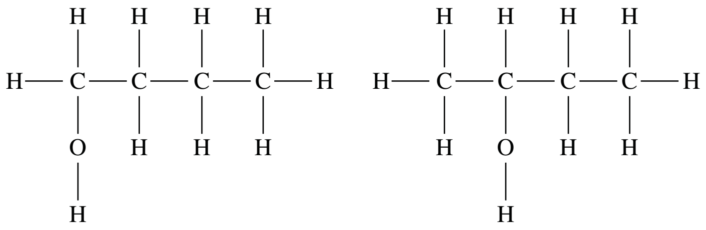
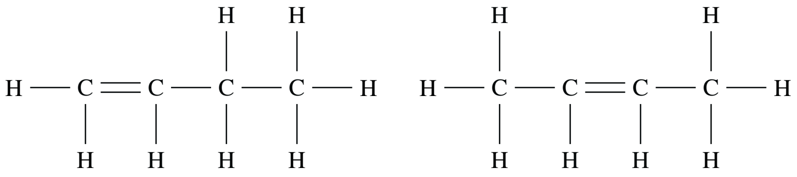


FIGURE 10.1.15 Two positional isomers of an alcohol with the formula $C_4H_{10}O$.

It is important to realise that alkenes and alkynes also contain functional groups—their double and triple carbon–carbon bonds. This means that positional isomers can be formed when the multiple bond is located in different locations. Figure 10.1.16 shows the two positional isomers of butene.



but-1-ene

but-2-ene

FIGURE 10.1.16 The two positional isomers of butene: but-1-ene and but-2-ene.

Positional isomers only exist for molecules that contain a functional group and have a long enough carbon chain that different positions of the functional group are possible. When drawing positional isomers, be careful that you do not just draw the same molecule from a different perspective. You can see that the two structural formulas of ethanol in Figure 10.1.17 do not represent positional isomers.

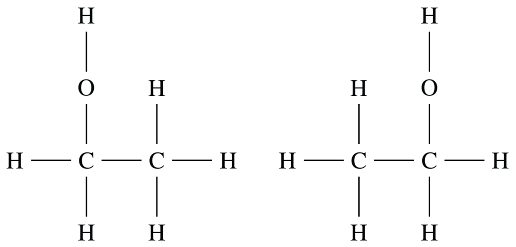


FIGURE 10.1.17 Two representations of the structure of ethanol (C_2H_6O). These are not positional isomers; if the first structure is flipped over, it is identical to the second.

It is possible for structural isomers to form both positional and chain isomers. Figure 10.1.18 shows two more isomers of an alcohol with the formula $C_4H_{10}O$. They are chain isomers of the molecules shown previously in Figure 10.1.15, and positional isomers of each other.

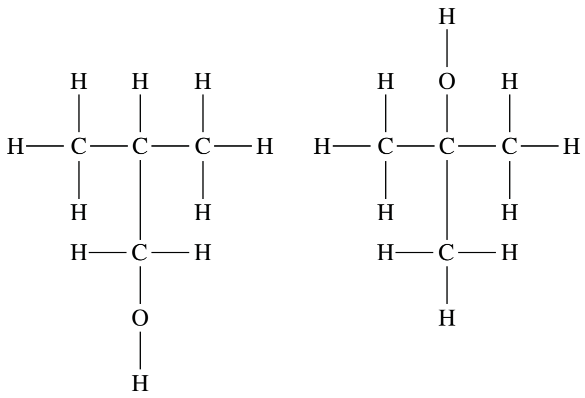


FIGURE 10.1.18 Two more molecules that are alcohols with the molecular formula $C_4H_{10}O$.

10.1 Review

SUMMARY

- Carbon has a valence number of four.
- Carbon atoms form covalent bonds with each other and with other non-metallic atoms such as hydrogen, oxygen and nitrogen.
- Carbon atoms can form single, double or triple bonds with other carbon atoms.
- Bond strength is the amount of energy required to break a bond. The covalent bonds between carbon and other non-metal atoms have different bond strengths.
- The bonds with the highest strength also have the highest stability.
- Carbon compounds can have structural isomers and stereoisomers. Structural isomers include chain and positional isomers.
- Chain isomers have the same molecular formula but different branching of the carbon chain.
- Positional isomers have the same molecular formula but at least one functional group in different positions on the carbon chain.

KEY QUESTIONS

1 Which of the following bonds is the most stable?

A C–S
B C–F
C C–Cl
D C–O

2 Define:

a structural formula
b semistructural formula
c saturated
d unsaturated
e positional isomer.

3 Which one or more of the following semistructural formulas represent an alkane?

A CH_3CH_3
B $CH_3CHCHCH_3$
C $CH_3CH_2CH_2CH_3$
D $CH_3CH_2CHCH_2$

4 **a** Which is the shortest alkane that can have chain isomers?
b Draw structural formulas for all the chain isomers of this alkane.

5 Explain why carbon chains in alkanes are not straight as commonly drawn in structural formulas.

10.2 Stereoisomers

Stereoisomers are isomers in which the atoms in two molecules are connected in the same order, but have different arrangements in space. Stereoisomers differ in their three-dimensional shape, so the name of this type of isomer begins with the stem ‘stereo-’. Molecules that are stereoisomers can have very different chemical properties.

There are two types of stereoisomers, called **optical isomers** and **geometric isomers**, and they can be formed by a range of organic molecules. In this section, you will learn about some simple examples of optical and geometric isomers.

OPTICAL ISOMERS

Optical isomers are a type of stereoisomer in which there is a different placement of groups around one atom in a molecule. The molecules have exactly the same molecular and semistructural formula.

These isomers are called optical isomers because they were first noticed by the different way they interact with plane-polarised light. (You can read more about this in the Extension box on page 285.)

Chirality

Substances that are optical isomers are said to be **chiral**. Two objects are chiral when they are mirror images of each other and the mirror images cannot be superimposed on top of each other.

The term ‘chiral’ comes from the Greek word for hand. Your hands are chiral objects. One hand is a mirror image of the other. A left and right hand are not superimposable in three dimensions. It is even simpler to think about your feet. Again, your left and right feet are mirror images but cannot be superimposed. Your left shoe does not fit on your right foot, as shown in Figure 10.2.1.

FIGURE 10.2.1 Your feet are chiral. They are mirror images but cannot be superimposed or fit in the same three-dimensional space, meaning that a right foot does not fit in a left shoe.

Another example of chiral objects is shown in Figure 10.2.2. The shell on the right is a mirror image that cannot be superimposed onto the shell on the left.

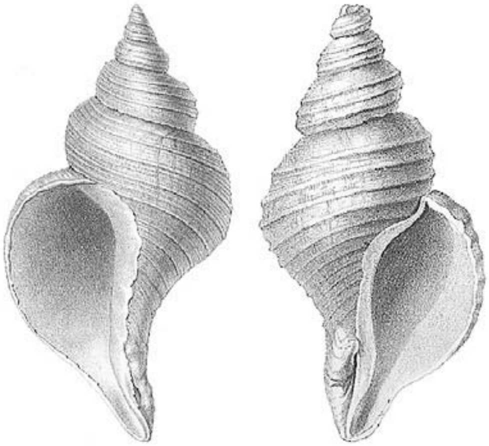


FIGURE 10.2.2 These shells are chiral. The shell on the right is the mirror image of the shell on the left. It cannot be superimposed on the left-hand shell.

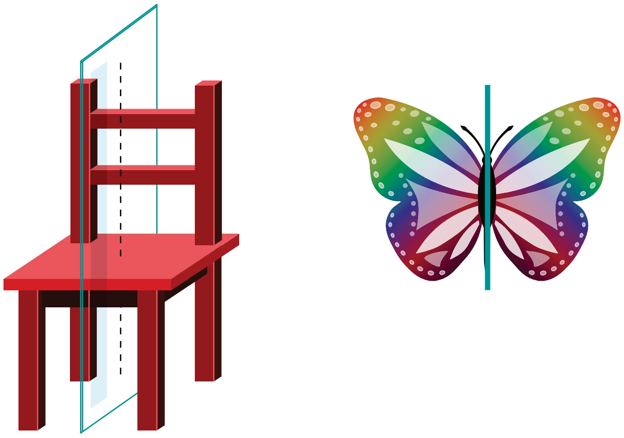


FIGURE 10.2.3 This chair and butterfly each have a plane of symmetry. The left side is exactly the same as the right. This means the chair and the butterfly are achiral.

Achiral objects (objects that are not chiral) are objects whose mirror images can be superimposed on the original. Chiral objects lack a **plane of symmetry**, whereas objects that are achiral have at least one plane of symmetry. A plane of symmetry exists when a three-dimensional figure can be divided into two halves that are mirror images. You can see some examples in Figure 10.2.3.

Chirality in organic molecules

Organic molecules that are chiral include molecules with a carbon atom joined to four different groups in a tetrahedral arrangement. A pair of chiral molecules are called **enantiomers**.

In Figure 10.2.4, you can see that molecule A is a mirror image of molecule B. The mirror image cannot be superimposed on the first molecule as the arrangement of the four groups in space is different. When molecule A is rotated so that the red and green groups are in the same position as in molecule B, the purple and yellow groups are in different places. The two molecules are chiral.

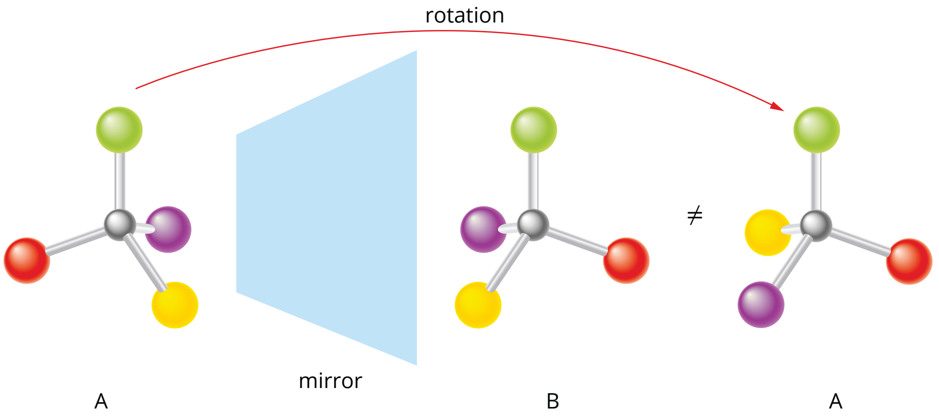


FIGURE 10.2.4 The molecules A and B represented by these ball and stick models are a pair of enantiomers.

A carbon atom attached to four different groups is called a **chiral centre**. A chiral molecule must contain at least one chiral centre. However, molecules with more than one chiral centre are not always chiral molecules. A chiral molecule must contain no planes of symmetry overall.

The molecule in Figure 10.2.5 is chiral and a pair of enantiomers is shown. The carbon in the centre is attached to four different groups, which makes it the chiral centre. Often the chiral centre is marked with an asterisk. The bonds from the carbon to the hydrogen and chlorine are shown as simple lines to show that these are flat against the page. The wedged line represents a bond coming out of the page and the dashed wedge represents a bond going into the page. A rotated view of enantiomer A is shown with the hydrogen and chlorine atoms in the same position as enantiomer B. This results in the bromine and fluorine atoms being in different places and shows that the mirror image is not the same.

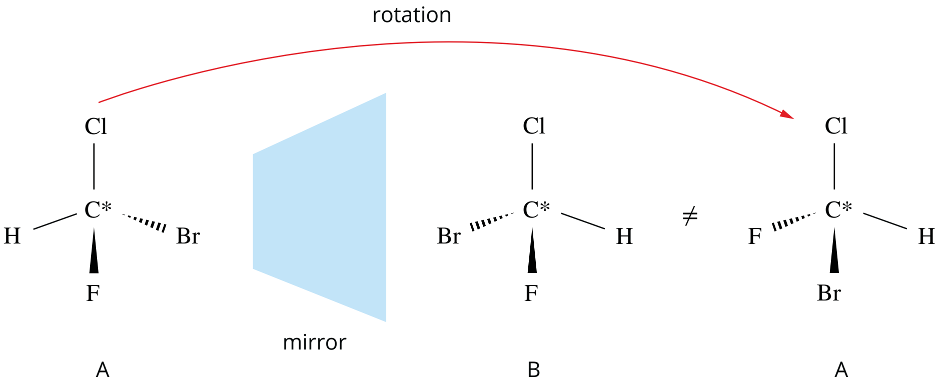


FIGURE 10.2.5 Bromochlorofluoromethane is a chiral molecule and has two enantiomers.

The molecule in Figure 10.2.6 does not contain a chiral centre because there are two identical groups bonded to the carbon atom. It is an achiral molecule. The mirror image of the molecule can be rotated to produce a structure that can be superimposed on the original. They are the same molecule and are not enantiomers.

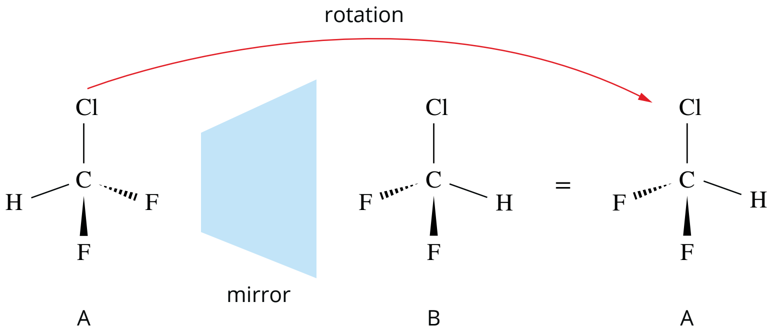


FIGURE 10.2.6 Chlorodifluoromethane is an achiral molecule because its mirror image can be superimposed.

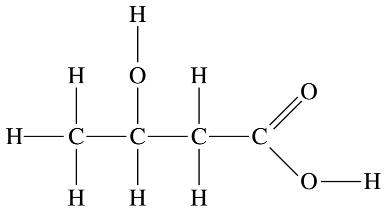
Identifying chiral centres

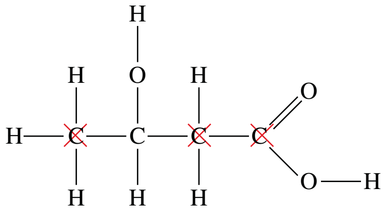
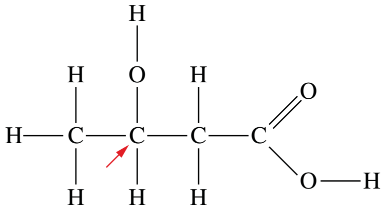
To identify a chiral centre, you need to determine if any of the carbon atoms in a molecule have four different groups attached. As Worked Example 10.2.1 illustrates, you often have to look further than just the next atom to see if the groups are the same.

Worked example 10.2.1

IDENTIFYING CHIRAL CENTRES IN ORGANIC MOLECULES

Identify any chiral centres in the following molecule.

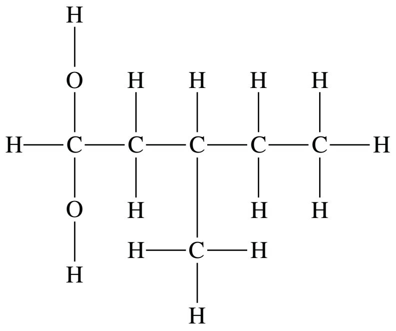


Thinking	**Working**
Eliminate the carbon atoms that cannot be chiral centres. This includes all $-CH_3$ and $-CH_2-$ groups and any atom that is part of a double or triple bond, because these carbon atoms cannot be bonded to four different groups.	 This leaves one carbon atom that may or may not be a chiral centre.
For each remaining carbon atom, examine the groups attached to the atom. If there are four different groups, the atom is a chiral centre.	 The remaining carbon atom has the following groups attached: $-CH_3$ $-H$ $-OH$ $-CH_2COOH$ The four groups are different so this carbon atom is a chiral centre.

Worked example: Try yourself 10.2.1

IDENTIFYING CHIRAL CENTRES IN ORGANIC MOLECULES

Identify any chiral centres in the following molecule.



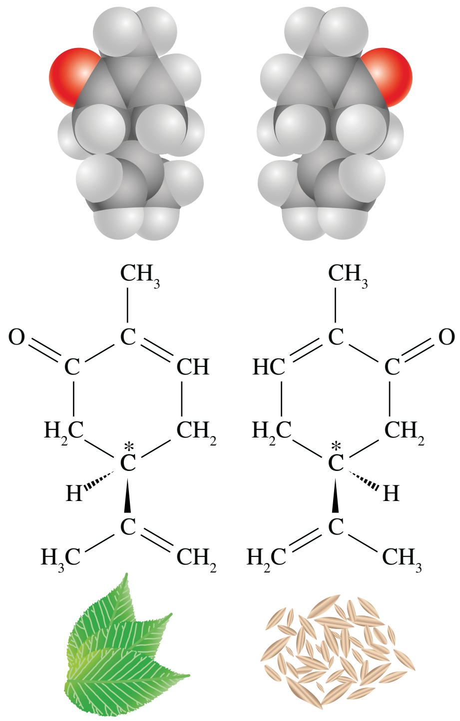


FIGURE 10.2.7 Carvone is a chiral molecule with two enantiomers. The enantiomer on the left has the odour of spearmint. The enantiomer on the right has the odour of caraway seeds.

Properties of enantiomers

Enantiomers have identical physical properties, apart from the way they rotate plane-polarised light. For example, they have the same melting and boiling points and the same solubility in water.

However, enantiomers usually interact differently with other chiral molecules. The human body contains mainly chiral molecules, so molecules that are chiral have different effects in the body. Figure 10.2.7 shows the example of the compound carvone. One enantiomer of carvone has the odour of spearmint, whereas the other enantiomer has the odour of caraway seeds. Many pharmaceutical drugs exist as enantiomers, with only one enantiomer having a beneficial effect on the body.

EXTENSION

Rotation of plane-polarised light

Optical isomers were first discovered because of the different ways they rotate plane-polarised light. This type of light is produced when light passes through polaroid glass or film, which is used in some sunglass lenses. Plane-polarised light contains waves that oscillate in a single plane.

When plane-polarised light shines through a chiral substance, its plane of polarisation is rotated. Different substances rotate the light to different extents and in different directions (clockwise or anticlockwise). A pair of enantiomers rotate plane-polarised light by the same amount but in opposite directions (Figure 10.2.8).

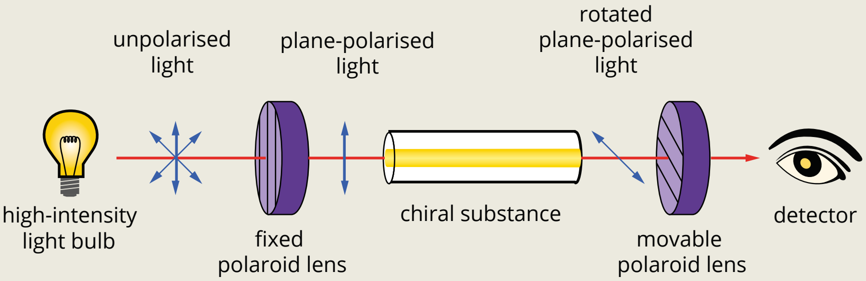


FIGURE 10.2.8 A chiral substance rotates plane-polarised light. The angle and direction of the rotation between the fixed and movable polaroid lenses allow the different enantiomers to be identified.

GEOMETRIC ISOMERS

Geometric isomers are another form of stereoisomer. These isomers can occur when there is restricted rotation somewhere in a molecule. Restricted rotation can occur about a carbon–carbon double bond or a ring.

cis–trans isomers

***cis–trans* isomers** of alkenes occur because the atoms associated with the carbon–carbon double bond are fixed in position.

Two atoms joined by a single bond can rotate freely around the single bond. You might think that the two models shown in Figure 10.2.9 show different molecules, but they are models of the same molecule because there is free rotation around the single bond. The first structure can rotate around the central single bond to look exactly the same as the second.

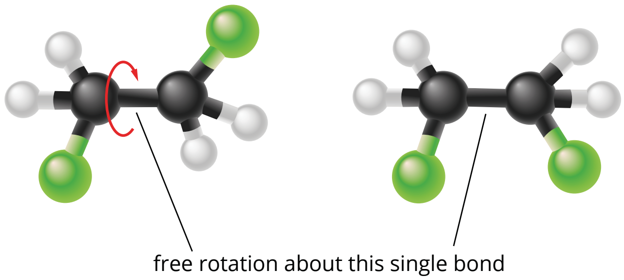


FIGURE 10.2.9 These two models represent the same molecule because the groups on either end can rotate around the single bond.

However, because of the way that the electrons are arranged in a double bond, groups attached to carbons on either side are unable to rotate freely. The models in Figure 10.2.10 represent two molecules that cannot be rotated to form the same structure because a double bond is present.

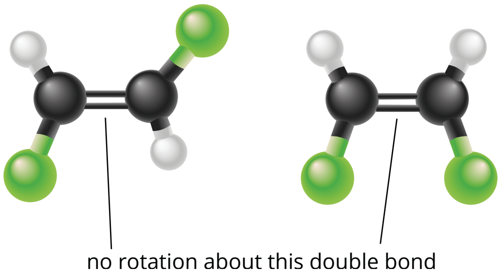


FIGURE 10.2.10 These two models represent different molecules because the groups on either end cannot rotate around the double bond.

cis–trans isomers can occur when there are two different groups attached to each carbon atom involved in the double bond. The different groups can be functional groups or hydrocarbon chains of different lengths. There are two possible arrangements: the groups can be on the same or opposite sides of the double bond. If the groups are on the same side, the isomer is called the ***cis* isomer**. If the groups are on opposite sides, the isomer is called the ***trans* isomer**.

Figure 10.2.11 shows the three possible structures of dibromoethene ($C_2H_2Br_2$). If both bromine atoms are attached to the first carbon atom, then it is called 1,1-dibromoethene. This molecule does not have geometric isomers. If the bromine atoms are attached to different carbon atoms, then it is called 1,2-dibromoethene, which has the semistructural formula BrCH=CHBr. There are two isomers that may form: *cis*-1,2-dibromoethene and trans-1,2-dibromoethene.

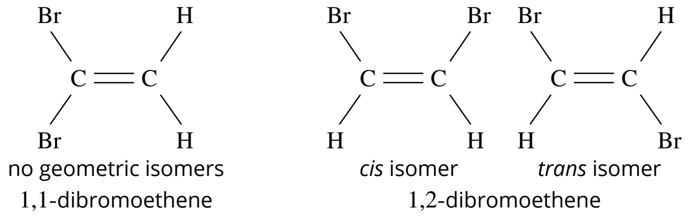


FIGURE 10.2.11 The possible structures of dibromoethene ($C_2H_2Br_2$). Note the position of the bromine atoms in the *cis* and *trans* isomers.

When considering longer alkenes, it is the longest alkyl groups attached to the carbon atoms in the double bond that are used to decide if the molecule is a *cis* or *trans* isomer.

- In *cis* isomers, the longest alkyl groups on each carbon are located on the same side of the double bond.
- In *trans* isomers, the longest alkyl groups on each carbon are located on opposite sides of the double bond.

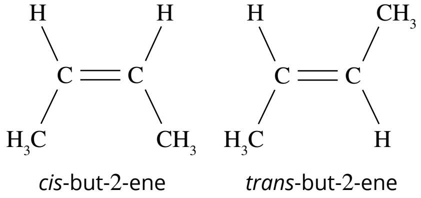


FIGURE 10.2.12 The two isomers of but-2-ene both have the semistructural formula $CH_3CH=CHCH_3$. The two methyl groups are on the same side of the double bond in the *cis* isomer. The methyl groups are opposite each other in the *trans* isomer.

10.2 Review

SUMMARY

- Stereoisomers are a type of isomer in which the atoms in two molecules are connected in the same order, but have different arrangements in space.
- Optical isomers are stereoisomers in which there is a different placement of groups around one or more atoms in a molecule. The different arrangements of atoms interact differently with plane-polarised light and different chiral environments.
- An object is achiral if it can be superimposed on its mirror image.
- An object is chiral if it cannot be superimposed on its mirror image. A pair of chiral molecules are called enantiomers.
- A chiral centre is a carbon atom that is attached to four different groups.
- Geometric isomers are stereoisomers that can occur when there is restricted rotation somewhere in a molecule. Restricted rotation can occur about a carbon–carbon double bond or a ring.
- *cis–trans* isomers are geometric isomers of alkenes that occur when there are two different groups attached to the carbon atoms at each end of a carbon–carbon double bond.
- In *cis–trans* isomers of alkenes, the atoms in the isomers are joined in the same order, but have a different arrangement in space (see FIgure 10.2.12 on page 286).
- In *cis* isomers, the longest alkyl groups are attached to the same side of the double bond.
- In *trans* isomers, the longest alkyl groups are attached to the opposite sides of the double bond.

KEY QUESTIONS

1 Consider the nail and screw in Figure 10.2.13. Explain why one of the two objects is chiral and the other is achiral.

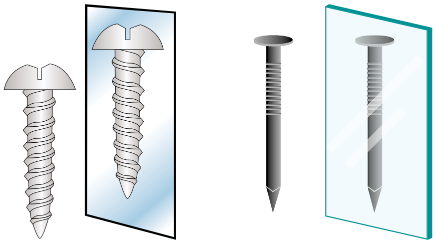


FIGURE 10.2.13 Explain chirality using a nail and a screw.

2 Which numbered carbon in the molecule shown in Figure 10.2.14 is a chiral centre?

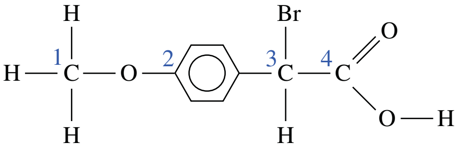
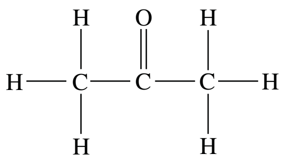


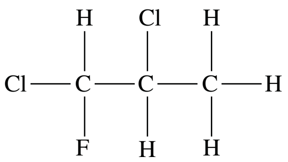
FIGURE 10.2.14 Locate a chiral centre.

3 How many chiral centres are present in each of the following molecules?

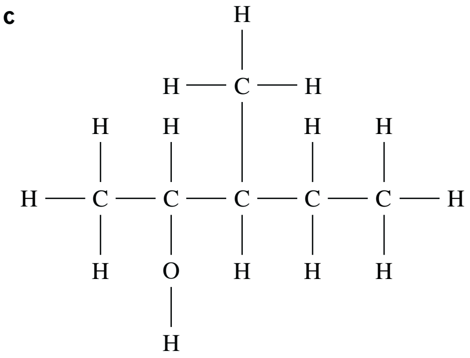
a



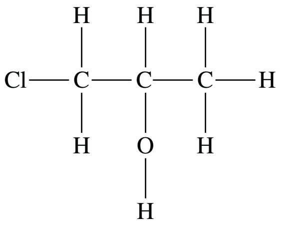
b



c



d



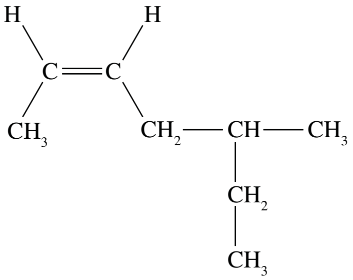
4 Look at the following alkenes.

a Which alkenes have *cis–trans* isomers?

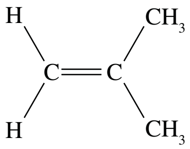
b Which alkenes are *cis* isomers?

c Which alkenes do have not *cis–trans* isomers? Explain why.

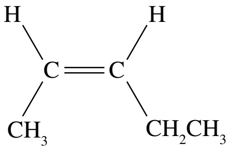
i



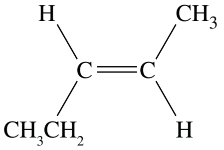
ii



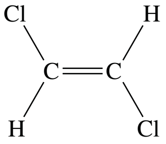
iii



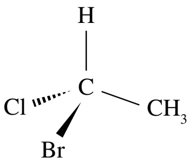
iv



v



5 Draw the enantiomer of the following molecule and show that it is a non-superimposable mirror image of this molecule.



10.3 Hydrocarbons

The simplest organic molecules are the hydrocarbons. Although they only contain the elements carbon and hydrogen, the different ways their atoms can be arranged to form molecules results in an enormous diversity of compounds. Crude oil, the source of many hydrocarbons used in industry, contains a mixture of different hydrocarbons and is shown in Figure 10.3.1.

In this section, you will learn about the molecules in the hydrocarbon families of alkanes, alkenes and alkynes. You will learn about their molecular, structural and semistructural formulas, as well as some of their isomers and the ways they are named.

FIGURE 10.3.1 Crude oil burning in a Petri dish.

HOMOLOGOUS SERIES

The study of organic chemistry is simplified by grouping the millions of different molecules that exist into families called homologous series. Compounds that are members of the same homologous series have:

- similar structures
- similar chemical properties
- the same general formula
- a pattern to their physical properties.

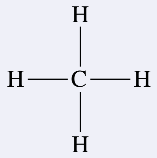
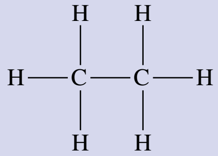
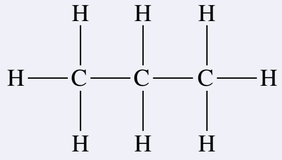
Homologous series contain members that have increasingly longer chains. These chains grow by the addition of a $-CH_2-$ unit to the previous member of the series. The hydrocarbons consist of three homologous series: the alkanes, the alkenes and the alkynes.

ALKANES

Alkanes are saturated molecules, which means all of the carbon atoms in a molecule have four single bonds. The Review section at the beginning of this chapter describes the naming of alkanes. Alkanes have the general formula C_nH_{2n+2}.

The molecular, structural and semistructural formulas of the first three members of the homologous series of alkanes are shown in Table 10.3.1. You can see that successive members differ by a $-CH_2-$ unit.

TABLE 10.3.1 Formulas of the first three members of the alkane homologous series

Name	Structural formula	Semistructural formula
Methane		CH_4
Ethane		CH_3CH_3
Propane		$CH_3CH_2CH_3$

Alkanes with more than three carbon atoms can form chain isomers. The isomers are named according to the steps shown in Figure 10.3.2.

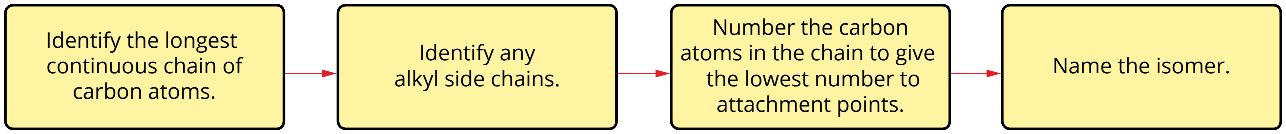


FIGURE 10.3.2 The steps used to name isomers of alkanes.

In the naming of an isomer, the following conventions are also used.

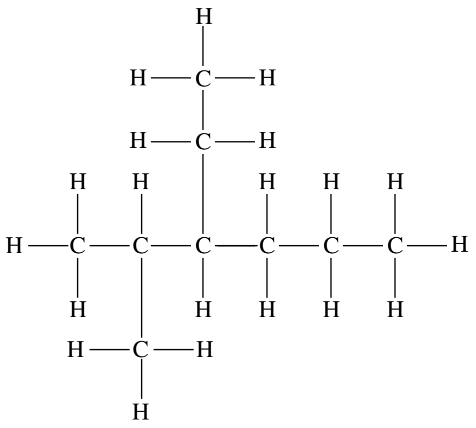
- Place the name of each alkyl group before the **parent molecule** name.
- If there is more than one type of alkyl group, list the groups in alphabetical order.
- If there is more than one of the same type of alkyl group, use the prefix ‘di-’, ‘tri-’ or ‘tetra-’.
- Specify the carbon atom to which each alkyl group is attached by a number before the alkyl group.
- Choose the direction of numbering to give the smallest possible number to each alkyl group.
- Do not have spaces in the name.
- Use dashes to separate numbers from words.
- Use commas to separate numbers from other numbers.

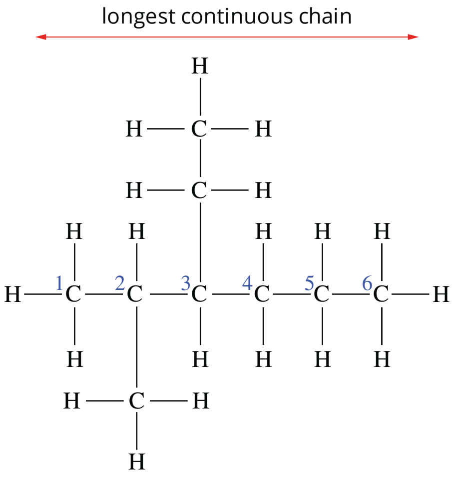
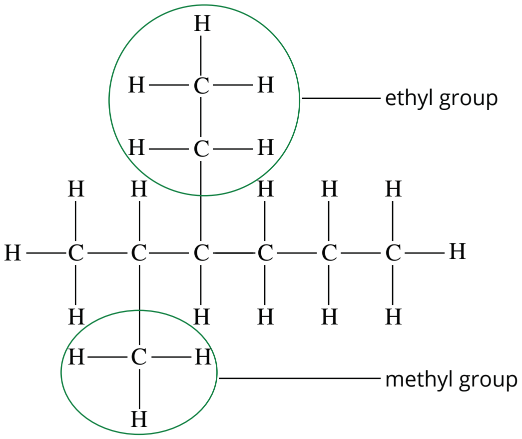
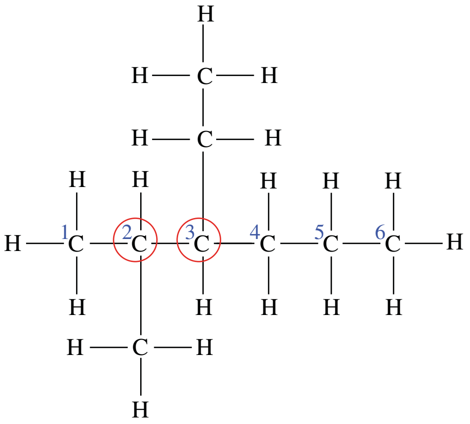
Worked Example 10.3.1 takes you through these steps for alkanes with more than one alkyl branch.

Worked example 10.3.1

NAMING AN ISOMER OF AN ALKANE WITH MORE THAN ONE ALKYL BRANCH

Write the systematic name of the molecule with the following structure.

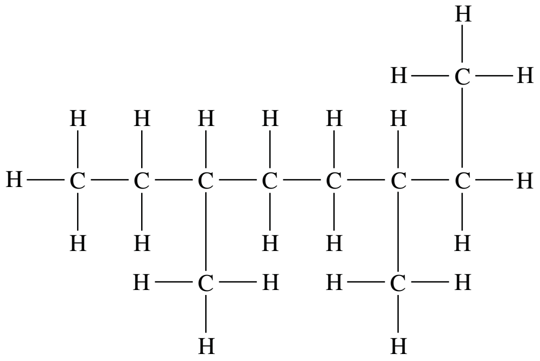


Thinking	**Working**
Identify the parent name by counting the longest continuous chain of carbon atoms.	 There are six carbon atoms in the longest continuous chain, so the parent name is hexane.
Identify any alkyl side chains by counting the number of carbon atoms in any branches.	 There is one carbon atom in the first alkyl group, so it is a methyl group. The second alkyl group has two carbon atoms, so it is an ethyl group.
Identify the number(s) of the carbon atom(s) to which any alkyl group is attached. Count from the end that will give the lowest possible number to the carbons the groups are attached to.	 The methyl group is attached to carbon number 2 and the ethyl group is attached to carbon number 3.
Assemble the name of the isomer, listing alkyl groups in alphabetic order with the number of the carbon atom before each group.	The name of the isomer is 3-ethyl-2-methylhexane.

Worked example: Try yourself 10.3.1

NAMING AN ISOMER OF AN ALKANE WITH MORE THAN ONE ALKYL BRANCH

Write the systematic name of the molecule with the following structure.



Cyclohexane

Cyclohexane is a hydrocarbon that is used as a solvent, in paint stripper and to make other chemicals such as nylon. Figure 10.3.3 shows that the carbon atoms in the cyclohexane molecule form a ring. Molecules that form rings are known as **cyclic molecules**.

Although cyclohexane can be drawn as a hexagonal ring, it does not have this shape in reality. The ability of the carbon atoms to rotate to a limited extent around the single bonds means that the ring can take on different shapes. The most common arrangement (or conformation) is known as the 'chair' conformation as it is said to resemble the shape of a chair.

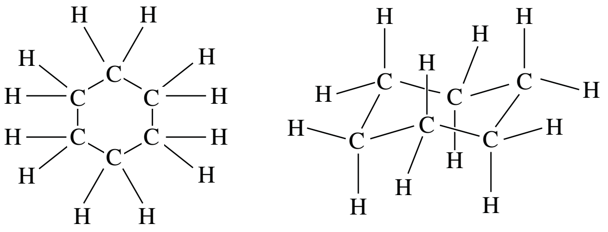


FIGURE 10.3.3 The structural formula of cyclohexane (C_6H_{12}) and a representation of the most common 'chair' conformation formed by the ring.

Just like straight-chain hexane, cyclohexane is a saturated molecule that contains six carbon atoms. Because of the extra carbon–carbon bond that closes the ring structure, there are two less hydrogen atoms, making the formula of cyclohexane C_6H_{12}, whereas hexane is C_6H_{14}. Cyclohexane is a member of the cycloalkane homologous series.

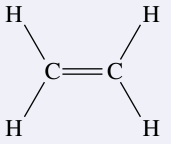
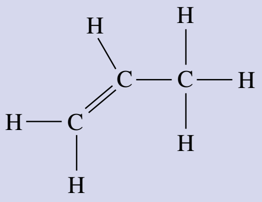
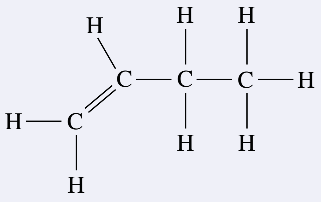
ALKENES AND ALKYNES

Alkenes and alkynes are unsaturated hydrocarbons and contain at least one multiple carbon–carbon bond. Because this bond is shared by a pair of carbon atoms, all alkene and alkyne molecules must have two or more carbon atoms.

The homologous series of hydrocarbons that contains a carbon–carbon double bond is called the alkenes. The molecular, structural and semistructural formulas of the first three members of the homologous series of alkenes are shown in Table 10.3.2. You can see that successive members differ by a $-CH_2-$ unit. Alkenes have the general formula C_nH_{2n}.

Alkenes with four or more carbon atoms can have structural isomers, where the location of the double bond changes, as well as *cis–trans* isomers, where the geometry of groups around the double bond changes.

TABLE 10.3.2 Formulas of the first three members of the alkene homologous series

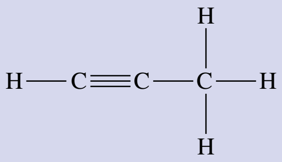
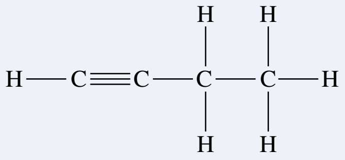
Name	Molecular formula	Structural formula	Semistructural formula
Ethene	C_2H_4		$CH_2{=}CH_2$
Propene	C_3H_6		$CH_2{=}CHCH_3$
But-1-ene	C_4H_8		$CH_2{=}CHCH_2CH_3$

The homologous series of hydrocarbons that contain a carbon–carbon triple bond are called alkynes. They have the general formula C_nH_{2n-2}.

Just as with alkenes, alkynes with four or more carbon atoms have structural isomers. However, alkynes do not form *cis–trans* isomers.

Representations of the first three members of the homologous series of alkynes are shown in Table 10.3.3.

TABLE 10.3.3 Formulas of the first three members of the alkyne homologous series

Name	Molecular formula	Structural formula	Semistructural formula
Ethyne	C_2H_2	$H-C\equiv C-H$	$CH\equiv CH$
Propyne	C_3H_4	 $H-C\equiv C-\overset{H}{\underset{H}{C}}-H$	$CH\equiv CCH_3$
But-1-yne	C_4H_6	 $H-C\equiv C-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-H$	$CH\equiv CCH_2CH_3$

Naming alkenes

The rules for naming alkenes follow the rules used for alkanes. In addition, the following conventions are applied.

- Use the ending '-ene' for the parent name.
- Number the carbon atoms from the end of the chain closest to the double bond.
- Specify the position of the double bond by the number of the lowest-numbered carbon atom in the double bond.
- Insert the number into the name immediately before '-ene'.

- Indicate *cis* and *trans* isomers by writing '*cis*-' or '*trans*-' in front of the compound's name.

The flowchart in Figure 10.3.4 shows the steps involved in naming an alkene.

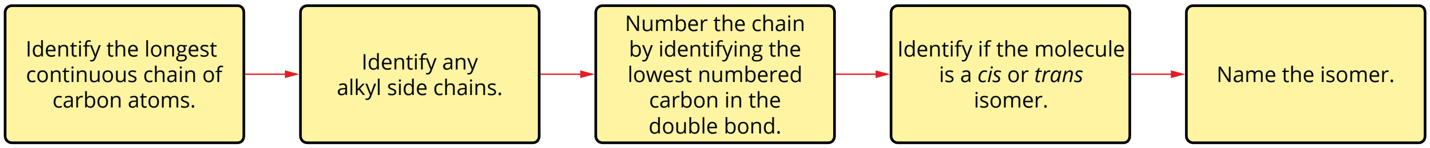
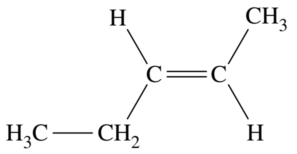


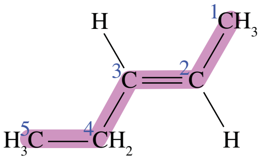
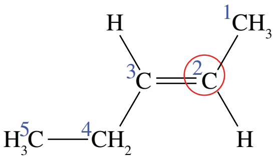
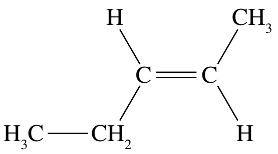
FIGURE 10.3.4 The steps used to name alkenes.

Worked example 10.3.2

NAMING A *cis–trans* ISOMER OF AN ALKENE

Write the systematic name of the following alkene.

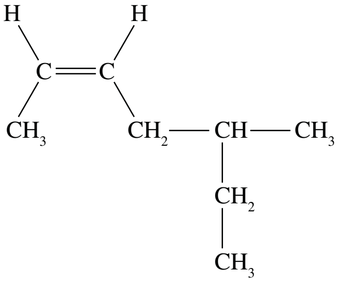


Thinking	Working
Identify the parent name by counting the longest continuous chain of carbon atoms.	 There are five carbon atoms in the longest continuous chain, so the parent name is pentene.
Identify any alkyl side chains by counting the number of carbon atoms in any branches.	There are no alkyl side chains.
Number the chain from the end closest to the double bond and identify the lowest numbered carbon atom in the double bond.	 The lowest numbered carbon atom in the double bond is 2, so the parent name becomes pent-2-ene.
Number any alkyl side chains using the numbers of the carbon atoms to which they are attached.	There are no alkyl side chains.
Identify whether the molecule is a *cis* or *trans* isomer.	 Both of the carbons in the double bond are attached to a hydrogen atom and another carbon in the chain. The carbon atoms are on opposite sides of the double bond so this is a *trans* isomer.
Name the isomer.	The name of the isomer is *trans*-pent-2-ene.

Worked example: Try yourself 10.3.2

NAMING A *cis–trans* ISOMER OF AN ALKENE

Write the systematic name of the following alkene.



Naming alkynes

The rules used for naming alkynes also follow the rules used for alkanes and alkenes. In addition, the following conventions are applied.

- Use the ending '-yne' for the parent name.
- Number the carbon atoms from the end of the chain closest to the triple bond.
- Specify the position of the triple bond by the number of the lowest-numbered carbon atom in the triple bond.
- Insert the number into the name immediately before '-yne'.

BENZENE

Benzene is an unsaturated cyclic hydrocarbon molecule. Its structure consists of six carbon atoms arranged in a ring. Three of the four outer-shell electrons from each carbon atom form normal covalent bonds, but the fourth electron is delocalised (shared) around all six carbons.

The structure of **benzene**, shown in Figure 10.3.5, is sometimes represented with alternating double and single bonds. Due to the shared nature of the **delocalised electrons**, it is more correct to describe each carbon as having one and a half bonds to each neighbour. For this reason, the bonds are often represented as a ring of normal single bonds with a circle inside the ring.

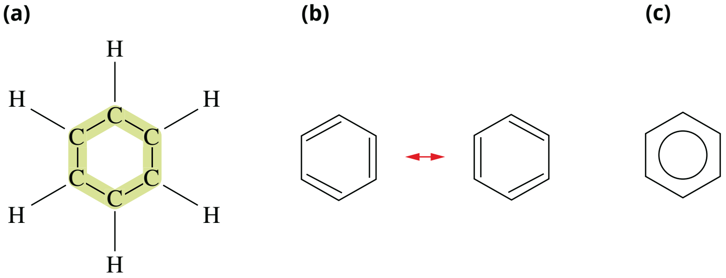


FIGURE 10.3.5 Representations of benzene's (C_6H_6) molecular structure showing (a) the delocalised electrons in green, (b) a shorthand representation with alternating double and single bonds, (c) the delocalised electrons represented as a circle inside the hexagon of carbon atoms.

10.3 Review

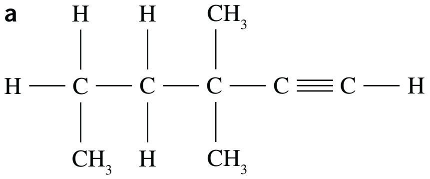
SUMMARY

- Alkanes are the simplest hydrocarbons. Their molecules contain carbon and hydrogen atoms and all bonds between atoms are single covalent bonds.
- Alkanes have the general formula C_nH_{2n+2}.
- Alkanes can have structural isomers.
- Cyclohexane is a saturated cyclic hydrocarbon with the molecular formula C_6H_{12}.
- The naming of isomers of alkanes follows a set of rules.
- Alkenes are a homologous series of hydrocarbons that contain a carbon–carbon double bond.
- Alkenes have the general formula C_nH_{2n}.
- Alkenes can have both structural and *cis–trans* isomers.
- *cis–trans* isomers occur when there are two different groups attached to each carbon atom in the carbon–carbon double bond.
- Alkynes are a homologous series of hydrocarbons that contain a carbon–carbon triple bond.
- Alkynes have the general formula C_nH_{2n-2}.
- Alkynes can have structural isomers, but not *cis–trans* isomers.
- The naming of isomers of alkenes and alkynes follows these additional rules:
  - Identify the longest unbranched carbon chain. This gives the parent name for the molecule. The ending of the parent name is '-ene' or '-yne'.
  - Number the carbons in the chain from the end of the chain that gives the smallest numbers to the double- or triple-bonded carbons.
  - A number is used to indicate the location of the double bond in alkenes and the triple bond in alkynes if there is more than one possible location for the group in the molecule.
  - The number and position of any alkyl side chains are given at the beginning of the molecule's name.
- Benzene is an unsaturated cyclic hydrocarbon with the formula C_6H_6.

KEY QUESTIONS

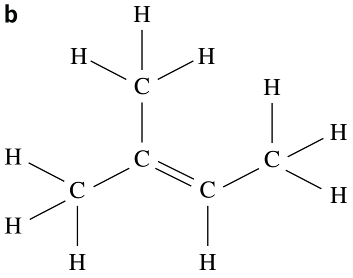
1 Name the following molecules.

a

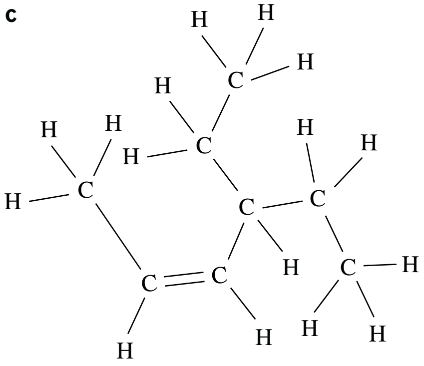


$$\begin{array}{ccccccccccccc} & & H & & H & & CH_3 & & & & & & \\ & & | & & | & & | & & & & & & \\ H & — & C & — & C & — & C & — & C & \equiv & C & — & H \\ & & | & & | & & | & & & & & & \\ & & CH_3 & & H & & CH_3 & & & & & & \end{array}$$

b



c



2 Draw the structure of:

a 2,3-dimethylpent-2-ene

b *cis*-4-ethylhex-2-ene

c 5-ethyl-2-methylhept-3-yne

d 2,2-dimethyloct-3-yne.

3 Which two of the molecules in Question **2** are structural isomers?

4 Draw all of the possible structural isomers with the formula C_6H_{14}.

10.4 Functional groups—Part 1

Most organic compounds can be regarded as derivatives of hydrocarbons which have one or more hydrogen atoms replaced by other atoms or groups of atoms called a **functional group**. You can revise the concept of functional groups in the Review section at the beginning of this chapter (page 272).

The presence of a particular functional group in a molecule gives a substance certain physical and chemical properties. For example, vinegar and wine (Figure 10.4.1) both contain organic molecules based on ethane. The difference between their tastes and other properties is due to the different functional groups in each molecule.

In this section, you will explore three homologous series:

- **haloalkanes**
- **alcohols**
- **primary amines**.

You will learn about the functional groups in each of these families of molecules as well as how to name them.

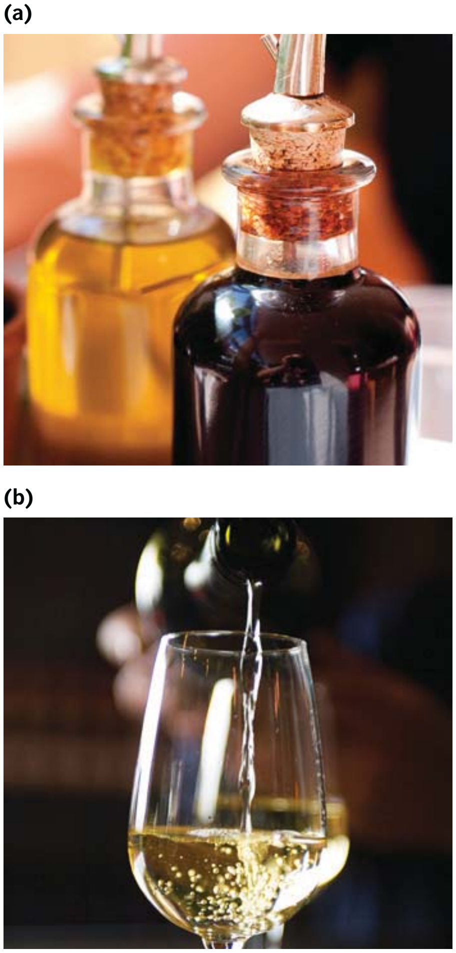


FIGURE 10.4.1 (a) Vinegar and (b) wine contain molecules with two carbon atoms. Vinegar contains ethanoic acid with a carboxyl functional group and wine contains ethanol with a hydroxyl group.

HALOALKANES

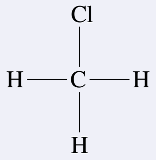
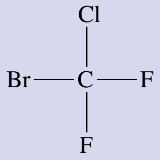
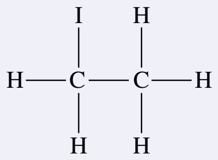
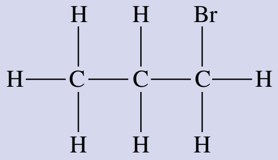
Haloalkanes are a homologous series derived from alkanes, in which one hydrogen atom is replaced with a **halogen** atom.

Haloalkanes are used widely in industry as flame retardants, refrigerants, propellants, pesticides (Figure 10.4.2), solvents and pharmaceuticals. Some haloalkanes are ozone-depleting chemicals and their use has been phased out in many applications.

FIGURE 10.4.2 Bromomethane (CH_3Br) is a colourless, odourless, non-flammable gas that was used as a pesticide in the past. This photo shows a field covered in plastic sheeting to minimise loss of the pesticide from the soil.

The halogen elements are in group 17 of the periodic table. All halogen atoms have seven valence electrons, which means they can form a single covalent bond with carbon atoms. The halogen elements that commonly form **halo functional groups** in organic compounds are fluorine, chlorine, bromine and iodine. Table 10.4.1 includes the names, structures and uses of some haloalkanes.

TABLE 10.4.1 Names, structures and uses of some haloalkanes

Name	Structural formula	Semistructural formula	Use
Chloromethane		CH_3Cl	Refrigerant
Bromochlorodifluoromethane		$CBrClF_2$	Fire extinguishers
Iodoethane		CH_3CH_2I	Production of chemicals
1-Bromopropane		$CH_3CH_2CH_2Br$	Industrial solvent

Naming haloalkanes

The names of haloalkane functional groups are derived from the name of the halogen, as shown in Table 10.4.2.

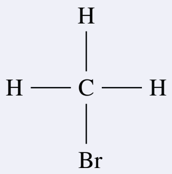
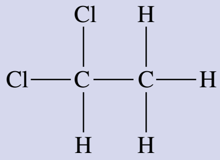
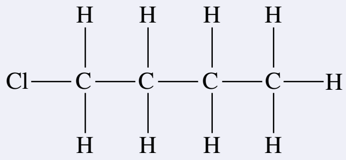
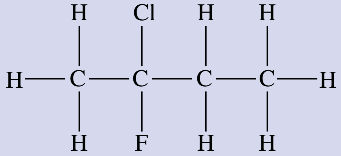
TABLE 10.4.2 Names of the haloalkane functional groups

Halogen	Functional group name
Fluorine	Fluoro-
Chlorine	Chloro-
Bromine	Bromo-
Iodine	Iodo-

The rules for naming haloalkanes follow the rules for naming alkanes. In addition, the following conventions are applied.

- Place the name of the specific halo functional group at the start of the parent alkane's name.
- If positional isomers are possible, use numbers to indicate the carbon to which the halo function group is attached.
- Number the carbons of the parent chain, beginning at the end of the first halo group or alkyl side chain.
- If there is more than one of the same type of halogen atom, use the prefix 'di-', 'tri-' or 'tetra-'.
- If more than one type of halo functional group is present, list them in alphabetical order.

TABLE 10.4.3 Examples of haloalkanes and their names

Name	Semistructural formula	Structural formula
Bromomethane	CH_3Br	
1,1-Dichloroethane	CH_3CHCl_2	
1-Chlorobutane	$CH_3CH_2CH_2CH_2Cl$	
2-Chloro-2-fluorobutane	$CH_3CClFCH_2CH_3$	

ALCOHOLS

Ethanol is a member of the homologous series of **alcohols**. Alcohols contain a **hydroxyl** (–OH) **functional group** attached to a saturated carbon atom. A representation of the hydroxyl group is shown in Figure 10.4.3.

Figure 10.4.4 shows the structural and semistructural formulas of three alcohols. You can think of the hydroxyl group as taking the place of a hydrogen atom in an alkane.

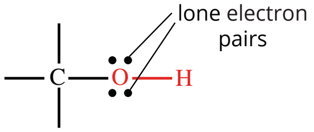
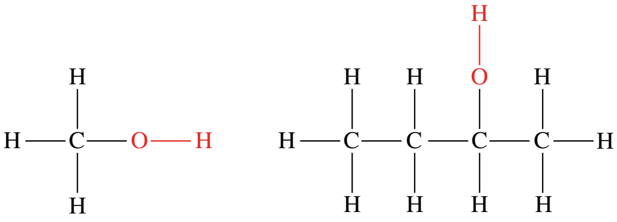


FIGURE 10.4.3 Alcohols contain the hydroxyl functional group, –OH (in red above). There are two pairs of non-bonding electrons on the oxygen atom.

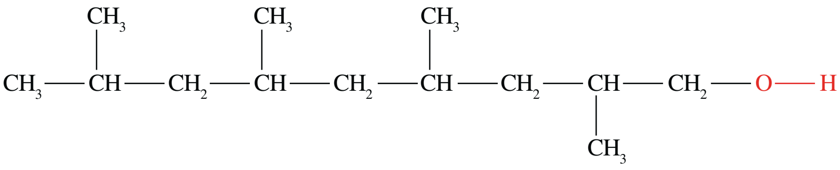


methanol

CH_3OH

butan-2-ol

$CH_3CH_2CHOHCH_3$



2,4,6,8-tetramethylnonan-1-ol

$(CH_3)_2CHCH_2CH(CH_3)CH_2CH(CH_3)CH_2CH(CH_3)CH_2OH$

FIGURE 10.4.4 Structural and semistructural formulas of three alcohols. Each contains the hydroxyl functional group (shown in red). Note that the non-bonding electron pairs on the oxygen atom are often omitted in structural formulas.

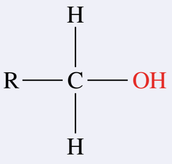
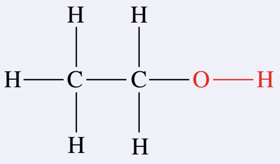
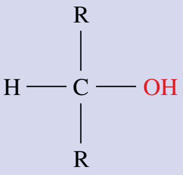
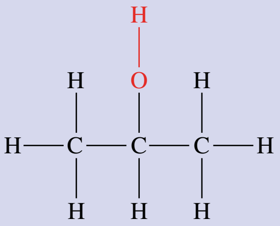
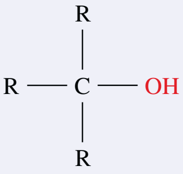
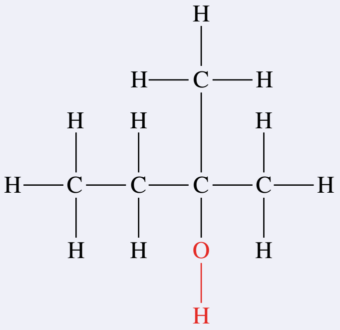
Types of alcohols

Alcohols are classified according to the number of alkyl groups attached to the carbon bonded to the hydroxyl group. The three different types of alcohols are:

- **primary alcohols**
- **secondary alcohols**
- **tertiary alcohols**.

The definition of each type and examples are shown in Table 10.4.4. Alkyl groups are represented by the general symbol R.

TABLE 10.4.4 The three different types of alcohols. The hydroxyl group is shown in red

Type of alcohol	Definition	General formula	Example
Primary	The carbon bonded to the –OH group is only bonded to one alkyl group.		
Secondary	The carbon bonded to the –OH group is also bonded to two alkyl groups.		
Tertiary	The carbon atom bonded to the –OH group is also bonded to three alkyl groups.		

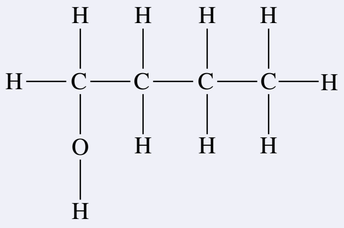
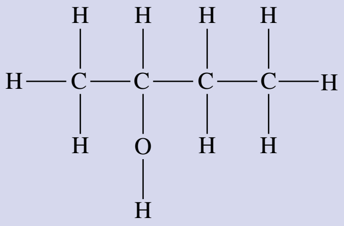
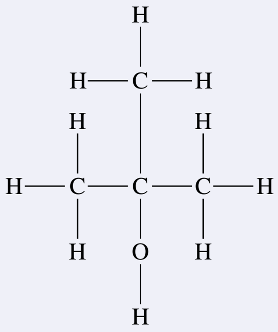
Naming alcohols

Alcohol names follow the rules used for alkanes, except that the '-e' at the end of the parent alkane's name is replaced with the suffix '-ol'.

The following rules also apply.

- Identify the parent name from the longest carbon chain containing the hydroxyl group.
- If positional isomers are possible, a number is inserted before the '-ol' to indicate the carbon to which the hydroxyl functional group is attached.
- Number the carbon chain commencing at the end closest to the hydroxyl group. Table 10.4.5 shows some examples.

TABLE 10.4.5 Examples of naming alcohols. These three structures are all isomers of $C_4H_{10}O$

Name	Semistructural formula	Structural formula
Butan-1-ol	$CH_3CH_2CH_2CH_2OH$	 This is an example of a primary alcohol.
Butan-2-ol	$CH_3CHOHCH_2CH_3$	 This is an example of a secondary alcohol.
2-Methylpropan-2-ol	$(CH_3)_3COH$	 This is an example of a tertiary alcohol.

PRIMARY AMINES

Amines are a homologous series of organic compounds that contain the **amino functional group**. An amino functional group consists of one nitrogen atom covalently bonded to two hydrogen atoms as shown in Figure 10.4.5.

Amino functional groups with two hydrogens and one alkyl group are called primary amines. Unlike alcohols, amines are classified as 'primary', 'secondary' and 'tertiary' according to the number of alkyl groups attached to the nitrogen atom. Secondary and tertiary amines exist, but these compounds are not covered in this course. Some primary amines are shown in Figure 10.4.6.

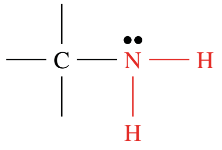
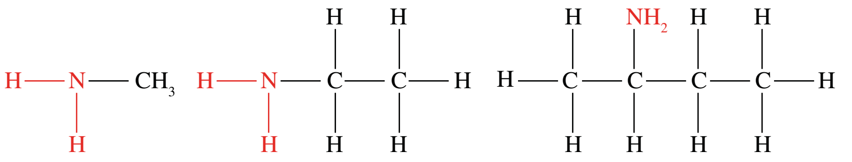


FIGURE 10.4.5 Primary amines contain the amino functional group, $-NH_2$ (in red above). There are two non-bonding electrons on the nitrogen atom.



methanamine
CH_3NH_2

ethanamine
$CH_3CH_2NH_2$

butan-2-amine
$CH_3CHNH_2CH_2CH_3$

FIGURE 10.4.6 Structural and semistructural formulas of three primary amines. The amino functional group is shown in red. Primary amines have one carbon atom bonded to the nitrogen atom.

CHEMFILE

Amines, chocolate and happiness

An active ingredient in chocolate (Figure 10.4.7) is the primary amine 2-phenylethanamine.

2-Phenylethanamine is also produced in the pleasure centres of the brain and has the effect of generating a general sense of wellbeing or happiness, as well as temporarily raising blood pressure and blood glucose levels.

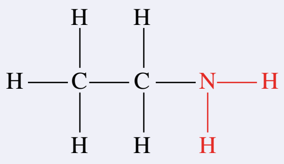
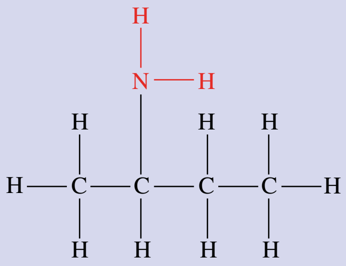
Eating chocolate provides you with a boost of 2-phenylethanamine, so the reason eating chocolate might make you feel happy is partly due to organic chemistry!

FIGURE 10.4.7 Chocolate contains an amine that makes humans feel happy.

Naming amines

Amines are named in a similar way to alcohols. The '-e' at the end of the parent alkane's name is replaced with the suffix '-amine'. If positional isomers are possible, a number is inserted before '-amine' to indicate the carbon to which the amino functional group is attached. Table 10.4.6 shows two examples.

TABLE 10.4.6 Examples of naming amines

Name	Condensed formula	Structural formula
Ethanamine	$CH_3CH_2NH_2$	
Butan-2-amine	$CH_3CHNH_2CH_2CH_3$	

10.4 Review

SUMMARY

- Organic molecules containing functional groups include:
  - haloalkanes, which contain the halo groups –F, –Cl, –Br and –I
  - alcohols, which contain hydroxyl (–OH) groups
  - primary amines, which contain amino (–NH_2) functional groups.
- Haloalkanes, alcohols and primary amines can be regarded as being derived from alkanes. The name of the parent alkane is used as the basis for their names.
  - Haloalkanes are named by adding the prefix for the halogen.
  - Alcohols are named by replacing the '-e' at the end of the parent alkane with the suffix '-ol'.
  - Primary amines are named by replacing the '-e' at the end of the parent alkane with the suffix '-amine'.
  - When isomers exist, a number is used to specify the position of the functional group.

KEY QUESTIONS

1 Give the systematic name for the molecule in Figure 10.4.8.

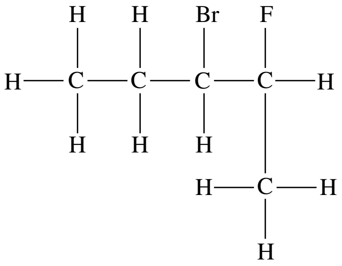


FIGURE 10.4.8 Molecule structure.

2 Write the semistructural formula of 3-chloro-2-fluoro-2-iodohexane.

3 Draw the structure and then write the name of a tertiary alcohol with the molecular formula $C_5H_{12}O$.

4 Give the systematic names of:

a $CH_3CH_2CH_2Br$

b $(CH_3)_2CHCH_2CHClCH_3$

c $CH_3(CH_2)_3CH_2OH$

d $CH_3(CH_2)_3CHNH_2(CH_2)_2CH_3$

5 Explain why the names 1-chloroethane and propan-3-amine are not used.

10.5 Functional groups—Part 2

FIGURE 10.5.1 The strong and often pleasant odours of organic chemicals are used in perfumes.

In this section you will look at five more homologous series:

- **aldehydes**
- **ketones**
- **carboxylic acids**
- primary **amides**
- **esters**.

You will learn about the functional groups and structures of the molecules of each homologous series, as well as the rules for naming carboxylic acids and esters.

The molecules in these homologous series are responsible for many natural fragrances as well as in essential oils and pheromones (Figure 10.5.1). They are also synthesised commercially to produce particular smells and flavourings.

ALDEHYDES AND KETONES

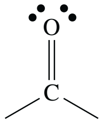


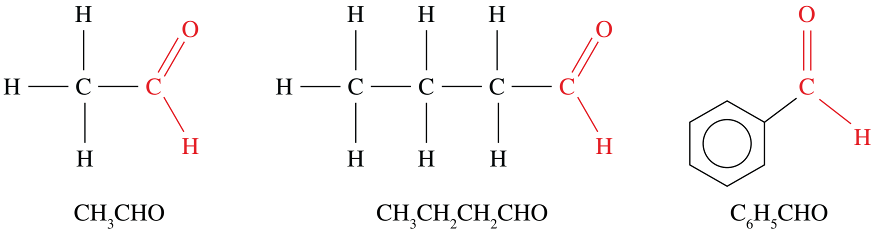
FIGURE 10.5.2 The carbonyl functional group. The non-bonding pairs of electrons shown on the oxygen atom are often not included in structural formulas.

Molecules of aldehydes, ketones, carboxylic acids, amides and esters all contain a **carbonyl functional group** as shown in Figure 10.5.2. A carbonyl functional group consists of a carbon atom connected to an oxygen atom by a double bond. All atoms bonded to the carbon atom are in a plane and the angles between bonds are 120°. The naming of aldehydes and ketones is not covered in this course.

Aldehydes

In aldehydes, the carbonyl group is always at the end of the hydrocarbon chain. As shown in Figure 10.5.3, the carbon atom of the carbonyl group is bonded to a hydrogen atom. The carbonyl functional group in an aldehyde is always written as –CHO at the end of the semistructural formula of aldehydes.

The simplest aldehyde, HCHO, is commonly known as formaldehyde and is used to preserve biological specimens, including embalming human remains.



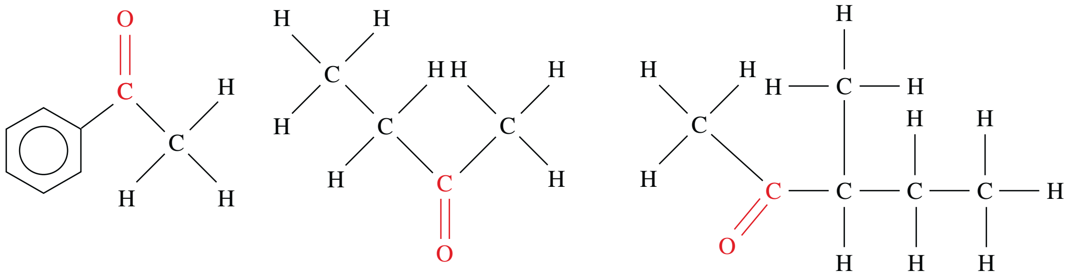
CH_3CHO $CH_3CH_2CH_2CHO$ C_6H_5CHO

FIGURE 10.5.3 Structural and semistructural formulas of three aldehydes. Each contains a carbonyl functional group with a hydrogen atom attached, shown in red.

Ketones

In ketones, the carbonyl carbon is attached to other carbon atoms. This means that the carbonyl group is never at the end of the molecule, as you can see in the examples in Figure 10.5.4. In semistructural formulas, the carbonyl functional group in a ketone is simply written as –CO–.

The simplest ketone, CH_3COCH_3, is commonly called acetone and is a useful polar organic solvent, frequently found in nail polish remover and paint thinner.



$C_6H_5COCH_3$ $CH_3CH_2COCH_3$ $CH_3COCH(CH_3)CH_2CH_3$

FIGURE 10.5.4 Structural and semistructural formulas of three ketones. Each contains a carbonyl functional group (shown in red) attached to two hydrocarbon groups.

CARBOXYLIC ACIDS

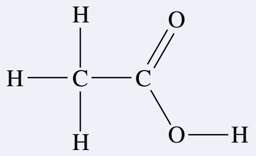
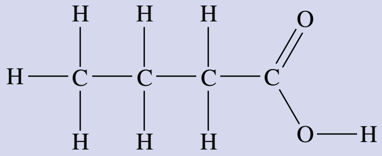
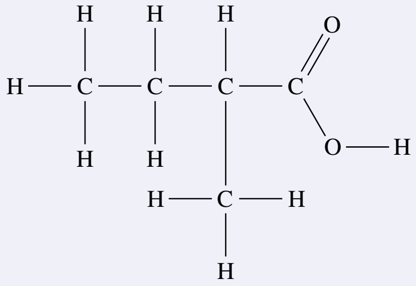
Carboxylic acids are a homologous series that contain the carboxyl functional group. The carboxyl functional group (Figure 10.5.5) consists of a carbonyl group attached to a hydroxyl group.

The **carboxyl functional group** is represented in a semistructural formula as –COOH and is always located at one end of a hydrocarbon chain. Figure 10.5.6 shows the structural and semistructural formulas of three carboxylic acids.

Naming carboxylic acids

Carboxylic acid names also follow the rules used for alkanes, except that the ‘-e’ at the end of the parent alkane’s name is replaced with the suffix ‘-oic acid’. As the carboxyl group is always on the end of a chain, the carbon atom in the carboxyl group is always carbon number 1. Table 10.5.1 shows three examples.

TABLE 10.5.1 Examples of naming carboxylic acids

Name	Semistructural formula	Structural formula
Ethanoic acid	CH_3COOH	
Butanoic acid	$CH_3CH_2CH_2COOH$	
2-Methylbutanoic acid	$CH_3CH_2CH(CH_3)COOH$	

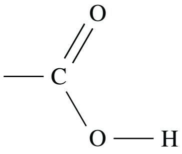
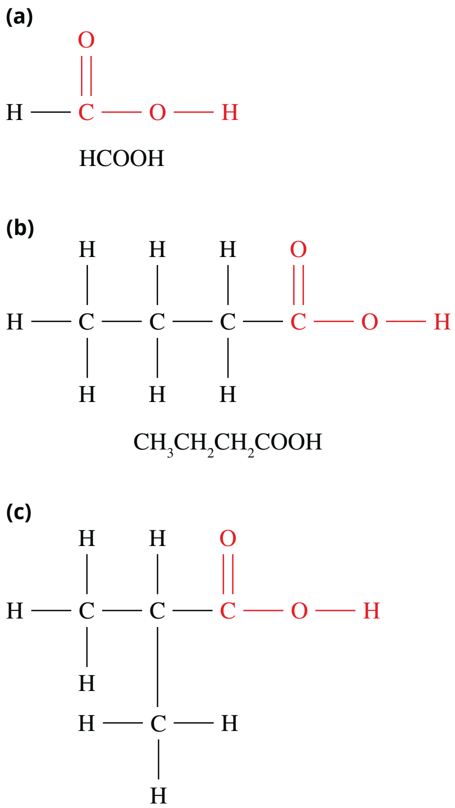


FIGURE 10.5.5 Structure of the carboxyl functional group.



(a) HCOOH

(b) $CH_3CH_2CH_2COOH$

(c) $(CH_3)_2CHCOOH$

FIGURE 10.5.6 Structural and semistructural formulas of three carboxylic acids. Each contains a carboxyl functional group shown in red. Note that molecules (b) and (c) are isomers with the molecular formula $C_4H_8O_2$.

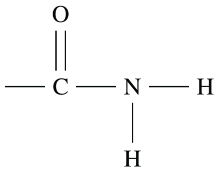


FIGURE 10.5.7 Structure of the amide functional group in a primary amide.

PRIMARY AMIDES

Primary amides contain a carbonyl functional group attached to an amino functional group. They are similar to carboxyl groups, except that the –OH is replaced with $-NH_2$ (Figure 10.5.7).

The nitrogen atom in primary amides is bonded to two hydrogen atoms. Secondary and tertiary amides exist, but these compounds are not covered in this course. The **amide functional group** is represented in a semistructural formula as $-CONH_2$ and is always located at one end of a hydrocarbon chain. The structural and semistructural formulas of three primary amides are shown in Figure 10.5.8.

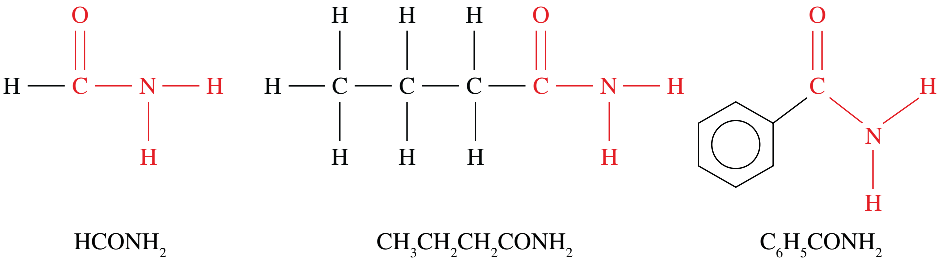


FIGURE 10.5.8 Structural and semistructural formulas of three amides, with the amide functional group shown in red.

CHEMFILE

Urea and organic chemistry

Urea ($(NH_2)_2CO$) is a small amide, which is the end product of the breakdown of proteins by mammals and is excreted in urine. This naturally produced urea can be used as a source of nitrogen to promote plant growth (see Figure 10.5.9).

Friedrich Wöhler, a German chemist, synthesised urea in his laboratory in 1828 by treating silver cyanate with ammonium chloride. In a letter to a colleague Wöhler excitedly wrote: 'I must tell you that I can make urea without the use of kidneys, either man or dog.'

Wöhler's synthesis of urea was remarkable because it was the first time someone had made an organic molecule. This discovery established the field of synthetic organic chemistry, which is responsible for millions of products in our society.

FIGURE 10.5.9 Urea is used commercially in fertiliser.

ESTERS

Esters are produced by the reaction of a carboxylic acid with an alcohol. The **ester functional group** (Figure 10.5.10) contains a carbonyl group attached to an oxygen linked to another carbon. It is similar to a carboxylic acid group, but the hydrogen of the –OH is replaced by an alkyl group.

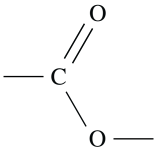
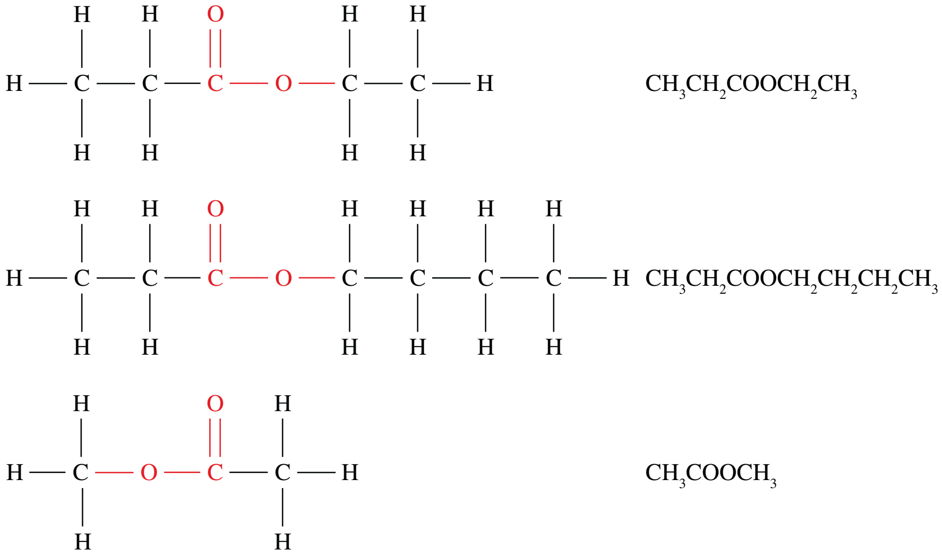


FIGURE 10.5.10 Structure of the ester functional group.

Figure 10.5.11 shows the structural and semistructural formulas of three esters. In semistructural formulas, the ester functional group is usually written as –COO–.



$CH_3CH_2COOCH_2CH_3$

$CH_3CH_2COOCH_2CH_2CH_2CH_3$

CH_3COOCH_3

FIGURE 10.5.11 Structural and semistructural formulas of three esters. Each contains the ester functional group shown in red.

Naming esters

The names of esters consist of two words. The name is built up from the names of the alcohol and carboxylic acid that reacted to form it. The first part is based on the number of carbon atoms in the chain attached to the singly bonded oxygen (–O–). The second part of the name is based on the number of carbon atoms in the chain containing the carbonyl group.

In the example in Figure 10.5.12, the chain attached to the single –O– contains one carbon atom, while the chain containing the carbonyl is three carbon atoms long.

The –O– section of an ester is derived from an alcohol and contributes the first word of the name. The name of the alcohol is adapted by changing the '-ol' suffix to '-yl'.

The section containing the carbonyl group is derived from a carboxylic acid and contributes the second word of the name. The name of the carboxylic acid is adapted by changing '-oic acid' to '-oate'.

Using these rules, you can work out that the name of the ester shown in Figure 10.5.9 is methyl propanoate.

The names, semistructural and structural formulas of some other esters are shown in Table 10.5.2 (page 308), with the part of each molecule derived from an alcohol in red and the part of each molecule derived from the carboxylic acid in blue.

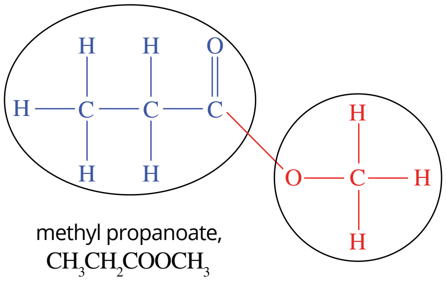
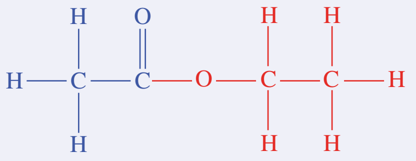
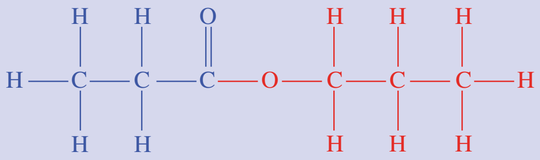
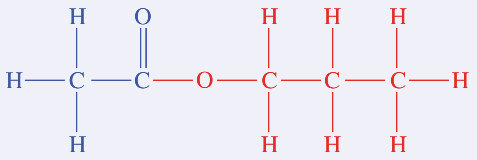


FIGURE 10.5.12 Esters are named using two words based on the two alkyl chains in the molecule.

TABLE 10.5.2 The names, semistructural and structural formulas of three esters

Name	Semistructural formula	Structural formula
Ethyl ethanoate	$CH_3COOCH_2CH_3$	
Propyl propanoate	$CH_3CH_2COOCH_2CH_2CH_3$	
Propyl ethanoate	$CH_3COOCH_2CH_2CH_3$	

CHEMFILE

Esters, sweet flavours and strong aromas

Esters are responsible for some of the natural and synthetic flavours and smells found in ice creams, lollies, flowers and fruit (Figure 10.5.13). Table 10.5.3 lists the names of some esters with distinctive smells or flavours.

Your favourite perfume or cologne is likely to contain esters that are responsible for its distinctive and appealing odour.

TABLE 10.5.3 Some sweet smelling esters

Ester	Smell or flavour
Pentyl propanoate	Apricot
Ethyl butanoate	Pineapple
Octyl ethanoate	Orange
2-Methylpropyl methanoate	Raspberry
Ethyl methanoate	Rum
Pentyl ethanoate	Banana

FIGURE 10.5.13 Esters are responsible for many of the flavours and odours of fruit.

10.5 Review

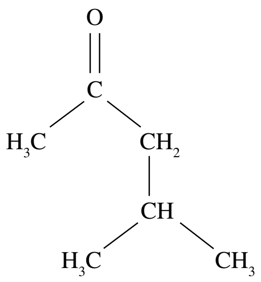
SUMMARY

- The carbonyl group (–CO–) is a component of a number of functional groups.
- Aldehydes and ketones are homologous series that contain a carbonyl group on its own.
- The carbonyl group is at the end of a hydrocarbon chain in aldehydes and within a hydrocarbon chain in ketones.
- Carboxylic acids are a homologous series of molecules that contain the carboxyl group (–COOH) at the end of a hydrocarbon chain.
- Carboxylic acids are named using the suffix '-oic acid'.
- Primary amides are a homologous series of molecules that contain the amide group ($-CONH_2$) at the end of the hydrocarbon chain.
- Esters are a homologous series of molecules that contain an ester group (–COO–) within the hydrocarbon chain.
- Esters have a two-word name.
  - The first part of the name comes from the section derived from an alcohol and the '-ol' suffix is changed to '-yl'.
  - The second part of the name is derived from the section that comes from a carboxylic acid and the suffix '-oic acid' is changed to '-oate'.

KEY QUESTIONS

1 What homologous series do each of the following molecules belong to?

a



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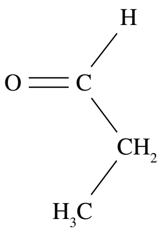

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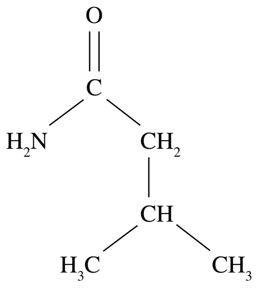

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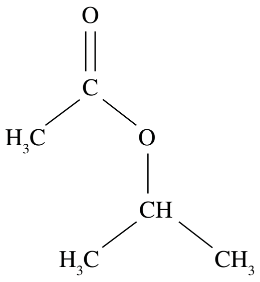


2 Write the systematic name for the following molecules.

a $HCOOCH_3$

b HCOOH

c $CH_3CH_2CH_2COOCH_2CH_2CH_3$

d CH_3COOCH_3

e $CH_3(CH_2)_4COOCH_2CH_3$

3 Draw and name an isomer of $HCOOCH_3$.

10.6 An overview of IUPAC nomenclature

In the early 1960s, the International Union of Pure and Applied Chemistry (IUPAC) endorsed a common naming system for carbon compounds. These rules are regularly updated and are used worldwide to enable scientists to communicate with each other. The rules ensure that a carbon compound is given a unique name that provides useful information about its structure and distinguishes it from any isomers.

The rules specify the names for different parts of an organic molecule and may include both words and numbers to indicate locations of functional groups and alkyl branches (for example, see Figure 10.6.1).

This section will summarise and extend your knowledge of the rules that you learnt in the previous sections for naming organic compounds. You will also learn how to name organic molecules that contain two different functional groups.

FIGURE 10.6.1 According to the IUPAC rules, the active ingredient in the antiseptic Dettol has the name 4-chloro-3,5-dimethylphenol.

IUPAC NOMENCLATURE

IUPAC nomenclature is the term used to describe the set of rules by which chemists can name a given compound. The rules can be used in reverse to derive a structure from the IUPAC name. IUPAC names of organic molecules can be short or very long, but, whether simple or complex, most IUPAC names follow the same basic pattern.

All organic molecules can be thought of as being derived from a hydrocarbon parent molecule, which provides the basis for the name of the molecule. Part of the IUPAC name reflects which alkane is the parent molecule.

The IUPAC name also indicates which functional groups are present in the molecule by adding a suffix to the end of the name or a prefix to the beginning of the name. The positions of functional groups are indicated by numbers. As an example, the meaning of each part of the name butan-2-ol, an alcohol, is shown in Figure 10.6.2 along with its structural formula.

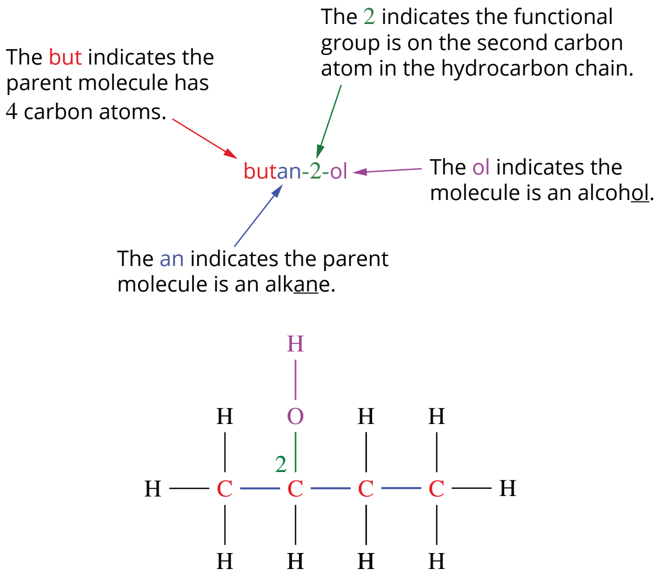


FIGURE 10.6.2 The name and structural formula of butan-2-ol. The colours of each part of the name correspond with the section of the structure that it represents.

SUMMARY OF IUPAC RULES FOR NOMENCLATURE

The following conventions are used for naming organic molecules.

- There are no spaces in a name, apart from the two-word names of esters and carboxylic acids.
- The longest carbon chain is used to derive the parent name. The longest chain must include the functional group for alkenes, alkynes, alcohols, amines, carboxylic acids and esters.
- The names and locations of branches and additional functional groups are added to this parent name.
- Numbers are used to identify the carbon atom that groups are attached to.
- Numbers and letters are separated by dashes.
- Numbers are separated from other numbers by commas.
- The names of branch alkyl groups are added before the parent name.
- If there is more than one type of functional group to be listed at the beginning of a name, they are listed in alphabetical order.
- If there is more than one of the same type of functional group, the prefixes 'di-', 'tri-' or 'tetra-' are used. Each group is still given a number to indicate its position on the carbon chain.

The presence of a particular functional group identifies the homologous series a molecule belongs to and changes the molecule's name, as shown in Table 10.6.1.

TABLE 10.6.1 The identity, functional groups and naming conventions of the homologous series.

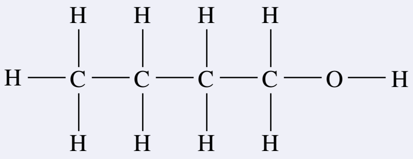
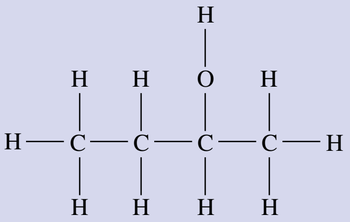
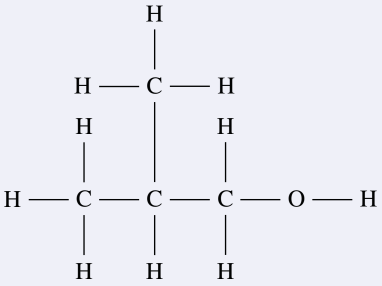
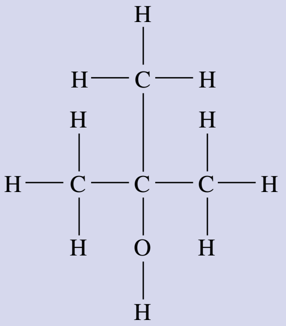
Homologous series	Functional group name	Semistructural formula	Naming convention
Alkane	Not applicable	Not applicable	Suffix -ane
Alkene	Carbon–carbon double bond	–C=C–	Suffix -ene
Alkyne	Carbon–carbon triple bond	–C≡C–	Suffix -yne
Haloalkane	Halo	–F, –Cl, –Br, –I	Prefix fluoro-, chloro-, bromo- or iodo-
Alcohol	Hydroxyl	–OH	Suffix -ol Occasionally prefix hydroxy-
Amine	Amino	$-NH_2$	Suffix -amine Occasionally prefix amino-
Carboxylic acid	Carboxyl	–COOH	Suffix -oic acid
Ester	Ester	–COO–	Two-word name with suffixes -yl and -oate
Aldehyde	Carbonyl (aldehyde)	–CHO	Not covered in this course
Ketone	Carbonyl	–CO–	Not covered in this course
Amide	Amide	$-CONH_2$	Not covered in this course

Naming organic molecules with a functional group and alkyl side chain

Organic molecules with functional groups can also have alkyl side chains. The names of alkyl groups are placed in alphabetical order in front of the parent name. The carbon chain is numbered from the end closest to the functional group to give the lowest possible number to the functional group.

This procedure is illustrated in Table 10.6.2 (page 312) with the naming of the structural isomers of an alcohol with the molecular formula $C_4H_{10}O$.

TABLE 10.6.2 Names of isomers of an alcohol with the molecular formula $C_4H_{10}O$

Structure	Name
	Butan-1-ol
	Butan-2-ol
	2-Methylpropan-1-ol
	2-Methylpropan-2-ol

Naming organic molecules with two functional groups

Many organic molecules have more than one functional group. If the functional groups are the same, a multiplier (di-, tri- etc.) can be used. If the molecule has different functional groups, you will need to know which one has the highest priority in order to work out what numbers and names to use.

IUPAC has designated a priority system for functional groups (Table 10.6.3). In an organic molecule with two functional groups, the following naming conventions are used.

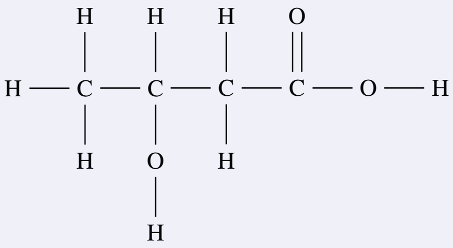
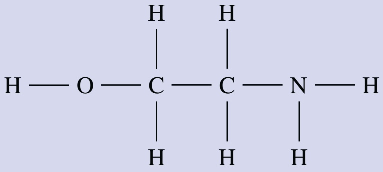
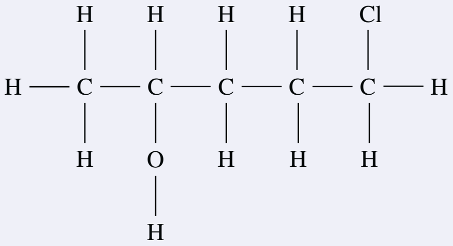
- The functional group with the highest priority is assigned the lowest possible number and the suffix for this functional group is used in the name.
- The lower priority functional group is indicated by a prefix or alternative name.

TABLE 10.6.3 IUPAC functional group priorities

	Functional group	Suffix	Alternative name (when needed)
Highest priority	carboxyl	-oic acid	–
	hydroxyl	-ol	hydroxy-
	amino	-amine	amino-
	alkene	-ene	-an- becomes -en-
	alkyne	-yne	-an- becomes -yn-
Lowest priority	halo	–	halo-

This priority system is illustrated in Table 10.6.4 with the naming of molecules with two functional groups.

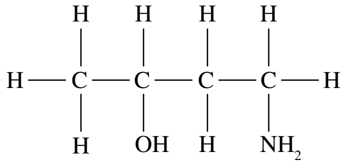
TABLE 10.6.4 Naming molecules with two functional groups

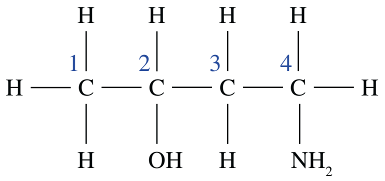
Structure	Name
	3-Hydroxybutanoic acid
	2-Aminoethanol
	5-Chloropentan-2-ol

Worked example 10.6.1

NAMING AN ORGANIC MOLECULE WITH TWO FUNCTIONAL GROUPS

Name this molecule according to IUPAC rules.

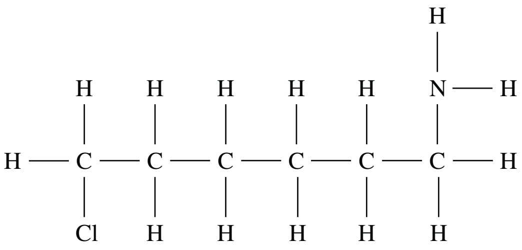


Thinking	Working
Identify the parent name by counting the longest continuous chain of carbon atoms.	There are four carbons in the longest chain, so the parent name is butane.
Identify the functional groups present.	The two functional groups present are hydroxyl and amino.
Determine which functional group has the higher priority and determine the prefixes and suffixes to use.	The hydroxyl group has the higher priority, so the molecule will end in -ol. The amino group has lower priority and so the prefix amino- will be used.
Number the carbon chain, giving the highest priority group the lowest number possible.	
Determine the number of the carbon each functional group is attached to.	The –OH is attached to carbon 2 and $–NH_2$ is attached to carbon 4.
Use the functional group names and carbon numbers to construct the full name.	The name of the molecule is 4-aminobutan-2-ol.

Worked example: Try yourself 10.6.1

NAMING AN ORGANIC MOLECULE WITH TWO FUNCTIONAL GROUPS

Name this molecule according to IUPAC rules.



10.6 Review

SUMMARY

- IUPAC nomenclature is a set of rules for naming an organic compound.
- The naming of organic molecules follows a series of steps.
  - Identify the longest unbranched carbon chain to determine the parent name.
  - Name functional groups by prefixes or suffixes, depending on their priority.
  - Number the carbon chain so that the carbon attached to the highest priority functional group has the lowest number.
  - Insert numbers before each functional group.
  - When multiples of a functional group are present, use a multiplier (e.g. 'di-').

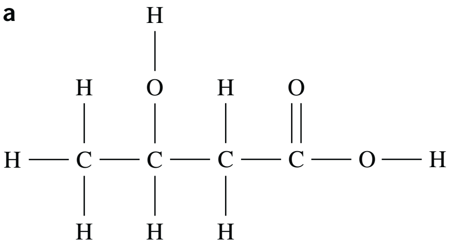
KEY QUESTIONS

1 Draw the structural formula of the functional group of each of the following homologous series.

a Alkyne
b Carboxylic acid
c Aldehyde
d Amide
e Alcohol
f Ester

2 Write the systematic name for the following molecules.

a



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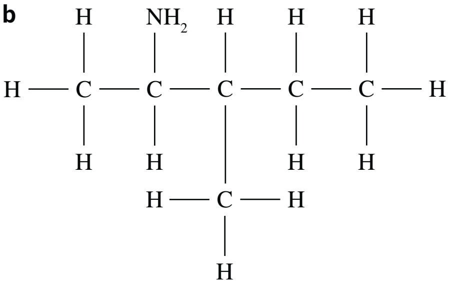

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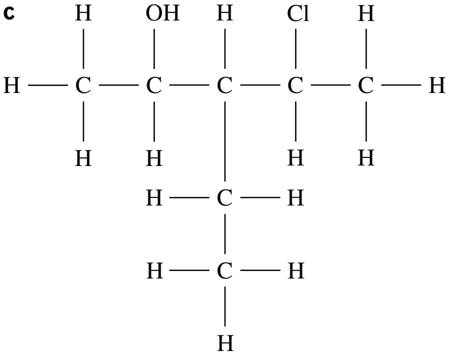

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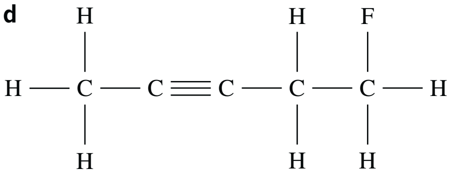


3 Draw the structure of:

a but-3-ynoic acid
b 4-chloropent-1-en-2-amine
c *trans*-6-bromohept-4-en-2-ol
d 3,4-diethylhex-3-ene.

4 **a** Write the semistructural formulas based on the following incorrect names.

  i 3-Aminoprop-1-ene
  ii 2-Chloropentan-5-oic acid
  iii 1-Ethyl-1-hydroxyprop-2-ene

b Explain why each name is incorrect and give the correct name.

Chapter review

10

KEY TERMS

achiral
alcohol
aldehyde
alkane
alkene
alkyl group
alkyne
amide
amide functional group
amine
amino functional group
benzene
bond energy
bond strength
carbonyl functional group
carboxylic acid
carboxylic functional group
chain isomers
chiral
chiral centre
cis isomer
cis–*trans* isomers
cyclic molecule
delocalised electrons
electronic configuration
enantiomer
ester
ester functional group
functional group
geometric isomer
halo functional group
haloalkane
halogen
homologous series
hydrocarbon
hydroxyl functional group
isomers
IUPAC nomenclature
ketone
molecular formula
optical isomers
organic molecule
parent molecule
plane of symmetry
positional isomer
primary alcohol
primary amine
saturated molecule
secondary alcohol
semistructural formula
side chain
stem name
stereoisomer
structural formula
structural isomers
tertiary alcohol
tetrahedral
trans isomer
unsaturated molecule
valence number
valence shell electron pair repulsion (VSEPR) theory

Diversity of carbon compounds

1 The structure of 1-chloropentane is shown in Figure 10.7.1.

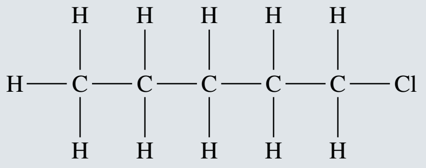


FIGURE 10.7.1 1-Chloropentane

- **a** How many positional isomers can be drawn of this structure?
- **b** Draw and name all the possible isomers of this structure.

2 How is a chain isomer different from a positional isomer?

3 Structures with the molecular formula C_4H_8 can be both chain and positional isomers. Write three semistructural formulas of C_4H_8 to explain the relationship between positional and chain isomers.

Stereoisomers

4 Draw the structures of the chiral molecules named below and label the chiral centres with an asterisk.

- **a** Butan-2-amine
- **b** 1-Chloropropan-2-ol
- **c** 4-Bromopentan-2-ol

5 Draw the structure of *cis*-but-2-en-1-ol.

6 What types of isomers exist for pent-3-en-2-ol?

Hydrocarbons

7 What is the molecular formula of:

- **a** an alkane with molar mass 72 g mol^{-1}?
- **b** an alkene with molar mass 84 g mol^{-1}?
- **c** an alkyne with molar mass 54 g mol^{-1}?
- **d** a hydrocarbon with molar mass 98 g mol^{-1}?

8 How many isomers of pentane exist?

9 Explain why 2-ethylpentane is an incorrect name for the alkane.

Functional groups—Part 1

10 What elements are present in the following functional groups?

- **a** Amino
- **b** Chloro
- **c** Hydroxyl

11 Use propan-1-ol and propan-2-ol to explain the difference between a primary and secondary alcohol.

12 Determine the systematic name of each of the following compounds.

- **a** $CH_3CHNH_2CH_2OH$
- **b** $CH_3CHOH(CH_2)_5CH_2Cl$
- **c** $CH_3CH_2CH_2CH_2CHNH_2CHICH_3$

Functional groups—Part 2

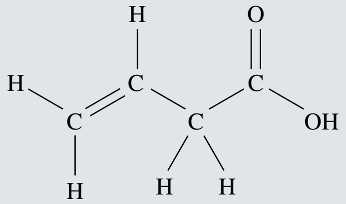
13 What is the structural difference between an aldehyde, a ketone, a carboxylic acid and an amide?

14 Why are carboxyl and primary amide groups only found at the end of a carbon chain?

An overview of IUPAC nomenclature

15 Name each of the following molecules.

a



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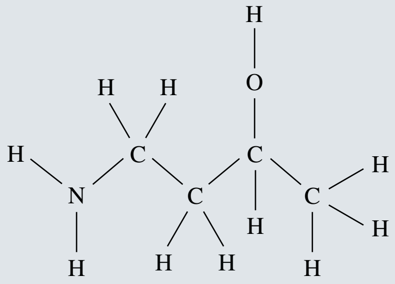

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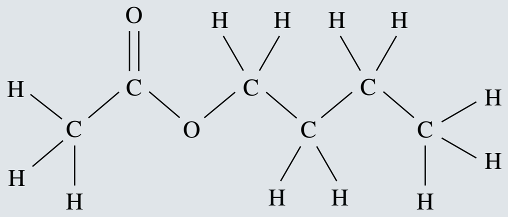

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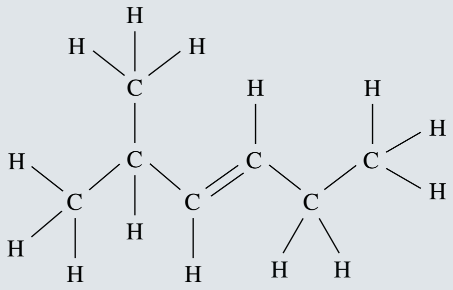

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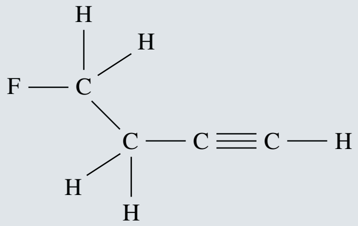

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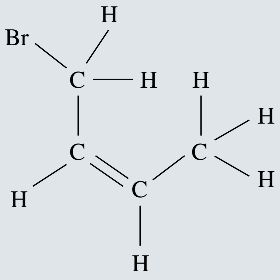


Connecting the main ideas

16 Draw the structure of:

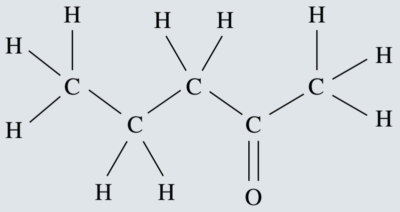
- **a** heptyl propanoate
- **b** *trans*-4-iodo-3-methylpent-2-ene
- **c** *cis*-oct-4-enoic acid
- **d** 3-methylbutan-1-amine.

17 Write the semistructural formulas of:

- **a** *cis*-oct-3-enoic acid
- **b** methyl hexanoate
- **c** 3-fluoropropan-1-ol
- **d** 4-hydroxybutanoic acid
- **e** 2,3-dimethylpentan-1-amine.

18 Convert the following structures to semistructural formulas.

a



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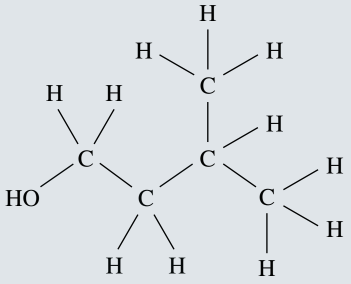

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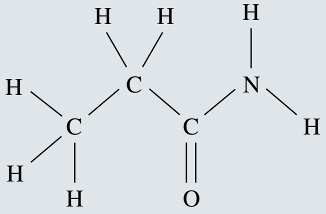

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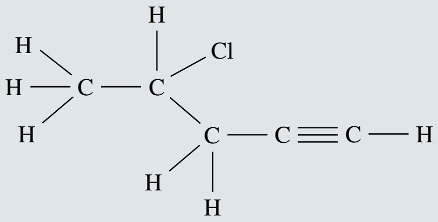
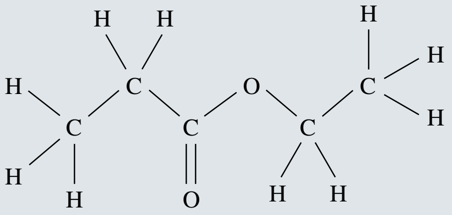


e



19 Explain why each of these names is incorrect, then determine its correct name.

- **a** But-4-ene
- **b** 2-Hydroxyethanamine
- **c** 4-Chlorohex-5-yne
- **d** 2-Chloro-3-ethylbutane
- **e** 2,2-Dimethylpent-3-ene
- **f** 1-Bromo-1,1-dipropylmethane

20 The semistructural formulas of some organic compounds are given below. For each compound:

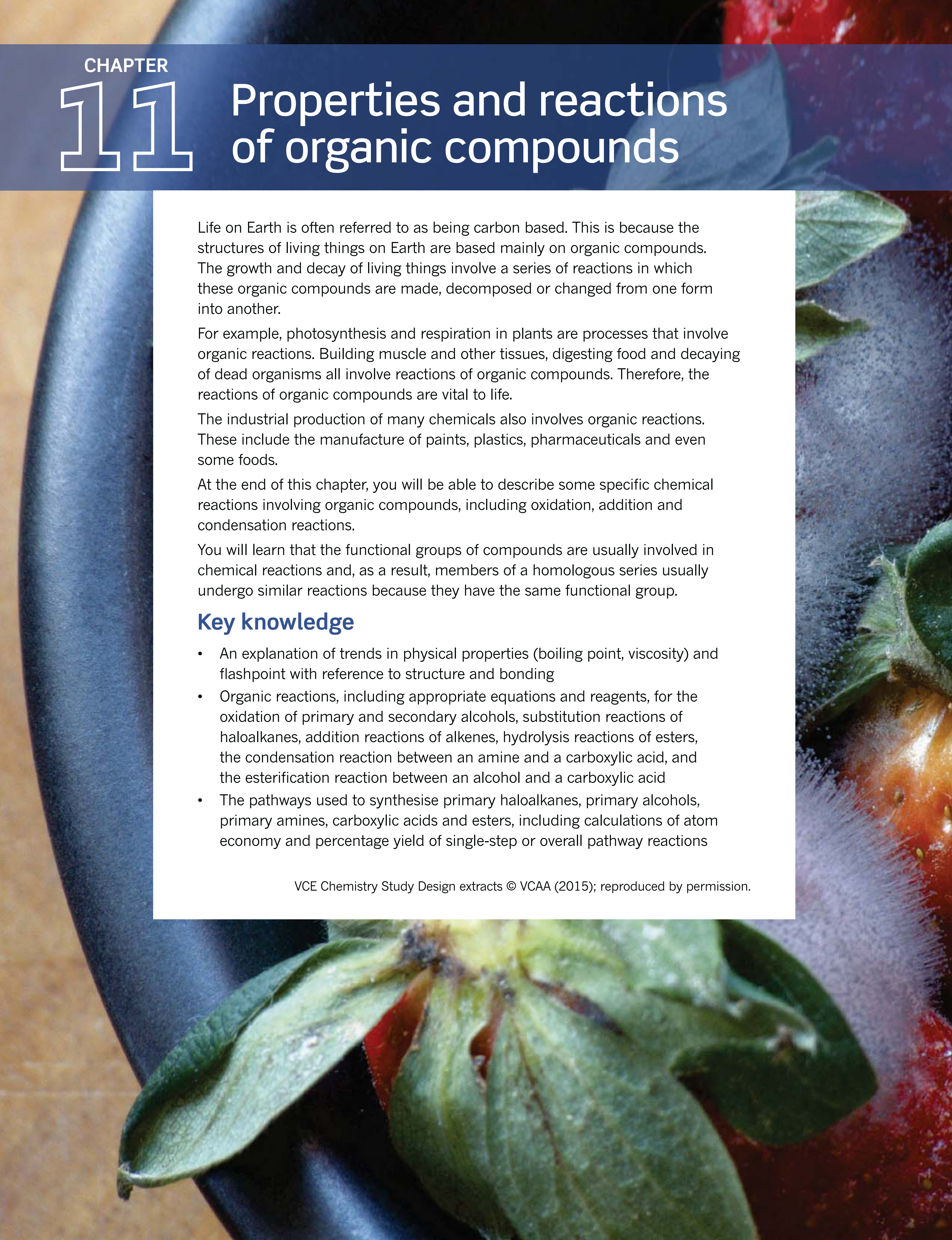
- **i** identify the homologous series to which it belongs
- **ii** give its systematic name.

- **a** $CH_3(CH_2)_5CH_2OH$
- **b** $CH_3(CH_2)_2CHCl(CH_2)_2CH_3$
- **c** $CH_3CHOH(CH_2)_3CH_3$
- **d** $CH_3(CH_2)_3COOH$
- **e** $CH_3CH_2CHNH_2CH_3$
- **f** $(CH_3)_2CH(CH_2)_5CH_3$
- **g** $(CH_3)_2C{=}CH_2$

21 For each of the substances whose molecular formulas are given below:

- **i** draw a structural formula of a molecule with this formula
- **ii** name the molecule you have drawn.

- **a** $C_5H_{11}Cl$
- **b** $C_4H_{10}O$
- **c** $C_3H_6O_2$
- **d** $C_4H_8O_2$
- **e** $C_5H_{11}N$



CHAPTER 11

Properties and reactions of organic compounds

Life on Earth is often referred to as being carbon based. This is because the structures of living things on Earth are based mainly on organic compounds. The growth and decay of living things involve a series of reactions in which these organic compounds are made, decomposed or changed from one form into another.

For example, photosynthesis and respiration in plants are processes that involve organic reactions. Building muscle and other tissues, digesting food and decaying of dead organisms all involve reactions of organic compounds. Therefore, the reactions of organic compounds are vital to life.

The industrial production of many chemicals also involves organic reactions. These include the manufacture of paints, plastics, pharmaceuticals and even some foods.

At the end of this chapter, you will be able to describe some specific chemical reactions involving organic compounds, including oxidation, addition and condensation reactions.

You will learn that the functional groups of compounds are usually involved in chemical reactions and, as a result, members of a homologous series usually undergo similar reactions because they have the same functional group.

Key knowledge

- An explanation of trends in physical properties (boiling point, viscosity) and flashpoint with reference to structure and bonding
- Organic reactions, including appropriate equations and reagents, for the oxidation of primary and secondary alcohols, substitution reactions of haloalkanes, addition reactions of alkenes, hydrolysis reactions of esters, the condensation reaction between an amine and a carboxylic acid, and the esterification reaction between an alcohol and a carboxylic acid
- The pathways used to synthesise primary haloalkanes, primary alcohols, primary amines, carboxylic acids and esters, including calculations of atom economy and percentage yield of single-step or overall pathway reactions

11.1 Boiling points and solubilities of organic compounds

The functional groups that are present in organic compounds are responsible for many of their chemical and physical properties. For example, the properties of methanoic acid (formic acid) HCOOH (Figure 11.1.1) are largely determined by the presence of the polar, acidic carboxyl functional group in its molecules.

FIGURE 11.1.1 Green tree ants weave leaf nests in the Gardner Plateau on the Kimberley Coast in Western Australia. Weaver ants can inflict painful bites and often spray methanoic acid directly at the bite wound, resulting in intense discomfort.

In this section and section 11.2, you will consider the effect of functional groups on physical properties such as boiling point, solubility and viscosity. Differences in chemical properties will be discussed in sections 11.3 and 11.4.

PHYSICAL PROPERTIES OF ALKANES, ALKENES, ALKYNES AND HALOALKANES

Boiling points of alkanes

Table 11.1.1 lists the boiling points of the first six alkanes from methane to hexane. The boiling points increase as the size of the alkane molecule increases.

TABLE 11.1.1 Boiling points of the first six alkanes

Alkane	Molecular formula	Boiling point (°C)
Methane	CH_4	–162
Ethane	C_2H_6	–89
Propane	C_3H_8	–45
Butane	C_4H_{10}	–0.5
Pentane	C_5H_{12}	36
Hexane	C_6H_{14}	69

Because alkane molecules are non-polar, the only intermolecular forces of attraction between them are weak **dispersion forces**. As the length of the carbon chain increases, the overall forces of attraction between molecules also increase (Figure 11.1.2). The dispersion forces between molecules increase because of the increased strength of temporary dipoles within the molecules. Because the boiling point of a molecular substance is determined by the strength of the intermolecular forces, boiling point increases as alkane chain length increases.

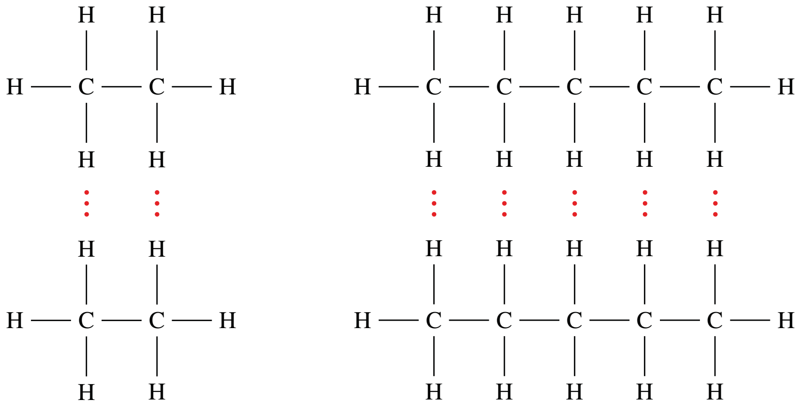


FIGURE 11.1.2 Dispersion forces are the strongest forces between alkane molecules. As molecules become longer, the dispersion forces become stronger.

Molecular shape also influences the strength of dispersion forces and, therefore, boiling points. Straight-chain alkanes are able to fit together more closely and tend to have higher boiling points than their corresponding branched-chain **isomers**, which are unable to come as closely together in the bulk substance.

Figure 11.1.3 shows how the shapes of butane and its branched isomer methylpropane influence the strength of the dispersion forces between the molecules. Butane ($CH_3CH_2CH_2CH_3$) boils at –0.5°C, whereas methylpropane ($(CH_3)_3CH$) boils at –11.7°C. Although both molecules have the same molecular formula of C_4H_{10}, molecules of $CH_3CH_2CH_2CH_3$ have a greater surface area and can fit more closely together, allowing more contact between the molecules and forming stronger intermolecular bonds.

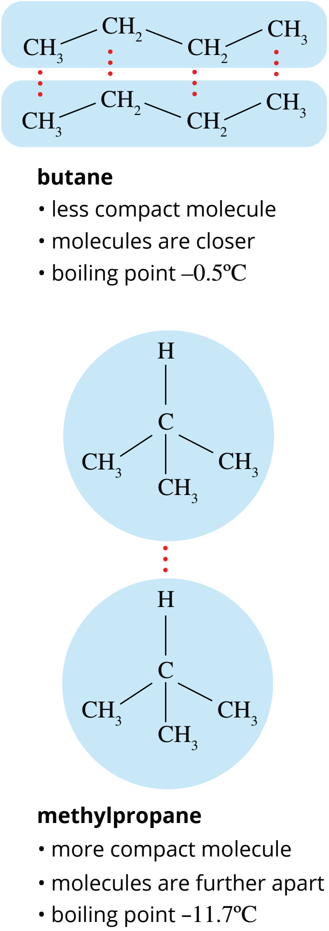


FIGURE 11.1.3 Molecular shape affects boiling point. Dispersion forces between butane molecules are stronger than those between methylpropane molecules because butane molecules are less compact and can come closer together.

The strength of dispersion forces between molecules depends on the size and shape of the molecules.

Boiling points of alkenes, alkynes and haloalkanes

Alkenes and alkynes, like alkanes, are hydrocarbons. These molecules are non-polar and the forces of attraction between them are only weak dispersion forces. As you can see in Table 11.1.2, members of these homologous series have relatively low boiling points similar to those observed for the alkanes with the same number of carbon atoms.

Like the alkanes, the boiling points of alkenes and alkynes increase with molecular size as the strength of dispersion forces between molecules increases.

TABLE 11.1.2 Boiling points of molecules containing four carbons with different functional groups

Compound	Boiling point (°C)
Butane (C_4H_{10})	–0.5
But-1-ene (C_4H_8)	–6.3
But-1-yne (C_4H_6)	–8.1
Chlorobutane (C_4H_9Cl)	78

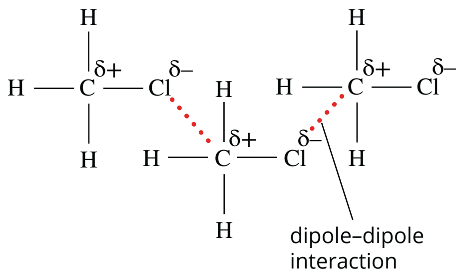


FIGURE 11.1.4 The carbon–chlorine bond in chloromethane is polar because the chlorine atom is more electronegative than the carbon atom. The presence of this permanent dipole allows for the formation of dipole–dipole attractions between chloromethane molecules.

Haloalkanes contain bonds that are quite polar. Chloromethane is a member of the haloalkane homologous series and contains a polar carbon–chlorine bond as shown in Figure 11.1.4. Like all alkanes, chloromethane contains weak dispersion forces between molecules. However, the presence of the carbon–chlorine dipole allows **dipole–dipole attractions** to also occur. Because the dipole–dipole attractions are stronger than the dispersion forces, the boiling points of the haloalkanes are generally higher than those of alkanes with a similar number of carbon atoms, as seen in Table 11.1.2 (page 321).

ℹ The addition of polar functional groups to a hydrocarbon increases the boiling point for molecules of a similar size when compared to purely non-polar families.

Solubility in water

The non-polar nature of alkanes, alkenes and alkynes makes them insoluble in water. You will recall from Unit 1 Chemistry that water molecules are polar and held together by strong **hydrogen bonds** (Figure 11.1.5). The weak dispersion forces between water molecules and hydrocarbon molecules are not strong enough to overcome the strong attraction between water molecules so the two substances remain separate and do not mix.

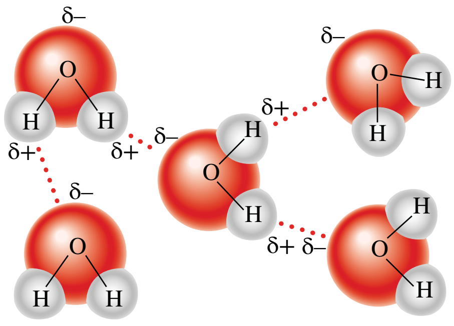


FIGURE 11.1.5 Water molecules are held to each other by hydrogen bonding.

For example, when hexane is added to water, it simply forms a layer on top of the water because hexane is less dense than water and the two liquids cannot dissolve in each other. Liquids that do not mix are said to be **immiscible**.

As a result of the polar halogen–carbon bond in haloalkanes, haloalkanes are slightly more soluble than hydrocarbons in water. However, the solubility is still very low because the overall influence of the dipole–dipole interaction is small. The influence of the **halogen** decreases as the length of the carbon chain increases. Many haloalkanes are denser than water and, unlike the hydrocarbons, these liquids settle to form a layer on the bottom when added to water.

Crude oil is a mixture of many different compounds. Most of these compounds are hydrocarbon compounds of varying lengths. While there are some alkenes in crude oil, many of the hydrocarbons are alkanes. Because alkanes are generally less dense than water, when crude oil spills occur at sea the crude oil floats on the surface, forming a thick insoluble layer. As the oil layer is moved by the waves of the sea, the oil can spread over many hundreds of square kilometres. The presence of the thick oil layer can have disastrous consequences for marine and bird life. Oil that reaches the shore, like the oil spill shown in Figure 11.1.6, has drastic effects on beaches and wildlife.

FIGURE 11.1.6 Oil spills at sea can contaminate shorelines and are very difficult to clean due to the lack of solubility of the oil in water. Other non-polar solvents or physical methods are required to disperse or remove the oil.

Solubility in organic solvents

Alkanes mix with other non-polar liquids such as alkenes and symmetrical haloalkanes. This is because the forces of attraction between molecules of these liquids are also weak dispersion forces and of similar strength to the alkane–alkane forces of attraction. Therefore, these liquids are **miscible**; that is, they are soluble in each other.

Many commercial cleaning agents contain non-polar liquids that are useful for removing oil stains. White spirit is a mixture of alkanes and other hydrocarbons obtained by the refining of crude oil. White spirit is a useful cleaning agent because it can dissolve other non-polar liquids, such as oils and greases. It is used as a solvent in aerosols and in the home as a degreasing solvent. White spirit is also used for cleaning paintbrushes and as a general cleaning agent (Figure 11.1.7).

FIGURE 11.1.7 White spirit contains a mixture of alkanes. It is a useful solvent for other non-polar liquids.

EXTENSION

A non-polar haloalkene

Tetrachlorethene is a solvent commonly used by commercial dry cleaners in Australia. It is also known as perchloroethene or 'perc'. This compound is a haloalkene as seen by the structure shown in Figure 11.1.8. The molecule contains polar carbon–chlorine bonds, but the molecule is symmetrical, so the dipoles cancel each other. This makes the overall molecule non-polar. The non-polar liquid can dissolve oil and grease from fabrics without the use of water or detergents. An advantage that chloroethene has over hydrocarbon solvents is that it is also non-flammable.

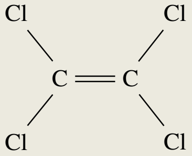


FIGURE 11.1.8 Tetrachlorethene is symmetrical and therefore non-polar. It is commonly used as a solvent in the dry-cleaning industry.

PHYSICAL PROPERTIES OF ALCOHOLS, CARBOXYLIC ACIDS, AMINES AND AMIDES

Compounds from the four homologous series **alcohols**, **carboxylic acids**, **amines** and **amides** will be considered together because their molecules contain functional groups that can form hydrogen bonds. The ability of molecules to form hydrogen bonds has a significant effect on their properties.

Boiling points

Hydrogen bonds are the strongest of the intermolecular forces and, as a result, molecules that can form hydrogen bonds generally exhibit higher boiling points. You can see in Table 11.1.3 that alcohols, carboxylic acids, amines and amides have higher boiling points than alkanes of similar molecular mass.

TABLE 11.1.3 Comparison of boiling points of compounds with different functional groups based on molecular mass

Homologous series	Compound	Formula	Molar mass (g mol^{-1})	Boiling point (°C)
Alkane	Butane	C_4H_{10}	58	–1
Alcohol	Propan-1-ol	C_3H_7OH	60	97.2
Carboxylic acid	Ethanoic acid	CH_3COOH	60	118
Amine	Propan-1-amine	$C_3H_7NH_2$	59	49
Amide	Ethanamide	CH_3CONH_2	59	210

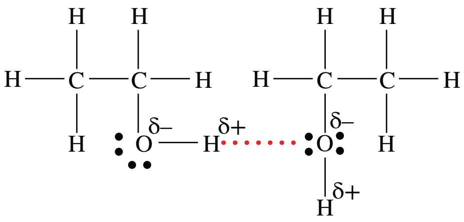


FIGURE 11.1.9 The red dotted line shows the hydrogen bonds that form between molecules such as ethanol that contain the polar hydroxyl functional group.

Boiling points of alcohols

The higher boiling points of the alcohols are due to the presence of hydrogen bonds between neighbouring alcohol molecules. In contrast, the only type of bonding present between non-polar alkane molecules is much weaker dispersion forces.

You will recall from Unit 1 Chemistry that oxygen is a more **electronegative** atom than hydrogen, so the oxygen–hydrogen bond in the hydroxyl functional group is a polar bond. Figure 11.1.9 shows how hydrogen bonding occurs between the partially charged hydrogen atom in the –OH group on one alcohol molecule and a non-bonding electron pair on the oxygen atom of a neighbouring alcohol molecule. The presence of the hydrogen bonds results in the higher boiling points observed.

Boiling points of amines and amides

The presence of highly polar nitrogen–hydrogen bonds in amine and amide molecules means that these molecules can also form hydrogen bonds. The formation of hydrogen bonds between amines and amides is illustrated in Figure 11.1.10.

In amines, the hydrogen bonds form between the non-bonding pair of electrons on the electronegative nitrogen atom and the partially positive hydrogen atom on another amine molecule. In amides, hydrogen bonds form between the non-bonding electron pairs on the oxygen atoms of one molecule and the partially positive hydrogen atom on a neighbouring molecule. The strength of the hydrogen bonding between molecules explains the relatively high boiling points of amines and amides when compared to hydrocarbon molecules of similar size.

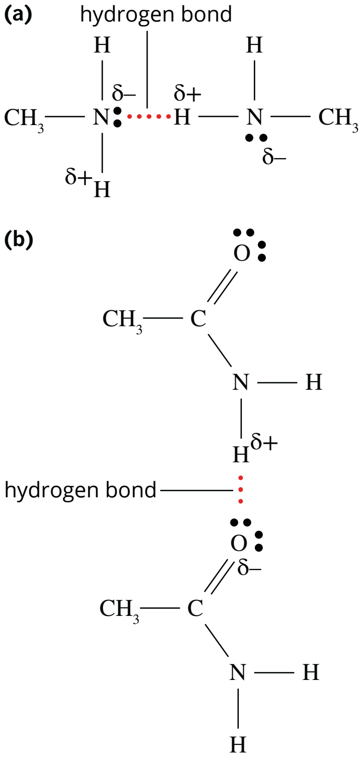


FIGURE 11.1.10 Hydrogen bonding between (a) amine molecules and (b) amide molecules.

Boiling points of carboxylic acids

Hydrogen bonding also has a marked effect on the boiling points of carboxylic acids. Figure 11.1.11 shows how two molecules of a carboxylic acid in the liquid state can form **dimers** in which two hydrogen bonds occur between the molecules.

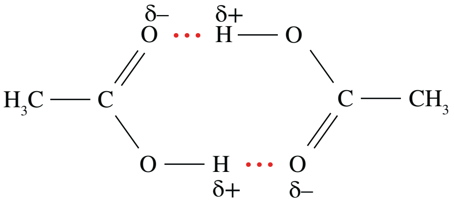


FIGURE 11.1.11 Hydrogen bonding between two ethanoic acid molecules results in the formation of a dimer.

The dimer produced is a stable species that has a molar mass that is double that of a single carboxylic acid molecule. The increase in size that results from the formation of the dimer increases the strength of the dispersion forces between one dimer and its neighbours. The higher dispersion forces combined with the hydrogen bonds between molecules results in the higher boiling point observed for carboxylic acids when compared to most other organic molecules of similar size.

Figure 11.1.12 highlights the higher boiling points of the carboxylic acid homologous series compared to alcohols.

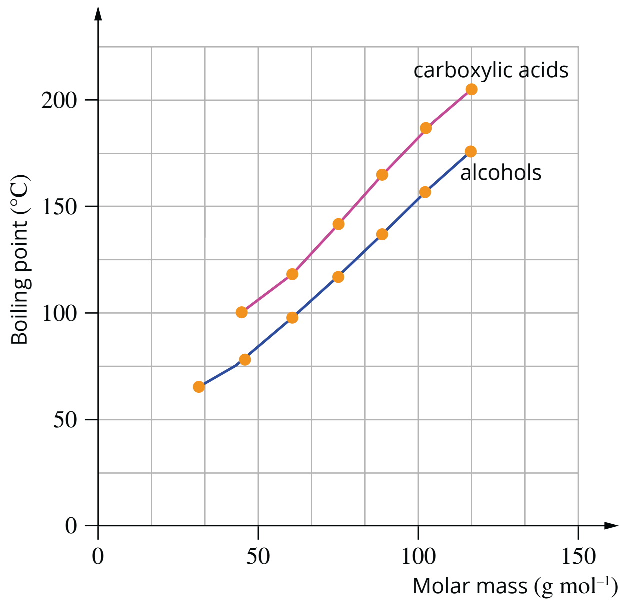


FIGURE 11.1.12 Boiling points of the carboxylic acid homologous series increases with increasing molar mass. The boiling points are higher than the boiling points of alcohols because of the formation of dimers stabilised by hydrogen bonds between molecules.

Effect of chain length on boiling point

The boiling points of alcohols, amines, amides and carboxylic acids increase as molar mass increases. For example, in alcohols the intermolecular hydrogen bonding between the –OH groups results in the higher boiling points. As the length of the hydrocarbon chain or 'tail' increases from one member of the homologous series to the next, the molar mass of the alcohols increases. With the increase in molecular size, the dispersion forces between molecules also get stronger. So the boiling points of alcohols increase as molar mass increases (Figure 11.1.12).

The three-dimensional structure of molecules can also affect the boiling point of a compound. In the case of alcohols, in addition to the impact of branching on the strength of dispersion forces, the position of the hydroxyl within the molecule affects the hydrogen bonding. Figure 11.1.13 shows molecular models for three isomers of butanol: butan-1-ol, butan-2-ol and 2-methylpropan-2-ol. These isomers are examples of **primary**, **secondary** and **tertiary alcohols**, respectively.

You can see from the models that the hydroxyl group becomes increasingly 'crowded' from the primary alcohol through to the secondary and tertiary alcohol isomers. The presence of the alkyl groups restricts a molecule's ability to form hydrogen bonds with other molecules. For this reason, the boiling points of these alcohols decrease in the sequence from primary to secondary to tertiary alcohol, as seen in Table 11.1.4.

TABLE 11.1.4 The boiling point of primary to secondary and tertiary alcohols with the formula C_4H_9OH

Alcohol	Type of alcohol	Boiling point (°C)
Butan-1-ol	Primary	118
Butan-2-ol	Secondary	100
2-Methylpropan-2-ol	Tertiary	82

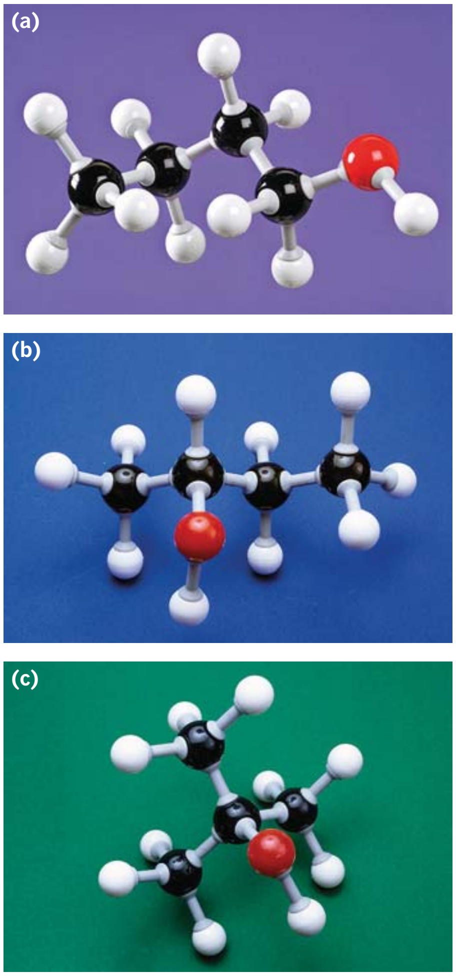


FIGURE 11.1.13 Molecular models of the three isomers of butanol: (a) butan-1-ol, (b) butan-2-ol, (c) 2-methylpropan-2-ol.

Solubility

Solubility in water

Small alcohols and amines dissolve well in water because hydrogen bonds can form between the polar functional groups of the molecules and adjacent water molecules. For alcohols, the hydrogen bonds form between the partially positive hydrogen atom of the hydroxyl group and the lone-pair electrons of an adjacent water molecule (Figure 11.1.14a). There is also attraction between the partially positive hydrogen within the water molecules and the lone-pair electrons on the alcohol. This is how ethanol dissolves in water in alcoholic drinks, such as beer or wine.

When amines interact with water molecules (Figure 11.1.14b), hydrogen bonds can form between the lone-pair electrons of the nitrogen and the partial positive hydrogen of an adjacent water molecule or between the hydrogen of an amine group and an oxygen of an adjacent water molecule.

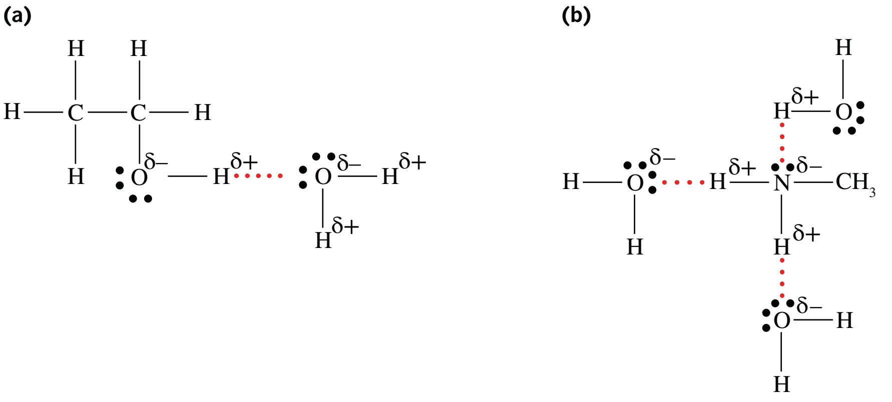


FIGURE 11.1.14 Hydrogen bonding between water molecules and (a) an ethanol molecule and (b) an amine molecule.

Small amide and carboxylic acid molecules are also soluble in water. When carboxylic acids dissolve in water, hydrogen bonding occurs between water molecules and both the C=O group and the –OH group, making these compounds more soluble than alcohols in water (Figure 11.1.15).

The high solubility of carboxylic acids and alcohols explains why they are frequently found in solutions, such as citric acid and vitamin C in orange and lemon juice (see Figure 11.1.16).

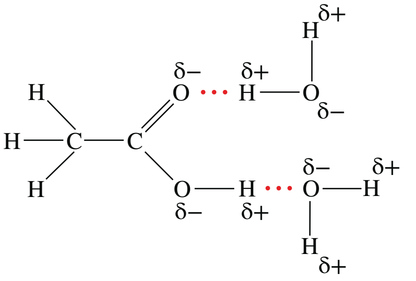


FIGURE 11.1.15 A small carboxylic acid molecule, such as ethanoic acid, is soluble in water due to hydrogen bonding between the carboxyl functional group and water molecules.

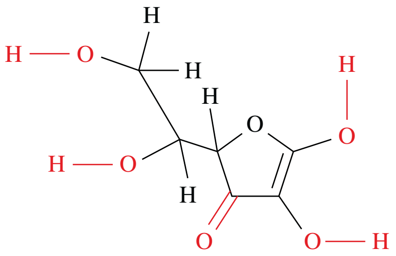


FIGURE 11.1.16 The presence of a large number of polar carbonyl and hydroxyl functional groups in a molecule of vitamin C makes it highly soluble in water. (Carbon atoms in the structure have been omitted for clarity.)

Solubility and chain length

The graph in Figure 11.1.17 shows the solubility of three alcohols. The solubility of alcohols, amines, amides and carboxylic acids in water decreases with increasing length of the carbon chain.

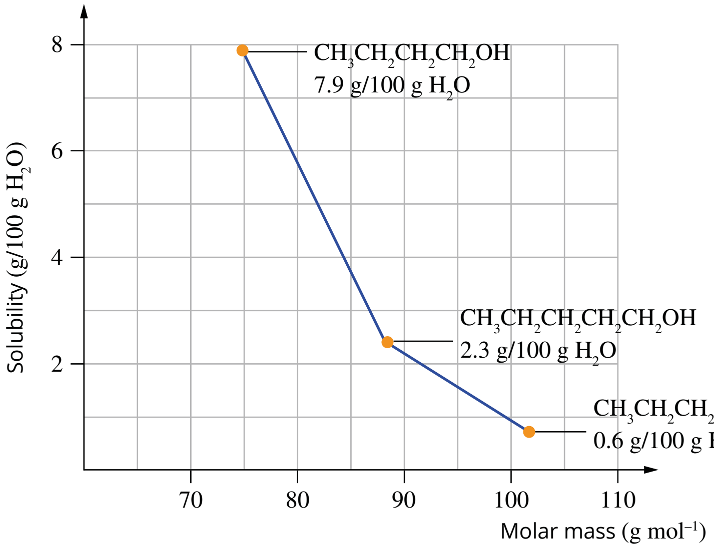


FIGURE 11.1.17 The solubility of alcohols in water decreases with increasing carbon chain length. This trend is also observed for other polar hydrocarbons such as amines, amides and carboxylic acids.

The longer hydrocarbon chains disrupt the hydrogen bonds between water molecules. While the hydroxyl group of an alcohol, for example, can form hydrogen bonds with water molecules, the hydrocarbon 'tail' cannot. Only dispersion forces occur between the hydrocarbon chain and water molecules, which are not as strong as hydrogen bonds, opposing the tendency for the molecule to dissolve. As the chain length increases, the non-polar nature of the molecule also increases and the alcohol becomes less soluble.

Solubility in organic solvents

In contrast to their solubility in water, alcohols become more soluble in organic solvents as they get larger. This is because organic solvents—such as hexane, benzene and toluene—are non-polar. Only relatively non-polar alcohols with long hydrocarbon chains dissolve well in non-polar solvents.

Small alcohols such as ethanol, which are very soluble in water, do not dissolve as well in organic solvents. The dispersion forces between their hydrocarbon chains and the solvent are not strong enough to disrupt the hydrogen bonds that hold the alcohol molecules together. Therefore, the alcohol molecules do not separate and disperse throughout the solvent.

The solubilities of amines, amides and carboxylic acids in organic solvents show similar trends to those of alcohols.

PHYSICAL PROPERTIES OF ALDEHYDES, KETONES AND ESTERS

Aldehydes, **ketones** and **esters** can be considered together because they are composed of molecules that are held together by dipole–dipole attractions. Their molecules cannot form hydrogen bonds with each other because they do not have a hydrogen atom bonded to an oxygen atom or a nitrogen atom in their molecules.

Boiling points

Aldehydes, ketones and esters all contain a carbon–oxygen double bond. Oxygen is much more electronegative than carbon, so the carbon–oxygen double bond is polar. This means that molecules of aldehydes, ketones and esters contain a permanent dipole, which can form dipole–dipole attractions with nearby molecules. The dipole–dipole interactions that arise between ketone molecules are shown in Figure 11.1.18.

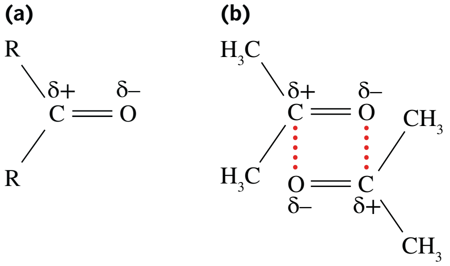


FIGURE 11.1.18 (a) A carbonyl bond is polar. (b) Dipole–dipole attractions between ketone molecules.

The strength of these dipole–dipole bonds between molecules give aldehydes, ketones and esters higher boiling points than similar sized alkanes. However, their boiling points are not as high as similar-sized alcohols because dipole–dipole bonds are not as strong as hydrogen bonds.

A comparison of the boiling points of members of each of these homologous series with that of an alkane is shown in Table 11.1.5.

TABLE 11.1.5 Comparison of boiling points of similar mass organic molecules from different homologous series

Homologous series	Semistructural formula	Molar mass (g mol^{-1})	Boiling point (°C)
Alkane	$CH_3CH_2CH_2CH_3$	58	–0.5
Alcohol	$CH_3CH_2CH_2OH$	60	97
Aldehyde	CH_3CH_2CHO	58	48
Ketone	CH_3COCH_3	58	56
Ester	$HCOOCH_3$	60	32

Effect of chain length on boiling point

As the hydrocarbon chain lengths of aldehydes, ketones and esters increase, their boiling points increase because the strength of the dispersion forces between molecules also increases. This trend is similar to that observed for alcohols and other compounds described earlier.

Solubility

Solubility in water

Molecules of aldehydes, ketones and esters cannot form hydrogen bonds with each other. However, Figure 11.1.19 shows how hydrogen bonds can form between a lone pair of electrons on the oxygen atom of the carbonyl group and the partially positive hydrogen atoms in water molecules. The strength of this interaction is enough to make small aldehydes, ketones and, to a lesser extent, esters quite soluble in water.

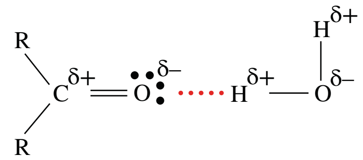


FIGURE 11.1.19 Hydrogen bonds form between the negatively charged electron pair on the oxygen atom in a carbonyl group and the positively charged hydrogen atom in a water molecule.

As for other soluble organic compounds such as alcohols, when the non-polar hydrocarbon chain length of aldehydes, ketones and esters increases, their solubility in water decreases.

Solubility in organic solvents

As the non-polar hydrocarbon chain length of aldehydes, ketones and esters increases, they become more soluble in non-polar solvents. This is opposite to the trend observed in water.

11.1 Review

SUMMARY

- The boiling points of organic molecules are determined by intermolecular forces. Dispersion forces are always present and there may also be dipole–dipole attractions or hydrogen bonds.
- The strength of dispersion forces between alkane molecules depends on the size and shape of the molecules.
- The only forces of attraction between molecules of the alkane, alkene and alkyne homologous series are dispersion forces. Molecules of haloalkanes are attracted to each other by dipole–dipole attractions, as well as by dispersion forces.
- Molecules of aldehydes, ketones and esters have polar carbonyl functional groups and they are attracted to each other by dipole–dipole attractions.
- Molecules of alcohols, carboxylic acids, amines and amides contain functional groups that can form hydrogen bonds with other molecules.
- Comparing molecules of similar size in different homologous series, it is generally true that their boiling points increase in the order: alkanes, alkenes, alkynes < aldehydes, ketones, esters < alcohols, carboxylic acids, amines, amides.
- The solubility of organic molecules in water is determined by the way the water molecules interact with the molecules of the solvent. This is affected by the polarity of functional groups and the length of the non-polar hydrocarbon tails.
- Alkanes, alkenes, alkynes and haloalkanes are insoluble in water.
- The smaller members of the aldehyde, ketone, ester, alcohol, amine and amide homologous series are generally soluble in water. Solubility rapidly decreases as the chain length increases.
- Alkanes, alkenes and alkynes are soluble in non-polar organic solvents.
- The solubility of aldehydes, ketones, esters, alcohols, amines and amides in non-polar organic solvents increases as the chain length of the molecules increases.

KEY QUESTIONS

1 Complete the following paragraph by filling in the gaps with the appropriate words.

Butane is a member of the ____________ homologous series. The forces of attraction holding butane molecules to each other are ____________. As the chain length of alkanes increases, their boiling points ____________. Alkanes are __________ in water. This is because the forces of attraction between water molecules and alkane molecules are __________ than the __________ __________ between water molecules.

2 Arrange the following compounds in increasing order of boiling point. Provide reasons for your answer.

$CH_3CH_2CH_2CH_3$, $CH_3CH(CH_3)CH_3$, $CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_3$, $CH_3CH_2CH_2CH_2CH_2CH(CH_3)CH_3$

3 Arrange the following compounds in increasing order of boiling point.

$CH_3CH_2CH_2CH_3$, $CH_3CH_2CH_2CH_2Cl$, CHCH, CH_3CHCH_2, $CH_3CH_2CH_2CH_2OH$, $CH_3CH_2CH_2COOH$

4 Identify each of the following pairs of compounds as either miscible or immiscible.

a Hexane and hex-2-yne

b Pentane and pent-1-ene

c Pent-1-yne and water

d 3-Bromobutane and 3-chloropentane

11.2 Viscosities and flashpoints of organic compounds

In the previous section you saw how two physical properties of organic compounds, boiling point and solubility, were affected by the structure and size of the molecules of the compounds. Two other physical properties of organic compounds—**viscosity** and **flashpoint**—are very important in the transport fuel and lubricating oil industries.

In this section you will see how the structures of organic molecules affect viscosity and flashpoint.

VISCOSITY

The viscosity of a liquid is its resistance to pouring or flowing. A liquid that pours slowly, such as honey, is said to be viscous or to have a high viscosity (Figure 11.2.1). Vegetable oil is less viscous than honey, but more viscous than water, and petrol is less viscous than all of these liquids.

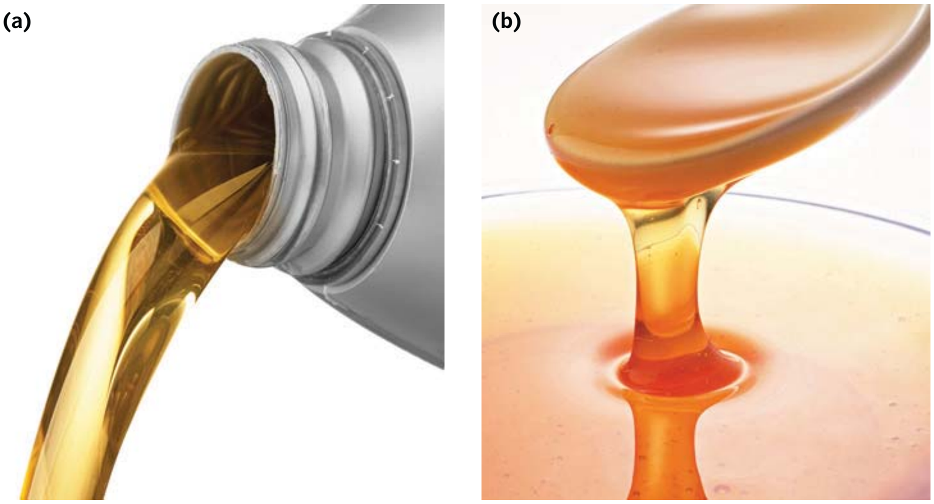


FIGURE 11.2.1 (a) Engine oil and (b) honey are both highly viscous liquids.

Honey is not a pure substance. It is made up of a mixture of different compounds. About 80% of honey is made up of glucose, fructose and other sugars. The molecules of these compounds have many hydroxyl groups (Figure 11.2.2) and so the molecules are held to each other by hydrogen bonds between these hydroxyl groups. The number and strength of these interactions is a major reason for the high viscosity of honey.

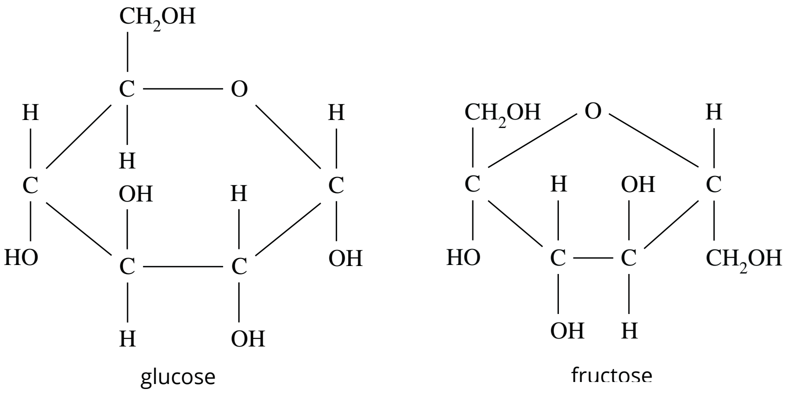


FIGURE 11.2.2 Glucose and fructose molecules contain many hydroxyl functional groups.

The viscosity of a liquid depends on the interactions between molecules. Like boiling point, viscosity increases as the forces of attraction between the molecules increase. As the chain length of organic molecules increases, the strength of dispersion forces between molecules also increases and, therefore, the viscosity increases.

ℹ The viscosity of a liquid depends on the interactions between molecules.

Table 11.2.1 shows different fractions obtained by the **fractional distillation** of crude oil. Crude oil is a mixture of hydrocarbons of different molar mass and chain length. During the fractional distillation process, molecules of approximately the same size are separated into different fractions. Molecules with 18–20 carbon atoms in their chains form fractions that are suitable for use as lubricating oils for motors.

TABLE 11.2.1 Fractions obtained from the fractional distillation of crude oil and their uses

Fraction	Composition	Boiling range (°C)	Uses
Gas	C_1–C_4	<30	Heating fuel, LPG
Petrol	C_5–C_{12}	30–250	Motor fuel/petrol
Kerosene	C_{12}–C_{16}	250–300	Jet and diesel fuel
Heating fuel oils	C_{16}–C_{18}	>300	Diesel fuel, heating fuel oil, material for cracking
Lubricating oils	C_{18}–C_{20}	>350	Lubrication, material for cracking
Paraffin waxes	C_{20}–C_{40}		Candles, wax
Bitumen	Above C_{40}		Roofing tar, road surfaces

The viscosity of motor engine oils enables them to protect an engine from wear. The high viscosity of oil makes it 'cling' to the metal. The oil forms a thin layer over bearings and gears, which prevents direct contact between metals and so reduces friction and wear (Figure 11.2.3). As the temperature of the engine increases, the viscosity of the engine oil decreases due to the disruption of the intermolecular forces. Engine oils must be specially formulated with a mixture of organic compounds of different viscosity and additives to produce oils that are effective in both cold and hot engines.

FIGURE 11.2.3 Lubricating oil protects gears from friction and wear.

FIGURE 11.2.4 A sample of pitch at room temperature appears solid and shatters when hit with a hammer.

CHEMFILE

Have you got the patience for slow science?

The longest running laboratory experiment in the world was set up in 1927 at the University of Queensland in Brisbane. The long-running 'pitch drop' experiment is designed to show that pitch, the name given to a mixture of highly viscous hydrocarbons, is actually a liquid. Pitch, otherwise known as bitumen (Figure 11.2.4), appears solid on first inspection and shatters if you strike it with a hammer.

Professor Thomas Purnell set up the pitch experiment as shown in Figure 11.2.5 by placing a sample of pitch into a funnel encased in a sealed container. He wanted to demonstrate to students that pitch was indeed a liquid—just a very, very viscous one. Over time, the pitch has settled and slowly flowed through the funnel producing a drop on average once every decade. The ninth drop was recorded in April of 2014.

Today bitumen is used extensively, forming the main component of road surfaces. Under normal conditions, the road surface appears solid. However, heating reduces the viscosity and road workers are able to work the pliable bitumen.

FIGURE 11.2.5 Professor Thomas Purnell set up the famous University of Queensland pitch drop experiment in 1927. Professor John Mainstone, shown here, oversaw the experiment for many years.

FLASHPOINT

When a candle burns, the solid candle wax must be converted to a vapour before it will ignite. The match used to light the candle first melts some of the wax soaked into the candlewick and vaporises it. It is the wax vapour, rather than the solid candle wax, that ignites and actually burns. Close observation of a burning candle, such as the one shown in Figure 11.2.6, confirms that this is the case.

Similarly, for liquid fuels such as petrol and methylated spirits, it is the vapour that burns, rather than the liquid. As the temperature of a liquid fuel increases, the concentration of vapour above the surface of the liquid rises. At a certain temperature, there will be enough fuel vapour mixed with the air for the fuel to burn. The temperature at which a vapour ignites is called the flashpoint.

FIGURE 11.2.6 Close observation of a candle shows that it is the candle-wax vapour rather than the solid wax that burns.

FIGURE 11.2.7 This apparatus measures the flashpoint of fuels. The fuel is heated steadily in a metal cup and, at intervals, a flame is brought above the liquid in the cup. The flashpoint is the lowest temperature at which the fuel will ignite when the flame is brought above it.

The flashpoint is defined as the lowest temperature at which a liquid forms sufficient vapour to ignite when an ignition source (such as a flame) is applied (Figure 11.2.7). The flashpoints of some common fuels are shown in Table 11.2.2.

TABLE 11.2.2 Flashpoints of some common fuels

Fuel	Flashpoint (°C)
Ethanol	16
Petrol	–43
Diesel	>52
Jet fuel	>38

ℹ The flashpoint of a liquid is the lowest temperature at which it will produce a vapour that will ignite to produce a flame when an ignition source is applied.

The flashpoints of hydrocarbon fuels, such as petrol, diesel and kerosene, are related to the boiling points of the fuels. The boiling points of hydrocarbons are a property of the carbon–carbon chain length of the hydrocarbon molecules in the fuels. This trend is also observed when measuring flashpoints (Table 11.2.3).

TABLE 11.2.3 Flashpoints of a selection of alkanes with increasing molecular size

Alkane	Number of carbon atoms in chain	Flashpoint (°C)
Butane	4	–76
Methylpropane	4	–83
Hexane	6	–7
Heptane	7	25
Octane	8	56

As you saw in section 11.1, the shape of a molecule can also affect a compound's physical properties. Methylpropane and butane are isomers, with a molecular formula of C_4H_{10}. The dispersion forces between methylpropane molecules are weaker, so it has a lower boiling point and lower flashpoint than butane.

While the low flashpoints of fuels make them useful in engines, their use also has dangers. That is why when putting petrol in a car, you should not smoke or use a naked flame of any kind. Gas supplies, including bottled gas, have additives with unpleasant odours, making it possible to detect and respond to gas leaks before an explosion occurs.

EXTENSION

Autoignition point

Another feature of fuels is their **autoignition point**, sometimes called the 'self-ignition point' or simply 'ignition point'. The autoignition point of a fuel is the lowest temperature at which it will spontaneously ignite in the absence of an external ignition source. Table 11.2.4 shows the autoignition points of some commonly used fuels along with their corresponding flash points.

TABLE 11.2.4 The autoignition temperatures of some fuels

Fuel	Flashpoint (°C)	Autoignition point (°C)
Ethanol	16	363
Petrol	–43	280
Diesel	>52	256
Jet fuel	>38	210

Car fuels need to have a low flashpoint so that they ignite readily in the combustion engine. Car fuels also need to have a relatively high autoignition point. If the autoignition point of a fuel is too low, there is a high risk the fuel will explode in the engine cylinder too early and reduce the efficiency of the engine.

Many fires in the home start in the kitchen. Some of these are due to pots or pans of cooking oil being left until the temperature of the oil reaches its autoignition point and the oil catches fire spontaneously (Figure 11.2.8).

FIGURE 11.2.8 An unattended pan of cooking oil can reach its autoignition point and self-ignite.

11.2 Review

SUMMARY

- The viscosity of a liquid is its resistance to flow.
- The viscosity of a homologous series of organic compounds increases as the length of the carbon chain in the molecules increases.
- The flashpoint of a liquid is the minimum temperature at which the vapour of the liquid ignites when an ignition source is applied to it.
- The flashpoint of an organic liquid increases as the carbon chain length of molecules of the compound increases.

KEY QUESTIONS

1 Arrange the following solutions in increasing order of viscosity.
  i A syrup made from two parts of water to one part of sugar
  ii A 240 mL cup of tea containing three teaspoons (12 g) of sugar
  iii Honey
  iv A 250 g can of soft drink that contains 25 g of sugar

2 The molecular structures of three organic compounds are shown in Figure 11.2.9.
  List the compounds in increasing order of viscosity.

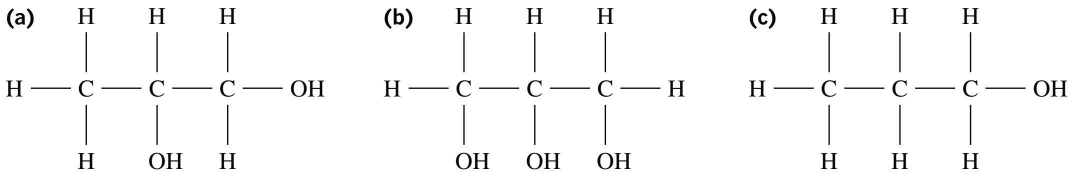


FIGURE 11.2.9 Molecular structures of (a) propan-1,2-diol, (b) glycerol and (c) propan-1-ol.

3 The hydrocarbon molecules in petrol typically have between 5 and 12 carbon atoms. The molecules in lubricating oil have more than 18 carbon atoms.
  Many lawnmowers have two-stroke engines, which use a fuel made by mixing lubricating oil with petrol. The mixture is added to the fuel tank and, as the fuel is taken into the engine, the oil in the mixture lubricates the moving parts of the engine.
  Which statement about the viscosity of two-stroke fuel is correct?
  A The viscosity of two-stroke fuel is greater than that of petrol.
  B The viscosity of two-stroke fuel is the same as that of lubricating oil.
  C The viscosity of two-stroke fuel is less than that of petrol.
  D The viscosity of two-stroke fuel is greater than that of lubricating oil.

4 By referring to Table 11.2.3 (page 333) of flashpoints, decide which one of the following would not ignite if a match flame were held just above the liquid.
  A Heptane at 20°C
  B Ethanol at 20°C
  C Hexane at 20°C
  D Petrol at 20°C

5 **a** Use the data provided in Table 11.2.5 to determine which of the following temperatures is a likely flashpoint for ethanal (CH_3CHO): –160°C, –39°C, 25°C or 56°C.
  b Explain your answer.

TABLE 11.2.5 The flashpoint temperatures of some organic compounds

Compound	Flashpoint (°C)
Ethane (C_2H_6)	–135
Ethanol (C_2H_5OH)	16.6
Ethanoic acid (CH_3COOH)	40

11.3 Chemical properties of alkanes, haloalkanes and alkenes

The properties and reactions of an organic compound are largely determined by the functional groups in the compound. As all members of a homologous series have the same functional group, the members of that group typically undergo reactions of the same type.

For example, alkenes are a homologous series of compounds that contain a carbon–carbon double bond. Vegetable oils are liquids that contain one or more carbon–carbon double bonds. Vegetable oils react with hydrogen gas to form semisolid substances that have a consistency suitable for spreading on bread. These semisolid products (for example, margarine) provide an alternative to **saturated** fats such as butter (Figure 11.3.1).

FIGURE 11.3.1 Vegetable oils are organic compounds that can be converted to margarine by reacting them with hydrogen gas.

Chemists who are involved in the synthesis of organic compounds are often required to prepare complex molecules from simpler starting materials. These chemists must have detailed knowledge of the reactions of functional groups in order to devise a way to produce the desired product.

In this section you will learn about some of the typical reactions that alkanes, alkenes and haloalkanes undergo and the reaction conditions required.

REACTIONS OF ALKANES

Combustion of alkanes in air

Although alkanes are relatively stable compounds and only undergo a few chemical reactions, they do burn readily in air in an exothermic reaction. As discussed in Chapter 1, alkanes are very good fuels.

Common fuels such as petrol, diesel and kerosene all contain mixtures of alkanes with other hydrocarbon molecules. The main component of natural gas is methane (CH_4), the simplest alkane.

The burning of hydrocarbon fuels in excess oxygen results in complete combustion, producing carbon dioxide and water vapour. The equation for the complete combustion of methane in air is:

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$$

Octane is a major component of petroleum. The reaction for the complete combustion of octane is:

$$2C_8H_{18}(g) + 25O_2(g) \rightarrow 16CO_2(g) + 18H_2O(g)$$

CHEMFILE

Burning ice

Large amounts of methane gas are stored around the world trapped as solid methane hydrate. These methane hydrates look very similar to ice with one main difference—they burn.

The burning ice is a result of the methane gas being released from the crystal structure of the ice as it melts (Figure 11.3.2).

Large deposits of methane hydrate are trapped in the Arctic regions of the Earth and deep in the oceans where low temperatures and high pressures trap methane. This source of methane is produced by the anaerobic decomposition of organic material by bacteria. The lattice structure of methane hydrate is shown in Figure 11.3.3.

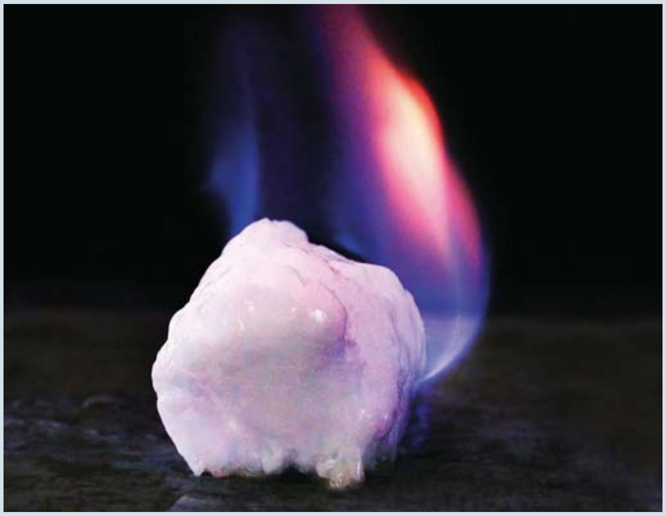


FIGURE 11.3.2 The combustion of blocks of methane hydrate give the appearance of burning ice. As the ice melts, methane gas is released from the lattice structure, providing the fuel for the combustion reaction.

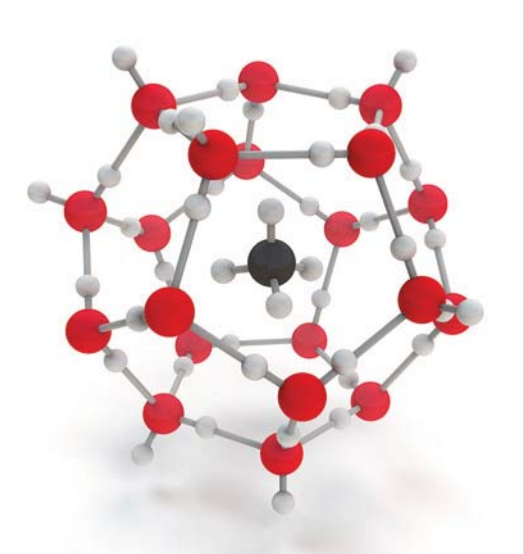


FIGURE 11.3.3 Structure of methane hydrate. Methane molecules are trapped inside the hexagonal structure of ice.

Oil companies have known of the existence of methane hydrate as far back as the 1930s. However, it is only now, with growing concerns over dwindling fossil fuel supplies and global warming, that scientists are endeavouring to find a way to safely use these large fuel sources.

One fear is that with rising ocean temperatures the deposits of methane hydrate throughout the oceans will melt, releasing large amounts of methane into the atmosphere. Methane is a major contributor to the enhanced greenhouse effect, so a release of this size is likely to accelerate the effects of global climate change.

Substitution reactions of alkanes

A **substitution reaction** occurs when an atom or functional group in a molecule is replaced or 'substituted' by another atom or group.

Alkanes are saturated hydrocarbons and undergo substitution reactions with halogens, such as chlorine and bromine, to produce haloalkanes. At room temperature and in the dark, a reaction vessel containing a mixture of an alkane such as methane and chlorine gas will not react. In order for the substitution reaction to occur, the reaction must be initiated by ultraviolet (UV) light.

The reaction between methane and chlorine in the presence of UV light is given by the equation:

$$CH_4(g) + Cl_2(g) \xrightarrow{\text{UV light}} CH_3Cl(g) + HCl(g)$$

For each molecule of chlorine gas (Cl_2) that reacts, a hydrogen atom on the alkane is replaced by a chlorine.

Chloromethane is said to be the substitution product of this reaction. As the reaction proceeds, the chloromethane product may continue to react with another chlorine molecule. If this occurs, the di-substituted product, dichloromethane (CH_2Cl_2) is produced.

If enough chlorine is available, further reactions can result in all four hydrogen atoms of the original methane molecule being substituted by chlorine atoms (see Figure 11.3.4 on page 338). The different substituted products have different boiling points so they may be separated from one another by fractional distillation.

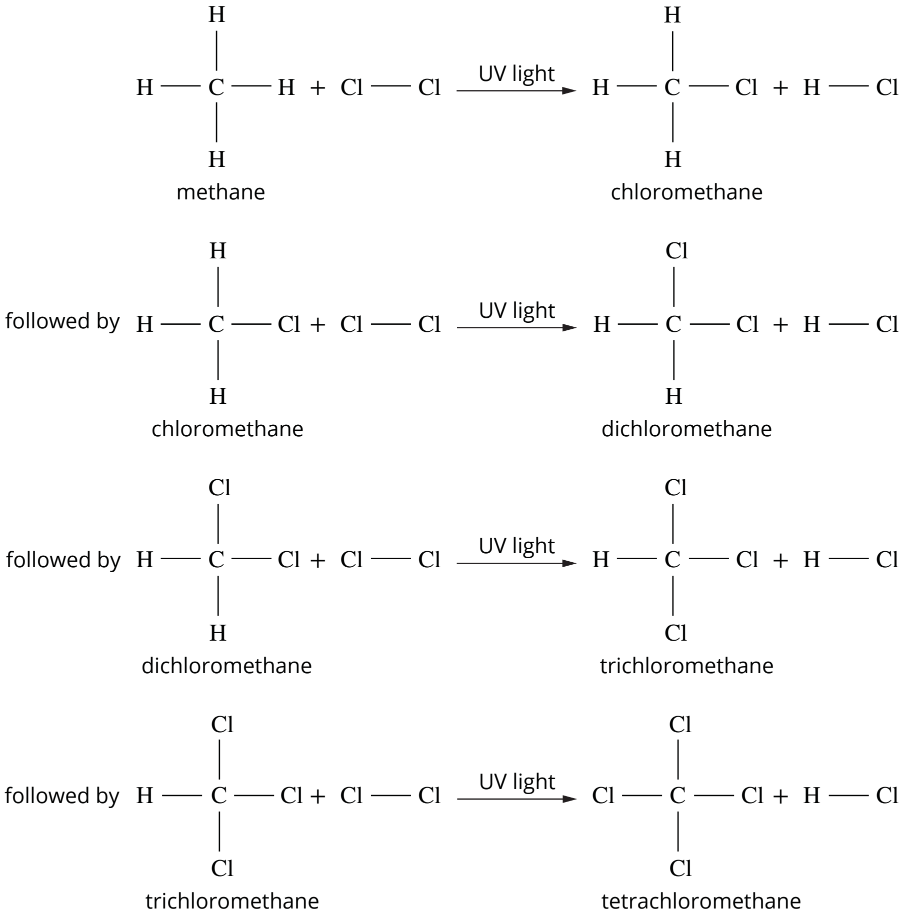


FIGURE 11.3.4 Substitution reactions between methane and chlorine.

Substitution reactions of alkanes using excess chlorine gas can result in a mixture of chloroalkane products with varying levels of substitution.

SUBSTITUTION REACTIONS OF HALOALKANES

Because of the large electronegativity difference between chlorine and carbon, the carbon–chlorine bond in a molecule of chloromethane is polar. Figure 11.3.5 shows that the carbon atom in the bond carries a partial positive charge and the more electronegative chlorine atom carries a partial negative charge.

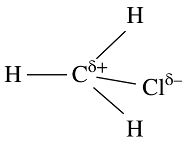


FIGURE 11.3.5 Structural formula of chloromethane. The electronegativity of carbon is 2.6 and that of chlorine is 3.2. This large difference in electronegativity results in a polar carbon–chlorine bond.

As a consequence of the highly polarised bond between carbon and chlorine, the partial positive charge on the carbon atom can be attacked by a negatively charged species such as a hydroxide ion. The new organic product is methanol. Because the chlorine atom of the chloroalkane has been 'swapped' for a hydroxyl group, this is a substitution reaction. Figure 11.3.6 shows the substitution reaction between chloromethane and hydroxide to form methanol.

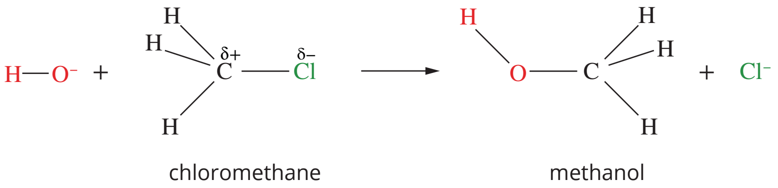


FIGURE 11.3.6 Reaction of a chloromethane molecule with a hydroxide ion to form methanol via a substitution reaction.

Chemists write the general unbalanced equation for a chloroalkane reacting with hydroxide ions in shorthand form as:

$$RCl \xrightarrow{OH^-} ROH$$

For all general equations, R represents an alkyl group. In general equations, it is standard that only the organic product is shown. It is important though that you remember the chloride ion (Cl^-) is generated as part of this substitution reaction.

It is also possible for haloalkanes to undergo substitution reactions with water to form alcohols. This reaction occurs much more slowly and requires a catalyst. In the reaction shown in Figure 11.3.7, ethanol is produced by a substitution reaction between chloroethane and water.

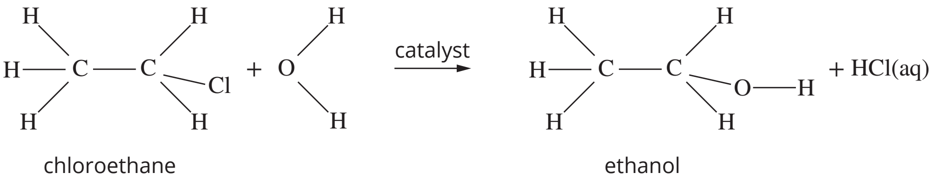


FIGURE 11.3.7 Reaction of chloroethane with water is a slower reaction and requires the use of a catalyst.

Ammonia also reacts with haloalkanes in substitution reactions. The product of these reactions is an amine.

The general equation for the formation of an amine by substitution with ammonia is:

$$RCl \xrightarrow{NH_3} RNH_2$$

Figure 11.3.8 shows the reaction of chloroethane with ammonia. The substitution reaction does not require a catalyst and produces ethanamine as the product. The production of propan-2-amine by reaction of 2-chloropropane with ammonia is also shown.

Other haloalkanes containing fluorine, bromine and iodine also undergo substitution reactions with strong bases and ammonia to produce the corresponding alcohols and amines.

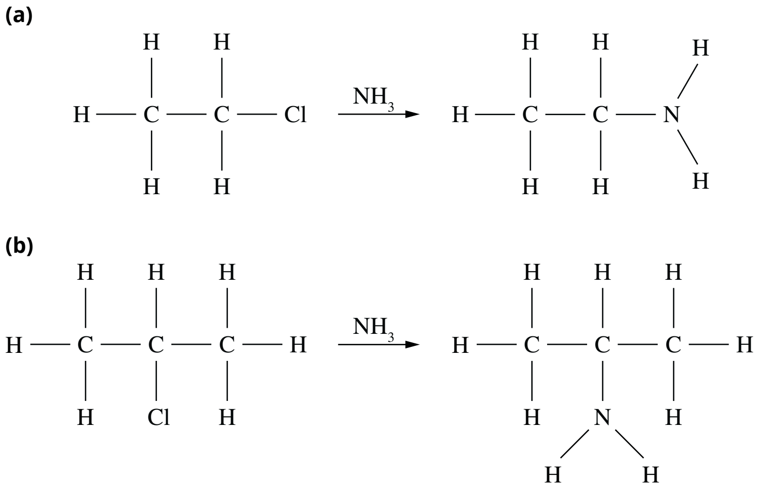


FIGURE 11.3.8 (a) Reaction of chloroethane with ammonia produces ethanamine. (b) Reaction of 2-chloropropane with ammonia produces propan-2-amine.

REACTIONS OF ALKENES

Combustion in air

You have previously learned that alkanes are rather unreactive, but they are good fuels and burn in oxygen to produce carbon dioxide and water. Alkenes also burn in an excess of oxygen to produce carbon dioxide and water. The equation for the combustion of ethene is:

$$C_2H_4(g) + 3O_2(g) \rightarrow 2CO_2(g) + 2H_2O(g)$$

Addition reactions of alkenes

The double carbon–carbon covalent bond in alkenes has a significant effect on the chemical properties of the homologous series. Alkenes are generally more reactive compounds, reacting more readily and with more chemicals than alkanes, which contain only single bonds. The reactions of alkenes usually involve addition of a small molecule to the double bond of the alkene. These reactions are called **addition reactions**.

During addition reactions:

- two reactant molecules combine to form one product molecule
- the carbon–carbon double bond becomes a single bond
- an **unsaturated** compound becomes saturated
- the atoms of the small molecule adding to the alkene are ‘added across the double bond’, so that one atom or group from the molecule forms a bond to each of the carbon atoms in the double bond. This can be seen in the reaction of hydrogen bromide with ethene in Figure 11.3.9.

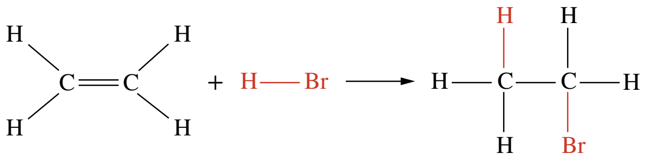


FIGURE 11.3.9 The reaction between ethene and hydrogen bromide. This is an example of an addition reaction between an alkene and a hydrogen halide.

When ethene reacts with hydrogen bromide an addition reaction occurs and bromoethane is the only product. During this reaction, the hydrogen atom from the HBr molecule forms a covalent bond to one carbon atom in the double bond of ethene and the bromine atom forms a bond to the other carbon atom. Unlike substitution reactions, there is no **inorganic** product formed. All the atoms in the reactants end up in the final product.

There are four different types of addition reactions of alkenes. These were all introduced in Unit 1 Chemistry and are explained in detail below.

Reaction of alkenes with hydrogen

Alkenes react with hydrogen gas in the presence of a metal catalyst such as nickel to form alkanes. This reaction is known as a hydrogenation reaction and forms a saturated alkane. The reaction shown in Figure 11.3.10 is hydrogenation of ethene with hydrogen gas to produce ethane.

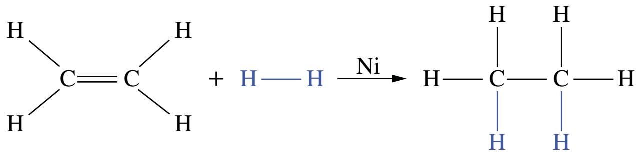


FIGURE 11.3.10 Addition reaction of ethene with hydrogen to form the corresponding saturated alkane, ethane.

The activation energy for the reaction is too high for the reaction to proceed at room temperature without a catalyst.

Reaction of alkenes with halogens

Figure 11.3.11 shows the reaction of ethene with bromine to form 1,2-dibromoethane. The halogen adds across the double bond of the molecule, so in the product there is one bromine atom attached to each carbon atom.

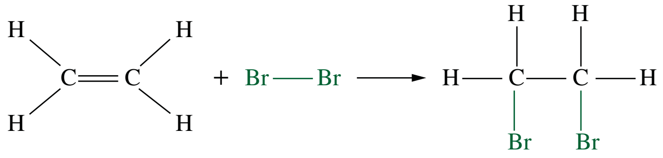


FIGURE 11.3.11 Addition reaction of ethene with bromine.

This reaction proceeds at room temperature without a catalyst. Other halogens such as Cl_2 and I_2 also undergo addition reactions with alkenes to form the corresponding di-substituted haloalkanes.

Bromine is often used as a test for the presence of a carbon–carbon double bond because of the ease and speed with which it reacts with an alkene. The orange colour of the bromine quickly disappears when it is mixed with an alkene (Figure 11.3.12).

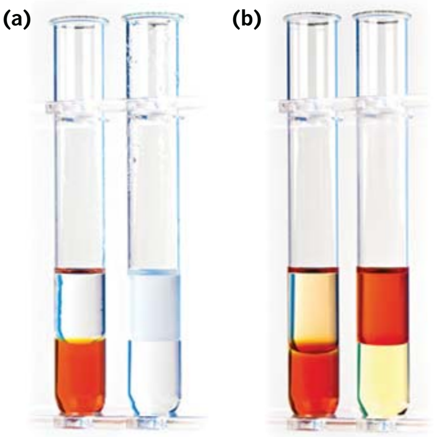


FIGURE 11.3.12 (a) When an alkene is added to aqueous bromine, the alkene reacts with the coloured bromine and the solution loses colour. (b) When an alkane is added to aqueous bromine, no addition reaction occurs and so the colour remains.

Reactions of alkenes with hydrogen halides

Just as you saw with the reaction of ethene and hydrogen bromide, but-2-ene reacts with hydrogen chloride, a **hydrogen halide**, in an addition reaction. Figure 11.3.13 shows the reaction of but-2-ene with hydrogen chloride to produce a single product, 2-chlorobutane. In this reaction, a hydrogen atom adds to one of the carbon atoms in the carbon–carbon double bond and a halogen atom adds to the other carbon atom.

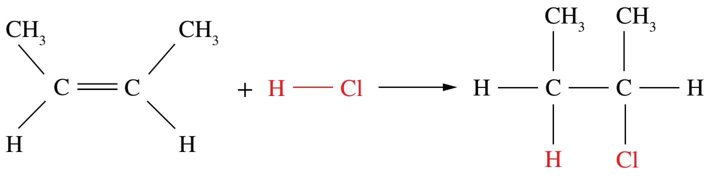


FIGURE 11.3.13 The addition reaction of but-2-ene with hydrogen chloride produces 2-chlorobutane.

However, as Figure 11.3.14 shows, when you react hydrogen chloride and but-1-ene, two products are possible.

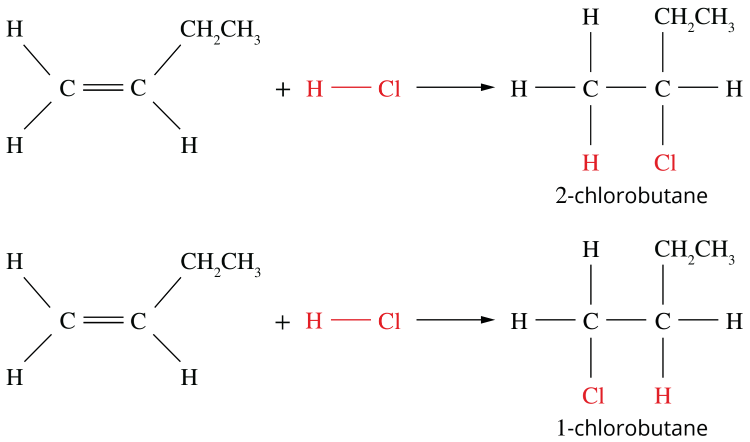


FIGURE 11.3.14 Addition reaction of but-1-ene with hydrogen chloride. Two isomers are possible as products.

The addition reaction can produce two isomers. In one product, the hydrogen atom from the hydrogen chloride molecule has been added to the carbon atom in the carbon–carbon double bond at the end of the but-1-ene molecule (C1). In the other product, the hydrogen atom has been added to a carbon atom at the other end of the carbon–carbon double bond (C2).

When you react an asymmetrical alkene such as but-1-ene with an asymmetrical reactant, isomers are produced. More of one isomer is usually produced than the other. The reasons for this are beyond the scope of this course and are not discussed here.

Reactions of alkenes with water

Alkenes react with water under specific conditions to form the corresponding alcohol. For example, ethanol can be produced by an addition reaction of ethene and water, using a catalyst to increase the rate of the reaction. Figure 11.3.15 shows the addition reaction of steam and ethene, using a phosphoric acid catalyst. This reaction is used extensively in industry for the production of ethanol.

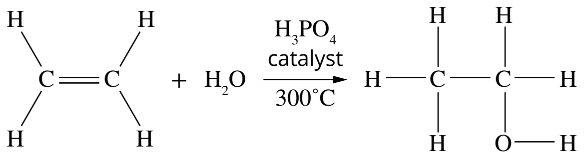


FIGURE 11.3.15 Addition reaction of ethene with water in the presence of a phosphoric acid catalyst.

The reaction is carried out at 300°C. The gaseous reactants are passed over a solid bed of the catalyst and gaseous ethanol is formed.

The reaction of ethene with steam is often described as a **hydration reaction**. Hydration reactions are reactions that involve water as a reactant. In the addition reaction, water is 'added' across the double bond. The reaction is used for the commercial manufacture of ethanol because it is a one-step process that uses little energy, apart from initial heating. The heterogeneous nature of the reaction system means it is easy for manufacturers to remove the product from the reaction mixture, leaving the catalyst intact.

Reactions that involve water as a reactant are referred to as hydration reactions.

Addition polymerisation

You will recall from Unit 1 Chemistry that alkenes can also react with each other in addition reactions to form **polymers** (meaning 'many units'). The reaction of ethene with itself to form polyethene, shown in Figure 11.3.16, is an example of an **addition polymerisation** process. The small molecule that undergoes the addition reaction, ethene, is called a **monomer** ('one unit'). Several thousand ethene monomers usually react to make one molecule of polyethene.

Large square brackets around the repeating unit, and the subscript *n*, are used to simplify the drawing of long polymer molecules. The value of *n* varies with each polymer molecule, but the average molecular chain formed may contain around 20 000 carbon atoms.

Note that the empirical formula of each monomer is the same as that of the polymer, since there are no other products in addition polymerisation reactions. When ethene polymerises, the double bonds break and new covalent bonds are formed between carbon atoms on nearby monomers. The polyethene formed does not contain any double bonds.

Other alkenes react in a similar way. For example, propene forms polypropene and butene forms polybutene.

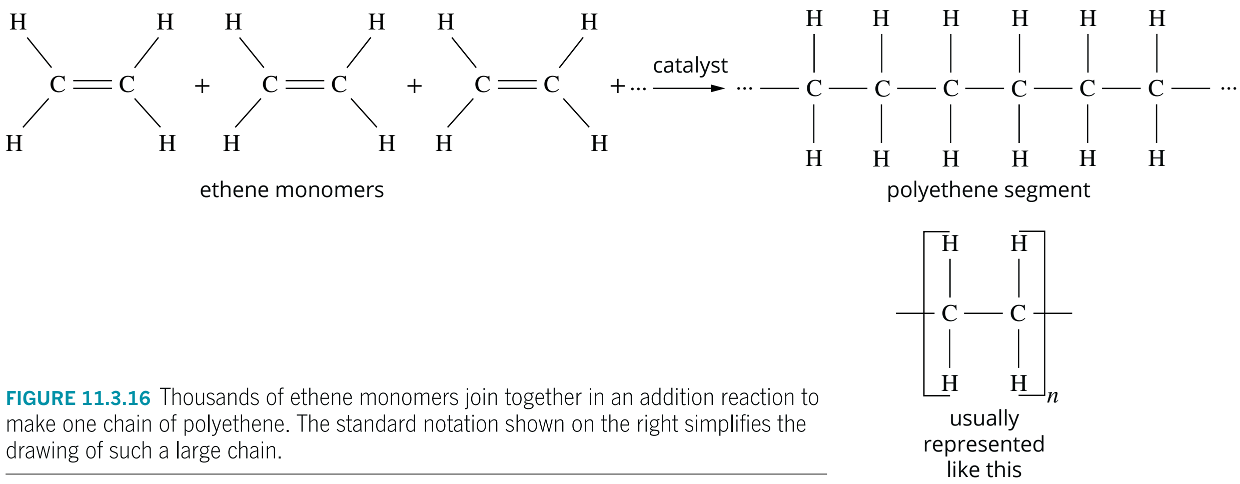


FIGURE 11.3.16 Thousands of ethene monomers join together in an addition reaction to make one chain of polyethene. The standard notation shown on the right simplifies the drawing of such a large chain.

CHEMFILE

Making margarine

The raw materials used to make many margarines include vegetable oils (Figure 11.3.17). Most vegetable oils are liquids and so cannot be spread on bread in the same way as butter.

Vegetable oils contain long hydrocarbon chains that are polyunsaturated; that is, they contain a number of carbon–carbon double bonds. If some of these double bonds are converted to single bonds, the molecules can pack more closely, resulting in stronger dispersion forces between the molecules and higher melting points. The liquids become semisolids and the product is then suitable for spreading.

One of the steps in making margarine from a vegetable oil usually involves reacting vegetable oils with hydrogen gas, using a metal catalyst such as nickel. In this step, some carbon–carbon double bonds react with the hydrogen in an addition reaction, and are converted into single bonds, as shown in Figure 11.3.18.

FIGURE 11.3.17 Margarines are made from vegetable oils that have been reacted with hydrogen to convert the liquids to semisolids.

Note that in the diagrams the carbon and hydrogen atoms have been omitted for clarity. Each 'kink' in the long chains represents a carbon atom with two hydrogen atoms attached. Where a double bond is shown, each carbon atom in the double bond has only one hydrogen atom attached to it.

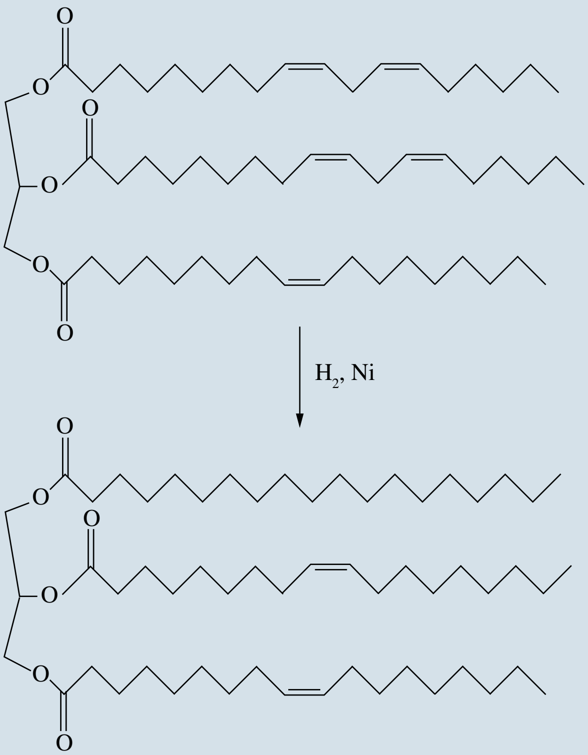


FIGURE 11.3.18 Hydrogenation of some of the carbon–carbon double bonds in a vegetable oil can convert it from a liquid into a 'spreadable' semisolid.

11.3 Review

SUMMARY

- Alkanes are generally unreactive, but they can undergo substitution reactions with halogens in the presence of ultraviolet light to produce haloalkanes.
- Haloalkanes undergo substitution reactions with:
  - sodium hydroxide to produce alcohols
  - ammonia to produce amines.
- Alkanes and alkenes burn in the presence of oxygen to produce carbon dioxide and water.
- Alkenes are unsaturated hydrocarbons. They undergo addition reactions to produce saturated compounds.
- Alkenes undergo addition reactions with:
  - hydrogen and a metal catalyst to produce alkanes
  - halogens to produce dihaloalkanes
  - hydrogen halides to produce haloalkanes
  - water and phosphoric acid catalyst to produce alcohols.
- Alkenes undergo addition polymerisation reactions to form polymers containing only carbon–carbon single bonds.

KEY QUESTIONS

1 Write balanced equations to represent the formation of all possible products of the reactions of chlorine with methane.

2 Name the products formed when ethene reacts with:

a hydrogen chloride
b chlorine
c water
d hydrogen.

3 Use structural formulas to write equations and name the products for the reactions of:

a but-1-ene with chlorine
b but-2-ene with hydrogen bromide.

4 Name the organic products formed when each of the following pairs of compounds react.

a Bromoethane and ammonia
b 2-Chlorobutane and sodium hydroxide
c 2-Bromopentane and water in the presence of a catalyst
d 2,3-Dibromobutane and aqueous sodium hydroxide

5 Write unbalanced equations for the production of:

a methanol from chloromethane
b propan-2-amine from 2-bromopropane
c propan-1-ol from 1-chloropropane.

11.4 Reactions of alcohols, carboxylic acids and esters

As you learned in section 11.3, alcohols can be produced by addition reactions of alkenes. Ethanol is the most widely used alcohol in society. You may have seen E10 fuel being sold at your local service station. The E10 classification indicates that the petrol contains 10% ethanol. In Brazil, the use of ethanol fuels is widespread with the percentage of ethanol being a minimum of 20–25% (Figure 11.4.1). Some cars have been developed to run on 100% ethanol.

FIGURE 11.4.1 Ethanol (*álcool*) is used as a fuel in Brazil and is cheaper than petrol (*gasolina*), although petrol delivers better fuel consumption.

The presence of the hydroxyl functional group means ethanol has very different properties from ethene or chloroethane. These properties make it useful across a wide variety of applications. Ethanol is a liquid at room temperature with high water solubility. It is widely used as a solvent in cosmetics and pharmaceuticals, as well as being the active ingredient in alcoholic drinks such as wine, beer and spirits. When consumed, ethanol acts as a depressant on the human body, slowing reactions and responses. Excess ethanol consumption also blocks the production of antidiuretic hormones, increasing urination and resulting in dehydration.

In this section, you will examine some of the common reactions that alcohols and other types of organic compounds undergo.

REACTIONS OF ALCOHOLS

Combustion of alcohols

Just like alkanes and alkenes, alcohols burn readily in air to form carbon dioxide and water as products. The equation for the combustion of ethanol is:

$$C_2H_5OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(g)$$

This is a highly exothermic reaction, so ethanol is used as a fuel. On a smaller scale, methylated spirits, which contains about 95% ethanol mixed with other chemicals, is used as a fuel for camping stoves. Some cooking techniques even make use of the burning of alcohol for drama and flavour. Figure 11.4.2 shows how the ethanol in the alcoholic drink, brandy, can also burn as it is added to enhance the flavour of a Christmas pudding.

FIGURE 11.4.2 Burning brandy is sometimes poured over a Christmas pudding. Brandy can contain as much as 40% ethanol.

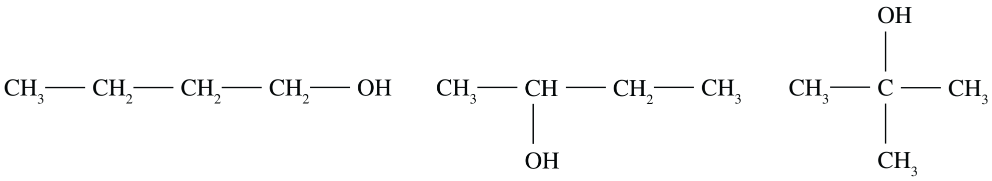
Oxidation of alcohols

The combustion of alcohols and other fuels can be classified as a type of oxidation–reduction (redox) reaction. Alcohols can also be oxidised by strong inorganic oxidising agents such as acidic solutions of potassium dichromate ($K_2Cr_2O_7$) and potassium permanganate ($KMnO_4$). The products of these oxidation reactions depend on the type of alcohol involved.

Alcohols can be classified (see Chapter 10) into three types—primary, secondary or tertiary—depending on the position of the hydroxyl group within the molecule.

- Primary alcohols are alcohols in which the –OH group is bonded to a carbon that is attached to only one alkyl group. These alcohols first oxidise to form aldehydes and then further oxidation forms the corresponding carboxylic acids.
- Secondary alcohols are alcohols in which the –OH group is bonded to a carbon that is bonded to two alkyl groups. These alcohols oxidise to form ketones.
- Tertiary alcohols are alcohols in which the –OH group is bonded to a carbon that is bonded to three alkyl groups. These alcohols are resistant to oxidation by inorganic oxidising agents and will not normally react.

You can see in Figure 11.4.3 how the different isomers of butanol can be classified as primary, secondary or tertiary alcohols. Chemists often use the symbols 1°, 2° and 3° as a shorthand way of indicating whether an alcohol is primary, secondary or tertiary, respectively.



butan-1-ol (primary alcohol)

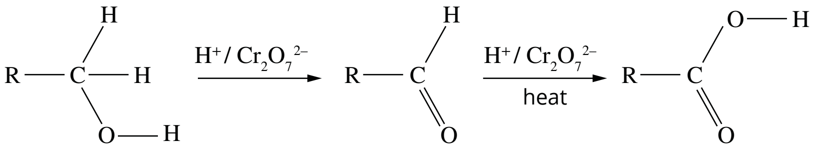
butan-2-ol (secondary alcohol)

2-methylpropan-2-ol (tertiary alcohol)

FIGURE 11.4.3 Structures of some primary, secondary and tertiary alcohols.

Oxidation of primary alcohols

Figure 11.4.4 shows how a primary alcohol can be oxidised to a carboxylic acid in two stages.



primary alcohol

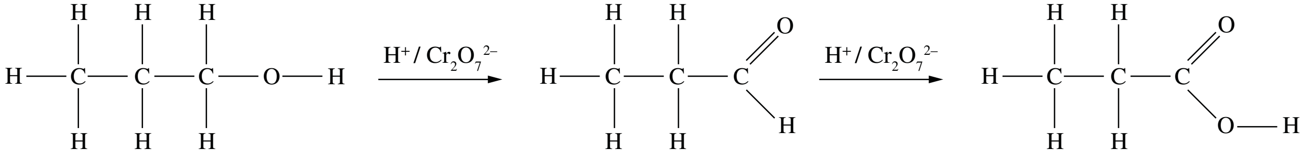
aldehyde

carboxylic acid

FIGURE 11.4.4 General equation for the oxidation of a primary alcohol.

In the first stage, the primary alcohol is oxidised to an aldehyde. In the second stage, further heating of the reaction mixture in the presence of the oxidising agent oxidises the aldehyde to a carboxylic acid.

The example in Figure 11.4.5 shows that propan-1-ol is oxidised first to propanal (an aldehyde) and then to propanoic acid (a carboxylic acid).



propan-1-ol

propanal

propanoic acid

FIGURE 11.4.5 Equations for the oxidation of the primary alcohol propan-1-ol.

If the desired product is an aldehyde rather than a carboxylic acid, milder conditions (lower temperatures and shorter reaction times) must be used and the aldehyde can be distilled from the reaction mixture as it is formed so that it is not oxidised further. Higher temperatures and longer reaction times favour the formation of the carboxylic acid over the aldehyde.

Aldehydes are produced as an intermediate in the oxidation of a primary alcohol to a carboxylic acid. If an aldehyde is the desired product, it can be distilled off as it forms to prevent further oxidation.

Oxidation of secondary alcohols

When secondary alcohols are oxidised by strong oxidising agents, such as solutions of acidified potassium dichromate ($K_2Cr_2O_7$) or potassium permanganate ($KMnO_4$), the corresponding ketones are produced. Figure 11.4.6 gives the general equation for the oxidation of secondary alcohols to ketones.

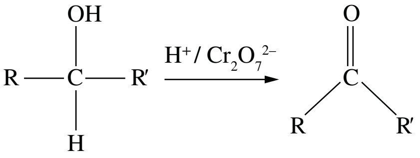


FIGURE 11.4.6 The general equation for the oxidation of a secondary alcohol. The R groups in the structures represent different alkyl groups.

Figure 11.4.7 gives the equation for the production of the ketone propanone by the oxidation of the secondary alcohol propan-2-ol.

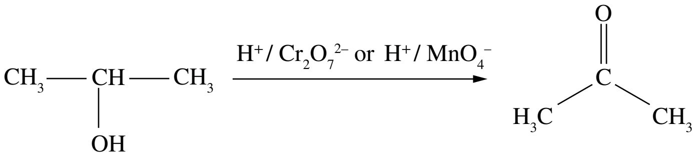


FIGURE 11.4.7 The secondary alcohol propan-2-ol can be oxidised to propanone.

Tertiary alcohols and oxidising agents

Tertiary alcohols are resistant to reaction with solutions of acidified potassium dichromate ($K_2Cr_2O_7$) or potassium permanganate ($KMnO_4$).

During the oxidation of alcohols, there is an increase in the number of C–O bonds and a simultaneous decrease (at the same carbon atom) in the number of C–H bonds. In tertiary alcohols, the carbon attached to the hydroxyl group does not have a C–H bond to break, so oxidation cannot occur at that carbon atom.

Tertiary alcohols are not normally oxidised by heating in the presence of a strong oxidant such as acidified dichromate or acidified permanganate.

Colour changes in oxidation reactions

The strong oxidising agents potassium dichromate and potassium permanganate are both highly coloured due to the presence of the transition metal elements chromium (Cr) and manganese (Mn).

A solution of dichromate ions in water is orange in colour. When this acidified dichromate solution is used to oxidise a primary or secondary alcohol, the dichromate is reduced to the chromium ion (Cr^{3+}), which is green in colour. This colour change from orange to green can be used as a qualitative test to indicate that oxidation of an organic compound has taken place. The colour changes observed for the reaction of primary, secondary and tertiary alcohols with potassium dichromate are shown in Figure 11.4.8.

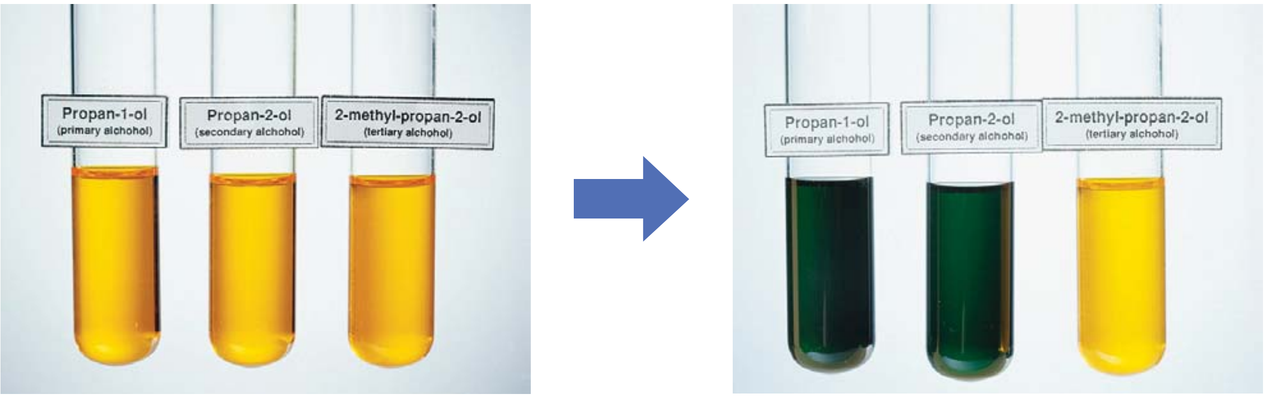


FIGURE 11.4.8 Solutions of the primary alcohol propan-1-ol and secondary alcohol propan-2-ol with acidified potassium dichromate change from orange to green on heating. Tertiary alcohols such as 2-methylpropan-2-ol will not react under these conditions so no change is observed.

A solution of acidified potassium permanganate reagent is a deep purple colour. When this solution reacts with primary or secondary alcohols, the manganese in the permanganate ion (MnO_4^-) is reduced to Mn^{2+}, which is colourless. Tertiary alcohols do not react so there is no change in the colour of the solution (Figure 11.4.9). You will look at how potassium dichromate and potassium permanganate are used in redox titrations as indicators in Chapter 14.

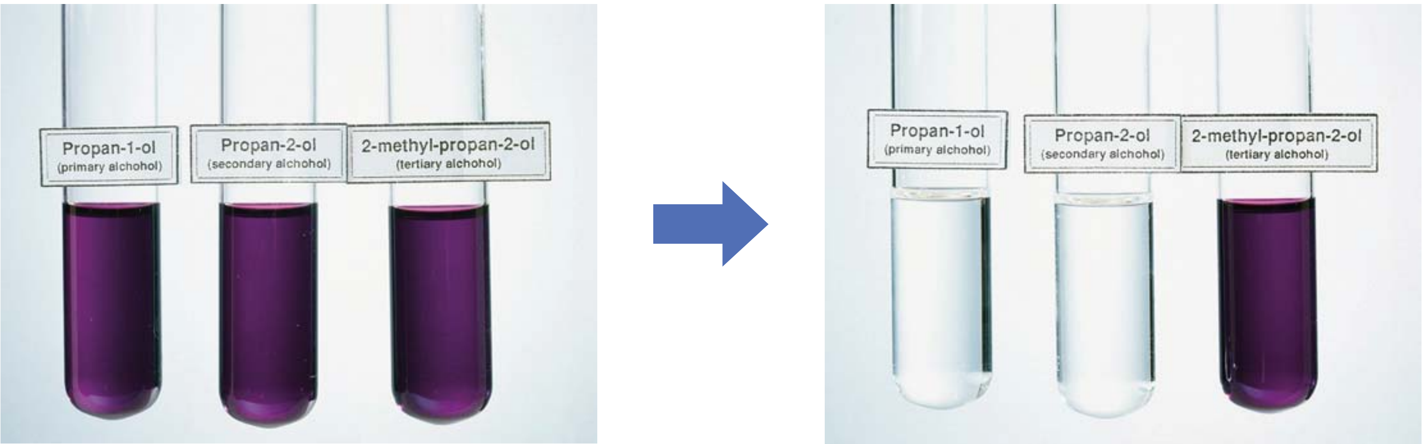


FIGURE 11.4.9 The strong oxidising agent potassium permanganate is deep purple in colour. On reaction with primary and secondary alcohols, the colour changes from purple to colourless. The tertiary alcohol is resistant to oxidation under these conditions and does not react, so the solution does not change colour.

Table 11.4.1 summarises the reactions of primary, secondary and tertiary alcohols with an acidified solution containing dichromate or permanganate ions.

TABLE 11.4.1 Summary of the oxidation reactions of primary, secondary and tertiary alcohols with acidified dichromate solution or acidified permanganate solution

Type of alcohol	Products
Primary (1°)	Mild conditions produce aldehydes. Higher temperatures and longer reaction times produce carboxylic acids.
Secondary (2°)	Ketones
Tertiary (3°)	No products because tertiary alcohols are resistant to oxidation by these oxidising agents.

REACTIONS OF CARBOXYLIC ACIDS

Molecules that contain carboxylic acids are common in the natural world and are present in most plants. Solutions of carboxylic acids taste sour. The sour taste of vinegar, lemons, yoghurt, rhubarb and most unripe fruits is due to the presence of carboxylic acids.

When fruits and berries like the blackberries in Figure 11.4.10 ripen, complex reactions take place. These include the conversion of carboxylic acids to other compounds. In some of these reactions, carboxylic acids react with alcohol molecules to produce esters. Esters give many fruits their characteristic aromas and tastes.

FIGURE 11.4.10 The ripening of blackberries involves many chemical reactions, including the conversion of carboxylic acids to esters.

Ionisation in water

You will remember from Chapter 8 that ethanoic acid is a weak acid and only ionises to a small extent in water to form hydronium ions. Other carboxylic acids react with water in a similar way.

The reaction of a carboxylic acid with water is a reversible process so the equation for ionisation is written using equilibrium arrows. The equation for the ionisation of ethanoic acid in water is:

$$CH_3COOH(aq) + H_2O(l) \rightleftharpoons CH_3COO^-(aq) + H_3O^+(aq)$$

The partial ionisation of carboxylic acids is because the equilibrium position of the reaction favours the reactants.

Reactions of carboxylic acids with alcohols

Reactions that involve the combination of two reactants and the elimination of a small molecule, such as water, are called **condensation reactions**. Esters are made by a condensation reaction between a carboxylic acid and an alcohol. A condensation reaction in which an ester is formed is also known as an **esterification reaction.**

For example, the ester ethyl ethanoate can be produced by gently heating a mixture of ethanol and pure ethanoic acid with a trace amount of sulfuric acid. The sulfuric acid acts as a catalyst. As well as the desired ester, water is a product.

The general equation for the esterification reaction involving a carboxylic acid and an alcohol is shown in Figure 11.4.11. Two examples of esterification reactions are also shown.

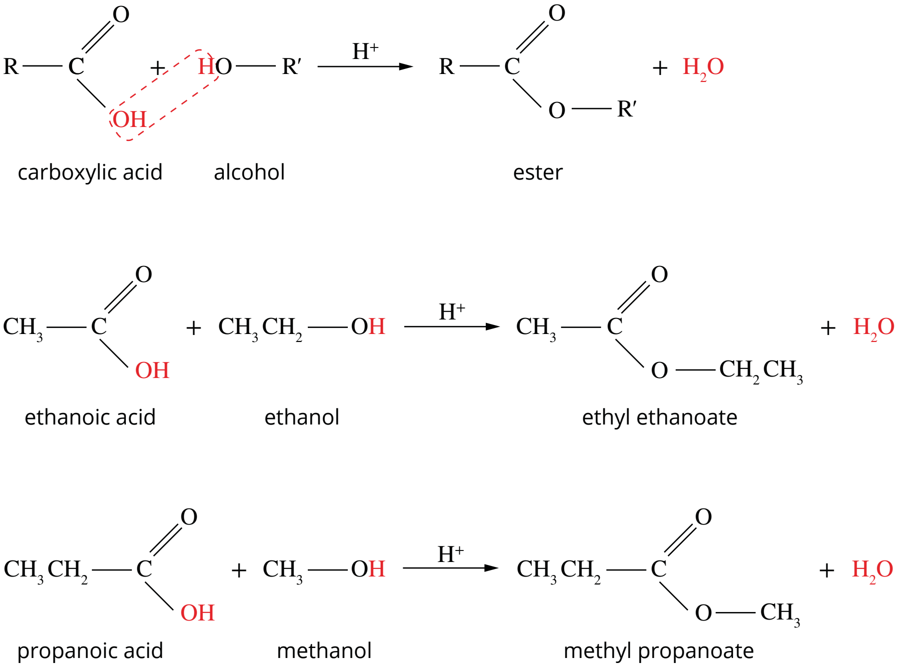


FIGURE 11.4.11 Esterification reactions occur when alcohols are heated with carboxylic acids and a small amount of sulfuric acid as a catalyst. The top reaction shows the general equation for esterification. Two specific examples are also shown: ethanoic acid with ethanol and propanoic acid with methanol.

In the esterification reaction, it is the hydrogen atom from the hydroxyl group of the alcohol and the –OH group from the carboxylic acid that combine to form water, which is the molecule eliminated in this condensation reaction.

As you learned in Chapter 10, the first part of the name of an ester is derived from the name of the alcohol from which it was made. The second part of the name is derived from the name of the carboxylic acid from which it was made. Therefore, the name of the ester formed from methanol (an alcohol) and propanoic acid (a carboxylic acid) is methyl propananoate.

CHEMFILE

Aspirin, an ester derived from a herbal remedy

Pharmaceutical products are often developed from substances found in a plant that has been used as a traditional medicine. For example, the origin of the mild painkiller aspirin is a naturally occurring substance called salicin, found in the leaves and bark of willow trees and in the herb meadowsweet.

As long ago as 400 BCE, the Greek physician Hippocrates (Figure 11.4.12) recommended the use of an infusion of willow leaves and bark to assist in childbirth and relieve other aches and pains. It wasn't until 1829 that the active ingredient, salicin, was identified and isolated.

It is now known that the body converts salicin to salicylic acid and this is the active substance that helps to reduce fever and acts as a painkiller. Pure salicylic acid can be hard to ingest and causes stomach irritation.

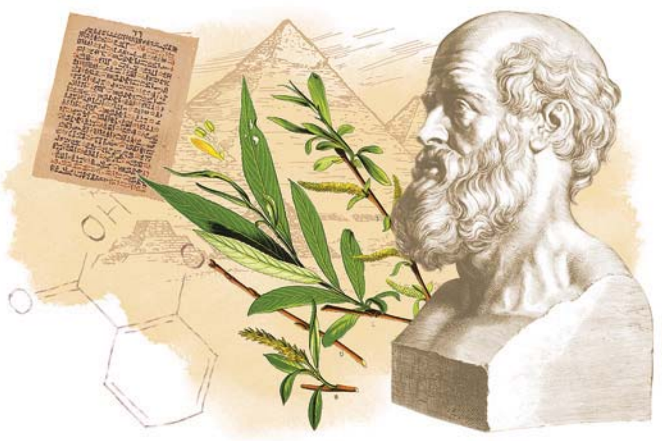


FIGURE 11.4.12 In 3000–1500 BCE willow was used as a medicine by ancient civilisations such as the Sumerians and Egyptians. In Greece, in about 400 BCE, Hippocrates administered willow leaf tea to people suffering pain.

In 1897, Felix Hoffmann replaced the hydroxyl functional group on salicylic acid with an ester functional group to form acetylsalicylic acid, later named aspirin, which was much gentler on the mouth and stomach than salicylic acid.

The preparation of aspirin is a relatively simple process. It has one main step in which the hydroxyl functional group of a salicylic acid molecule reacts with the carboxylic acid functional group of an ethanoic acid molecule in a condensation reaction as shown in Figure 11.4.13. The product, aspirin, has properties that are quite different from those of either of the two reactant molecules.

Although this reaction can be easily carried out in a laboratory, the yield is quite low. A more complex reaction is used to produce aspirin on an industrial scale.

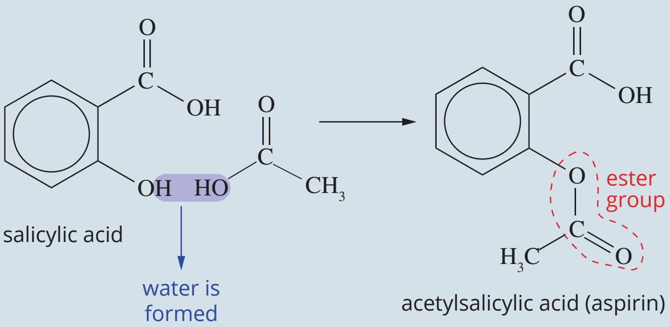


FIGURE 11.4.13 Aspirin can be made from salicylic acid and ethanoic acid. The process involves a reaction between hydroxyl and carboxyl functional groups to form an ester.

HYDROLYSIS OF ESTERS

The condensation reaction between carboxylic acids and alcohols is a reversible reaction. You can see in Figure 11.4.14 that esters can react with water to form a carboxylic acid and an alcohol. Reactions of this type are described as **hydrolytic reactions**, or simply **hydrolysis**. This reaction is catalysed by an alkali or dilute acid.

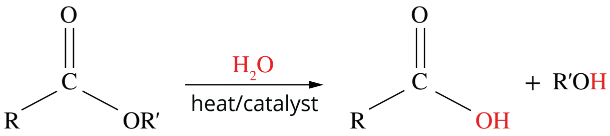


FIGURE 11.4.14 General equation for the hydrolysis of an ester.

Figure 11.4.15 shows the equation for the hydrolysis of ethyl propanoate to form ethanol and propanoic acid using an acid catalyst.

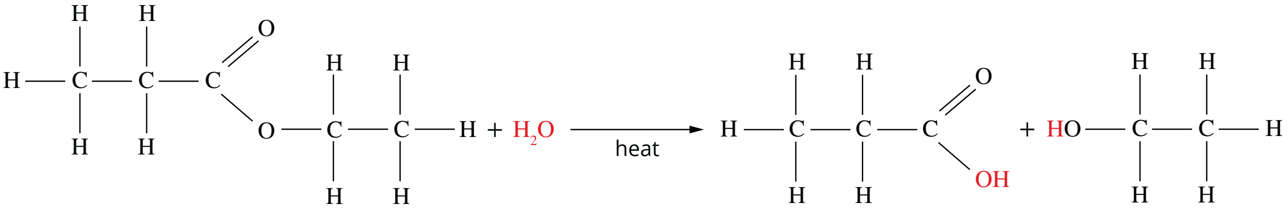


FIGURE 11.4.15 Equation for the acid-catalysed hydrolysis of ethyl propanoate to produce propanoic acid and ethanol.

When the hydrolysis of an ester is catalysed by an alkali such as sodium hydroxide, the products are an alcohol and the sodium salt of the carboxylic acid. The sodium salt can be easily converted to the carboxylic acid by adding dilute acid solution, such as hydrochloric acid.

Esters hydrolysed by metal hydroxides form a salt of the carboxylic acid. Addition of excess acid regenerates the protonated carboxylic acid.

CHEMISTRY IN ACTION

Saponification—the manufacture of soap

Traditionally, soap was made by heating an animal fat or vegetable oil with a strong alkali, such as sodium hydroxide solution. Fats and oils are triglycerides—ester molecules made from a combination of a glycerol molecule and three molecules of long-chain carboxylic acids called **fatty acids**. This reaction can be easily carried out using equipment you will find in your school laboratory (Figure 11.4.16).

When triglyceride molecules are heated with sodium hydroxide, the three ester links in the triglyceride are hydrolysed. The equation for this reaction is shown in Figure 11.4.17. The products of the hydrolysis are glycerol and the sodium salts of the three fatty acids. This process is called **saponification** and the sodium salts are the main components of soap.

The metal hydroxide used as an alkali can alter the effects of the soap produced. The fatty acid sodium salts produced when sodium hydroxide is used tend to be solids at room temperature. However, if potassium hydroxide is used, the fatty acid potassium salts produce a liquid soap.

FIGURE 11.4.16 Making soap from vegetable oil and sodium hydroxide solution is a relatively easy reaction to perform in the school laboratory.

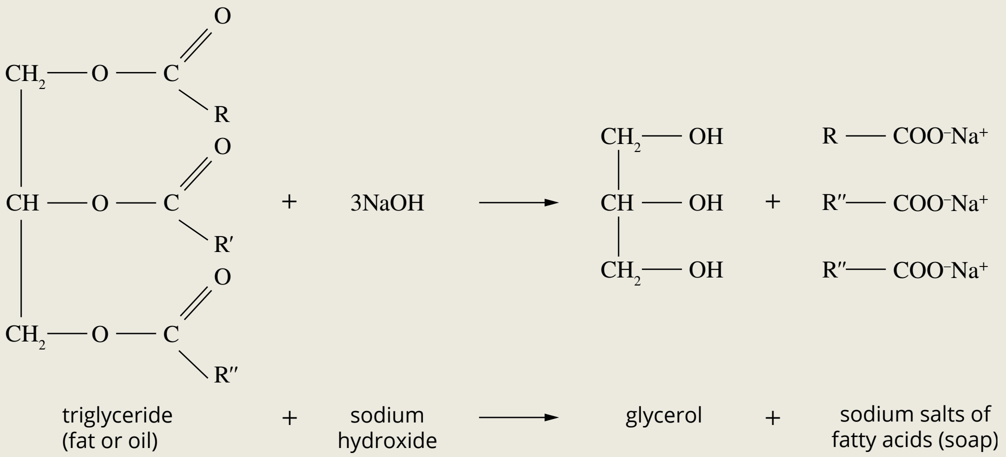


FIGURE 11.4.17 The alkaline hydrolysis of a triglyceride molecule to form glycerol and soap.

REACTIONS OF CARBOXYLIC ACIDS TO FORM AMIDES

Primary amides ($RCONH_2$) can be prepared by the reaction of a carboxylic acid with ammonia. In Figure 11.4.18, you can see the production of ethanamide from ethanoic acid and ammonia. The reaction is a condensation reaction similar to the one you saw between a carboxylic acid and an alcohol to form an ester. A water molecule is eliminated during the reaction.

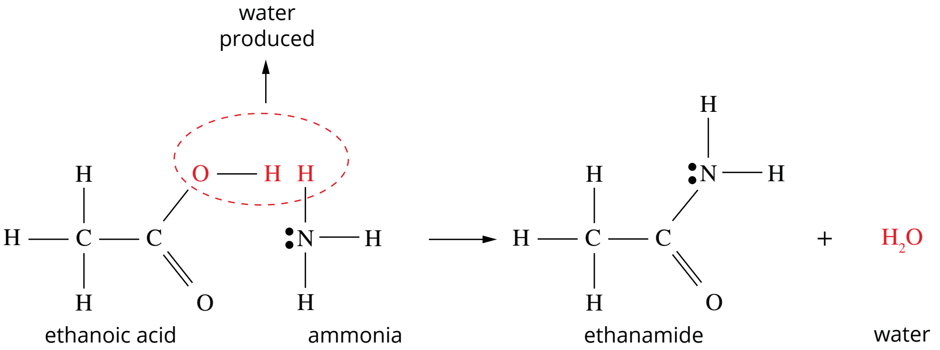


FIGURE 11.4.18 Reaction of ethanoic acid with ammonia to produce the primary amide ethanamide. Note the formation of the amide functional group, $RCONH_2$.

Secondary amides have the general formula RCONHR´, where R and R´ represent alkyl groups. Secondary amides are formed when carboxylic acids react with primary amines. An amide link is formed in this reaction.

You can see in Figure 11.4.19 that the formation of a secondary amide is also a condensation reaction that produces a water molecule. The hydrogen of the primary amine is lost and combines with the –OH from the carboxylic acid. A new covalent bond is formed between the carbon of the carboxylic acid and the nitrogen of the primary amine.

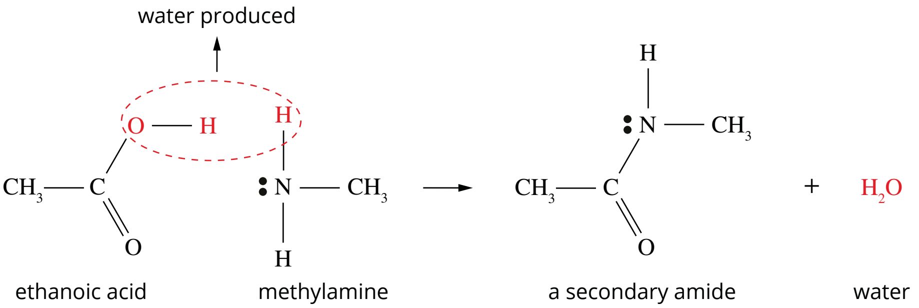


FIGURE 11.4.19 Formation of a secondary amide—reaction of ethanoic acid and methylamine to form the secondary amide *N*-methylethanamide.

11.4 Review

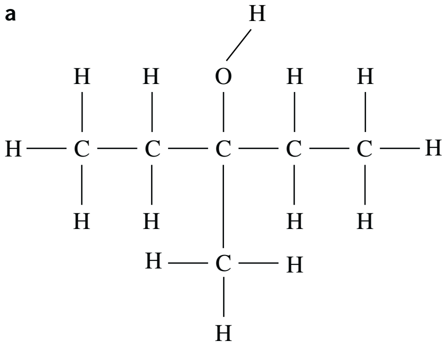
SUMMARY

- Alcohols react with oxidising agents such as acidified solutions of dichromate ions and permanganate ions in different ways.
  - Primary alcohols are oxidised first to aldehydes, which may be oxidised further to carboxylic acids.
  - Secondary alcohols are oxidised to ketones.
  - Tertiary alcohols are resistant to oxidation by these oxidising agents.
- Carboxylic acids can react with alcohols in the presence of an acid catalyst to produce esters.
- Esters can be hydrolysed by acids or alkalis to produce alcohols and carboxylic acids or their sodium salts, respectively.
- Carboxylic acids react with ammonia and amines to form amides.
- Each of the different types of reactions you have studied in this section can be represented by chemical equations.

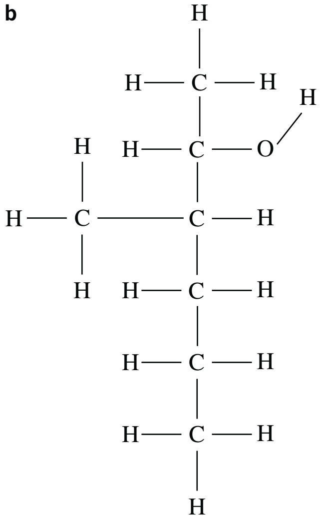
KEY QUESTIONS

1 Identify each of the following alcohols as primary, secondary or tertiary.

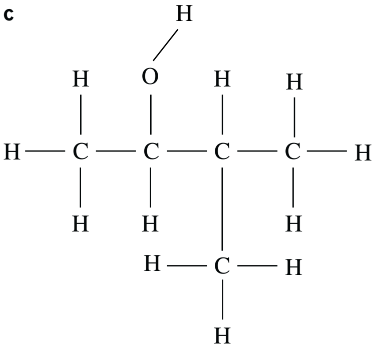
a



b



c



2 Pentan-3-ol, 2-methylbutan-2-ol and pentan-1-ol are all isomers of $C_5H_{12}O$.

a Write an equation for the complete combustion of $C_5H_{12}O$.

b Identify each isomer as a primary, secondary or tertiary alcohol.

c For each isomer, write the equation (using structural formulas) for all the reactions that would occur if the alcohol was heated with acidified potassium permanganate solution. Describe any colour changes that would be observed.

3 **a** What reaction conditions are required for the hydrolysis of an ester?

b Give the name of the products that would be formed from the acid hydrolysis of each of the following esters.

i $CH_3CH_2CH_2CH_2COOCH_3$

ii $CH_3COOCH_2CH_2CH_3$

iii $CH_3CH_2COOCH_2CH_2CH_2CH_2CH_2CH_3$

4 Complete the following sentences by filling in the blanks with the appropriate terms.

When pentanoic acid reacts with ammonia, the organic product ____________is formed. The other product in this reaction is ___________. This is an example of a ___________ reaction.

5 Draw and name the products of the reaction between:

a methyl butanoate and sodium hydroxide solution. If an acid was added, what additional product would form?

b ammonia and propanoic acid

c ethanol and propanoic acid, using concentrated sulfuric acid as a catalyst

d butanoic acid and ammonia.

11.5 Reaction pathways

FIGURE 11.5.1 Ibuprofen is the analgesic (pain reliever) found in many commercially available products.

Organic chemists are highly skilled at developing compounds that have exactly the right properties needed for a particular purpose. These may be new pharmaceuticals, polymers or nano-materials. Once the desired compound has been identified, chemists must devise a way to make it. Chemists have to design an efficient method for converting readily available starting materials—often alkenes or alkanes—into the more complex product they want.

Modern chemists are also interested in devising environmentally friendly synthetic routes. These pathways are designed to minimise waste, use 'greener' solvents, require less energy, and help to preserve the world's resources. The preparation of ibuprofen (Figure 11.5.1), a commonly used analgesic, is an example. Figure 11.5.2 illustrates two pathways for the preparation of ibuprofen, one more efficient than the other.

In this section, you will learn how to devise **reaction pathways** for the synthesis of some simple organic compounds by utilising the reactions you have learned about in sections 11.3 and 11.4.

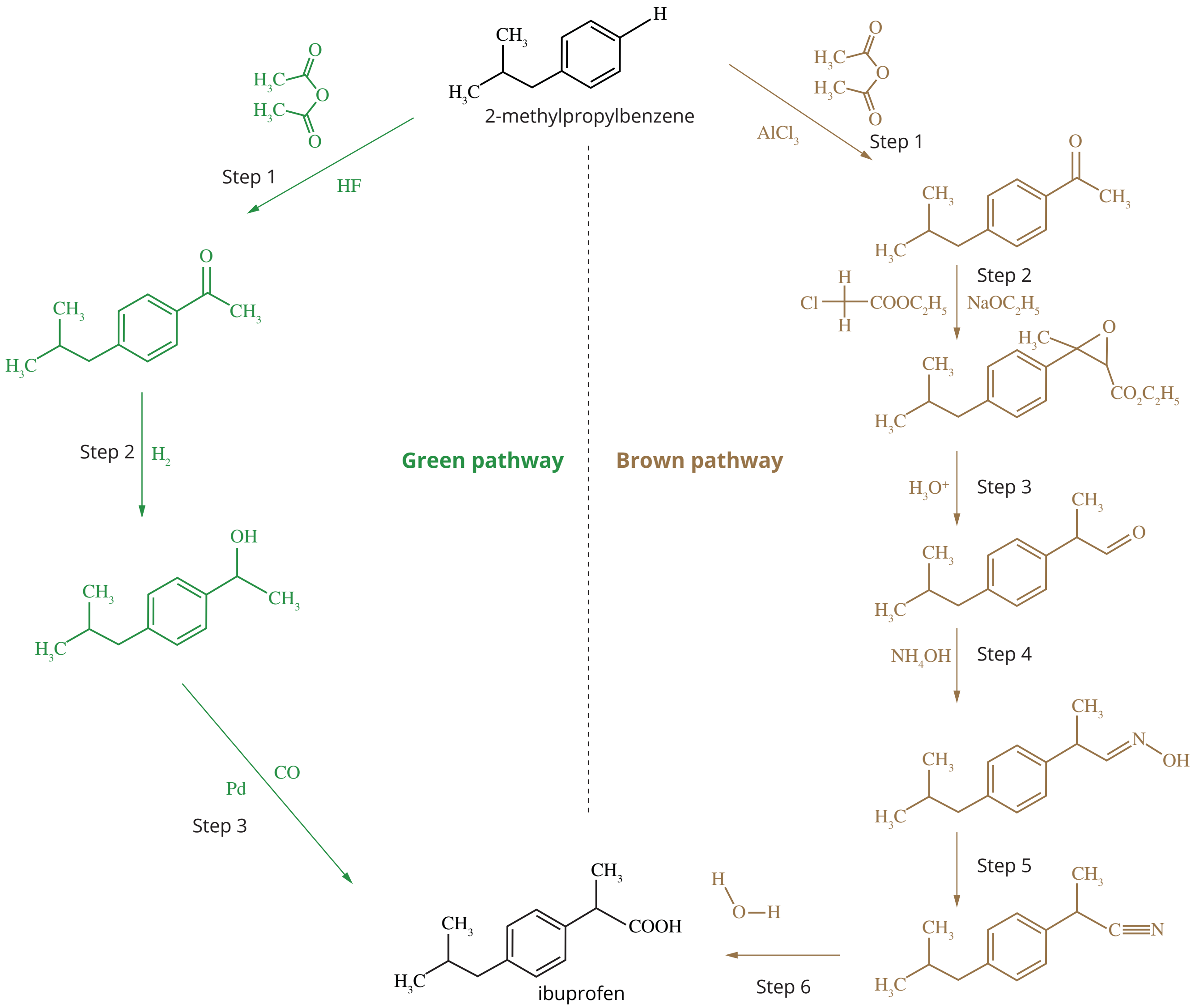


FIGURE 11.5.2 Two alternative reaction pathways for the production of ibuprofen. The green pathway is more efficient than the brown one. In the green pathway, fewer reactants are needed and a higher proportion of atoms in the reactants are present in the final product. This means that there is less waste in the green pathway.

SIMPLE REACTION PATHWAYS

Figure 11.5.3 shows chemical reaction pathways that can be used to form some compounds based on ethane and ethene. A reaction pathway is a series of one or more steps, or reactions, that can be used to convert a reactant containing certain functional groups to a desired product with different functional groups. Pathways for other alkanes can be constructed using the same inorganic reactants and reaction conditions.

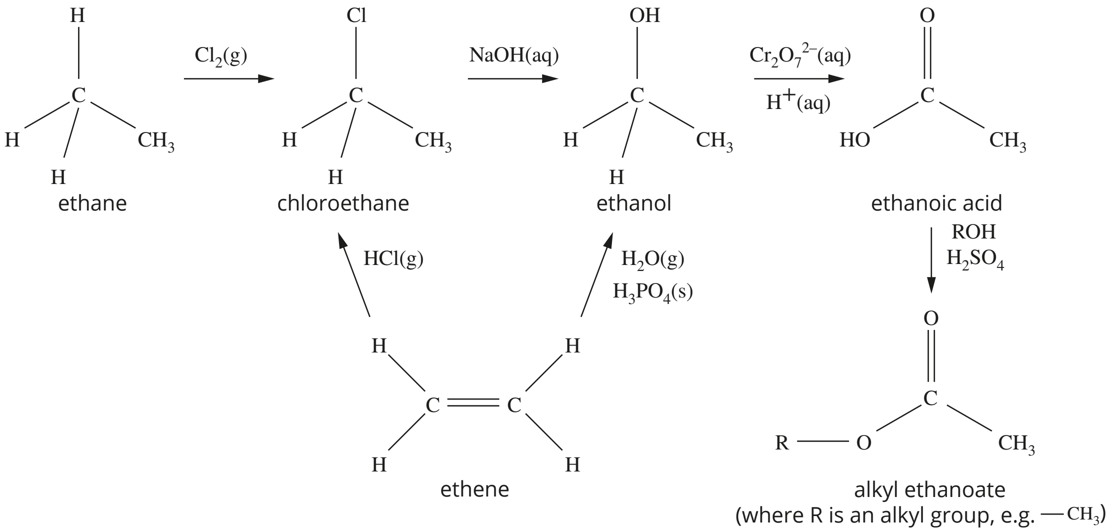


FIGURE 11.5.3 Some reaction pathways based on ethane and ethene. The same reaction conditions can be used to develop pathways for other members of the alkane and alkene homologous series.

CHEMFILE

Building the impossible

The American chemist Professor Robert Burns Woodward (Figure 11.5.4) was awarded the Nobel Prize in Chemistry in 1965 for his synthesis of complex organic molecules. Woodward devised synthetic procedures for the production of complex natural products that many considered to be impossible to replicate in the laboratory. His methodical approach resulted in the development of a number of rules that are now used by modern organic chemists to plan and predict how reactions will occur in order to devise sequential pathways like the ones you will investigate in this chapter.

By the time he was awarded the Nobel Prize, Woodward had successfully proposed and conducted the synthesis of large complex molecules such as quinine, cholesterol, cortisone, lysergic acid (LSD), strychnine, reserpine and chlorophyll. His work on the total synthesis of vitamin B_{12} is considered to be the most complex. As you can see in Figure 11.5.5 (on page 356), vitamin B_{12} is a large molecule. The synthesis required 69 steps and took more than 12 years to develop with the combined efforts of over 100 people from all around the world.

The discoveries that were made during the synthesis of vitamin B_{12} have contributed greatly to the field of organic chemistry and were recognised with another Nobel Prize, in 1981. The prize was awarded to Roald Hoffmann, who worked closely with Woodward on the synthesis, and Kenichi Fukui, who had devised an alternative approach with a similar result to Hoffman and Woodward. Woodward was not named on the 1981 Nobel Prize because he had died in 1979 and Nobel Prizes are not awarded posthumously.

FIGURE 11.5.4 Professor Robert Burns Woodward (1917–1979) synthesised complex organic molecules.

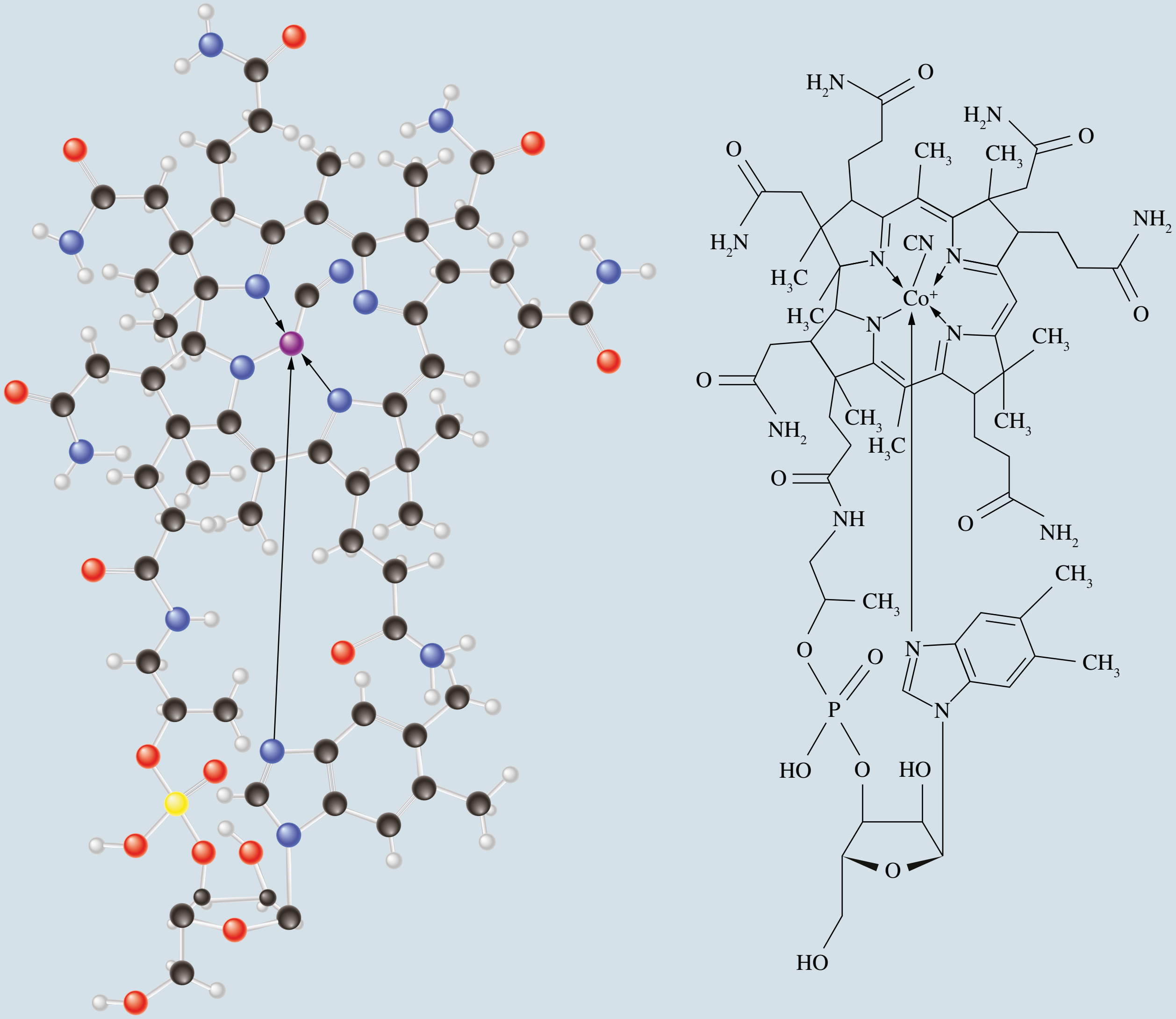


FIGURE 11.5.5 The structure of vitamin B_{12}. The manipulation of the functional groups and reaction conditions required to synthesise this large molecule from small starting materials takes 69 steps.

MORE COMPLEX REACTION PATHWAYS

Suppose you wanted to form ethyl propanoate using only alkanes or alkenes as starting materials. A close look at the structure of the compound shown in Figure 11.5.6 will show you that it is an ester produced by the condensation reaction between propanoic acid and ethanol, so each of these compounds need to be prepared first as described below.

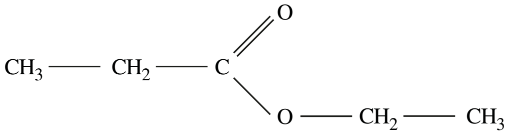


FIGURE 11.5.6 Structure of ethyl propanoate.

Making ethanol

Ethanol is an alcohol containing two carbon atoms. Ethanol can be synthesised from ethene in two ways: in one step by the direct addition reaction with water, or in two steps via the intermediate product chloroethane. In this case, the best option is the more direct route, the addition reaction with water. Figure 11.5.7 shows both possible pathways for the production of ethanol from ethene. You can see in each pathway the inorganic reactant is placed above the arrow for each step.

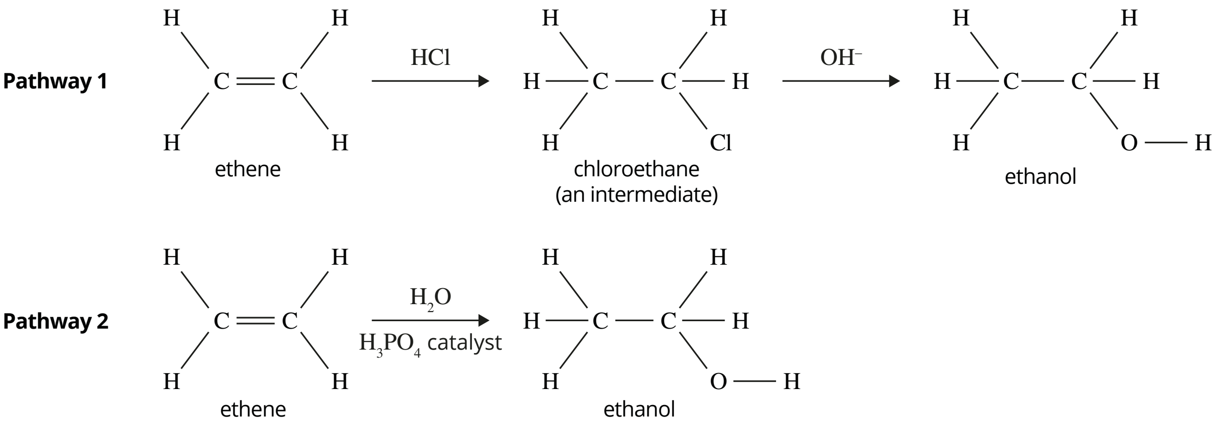


FIGURE 11.5.7 Synthetic pathways for making ethanol from ethene.

Making propanoic acid

Propanoic acid is a carboxylic acid containing three carbon atoms. It can be prepared by the pathway shown in Figure 11.5.8. If you work backwards from propanoic acid, you can see that it can be formed from the oxidation of the primary alcohol propan-1-ol. This in turn can be formed by the reaction of 1-chloropropane with sodium hydroxide.

You will recall that 1-chloropropane can be prepared by reacting propane with chlorine. In this way you can devise the sequence of reactions to reach a particular product. The pathway shown for the preparation of propanoic acid would produce several products, which are separated by fractional distillation.

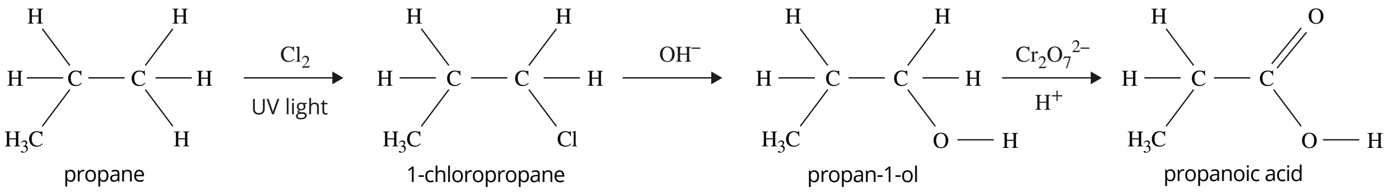


FIGURE 11.5.8 Synthesis of propanoic acid from propene.

For the pathway shown in Figure 11.5.8, the substitution reaction of propane is a better choice than an addition reaction of propene. This is because the addition of HCl to propene results in the formation of unwanted 2-chloropropane.

Making ethyl propanoate

Having synthesised ethanol and propanoic acid, you can now prepare the ester, ethyl propanoate, using a condensation reaction as shown in Figure 11.5.9.

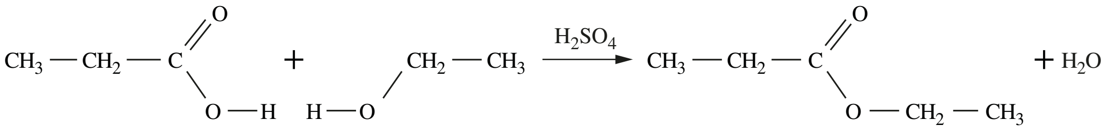


FIGURE 11.5.9 The formation of ethyl propanoate from the condensation reaction of ethanol and propanoic acid.

A reaction pathway summarises the reactions required to produce a product from simple starting materials.

The full reaction pathway for the preparation of ethyl propanoate from ethene and propane via ethanol and propanoic acid is summarised in Figure 11.5.10.

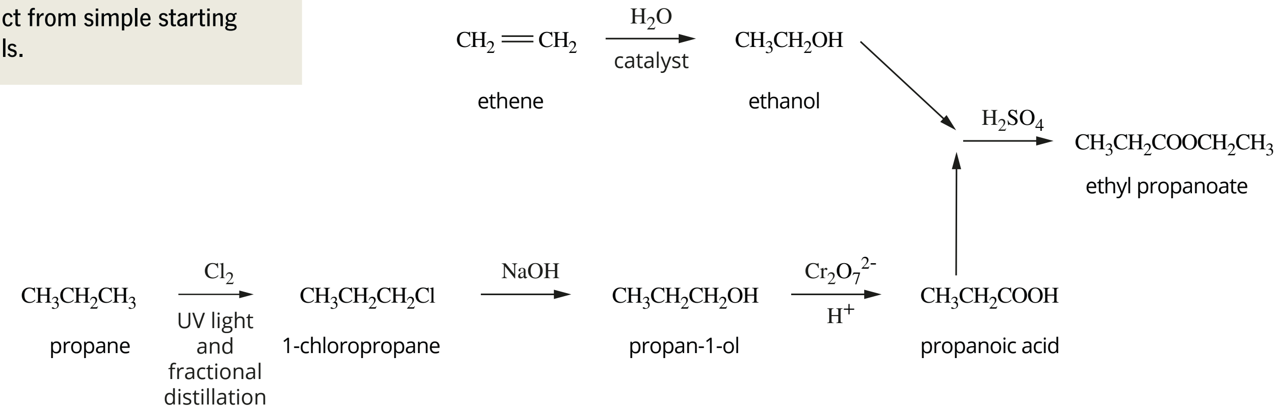


FIGURE 11.5.10 Reaction pathway for the preparation of ethyl propanoate.

The desired ester product can be separated from the reaction mixture and purified by fractional distillation. In Chapter 12, you will learn how to verify the identity of the product by instrumental analysis techniques such as infrared and nuclear magnetic resonance spectroscopy and mass spectrometry.

A summary of the reaction pathways described in this chapter is shown in Figure 11.5.11.

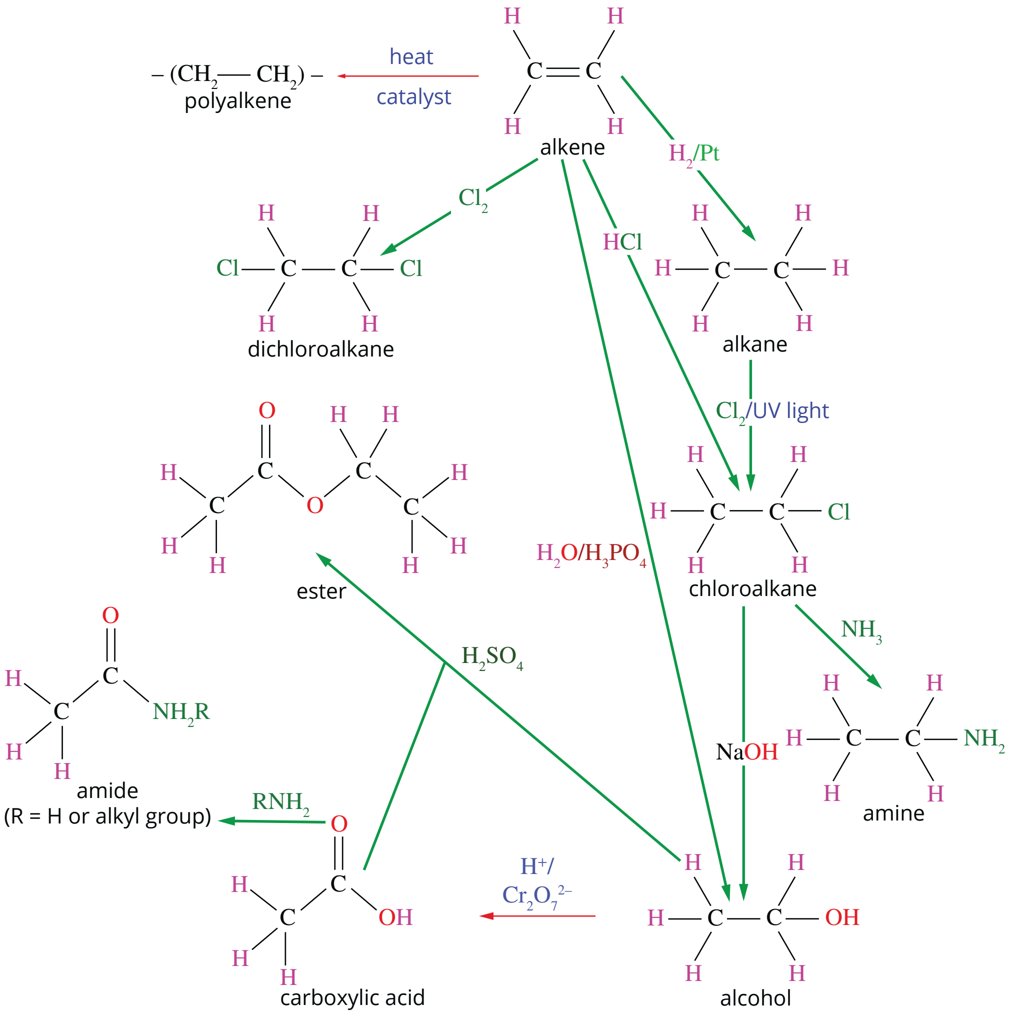


FIGURE 11.5.11 Synthetic pathways for the production of a variety of functional groups from an alkene starting product.

OTHER CONSIDERATIONS IN DEVISING A SYNTHESIS

When planning a reaction pathway, there are a number of considerations in addition to simply identifying a possible reaction sequence. As you will recall from Chapter 8, the equilibrium position of a reaction can have a considerable impact on the overall yield. The principles of 'green' chemistry must also be considered in terms of the solvents required and the by-products that are formed. The flowchart in Figure 11.5.12 shows some of the stages in the planning process.

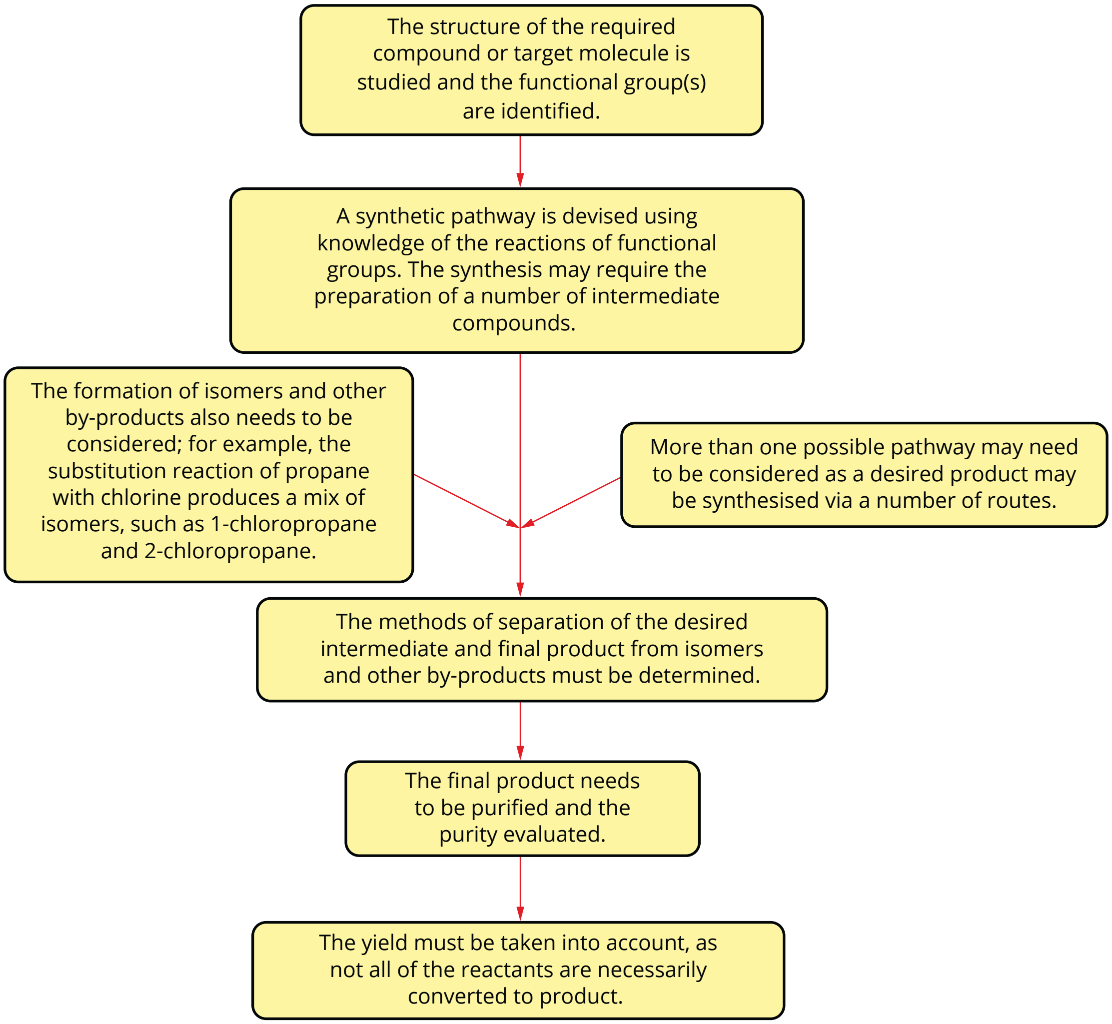


FIGURE 11.5.12 Steps in the design of a synthetic pathway of an organic compound.

11.5 Review

SUMMARY

- A reaction pathway is a sequence of more than one reaction that is used to convert a reactant into a product.
- Reaction pathways can be constructed using the organic reactions studied in this chapter.
- Reaction pathways indicate the reaction conditions and reagents required for each step.

KEY QUESTIONS

1 Devise reaction pathways for the following reactions.
  a Ethylamine from ethene
  b Butan-1-ol from butane
  c Pentanoic acid from 1-chloropentane

2 Propose the shortest reaction pathway that will synthesise:
  a methanoic acid from methane
  b ethanol from ethene
  c propyl methanoate from propane and methane.

3 Pentanamide can be made from 1-chloropentane in the following reaction pathway.

1-Chloropentane → compound A → compound B → pentanamide
  a Identify compound A.
  b Name the chemical used to convert 1-chloropentane to compound A.
  c Identify compound B.
  d Name the chemicals and the reaction conditions used to convert compound A to compound B.
  e Give the name of the reagent used to convert compound B to pentanamide.

4 Describe a reaction pathway to synthesise butyl ethanoate from appropriate alkane or alkene starting materials.

11.6 Yield and the chemical industry

As you learned in Chapter 8, a major consideration in industrial chemistry is the amount of product that can be produced from a given amount of reactants in a given time. Many industrial processes involve a number of steps in order to make the final product. At each step, the conversion from reactants to products is usually less than complete. For every step in a reaction pathway, the amount of final product diminishes. Industrial chemists must consider the efficiency of a reaction pathway and the wastes that are produced (Figure 11.6.1)

In this section, you will learn to perform calculations that can be used to determine the efficiency of processes that involve chemical reactions and help in the development of strategies to minimise waste. While the focus in this chapter is on reactions involving organic chemicals, the principles discussed in this section apply to all chemical industries and research.

FIGURE 11.6.1 Most chemical reactions carried out in industrial processes are not 100% efficient and so waste chemicals are produced. The reduction or elimination of waste chemicals is a major concern for industrial chemists.

YIELD

Theoretical and actual yields

The mass of product that can be formed if all reactants react to produce products according to the reaction equation is known as the **theoretical yield**. The theoretical yield is calculated using the mole ratios of the equation and assumes 100% conversion of the reactants. However, as you learned in Chapter 8, when reactants are mixed together in the correct mole ratio, the amount of products will not always be exactly as predicted from stoichiometric calculations.

Theoretical yield is the maximum amount of product that can be formed using stoichiometric ratios of the limiting reactant and assumes 100% conversion.

A number of factors can influence the amount of product that will be produced for a given reaction.

- When a reaction reaches equilibrium rather than continuing on to completion, the **actual yield** will be less than the theoretical yield.
- If the reaction rate is slow, the reaction may not proceed to completion in the time available. This will reduce the actual yield so that the theoretical yield is not obtained.
- Loss of reactants and products during transfers between reaction vessels and in separation and purification stages such as filtration will all result in smaller amounts of the product being obtained than expected.

Percentage yield

The **percentage yield** compares the actual yield to the theoretical yield. It is a measure of the efficiency of a production process, for the particular conditions and method used for the synthesis. The higher the value of the percentage yield, the greater the degree of conversion from reactants to products for the reaction.

Percentage yield can be calculated using the formula:

$$\text{percentage yield} = \frac{\text{actual yield}}{\text{theoretical yield}} \times \frac{100}{1}$$

Worked example 11.6.1

CALCULATING THE PERCENTAGE YIELD OF A REACTION

30.0 g of propan-2-ol was oxidised to propanone using an acidified solution of $K_2Cr_2O_7$. The propanone that was distilled from the reaction mixture had a mass of 20.0 g. Calculate the percentage yield of this oxidation reaction.

Thinking	**Working**
Write an equation for the reaction.	$CH_3CH(OH)CH_3 \xrightarrow{H^+/Cr_2O_7^{2-}} CH_3COCH_3$ Note that in this case it is not necessary to write a full equation. Because a molecule of the organic product has the same number of carbon atoms as the organic reactant, the number of moles of the product is equal to the number of moles of the reactant.
Use the formula $n = \frac{m}{M}$ to determine the amount of reactant.	$n(CH_3CH(OH)CH_3) = \frac{m}{M}$ $= \frac{30.0}{60.0}$ $= 0.500$ mol
Use the mole ratio for the reaction to determine the amount, in moles, of the product that would be made if all of the reactant reacted.	Mole ratio $= \frac{n(CH_3COHCH_3)}{n(CH_3CH(OH)CH_3)} = \frac{1}{1}$ $n(CH_3COCH_3) = \frac{1}{1} \times n(CH_3CH(OH)CH_3)$ $= 0.500$ mol
Use the formula $m = n \times M$ to determine the mass of the product if all of the reactant reacts. This is the theoretical yield of the product.	$m(CH_3COCH_3) = n \times M$ $= 0.500 \times 58.0$ $= 29.0$ g
Calculate the percentage yield for this reaction from the formula: percentage yield $= \frac{\text{actual yield}}{\text{theoretical yield}} \times \frac{100}{1}$	percentage yield $= \frac{20.0}{29.0} \times \frac{100}{1}$ $= 69.0\%$

Worked example: Try yourself 11.6.1

CALCULATING THE PERCENTAGE YIELD OF A REACTION

80.0 g of propan-1-ol was oxidised to propanoic acid using an acidified solution of $K_2Cr_2O_7$. The propanoic acid obtained at the end of the reaction had a mass of 55.0 g. Calculate the percentage yield of this oxidation reaction.

Percentage yields in multistep syntheses

When a reaction proceeds by a number of steps, the overall percentage yield is reduced at each step. The yield for each step has an effect on the overall yield. A low yield in one of the intermediate reactions can have a significant effect on the amount of final product obtained.

Comparison of the overall percentage yields for different pathways to the same product can be used to determine whether a particular synthetic pathway is the best way to produce an organic compound. Finding the most efficient pathway for the production of a desired chemical is critical to industry because wasting valuable reactants is not a good option, economically or environmentally.

Worked example 11.6.2

CALCULATING THE PERCENTAGE YIELD OF A MULTISTEP SYNTHESIS

Calculate the overall percentage yield for the preparation of C from A if it proceeds by a two-step synthesis:

$$A \rightarrow B \text{ followed by } B \rightarrow C$$

The yield of A → B is 80% and the yield of B → C is 70%.

Thinking	Working
Calculate the overall yield of C by multiplying the percentage yields together and expressing as a percentage (multiplying by 100).	The overall yield of C is: $\frac{80}{100} \times \frac{70}{100} \times \frac{100}{1}$ = 56%

Worked example: Try yourself 11.6.2

CALCULATING THE PERCENTAGE YIELD OF A MULTISTEP SYNTHESIS

Calculate the overall percentage yield for the preparation of D from A if it proceeds by a three-step synthesis:

$$A \rightarrow B \text{ followed by } B \rightarrow C \text{ followed by } C \rightarrow D$$

The yield of A → B is 90%, the yield of B → C is 80% and the yield of C → D is 60%.

ATOM ECONOMY

An important objective for an industrial chemist who is developing a reaction pathway is to use a sequence of chemical reactions that minimises energy consumption, reduces waste and has a low impact on the environment.

One consideration when planning reaction pathways is to maximise **atom economy**. The atom economy for a chemical reaction is a measure of how many of the atoms in the reactants end up in the desired product. As you can see in Figure 11.6.2, if the atom economy of a reaction is high, then there are few, if any, waste products.

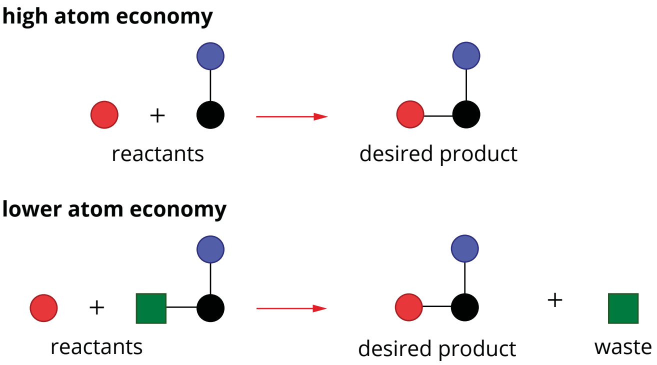


FIGURE 11.6.2 The different coloured symbols represent atoms or groups of atoms. In a high-atom economy reaction, all or most of the atoms in the reactant molecules end up in the desired product molecule. In a lower-atom economy reaction, not all of the reactant atoms end up in the desired product. The atoms that don't end up in the desired product are waste products of the reaction.

Calculating the atom economy of a reaction provides a method of accounting for the use of materials in a manufacturing process. It tracks all the atoms in a reaction and calculates the mass of the atoms of reactants actually used to form products as a percentage of the total mass of reactants. From this, the mass of reactant atoms that end up as waste can also be calculated.

Once the balanced equation for a reaction is known, the atom economy can be calculated using the formula:

$$\text{Atom economy} = \frac{\text{molar mass of desired product}}{\text{molar mass of all reactants}} \times 100$$

Since in a chemical reaction, the total mass of products is equal to the total mass of reactants, this alternative formula can also be used:

$$\text{Atom economy} = \frac{\text{mass of desired product}}{\text{mass of all products}} \times 100$$

Use Worked Example 11.6.3 to help you with calculations of atom economy.

Worked example 11.6.3

CALCULATING ATOM ECONOMY

Calculate the atom economy in the production of ethanol from chloroethane. In this process, chloroethane is heated with a solution of sodium hydroxide. The equation for the reaction is:

$$C_2H_5Cl(aq) + NaOH(aq) \rightarrow C_2H_5OH(aq) + NaCl(aq)$$

Thinking	**Working**
Calculate the total molar mass of the reactants.	$M(C_2H_5Cl) + M(NaOH)$ $= [(2 \times 12.0) + (5 \times 1.0) + 35.5] + [23.0 + 16.0 + 1.0]$ $= 104.5 \text{ g mol}^{-1}$
Calculate the molar mass of the required product.	$M(C_2H_5OH)$ $= (2 \times 12.0) + (6 \times 1.0) + 16.0$ $= 46.0 \text{ g mol}^{-1}$
Calculate the atom economy for the reaction using the formula: atom economy = $\frac{\text{molar mass of desired product}}{\text{molar mass of all reactants}} \times 100$	Atom economy = $\frac{46.0}{104.5} \times 100$ $= 44.0\%$ So in this process, only 44.0% of the starting materials are converted to the desired product. The remainder of the chemicals used is waste.

Worked example: Try yourself 11.6.3

CALCULATING ATOM ECONOMY

Calculate the percentage atom economy in the formation of 1-iodopropane ($CH_3CH_2CH_2I$) from propan-1-ol. The equation for the reaction is:

$$CH_3CH_2CH_2OH(aq) + NaI(aq) + H_2SO_4(aq) \rightarrow CH_3CH_2CH_2I(aq) + NaHSO_4(aq) + H_2O(l)$$

11.6 Review

SUMMARY

- The theoretical yield of a chemical reaction is the mass of the product that would be formed if the limiting reactant reacted completely.
- To calculate the percentage yield, divide the actual yield obtained by the theoretical yield that would be obtained, if all of the limiting reactant reacted completely and multiply by 100:

  $$\text{percentage yield} = \frac{\text{actual yield}}{\text{theoretical yield}} \times \frac{100}{1}$$
- When a reaction proceeds by a number of steps, the overall percentage yield is reduced at each step.
- The overall yield of the product of a multistep reaction is found by multiplying the percentage yields of each step together and expressing as a percentage (multiplying by 100). For example, for the multistep reaction A → B → C → D with the yields: 90%, 50% and 60%:

  $$\text{overall yield} = \frac{90}{100} \times \frac{50}{100} \times \frac{60}{100} \times \frac{100}{1}$$
  $$= 27\%$$
- The atom economy for a chemical reaction is a measure of how many of the atoms in the reactants end up in the desired product for the reaction. Atom economy can be calculated from the formula:

  $$\text{atom economy} = \frac{\text{molar mass of desired product}}{\text{molar mass of all reactants}} \times 100$$

KEY QUESTIONS

1 Calculate the percentage yield for the reaction in which 20.0 g of ethanol is oxidised to produce 21.5 g of ethanoic acid according to the equation:

$$C_2H_5OH \xrightarrow{H^+/Cr_2O_7^{2-}} CH_3COOH$$

2 Compound D can be synthesised by a reaction pathway that involves a number of intermediate steps. The yield for each step is shown:

$$A \xrightarrow{70\%} B \xrightarrow{50\%} C \xrightarrow{90\%} D$$

a Determine the overall yield for the preparation of compound D from compound A.

b How would the overall yield be affected if the yield for B → C was only 10%?

3 During a trial experiment for the industrial production of ethanol from ethene, 150 g of ethene was reacted with water to produce ethanol according to the equation:

$$C_2H_4(g) + H_2O(g) \rightarrow C_2H_5OH(g)$$

Calculate the theoretical yield, in grams, of ethanol for this reaction.

4 Ethylene oxide has been manufactured in the past by what was known as the chlorohydrin route, as shown in Figure 11.6.3.

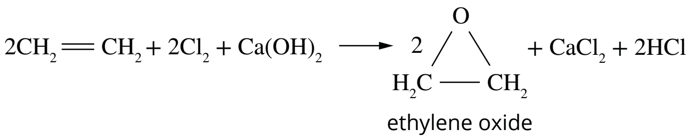


FIGURE 11.6.3 The chlorohydrin method for the production of ethylene oxide.

Ethylene oxide is now produced using a catalytic method according to the pathway shown in Figure 11.6.4.

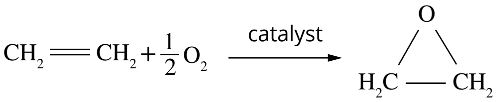


FIGURE 11.6.4 The catalytic method for the production of ethylene oxide.

Calculate the atom economy for the preparation of ethylene oxide by both of these reactions.

5 An old method for the manufacture of phenol (C_6H_5OH) from benzene (C_6H_6) used sulfuric acid and sodium hydroxide in several steps. The overall equation is:

$$C_6H_6(l) + H_2SO_4(aq) + 2NaOH(aq) \rightarrow C_6H_5OH(aq) + Na_2SO_3(aq) + 2H_2O(l)$$

Calculate the atom economy of this process when phenol is the desired product.

6 When ethanamide is produced by the reaction of ethanoic acid and ammonia, the atom economy is 76.7%. Calculate the total mass of reactants, in kilograms, required to make 2.00 kg of ethanamide.

Chapter review

11

KEY TERMS

actual yield
addition polymerisation
addition reaction
alcohol
aldehyde
atom economy
autoignition point
carboxylic acid
condensation reaction
dimer
dipole–dipole attraction
dispersion force
electronegative
esterification reaction
fatty acid
flashpoint
fractional distillation
haloalkane
hydration reaction
hydrogen bond
hydrogen halide
hydrolysis
hydrolytic reaction
immiscible
inorganic
isomers
ketone
miscible
monomer
percentage yield
polar bond
polymer
primary alcohol
reaction pathway
saponification
saturated
secondary alcohol
substitution reaction
tertiary alcohol
theoretical yield
unsaturated
viscosity

Boiling points and solubilities of organic compounds

1 Table 11.7.1 gives the relative molecular masses and boiling points of methylpropane, butane, methyl methanoate and propan-1-ol. Explain why the boiling points differ even though the compounds have similar molar masses.

TABLE 11.7.1 Boiling points of some organic compounds

Compound	Relative molecular mass (g mol^{-1})	Boiling point (°C)
Methylpropane	58	–11.17
Butane	58	–0.5
Methyl methanoate	60	32.0
Propan-1-ol	60	97.0

2 Explain why, when comparing the effect of functional groups on the boiling points of different homologous series, it is important to compare molecules with a similar molar mass.

3 Consider the following compounds:
$CH_3CH(CH_3)CH(CH_3)CH_2CH_2OH$, $CH_3(CH_2)_5CH_2OH$, $CH_3CH(CH_3)CH_2CH_2CH_2CH_2OH$.
- **a** Place the compounds in order of increasing boiling point.
- **b** Would the compounds have a greater solubility in water or in hexane? Explain your answer.

Viscosities and flashpoints of organic compounds

4 Define:
- **a** viscosity
- **b** flashpoint.

5 Which alkane has the higher viscosity and flashpoint: pentane or octane? Explain your answer in terms of the intermolecular forces between molecules.

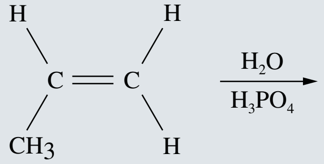
Chemical properties of alkanes, haloalkanes and alkenes

6 Complete this table about the different types of reactions of alkenes.

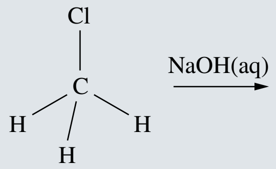
Reactants	Type of reaction	Product(s)
Alkene and hydrogen		
Alkene and hydrogen bromide		
Alkene and water (with a catalyst)		
Alkene and bromine		
Alkene in the presence of a catalyst		

7 Write the structural formulas of the products of the following reactions.

a



b



8 Write an unbalanced chemical equation for the reaction between:
- **a** butane and chlorine
- **b** 1-chlorobutane and sodium hydroxide solution
- **c** ethane and oxygen.

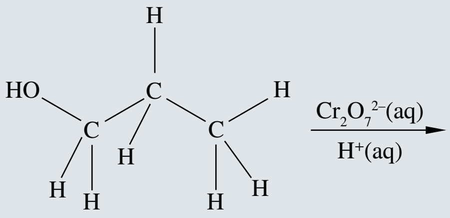
Reactions of alcohols, carboxylic acids and esters

9 State the name of the functional group that will be formed in reactions of the following types of alcohols with potassium permanganate solution. If there is more than one possible product, state both names.

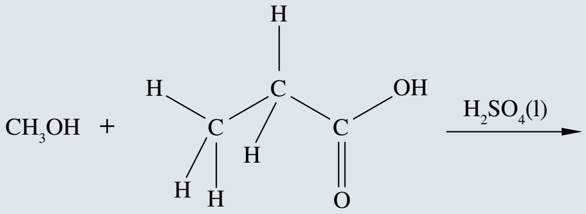
- **a** Primary alcohol
- **b** Secondary alcohol
- **c** Tertiary alcohol

10 Write the structural formulas of the products of the following reactions.

a

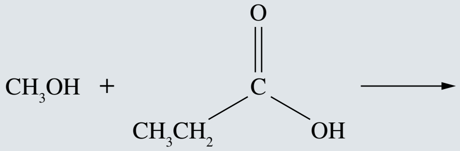


b

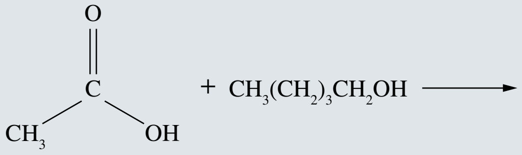


11 Complete the following reactions.

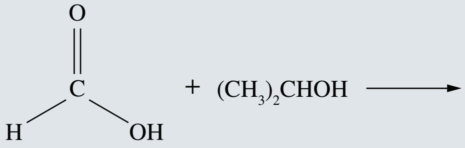
a



b



c



12 Give the semistructural formulas for the products of the hydrolysis of each of the following esters when an acid is used as a catalyst.

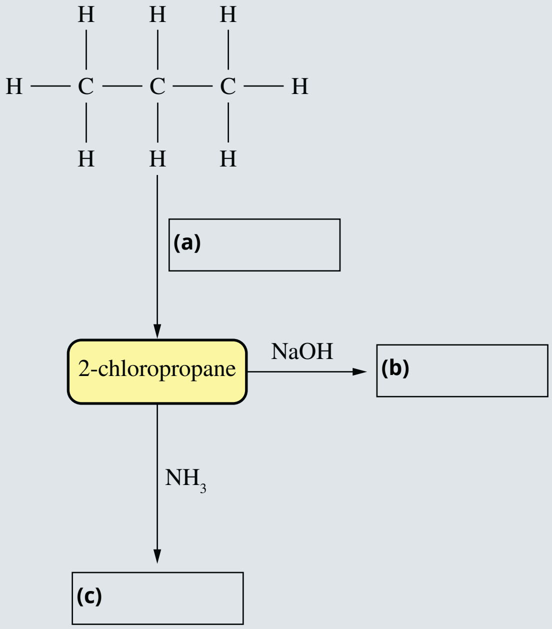
- **a** Methyl ethanoate
- **b** Propyl ethanoate
- **c** Ethyl methanoate

13 Write the structural formula of the product that will be formed from the reaction of:

- **a** ethanoic acid and ammonia
- **b** methanamine and methanoic acid
- **c** pentan-3-ol heated with $H^+/Cr_2O_7^{2-}$
- **d** butan-1-ol with $H^+/Cr_2O_7^{2-}$, mild heat; the product is distilled off as it forms.

Reaction pathways

14 Complete the flowchart of organic reactions by providing the correct reagents/products as required.



15 Write chemical pathways in the form of flow diagrams (like the one in Question **14**) to describe the preparation of propanoic acid from an:

- **a** alkane
- **b** alkene.

16 Write a reaction pathway for the synthesis of:

- **a** ethyl propanoate from ethene and 1-chloropropane
- **b** ethyl ethanoate from an alkene.

Yield and the chemical industry

17 Chloroethane (C_2H_5Cl) is a product in the reaction between ethane and chlorine in the presence of sunlight. The equation for the reaction is:

$C_2H_6(g) + Cl_2(g) \rightarrow C_2H_5Cl(g) + HCl(g)$

Calculate the atom economy for the production of chloroethane in this reaction.

18 Aspirin can be synthesised by an esterification reaction according to the pathway shown in Figure 11.7.1.

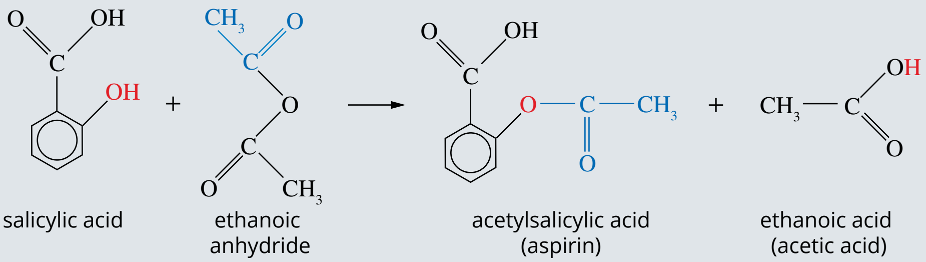


FIGURE 11.7.1 The synthesis of aspirin from salicylic acid and ethanoic anhydride.

A student reacted a 2.50 g sample of salicylic acid with an excess of ethanoic anhydride, using sulfuric acid as a catalyst. After purification a mass of 2.35 g of pure aspirin was obtained.

- **a** Calculate the theoretical yield of aspirin for the reaction.
- **b** Calculate the percentage yield of aspirin for the reaction.

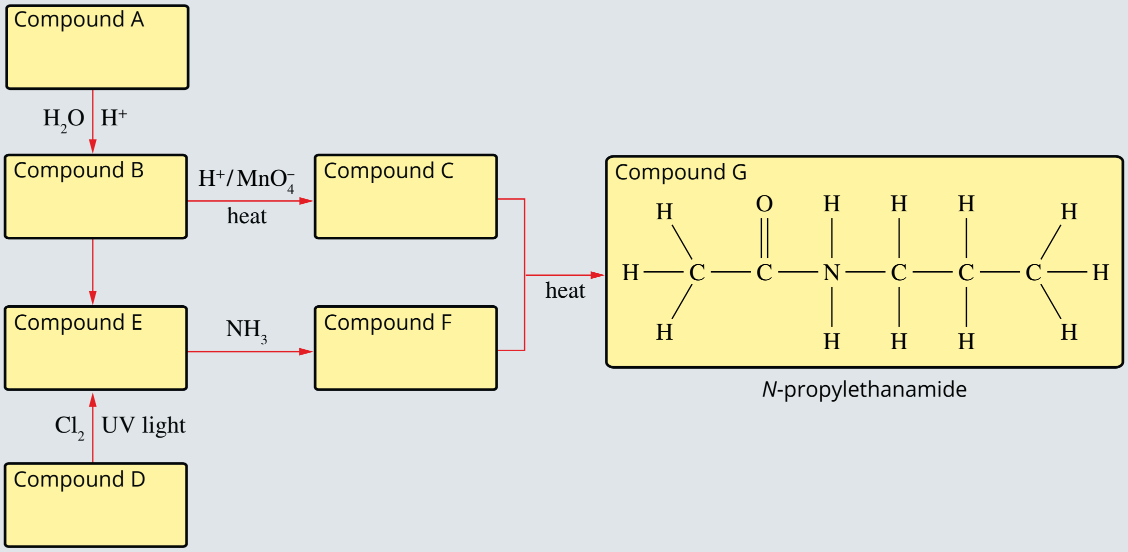
Connecting the main ideas

19 **a** Write unbalanced equations for the production of:
  - **i** chloroethane from ethane
  - **ii** ethanol from ethene
  - **iii** ethanol from chloroethane
  - **iv** ethanoic acid from ethanol.

- **b** Classifiy each of the reactions in part **a** as addition, substitution or oxidation.

20 The reaction pathway shown below leads to the organic compound G (*N*-propylethanamide).

- **a** Complete the pathway by filling in the boxes with the structural formulas of the appropriate compound for A–F.
- **b** Describe a chemical test that could be carried out to distinguish between compounds A and D in the pathway.
- **c** Which compound would be expected to have greater water solubility: B or F? Explain your answer.



CHAPTER

12

Analysis of organic compounds by spectroscopic techniques

In Units 1 and 2, you were introduced to chemical methods of analysis such as volumetric analysis and gravimetric analysis. You were also introduced to instrumental methods of analysis such as atomic absorption spectroscopy. These methods are based on the chemical and physical properties of substances, and help analytical chemists to determine how much of a substance is present in a sample.

The properties of substances can also be used to determine their identity. Analytical chemists combine knowledge of the properties of chemicals with instrumental methods to identify and quantify substances. Analytical instruments coupled with computers are fast and accurate and are able to detect and identify very small amounts of complex substances.

In this chapter, you will learn about three instrumental techniques used to determine the structure of organic compounds—infrared spectroscopy, nuclear magnetic resonance spectroscopy and mass spectrometry. You will also investigate how data from a combination of these techniques can be interpreted to identify an organic compound and determine its structure.

Key knowledge

- The principles and applications of mass spectrometry (excluding features of instrumentation and operation) and interpretation of qualitative and quantitative data, including identification of molecular ion peak, determination of molecular mass and identification of simple fragments
- The principles and applications of infrared (IR) spectroscopy (excluding features of instrumentation and operation) and interpretation of qualitative and quantitative data including use of characteristic absorption bands to identify bonds
- The principles (including spin energy levels) and applications of proton and carbon-13 nuclear magnetic resonance (NMR) spectroscopy (excluding features of instrumentation and operation); analysis of carbon-13 NMR spectra and use of chemical shifts to determine number and nature of different carbon environments in a simple organic compound; and analysis of high-resolution proton NMR spectra to determine the structure of a simple organic compound using chemical shifts, areas under peaks and peak splitting patterns (excluding coupling constants) and application of the $n + 1$ rule
- Determination of the structures of simple organic compounds using a combination of mass spectrometry (MS), infrared (IR) spectroscopy and proton and carbon-13 nuclear magnetic resonance (NMR) spectroscopy limited to data analysis

12.1 Infrared spectroscopy

INTERACTION OF ELECTROMAGNETIC RADIATION WITH MATTER

All types of spectroscopy use electromagnetic radiation to give information about materials found around you. Electromagnetic radiation interacts with atoms and molecules. The nature of this interaction depends upon the energy of the radiation. Different types of spectroscopy utilise the effects electromagnetic radiation has on atoms and molecules to learn about their structure.

The **electromagnetic spectrum** represented in Figure 12.1.1 is divided into different regions of radiation, with different frequencies, wavelengths and energies. Ultraviolet light has short wavelengths with high frequency and energy, while radio waves have long wavelengths and low frequency and energy.

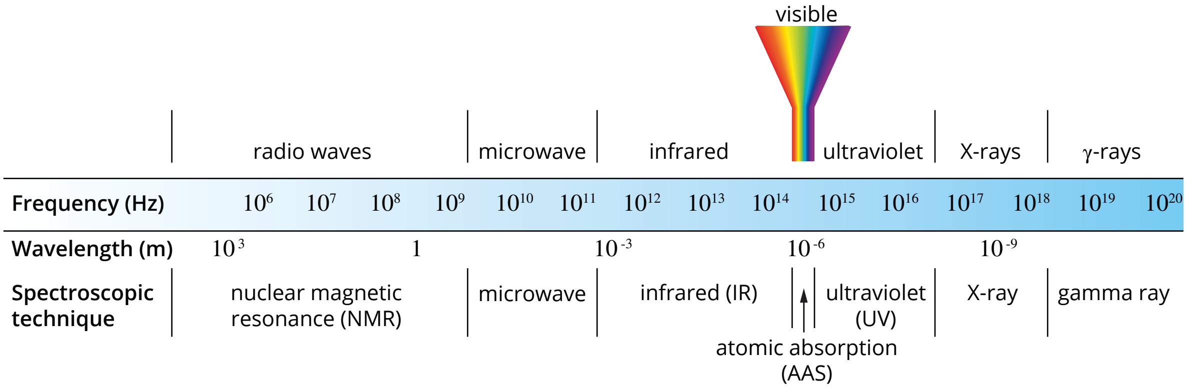


FIGURE 12.1.1 The electromagnetic spectrum showing the frequency and wavelength of different regions and their applications to spectroscopy.

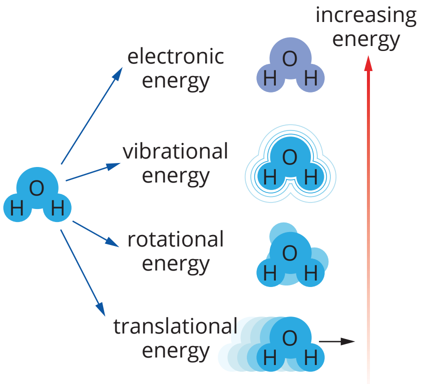


FIGURE 12.1.2 A water molecule has different types of energy.

Atoms and molecules have different types of energy. The water molecule in Figure 12.1.2 shows four different types of energy in order of increasing energy.

When you studied atomic absorbance spectroscopy you learned how electrons in an atom can absorb fixed amounts of energy and move to higher energy levels. In a similar way, molecules can also absorb energy and move to higher electronic, vibrational, rotational and nuclear energy levels.

The measurement of these energy transitions forms the basis of the spectroscopic techniques studied in this course. The electromagnetic radiation associated with some spectroscopic techniques are summarised in Table 12.1.1.

TABLE 12.1.1 Spectroscopic techniques and the regions of the electromagnetic spectrum they use

Spectroscopic technique	Region of the electromagnetic spectrum used	Type of energy level transition
Nuclear magnetic resonance (NMR) spectroscopy	Radio waves	Nuclear spin states—makes the nucleus flip in an applied magnetic field
Infrared (IR) spectroscopy	Infrared	Vibrations of bonds in molecules—makes the bonds bend and stretch
Colorimetry, ultraviolet–visible (UV–visible) spectroscopy and atomic absorption spectroscopy (AAS)	Visible and ultraviolet	Valence electrons in molecules and atoms—makes outer-shell electrons jump to higher energy levels

These spectroscopic techniques use the facts that:

- atoms and molecules absorb and emit electromagnetic radiation of specific energies
- atoms and molecules undergo a change when they absorb electromagnetic radiation
- different parts of the electromagnetic spectrum affect atoms or molecules in different ways.

Colorimetry, atomic absorption spectroscopy and UV–visible spectroscopy were covered in Unit 2 of this course. In this and the following sections, you will study the principles of IR and NMR spectroscopy and learn to interpret the respective spectra.

FIGURE 12.1.3 A food chemist uses an infrared spectrometer to evaluate the quality of raisins.

PRINCIPLES OF INFRARED SPECTROSCOPY

Infrared (IR) spectroscopy is a powerful analytical tool that can be applied to the analysis of many organic and inorganic compounds.

IR spectroscopy can be used to analyse solids, liquids and gases. IR spectroscopy is used as a quality control tool in the pharmaceutical industry, agriculture, food processing (Figure 12.1.3), paint, paper and other industries (Figure 12.1.4). Researchers combine IR spectroscopy with other techniques to study biological molecules. The technique is used to analyse blood and urine samples and is also used to determine the level of atmospheric pollutants.

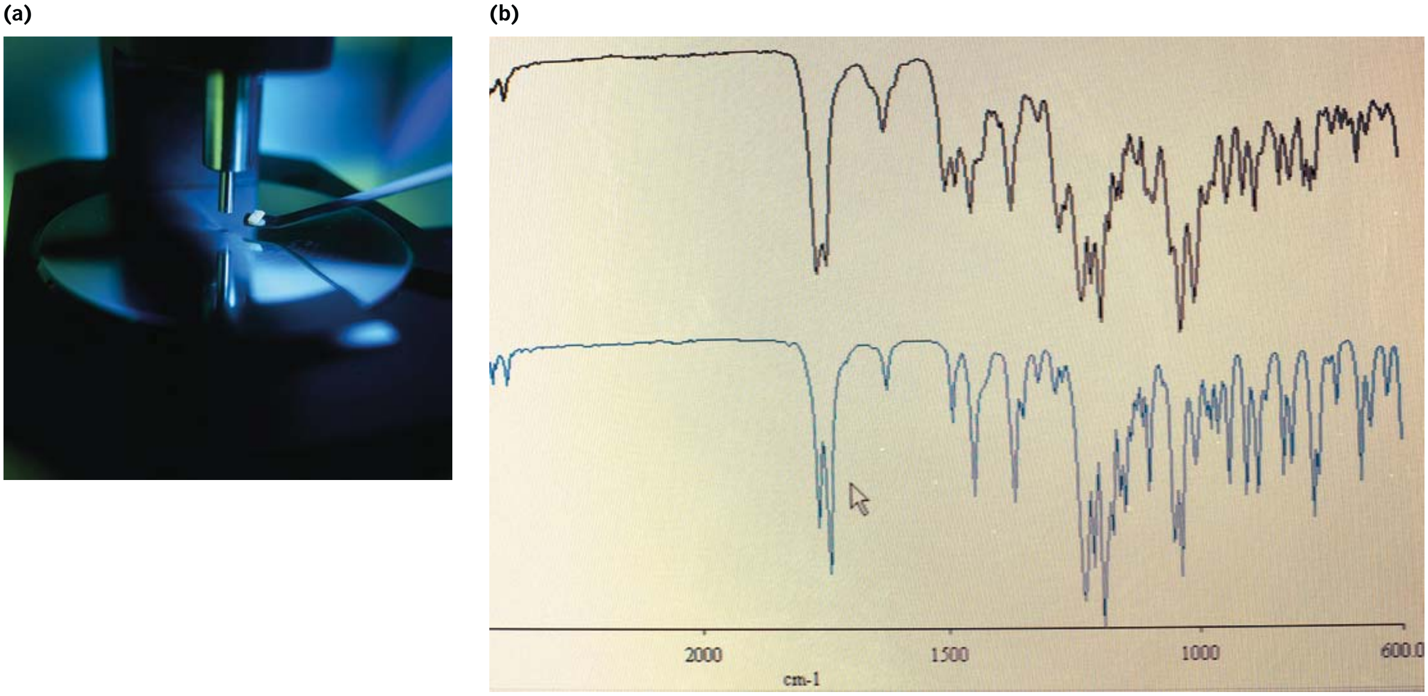


FIGURE 12.1.4 (a) Obtaining the infrared spectrum of a suspected illegal drug. (b) The spectrum of the substance (black) closely matches that of a heroin sample (blue), indicating that the substance contains the illegal drug.

IR spectroscopy is particularly useful because it can give you information about the functional groups present in an organic molecule. This information helps to clarify its structure.

IR light has a lower energy and a longer wavelength than visible and ultraviolet light. The energy from infrared light is not enough to promote electrons to very high energy levels, but it is enough to change the vibration of the bonds in molecules.

Covalent bonds can be compared to springs that can undergo specific amounts of bending or stretching. The atoms in a molecule can change position due to bending or stretching of the bonds, as shown in Figure 12.1.5 (page 372), and the molecule vibrates.

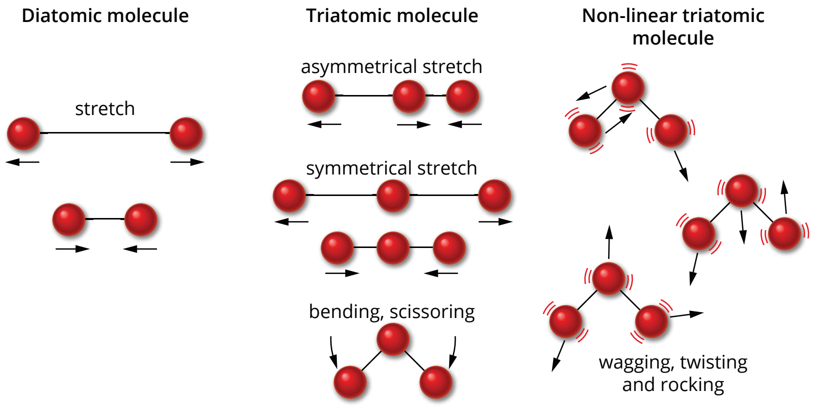


FIGURE 12.1.5 Stretching and bending motions in diatomic and triatomic molecules.

Infrared spectroscopy exploits the ability of molecules to bend and stretch. Molecules are only able to occupy discrete **vibrational energy levels** (Figure 12.1.6). The amount of energy required to move from one vibrational energy level to the next is the same as the amount of energy contained in electromagnetic radiation from the infrared region.

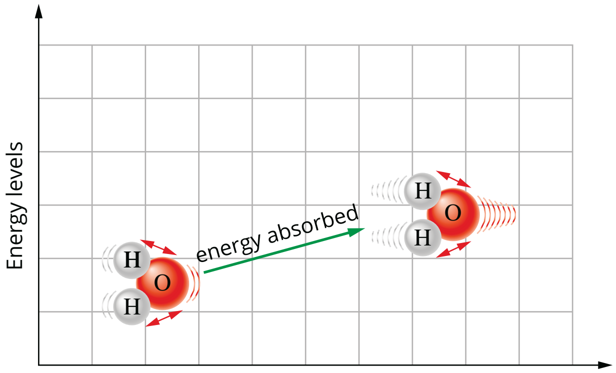


FIGURE 12.1.6 A molecule can absorb energy and move to a higher vibrational energy level.

When molecules absorb infrared radiation, the stretching or bending vibrations of the bonds become more energetic.

IR spectroscopy is a powerful analytical technique because almost all molecules absorb IR radiation. For a molecule to absorb IR radiation, the bending or stretching vibrations must change the overall **dipole** of the molecule.

The frequency of vibration of the bond between two identical atoms depends on the strength of the bond, as shown in Table 12.1.2. The C–C bond is weaker and absorbs infrared radiation of a lower frequency than that absorbed by the C≡C bond. It is important to realise that the frequency of a vibration is directly proportional to the energy of the vibration. Note that in infrared spectroscopy the frequency is expressed as the **wavenumber**, or waves per unit distance, and has the unit cm^{-1}.

TABLE 12.1.2 Bond energy, representing strength of the bond, compared to the frequency of infrared light absorbed

Bond	Bond energy ($kJ\ mol^{-1}$)	Infrared absorption frequency (cm^{-1})	Increasing energy of vibration
C≡C	839	2300	↑
C=C	614	1720	
C–C	346	880	

The mass of the atoms attached to a bond also affects the frequency of the IR radiation that will be absorbed. Atoms with higher masses absorb lower frequency radiation. Table 12.1.3 compares the energy absorbed when atoms of different masses are bonded to carbon with a single bond.

TABLE 12.1.3 Atomic mass affects the frequency of infrared light absorbed

Bond	Typical absorption frequency (cm^{-1})	Increasing energy of vibration
C–H	3000	↑
C–C	1200	
C–O	1100	
C–Cl	750	
C–Br	600	

EXTENSION

Instrumentation

Figure 12.1.7 shows the main components of a simple infrared spectrophotometer. These include:

- a source of infrared radiation
- a sample and reference cell or disc made of NaCl, KBr or similar; glass and plastic cannot be used as they absorb IR radiation and are so opaque to IR radiation
- a wavelength selector (monochromator)
- an infrared detector.

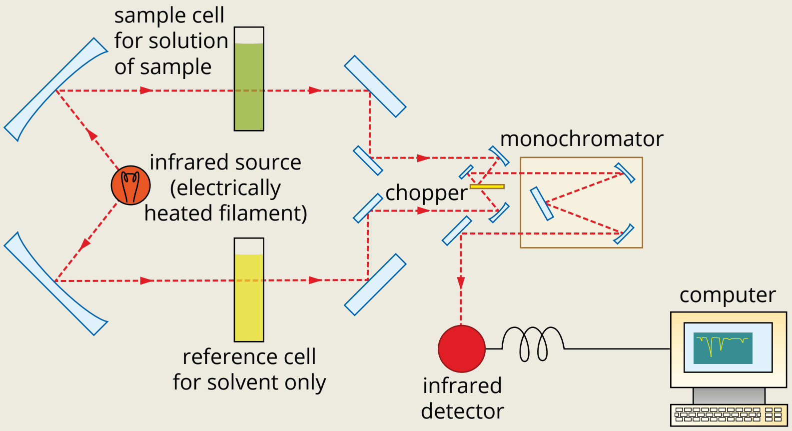


FIGURE 12.1.7 Essential features of a simple IR spectrophotometer.

The IR radiation from the source is split into two beams and passed separately through the sample cell and a reference cell. The reference cell is used to discount the effect of the material of the sample cell, the solvent, and any interference from water or carbon dioxide in the atmosphere.

The difference in **transmittance**, or transmitted radiation, between the sample and reference cell is due to the absorption of certain frequencies by the molecules of the sample. These absorptions result in changes in the vibrational energy in the molecule under examination.

INTERPRETATION OF INFRARED SPECTRA

Features of an infrared spectrum

The frequency of the electromagnetic radiation in IR spectroscopy is usually expressed in wavenumbers (cm^{-1}). The wavenumber is the number of waves per centimetre and is inversely proportional to wavelength. A bond that vibrates at a higher frequency absorbs IR radiation with a higher wavenumber and greater energy than a bond that vibrates at a lower frequency.

The horizontal axis of an IR spectrum shows the wavenumber and the highest wavenumber is usually shown on the left. This axis often has two scales to ensure all features are visible. In the infrared spectrum of 2-methylpropan-2-ol, shown in Figure 12.1.8, you can see that the scale starts with intervals of 1000 cm^{-1} and then changes to intervals of 500 cm^{-1} in the region below 2000 cm^{-1}.

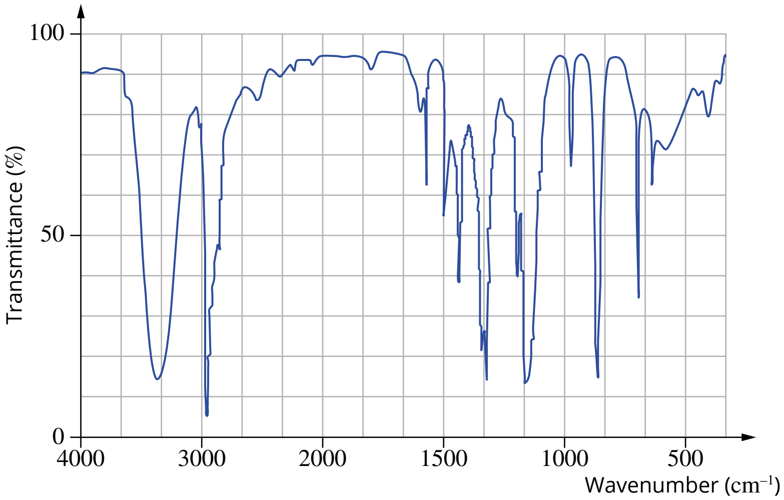


FIGURE 12.1.8 The infrared spectrum of 2-methylpropan-2-ol.

The vertical axis of an IR spectrum shows the percentage transmittance on a scale of 0 to 100. The 'baseline' of the spectrum is where all of the light, 100%, is passed through the sample. Where the molecule absorbs IR radiation the spectrum dips down to lower transmittance. These **absorption bands** appear as inverted peaks in the spectrum.

Different terms can be used to describe absorption bands in IR spectra. Narrow absorption bands span only a few wavenumbers. This usually means that the peak corresponds to one specific type of molecular vibration. Broader bands may be the result of a number of related vibrational changes that have similar energies. Absorption bands are also described as 'strong', 'medium' or 'weak' (Figure 12.1.9) if they absorb a large, moderate or small amount of radiation.

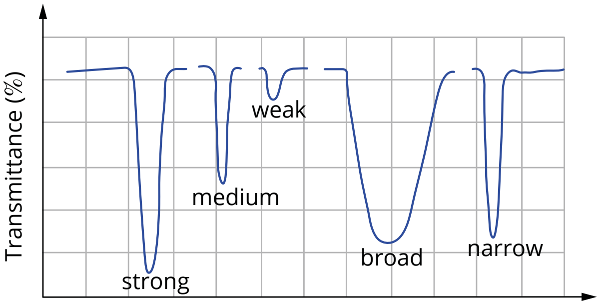


FIGURE 12.1.9 Descriptions used for different shapes and strengths of infrared absorption bands.

Absorption bands above about 1400 cm^{-1} are used to identify **functional groups** because this region coincides with the energy associated with the characteristic stretching vibrations of the atoms in these groups. The region below 1400 cm^{-1} is called the **fingerprint region** as absorption bands of this frequency tend to be unique to each compound. If a known compound and an unknown compound have the same absorption spectrum below 1400 cm^{-1}, they are almost certainly the same.

Interpreting infrared spectra

Each type of bond absorbs IR radiation over a typical range of wavenumbers. For example, it takes energy in the 2850–3300 cm^{-1} region to stretch a C–H bond and energy in the in the 750–1100 cm^{-1} region to stretch a C–C bond. The characteristic regions of absorption for different bonds in an IR spectrum are shown Figure 12.1.10.

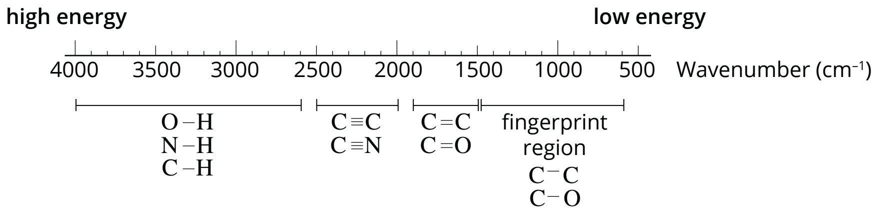


FIGURE 12.1.10 Typical regions for absorption bands from different bonds in the infrared spectrum.

When chemists look at the IR spectrum of an unidentified organic compound, they often refer to tables and charts showing the wavenumbers at which the main functional groups absorb. This can give broad clues to the bond types and functional groups present in the molecule. For positive identification, the entire spectrum of an unidentified compound can be compared to a computer library of spectra, often containing tens of thousands of spectra of known compounds.

The characteristic range for IR absorptions of common functional groups are summarised in Table 12.1.4.

TABLE 12.1.4 Infrared absorption data for some common functional groups

Bond	Wavenumber (cm^{-1})
C–Cl	700–800
C–C	750–1100
C–O	1000–1300
C=C	1610–1680
C=O	1670–1750
O–H (acids)	2500–3300
C–H	2850–3300
O–H (alcohols)	3200–3550
N–H (primary amines)	3350–3500

IR spectroscopy can be useful for distinguishing between very similar compounds. Consider the molecules propanoic acid and methyl ethanoate. These two compounds are isomers with the molecular formula $C_3H_6O_2$.

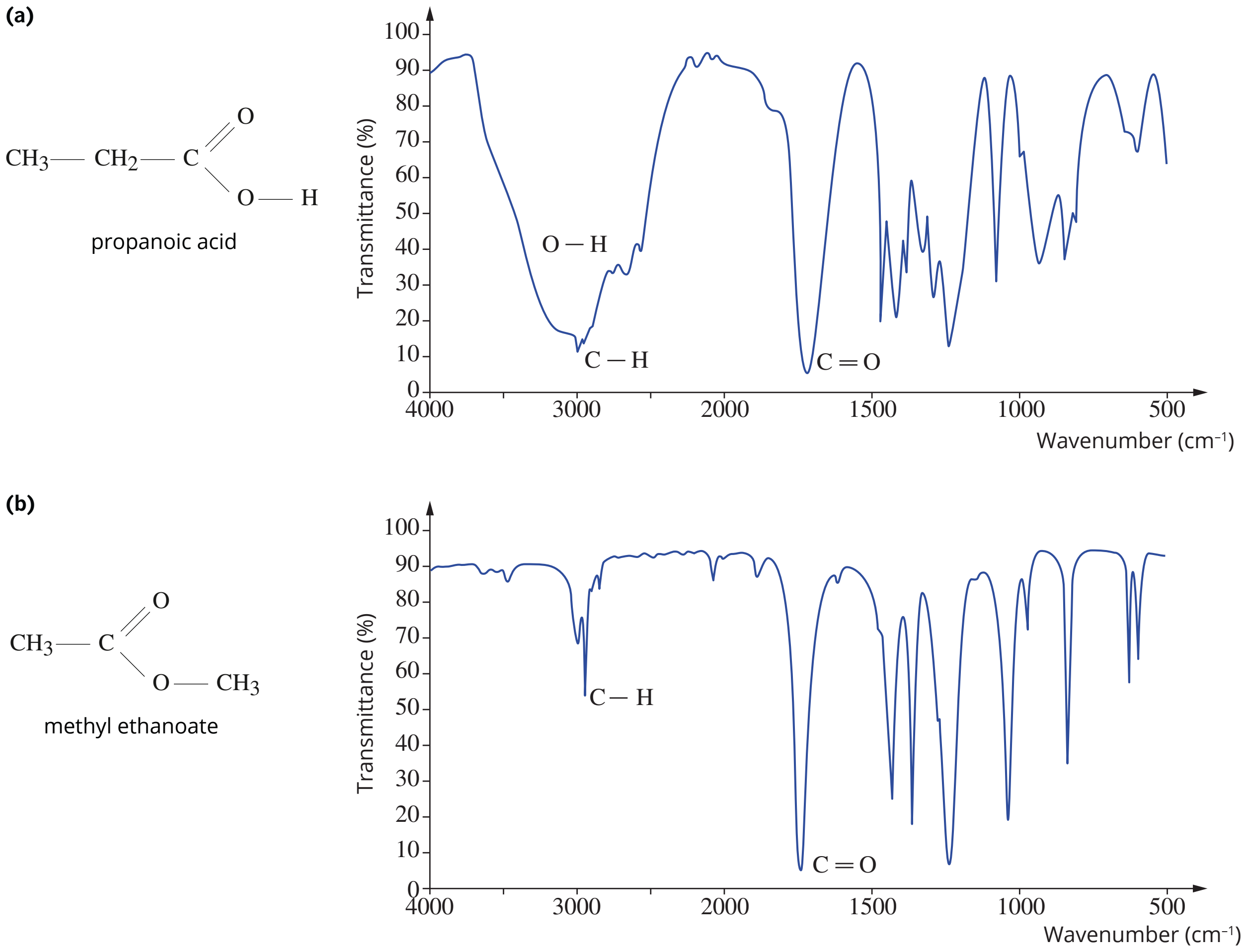


FIGURE 12.1.11 Infrared spectra of (a) propanoic acid and (b) methyl ethanoate.

The infrared spectra of these compounds (Figure 12.1.11) have some features in common and some differences. Both spectra have an absorption band at about 1700 cm^{-1} due to the stretching of the carbonyl (C=O) bond. In methyl ethanoate, the narrow absorption band at around 3000 cm^{-1} is due to the C–H bonds. In propanoic acid, the broad absorption band from 2700 cm^{-1} to 3600 cm^{-1} is due to the O–H bond. This broad absorption band partly masks the absorption due to C–H bonds that are also present in this spectrum.

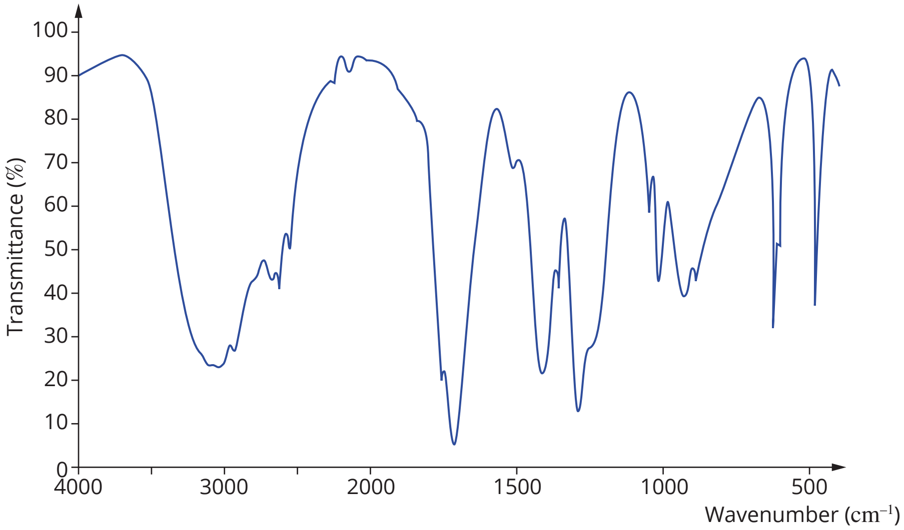
Using the data in Table 12.1.4 (page 375), you can identify the bonds that are likely to be present in an unidentified compound from their characteristic absorption bands. This information allows you to determine which of the main functional groups are present. The IR spectrum may also be used to prove that a functional group is not present, helping you to narrow down the possible structure of the compound.

Different types of covalent bonds absorb IR radiation within a characteristic range of frequencies (wavenumbers), allowing the functional groups in an organic compound to be identified.

Worked example 12.1.1

INTERPRETING THE IR SPECTRUM OF AN UNIDENTIFIED COMPOUND

Use the infrared spectrum of an unidentified compound to identify the functional groups present. The molecular formula of the compound is $C_2H_4O_2$. You will need to refer to the IR absorption data in Table 12.1.4 (page 375).

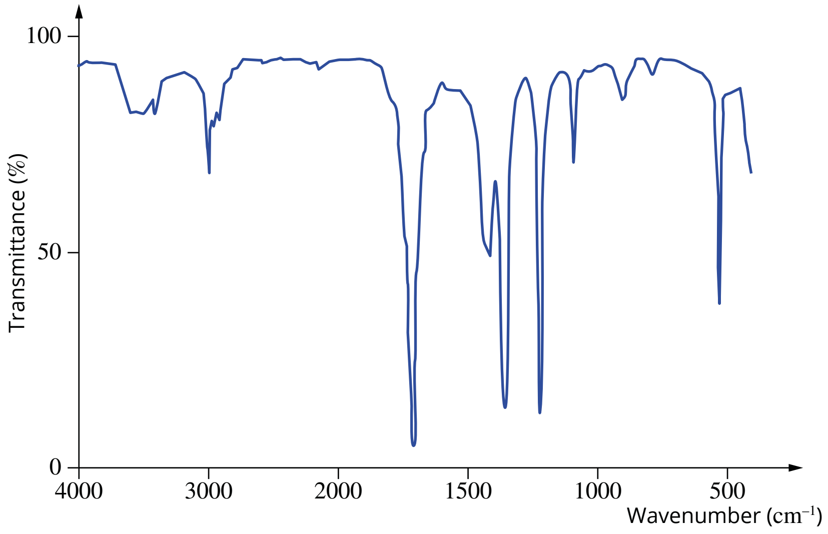


Thinking	**Working**
Identify the absorption bands that correspond to the absorption bands of bonds in the IR absorption data table.	There is a strong, narrow band at approximately 1700 cm^{-1}, which corresponds to the absorption by a carbonyl, C=O, group. The broad band centred at about 3000 cm^{-1} corresponds to the absorption by the O–H bond of a carboxylic acid.
Identify the functional group or groups that are present.	The spectrum shows absorption bands corresponding to the presence of C=O and carboxylic acid O–H bonds. This suggests the presence of a carboxyl functional group, –COOH. From the formula, it can be concluded that the compound is ethanoic acid, CH_3COOH.

Worked example: Try yourself 12.1.1

INTERPRETING THE IR SPECTRUM OF AN UNKNOWN COMPOUND

Use the infrared spectrum of an unidentified compound to identify the functional groups present. The molecular formula of the compound is C_3H_6O. You will need to refer to the IR absorption data in Table 12.1.4 (page 375).



IR SPECTROSCOPY AND QUANTITATIVE ANALYSIS

In Unit 2 of this course you saw that UV–visible spectroscopy can be used to determine the concentration of a solution by comparing its **absorbance** at a specific wavelength to the absorbance of solutions of known concentrations. In a similar way, the amount of light absorbed by a particular bond in an IR spectrum is directly related to the amount of the compound being tested. This means IR spectroscopy can be used for **quantitative analysis**. Measurements of the concentrations of toxic gases in the atmosphere, such as sulfur dioxide and hydrogen cyanide, are often carried out by infrared spectroscopy.

In practice, a molecule can be analysed in this way if its spectrum contains a strong sharp peak. As with chromatography and other spectroscopic techniques, a **calibration curve** is constructed by using standards of known concentration. The concentration of the sample is found by comparison with the calibration curve. Unfortunately, the correlation of absorbance to concentration is not always reliable because the calibration curves obtained from IR absorbances are often significantly curved rather than linear.

FIGURE 12.1.12 A driver's blood alcohol level is tested in a roadside breath test.

CHEMFILE

IR spectroscopy and breath tests

If a roadside breath test (Figure 12.1.12) shows that a driver is over the legally allowed blood alcohol limit, the driver is required to undergo a second test in a 'booze bus'. During the second test, the driver breathes into the cell of an IR spectrometer. The absorption bands due to C–O, O–H and C–H bonds are measured to determine the ethanol concentration.

If the reading is above the legal limit, or the driver is unable to provide a breath test, a blood or urine sample may be taken for testing by gas chromatography.

12.1 Review

SUMMARY

- Matter interacts with electromagnetic radiation in different ways depending on the energy of the radiation.
- Molecules have discrete vibrational energy levels. The absorption of IR radiation causes molecules to move to higher vibrational energy levels.
- Different types of covalent bonds absorb IR radiation within a characteristic range of frequencies (wavenumbers), allowing the functional groups in an organic compound to be identified.
- Each compound has a unique absorbance pattern in the fingerprint region of the IR spectrum and this can be used to identify the compound.
- IR spectroscopy can also be used in quantitative analysis.

KEY QUESTIONS

1 What kind of energy level transition is caused by the absorption of:

- **a** infrared radiation?
- **b** ultraviolet radiation?
- **c** visible radiation?

2 Refer to Figure 12.1.1 (page 370). What parts of the electromagnetic spectrum does radiation with the following frequency belong to?

- **a** 3.2×10^{10} Hz
- **b** 8.6×10^{13} Hz
- **c** 2.4×10^{6} Hz
- **d** 9.1×10^{20} Hz

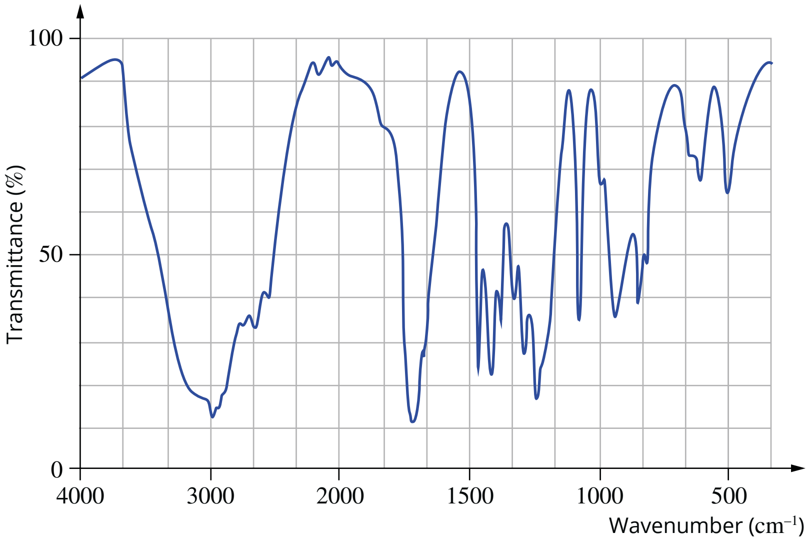
3 What absorption bands would you expect to see from the following functional groups?

- **a** Alcohol
- **b** Amide
- **c** Amine
- **d** Carboxyl
- **e** Ester
- **f** Ketone

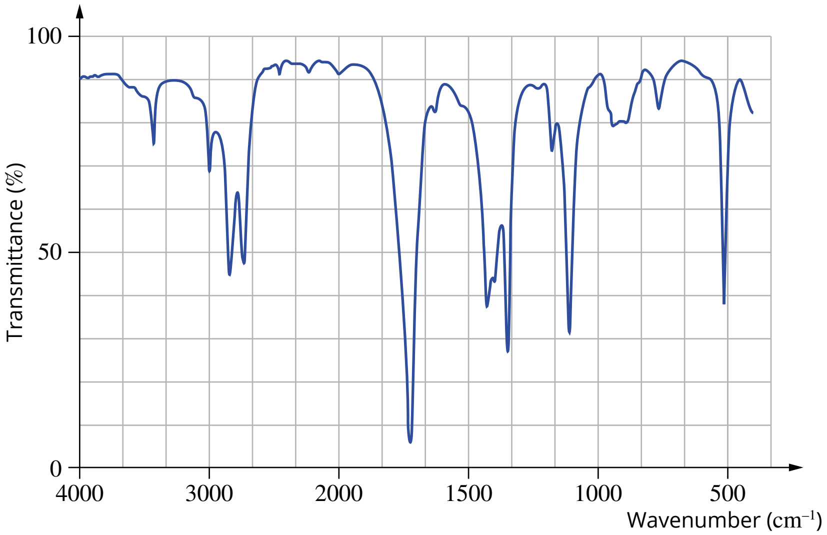
4 The absorption bands due to C–O and C–C bonds are often of little help when determining the structure of an unidentified compound, but are valuable in the confirmation of the identity of a known compound. Why is this so?

5 Identify the vibrations causing the major peaks above the fingerprint region (500–1400 cm^{-1}) in the following spectra.

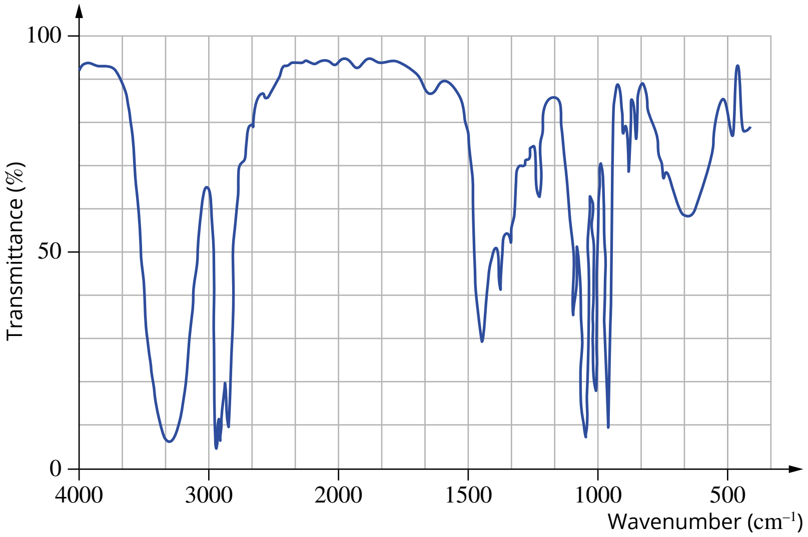
a



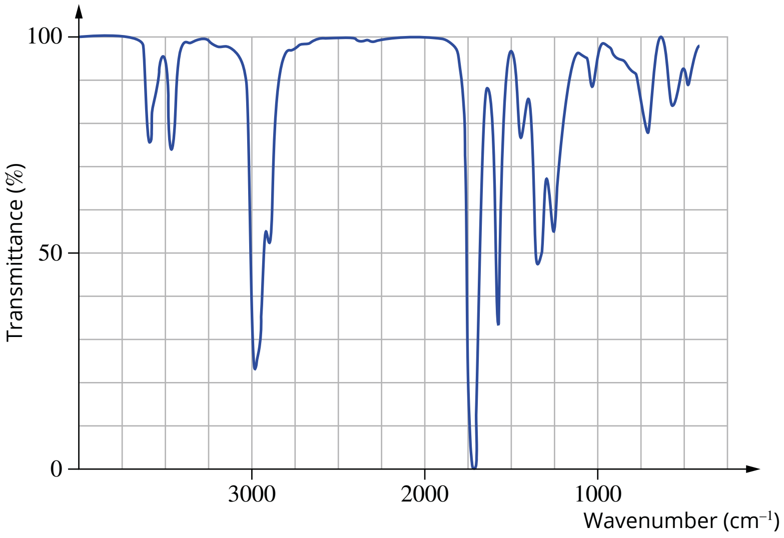
b


Transmittance (%)
100
50
0
4000
3000
2000
1500
1000
500
Wavenumber (cm⁻¹)

c


Transmittance (%)
100
50
0
4000
3000
2000
1500
1000
500
Wavenumber (cm⁻¹)

d


Transmittance (%)
100
50
0
3000
2000
1000
Wavenumber (cm⁻¹)

12.2 Nuclear magnetic resonance spectroscopy

Nuclear magnetic resonance (NMR) spectroscopy is one of most powerful techniques for determining the structure of complex molecules. NMR spectroscopy is used to distinguish between atoms in a molecule. As you saw in the previous section, IR spectroscopy provides general information about functional groups. In combination with IR spectroscopy and other techniques, NMR spectroscopy enables chemists to determine the exact structure of a molecule (Figure 12.2.1).

A form of NMR technology called magnetic resonance imaging (MRI) is used as a tool in medicine to provide a highly detailed picture of anatomical features and diseased tissue without the use of harmful radiation such as X-rays.

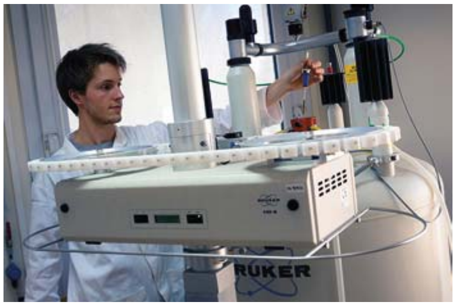


FIGURE 12.2.1 A research chemist places a sample tube into an NMR spectrometer.

PRINCIPLES OF NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

NMR spectroscopy uses electromagnetic radiation in the radio frequency range to obtain information about the structure of molecules. The energy of the radio waves is too low to cause electronic, vibrational or rotational transitions.

In order to interact with radio waves, the nuclei of the atoms must have a property called **nuclear spin**. Only nuclei that have an odd number of protons and/or neutrons, such as ^{1}H, ^{13}C and ^{31}P, have a nuclear spin. The odd number of nuclear particles causes these nuclei to behave like tiny bar magnets.

In the presence of an external magnetic field, magnets, or nuclei with spin, can either line up in the same direction as the field (lower energy) or line up in the opposite direction (higher energy), as shown in Figure 12.2.2. A magnet, or nucleus, that is aligned against an external field is in an unstable arrangement.

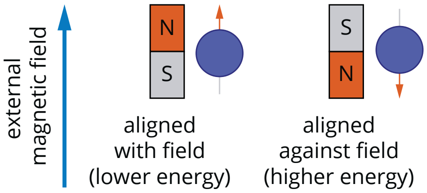


FIGURE 12.2.2 Small magnets and nuclei with spin interact with an external magnetic field.

When inside the NMR spectrometer, the nuclei are normally in a low energy state and aligned with a strong magnet. A radio transmitter is used to provide the energy to 'flip' the nuclei into a high-energy state. Over time, the nuclei tend to flip back into a lower energy spin (see Figure 12.2.3). As they do, they release a pulse of energy, which is measured and represented in graphical form as an **NMR spectrum**.

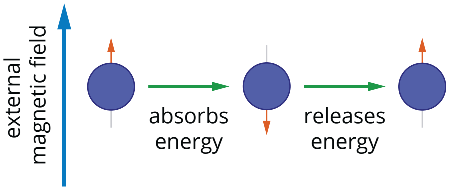


FIGURE 12.2.3 Absorption and release of energy as a nucleus changes spin.

The difference in energy between the higher and lower energy spin states depends on the type of nucleus and the chemical environment surrounding the nucleus.

The most common form of NMR spectroscopy is based on the hydrogen-1 (^{1}H) nucleus. This nucleus contains one proton and no neutrons. This type of spectroscopy is usually called **proton NMR** or ^{1}H NMR spectroscopy. It can give information about the structure of any molecule containing hydrogen atoms. Another common type of spectroscopy, called **carbon-13 NMR spectroscopy**, examines the ^{13}C nucleus and is useful in investigating the carbon atoms inside organic molecules.

A hydrogen nucleus is a proton, and chemists using NMR spectroscopy tend to use the words 'hydrogen' and 'proton' interchangeably.

EXTENSION

NMR instrumentation

The main features of an NMR spectrometer are shown in Figure 12.2.4.

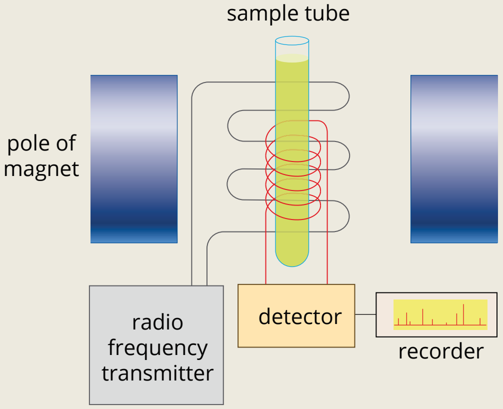


FIGURE 12.2.4 Schematic diagram of an NMR spectrometer.

The procedure used to produce an NMR spectrum is summarised below.

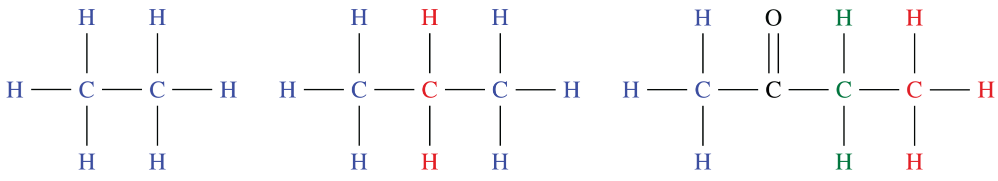
- The sample is dissolved in a solvent that does not produce a signal. Typical solvents are $CDCl_3$, D_2O and CD_2Cl_2. (Deuterium (D or ^2H), ^{16}O and ^{12}C nuclei do not show up in proton and carbon NMR spectroscopy.)
- A glass tube containing the dissolved sample is placed in the centre of a powerful magnet. The tube spins so that the sample is subjected to a uniform magnetic field.
- A radio transmitter produces a short powerful pulse of radio waves that is absorbed by the nuclei and causes them to flip to high-energy spin states.
- A radio receiver detects the radio frequency energy emitted as nuclei return to lower energy spin states.
- A computer analyses the signals and outputs the data as a NMR spectrum.

Hydrogen and carbon chemical environments

An NMR spectrum provides information about the number and type of hydrogen and carbon nuclei in an organic compound. Atoms that are in the same chemical environments absorb the same energy and produce a single signal in the NMR spectrum.

A chemical environment is made up of the atoms and electrons that surround a specific atom. Inside a molecule, atoms can be said to have the same chemical environment if they are attached in the same way to the same atoms. For example, the simplest organic molecule, methane, contains only one hydrogen environment and one carbon environment and gives only one signal in its NMR spectrum.

Figure 12.2.5 shows the structures of three organic molecules with their atoms colour-coded to show the different hydrogen and carbon environments.



ethane
one H environment
one C environment

propane
two H environments
two C environments

butanone
three H environments
four C environments

FIGURE 12.2.5 The different chemical environments in ethane, propane and butanone shown using different colours.

The six hydrogen atoms in ethane are in the same environment because each is part of a $-CH_3$ group attached to the other $-CH_3$ group. Similarly, the two carbon atoms are also in the same environment. As a result, ethane has just one signal in its proton NMR spectrum and one signal in its carbon NMR spectrum.

Propane has two different hydrogen and two different carbon environments. The six hydrogen atoms in the $-CH_3$ groups are all in the same environment, each being part of three hydrogens on a carbon attached to a $-CH_2-$ group.

The two hydrogen atoms in $–CH_2–$ make up the second environment, which is different from each of the hydrogen atoms in the $–CH_3$ groups on the ends. Again, the carbons in the $–CH_3$ groups are similar and occupy one environment, and the carbon in the centre occupies a second and different environment. The proton NMR and carbon NMR spectra each show two signals.

Butanone has three different hydrogen environments and four carbon environments. The hydrogen atoms in the two $–CH_3$ groups at either end of the molecule are not similar. One group is bonded directly to the carbonyl group, while the other is bonded to the $–CH_2–$ group. The proton NMR spectrum contains three signals. Each of the carbon atoms in the backbone of the molecule can be distinguished from the others by how close it is to the carbonyl group and whether it is on the end or within the chain. The carbon NMR spectrum of butanone contains four different signals.

As a general rule, molecules that contain symmetry have fewer different chemical environments than molecules that do not have symmetry. More planes of symmetry lead to fewer unique chemical environments

Chemical shifts

Nuclei emit different frequencies of radio energy when analysed in different spectrometers. To ensure that chemists can share results obtained using different experimental conditions, the signals emitted by nuclei are compared with the signal from a reference compound, tetramethylsilane (TMS). The structure of TMS is shown in Figure 12.2.6.

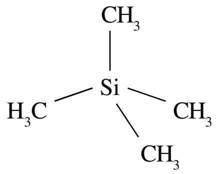


FIGURE 12.2.6 Structural formula of tetramethylsilane (TMS).

Tetramethylsilane is chemically inert and can be added to a sample without causing a chemical reaction. It contains protons, carbon atoms and a silicon atom in a symmetrical arrangement (so it has only one chemical environment in each type of NMR spectroscopy). TMS forms a single peak in an NMR spectrum that is well away from the peaks that most chemists are interested in.

The difference in energy needed to change spin state in a sample is compared to the energy needed to change spin states in TMS. This energy difference is called the **chemical shift**, and is measured in parts per million, ppm. The chemical shift of TMS is defined as zero. The symbol δ (difference) is often used to represent the chemical shift.

The actual magnetic field experienced by the nucleus is not the same as the applied external magnetic field. Electrons around each nucleus also have spin and so have an associated magnetic field that shields the nucleus from the applied magnetic field. The amount of **nuclear shielding** depends on the other atoms surrounding the nucleus. This in turn affects the amount of energy needed for the nucleus to change its spin.

The energy emitted when the nucleus flips to the lower spin state depends on the amount of nuclear shielding experienced. For example, a hydrogen atom in a $–CH_2–$ group absorbs at a slightly different frequency from hydrogen in a $–CH_3$ group or a hydrogen in an –OH group. As a consequence, the chemical shift of hydrogen in each of these species is different.

Proton NMR spectroscopy

Proton NMR spectroscopy is used to identify the different hydrogen atoms in a molecule. This involves finding the number of chemically distinct hydrogen environments there are in a molecule.

The number of signals in a proton NMR spectrum is the same as the number of different hydrogen environments. Hydrogen atoms that are in the same chemical environment are said to be **equivalent**. Equivalent atoms have the same chemical shift, and hence form one signal.

The structural formula and proton NMR spectrum of propanone are shown in Figure 12.2.7 (page 384). All six hydrogen atoms are in equivalent $–CH_3$ groups, which are bonded to the central carbonyl group. Equivalent protons have the same chemical shift, so the NMR spectrum shown in Figure 12.2.7 has only a single signal.

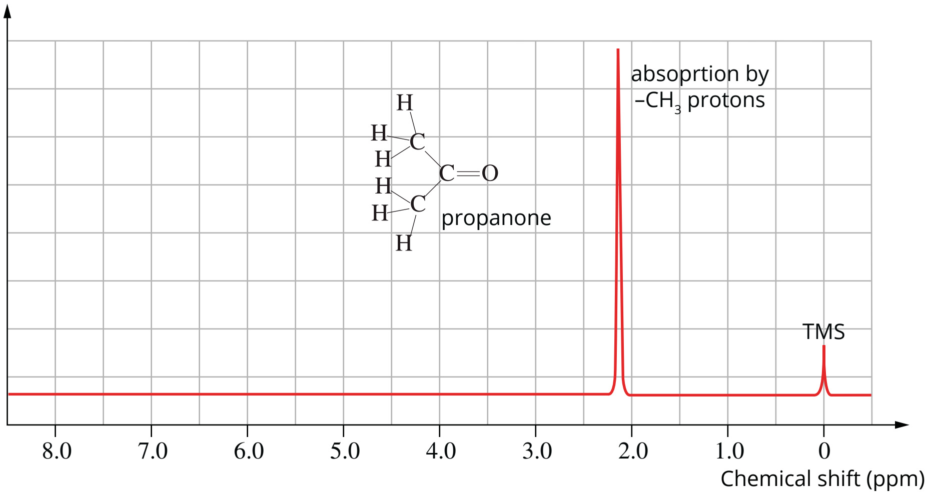


FIGURE 12.2.7 Proton NMR spectrum of propanone.

Figure 12.2.8 shows the structural formula and spectrum of dimethoxymethane, CH_3–O–CH_2–O–CH_3, which has two signals. The signal with the chemical shift of 4.6 ppm is due to the protons on the central carbon. The signal with the chemical shift of 3.4 is due to the protons in the –CH_3 groups, as they are in equivalent chemical environments.

The size of the signals is measured by the area under the curve of each signal. The peak area of each signal is proportional to the number of hydrogen atoms in the environment it corresponds with. In the spectrum of dimethoxymethane, you can see that the signals have relative peak areas of one and three, corresponding to the ratio of hydrogens in the two environments in the molecule.

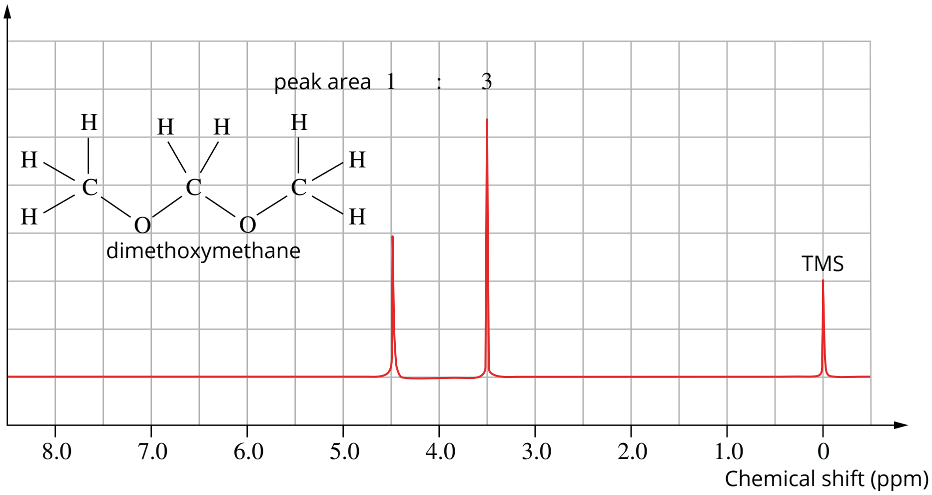


FIGURE 12.2.8 Proton NMR spectrum of dimethoxymethane.

Signal splitting

Figure 12.2.9 shows the structural formula and proton NMR spectrum of chloroethane. The hydrogen atoms in the molecule are in two different environments. The signals generated by the different types of hydrogen atoms are shown in matching colours. The relative peak areas are indicated above each peak and correspond to the number of hydrogens in each environment.

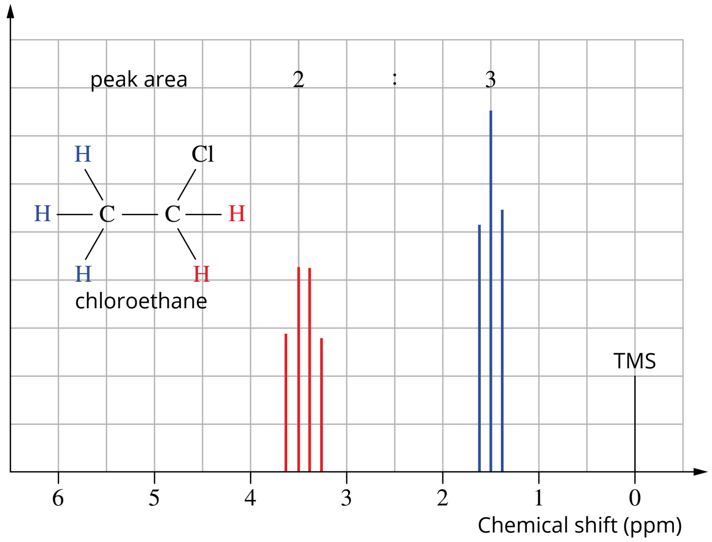


FIGURE 12.2.9 A simplified representation of the proton NMR spectrum of chloroethane.

You will notice that each signal is not a single peak, but a series of fine peaks. In high-resolution NMR spectra, some signals are seen to split into line (peak) patterns. This is due to the effect of neighbouring protons. The number of lines in a signal is related to the number of protons connected to adjacent atoms by the relationship of $n + 1$, where n is the number of protons that are equivalent to each other in neighbouring environments but not equivalent to the proton(s) giving rise to the signal. This is called the '$n + 1$ rule'.

An environment can be said to be 'neighbouring' if it is up to three bonds away from the hydrogen atoms in question. In the structure of chloroethane, you can see that there are two protons (in red) three bonds away from the protons shown in blue (the $-CH_3$ group). The number of neighbours plus one would be three for this group ($n + 1 = 2 + 1 = 3$), and the signal shows a three-line pattern. In a similar way, the $-CH_2-$ group has three neighbouring protons and gives a signal with a four-line pattern ($n + 1 = 3 + 1 = 4$).

The **splitting pattern** gives important information about which environments are caused by hydrogen atoms close to one another in a molecule. The number of neighbours causes a splitting pattern in a predictable way.

- A hydrogen atom with no **neighbours** gives a one-line signal (a singlet).
- A $-CH-$ group splits the signal from protons attached to adjacent atoms into two lines (a doublet).
- A $-CH_2-$ group splits the signal from protons attached to adjacent atoms into three lines (a triplet).
- A $-CH_3$ group splits the signal from protons attached to adjacent atoms into four lines (a quartet).

If the neighbouring protons are in an equivalent chemical environment they will not cause splitting of the signal and are not counted as neighbours as they are 'the same'. Also, note that the signal produced by the hydrogen atom in the hydroxyl group of alcohols is not usually split by hydrogen atoms attached to a neighbouring carbon atom, and does not count as a neighbour. The signal for a hydroxyl group is usually a singlet.

Signal splitting acts over small distances only. The interacting hydrogens must be bonded to adjacent atoms. For example, $CH_3OCH_2OCH_3$ shows no peak splitting because the hydrogens are not joined to adjacent atoms—they are separated by an oxygen atom.

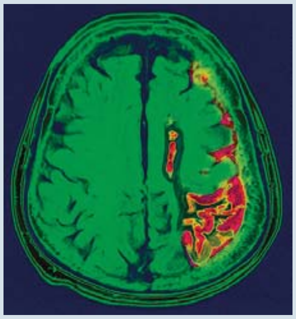


FIGURE 12.2.10 An MRI scan of the human brain showing a diseased section in red.

CHEMFILE

Magnetic resonance imaging

NMR is used in medicine in the form of magnetic resonance imaging (MRI). The scanner is effectively an NMR machine; the patient takes the place of the sample and is passed into the opening of a huge magnet and radio receiver.

The human body contains a large amount of water, which is an abundant source of protons. Normally, MRI measures the strength of the water signal in each area of the body, creating a detailed three-dimensional map. Bone, fat, muscle and tissues contain different amounts of water, allowing them to be distinguished from one another. Normal, healthy tissue gives a different response from the response from a tumour (see Figure 12.2.10). A powerful computer is used to analyse the data and present a coloured image of the patient's body.

INTERPRETATION OF PROTON NMR SPECTRA

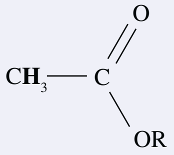
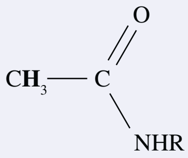
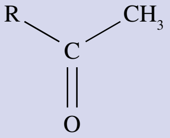
A proton NMR spectrum provides a number of pieces of information about the structure of a molecule, including the:

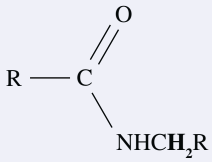
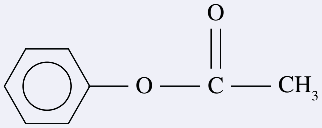
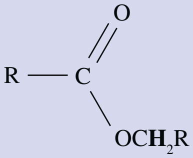
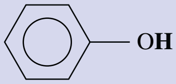
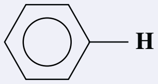
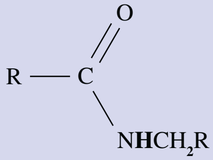
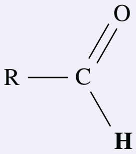
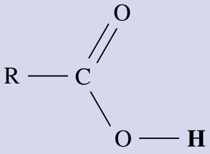
- number of signals, which shows the number of different proton environments
- relative peak area, which helps to determine the number of protons in each environment
- splitting of the signals, which provides information about the hydrogen atoms in adjacent environments
- chemical shift of the signals, which helps to identify the chemical environment in which the protons are located.

By using each piece of this information in turn and considering how the different environments would affect each other, it is often possible to determine an overall structure of a molecule.

Some typical chemical shifts for different types of protons relative to TMS are found in Table 12.2.1. These can differ slightly in different solvents. Where more than one proton environment is shown in the formula, the shift refers to the protons shown with bold letters.

TABLE 12.2.1 Typical proton NMR chemical shifts

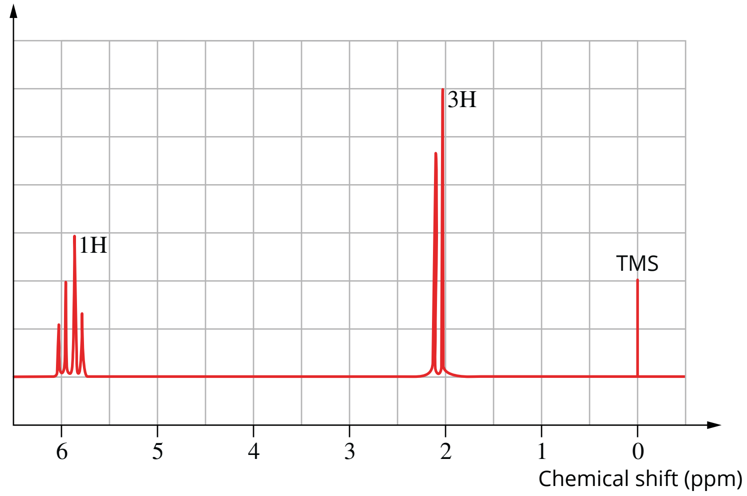
Type of proton	Chemical shift (ppm)
$\mathrm{R{-}}\mathbf{CH_3}$	0.8–1.0
$\mathrm{R{-}}\mathbf{CH_2}\mathrm{{-}R}$	1.2–1.4
$\mathrm{RCH{=}CH{-}}\mathbf{CH_3}$	1.6–1.9
$\mathrm{R_3{-}}\mathbf{CH}$	1.4–1.7
 or 	2.0
	2.1–2.7

Type of proton	Chemical shift (ppm)
$\mathrm{R-\mathbf{CH_2}-X}$ (X = F, Cl, Br or I)	3.0–4.5
$\mathrm{R-\mathbf{CH_2}-OH,\ R_2-\mathbf{CH}-OH}$	3.3–4.5
	3.2
$\mathrm{R-O-\mathbf{CH_3}}$ or $\mathrm{R-O-\mathbf{CH_2}R}$	3.3
	2.3
	4.1
$\mathrm{R-O-\mathbf{H}}$	1–6 (varies considerably under different conditions)
$\mathrm{R-\mathbf{NH_2}}$	1–5
$\mathrm{RHC=\mathbf{CH_2}}$	4.6–6.0
	7.0
	7.3
	8.1
	9–10
	9–13

Worked example 12.2.1

INTERPRETATION OF A ^{1}H NMR SPECTRUM

The proton NMR spectrum of a compound with a molecular formula of $C_2H_4Cl_2$ is shown below. Relative peak areas are shown on the spectrum.



Identify this compound using the information provided in the NMR spectrum.

Thinking	**Working**
What information does the formula provide about the compound?	Two molecules are possible from the formula: either 1,2-dichloroethane or 1,1-dichloroethane.
Summarise the information provided in the NMR spectrum in a table.	See table below.
Identify the number of different hydrogen environments.	There are two signals so there must be two different hydrogen environments.
If possible, use the chemical shifts in Table 12.2.1 (page 386) to identify the types of protons. Remember the ranges are broad.	The table does not give information about compounds containing two chloro groups, so continue on to the next step.
Use the relative peak area to deduce the number of hydrogen atoms in each environment.	The relative peak areas of the signals at 5.9 and 2.1 ppm are 1:3, so the relative number of hydrogen atoms must be 1:3. The sum of hydrogen atoms in the formula is 4, which means that the peak areas are directly equal to the number of hydrogens in each environment. This suggests that the molecule contains one –CH– group and one $–CH_3$ group.

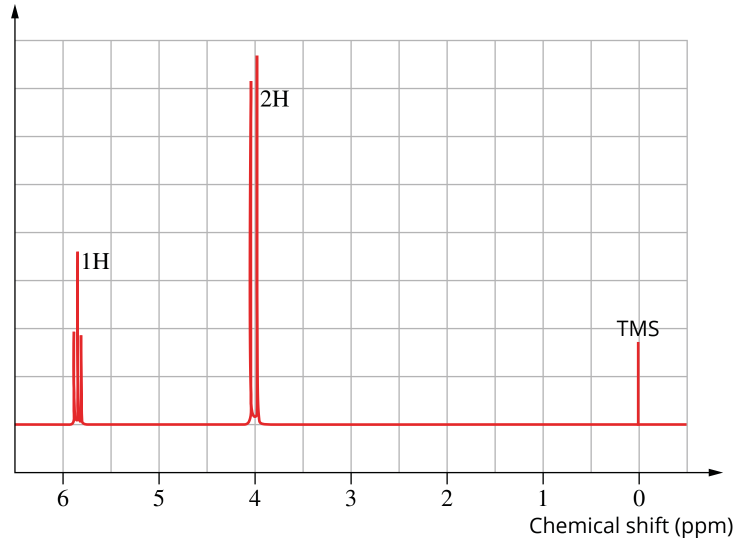
Chemical shift	Peak splitting	Relative peak area
2.1	doublet (2-line pattern)	3
5.9	quartet (4-line pattern)	1

Use the peak splitting of the signals to identify the types of hydrogen environments.	The signal at 2.1 ppm is a doublet (2-line pattern). The number of lines in the pattern is given by *n* + 1, so this signal must be generated by an environment that has 1 neighbouring hydrogen atom, i.e. a –CH– group. The signal at 5.9 ppm is a quartet (4-line pattern). The number of lines in the pattern is given by *n* + 1, so this signal must be generated by an environment that has 3 neighbouring hydrogen atoms, i.e. a $-CH_3$ group.
Use the information you gathered to identify the compound.	The molecular formula of the compound is $C_2H_4Cl_2$. The compound is either 1,2-dichloroethane or 1,1-dichloroethane. The splitting patterns and peak area indicates that the molecule contains a $-CH_3$ group adjacent to a –CH– group. The molecule must be 1,1-dichlorethane as the structure fits the evidence from the spectrum.

Worked example: Try yourself 12.2.1

INTERPRETATION OF A ^{1}H NMR SPECTRUM

The proton NMR spectrum of a compound with a molecular formula of $C_2H_3Cl_3$ is shown below. Relative peak areas are shown on the spectrum.



Identify this compound using the information provided in the NMR spectrum.

^{13}C NMR SPECTROSCOPY

Carbon-13 is a naturally occurring isotope of carbon, which has a nuclear spin. The abundance of the carbon-13 isotope is only 1.1%. The most abundant isotope of carbon is carbon-12, which has no spin and is therefore not detected by NMR spectroscopy.

The carbon-13 isotope can be used in NMR spectroscopy to identify different carbon atom environments within a molecule. TMS is also used as a reference in carbon NMR spectroscopy. As in proton NMR spectroscopy, the chemical shift relative to the TMS reference is dependent on the chemical environment a carbon atom experiences within a molecule. As shown in Table 12.2.2, chemical shifts in carbon NMR spectra range from 0 ppm to about 200 ppm.

TABLE 12.2.2 Typical carbon NMR chemical shifts

Type of carbon	Chemical shift (ppm)
$R-CH_3$	8–25
$R-CH_2-R$	20–45
R_3CH	40–60
R_4C	36–45
$R-CH_2-X$ (X = F, Cl, Br or I)	15–80
R_3C-NH_2	35–70
$R-CH_2-OH$	50–90
RC≡CR	75–95
$R_2C=CR_2$	110–150
RCOOH	160–185

Because of the low abundance of carbon-13 atoms, any particular carbon-13 atom is unlikely to be adjacent to another carbon-13 atom. For this reason, carbon-13 NMR spectra do not display splitting and all the peaks in a spectrum appear as single lines for each different carbon environment. In addition, the peak areas in a carbon NMR spectrum are not directly proportional to the number of carbon atoms in each environment.

The proton and carbon-13 NMR spectra, along with the structural formula, of chloroethane are shown in Figure 12.2.11. The proton NMR spectrum shows two signals representing the two different hydrogen environments. The carbon-13 NMR spectrum shows two signals representing the two carbon environments.

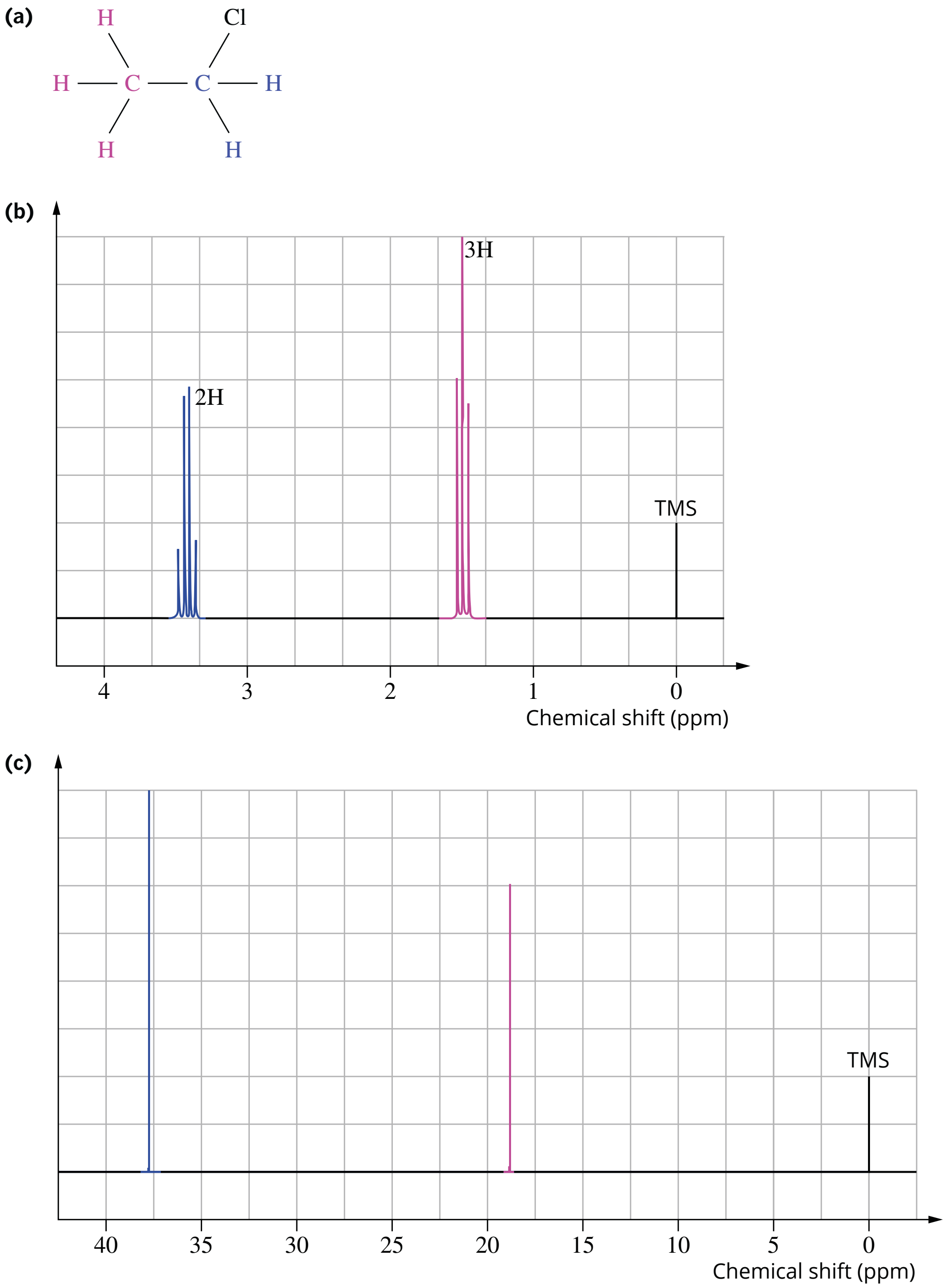


FIGURE 12.2.11 The (a) structure, (b) proton NMR spectrum and (c) carbon NMR spectrum of chloroethane, showing the atoms and their signals in different colours.

12.2 Review

SUMMARY

- Atomic nuclei within a strong magnetic field can absorb energy from radio waves and flip into a high-energy spin state. The nuclei emit a signal as they flip back to a low-energy spin state.
- Each signal in a nuclear magnetic resonance (NMR) spectrum corresponds to nuclei in a different chemical environment.
- Chemical shift is characteristic of an atom's environment.
- Proton (^1H) NMR spectroscopy provides information about the different hydrogen atoms in a molecule.
- The peak area of each signal in a proton NMR spectrum is proportional to the number of hydrogen atoms in the corresponding environment.
- Signals in a proton NMR spectrum may be split into line patterns due to the interaction of hydrogen atoms in neighbouring environments. The number of lines in the splitting pattern indicates the number of hydrogen neighbours by the rule $n + 1$.
- Carbon-13 (^{13}C) NMR spectroscopy provides information about the number and identity of different carbon atom environments in a molecule.
- Analysis of an NMR spectrum involves the study of the:
  - number of signals
  - relative peak area of each signal
  - chemical shift of the signal
  - splitting pattern.

KEY QUESTIONS

1 Proton NMR spectra give a number of pieces of information about a molecule's structure. What information can be gained from the:

a number of signals?

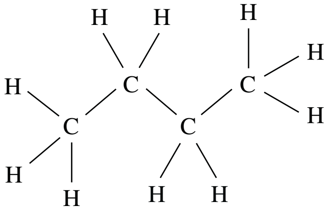
b chemical shift of a signal?

c relative peak areas?

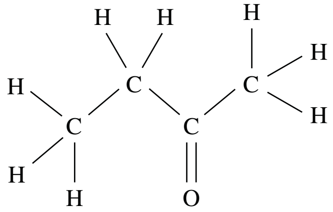
d splitting pattern of a signal?

2 Consider the following molecules.

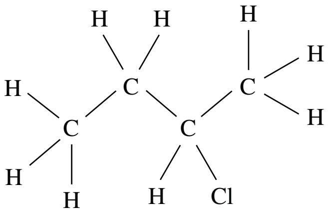
i



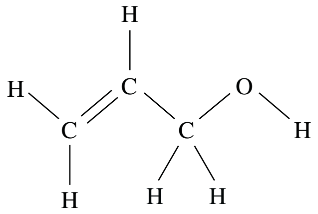
ii



iii



iv



a How many different hydrogen environments are in each molecule?

b How many different carbon environments are in each molecule?

c What splitting pattern would you expect to see from the hydrogen environments in molecule **ii**?

d What ratio would you expect to see in the relative peak areas of the signals from molecule **i**?

3 The proton NMR spectrum of a compound shows a doublet (two-line signal) with a chemical shift of 1.8, and a relative peak area of 3. Identify what this environment is likely to be.

4 Ethyl ethanoate is a solvent commonly used in nail varnish remover. The proton NMR spectrum and semistructural formula of ethyl ethanote are shown in Figure 12.2.12.

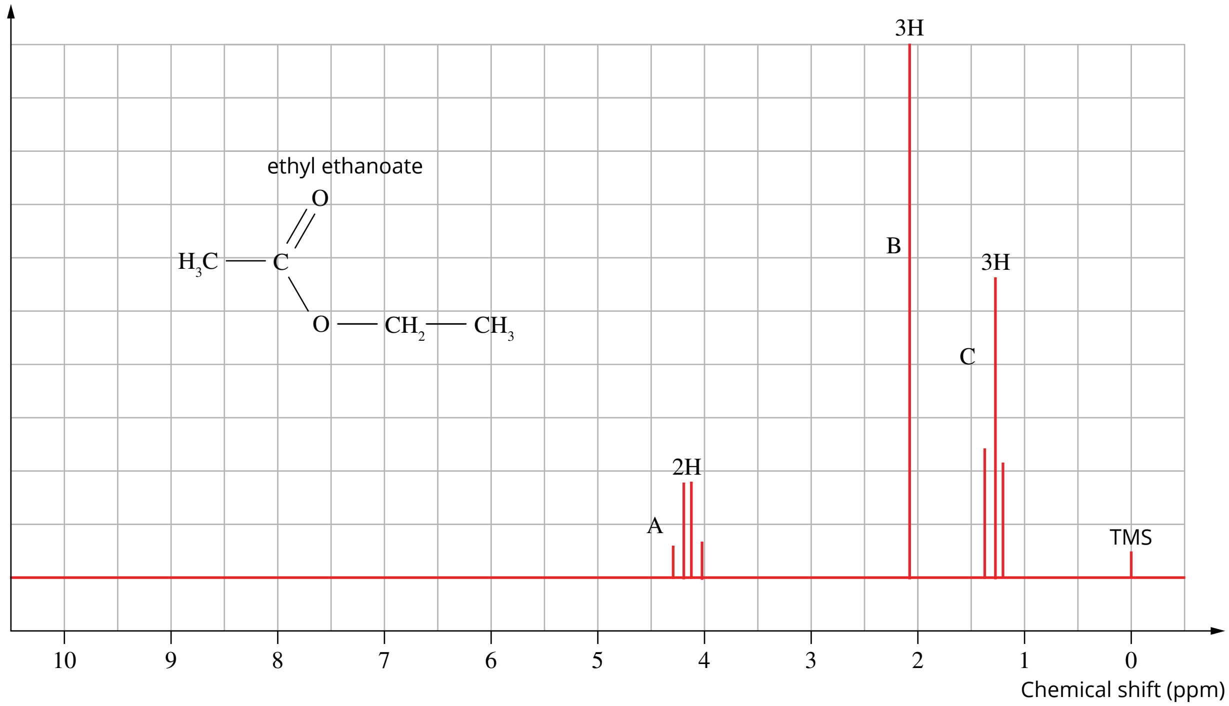


FIGURE 12.2.12 Proton NMR spectrum of ethyl ethanoate.

To answer this question you may need to refer to the chemical shift data in Table 12.2.1 (pages 386–7).

a How many hydrogen environments are there in ethyl ethanoate?

b Refer to Table 12.2.1 and identify the expected chemical shift for the groups present in the ethyl ethanoate molecule.

c What is the relative number of protons in each peak set A, B and C?

d Explain why:

- **i** peak set A is split into a quartet (four peaks)
- **ii** peak set B is a single peak
- **iii** peak set C is a triplet.

e Identify the protons responsible for each peak set and the carbon atoms to which they are bonded.

f How many peaks would you expect in the ^{13}C NMR spectrum of ethyl ethanoate?

12.3 Mass spectrometry

Mass spectrometry is one of the most commonly used analytical tools. It is used to analyse samples of solids, liquids and gases. It is a very sensitive quantitative technique that can detect concentrations in the parts per billion to parts per trillion range.

In Unit 1 of this course, you studied the use of mass spectrometry in the analysis of isotopes. Mass spectrometry can also be applied to the study of molecules. Each molecule produces its own unique mass spectrum, so a molecule can be identified by comparing its mass spectrum with the mass spectra held in a data base.

Mass spectrometry is used to determine the structure of proteins and drugs. It can also detect molecules that are common markers for diseases such as cancer. Mass spectrometers have also been used in space exploration to analyse the atmosphere on Mars and on the moons of Saturn. The Mars rover Curiosity, shown in Figure 12.3.1, is a robotic laboratory that NASA landed on Mars in 2012. Curiosity carries a number of miniaturised analytical instruments, including a mass spectrometer.

FIGURE 12.3.1 Curiosity, a robotic rover, on the surface of Mars.

Mass spectrometry is often combined with other instrumental techniques, in particular chromatography, for the analysis of mixtures.

PRINCIPLES OF MASS SPECTROMETRY

A schematic diagram of a **mass spectrometer** is shown in Figure 12.3.2.

In a mass spectrometer:

- ions are formed in the ionisation chamber where the sample is exposed to high voltages
- the ions are separated in a magnetic field on the basis of their mass-to-charge ratio (m/z)
- the number of ions with different m/z values are measured by a detector and the data is recorded as a **mass spectrum**.

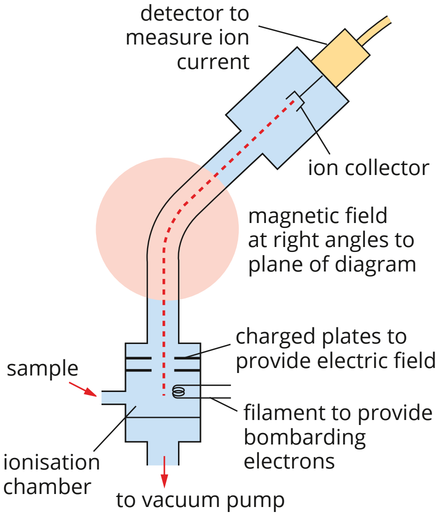


FIGURE 12.3.2 A representation of the components of a mass spectrometer.

A mass spectrometer does not use electromagnetic radiation like the spectroscopic techniques outlined in earlier sections of this chapter. The mass spectrometer gives very accurate information about the mass of positive ions formed in the instrument.

Features of a mass spectrum

A mass spectrum of a sample of pentane is shown in Figure 12.3.3. It is a plot of the abundance, measured as relative intensity, of ions of different *m*/*z*. This spectrum shows the positive ions formed when a sample of pentane was injected into the mass spectrometer.

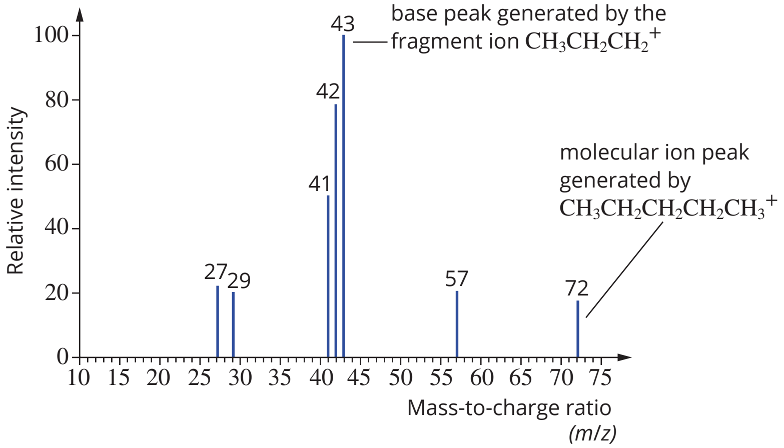


FIGURE 12.3.3 A mass spectrum of pentane ($CH_3CH_2CH_2CH_2CH_3$).

The peak at $m/z = 72$ in pentane's mass spectrum is caused by the **molecular ion**. A molecular ion is formed when the entire molecule loses an electron and becomes positively charged. When ions are singly charged, meaning $z = 1$, then the *m*/*z* ratio is the same as the molecular mass of the ion. In most cases, the peaks in a mass spectrum are generated by singly charged ions. Mass spectra of ions that have a larger charge are not covered in this course.

The other peaks in the spectrum, which have smaller *m*/*z* values than the molecular ion, represent fragment ions. These are formed when the high-energy electrons in the ionisation chamber cause bonds to break, which then causes the molecule to break into pieces.

The most intense peak, $m/z = 43$, is called the **base peak** and is produced by the most abundant fragment ion. The base peak is assigned a relative intensity of 100%. The intensity of all the other peaks are measured relative to the base peak. In some spectra, the peak with the highest intensity is also the molecular ion. In other spectra, the base peak may correspond to a smaller fragment. The relative intensities of the peaks in the spectrum depend on the:

- energy of the ionising electrons
- ease with which fragments can be formed
- stability of the fragment ions formed.

TABLE 12.3.1 Common positive fragment ions

m/*z*	Formula
15	CH_3^+
17	OH^+
29	$CH_3CH_2^+$, CHO^+
31	CH_3O^+
35 and 37	$^{35}Cl^+$, $^{37}Cl^+$
43	$CH_3CH_2CH_2^+$, CH_3CO^+
45	$COOH^+$
79, 81	$^{79}Br^+$, $^{81}Br^+$

Fragmentation

Inside the ionisation chamber, high-energy electrons ionise the sample by knocking off or adding an electron, leading to a positive or negative molecular ion. Because covalent bonds are formed from the sharing of electrons, the addition or removal of electrons can cause the bonds to weaken and break.

The **fragmentation** of the molecule into smaller pieces is represented in the mass spectrum by peaks with a *m*/*z* smaller than the molecular ion. Fragments can be produced by the breaking of almost any bond in the molecular ion. They may represent single atoms, small groups of atoms or large sections of the parent molecule.

The *m*/*z* values and formulas of some common fragment ions in mass spectra of organic molecules are listed in Table 12.3.1.

INTERPRETATION OF MASS SPECTRA

The information that is provided by mass spectrometry can be illustrated by examining the mass spectrum of ethanoic acid.

Ethanoic acid (CH_3COOH) can be ionised in a mass spectrometer by removing an electron in the following process:

$$CH_3COOH + e^- \rightarrow CH_3COOH^+ + 2e^-$$

The molecular ion, CH_3COOH^+, is unstable and can break into a number of fragment ions as shown in Figure 12.3.4.

The molecular and fragment ions generate peaks in the mass spectrum of ethanoic acid, shown in Figure 12.3.5.

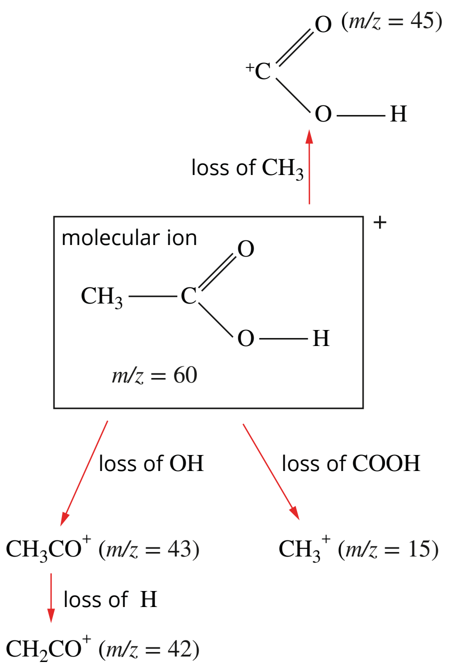


FIGURE 12.3.4 Formation of fragment ions from ethanoic acid.

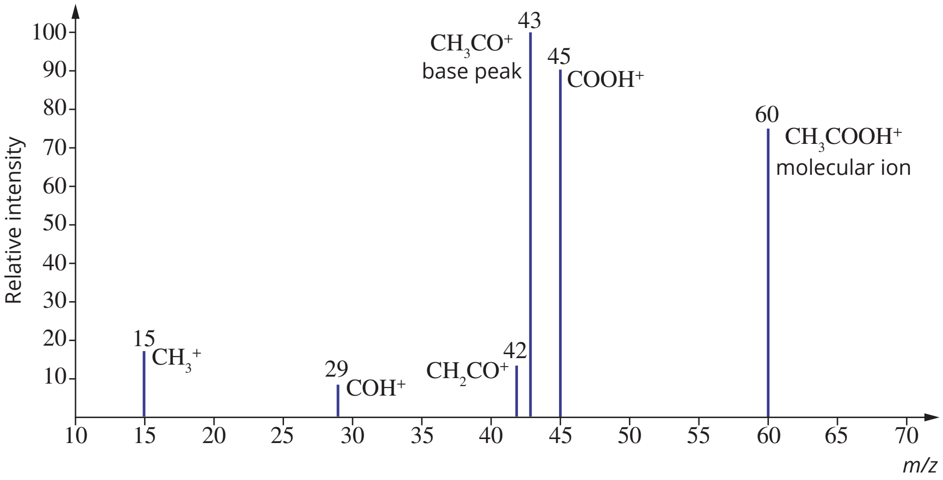


FIGURE 12.3.5 Mass spectrum of ethanoic acid.

The mass spectrum of ethanoic acid indicates that the molecular ion has a mass of 60. The mass of the molecular ion is the same as the relative molecular mass of the ethanoic acid molecule. The fragment ions provide information about the structure of the ethanoic acid molecule, as shown in Table 12.3.2.

TABLE 12.3.2 Identity of peaks in ethanoic acid mass spectrum

m/z	Ion identity	
60	CH_3COOH^+	Molecular ion caused by loss of an electron
45	$COOH^+$	Loss of CH_3 from molecular ion
43	CH_3CO^+	Loss of OH from molecular ion
42	CH_2CO^+	Loss of H from CH_3CO^+
29	COH^+	Loss of an O atom from $COOH^+$
15	CH_3^+	Loss of COOH from molecular ion

Worked example 12.3.1

DETERMINING THE IDENTITY OF A COMPOUND FROM ITS MOLECULAR ION

The mass spectrum of an unbranched alkane has a molecular ion peak of $m/z = 86$. Determine the molecular formula of the alkane and give its name.

Thinking	Working
The m/z value of the molecular ion is equal to the relative molecular mass of the molecule.	The relative molecular mass of the alkane is 86.
Identify the general formula for the molecule.	The general formula for an alkane is C_nH_{2n+2}.
Use the general formula to set up an equation linking the relative molecular mass to the relative atomic masses of the constituent atoms.	$M_r(C) = 12$ $M_r(H) = 1$ $(12 \times n) + (1 \times (2n + 2)) = 86$
Solve the equation for n.	$12n + 2n + 2 = 86$ $14n + 2 = 86$ $14n = 84$ $n = 6$
Use the value of n to find the molecular formula and the name.	C_6H_{14}, which is hexane.

Worked example: Try yourself 12.3.1

DETERMINING THE IDENTITY OF A COMPOUND FROM ITS MOLECULAR ION

The mass spectrum of an unbranched alkane has a molecular ion peak at $m/z = 58$. Determine the molecular formula of the alkane and give its name.

Isotope effects

Most elements exist as mixtures of **isotopes**, as shown in Table 12.3.3. The presence of isotopes in molecules leads to the appearance of additional peaks in a mass spectrum.

TABLE 12.3.3 Isotopes of some atoms and their percentage abundance

Element	Isotope	Isotopic mass	Percentage abundance	Isotope	Isotopic mass	Percentage abundance
Hydrogen	^{1}H	1.0	99.98	^{2}H	2.0	0.02
Carbon	^{12}C	12.0	98.9	^{13}C	13.0	1.1
Oxygen	^{16}O	16.0	99.8	^{18}O	18.0	0.2
Chlorine	^{35}Cl	35.0	75.8	^{37}Cl	37.0	24.2
Bromine	^{79}Br	79.0	50.7	^{81}Br	81	49.3

The percentage abundance of ^{2}H, ^{13}C and ^{18}O in samples is very small, so ions containing them only produce very small peaks in the mass spectra. The presence of these isotopes can be ignored in most instances. However, chlorine and bromine have high proportions of each isotope, and so samples that contain them have significant peaks for each isotope in their mass spectra.

The mass spectrum of chloromethane (CH_3Cl) shows peaks for two molecular ions (Figure 12.3.6).

- The peak at $m/z = 50$ is due to the molecular ion containing ^{35}Cl.
- The peak at $m/z = 52$ is due to the other molecular ion containing ^{37}Cl.

The relative heights of these peaks reflects the relative abundance of the two isotopes.

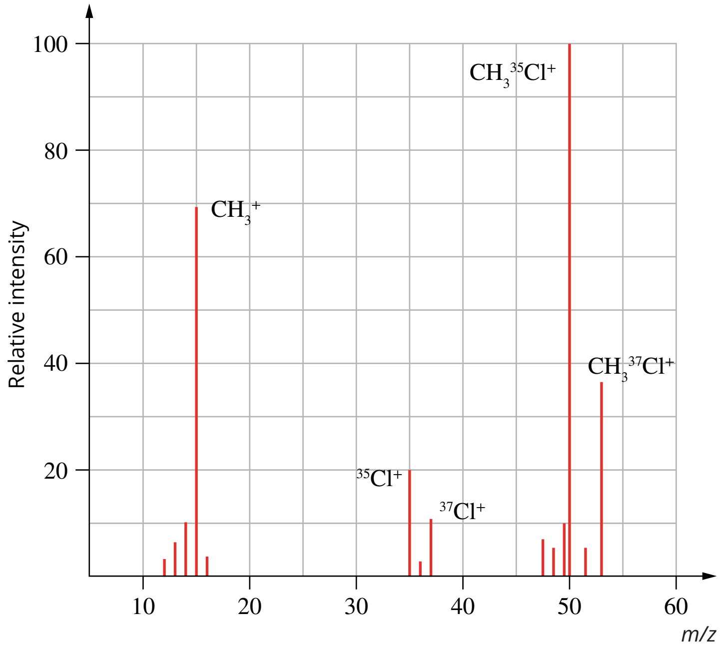


FIGURE 12.3.6 The mass spectrum of chloromethane (CH_3Cl). Note the two molecular ion peaks due to the isotopes of chlorine.

As the number of atoms that have significant proportions of isotopes increases, the mass spectrum can become more complex. The mass spectrum of dichloromethane (CH_2Cl_2) shows three **molecular ion peaks** (Figure 12.3.7).

- The peak at $m/z = 84$ is due to the molecular ion containing two ^{35}Cl atoms.
- The peak at $m/z = 86$ is due to the molecular ion containing one ^{35}Cl atom and one ^{37}Cl atom.
- The peak at $m/z = 88$ is due to the molecular ion containing two ^{37}Cl atoms.

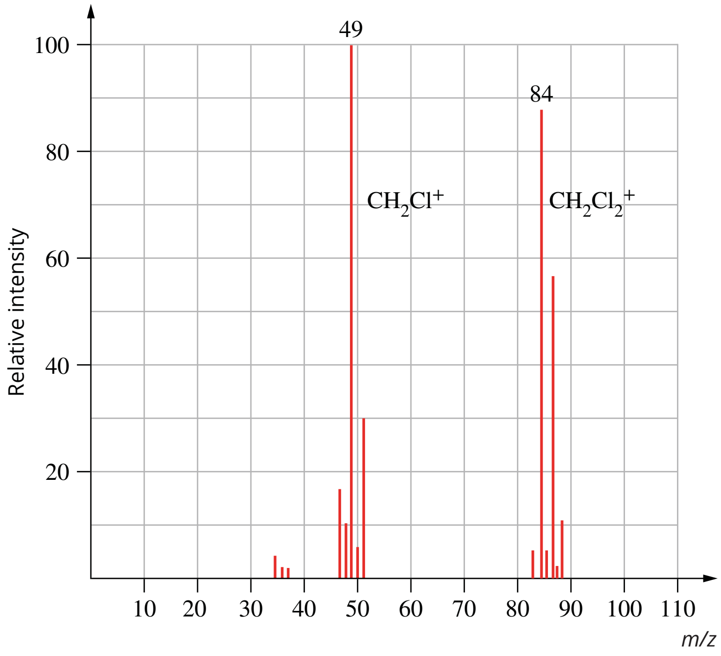


FIGURE 12.3.7 The mass spectrum of dichloromethane (CH_2Cl_2). Note the three molecular ion peaks at m/z = 84, 86 and 88 due the isotopes of chlorine.

Dichloromethane is found in a wide range of household products, including paints, polishes, air fresheners, hairsprays, household insecticides, shoe polish, pet flea and tick products, and waterproofing compounds.

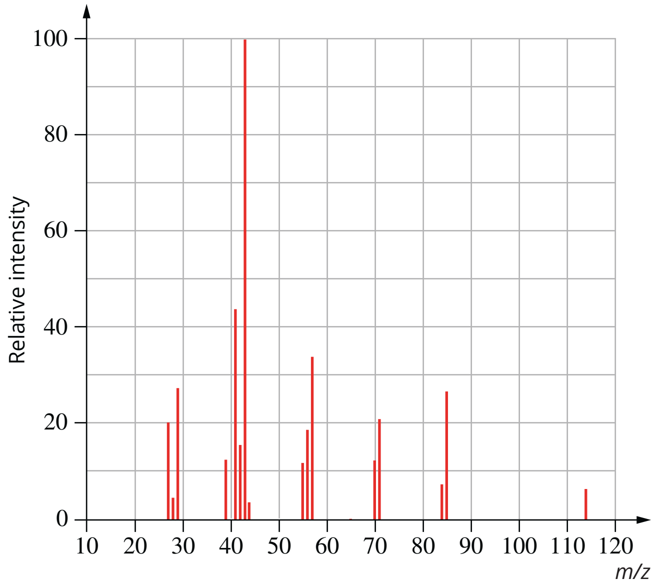
12.3 Review

SUMMARY

- A mass spectrometer measures the mass-to-charge ratio, *m*/*z*, of ions.
- The peak that has the highest *m*/*z* is usually caused by the entire molecule becoming ionised and is called the molecular ion peak.
- The molecular ion can break into pieces called fragment ions.
- Fragmentation of a molecule in a mass spectrometer can help to determine its molecular structure.
- Each compound has a unique mass spectrum that can be used to identify it.
- The mass spectrum of a compound containing chlorine or bromine atoms has significant additional peaks due to the isotopes of chlorine and bromine.

KEY QUESTIONS

1 The following mass spectrum is of a straight-chain alkane.



a What is the relative molecular mass of the compound?
b What is the *m*/*z* value of the base peak?
c What is the formula for the fragment ion with an *m*/*z* value of 85?
d What is the name of the alkane represented?

2 What are the molecular ions that would be found in the mass spectrum of 1,1-dibromoethane?

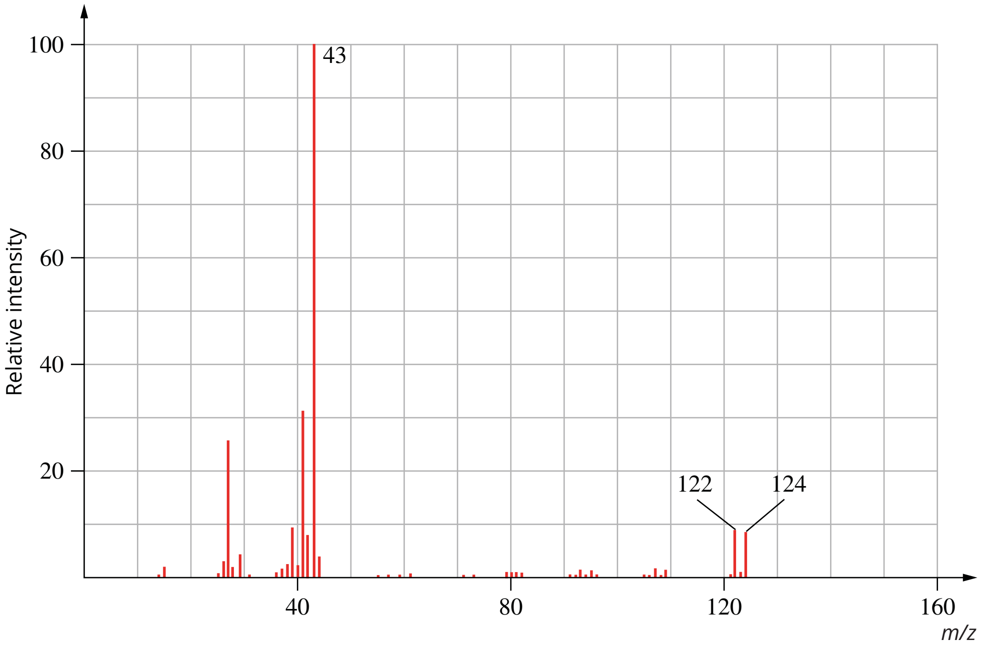
3 The mass spectrum of a bromoalkane is shown here.

a What is the formula of the bromoalkane?

b Explain why the mass spectrum has two peaks at *m/z* = 122 and *m/z* = 124.

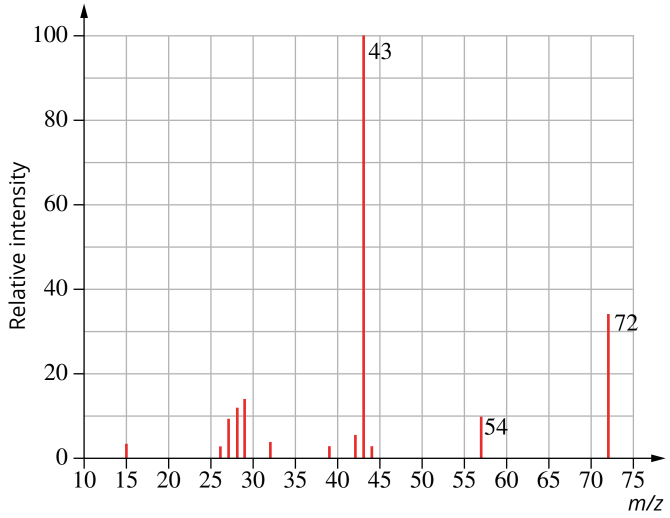
c Account for the relative heights of these two peaks.

d Write a possible formula for the ion responsible for the peak at *m/z* = 43.

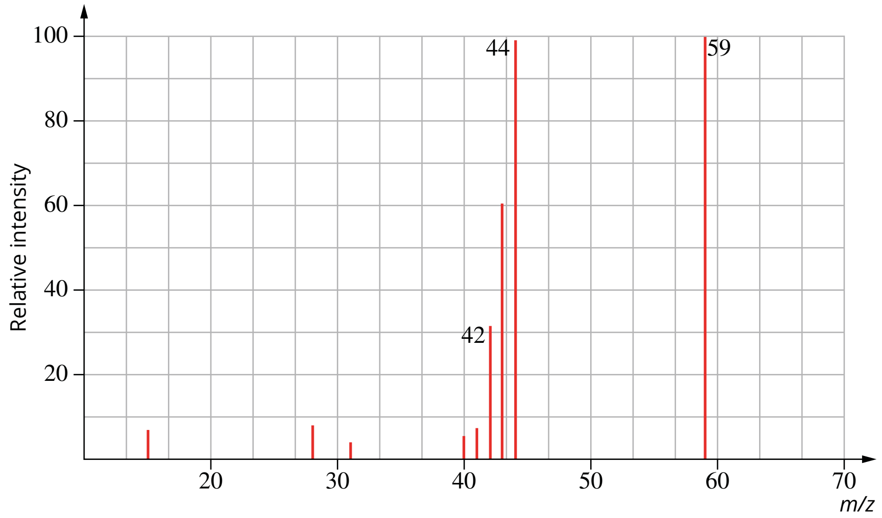


4 Use the following mass spectra to determine the identity of the molecules represented by the following mass spectra.

a A ketone



b An amide



12.4 Determination of molecular structure by spectroscopy

Chemists determine the structure and identity of unknown compounds by employing a range of analytical techniques. Each technique provides a different piece of information about the compound's structure, which, when considered together (along with educated guesses), can identify the substance. The process can be compared to piecing together the pieces of a jigsaw puzzle.

The structures of organic compounds are often determined using a combination of IR spectroscopy, NMR spectroscopy and mass spectrometry. Chemical and physical properties can also provide clues about the identity of a compound.

In this section, you will investigate how the structure of an unidentified compound can be determined.

As you read through and complete the questions in this section, you will need to refer to the IR and NMR tables (Tables 12.1.4 on page 375, 12.2.1 on page 386 and 12.2.2 on page 389) provided earlier.

COMBINING ANALYSES TO LEARN MORE

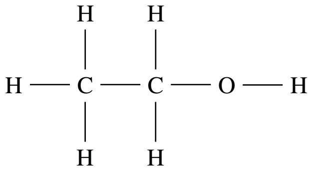


FIGURE 12.4.1 Molecular structure of ethanol.

Ethanol will be used as an example of how the results of different types of analysis can be used to identify an unknown organic compound. Ethanol has a molar mass of 46 g mol^{-1}. The structural formula of ethanol is shown in Figure 12.4.1.

The mass spectrum for ethanol can be seen in Figure 12.4.2. Using this spectrum, the following can be determined.

- There is a molecular ion peak at $m/z = 46$, which corresponds to a relative molecular mass of 46.
- The fragment ion peaks are identified on the spectrum and are consistent with the fragmentation of a molecule with the formula C_2H_6O.

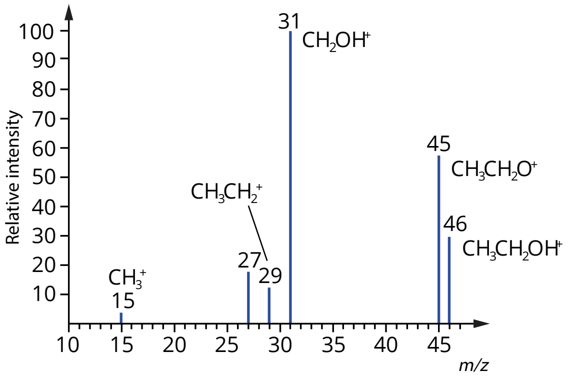


FIGURE 12.4.2 Mass spectrum of ethanol.

The infrared spectrum of ethanol (see Figure 12.4.3) provides the following information.

- The most prominent feature is the broad stretch at 3400 cm^{-1} due to the O–H bond and confirms the presence of an alcohol hydroxyl group.
- The absorption bands due to the C–H and C–O bonds are also shown.

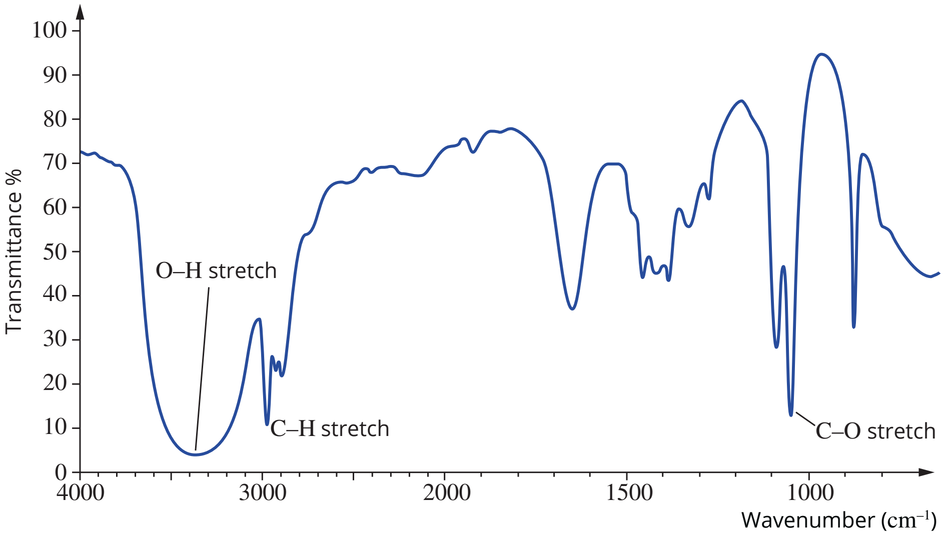


FIGURE 12.4.3 IR spectrum of liquid ethanol.

The proton NMR spectrum for ethanol is shown in Figure 12.4.4. It provides the following information.

- There are three signals, which means that the molecule contains three different proton environments.
- The signal with chemical shift of approximately 3.7 ppm is a four-line pattern and has a relative peak area of 2. The chemical shift and peak area are consistent with the signal of a $-CH_2-$ group adjacent to a hydroxyl group. The splitting pattern indicates there are three protons in a neighbouring environment. (Remember that a proton on an –OH group does not usually split the signals of adjacent protons.)
- The signal at 1.2 ppm is a three-line pattern with a relative peak area of 3. This is consistent with the signal of a $-CH_3$ group adjacent to a $-CH_2-$ group.
- The singlet at 2.6 ppm is consistent with the signal of an alcohol hydroxyl group.

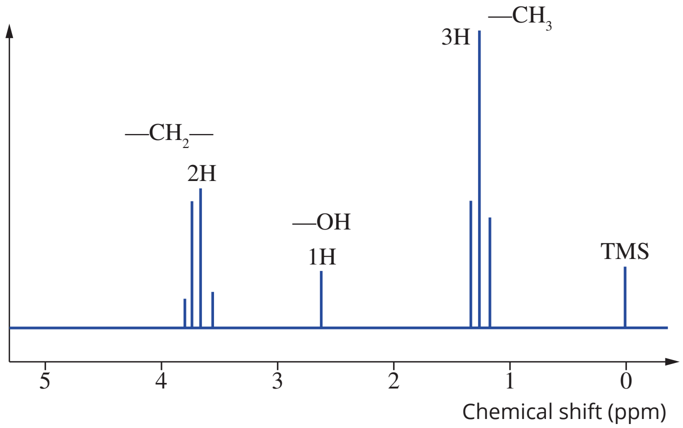


FIGURE 12.4.4 Proton NMR spectrum of ethanol.

The carbon NMR spectrum for ethanol shown in Figure 12.4.5 provides the following information.

- There are two signals, meaning that the molecule contains two different carbon environments.
- The signal at 58 ppm corresponds to the signal of a carbon attached to a hydroxyl group, $R-CH_2-OH$.
- The signal at 18 ppm is consistent with the signal from a methyl group, $-CH_3$.

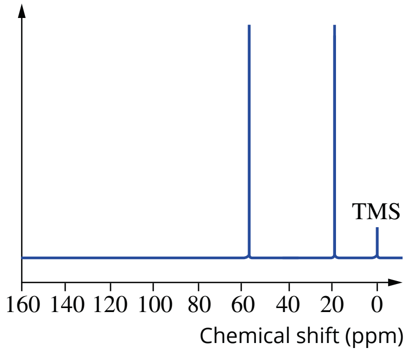


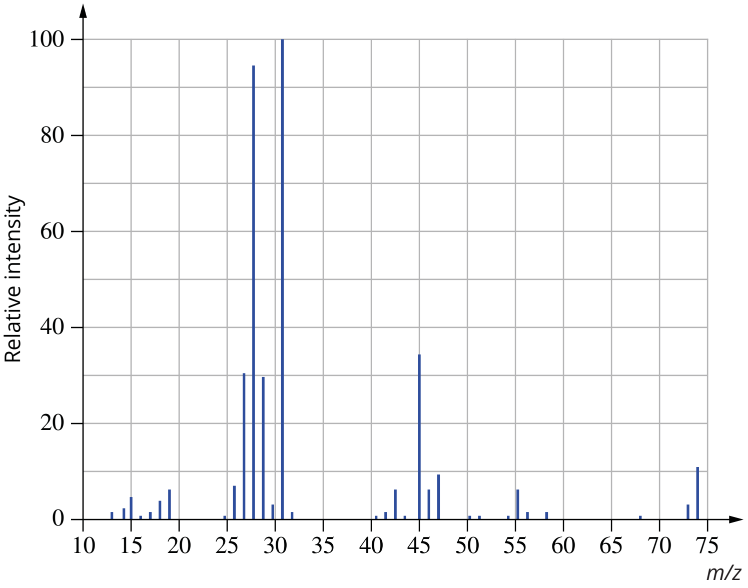
FIGURE 12.4.5 Carbon NMR spectrum of ethanol.

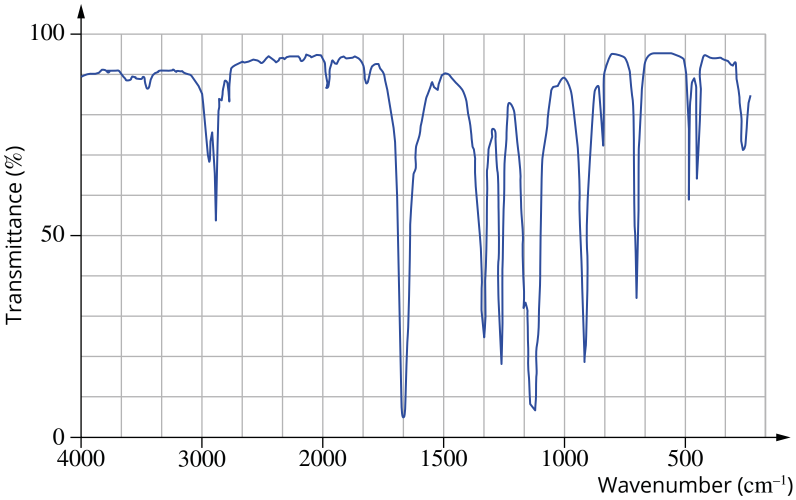
When each piece of evidence from analysing the different spectra is put together, you can see that the structure must be CH_3CH_2OH. Each of the spectra contains the peaks expected of ethanol, and none of the spectra contains information that is inconsistent with ethanol.

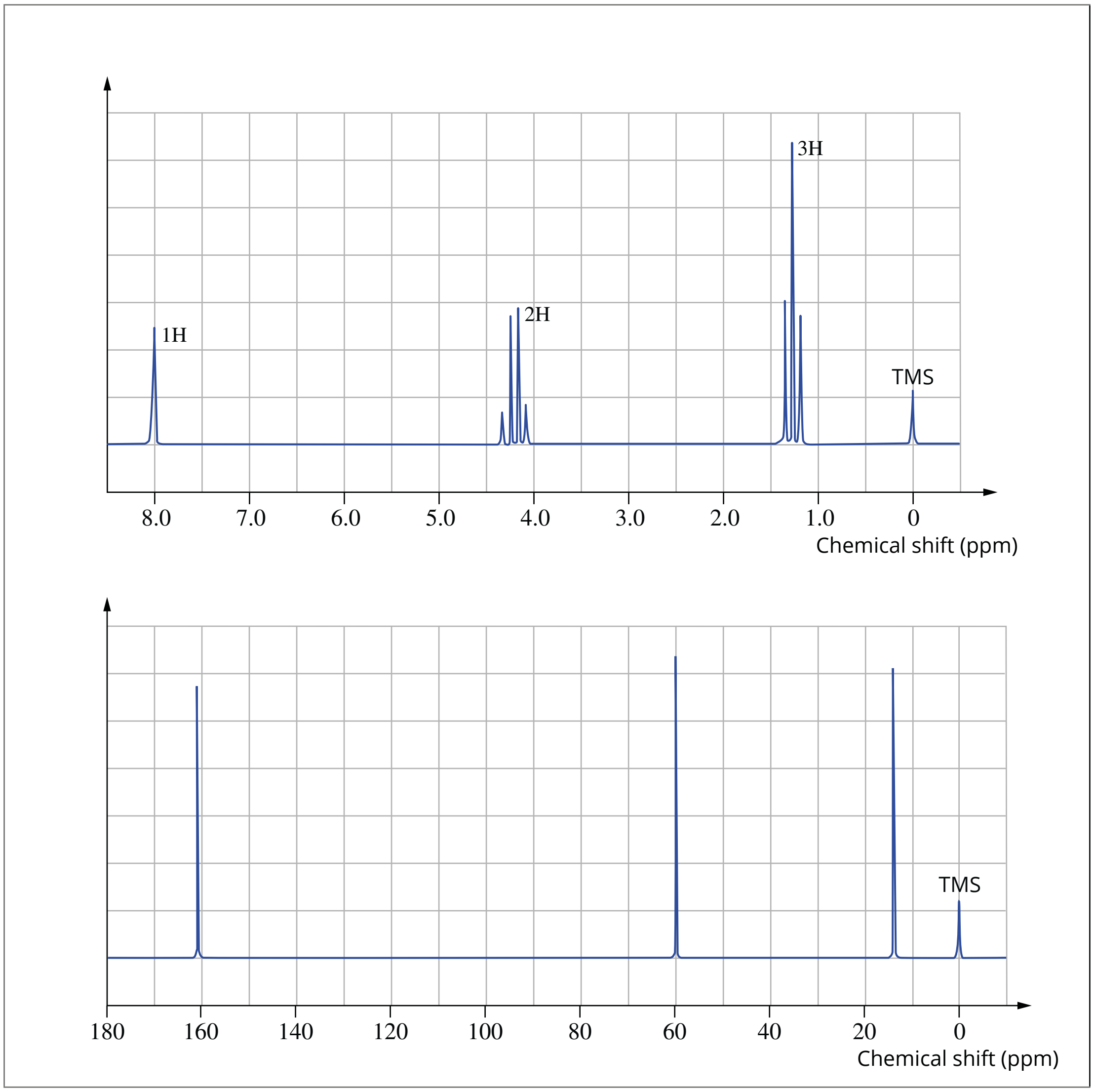
Worked example 12.4.1

DEDUCING MOLECULAR STRUCTURE FROM SPECTROSCOPIC DATA

A sweet-smelling liquid has an empirical formula of $C_3H_6O_2$. Chemical tests show that the compound is not an aldehyde or a ketone. Use this information and the mass, IR and NMR spectra provided to deduce the structure and name of the compound.







Thinking	**Working**
Use the mass spectrum to identify the molecular ion and relative molecular mass.	The peak with the largest mass-charge ratio is at *m/z* = 74, so the relative molecular mass is 74. This mass is consistent with the molecular formula of $C_3H_6O_2$.
Use the IR spectrum to identify functional groups present in the compound. (Refer to Table 12.1.4 on page 375.)	The IR spectrum shows a strong absorption band at 1700 cm^{-1}, suggesting the presence of a C=O bond, and hence a carbonyl group. The IR spectrum does not contain a strong, broad absorption in the range of 2500–3300 cm^{-1}, indicating there is no O–H bond in the molecule.

<table>
<tr>
<td>Use the proton NMR spectrum to identify the different hydrogen environments. (Refer to Table 12.2.1 on page 386.)</td>
<td>
The NMR data is summarised in the following table.

<table>
<tr><th>Chemical shift (ppm)</th><th>Splitting pattern</th><th>Relative peak area</th></tr>
<tr><td>1.3</td><td>Triplet (3-line pattern)</td><td>3</td></tr>
<tr><td>4.2</td><td>Quartet (4-line pattern)</td><td>2</td></tr>
<tr><td>8.0</td><td>Singlet (1-line pattern)</td><td>1</td></tr>
</table>

The spectrum contains three signals and so there are three different hydrogen environments.

The sum of the relative peak areas is 6, which is consistent with the molecular formula, each unit of peak area corresponds to one hydrogen atom.

The signal at 1.3 ppm is consistent with the signal produced by a $–CH_3$ group with two hydrogens in a neighbouring environment.

The signal at 4.2 ppm is consistent with the signal produced by a $–CH_2–$ group singly bonded to the oxygen of an ester group, with three hydrogens in a neighbouring environment.

The signal at 8.0 ppm is a singlet, indicating that there are no hydrogen atoms attached to adjacent atoms. The chemical shift is quite large and could be consistent with a proton attached to a carbonyl group.
</td>
</tr>
<tr>
<td>Use the carbon NMR spectrum to identify the different carbon environments. (Refer to Table 12.2.2 on page 389.)</td>
<td>
There are three signals in the carbon NMR spectrum and so the molecule contains three different carbon environments.

The number of carbon environments corresponds to the number of carbons in the molecular formula, so each environment represents one carbon atom.

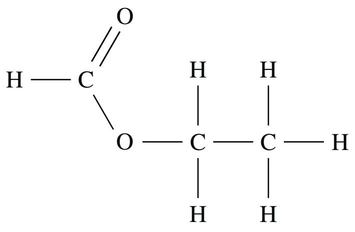
The signal at 161 ppm is consistent with a carbon in a carbonyl group.

The signal at 60 ppm is consistent with a carbon attached to an oxygen atom by a single bond to an oxygen.

The signal at 14 ppm is consistent with a methyl group, $R–CH_3$.
</td>
</tr>
<tr>
<td>Use the data from the spectra to deduce the structure of the compound.</td>
<td>
The data provided by the spectra show that:

- the molecular formula of the compound is $C_3H_6O_2$
- the compound has a carbonyl group, but no hydroxyl group
- it is an ester
- the compound has a $CH_3CH_2–$ group attached by a single bond to an oxygen atom
- the compound has a HC=O group.

A structure consistent with this data is:

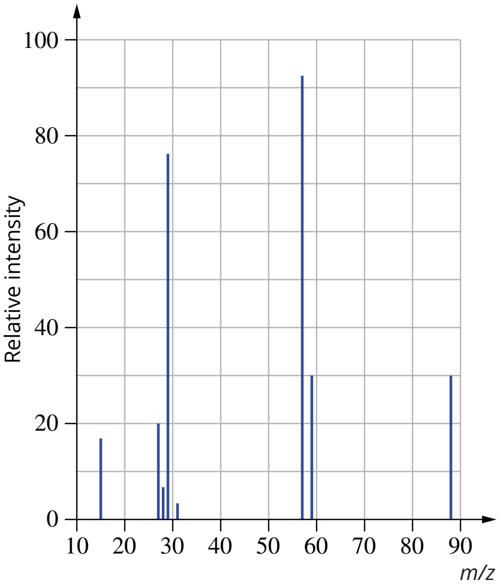


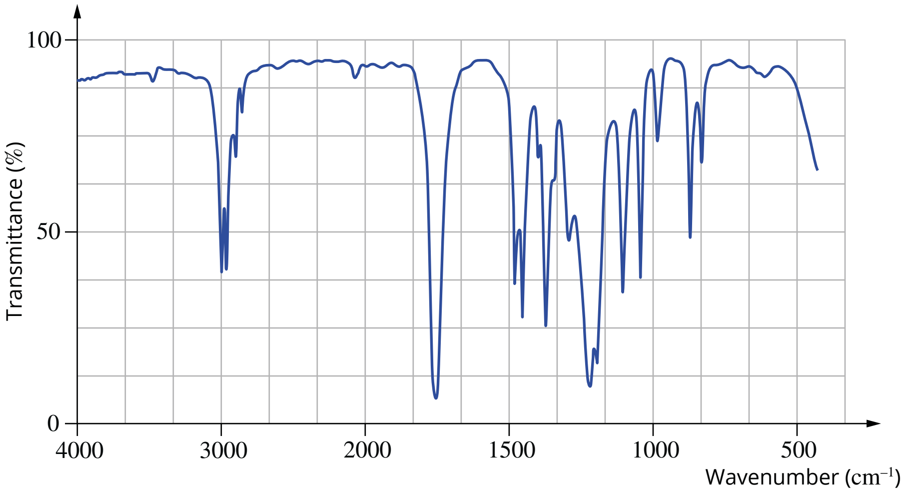
</td>
</tr>
<tr>
<td>Name the compound.</td>
<td>Ethyl methanoate</td>
</tr>
</table>

Worked example: Try yourself 12.4.1

DEDUCING MOLECULAR STRUCTURE FROM SPECTROSCOPIC DATA

A sweet-smelling liquid has an empirical formula of C_2H_4O. Chemical tests show that the compound is not an aldehyde or ketone. Use this information and the mass, IR and NMR spectra provided to deduce the structure and name of the compound.





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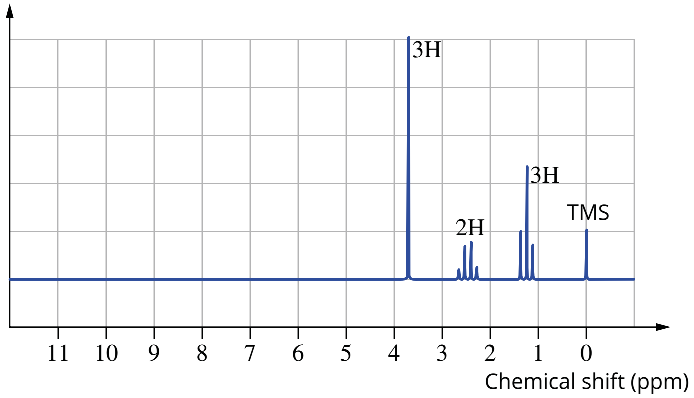
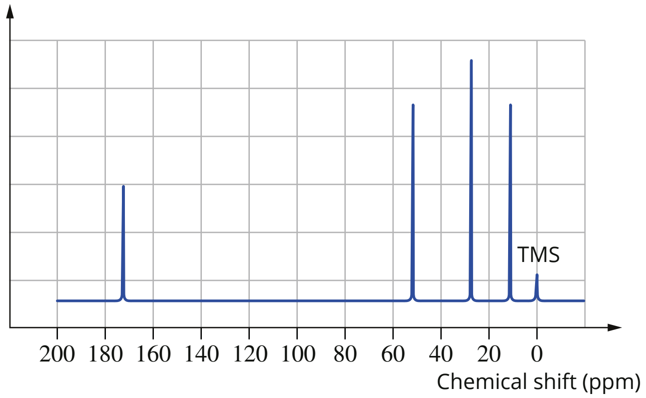
Worked example: Try yourself 12.4.1 (*continued*)





12.4 Review

SUMMARY

- A combination of information derived from mass spectrometry, infrared spectroscopy, proton NMR spectroscopy and carbon NMR spectroscopy can be used to determine the molecular structure of organic compounds.
- The molecular formula of a molecule can be determined from its mass spectrum if its empirical formula is known.
- The infrared spectrum of a compound provides evidence about functional groups present in a molecule.
- The proton and carbon NMR spectra provide detailed information that can be used to determine the connectivity of atoms and overall structure of a molecule.

KEY QUESTIONS

1 An industrial solvent has the molecular formula C_4H_8O. Use the infrared, proton NMR and carbon-13 NMR spectra in Figure 12.4.6 (on page 408) to determine the semistructural formula of this molecule.

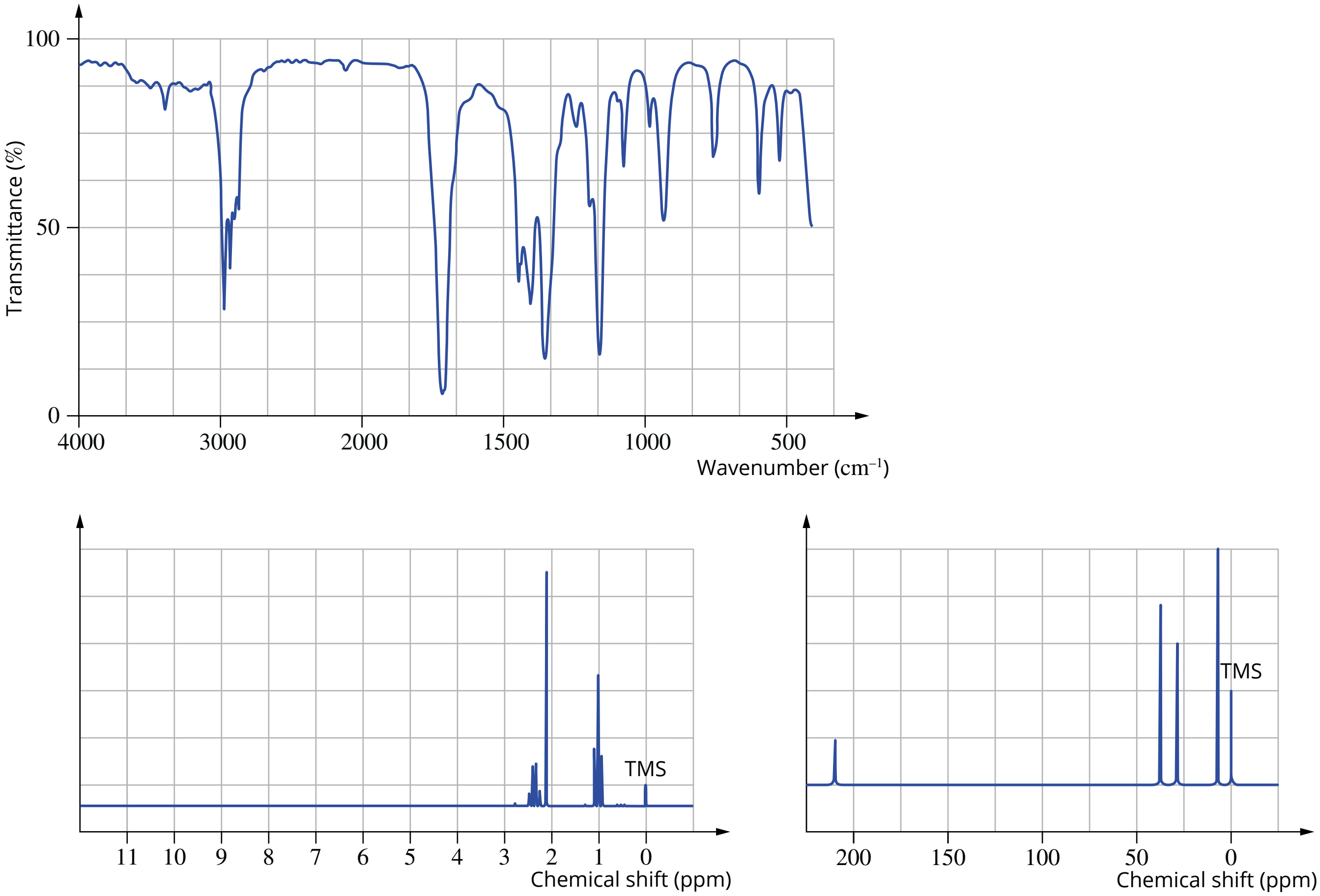


FIGURE 12.4.6 Spectra for an unknown molecule.

2 An unidentified organic compound is composed of 48.6% carbon, 8.2% hydrogen and 43.2% oxygen. Use this information and the spectra in Figures 12.4.7 and 12.4.8 to determine the name of the compound.

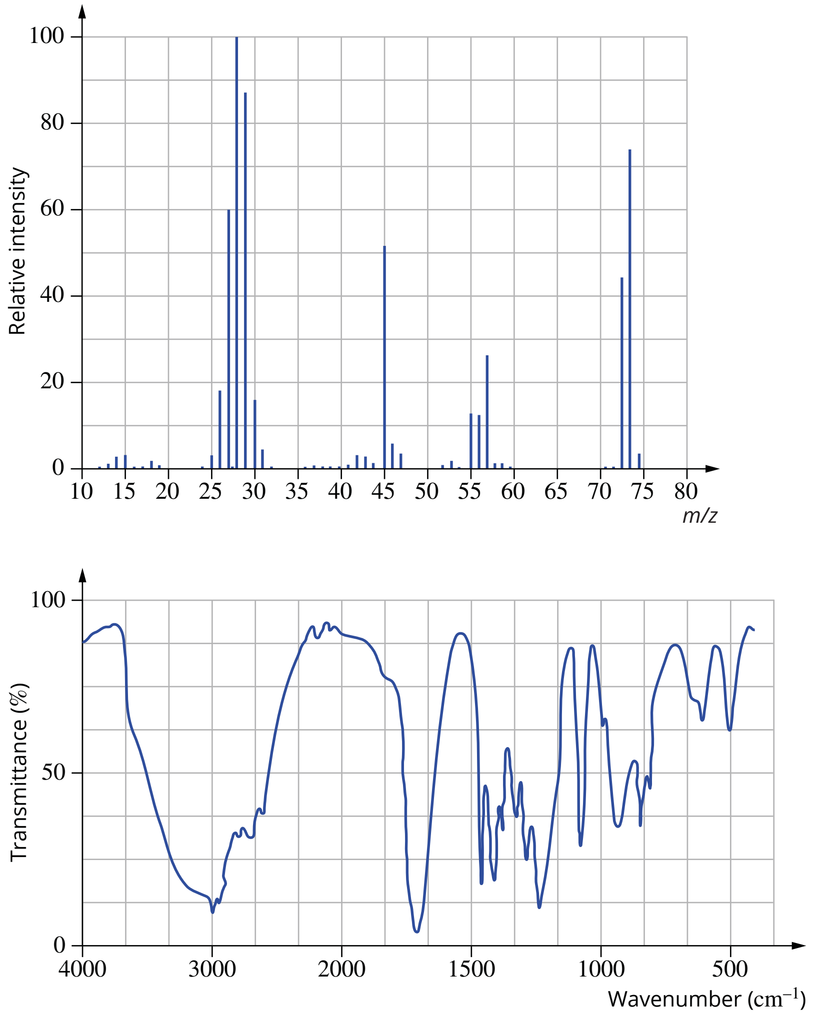


FIGURE 12.4.7 Spectra for an unknown molecule.

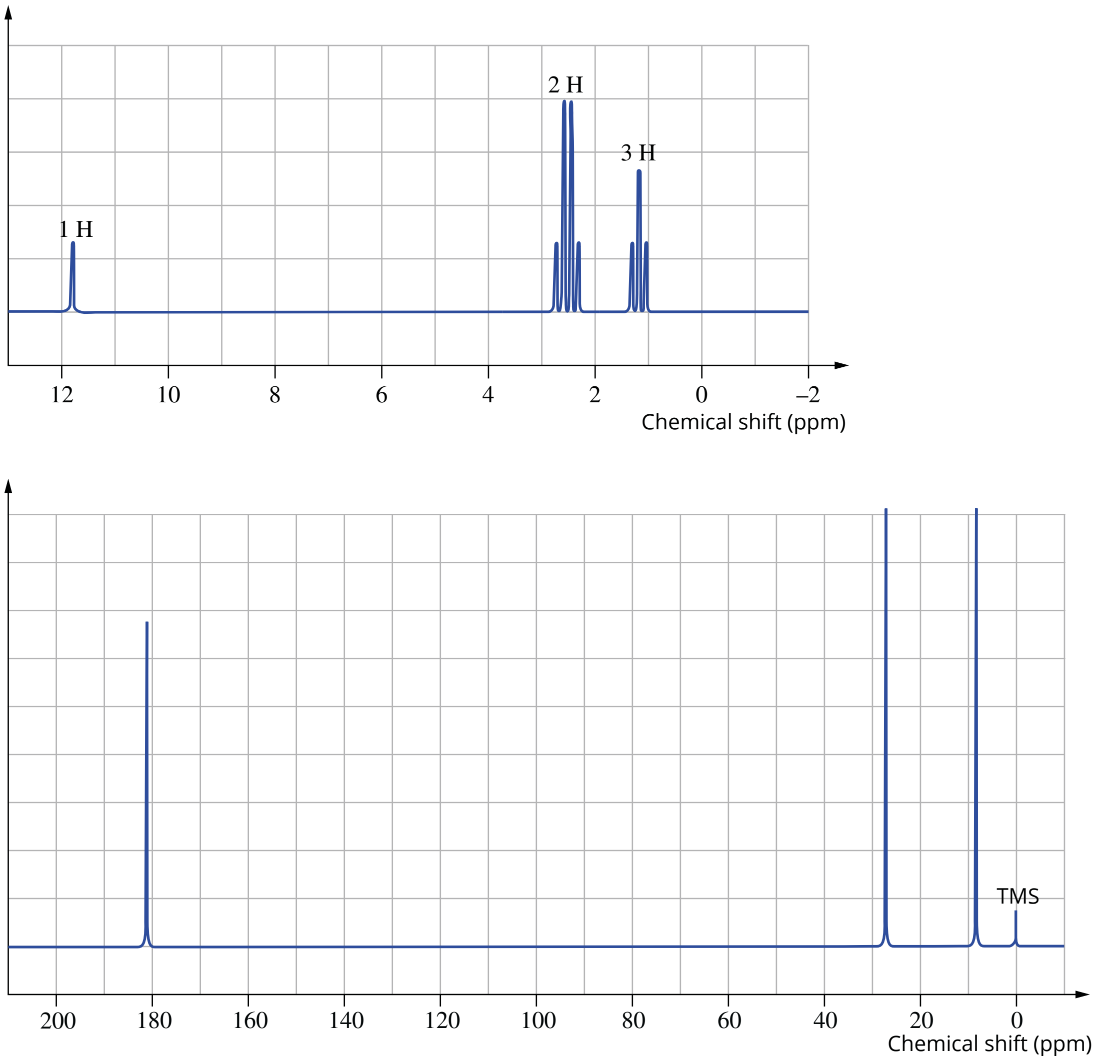


FIGURE 12.4.8 Spectra for an unknown molecule.

Chapter review

12

KEY TERMS

absorbance
absorption band
base peak
calibration curve
carbon-13 NMR spectroscopy
chemical shift
dipole
electromagnetic spectrum
equivalent
fingerprint region
fragmentation
functional group
infrared spectroscopy
isotope
mass spectrometer
mass spectrometry
mass spectrum
molecular ion
molecular ion peak
neighbour
nuclear magnetic resonance (NMR) spectroscopy
nuclear magnetic resonance (NMR) spectrum
nuclear shielding
nuclear spin
proton NMR spectroscopy
quantitative analysis
splitting pattern
transmittance
vibrational energy level
wavenumber

Infrared spectroscopy

1 List the bonds in 2-bromoethan-1-ol from the bond that will absorb the lowest energy infrared radiation to the bond that will absorb the highest energy infrared radiation.

2 The IR spectra of two liquid samples, A and B, are provided in Figure 12.5.1.

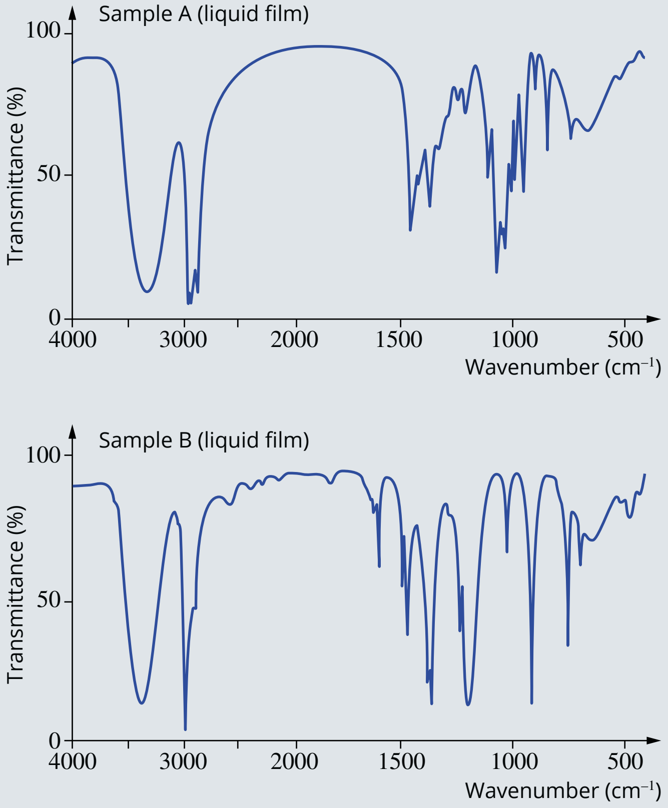


FIGURE 12.5.1 IR spectra of two liquid samples, A and B.

a Explain how these two spectra confirm that both samples are alcohols.

b Are these two spectra of the same compound? Explain your answer.

3 What absorption bands in an infrared spectrum are required to indicate the presence of:

a a hydroxyl group?

b an amide group?

c an aldehyde?

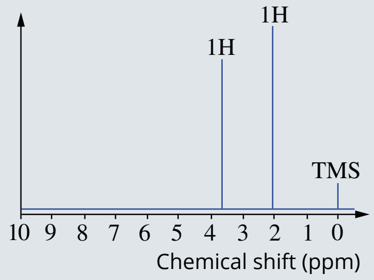
d a chloroalkane?

Nuclear magnetic resonance spectroscopy

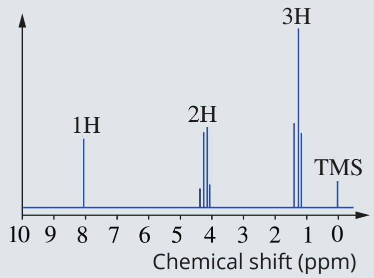
4 Explain the use of TMS in NMR spectroscopy.

5 Ethyl methanoate, methyl ethanoate and propanoic acid are isomers with the formula $C_3H_6O_2$. Match each of these compounds with the following spectra.

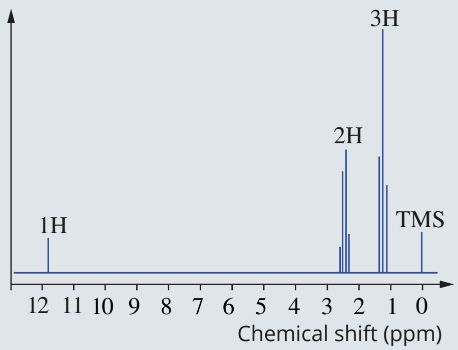
a



b



c



6 A chemist isolated a molecule with the molecular formula C_3H_6O. It is suspected that the molecule is a ketone due to its chemical properties. Explain how the chemist could use the proton and carbon NMR spectra to identify the correct structure.

7 Draw a table to predict the expected proton NMR spectrum of each of the molecules listed below. Include the expected chemical shift, relative peak area and splitting pattern.

- **a** Propane
- **b** CH_3CH_2Br
- **c** CH_3COOCH_2OH

Mass spectrometry

8 The mass spectrum of an alkane is shown in Figure 12.5.2.

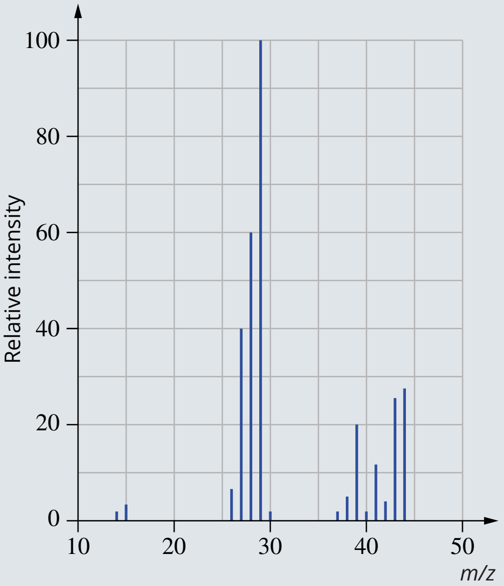


FIGURE 12.5.2 Mass spectrum of an unknown alkane.

Identify the formula of molecular and base ions.

9 The mass spectrum of an alkyne is shown in Figure 12.5.3.

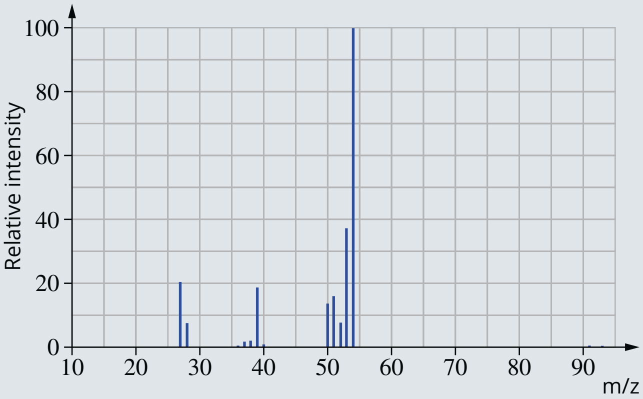


FIGURE 12.5.3 Mass spectrum of an unknown alkyne.

What is the molecular formula of the alkyne?

10 A number of compounds with different structures may form molecular ions with the same *m/z* ratio. Give the molecular formula of a compound that would give a *m/z* value of 58 if the molecule:

- **a** is an alkane
- **b** contains one oxygen atom
- **c** contains two amine groups.

11 The mass spectrum of dichloroethane is shown in Figure 12.5.4.

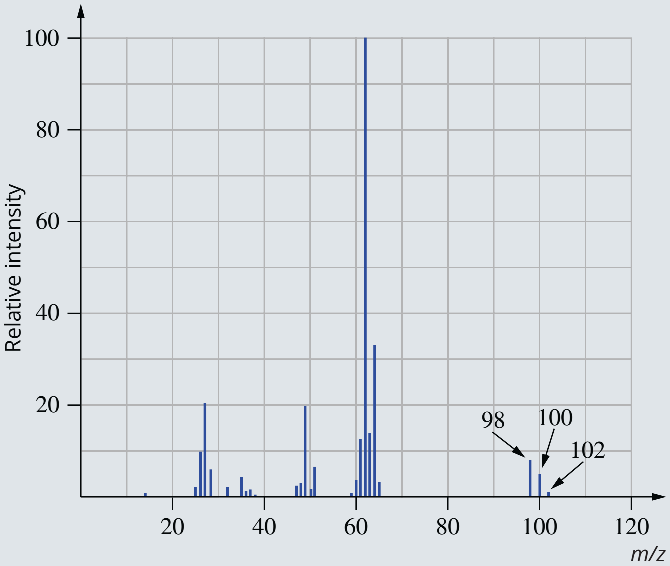


FIGURE 12.5.4 Mass spectrum of dichloroethane.

- **a** Explain why the mass spectrum has the peaks with the *m/z* values of:
  - **i** 98
  - **ii** 100
  - **iii** 102
- **b** Why is the peak with *m/z* = 98 the largest of these peaks?
- **c** Write a possible formula for the ion responsible for the base peak.

Determination of molecular structure by spectroscopy

12 An unknown compound has a molecular formula C_3H_6O. Its IR spectrum has a strong, sharp absorption at 1750 cm^{-1}. The proton NMR spectrum has three sets of peaks: a singlet, a triplet and a quartet. The carbon NMR has three peaks. What is the identity of this compound?

13 A hydrocarbon has the empirical formula C_5H_{12}. The *m/z* of the molecular ion peak is 72. The proton NMR spectrum has a single peak. The carbon NMR has two peaks. What is the identity of this compound?

14 A combination of different instrumental techniques was used to analyse a compound that had an empirical formula of C_2H_4O. The mass, IR, proton NMR and carbon NMR spectra of this compound are provided in Figure 12.5.5. Details of the proton NMR spectrum are given in Table 12.5.1.

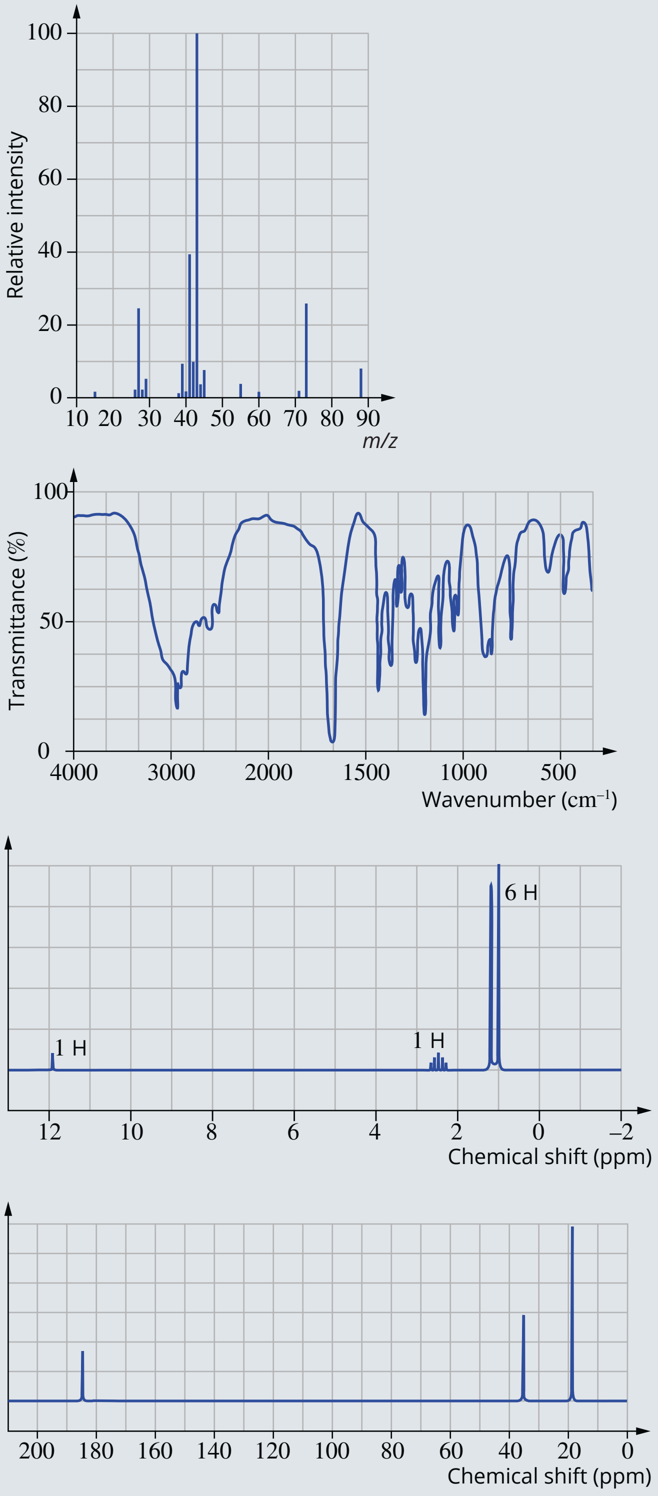


FIGURE 12.5.5 Various spectra for a compound of empirical formula C_2H_4O.

TABLE 12.5.1 Proton NMR data summary

Chemical shift (ppm)	Peak splitting	Relative peak area
1.1	doublet (2)	6
2.6	septet (7)	1
11.8	singlet (1)	1

What specific information about the compound does each of these spectra provide? Use this information to determine the semistructural formula and name of the compound.

Connecting the main ideas

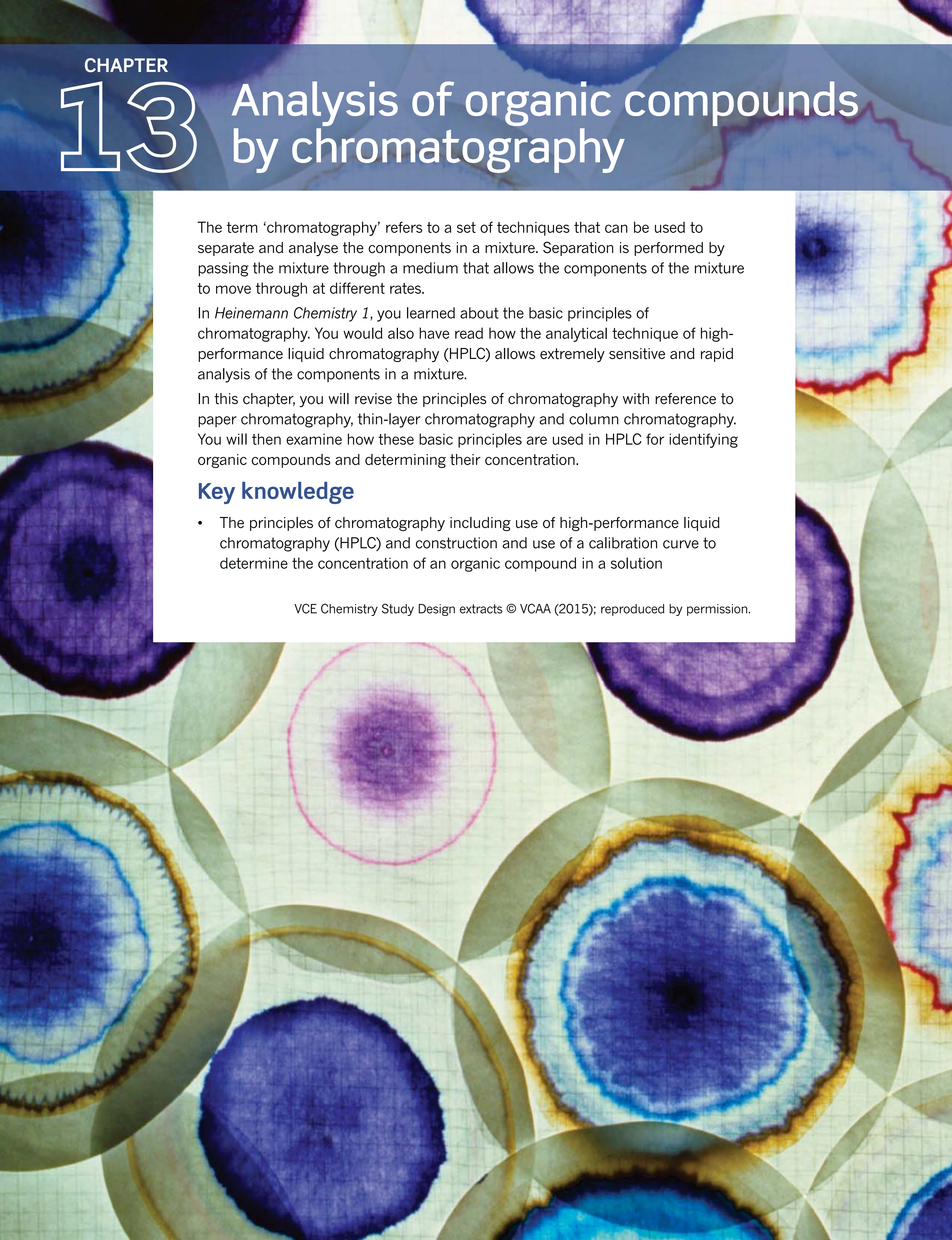
15 Explain how each of the techniques of NMR spectroscopy, IR spectroscopy and mass spectrometry, can be used in the identification of an organic molecule.

16 Some chemists suggest that proton NMR spectroscopy is the only analytical technique needed for organic molecules.

a Explain why proton NMR spectroscopy is such a useful technique.

b What other techniques are needed for a complete analysis of organic molecules?

17 Automatic detectors that use mass spectrometry are often employed by security guards and police officers to search for explosives and illicit drugs. They are powered by a computer that can tell if an illegal substance is present and identify what it is. Explain what the computer should look for in the mass spectrum.



CHAPTER 13

Analysis of organic compounds by chromatography

The term ‘chromatography’ refers to a set of techniques that can be used to separate and analyse the components in a mixture. Separation is performed by passing the mixture through a medium that allows the components of the mixture to move through at different rates.

In *Heinemann Chemistry 1*, you learned about the basic principles of chromatography. You would also have read how the analytical technique of high-performance liquid chromatography (HPLC) allows extremely sensitive and rapid analysis of the components in a mixture.

In this chapter, you will revise the principles of chromatography with reference to paper chromatography, thin-layer chromatography and column chromatography. You will then examine how these basic principles are used in HPLC for identifying organic compounds and determining their concentration.

Key knowledge

- The principles of chromatography including use of high-performance liquid chromatography (HPLC) and construction and use of a calibration curve to determine the concentration of an organic compound in a solution

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13.1 Principles of chromatography

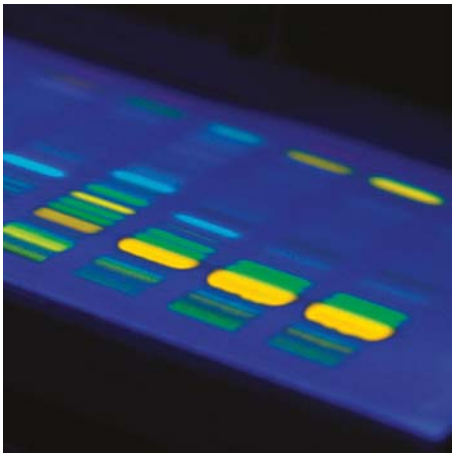


FIGURE 13.1.1 These glowing bands, viewed under fluorescent lighting, are individual chemical components that have been separated from a mixture by a form of thin-layer chromatography. The individual components can then be identified by mass spectrometry.

Chromatography is a widely used technique for separating and analysing complex mixtures of organic compounds. Food, petrochemicals, perfumes and pharmaceuticals are all mixtures that can be separated by chromatography. A feature of chromatography is that it can be performed on very small samples and for low concentrations. When separated, the various components often appear as distinct bands, as seen in Figure 13.1.1.

In this section, you will revise the principles of chromatography that you learned in Chapter 19 of *Heinemann Chemistry 1*. The next section describes the use of the analytical technique of high-performance liquid chromatography for the analysis of organic compounds.

HOW CHROMATOGRAPHY WORKS

You can perform a simple chromatography experiment by putting spots of ink from felt-tip pens near one end of a strip of filter paper. The filter paper can then be suspended so the end closest to the ink spots is just immersed in water.

The original position of the ink spots on the paper is called the **origin**. The inks are a mixture of different-coloured chemicals. As the water soaks up the paper, the **components** of the inks are carried upwards at different rates and separate into spots of different colours, as seen in Figure 13.1.2.

Each spot contains one of the components that are present in the ink mixture. The pattern of bands or spots is called a **chromatogram**.

This is an example of **paper chromatography**. In the laboratory, paper chromatography is performed with high-quality absorbent paper, similar to filter paper.

All methods of chromatography have a:

- **stationary phase**
- moving or **mobile phase**.

In the simple experiment using inks and paper, the stationary phase is a thin layer of water adsorbed to the paper and the mobile phase is the water.

As the components in the ink are swept upwards over the stationary phase by the solvent, they undergo a continual process of **adsorption** (onto the stationary phase), followed by **desorption** and dissolving (into the mobile phase).

The rate of movement of each component mainly depends on:

- how strongly the component adsorbs onto the stationary phase
- how readily the component dissolves in the mobile phase.

The components separate because they undergo these two processes to a different degree. Water is a polar solvent. If water is used as the mobile phase, the more polar components tend to move more quickly than the less polar components. These more soluble components move further up the paper in a given time interval.

FIGURE 13.1.2 Paper chromatography can be used to separate mixtures of inks into their separate components.

The term 'adsorption' describes the adhesion of molecules or substances to the surface of a solid or liquid. This is why the stationary phase in chromatography is either a solid or a liquid. The mobile phase is in either a liquid or a gas state.

CHEMFILE

Chromatography

The term 'chromatography' comes from the Greek *khromatos*, meaning 'of colour', and *graphos*, meaning 'written'. The technique was developed by the Russian botanist Mikhail Tsvet (Figure 13.1.3) to separate plant pigments.

Tsvet used ether and alcohol to extract the plant pigments. He then passed them through a column of calcium carbonate. The calcium carbonate acted as the stationary phase. The different pigments produced different coloured bands within the calcium carbonate column. Tsvet's work allowed people to see that there were two different forms of chlorophyll and eight other different plant pigments at a time when scientists believed there were only two.

FIGURE 13.1.3 Russian botanist Mikhail Tsvet invented the technique of chromatography.

Thin-layer chromatography

Thin-layer chromatography (TLC) is similar to paper chromatography. In TLC, a thin layer of a fine powder, such as alumina (aluminium oxide), is spread on a glass or plastic plate, which acts as the stationary phase.

Both paper chromatography and TLC are useful for **qualitative analysis**. They can indicate which chemicals are present in the mixture but cannot give their specific concentration.

Although the components of inks can be seen easily in chromatograms, most compounds are colourless and must be made visible. Many organic compounds fluoresce and appear blue when viewed under ultraviolet light. Another way to make colourless components visible is to spray them with a chemical that reacts to form coloured or fluorescent compounds.

Interpreting thin-layer and paper chromatograms

The components in a mixture can be identified by chromatography in one of two ways:

1 by including **standards** of known chemicals on the same chromatogram as the unknown sample

2 by calculating the **retardation factor (R_f)** of the sample.

Method 1—Using standards

Suppose you wish to find out whether a lolly contains the sugars fructose and glucose. You could place a sample of the lolly on the same chromatogram as a pure sample of each of fructose and glucose (the 'standards'). If spots from the lolly sample move the same distance from the origin as the spots from the pure samples, then the lolly is likely to contain the sugars (Figure 13.1.4).

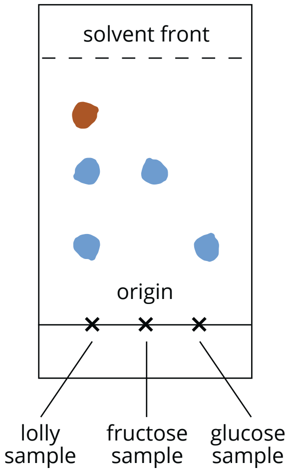


FIGURE 13.1.4 Identification of sugars in a lolly using paper or thin-layer chromatography. The lolly is likely to contain fructose and glucose, as well as a brown-coloured component.

For this method, you need to have an idea of the chemical that might be present in the sample. The sample and standards are 'run' on the same chromatogram because the distances moved from the origin will depend on the distance moved by the **solvent front**. The further the solvent front is allowed to travel, the further the spots travel.

'Solvent front' is the term used to describe the movement of the solvent during chromatography. It is visible as the wet moving edge of the solvent as it travels along the stationary phase.

Method 2—Calculating R_f *values*

Another way of identifying the components of a mixture is by calculating the distance they travel up the stationary phase compared to the distance travelled by the solvent front. This is expressed as a retardation factor (R_f) for a component:

$$R_f = \frac{\text{distance the component travels from the origin}}{\text{distance the solvent front travels from the origin}}$$

You can see from Figure 13.1.5 that:

- R_f values are always less than one
- the component most strongly adsorbed onto the stationary phase moves the shortest distance and has the lowest R_f value.

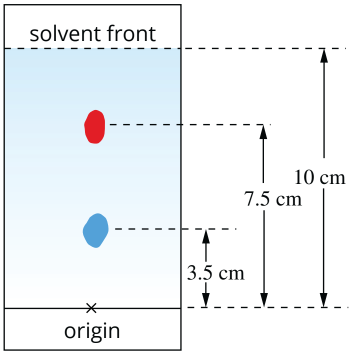


FIGURE 13.1.5 A thin-layer chromatogram of a sample with two components. The distances from the origin enable you to calculate R_f.

Each component has a characteristic R_f value for the conditions under which the chromatogram was obtained. By comparing the R_f values of components of a particular mixture with the R_f values of known substances determined under identical conditions, you can identify the components present in a mixture.

In this method, the distance moved by the solvent front is no longer critical. The proportion of the distance moved from the origin (the R_f value) stays the same provided the conditions under which the chromatogram is obtained are the same.

This means the R_f values of unknown spots can be compared against a table of R_f values of common materials.

However, changes in the temperature, the type of stationary phase, the amount of water vapour (around the plate or paper) and the type of solvent all change the R_f value for a particular chemical.

For the R_f value of a component to be comparable to a set of standard R_f values, they must be determined under identical conditions.

Worked example 13.1.1

CALCULATING R_f VALUES

Using Figure 13.1.5, calculate the R_f value of the blue component.

THINKING	WORKING
Record the distance the component has moved from the origin and the distance the solvent front has moved from the origin.	The distance the blue component has moved from the origin is 3.5 cm. The distance the solvent front has moved from the origin is 10 cm.
$R_f = \frac{\text{distance the component travels from the origin}}{\text{distance the solvent front travels from the origin}}$	R_f (blue component) $= \frac{3.5}{10}$ $= 0.35$

Worked example: Try yourself 13.1.1

CALCULATING R_f VALUES

Using Figure 13.1.5, calculate the R_f value of the red component.

The choice between paper and thin-layer chromatography depends upon the sample being analysed. Advantages of each method are given in Table 13.1.1.

TABLE 13.1.1 A comparison of paper and thin-layer chromatography

Paper chromatography	Thin-layer chromatography
Is cheap	Detects smaller amounts
Requires little preparation	Achieves better separation of less polar compounds
Is more efficient for polar and water-soluble compounds	Can use corrosive materials
Is easy to handle and store	Has a wide range of stationary phases

COLUMN CHROMATOGRAPHY

Figure 13.1.6 shows another form of chromatography, **column chromatography**, which can also be used to separate the components of a mixture.

In column chromatography, the solid stationary phase is packed into a glass column. The sample mixture is applied carefully to the top of the packed solid, and a solvent, which acts as the mobile phase, is dripped slowly onto the column from a reservoir above. A tap at the bottom of the column allows the solvent, which is now called the **eluent**, to leave the column at the same rate as it enters it at the other end.

As the components are carried down the column, they are repeatedly adsorbed to the stationary phase and desorbed back into the mobile phase. The components of a mixture undergo the processes of adsorption and desorption to different degrees, so the components separate as they move downwards.

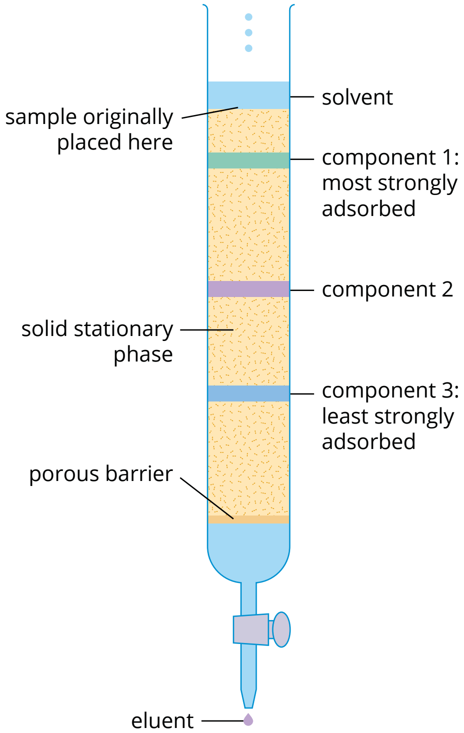


FIGURE 13.1.6 Column chromatography is used to separate the components in a mixture.

13.1 Review

SUMMARY

- The components in a mixture can be separated and identified by chromatography.
- Two simple forms of chromatography are paper chromatography and thin-layer chromatography.
- A mobile phase and a stationary phase are present in all forms of chromatography.
- The components of a mixture separate during chromatography as a consequence of how strongly they adsorb to the stationary phase and desorb back into the mobile phase.
- Paper and thin-layer chromatography can be used to identify the components in a mixture by comparing them with known standards or by determining their R_f values.

KEY QUESTIONS

1 Describe how the rate of adsorption and desorption of a component that appears at the top of a paper chromatogram compares to that of a component that appears at the bottom of the chromatogram.

2 Describe how an R_f value is calculated.

3 For each of the following types of chromatography, identify the:
   i mobile phase
   ii stationary phase.
  a Paper chromatography
  b Column chromatography
  c Thin-layer chromatography

4 Explain why the level of the solvent must be below the level of the origin where the samples are placed in paper chromatography.

13.2 High-performance liquid chromatography

In the previous section, you learned how the techniques of paper and thin-layer chromatography can separate the components in a mixture. In these techniques, a liquid mobile phase is used to carry the components of the mixture past a stationary phase. The components undergo a continual process of adsorption to the stationary phase and desorption back into the liquid. The components of a mixture undergo the processes of adsorption and desorption to different degrees, so the components separate as they move over the stationary phase.

In this section, you will learn about a highly sensitive technique capable of detecting miniscule amounts of a compound—**high-performance liquid chromatography (HPLC)**.

HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY

High-performance liquid chromatography (HPLC) is sometimes also referred to as high-pressure liquid chromatography.

High-performance liquid chromatography (HPLC) is a modern instrumental chromatographic technique based on column chromatography.

HPLC allows scientists to perform extremely sensitive analyses of a wide range of mixtures. It is commonly used for the separation and identification of very complex mixtures of similar compounds, such as drugs in blood, and hydrocarbons in oil samples. Compounds in trace concentrations as low as parts per trillion (ppt) may easily be identified. HPLC is therefore a much more sensitive technique than volumetric analysis, which is discussed in the following chapter.

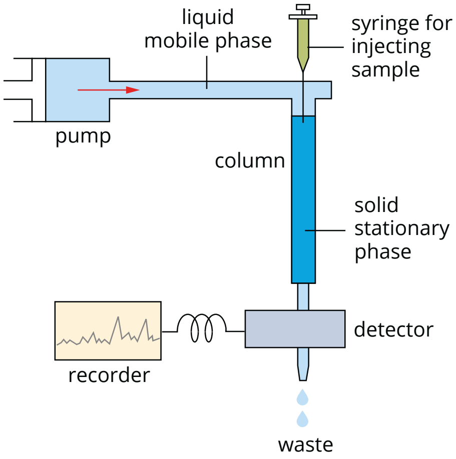


FIGURE 13.2.1 The construction of a high-performance liquid chromatograph.

Figure 13.2.1 shows the apparatus used for HPLC. The basic principles of HPLC are the same as for column chromatography described in the previous section. The main differences between simple column chromatography and HPLC are the:

- particles in the solid used in the HPLC column are often 10–20 times smaller than those used in column chromatography. Their higher surface area allows more frequent adsorption and desorption of the components. This greater surface area therefore gives much better separation of similar compounds.
- small particle size used in HPLC creates a considerable resistance to the flow of the mobile phase. Therefore, the solvent is pumped through the column under high pressure.

A range of solids is available for use in HPLC columns, including alumina (Al_2O_3) and silica (SiO_2). Some solids also have chemicals specially bonded to their surfaces to improve the separation of particular classes of compounds.

In the most common form of HPLC, called **reversed-phase HPLC**, the stationary phase is silica. The silica used has been modified to make it non-polar by attaching long hydrocarbon chains to its surface. A polar solvent is used as the mobile phase, such as a mixture of water and methanol.

Polar molecules in the sample form relatively strong hydrogen bonds and dipole–dipole attractions with solvent molecules, but are only weakly adsorbed to the non-polar stationary phase. Therefore, polar molecules in the sample spend most of their time moving with the solvent.

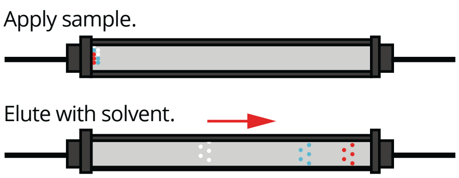


FIGURE 13.2.2 A diagram showing how HPLC can be used to separate and collect different components.

On the other hand, non-polar compounds in the sample tend to adsorb to the non-polar stationary phase by dispersion forces. They are also less soluble in the solvent because they cannot form hydrogen bonds with the polar mobile phase. Non-polar compounds spend less time in solution, so they move through the column more slowly than polar molecules.

The way this separation occurs can be seen in Figure 13.2.2.

In HPLC, the components are usually detected by passing the eluent stream through a beam of ultraviolet (UV) light. Many organic compounds absorb UV light. When an organic compound passes in front of the beam of light, a reduced signal is picked up by a detector. The amount of light received by the detector is converted into an absorbance measurement and recorded on a chart that moves slowly at a constant speed or on a computer. The resulting trace is called a chromatogram.

The time taken for a component to pass through the column is called the **retention time (R_t)** and this is characteristic of the component for the conditions of the experiment. It is similar to the R_f value in paper chromatography and thin-layer chromatography.

Retention times are used to identify the components associated with the peaks on a chromatogram (**qualitative analysis**). The relative amounts of each component in a mixture may be determined by comparing the areas under each peak with areas under the peaks for standard samples (**quantitative analysis**).

In Figure 13.2.3 you can see an example of the component peaks found in a HPLC chromatogram.

FIGURE 13.2.3 A research chemist uses HPLC to analyse the components in a mixture for medical research.

Paper chromatography and thin-layer chromatography provide qualitative analysis of components in a mixture. That is, the components that make up a mixture can be identified. HPLC provides qualitative and quantitative analysis of components in a mixture. The size of the peaks is due to the amount of light absorbed by each component, and this can be used to calculate the relative amount of each component within the mixture.

APPLICATIONS OF HPLC

Chemists use the technique of HPLC in chemical analysis to answer two questions.

- What chemicals are present in the sample (qualitative analysis)?
- How much of each chemical is present (quantitative analysis)?

Qualitative analysis

In HPLC, the same compound gives the same retention time if the conditions (temperature, mobile phase, stationary phase, flow rate, pressure etc.) remain the same. Each component forms one peak in the chromatogram.

Figure 13.2.4 shows the chromatogram of a sample of body fluid produced by HPLC. The smaller, more polar components are more soluble in the solvent used and are eluted more quickly. Therefore, these components have a lower retention time.

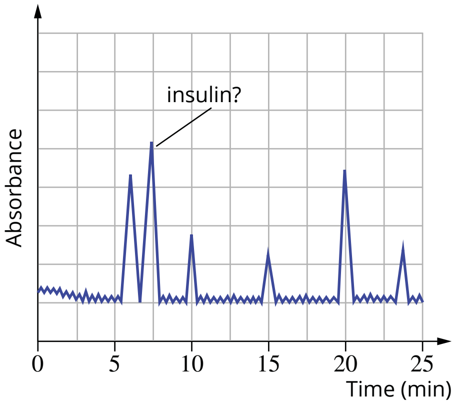


FIGURE 13.2.4 A chromatogram of body fluid.

The peaks can be tentatively identified by running a sample containing a known pure compound (such as insulin) under exactly the same conditions as the sample (see Figure 13.2.5).

A component can also be tentatively identified by adding a known compound to the sample (**spiking**). Figure 13.2.6 shows the sample spiked with insulin. Insulin was added to the sample and the spiked chromatogram shows the second peak to be larger than it was in the unspiked sample. There are no extra peaks, indicating that insulin is very likely to have been present in the sample.

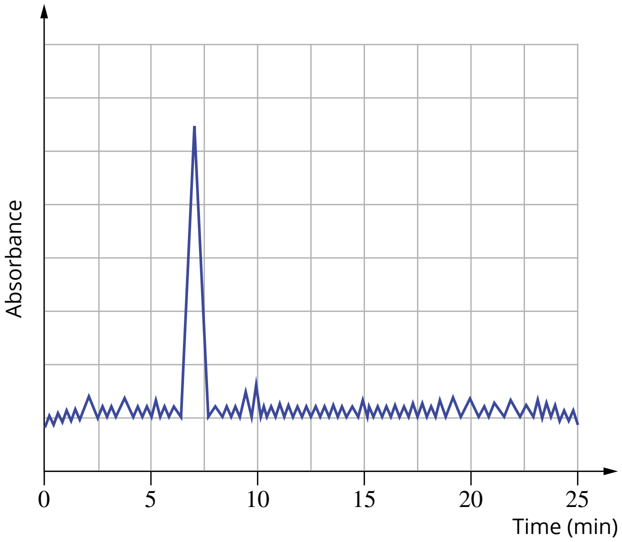


FIGURE 13.2.5 A chromatogram of a reference sample containing insulin.

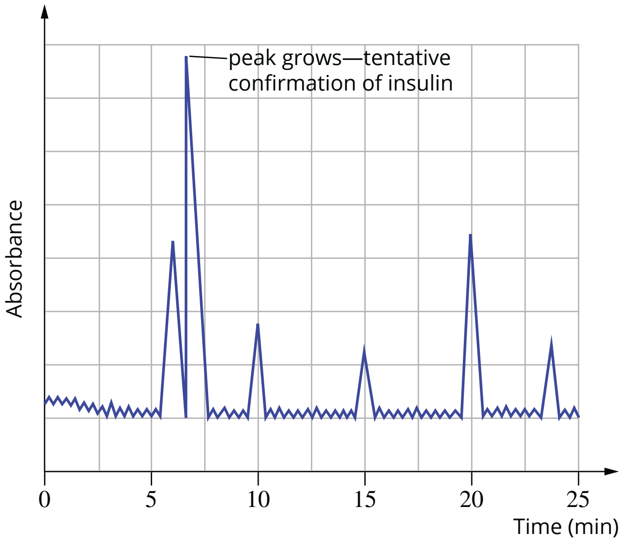


FIGURE 13.2.6 A body fluid sample spiked with insulin.

Quantitative analysis

To determine the concentration of an individual component in a mixture, its peak area is compared with the peak areas of samples of the same chemical at known concentrations. A solution with an accurately known concentration is called a **standard solution**.

By plotting the peak areas against the concentrations of the standard solutions, you can draw a **calibration curve** and use it to determine unknown concentrations.

Worked Example 13.2.1 shows how HPLC can be used to find the concentration of a component in a mixture.

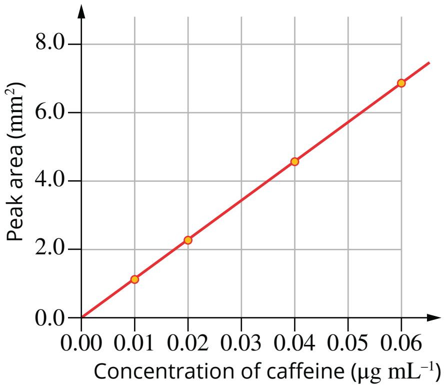
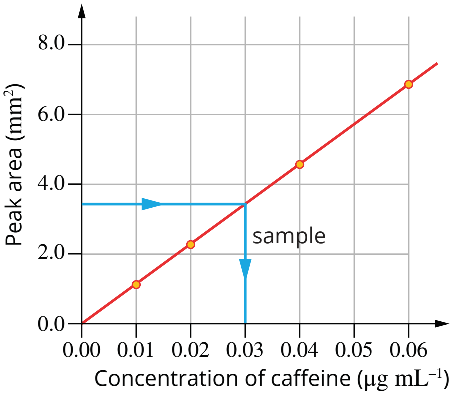
Worked example 13.2.1

CONCENTRATION OF A COMPONENT IN A MIXTURE

The concentration of caffeine in an energy drink was determined by HPLC. Chromatograms of standards with accurately known concentrations of caffeine were also obtained under the same conditions as the sample.

The peak areas of the sample and the standards are shown in the table. Calculate the concentration of caffeine in the sample.

Caffeine standards (μg mL^{-1})	Peak area (mm^2)
0.010	1.0
0.020	2.4
0.040	4.6
0.060	7.0
Sample	3.6

Thinking	**Working**
Construct a calibration curve by plotting peak area versus concentration.	
Use the calibration curve to find the concentration corresponding to the peak area of the sample.	A line (blue) can be drawn on the calibration curve from the peak area of the sample to find the corresponding concentration on the graph.  The concentration of caffeine in the energy drink is 0.030 μg mL^{-1}.

Worked example: Try yourself 13.2.1

CONCENTRATION OF A COMPONENT IN A MIXTURE

Trinitrotoluene (TNT) is often blended with other explosives to suit particular applications. A sample from a solution of an explosive mixture was injected onto an HPLC column using a water/methanol mobile phase. The peak corresponding to TNT had an area of 8.8 mm^2. The peak areas for three standard solutions were also measured, as shown in the table.

Determine the concentration of TNT in the sample solution in μg mL^{-1}.

TNT standards (μg mL^{-1})	Peak area (mm^2)
2.0	6.0
4.0	11.6
6.0	17.6

CHEMISTRY IN ACTION

Making the grade

Gourmet cooks value olive oil (Figure 13.2.7) for its distinctive taste and aroma. Nutritionists favour it because it is rich in monounsaturated triglycerides, which are believed to lower blood cholesterol levels and reduce the risk of heart disease. But some of the companies that process and distribute olive oil succumb to the temptation to mix their olive oil with less expensive oils such as corn, peanut and soybean.

A European company sent a shipment of olive oil to the United States. A routine sample was taken and forwarded to chemist Richard Flor at the US Customs Service laboratory in Washington, DC. The sample looked and poured like olive oil, but it didn't taste quite right. Because taste is a subjective test and doesn't always stand up in court, Flor and his colleague Le Tiet Hecking developed an analytical test based on olive oil's unique composition.

Flor used HPLC to separate the oils into their component triglycerides. (An example of the chromatographs obtained can be seen in Figure 13.2.8.) Flor and Hecking found that the oil in the suspect sample had too much of the polyunsaturated triglycerides, confirming their suspicion that the imported sample was diluted with corn oil.

FIGURE 13.2.7 Pure olive oil is highly regarded for its aroma and taste, and because it is thought to reduce blood cholesterol levels.

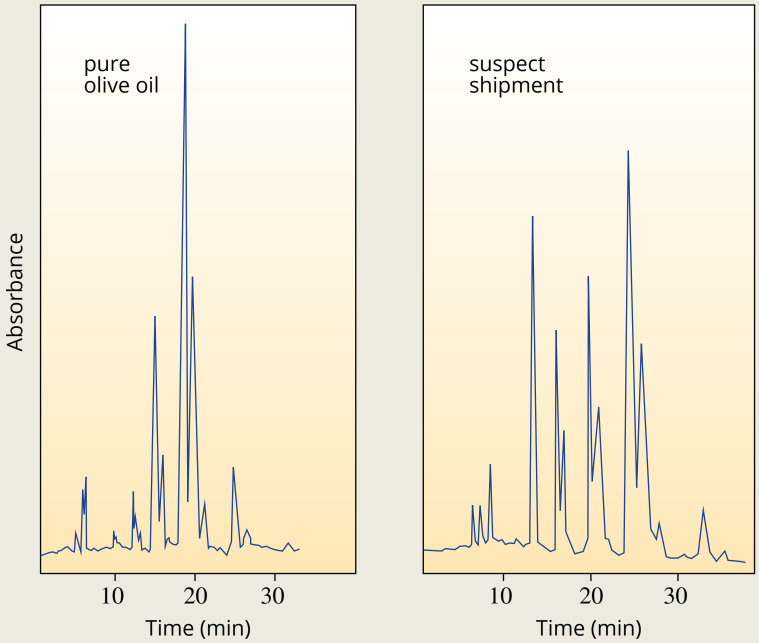


FIGURE 13.2.8 Peaks in the chromatogram of the suspect oil indicate the presence of compounds found in corn oil, rather than olive oil.

HPLC can be combined with another analytical technique called mass spectroscopy (MS) (see Chapter 12). Together, the techniques allow chemists to determine smaller and smaller quantities and identify a wider range of materials.

EXTENSION

Gas chromatography—detecting the smallest amounts

The most sensitive of the chromatographic techniques is gas chromatography (GC). GC is capable of detecting as little as 10^{-12} g of a compound. However, it is limited to compounds that can be readily vaporised without decomposing. Such compounds usually have relative molecular masses less than 300. HPLC, on the other hand, can separate compounds with relative molecular masses of 1000 or more.

The extreme sensitivity of GC makes it ideal for the analysis of trace contaminants in samples or for the detection of tiny amounts of very potent compounds. For example, urine samples are routinely taken from athletes competing in major sporting events to check whether the athletes are using illegal, performance-enhancing drugs. These samples are analysed by GC.

There are two types of GC, gas–liquid chromatography (GLC) and gas–solid chromatography (GSC). Both GC techniques operate in a similar way as outlined below. A generalised diagram of the equipment used in GC is shown in Figure 13.2.9.

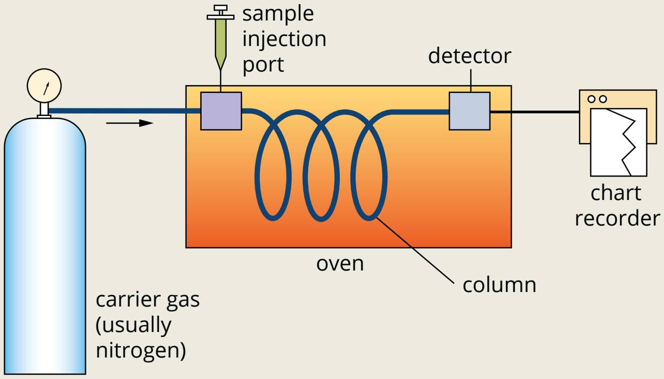


FIGURE 13.2.9 A gas chromatograph.

Gas chromatography has the following features.

- The mobile phase is a gas, generally nitrogen, called the carrier gas.
- A small amount of sample is injected into the top of the column through an injection port.
- The injection port is heated to a temperature sufficient to instantly vaporise the sample, which is then swept into the column by the carrier gas.
- The column is a loop, or series of loops, of glass that has an internal diameter of about 4 mm and is 2–3 m long in total. In GLC, the column is packed with a porous solid that has been coated with a liquid hydrocarbon or ester with a high boiling point. This liquid acts as a liquid stationary phase. In GSC, the column is packed with an adsorbant solid such as silica gel or alumina. The solid acts as a solid stationary phase.
- The column is mounted in an oven and heated.
- The components of the sample repeatedly adsorb onto and desorb from the stationary phase. The least soluble components are swept out first by the gas into the detector (see Figure 13.2.10).

The chromatogram shows the response of the detector against time. The response of the solvent is constant and gives a flat baseline. As components pass through the detector, the response changes and a peak is formed. The sample is injected into the column at time zero. Different chemicals show different strengths of attraction for the stationary phase and the mobile phase, and so pass through the column at different rates. As in HPLC, the time a component takes to pass through the column is called the retention time, R_t. The same compound gives the same retention time if the conditions (temperature, mobile phase, stationary phase, flow rate, pressure etc.) remain the same.

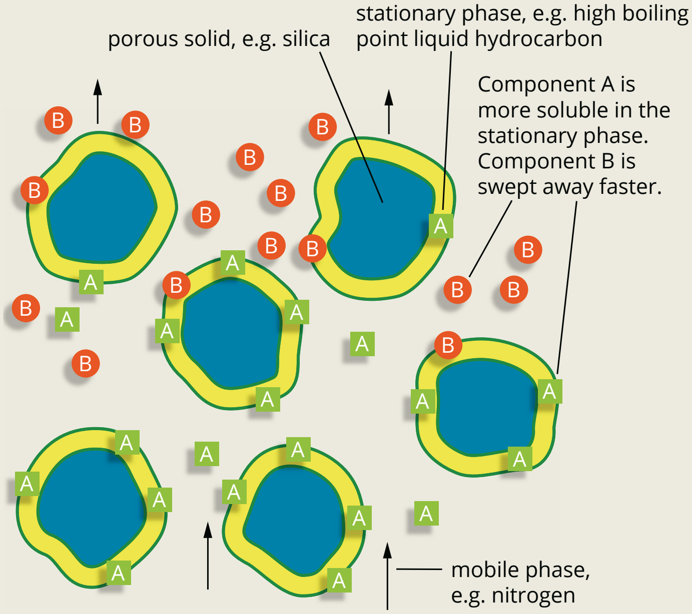


FIGURE 13.2.10 A cross-section through a GLC column.

Extension question

Australian wines are routinely tested for ethanol content. A quick and reliable method for testing is GLC. The peak areas produced by a sample of wine and a number of standard solutions of ethanol are shown in Table 13.2.1.

TABLE 13.2.1 Peak areas from GLC analysis of a wine sample and standards

	Ethanol content (%)	Relative ethanol peak area
Wine	?	82 400
Standard 1	4.00	31 200
Standard 2	8.00	62 900
Standard 3	12.00	94 200
Standard 4	16.00	125 700

a Plot a calibration curve of concentration of ethanol against peak area.

b Determine the percentage of ethanol in the wine sample.

c Why is it necessary to measure the peak areas produced by a number of standards?

13.2 Review

SUMMARY

- High-performance liquid chromatography (HPLC) is a very sensitive technique and is used for qualitative and quantitative analysis.
- In HPLC, the mobile phase is a liquid under pressure.
- In HPLC, retention time is used to identify components in a mixture.
- The concentration of an individual component in a mixture can be determined by comparing its peak area on a chromatogram with the peak areas of samples with known concentrations of the same chemical.
- The peak areas of standard solutions are used to construct a calibration curve, which can be used to determine unknown concentrations.

KEY QUESTIONS

1 A sample containing compounds A, B and C is mixed with ethanol and applied to the top of an HPLC instrument that uses ethanol as the solvent and alumina as the stationary phase. The three compounds have the following properties.

- Solubility in ethanol: C is much more soluble than A and B. A and B are equally soluble.
- Adsorption to alumina: B is more strongly absorbed than A. C is least strongly adsorbed.

Which of the following lists shows the retention times of the components, from lowest to highest?

A A, B, C
B C, B, A
C C, A, B
D B, A, C

2 EPO is a protein hormone produced by the kidneys. Although banned, some endurance athletes use it to improve performance because it increases the body's oxygen-carrying capacity. Athletes are routinely tested for EPO levels by HPLC. The peak areas produced from HPLC analysis of an athlete's blood and the peak areas of a number of standard solutions of EPO are shown in Table 13.2.2.

TABLE 13.2.2 Peak areas from HPLC analysis of an athlete's blood and standards

	EPO (μg mL^{-1})	Relative EPO peak area
Blood sample	?	5.6
Standard 1	2.0	1.6
Standard 2	4.0	3.2
Standard 3	6.0	4.8
Standard 4	8.0	6.4

a Plot a calibration curve of relative peak area against concentration of EPO (μg mL^{-1}).

b Determine the concentration of EPO in the blood sample correct to one decimal place.

3 Why is it necessary to construct a calibration curve to determine the concentration of a component in a mixture that has been analysed by HPLC?

4 A mixture was composed of four primary alcohols with formula ROH, where R is a straight-chain alkyl group. The mixture was analysed by HPLC using a non-polar stationary phase and a blend of water and methanol as the mobile phase. The chromatogram in Figure 13.2.11 was obtained.

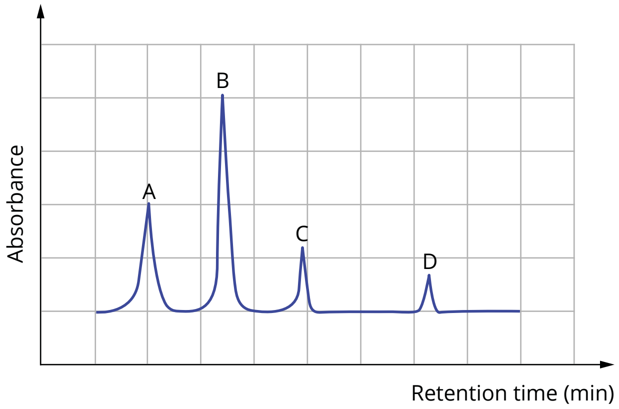


FIGURE 13.2.11 A chromatogram of a mixture of alcohols.

Determine the order from smallest to largest molar mass of the primary alcohols found in peaks A to D.

Chapter review

13

KEY TERMS

adsorption
calibration curve
chromatogram
chromatography
column chromatography
component
desorption
eluent
high-performance liquid chromatography (HPLC)
mobile phase
origin
paper chromatography
qualitative analysis
quantitative analysis
retardation factor (R_f)
retention time (R_t)
reversed-phase HPLC
solvent front
spiking
standard
standard solution
stationary phase
thin-layer chromatography (TLC)

Principles of chromatography

1 Consider Figure 13.3.1.

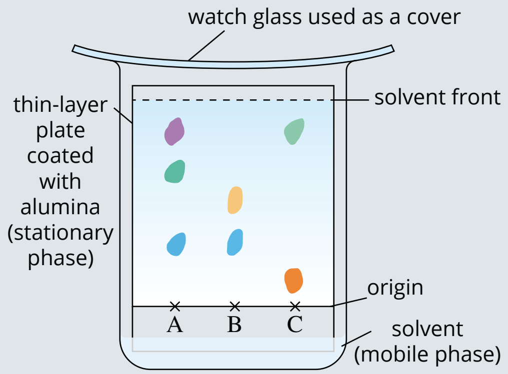


FIGURE 13.3.1 A thin-layer chromatogram of three different samples (A, B and C).

a How many different components are present in sample B?

b Which component of colour A is least strongly adsorbed on the stationary phase?

c Which samples are likely to have one component in common?

d The green spot in sample A is 8.0 cm above the origin. The R_f value of this green spot is 0.74. The orange and green spots of sample C are 3.0 cm and 9.0 cm above the origin, respectively. Calculate the R_f values of each component of sample C. Give your answer to two decimal places.

2 The amino acids present in a sample of fruit juice can be detected by thin-layer chromatography. R_f values of some amino acids in two separate solvents are given in Table 13.3.1.

To achieve better separation of the complex mixture of substances present in the juice, a 'two-way' chromatogram was prepared. The first step in this procedure was to run a chromatogram using solvent 1. The results of this chromatogram are shown in Figure 13.3.2

TABLE 13.3.1 R_f values for some amino acids

Amino acid	Solvent 1 R_f	Solvent 2 R_f
Lysine	0.12	0.55
Leucine	0.58	0.82
Proline	0.39	0.88
Valine	0.40	0.74
2-Aminobutyric acid	0.28	0.58
Threonine	0.21	0.49
Hydroxyproline	0.21	0.67
β-Phenylamine	0.50	0.86
Isoleucine	0.57	0.81
Alanine	0.24	0.55
Serine	0.19	0.34
Glutamic acid	0.25	0.33
Glycine	0.20	0.40
Arginine	0.13	0.60
Taurine	0.12	0.33
Tyrosine	0.38	0.62

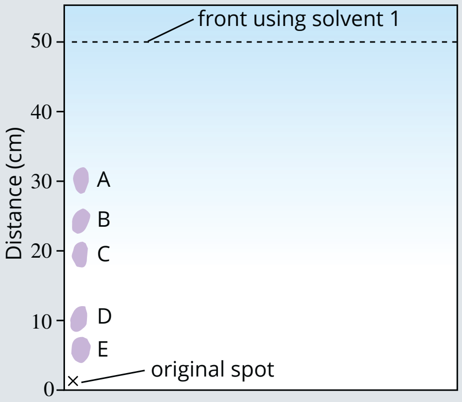


FIGURE 13.3.2 Chromatogram using solvent 1.

a Calculate the R_f value of each spot on the chromatogram.

b Try to identify the amino acids responsible for each spot. The TLC plate was then turned around so that it lay at a right angle to the original and a second chromatogram was produced using solvent 2. Figure 13.3.3 shows the appearance of the TLC plate after some time.

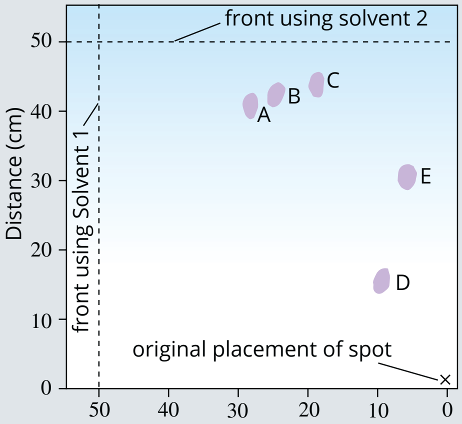


FIGURE 13.3.3 Appearance of the TLC plate after a second run with solvent 2 at right angles to the original spot.

c Use Table 13.3.1 to identify each component in the mixture.

d What is the advantage of a two-way chromatogram?

3 Figure 13.3.4 shows a thin-layer chromatogram obtained for individual amino acids and a medicine.

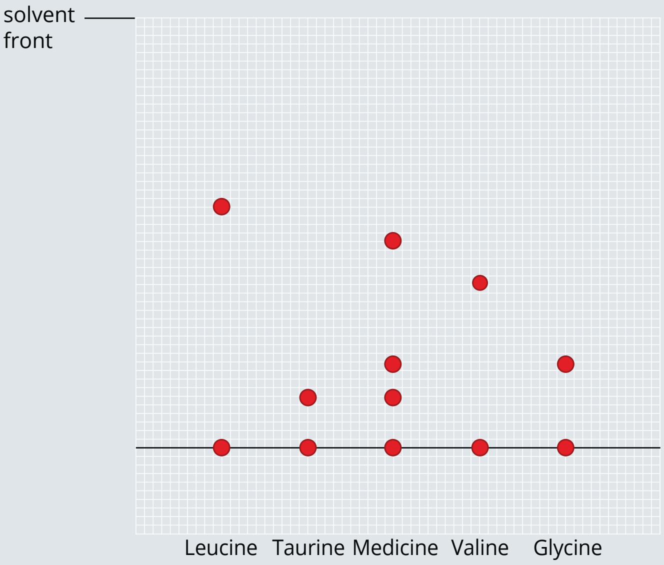


FIGURE 13.3.4 Chromatogram of amino acids.

a The following materials are commonly used in chromatography: water, ethanol, paraffin wax, glass sheets, paper strips, powdered alumina, nitrogen gas and hexane. Choose a suitable stationary phase and mobile phase from the list to use in the analysis of amino acids by thin-layer chromatography.

b Calculate the distance moved by the sample of leucine if the solvent front moves 13 cm from the origin.

c The separation of taurine and glycine on the chromatogram is not very great. State what would happen to the R_f values of the two amino acids if the separation was carried out for a longer period so the solvent front moved 20 cm instead of 13 cm from the origin. Explain your answer.

d What amino acids are present in the medicine? Explain your answer.

High-performance liquid chromatography

4 Consider the following changes that could be made to an analysis to be performed by HPLC. Which change is most likely to increase the retention time of a component?

A Reducing the length of the column

B Increasing the amount of sample injected into the instrument

C Using a less tightly packed column

D Reducing the pressure of the mobile phase

5 A chemist working for a sports anti-doping agency analyses the testosterone levels of an athlete's blood by HPLC.

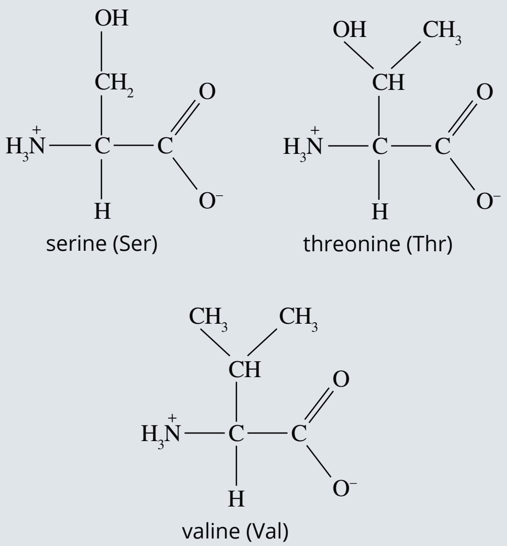
a Outline the steps that the scientist would undertake in the analytical process.

b The chemist obtained the results shown in Table 13.3.2 for four testosterone standards and the athlete's blood sample. The concentrations of the standards were measured in nanograms per litre. What is the testosterone concentration in the athlete's blood?

TABLE 13.3.2 Results of blood analysis

Concentration (ng L^{-1})	Peak area
20.0	0.12
40.0	0.22
60.0	0.36
80.0	0.46
Blood sample	0.28

6 Reversed-phase HPLC, uses a polar mobile phase and a non-polar stationary phase. A mixture of the amino acid molecules serine, threonine and valine (Figure 13.3.5) was analysed by reversed-phase HPLC. List the amino acids in the order that they would reach the detector.


serine (Ser)

threonine (Thr)

valine (Val)

FIGURE 13.3.5 Structures of three amino acids.

7 A government department analysed some imported olive oil by HPLC and found that the oil was impure and contained chemicals found only in corn oil. The peak area of one of the corn oil components in the chromatogram of a sample of the impure oil was 15.5 mm^2. The peak areas of four standard solutions of the component were also measured (Table 13.3.3).

Calculate the concentration of the corn oil component in the sample.

TABLE 13.3.3 Results of olive oil analysis

Corn oil component standards (%)	Peak area (mm^2)
1.0	5.8
2.0	11.6
3.0	17.6
4.0	23.0

8 What are the advantages of HPLC for the analysis of drugs compared to an analysis technique based on column chromatography?

9 Which feature of a chromatogram obtained during a HPLC analysis is:

a used to identify the components of a mixture?

b least affected by a change in concentration of the sample components?

c used to determine the concentration of each component in a mixture?

Connecting the main ideas

10 Write a definition for each of the following terms: adsorption, chromatography, desorption, eluent, mobile phase, stationary phase, retention time.

11 A herbal tea extract was analysed by HPLC. The chromatogram obtained is shown in Figure 13.3.6.

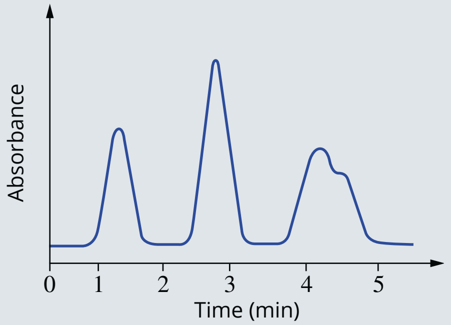


FIGURE 13.3.6 Chromatogram obtained from a herbal tea extract.

a Explain what information chemists can obtain from this chromatogram.

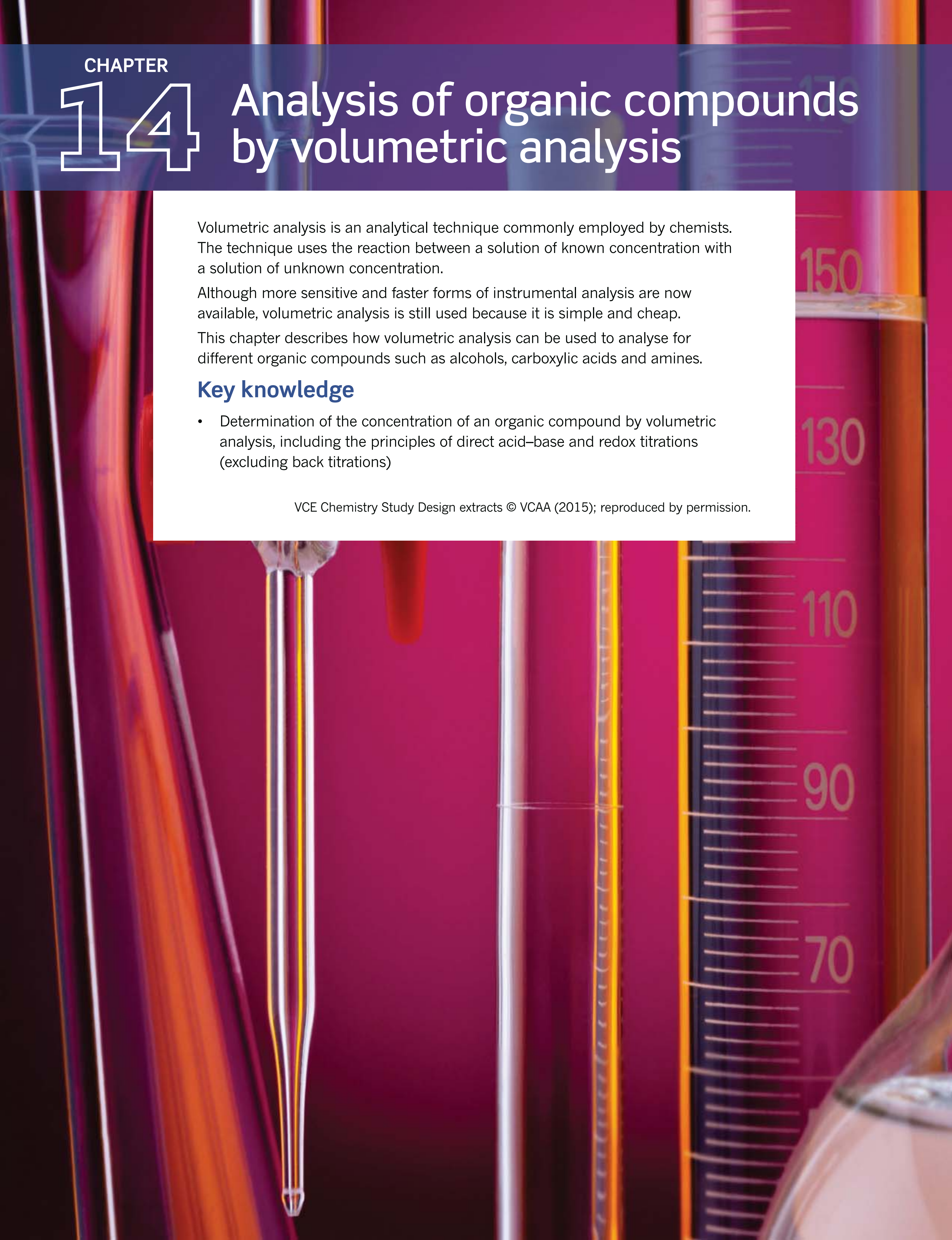
b How many components are evident?

c Briefly explain how the components are separated by HPLC.

12 Explain why paper or thin-layer chromatography might be used as the initial investigation of a mixture rather than HPLC.

CHAPTER

14 Analysis of organic compounds by volumetric analysis



Volumetric analysis is an analytical technique commonly employed by chemists. The technique uses the reaction between a solution of known concentration with a solution of unknown concentration.

Although more sensitive and faster forms of instrumental analysis are now available, volumetric analysis is still used because it is simple and cheap.

This chapter describes how volumetric analysis can be used to analyse for different organic compounds such as alcohols, carboxylic acids and amines.

Key knowledge

- Determination of the concentration of an organic compound by volumetric analysis, including the principles of direct acid–base and redox titrations (excluding back titrations)

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14.1 Principles of volumetric analysis

If you've ever eaten too quickly and experienced indigestion, then you have suffered the effects of excess acid within your body. The pain of indigestion is caused by your stomach producing excessive quantities of acidic gastric juices.

The protein-digesting enzyme in gastric secretions (pepsin) works best at pH 1.5. Gastric juice contains large amounts of hydrochloric acid, which produces the optimum pH. The discomfort of indigestion can be relieved by taking an antacid, which contains a base (such as magnesium hydroxide, sodium hydrogen carbonate or aluminium hydroxide) to neutralise the acidic secretions.

Manufacturers of antacids compare their effectiveness in experiments designed to find out the volume of hydrochloric acid that reacts with each brand of antacid. In this section, you will learn about the experimental techniques that are used by chemists to perform such analyses involving acid–base reactions.

PREPARING SOLUTIONS

Volumetric analysis can be used to determine the **amount** or **concentration** of a dissolved substance in a solution. For example, vinegar is a solution of ethanoic acid (CH_3COOH). In order to find the concentration of ethanoic acid in vinegar, the vinegar can be titrated against a **standard solution** of a strong base such as sodium hydroxide ($NaOH$). A standard solution is a solution with an accurately known concentration.

Before discussing the procedure of volumetric analysis further, it is important to recall how standard solutions are prepared.

Primary standards

Pure substances are widely used in the laboratory to prepare standard solutions. Substances that are so pure that the amount, in moles, can be calculated accurately from their mass are called **primary standards**.

A primary standard should:

- be readily obtainable in a pure form
- have a known chemical formula
- be easy to store without deteriorating or reacting with the atmosphere
- have a high molar mass to minimise the effect of errors in weighing
- be inexpensive.

Examples of primary standards are:

- bases: anhydrous sodium carbonate (Na_2CO_3) and sodium borate ($Na_2B_4O_7.10H_2O$)
- acids: hydrated oxalic acid ($H_2C_2O_4.H_2O$) and potassium hydrogen phthalate ($KH(C_8H_4O_4)$).

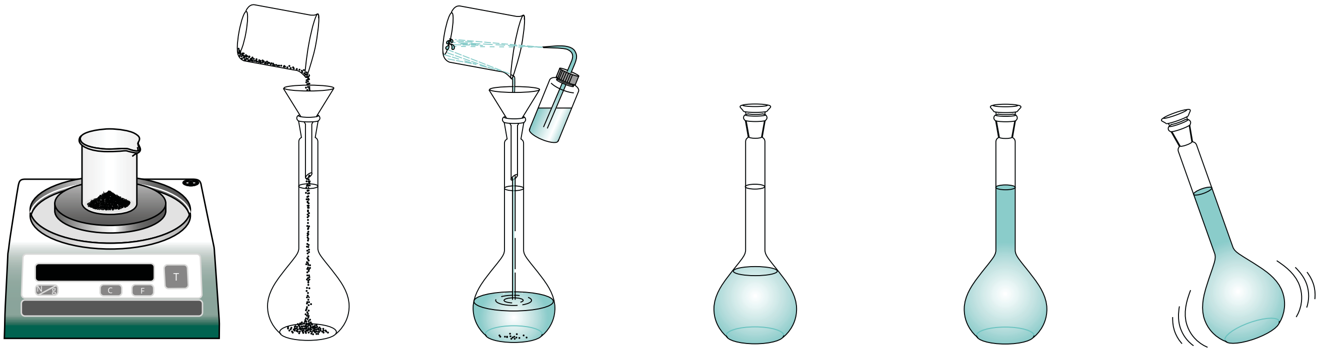
The term 'anhydrous' indicates there is no water present in the compound. To produce anhydrous sodium carbonate, a sample of sodium carbonate is heated to above 100°C to ensure all of the water is removed. The sodium carbonate is then quickly placed in a desiccator to prevent it absorbing any water from the atmosphere.

Standard solutions

Standard solutions are prepared by:

- dissolving an accurately measured mass of a primary standard in water to make an accurately measured volume of solution, or
- performing a **titration** with another standard solution in order to determine its exact concentration.

To prepare a standard solution from a primary standard, you need to dissolve an accurately known amount of the substance in deionised water to produce a known volume of solution. (You may recall this process from Unit 2 Chemistry.) The steps in preparing a standard solution from a primary standard are outlined in Figure 14.1.1.



Weigh the pure solid on an electronic balance.

Transfer to a volumetric flask using a clean, dry funnel.

Rinse any remaining solid particles into the flask with deionised water.

Half-fill the flask and stopper it. Swirl to ensure the solid particles dissolve.

Add deionised water up to the calibration line on the neck of the flask.

Stopper the flask and shake the solution to ensure an even concentration throughout.

FIGURE 14.1.1 The steps taken to prepare a standard solution from a primary standard.

The molar concentration of the standard solution can then be found from the following formulas:

$$\text{Amount in moles, } n = \frac{\text{mass of solute (in g)}}{\text{molar mass (in g mol}^{-1}\text{)}} = \frac{m}{M}$$

$$\text{Concentration, } c = \frac{\text{amount of solute (in mol)}}{\text{volume of solution}} = \frac{n}{V} = \frac{m}{M \times V}$$

In practice, making a standard solution directly from a primary standard is only possible for a few of the chemicals encountered in the laboratory. Many chemicals are impure because they decompose or react with chemicals in the atmosphere. For example:

- strong bases, such as sodium hydroxide (NaOH), absorb water and react with carbon dioxide in the air
- many hydrated salts, such as $Na_2CO_3.10H_2O$, lose water to the atmosphere over time.

Solutions such as hydrochloric acid (HCl), sulfuric acid (H_2SO_4), sodium hydroxide (NaOH) and potassium hydroxide (KOH) must be **standardised** to determine their concentration by titration against a standard solution. Common standard solutions used are sodium carbonate (Na_2CO_3) or potassium hydrogen phthalate ($KH(C_8H_4O_4)$).

CONDUCTING VOLUMETRIC ANALYSES

Now that you have seen how to prepare a standard solution, you will also need to recall how to undertake a titration.

Dilution

In general, many standard solutions, such as sodium hydroxide, are prepared as relatively high concentration **stock solutions**. To obtain a convenient concentration to use in a titration, these stock solutions must first be **diluted**.

Stock solutions are large volumes of common chemicals such as those used in volumetric analysis.

Titration

Volumetric analysis involves reacting a measured volume of a standard solution with a measured volume of the solution of unknown concentration.

The solutions are mixed until they have just reacted completely in the mole ratio indicated by the balanced chemical equation (the **equivalence point**). This process is known as performing a titration.

The number of moles of solute in the standard solution can be calculated from its concentration and volume. By using the mole ratio from the equation for the reaction, the number of moles of the solute in the solution of unknown concentration can be determined. The unknown solution concentration can then be calculated from the number of moles and the volume of solution.

Once the concentration of a solution has been determined from a titration, the solution can be described as a standard solution and it is said to be standardised.

The steps involved in an acid–base titration are as follows.

1 A known volume of one of the solutions is measured using a **pipette** and transferred into a conical flask (see Figure 14.1.2). The fixed volume of solution transferred by pipette is called an **aliquot**.

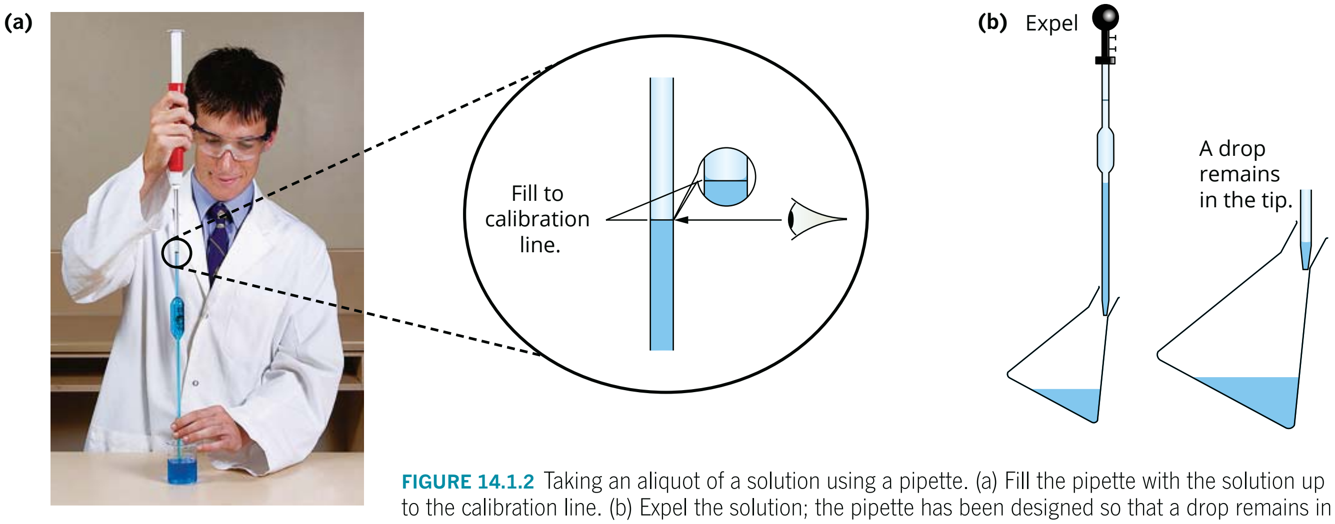


FIGURE 14.1.2 Taking an aliquot of a solution using a pipette. (a) Fill the pipette with the solution up to the calibration line. (b) Expel the solution; the pipette has been designed so that a drop remains in the tip after an aliquot has been delivered.

2 A few drops of an appropriate **acid–base indicator** are added so that a colour change signals the point at which the titration should stop.

3 The other solution is dispensed slowly into the conical flask from a **burette** until the indicator changes colour permanently (see Figure 14.1.3).

The volume of solution delivered by the burette is known as the **titre**. The titre is calculated by subtracting the initial burette reading from the final burette reading.

To minimise errors, the titration is repeated several times and the **average titre** is found. Usually three **concordant titres** (titres that are within 0.10 mL from highest to lowest of each other) are used to find this average.

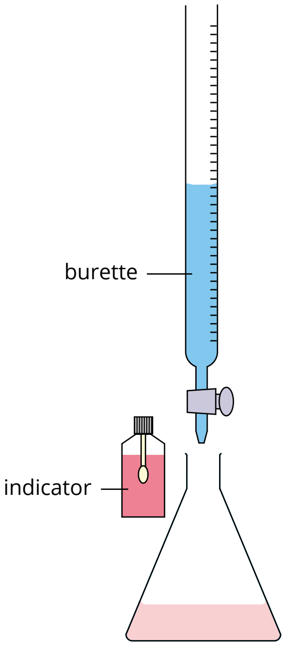


FIGURE 14.1.3 Titration from the burette into the conical flask containing the aliquot of the first solution.

Selecting an indicator

During a volumetric analysis, the pH of the solution in the conical flask changes as liquid is delivered from the burette. The graphical depiction of this change in pH is called a **titration curve** or **pH curve**.

The equivalence point is the point in the titration when the two chemicals have reacted in the mole ratio indicated by the balanced chemical equation. The equivalence point occurs when the gradient of the titration curve is steepest (see Figure 14.1.4).

The point during a titration when the indicator changes colour is known as the **end point**. It is important to select an indicator that changes colour during the steep section of the pH change, so that the end point and equivalence point occur at the same time during the titration.

The colours of common acid–base indicators and the pH range over which they change colour are shown in Figure 14.1.5 and listed in Table 14.1.1.

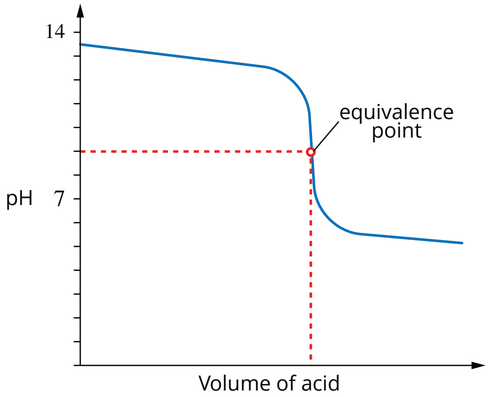


FIGURE 14.1.4 Change in pH during a titration between a strong base (sodium hydroxide solution) and a weak acid (ethanoic acid, present in vinegar). Phenolphthalein indicator (pH range 8.3–10.0) would be suitable for use in this titration.

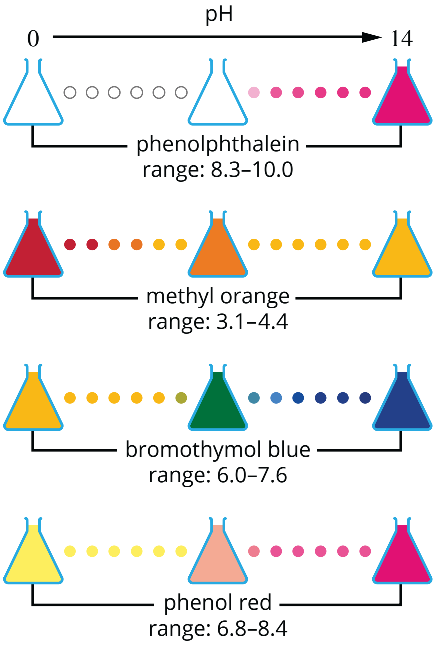


FIGURE 14.1.5 To identify the equivalence point of a titration, you must use a suitable indicator. Although all of these indicators display different colours at low pH and high pH, the pH range in which they change is different.

TABLE 14.1.1 pH range of some common indicators

Indicator	Colour in acid solution	pH range	Colour in basic solution
Phenolphthalein	Colourless	8.3–10.0	Dark pink
Methyl violet	Yellow	0.0–1.6	Violet
Methyl orange	Red	3.1–4.4	Yellow
Methyl red	Red	4.4–6.2	Yellow
Bromothymol blue	Yellow	6.0–7.6	Blue
Phenol red	Yellow	6.8–8.4	Red/violet
Alizarin yellow	Yellow	10.0–12.0	Red

For more accurate volumetric analyses, a pH meter can be used instead of an indicator. Data from the meter is used to plot a titration curve and the equivalence point can be identified from the steepest section of the curve.

Rinsing volumetric glassware

To ensure that glassware is completely clean, it is often rinsed before a volumetric analysis is conducted. This removes any trace chemicals from the glassware, and makes the analytical results more precise and accurate.

Table 14.1.2 describes how the glassware used in volumetric analysis should be rinsed. Rinsing with the wrong liquid can cause errors in the analysis.

TABLE 14.1.2 Techniques for rinsing equipment for volumetric analysis

Glassware	Correct	Incorrect
Burette Pipette	Final rinse should be with the acid or base to be transferred by them.	Rinsing with water will dilute the acid or base solution.
Volumetric flask Conical flask	Only rinse with deionised water.	Rinsing with acidic or basic solutions will introduce unmeasured amounts of acids or bases into the flask that can react and affect the results.

14.1 Review

SUMMARY

- A solution of accurately known concentration is referred to as a standard solution.
- Standard solutions can be prepared from primary standards or by titrating an existing solution with another standard solution to determine its concentration.
- In a titration, a measured volume of a standard solution is reacted with a measured volume of the solution whose concentration is to be determined.
- The equivalence point of a reaction occurs when the reactants have been mixed in the mole ratio shown by the reaction equation.
- The end point is the point during the titration when the indicator changes colour.
- Indicators for a titration should be selected so that the end point occurs when the equivalence point has been reached.
- Concordant titres vary within narrowly specified limits. Three concordant titres are usually obtained during a titration.
- When rinsing glassware before a titration, it is important to ensure that:
  - conical and volumetric flasks are rinsed with deionised water
  - the burette and pipette are rinsed with the acid or base to be transferred by them.

KEY QUESTIONS

1 Methanoic acid (HCOOH) is found in stinging nettles. In an analysis of the concentration of methanoic acid in a solution extracted from nettles, the solution was titrated with a standard solution of potassium hydroxide. Aliquots of the methanoic acid were transferred to a conical flask and titrated against the potassium hydroxide solution in a burette.

Which one of the following would cause the calculated concentration of methanoic acid to be higher than it actually is?

A Rinsing the conical flask with deionised water
B Rinsing the burette with deionised water
C Rinsing the pipette with deionised water
D Rinsing the conical flask with potassium hydroxide solution

2 Explain the difference between:

a a standard solution and a primary standard
b the equivalence point and the end point
c a burette and a pipette
d an aliquot and a titre.

3 Use the following words to complete the paragraph about a titration: pipette, measuring cylinder, beaker, volumetric flask, primary standard, indicator, base, standard solution, burette, indicator, titre, dessicator, aliquot.

A sample of anhydrous sodium carbonate of approximately 2 g is weighed accurately. (The solid must be dry if it is to be used as a __________________.) The solid is tipped into a ____________________ and shaken with about 50 mL of distilled water until the solid dissolves. More water is added to make the solution to a volume of exactly 100.0 mL. A 20.00 mL ______________ of the solution is taken by using a _____________ and placed in a conical flask. A few drops of methyl orange _____________ are are added and the mixture is titrated against dilute hydrochloric acid.

4 Use Table 14.1.1 (page 433) to match the equivalence points with the following pH values with an appropriate indicator.
   - **a** 3.4
   - **b** 11.2
   - **c** 7.6
   - **d** 5.2

5 If a solution was dark pink in phenolphthalein indicator, what colour would the same solution be in methyl orange indicator?

6 The graphs in Figure 14.1.6 show the pH curves for titrations involving combinations of acids and bases of various strengths. Phenolphthalein changes colour over a pH range of 8.3–10.0. Methyl orange changes colour over a pH range of 3.1–4.4.

   Decide which indicator(s), if any, would be suitable to identify the equivalence point for each reaction a–d. Provide reasons for your selections.

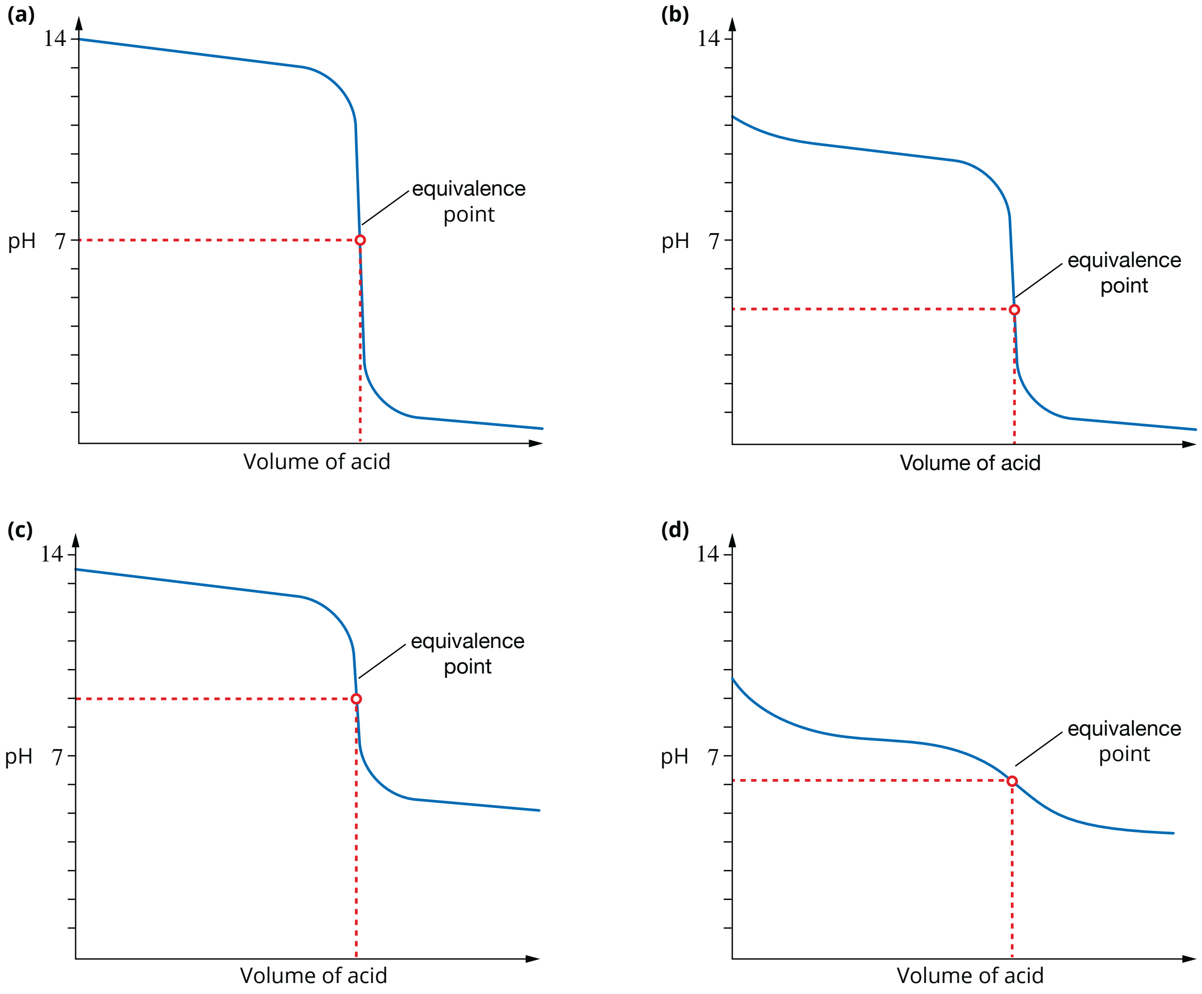


FIGURE 14.1.6 Change in pH during a titration of: (a) a strong acid with a strong base; (b) a strong acid with a weak base; (c) a weak acid with a strong base; (d) a weak acid with a weak base.

14.2 Acid–base titrations of organic compounds

You will recall from Chapter 10 that **organic compounds** make up over 90% of all compounds. The properties of different organic compounds can be dramatically different, depending on the **functional groups** present within the molecules of the compounds. In this section, you will look at how organic compounds with acidic or basic functional groups can be analysed by volumetric analysis.

Review

Quantities and errors in volumetric analysis

Quantities relevant to volumetric analysis

When you complete practical activities or answer questions involving volumetric analysis, you need to be able to calculate different quantities from different types of data.

For example, you may need to prepare a standard solution from a particular mass of a primary standard. Or you may need to calculate the concentration of a solution using the results from a titration.

The quantities that are most relevant to volumetric analysis calculations are:

- number of moles
- mass
- volume
- concentration.

Mole

The mole (unit mol) is a unit used by chemists for counting particles. One mole of any type of particle is a standard amount of substance. This amount contains the same number of specified particles as there are atoms in exactly 12 grams of carbon-12. The symbol for the amount of substance is *n*.

Because atoms are so small, chemists have defined the mole so that it represents a very large number. There are 6.02×10^{23} particles in 1 mole. This number is called Avogadro's number and has the symbol N_A.

The following formula links the amount of a substance (n) in mol, Avogadro's number (N_A) and the number of particles in a substance (N):

$$n = \frac{N}{N_A}$$

which can be rearranged to:

$$N = n \times N_A$$

Mass

Chemists often use mass, in grams, to measure an exact number of moles of an element or compound. In volumetric analysis, this would typically involve weighing out a predetermined mass of a primary standard in the preparation of a standard solution.

The molar mass of an element or compound is the mass of 1 mol of the element or compound, and is derived from the relative atomic mass, relative molecular mass or relative formula mass. The following formula links the amount of a substance (n) in mol, its molar mass (M) in g mol^{-1}, and the given mass of the substance (m) in g:

$$n = \frac{m}{M}$$

which can be rearranged to:

$$m = n \times N \text{ or } M = \frac{m}{n}$$

Volume

The unit of volume mainly used by chemists in calculations and in many units of concentration is the litre (L).

However, volumes delivered by a burette or pipette or made up in a volumetric flask are usually measured in millilitres (mL). For calculations, you must convert the volume from millilitres to litres.

1 L is equivalent to 1000 mL. Figure 14.2.1 shows a useful relationship for conversion between these units.

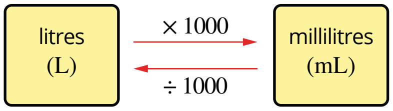


FIGURE 14.2.1 The relationship for conversions between L and mL.

Measuring concentration

Molar concentration

Preparing a standard solution of accurately known concentration and determining the concentration of the solution under analysis is at the heart of volumetric analysis.

Concentration is a measure of the amount of solute in a specified volume of solution. Chemists often express concentration as molar concentration, referred to as molarity. Molarity is defined as the amount of solute, in mol, dissolved in 1 litre of solution:

$$\text{Concentration} = \frac{\text{amount of solute (in mol)}}{\text{volume of solution (in L)}}$$

The unit of molarity is mol L^{-1}, which has the symbol M.

The following formula links the amount of substance (*n*) in mol, the concentration (*c*) in mol L^{-1} or M, and the volume (*V*) in L of a solution:

$$c = \frac{n}{V} \text{ or } n = c \times V \text{ or } V = \frac{n}{c}$$

Other units of concentration

Another concentration measure often used in volumetric analysis is mass per unit volume. Examples are shown in Table 14.2.1.

TABLE 14.2.1 Some concentration measures based on mass per unit volume

Unit of concentration	Unit of mass	Unit of volume
g L^{-1}	g	L
mg L^{-1}	mg	L
mg mL^{-1}	mg	mL
μg mL^{-1}	μg	mL

These are easily calculated by dividing the mass of solute, in the desired unit, by the volume of solution, in the desired unit.

For example, concentration (in g L^{-1}) = $\frac{m \text{ (in g)}}{V \text{ (in L)}}$.

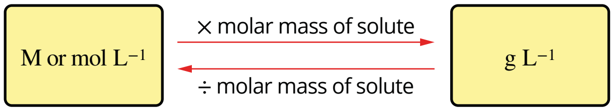


FIGURE 14.2.2 The relationship for conversions between mol L^{-1} and g L^{-1}.

Many commercial products express concentration in other ways such as:

- parts per million (ppm), i.e. grams per million grams, mg kg^{-1} or mg L^{-1} of solution
- parts per billion (ppb), i.e. grams per billion grams or μg kg^{-1}
- percentage mass/volume (%m/v), i.e. grams per 100 mL
- percentage by mass (%m/m), i.e. grams per 100 g
- percentage by volume (%v/v), i.e. mL per 100 mL.

Parts per million (ppm) and parts per billion (ppb) are very low concentrations. They are used to measure air pollution or effluent contamination by very sensitive analytical techniques such as atomic absorption spectroscopy. For example, the amount of mercury in a water sample from a stream might be given as 0.034 ppm or 34 ppb.

Converting between concentration units

Different units of concentration can be interconverted, for example from mol L^{-1} to g L^{-1}.

Figure 14.2.2 shows a useful relationship for conversion between the two concentration units most often used in volumetric analysis, mol L^{-1} (M) and g L^{-1}.

Uncertainties

Uncertainties are errors in measurements made during an experiment. Each piece of volumetric equipment has an associated uncertainty in its reading or measurement. Typical uncertainties associated with volumetric analysis are:

- 20 mL pipette: ±0.03 mL
- 50 mL burette: ±0.02 mL for each reading
- 250.0 mL volumetric flask: ±0.3 mL
- 100 g capacity top-loading balance: ±0.001 g
- 60 g capacity analytical balance: ±0.0001 g.

Other graduated laboratory glassware provides less precise measures:

- 50 mL measuring cylinder: ±0.3 mL
- 50 mL graduated beaker: ±5 mL.

Precision and accuracy

If repeated measurements of the same quantity give values that are in close agreement, the measurements are said to be precise. A titration is generally repeated until at least three titres are obtained that are within narrowly specified limits. These are called concordant titres. Repeating the analysis increases the the precision of the result.

If the average of a set of measurements is very close to the true or accepted value of the quantity being measured, then the measurement is said to be accurate.

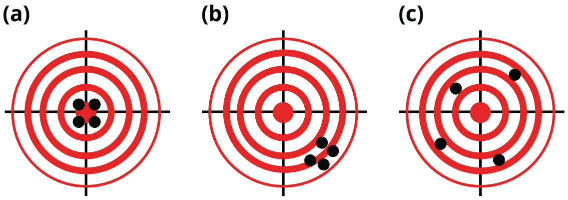


FIGURE 14.2.3 The holes in the targets illustrate the difference between accuracy and precision. Target (a) shows good accuracy and good precision. Target (b) shows poor accuracy but good precision. Target (c) shows both poor accuracy and poor precision.

Analytical chemists aim to produce results that are both precise and accurate.

Types of error

Mistakes

Mistakes are avoidable errors. Mistakes made during acid–base titrations could include:

- misreading the numbers on a scale
- using a pipette of incorrect volume
- spilling a portion of a sample.

A measurement that involves a mistake should be rejected and not included in calculations.

Systematic errors

A systematic error produces a constant bias in a measurement that cannot be eliminated by repeating the measurement. Systematic errors that affect an acid–base titration could include:

- using a 20 mL pipette that delivers 20.2 mL
- using an unsuitable indicator
- the presence of extra components in the sample other than the chemical being analysed that react during the titration.

Whatever the cause, the resulting error is in the same direction for every measurement and the average is either higher or lower than the true value.

Random errors

Random errors follow no regular pattern. The measurement is sometimes too large and sometimes too small. Random errors in volumetric analysis include:

- errors in judging the last digit in measurements of mass on an analytical balance
- changes in the volume of a titre due to fluctuations of temperature or minor variations in concentration
- difficulty in judging the fraction between two 0.1 mL scale markings on a burette.

The effects of random errors can be reduced by taking the average of several observations. In volumetric analysis, the average of three concordant titres is used to reduce random error.

ORGANIC ACIDS AND BASES

Organic acids are common in many everyday materials. Chemicals used for treating oil and removing rust commonly contain organic acids. Organic acids are also found in the home. For example, they are often incorporated in foods as preservatives to slow the growth of bacteria. Figure 14.2.4 shows some common organic acids found in nature.

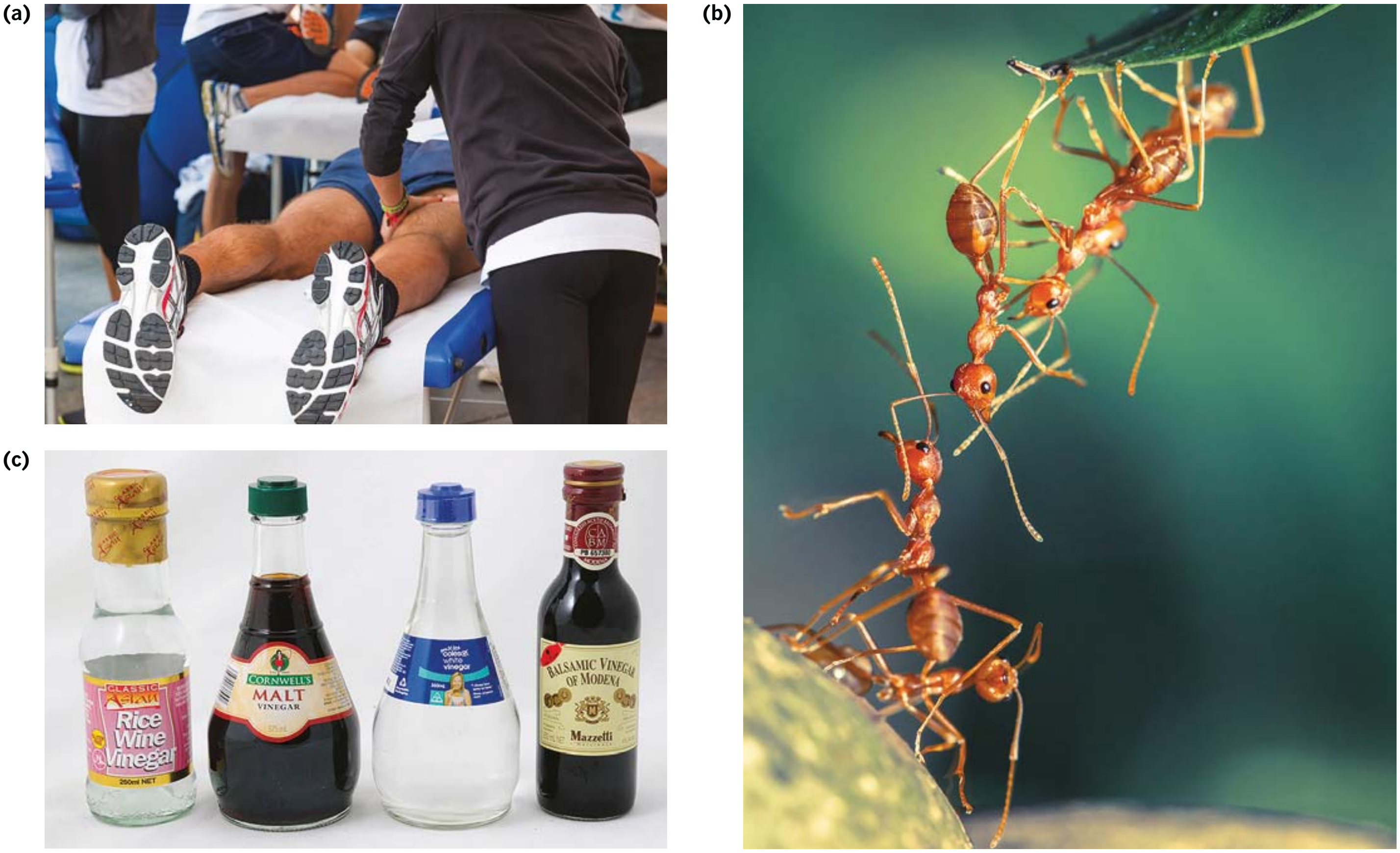


FIGURE 14.2.4 (a) Lactic acid can build up in muscles after intense exercise. Massaging can help release the lactic acid and decrease recovery time and soreness from exercise. (b) Ant venom contains methanoic acid (HCOOH), the simplest of the organic acids. (c) The sour-tasting ingredient in vinegar is ethanoic acid (CH_3COOH).

Organic bases are less common in our immediate environment, but are used in industry in the production of resins and dyes. Organic bases are also used to make many other industrial chemicals such as chloroform.

Carboxyl functional group

Although many different types of organic molecules can act as acids, **carboxylic acids** are the most common organic acids. Consequently, this section focuses on the analysis of carboxylic acids.

You will recall from Chapter 10 that a carboxylic acid is an organic molecule that contains the carboxyl functional group (–COOH). These compounds are weak acids because they can partially donate a hydrogen ion (H^+). Benzoic acid is shown in Figure 14.2.5 as an example.

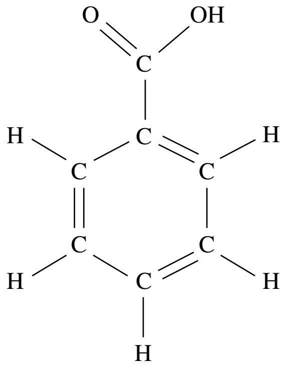


FIGURE 14.2.5 Benzoic acid is used in some foods as a preservative. The carboxyl group, depicted at the top of the molecule in this diagram, allows it to function as a weak acid.

In Unit 2, the properties of acids and bases were discussed in detail. As a general rule, acids are compounds that can donate a proton (a hydrogen ion) and bases are proton acceptors.

Most organic acids that contain a carboxyl group are **monoprotic acids**—they can donate only one proton. For example, ethanoic acid reacts with sodium hydroxide according to the equation:

$$CH_3COOH(aq) + NaOH(aq) \rightarrow CH_3COONa(aq) + H_2O(l)$$

Some organic acids are **polyprotic acids** and can donate more than one proton. For example, oxalic acid ($C_2H_2O_4$) contains two carboxyl functional groups and can therefore donate two protons. One mole of oxalic acid reacts with two moles of sodium hydroxide as follows:

$$C_2H_2O_4(aq) + 2NaOH(aq) \rightarrow Na_2C_2O_4(aq) + 2H_2O(l)$$

Amino functional group

Organic bases typically contain a nitrogen atom in the molecule, which can accept a hydrogen ion. The most common of these organic bases is the **amines**. You will recall from Chapter 10 that an amine molecule contains an amino functional group (–NH_2). Examples of some amines are shown in Figure 14.2.6.

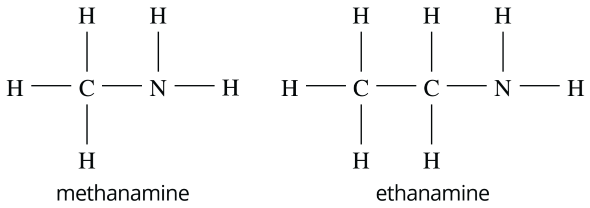


FIGURE 14.2.6 Amines contain the amino functional group (–NH_2). The presence of an amino group allows amines to accept protons and act as bases.

Amines have similar properties to ammonia as a consequence of the lone pair of electrons on the nitrogen atom. This means amines can act as bases and accept protons. Amines react with acids to produce salts as shown in the following equation:

$$C_2H_5NH_2(aq) + HCl(aq) \rightarrow C_2H_5NH_3Cl(aq)$$

ethanamine + hydrochloric acid → ethyl ammonium chloride

(composed of $C_2H_5NH_3^+$ and Cl^- ions)

ANALYSING ORGANIC ACIDS AND BASES

Carboxylic acids are weak acids and amines are weak bases. The volumetric analysis of organic acids and bases is performed using strong acid and bases. For example, a solution of benzoic acid, which is an organic acid, could be titrated against a solution of a strong base such as sodium hydroxide (NaOH). This ensures a near-complete reaction, sharper colour change in the indicator, with a more precise end point.

Calculations in volumetric analysis usually involve several steps. The flowchart in Figure 14.2.7 depicts the steps in performing these calculations.

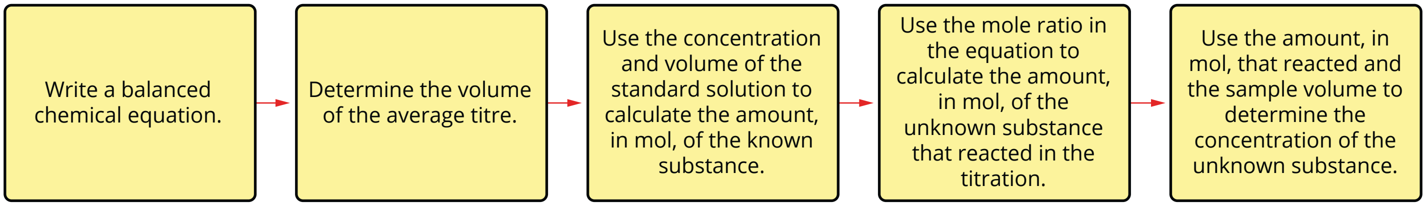


FIGURE 14.2.7 A flowchart summarising the steps in the calculation of the concentration of an unknown substance using data from a titration.

It is also important to use correct significant figures when giving an answer to a calculation. Appendix 2 (page 600) describes how to use significant figures.

Worked Examples 14.2.1 and 14.2.2 show how the concentration of an organic acid or base can be determined by an acid–base titration.

Worked example 14.2.1

VOLUMETRIC ANALYSIS OF ORGANIC ACIDS WITH STRONG BASES

The concentration of ethanoic acid (CH_3COOH) in a vinegar solution was determined by titration with standard sodium hydroxide solution using phenolphthalein indicator.

A 25.00 mL aliquot of vinegar was titrated with a 1.00 M solution of sodium hydroxide. Titres of 24.05, 22.10, 22.05 and 22.00 mL were required to reach the end point. What was the molar concentration of ethanoic acid in the vinegar?

Thinking	Working
Write a balanced chemical equation for the reaction.	Ethanoic acid is a monoprotic acid. An acid reacting with a base will form a salt and water: $CH_3COOH(aq) + NaOH(aq) \rightarrow NaCH_3COO(aq) + H_2O(l)$
Determine the volume of the average titre.	The titre of 24.05 mL is discarded because it is not concordant, i.e. it is not within a range of 0.10 mL from the highest to lowest titre volumes. $\text{Average titre} = \frac{22.10 + 22.05 + 22.00}{3}$ $= 22.05\text{ mL}$
Calculate the amount, in mol, of the standard solution that was required to reach the end point.	$n(NaOH) = c \times V$ $= 1.00 \times 0.02205$ $= 0.02205\text{ mol}$
Use the mole ratio in the equation to calculate the amount, in mol, of the unknown substance that reacted with the standard solution.	$\text{Mole ratio} = \frac{n(CH_3COOH)}{n(NaOH)} = \frac{1}{1}$ So $n(CH_3COOH) = n(NaOH)$ $= 0.02205\text{ mol}$
Determine the concentration of the unknown substance. Express your answer to the appropriate number of significant figures.	$c(CH_3COOH) = \frac{n}{V}$ $= \frac{0.02205}{0.02500}$ $= 0.8820\text{ M}$ The final result is rounded off to three significant figures corresponding to the smallest number of significant figures in the original data. Four significant figures are used in the earlier steps of the calculation to avoid rounding off errors. Concentration of CH_3COOH = 0.882 M

Worked example: Try yourself 14.2.1

VOLUMETRIC ANALYSIS OF ORGANIC ACIDS WITH STRONG BASES

The concentration of a solution of oxalic acid ($C_2H_2O_4$) was determined by titration with standard sodium hydroxide solution using phenolphthalein indicator.

A 20.00 mL aliquot of oxalic acid solution was titrated with a 1.00 M solution of sodium hydroxide. Titres of 22.10, 22.02, 18.80 and 22.06 mL were required to reach the end point. What was the molar concentration of the oxalic acid solution? (Oxalic acid is diprotic; the end point occurred when both protons on each acid molecule reacted.)

Worked example: 14.2.2

VOLUMETRIC ANALYSIS OF ORGANIC BASES WITH STRONG ACIDS

The concentration of a solution of methanamine (CH_3NH_2) was determined by titration with a standard solution of hydrochloric acid, using methyl red indicator.

A 10.00 mL aliquot of CH_3NH_2 solution was titrated with a 0.125 M solution of HCl. Titres of 17.23, 17.28 and 17.21 mL of HCl were required to reach the end point. What was the molar concentration of the methanamine solution?

Thinking	**Working**
Write a balanced chemical equation for the reaction.	A weak organic base, such as methanamine, reacts with an acid to form a salt: $CH_3NH_2(aq) + HCl(aq) \rightarrow CH_3NH_3Cl(aq)$
Determine the volume of the average titre.	The three titres are concordant, i.e. they are all within a range of 0.10 mL from highest to lowest titre volumes. $\text{Average titre} = \frac{17.23 + 17.28 + 17.21}{3}$ $= 17.24 \text{ mL}$
Calculate the amount, in mol, of the standard solution that was required to reach the end point.	$n(HCl) = c \times V$ $= 0.125 \times 0.01724$ $= 0.002155 \text{ mol}$
Use the mole ratio in the equation to calculate the amount, in mol, of the unknown substance that reacted with the standard solution.	$\text{Mole ratio} = \frac{n(CH_3NH_2)}{n(HCl)} = \frac{1}{1}$ $= 0.002155 \text{ mol}$ So $n(CH_3NH_2) = n(HCl)$ $= 0.002155 \text{ mol}$
Determine the concentration of the unknown substance.	$c(CH_3NH_2) = \frac{n}{V}$ $= \frac{0.002155}{0.0100}$ $= 0.2155 \text{ M}$ The final result is rounded off to three significant figures corresponding to the smallest number of significant figures in the original data. Four significant figures are used in the earlier steps of the calculation to avoid rounding off errors. Concentration of CH_3NH_2 = 0.216 M

Worked example: Try yourself 14.2.2

VOLUMETRIC ANALYSIS OF ORGANIC BASES WITH STRONG ACIDS

The concentration of a solution of ethanamine ($CH_3CH_2NH_2$) was determined by titration with a standard solution of hydrochloric acid using methyl orange indicator.

A 20.00 mL aliquot of $CH_3CH_2NH_2$ solution was titrated with a 0.100 M solution of HCl. Titres of 21.50, 21.40 and 21.48 mL of HCl were required to reach the end point. What was the molar concentration of the ethanamine solution?

14.2 Review

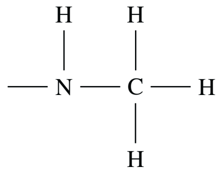
SUMMARY

- Carboxylic acid molecules contain the carboxyl functional group (–COOH), which has acidic properties.
- The concentration of organic acids, such as carboxylic acids, can be analysed in titrations with standardised solutions of strong bases, such as potassium hydroxide (KOH) and sodium hydroxide (NaOH).
- Amine molecules contain the amino functional group (–NH_2), which has basic properties.
- The concentration of organic bases, such as amines, can be determined from titrations with standardised solutions of strong acids, such as hydrochloric acid (HCl).

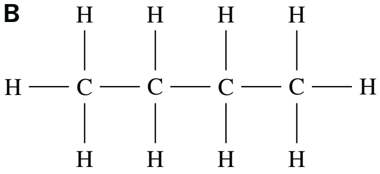
KEY QUESTIONS

1 Which of the following molecules can act as an acid?

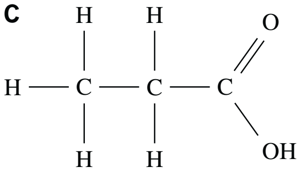
A



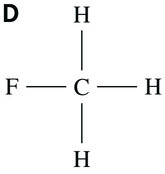
B



C



D



2 The concentration of ethanoic acid (CH_3COOH) in vinegar was determined by titration with a standardised solution of potassium hydroxide, using phenol red indicator. A 25.00 mL aliquot of vinegar required 21.56 mL of 0.995 M KOH to reach the end point.

a Write an equation for the reaction between ethanoic acid and potassium hydroxide.

b Calculate the amount, in mol, of KOH used in the titration.

c Calculate the amount, in mol, of ethanoic acid that reacted.

d Calculate the molar concentration of ethanoic acid in the vinegar.

e Calculate the concentration of ethanoic acid in g L^{-1}.

3 20.00 mL aliquots of 0.386 M sulfuric acid solution (H_2SO_4) are titrated against an ethanamine solution ($CH_3CH_2NH_2$) of unknown concentration. The equation for the reaction is:

$2CH_3CH_2NH_2(aq) + H_2SO_4(aq) \rightarrow (CH_3CH_2NH_3)_2SO_4(aq) + 2H_2O(l)$

Given the average titre was 21.02 mL, calculate the molar concentration of the ethylamine solution.

4 Oxalic acid ($C_2H_2O_4$) is a diprotic acid. The concentration of an oxalic acid solution was determined by titration with a standard sodium hydroxide solution, using phenolphthalein indicator. A 20.00 mL aliquot of oxalic acid was titrated with a 1.25 M solution of sodium hydroxide. Titres of 21.06, 21.00, 21.08 and 22.06 mL were required to reach the end point.

Given that the end point occurred when both acidic protons on each oxalic acid molecule had reacted, calculate the oxalic acid solution's:

a molar concentration

b %m/m concentration.

14.3 Redox titrations of organic compounds

You will recall from Chapter 4 that oxidation reactions occur when a substance loses electrons and reduction occurs when a substance gains electrons. Reactions involving the loss and gain of electrons are commonly referred to as **redox reactions**.

The effects of organic compounds undergoing redox reactions are easily observed in our everyday lives. Oxygen from the atmosphere slowly oxidises molecules in fruit, such as apples and bananas, to make the fruit turn brown. This can be prevented by adding lemon or lime juice to the cut fruit (Figure 14.3.1). The oxidation of molecules in butter causes it to become rancid. Within the human body, oxidation reactions in cells are the source of the body's energy.

FIGURE 14.3.1 Juice from citrus fruits is often added to guacamole (avocado) and cut apples to stop them from going brown. The ascorbic acid (vitamin C) in the juice is preferentially oxidised by the oxygen in the air, preventing the food from spoiling.

In this section you will see how the capacity of some organic molecules to undergo redox reactions can be used as a basis for volumetric analysis.

ANALYSING ORGANIC COMPOUNDS BY REDOX TITRATIONS

A redox titration involves the reaction of an oxidising agent with a reducing agent. As for acid–base titrations, one solution is usually pipetted into a conical flask and the other is dispensed into the flask from a burette.

For some redox titrations, such as those involving the permanganate ion (MnO_4^-), the equivalence point is indicated by a colour change in one of the reacting solutions. For other redox titrations, an indicator must be added in order to detect the equivalence point.

Volumetric analysis involving redox reactions can be used to determine the composition of a range of substances, including organic chemicals in fruit juice and wine. Table 14.3.1 gives examples of how these substances are analysed.

TABLE 14.3.1 Examples of analysis using redox titrations

Substance	Ingredients for analysis	Titrate with
Wine	Ethanol	Acidified potassium permanganate or potassium dichromate solution (in practice ethanol is analysed by back titration—see the Extension on page 448)
Fruit juice	Vitamin C (ascorbic acid)	Iodine solution
Wine	Sulfur dioxide	Iodine solution
Wound disinfectant	Hydrogen peroxide	Acidified potassium permanganate solution

Analysing alcohols

In Chapter 10, you learned that organic compounds with a hydroxyl functional group (–OH) belong to the family of molecules known as **alcohols**. Typical uses of alcohols are as fuels, in alcoholic beverages, as industrial solvents and as cleaning products, as shown in Figure 14.3.2.

The words OIL RIG can be used to remember that 'Oxidation Is Loss of electrons' and 'Reduction Is Gain of electrons'. Redox reactions were described in further detail in Chapter 4.

FIGURE 14.3.2 Methylated spirits is primarily made from ethanol. It is widely used in households as a solvent for cleaning.

Alcohols can undergo oxidation and act as weak reducing agents. When a primary alcohol such as ethanol is oxidised, the hydroxyl functional group is converted into an aldehyde group (–CHO). The aldehyde group can then be further oxidised to a carboxyl functional group (–COOH), as shown in Figure 14.3.3.

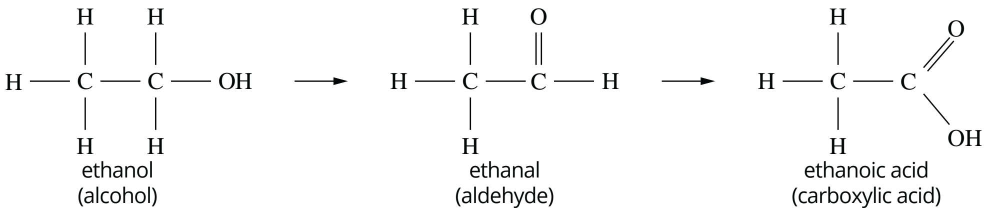


FIGURE 14.3.3 When alcohols such as ethanol are oxidised, an aldehyde is first formed, which may then be further oxidised to a carboxylic acid.

These oxidation reactions can be used as the basis for volumetric analysis to determine the concentration of an alcohol in a solution. Typically, a strong oxidising agent, such as acidified potassium dichromate solution ($K_2Cr_2O_7$) or acidified potassium permanganate solution ($KMnO_4$), is used to react with the alcohol in a titration.

If, for example, ethanol is oxidised to ethanoic acid by an acidified solution of potassium dichromate ($K_2Cr_2O_7$), the dichromate ion is involved in the reaction while the potassium ion is a spectator ion. The overall equation and half-equations are:

- Reduction half-equation:
  $Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$
- Oxidation half-equation:
  $CH_3CH_2OH(aq) + H_2O(l) \rightarrow CH_3COOH(aq) + 4H^+(aq) + 4e^-$
- Overall equation:
  $$\underset{\text{ethanol}}{3CH_3CH_2OH(aq)} + 2Cr_2O_7^{2-}(aq) + 16H^+(aq) \rightarrow \underset{\text{ethanoic acid}}{3CH_3COOH(aq)} + 4Cr^{3+}(aq) + 11H_2O(l)$$

Note that acid must be present for this reaction to occur because hydrogen ions (H^+) are consumed.

The calculations using data from a redox titration are similar to those from an acid–base titration. An example of these calculations is shown in Worked Example 14.3.1.

Worked example 14.3.1

VOLUMETRIC ANALYSIS OF AN ALCOHOL

The concentration of ethanol in a beer was determined by titration with a standard solution of acidified potassium dichromate. The equation for the reaction is:

$$3CH_3CH_2OH(aq) + 2Cr_2O_7^{2-}(aq) + 16H^+(aq) \rightarrow 3CH_3COOH(aq) + 4Cr^{3+}(aq) + 11H_2O(l)$$

A 20.00 mL aliquot of beer was titrated with a 0.00788 M solution of potassium dichromate. Titres of 17.05, 21.15, 21.13 and 21.17 mL were required to reach the end point. What was the molar concentration of ethanol in the beer?

Thinking	**Working**
Determine the volume of the average titre.	The titre of 17.05 mL is discarded because it is not concordant, i.e. it is not within a range of 0.10 mL from highest to lowest titre volumes. Average titre = $\frac{21.15 + 21.13 + 21.17}{3}$ = 21.15 mL
Calculate the amount, in mol, of the standard solution that was required to reach the end point.	$n(K_2Cr_2O_7) = c \times V$ $= 0.00788 \times 0.02115$ = 0.001667 mol
Use the mole ratio in the equation to calculate the amount, in mol, of the unknown substance that reacted with the standard solution.	Mole ratio = $\frac{n(CH_3CH_2OH)}{n(K_2Cr_2O_7)} = \frac{3}{2}$ So $n(CH_3CH_2OH) = \frac{3}{2} \times n(K_2Cr_2O_7)$ = 0.0002500 mol
Determine the concentration of the unknown substance. Express your answer to the appropriate number of significant figures.	$c(CH_3CH_2OH) = \frac{n}{V}$ $= \frac{0.0002500}{0.02000}$ = 0.01250 M The final result is rounded off to three significant figures, corresponding to the smallest number of significant figures in the original data. Four significant figures are used in the earlier steps of the calculation to avoid rounding off errors. Concentration of CH_3CH_2OH = 0.0125 M

Worked example: Try yourself 14.3.1

VOLUMETRIC ANALYSIS OF AN ALCOHOL

The concentration of a solution of methanol (CH_3OH) was determined by titration with a standard solution of acidified potassium permanganate ($KMnO_4$). The equation for the reaction is:

$$5CH_3OH(aq) + 4MnO_4^-(aq) + 12H^+(aq) \rightarrow 5HCOOH(aq) + 4Mn^{2+}(aq) + 11H_2O(l)$$

A 10.00 mL aliquot of CH_3OH solution was titrated with a 0.125 M solution of $KMnO_4$. Titres of 14.13, 14.18 and 14.11 mL were required to reach the end point. What was the molar concentration of the methanol solution?

Selecting indicators for redox titrations

It can be more difficult to select suitable indicators for redox titrations than for acid–base titrations. Redox indicators must behave as oxidants or reductants after the equivalence point has been reached and a small excess of solution from the burette is present. They must also be highly coloured in either oxidised or reduced form.

The permanganate ion is often used in redox titrations. The permanganate ion is purple while the manganese(II) ion is colourless (see Figure 14.3.4):

$$\underset{\text{purple}}{MnO_4^-(aq)} + 8H^+(aq) + 5e^- \rightarrow \underset{\text{colourless}}{Mn^{2+}(aq)} + 4H_2O(l)$$

As a consequence, there is no need to use a redox indicator in titrations using the permanganate ion.

Starch is used as an indicator in titrations in which iodine (I_2) is either a reactant or a product. When iodine is present in excess, it reacts with starch to form a dark blue complex (see Figure 14.3.5).

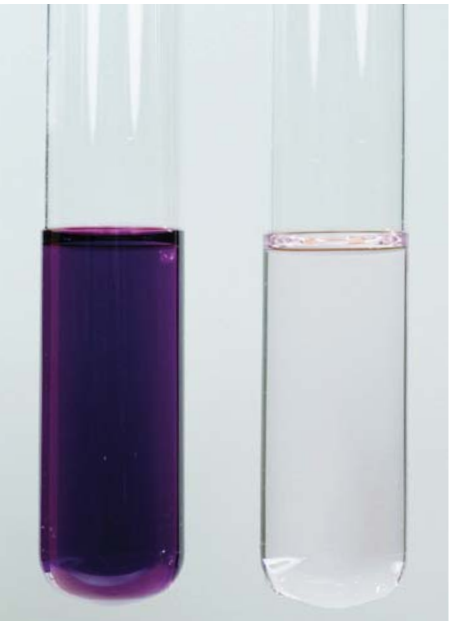


FIGURE 14.3.4 Oxidation of ethanol by potassium permanganate. Potassium permanganate ($KMnO_4$), a good oxidising agent, is dissolved in the liquid in the test tube on the left. When it reacts with ethanol, it forms the colourless solution on the right which contains Mn^{2+} ions.

FIGURE 14.3.5 Iodine (I_2) in the presence of starch forms a dark blue complex.

EXTENSION

Back titrations in determination of ethanol content of wine

Although direct titrations between alcohols and oxidising agents, such as dichromate ions, have been described in this section to illustrate the principles of redox titrations, in practice such titrations would yield inaccurate results. Ethanol and other alcohols react only slowly with dichromate ions at room temperature. To overcome this problem, the ethanol content of wine is usually determined by a technique called a back titration.

A known excess of dichromate ions is first added to the wine and the mixture is heated so that all the ethanol is oxidised. The amount of dichromate ions in excess is then found by reacting the excess dichromate ions with iodide ions to produce iodine (I_2) and titrating the iodine with sodium thiosulfate ($Na_2S_2O_3$).

The steps and reactions involved in determining the ethanol content of wine are as follows.

1 Ethanol is oxidised to ethanoic acid by heating it with dichromate ions.

$3C_2H_5OH(aq) + 2Cr_2O_7^{2-}(aq) + 16H^+ \rightarrow 3CH_3COOH(aq) + 4Cr^{3+}(aq) + 11H_2O$

2 Excess dichromate ions are reacted with iodide ions to produce iodine (I_2).

$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6I^-(aq) \rightarrow 2Cr^{3+}(aq) + 7H_2O(l) + 3I_2(aq)$

3 The iodine is titrated with standard sodium thiosulfate solution.

The equation for this reaction is:

$I_2(aq) + 2S_2O_3^{2-}(aq) \rightarrow 2I^-(aq) + S_4O_6^{2-}(aq)$

Calculations involving the amount of sodium thiosulfate, the amount of iodine reacted and the amount of dichromate in excess will enable you to determine the amount of ethanol, in moles, and hence the actual concentration of ethanol.

14.3 Review

SUMMARY

- Some organic compounds undergo redox reactions, which can form the basis of volumetric analysis.
- Primary alcohols can react with strong oxidising agents, such as compounds containing the permanganate (MnO_4^-) and dichromate ($Cr_2O_7^{2-}$) ions to form a carboxylic acid.
- Some redox titrations involve a change in colour and therefore do not require the addition of an indicator.

KEY QUESTIONS

1 Some alcohols can be converted into ketones by oxidising agents. Write a balanced half-equation for the oxidation of propan-2-ol ($CH_3CHOHCH_3$) to form propanone (CH_3COCH_3).

2 An artist uses 10.0 mL of 15.0 M HNO_3 to etch a design into a sheet of copper according to the following equation:

$Cu(s) + 4HNO_3(aq) \rightarrow Cu(NO_3)_2(aq) + 2H_2O(l) + 2NO_2(g)$

What mass of copper reacts with the acid?

3 Potassium permanganate reacts with hydrogen peroxide according to the following equation:

$2MnO_4^-(aq) + 5H_2O_2(aq) + 6H^+(aq) \rightarrow 2Mn^{2+}(aq) + 8H_2O(l) + 5O_2(g)$

25.0 mL of 0.0200 M $KMnO_4$ solution is reduced by 20.0 mL of H_2O_2 solution. What is the concentration of the hydrogen peroxide solution?

4 The amount of vitamin C in fruit juice can be determined by titration with a standard 0.0100 M iodine solution:

$C_6H_8O_6(aq) + I_2(aq) \rightarrow C_6H_6O_6(aq) + 2H^+(aq) + 2I^-(aq)$

If the maximum concentration of vitamin C is likely to be 0.00050 g mL^{-1}, describe how you would perform the analysis. You should mention the volume of the fruit juice used and the maximum titre of iodine you would expect to obtain.

5 The alcohol content of an imported brandy was found by diluting 10.0 mL of brandy to 500 mL. 20.00 mL aliquots of this solution were then titrated against 0.100 M potassium dichromate ($K_2Cr_2O_7$) solution. The mean titre was 17.98 mL. The overall equation for this reaction is:

$2Cr_2O_7^{2-}(aq) + 3CH_3CH_2OH(aq) + 16H^+(aq) \rightarrow 4Cr^{3+}(aq) + 3CH_3COOH(aq) + 11H_2O(l)$

Calculate the concentration of ethanol in the sample of brandy in units of:

a mol L^{-1}

b g L^{-1}.

Chapter review

14

KEY TERMS

acid–base indicator
alcohol
aliquot
amine
amount
average titre
burette
carboxylic acid
concentration
concordant titres
dilute
end point
equivalence point
functional group
monoprotic acid
organic acid
organic base
organic compound
pH curve
pipette
polyprotic acid
primary standard
redox reaction
standard solution
standardised
stock solution
titration
titration curve
titre
volumetric analysis

Principles of volumetric analysis

1 Anhydrous sodium carbonate is used as a primary standard in determining the concentration of hydrochloric acid by volumetric analysis.

  a What criteria are used to determine whether or not a substance is suitable for use as a primary standard?

  b How would you prepare a standard solution of anhydrous sodium carbonate?

2 A volumetric analysis was performed and the following five titres were obtained: 24.22, 25.02, 24.20, 24.16 and 25.14 mL.

  a Which of these titres would be considered concordant titres?

  b What is the average volume based on the concordant titres?

3 A student uses aliquots of a standard solution of hydrochloric acid to determine the concentration of an ethanamine ($CH_3CH_2NH_2$) solution by volumetric analysis. What should the student use for the final rinsing of each piece of glassware used in the titration?

4 A student accidentally rinsed the pipette needed to take an aliquot of standard solution with deionised water rather than the solution.

  a What would be the effect on the concentration of an aliquot of the standard solution?

  b What would be the effect on the determined concentration of the unknown solution?

5 Oxalic acid ($C_2H_2O_4$) is added to sugar syrup by some European beekeepers to prevent infestations of mites. To determine the concentration of oxalic acid in a particular sugar syrup, a chemist titrates the oxalic acid against a standard sodium hydroxide solution. Why can't the chemist prepare a standard solution of sodium hydroxide from solid sodium hydroxide?

Acid–base titrations of organic compounds

6 A 20.00 mL solution of sodium hydroxide is standardised in a titration with a solution of 0.0615 M malonic acid ($C_3H_4O_4$). An average titre of 12.82 mL of malonic acid was needed to neutralise the sodium hydroxide solution.

  a What amount, in mol, of malonic acid reacted with the sodium hydroxide?

  b The equation for the reaction between malonic acid and sodium hydroxide is:

$$C_3H_4O_4(aq) + 2NaOH(aq) \rightarrow Na_2C_3H_2O_4(aq) + 2H_2O(l)$$

  How many moles of NaOH were in the 20.00 mL sample?

  c What is the molar concentration of the sodium hydroxide solution?

7 Indicate whether the following organic compounds are acidic, basic or neither.

  a Methane

  b Ethanoic acid

  c Pentan-2-amine

  d 3-Methyloctanoic acid

8 The ethanoic acid content of white vinegar was determined by titrating a 20.00 mL aliquot of the vinegar with 0.9952 M sodium hydroxide solution. The phenolphthalein indicator changed permanently from colourless to pink when 20.34 mL of sodium hydroxide solution was added from the burette.

  a Write an equation for the reaction.

  b Calculate the amount of sodium hydroxide, in mol, used in the titration.

  c Calculate the amount of ethanoic acid, in mol, used in the titration.

  d Calculate the molar concentration of ethanoic acid in the vinegar.

Redox titrations of organic compounds

9 Given the half-equations below, write a balanced overall equation for the reaction between butan-1-ol and a solution of acidified potassium dichromate:

$$CH_3CH_2CH_2CH_2OH(aq) + H_2O(l) \rightarrow CH_3CH_2CH_2COOH(aq) + 4H^+(aq) + 4e^-$$

$$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$$

10 A vitamin C tablet with a mass of 1.306 g was crushed and dissolved in deionised water. The solution was titrated against 0.0500 M iodine solution using starch solution as an indicator to determine the vitamin C ($C_6H_8O_6$) content of the tablet. The reaction can be represented by the equation:

$$C_6H_8O_6(aq) + I_2(aq) \rightarrow C_6H_6O_6(aq) + 2H^+(aq) + 2I^-(aq)$$

The end point occurred when 28.40 mL of iodine solution had been added.

- **a** Find the mass of vitamin C in the tablet.
- **b** Calculate the percentage of vitamin C in the tablet by mass.
- **c** Suggest the function of the other substance that makes up the remainder of the mass of the tablet.

11 A food and drugs authority analysed a sample of light beer to see if it conformed with the regulation of 2% by mass of alcohol (ethanol). The alcohol content was determined by volumetric analysis according to the reaction:

$$2Cr_2O_7^{2-}(aq) + 3C_2H_5OH(aq) + 16H^+(aq) \rightarrow 4Cr^{3+}(aq) + 3CH_3COOH(aq) + 11H_2O(l)$$

The beer was tested by taking a 10.00 mL sample and making it up to 250.0 mL in a standard flask. 20.00 mL aliquots were titrated against a 0.0500 M solution of potassium dichromate ($K_2Cr_2O_7$). Three separate titrations gave titres of 9.20, 9.16 and 9.22 mL. Calculate the:

- **a** amount, in mol, of $Cr_2O_7^{2-}$ present in the average of the titres
- **b** amount, in mol, of ethanol present in each 20.00 mL aliquot
- **c** amount, in mol, of ethanol in the original 10.00 mL sample of beer
- **d** mass of ethanol in the original sample
- **e** percentage by mass of alcohol in the beer, if the density of light beer is 1.10 g mL^{-1}. Would this product conform with regulations for low-alcohol beer?

12 The active ingredient in bathroom mould killers is the bleach sodium hypochlorite (NaOCl). The concentration of this chemical in a 20.00 mL sample was determined by adding an acidified solution containing an excess of I^- ions to the sample. This reacted according to the equation:

$$OCl^-(aq) + 2I^-(aq) + 2H^+(aq) \rightarrow I_2(aq) + Cl^-(aq) + H_2O(l)$$

The iodine formed by this reaction was titrated against 0.750 M sodium thiosulfate ($Na_2S_2O_3$) solution.

$$I_2(aq) + 2S_2O_3^{2-}(aq) \rightarrow 2I^-(aq) + S_4O_6^{2-}(aq)$$

25.10 mL of the thiosulfate solution was required to reach the end point. Calculate the:

- **a** amount, in mol, of I_2 reacting with the $S_4O_6^{2-}$ ions
- **b** amount of NaOCl in the sample
- **c** percentage of NaOCl by mass, in the mould killer. (Assume the density of the solution is 1.0 g mL^{-1}.)

13 Megavit multivitamin tablets contain iron(II) sulfate. The iron content of a sample of Megavit tablets was analysed. Ten tablets were crushed and ground into a paste with a little dilute sulfuric acid. All of the paste was carefully transferred into a 250.0 mL volumetric flask and the solution was made up to the mark with more dilute sulfuric acid. 20.00 mL aliquots of the solution were titrated with 0.0200 M potassium permanganate solution and a mean titre of 12.95 mL was obtained.

- **a** Write the half-equation for the oxidation of Fe^{2+} to Fe^{3+}.
- **b** Write the half-equation for the reduction of purple MnO_4^- to colourless Mn^{2+} in acidic solution.
- **c** Write a balanced ionic equation to represent the overall equation.
- **d** Calculate the amount, in mol, of Fe^{2+} present in each aliquot.
- **e** Calculate the amount, in mol, of Fe^{2+} in the 250.0 mL volumetric flask.
- **f** Calculate the mass of iron(II) sulfate present in each tablet.
- **g** The label says that each tablet contains 250 mg $FeSO_4$. How do these results compare with the manufacturer's specification? List two possible sources of error that could account for any discrepancy.

14 The iron content in a 0.200 g sample of fencing wire was determined by dissolving the wire in dilute sulfuric acid and making up the resulting pale green solution of Fe^{2+} ions to 25.0 mL. The solution was titrated with 0.0300 M potassium permanganate ($KMnO_4$) solution, which is purple in colour. A titre of 20.22 mL was obtained. The solution of Mn^{2+} and Fe^{3+} ions produced by the reaction was almost colourless.

- **a** Write an overall equation for the titration reaction.
- **b** Calculate the amount, in mol, of Fe^{2+} ions in the 25.0 mL volume of solution.
- **c** Calculate the percentage, by mass, of iron in the wire.
- **d** An indicator was not required for this titration. Why not?
- **e** Briefly describe two safety precautions that should be observed when carrying out this titration.

Connecting the main ideas

15 A scientist accidentally leaves unlabelled bottles containing 14.00 g L^{-1} solutions of propan-1-ol, butan-1-ol and pentan-1-ol on the laboratory bench. When the scientist returns she can't remember which solution is in each bottle.

The scientist selects one of the bottles and fills a burette with the alcohol solution. In a titration with 20.00 mL aliquots of a 0.1971 M acidified potassium permanganate solution ($KMnO_4$), an average titre of 21.11 mL was required to reach the end point of the titration.

The two half-equations are:

$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l)$

$\text{alcohol}(aq) + H_2O(l) \rightarrow$
$\text{carboxylic acid}(aq) + 4H^+(aq) + 4e^-$

a What is the mole ratio $\frac{n(\text{alcohol})}{n(MnO_4^-)}$ equal to?

b What is the molar mass of the alcohol?

c What is the identity of the alcohol?

16 Potassium permanganate is used in many redox titrations as an oxidising agent. No indicator is required because the permanganate ion is purple while the managanese(II) ion is colourless. The half-equation is:

$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l)$

Potassium permanganate cannot be used as a primary standard because it is slightly unstable. Prior to use in analysis, a potassium permanganate solution must be standardised. Sodium oxalate ($Na_2C_2O_4$) can be used as a primary standard for this purpose. During the analysis, the oxalate ions are oxidised to CO_2:

$$C_2O_4^{2-}(aq) \rightarrow 2CO_2(g) + 2e^-$$

a Write a balanced equation for the reaction between the permanganate and oxalate ions.

b A solution containing 0.161 g of sodium oxalate reacted with 26.7 mL of acidified potassium permanganate solution. Determine the molar concentration of potassium permanganate in this solution.

UNIT 4 • Area of Study 1

REVIEW QUESTIONS

How can the diversity of carbon compounds be explained and categorised?

Multiple-choice questions

1 The flashpoint of petrodiesel is around 50°C and that of biodiesel is closer to 150°C. Which of the following statements can be concluded from this information?

- **I** The intermolecular bonding in biodiesel is stronger than in petrodiesel.
- **II** Neither fuel is likely to be ignited by a spark if spilt at room temperature.
- **III** Biodiesel is likely to have a higher viscosity than petrodiesel.

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

Refer to the following table when answering Questions 2 and 3.

Covalent bond	Bond energy (kJ mol^{-1})
C–C	348
C–H	413
C–F	488
C–Si	318
Si–Si	217

2 In tetramethylsilane (TMS, $Si(CH_3)_4$) the weakest covalent bonds present are:

A C–C
B C–H
C Si–Si
D C–Si.

3 Diamond (C) and silicon carbide (SiC) are both tetrahedral covalent lattices. In diamond, each carbon is bonded to four other carbon atoms, and in silicon carbide, each carbon is bonded to four silicon atoms. When heated strongly, both decompose to gaseous atoms (sublime). The temperature required for this will be:

A higher for diamond because C–C bonds are stronger than C–Si bonds
B higher for diamond because C–C bonds are stronger than Si–Si bonds
C higher for silicon carbide because C–C bonds are weaker than C–Si bonds
D higher for silicon carbide because C–C bonds are weaker than Si–Si bonds.

4 In which of the following homologous series does the smallest molecule contain two carbon atoms?

A Alkanes
B Alkanols
C Alkenes
D Alkanoic acids

5 What is the systematic name for $CH_3CH_2CH_2CH(CH_3)_2$?

A 1,1-Dimethylbutane
B 2-Methylpentane
C 2-Methylpentene
D Propyldimethylmethane

6 Which compound would be expected to have the lowest boiling point?

A $CH_3CH_2CH_2OH$
B $CH_3CH_2CH_2CH_3$
C $CH_3CH_2CH_2Cl$
D $CH_3CH_2CH_3$

7 Which of the following statements are true of the homologous series of primary alkanols?

- **I** The members differ by one CH_2 unit.
- **II** They are all strong bases.
- **III** They can be oxidised to form carboxylic acids.

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

8 What is the product formed by the reaction of CH_2CH_2 with Br_2?

A CH_2BrCH_2Br
B CH_2CHBr
C CH_3CH_2Br
D CHBrCHBr

9 Consider the following reaction pathway.

ethene $\xrightarrow{\text{I}}$ chloroethane $\xrightarrow{\text{II}}$ ethanol $\xrightarrow{\text{III}}$ ethanoic acid

What reactions occur in steps I, II and III of the pathway?

A Substitution, addition, hydrolysis
B Chlorination, substitution, addition
C Addition, substitution, oxidation
D Addition, reduction, hydrolysis

10 When ethanol is heated under reflux with an acidified solution of potassium dichromate, what is the formula of the final product?

A $CH_3CH_2CH_2OH$

B CH_3COOCH_3

C CH_3COOH

D $CH_3CH_2CH_3$

11 The ester methyl ethanoate could be made by reacting together which of the following?

A CH_3CH_2OH and CH_3COOH

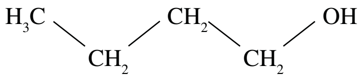
B CH_3CH_2OH and $HCOOH$

C CH_3OH and CH_3CH_2COOH

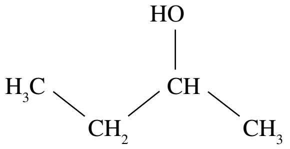
D CH_3OH and CH_3COOH

12 Which of the structures shown does **not** have a IUPAC name that ends with 'ol'?

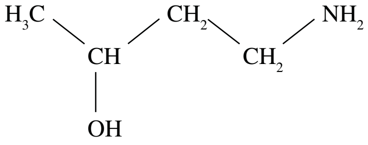
I



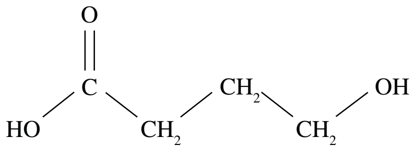
II



III



IV



A II and III

B III only

C IV only

D III and IV

13 Which statement about propan-1-ol and propan-2-ol is **not** true?

A The ^{13}C NMR spectrum of propan-1-ol has three peaks, and that of propan-2-ol has two peaks.

B The ^1H NMR spectrum of propan-1-ol has four peaks, and that of propan-2-ol has three peaks.

C The mass spectra of both will show a peak at a mass-to-charge ratio of 60.

D The fingerprint region of the IR spectra will be identical for both compounds.

14 In the mass spectrum of an organic compound, the signal produced by the unfragmented molecular ion and the signal produced by the most abundant particle correspond respectively to the:

A parent (molecular) ion peak and main ion peak

B main ion peak and base peak

C parent (molecular) ion peak and base peak

D base peak and parent (molecular) ion peak.

15 In high-performance liquid chromatography (HPLC), the stationary phase comprises small particles so densely packed that the mobile phase must be forced through it under pressure. Small particles are used in preference to large particles because:

A they are cheaper to manufacture

B it reduces the overall mass of the column

C increasing the surface area of the stationary phase improves separation

D it makes it easier to fill the column.

16 The retention time can be used in high-performance liquid chromatography (HPLC) to determine:

A the identity of a chemical

B the concentration of a chemical

C the amount of a chemical in the sample

D all of the above.

17 The concentration of a substance is most accurately determined in high-performance liquid chromatography (HPLC) by measuring:

A peak area

B peak height

C retention time

D R_f value.

18 Consider the following equation for the reaction of methanol with acidified potassium dichromate.

$2K_2Cr_2O_7(aq) + 3CH_3OH(aq) + 8H_2SO_4(aq) \rightarrow$
$2Cr_2(SO_4)_3(aq) + 3HCOOH(aq) + 2K_2SO_4(aq)$

Which statement about this reaction is **not** true?

A Dichromate ions have been reduced.

B Methanol has been oxidised.

C Hydrogen ions have been reduced.

D Sulfate ions have not been oxidised or reduced.

19 More energy is required to vibrate:

A C–C compared to C=C

B C–Cl compared to C–Br

C C–O compared to C–H

D C=C compared to C≡C.

20 How many peaks are expected in the low-resolution ^{1}H NMR and ^{13}C NMR spectra of methyl ethanoate, CH_3COOCH_3?

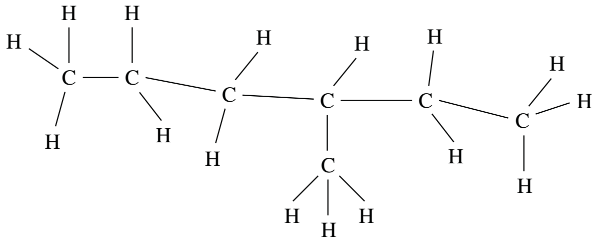
	^{1}H NMR spectrum (low resolution)	**^{13}C NMR spectrum**
A	2	3
B	3	2
C	6	3
D	1	3

Short-answer questions

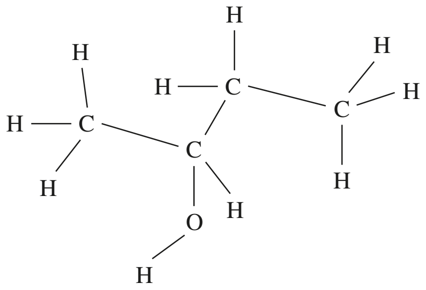
21 For each of the following structures, write a:

- **i** molecular formula
- **ii** condensed, or semistructural, formula.

a



b



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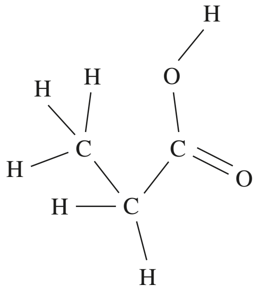

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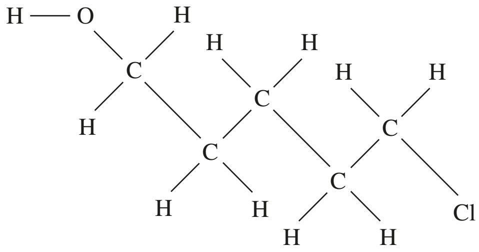

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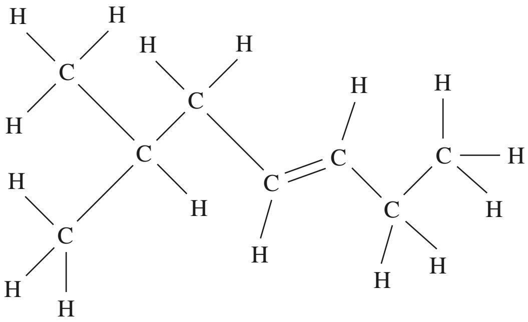

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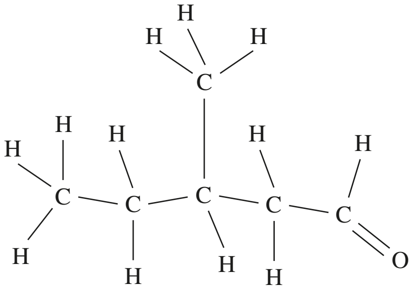

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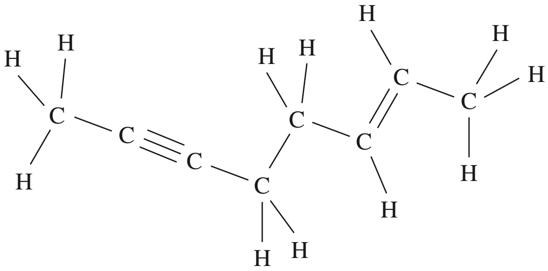

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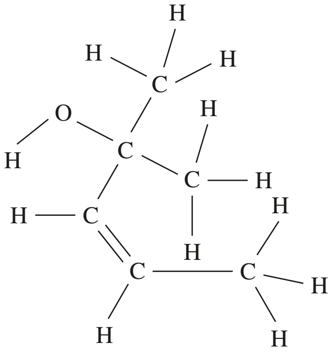
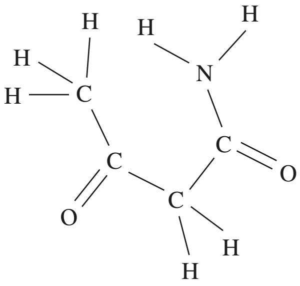
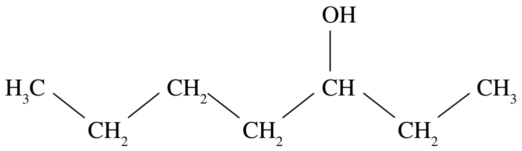


i



22 Give correct IUPAC names for the following structures, and state the number of chiral centres present in each.

a



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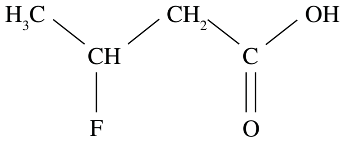

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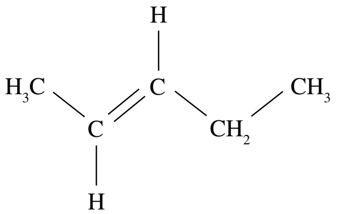

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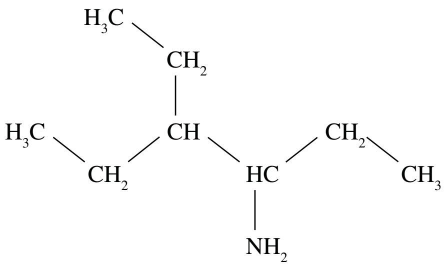

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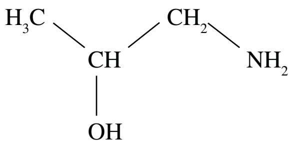

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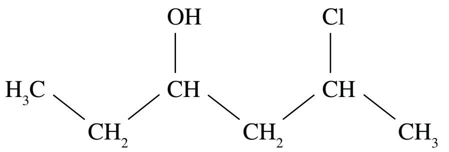

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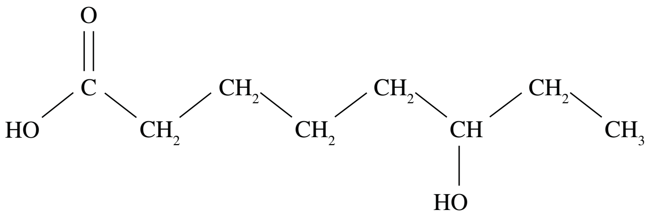

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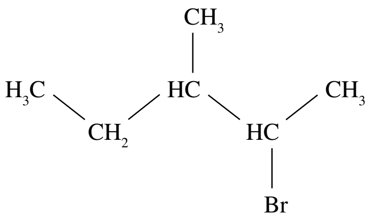
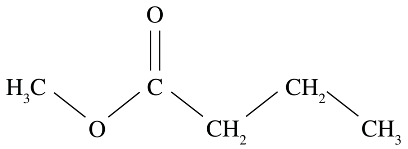


i



23 Draw full structures for each of the following, showing all bonds.

a $CH_3(CH_2)_3CH_3$

b $CH_2CHCH_2CHOHCH_3$

c $CH_2ClCH_2COCH_3$

d $CH_3(CH_2)_2CONH_2$

e $(CH_3)_2CHCHCH_2$

f $CH_3CH_2C(CH_3)OHCH_3$

g $CH_3OCOCH_2CH_3$

h 4-Ethylheptanoic acid

i 1-Bromopropan-1-ol

j *cis*-4-Methylpent-2-ene

k 1-Iodobutan-2-amine

l 3-Aminohexan-2-ol

24 Give appropriate reagents/conditions to effect the conversion of:

a butan-2-ol to butanone

b 1-chloropropane to propan-1-ol

c pent-2-ene to pentan-3-ol and pentan-2-ol

d propan-1-ol to propanoic acid

e cyclohexene to cyclohexane

f chloromethane to methanamine.

25 Design synthetic pathways/sequences, showing all organic intermediates and the reagents/conditions used, to prepare:

a propanoic acid from propane

b methyl ethanoate from methane and ethene

c propyl propanoate from propyl methanoate.

26 Write balanced chemical equations (excluding states) for the:

a acid–base reaction between propanoic acid and sodium hydrogen carbonate ($NaHCO_3$)

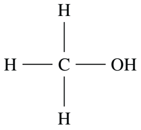
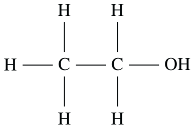
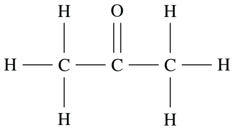
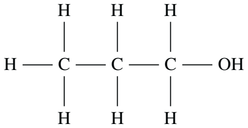
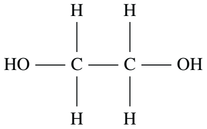
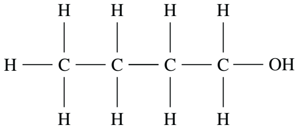
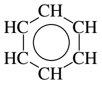
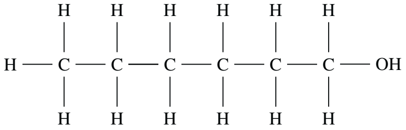
b oxidation of propan-1-ol to propanoic acid under acidic conditions (redox half-equation)

c condensation of ethanol and propanoic acid to form ethyl propanoate

d acid–base reaction between ethanamine and propanoic acid

e complete combustion of propanoic acid.

27 The following table gives a range of properties for a number of organic compounds arranged in order of increasing molecular mass.

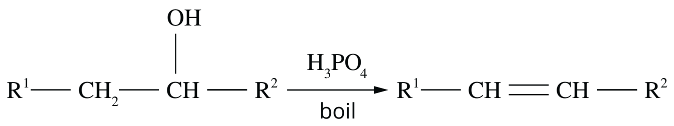
Name	Structure	Molecular mass	Viscosity (relative to methanol)	Boiling point (°C)	Water solubility
Methanol	 $\mathrm{H-\overset{H}{\underset{H}{C}}-OH}$	32	1.0	65	Miscible
Ethanol	 $\mathrm{H-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-OH}$	44	2.0	78	Miscible
Propanone	 $\mathrm{H-\overset{H}{\underset{H}{C}}-\overset{O}{\overset{\Vert}{C}}-\overset{H}{\underset{H}{C}}-H}$	54	0.6	57	Miscible
Propan-1-ol	 $\mathrm{H-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-OH}$	56	3.6	98	Miscible
Ethane-1,2-diol	 $\mathrm{HO-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-OH}$	62	29.6	197	Miscible
Butan-1-ol	 $\mathrm{H-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-OH}$	74	4.7	118	73 g L^{-1}
Benzene		78	1.1	80	<2 g L^{-1}
Hexan-1-ol	 $\mathrm{H-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-OH}$	102	8.3	159	~6 g L^{-1}

a What is viscosity a measure of?

b For each of the following statements concerning property trends, select compounds from the table that illustrate the trend, and account for the trend in terms of intermolecular bonding.

- **i** Within any homologous series, viscosity increases as the molecules get larger.
- **ii** Within any homologous series, water solubility decreases as the molecules get larger.
- **iii** For compounds with similar carbon skeletons, an additional hydrogen-bonding functional group significantly increases boiling point and viscosity.
- **iv** Compared with polar compounds of similar mass, non-polar compounds tend to have very low viscosity and low water solubility.

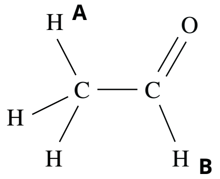
28 Alcohols can be 'dehydrated' by heating in acid to produce alkenes as shown below.

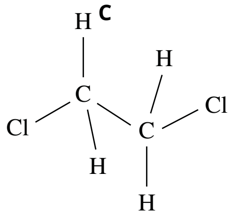


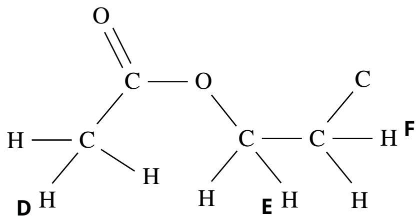
$$R^1—CH_2—\overset{\overset{\displaystyle OH}{|}}{CH}—R^2 \xrightarrow[\text{boil}]{H_3PO_4} R^1—CH{=}CH—R^2$$

When hexan-3-ol was heated with phosphoric acid, the resultant mixture was found to contain four distinct isomeric products: two pairs of geometric (*cis–trans*) isomers. Name and draw structures for the four products obtained.

29 ^{1}H NMR spectra of the following three compounds were recorded.

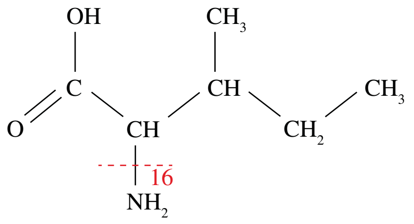






- **a** What type of electromagnetic radiation is absorbed and emitted in NMR spectroscopy?
- **b** What changes in the molecules are associated with this emission and absorption?
- **c** Describe the role of tetramethylsilane (TMS) in NMR spectroscopy.
- **d** The spectra of the three compounds included the following signals. In each case, select the letter labelling the H atoms most likely to be responsible for the signal, and give a brief justification.
  - **i** quartet at δ 8.5
  - **ii** singlet at δ 2.1
  - **iii** quartet at δ 4.1
  - **iv** singlet at δ 3.7
  - **v** triplet at δ 1.2
  - **vi** doublet at δ 2.2

30 The following is the structure of the amino acid isoleucine.



- **a** What is its molecular formula?
- **b** What is its molecular mass?
- **c** Copy the structure and mark the chiral centres with an asterisk (*).
- **d** The mass spectrum of isoleucine includes a signal at $m/z = 16$. The dotted line shows how cleavage might occur to produce the $[NH_2]^+$ fragment that would account for this signal.

  For each of the following m/z values from the spectrum of isoleucine, write the formula of the fragment ion likely to be responsible for it and add a dotted line to your diagram to show a simple bond cleavage that could produce this fragment ion.
  - **i** $m/z = 15$
  - **ii** $m/z = 29$
  - **iii** $m/z = 57$
- **e** The base peak in the mass spectrum is at $m/z = 86$.
  - **i** What is meant by the 'base peak' in a mass spectrum?
  - **ii** Suggest the fragment that has been *lost* from the molecular ion to produce the ion responsible for the base peak.

31 Chloroform (trichloromethane, $CHCl_3$) is synthesised commercially by the chlorination of methane:

$$CH_4 + 3Cl_2 \rightarrow CHCl_3 + 3HCl$$

The final mixture contains a mixture of chloroform along with chloromethane, dichloromethane and tetrachloromethane. Distillation allows separation of the chloroform and at one plant yields of 75%.

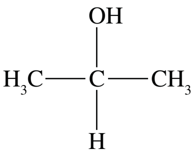
- **a** Calculate the atom economy of the reaction forming chloroform.
- **b** What mass of chloroform would be obtained from 1.0 kg of methane, assuming 75% yield?

An alternative source of chloroform is the reaction of sodium hypochlorite (bleach) with propanone (acetone):

$$CH_3COCH_3 + 3NaOCl \rightarrow CHCl_3 + 2NaOH + CH_3COONa$$

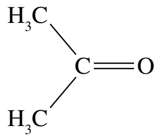
- **c** Name the by-products in this synthesis.
- **d** Calculate the atom economy for this process and compare it with that for the commercial method above.
- **e** Give an example of an organic reaction that has an atom economy of 100%.

32 The structures of propan-2-ol and propanone are shown below. The infrared spectra of these compounds are labelled IR spectrum A and IR spectrum B.

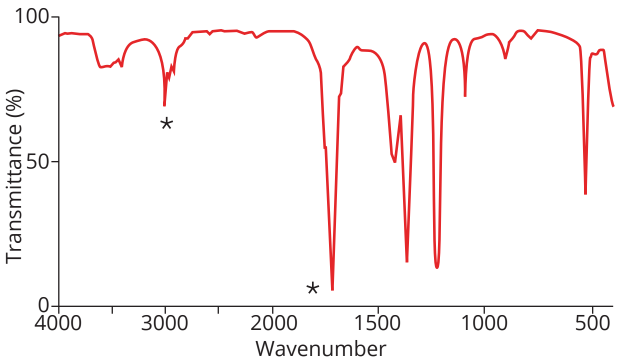


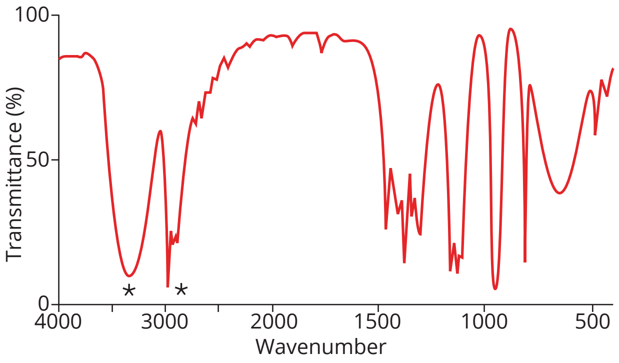
$$H_3C-\overset{\displaystyle OH}{\underset{\displaystyle H}{\overset{|}{\underset{|}{C}}}}-CH_3$$

propan-2-ol



propanone

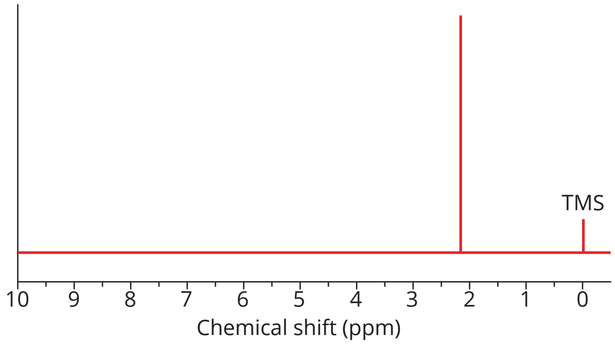




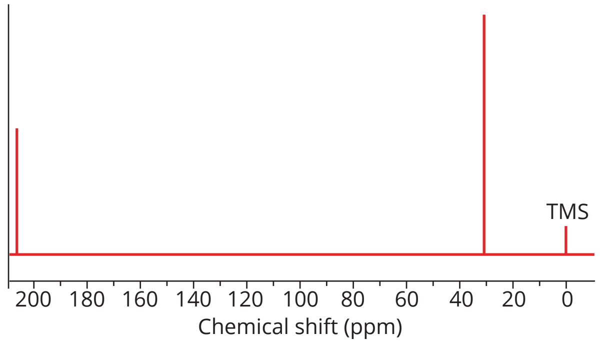
a Identify the bonds that produced the IR absorption marked with an asterisk (*) in each spectrum.

b Determine which spectrum represents which molecule.

c The ^1H NMR spectrum of propanone is shown below. Explain why there is only a single peak although there are six hydrogen atoms in the molecule.

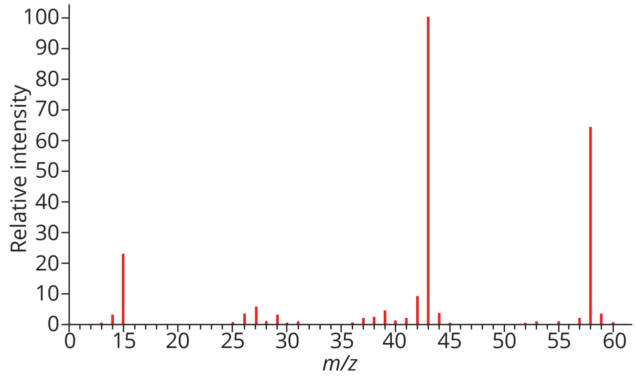


d The ^{13}C NMR spectrum of propanone is shown below. Explain why there are two peaks although there are three carbon atoms in the molecule.



e How many sets of peaks would you expect in ^1H NMR and ^{13}C NMR spectra of propan-2-ol? Provide an explanation for your answers.

f The mass spectrum of propanone is shown below.

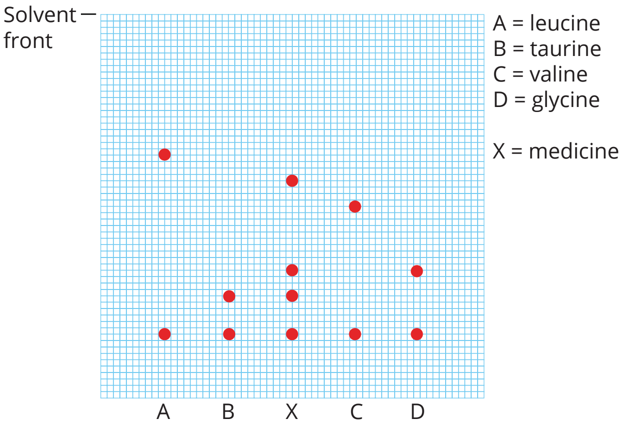


i What is the mass of the molecular ion?

ii What information does this provide about the molecule?

iii Suggest a formula for the molecular fragment that produces the peak at *m/z* 43.

33 The following diagram shows a thin-layer chromatogram of amino acids in a medicine.



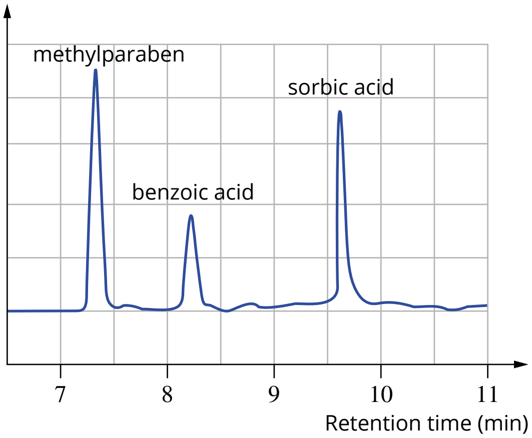
a What amino acids are in the medicine?

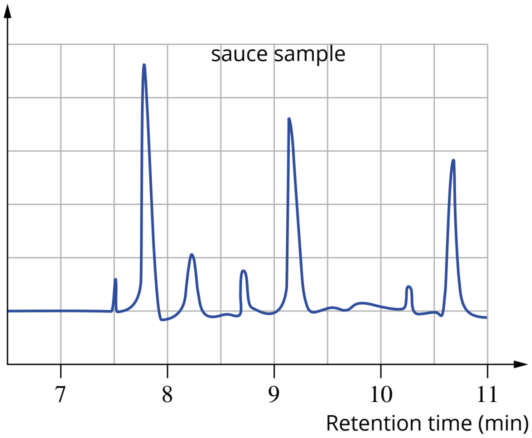
b Amino acids are colourless. What technique could be used to visualise the amino acid spots?

c Calculate the R_f value of taurine.

d Which amino acid is bonded least strongly to the mobile phase?

34 High-performance liquid chromatography (HPLC) is ideally suited to identify and measure food additives such as preservatives. A mixture of three common food preservatives was analysed by HPLC. A sample of sauce was prepared by dissolving 1.50 g of sauce in a total of 10.0 mL in a volumetric flask and this solution was analysed using the same mobile and stationary phases under the same conditions. The resultant chromatograms are shown below.





a Given that the preservatives are all equally soluble in the mobile phase, which of the three adsorbs most strongly on the stationary phase? Explain.

b Which of the preservatives appear to be present in the sauce sample?

c To measure the concentration of the preservative in the diluted sauce, its peak area was compared to that for standard solutions of the preservative, as shown in the following table.

Sample	Relative peak area
Sauce sample	31.5
0.00 mg/10.0 mL	0
2.00 mg/10.0 mL	13.3
4.00 mg/10.0 mL	26.6
6.00 mg/10.0 mL	39.9
8.00 mg/10.0 mL	53.2

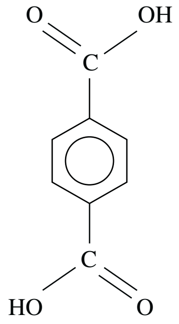
Construct a calibration graph for the standard samples and use it to estimate the concentration of the diluted sauce.

d Calculate the concentration of the preservative in the original sauce sample, in mg/10.0 g.

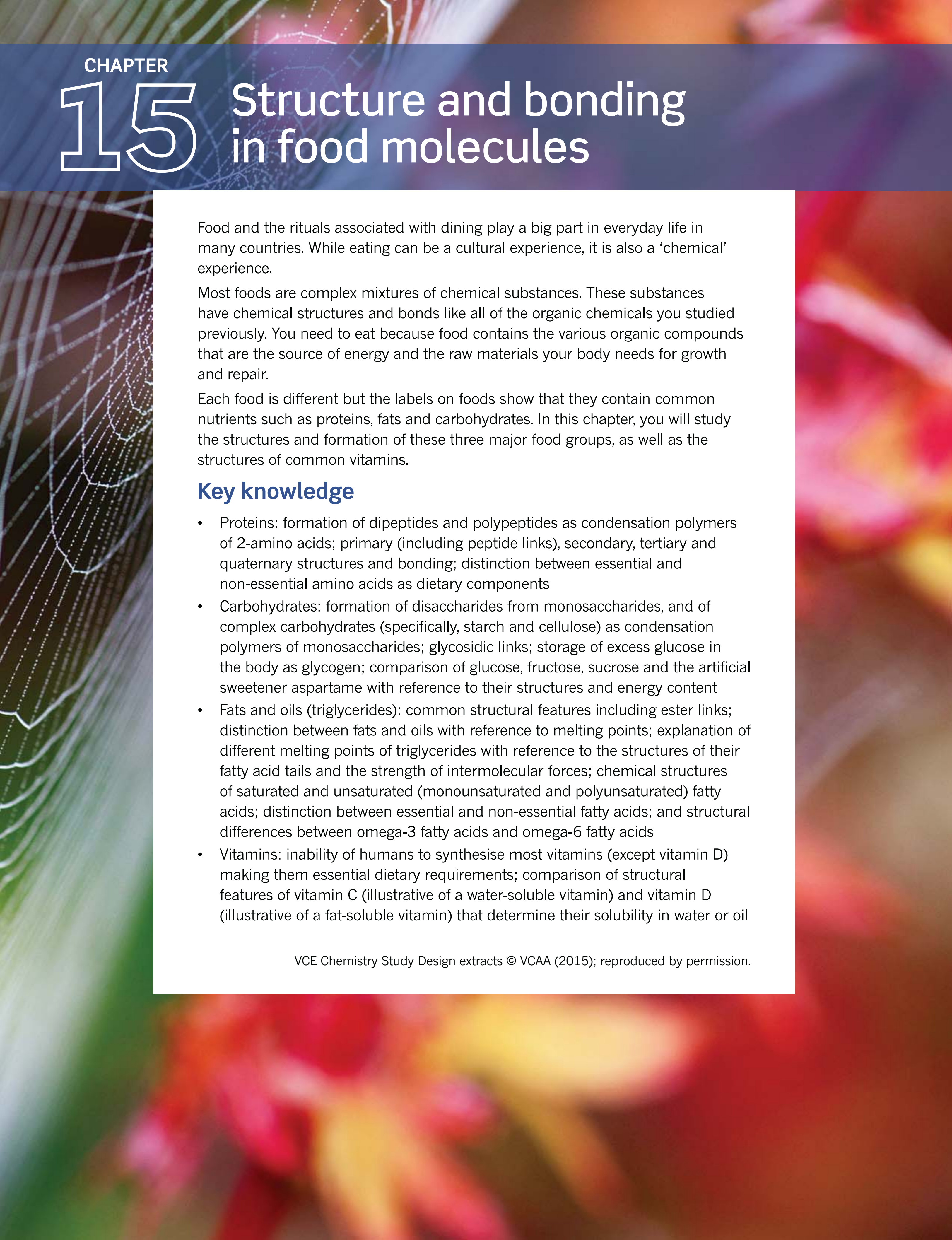
35 Terephthalic acid (benzene-1,4-dicarboxylic acid, $M = 166.1$ g mol^{-1}), whose structure is shown below, is one of the monomers used in the production of the polymer PET. It is a diprotic acid. As a preliminary test of the purity of a new sample, 5.26 g of the sample was dissolved in ethanol and water was added to make up a total of 100.0 mL in a volumetric flask. Then 10.00 mL aliquots were titrated against 0.350 M KOH(aq). An average titre of 17.48 mL was required. The equation for the reaction occurring is:

$C_8H_6O_4(aq) + 2KOH \rightarrow K_2C_8H_4O_4(aq) + 2H_2O(l)$

Calculate the percentage, by mass, of terephthalic acid in the original sample.



terephthalic acid



CHAPTER 15

Structure and bonding in food molecules

Food and the rituals associated with dining play a big part in everyday life in many countries. While eating can be a cultural experience, it is also a ‘chemical’ experience.

Most foods are complex mixtures of chemical substances. These substances have chemical structures and bonds like all of the organic chemicals you studied previously. You need to eat because food contains the various organic compounds that are the source of energy and the raw materials your body needs for growth and repair.

Each food is different but the labels on foods show that they contain common nutrients such as proteins, fats and carbohydrates. In this chapter, you will study the structures and formation of these three major food groups, as well as the structures of common vitamins.

Key knowledge

- Proteins: formation of dipeptides and polypeptides as condensation polymers of 2-amino acids; primary (including peptide links), secondary, tertiary and quaternary structures and bonding; distinction between essential and non-essential amino acids as dietary components
- Carbohydrates: formation of disaccharides from monosaccharides, and of complex carbohydrates (specifically, starch and cellulose) as condensation polymers of monosaccharides; glycosidic links; storage of excess glucose in the body as glycogen; comparison of glucose, fructose, sucrose and the artificial sweetener aspartame with reference to their structures and energy content
- Fats and oils (triglycerides): common structural features including ester links; distinction between fats and oils with reference to melting points; explanation of different melting points of triglycerides with reference to the structures of their fatty acid tails and the strength of intermolecular forces; chemical structures of saturated and unsaturated (monounsaturated and polyunsaturated) fatty acids; distinction between essential and non-essential fatty acids; and structural differences between omega-3 fatty acids and omega-6 fatty acids
- Vitamins: inability of humans to synthesise most vitamins (except vitamin D) making them essential dietary requirements; comparison of structural features of vitamin C (illustrative of a water-soluble vitamin) and vitamin D (illustrative of a fat-soluble vitamin) that determine their solubility in water or oil

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15.1 Amino acids

In this section, you will investigate the structure and properties of amino acids. Amino acids are the monomers that make the thousands of different **proteins** that are essential to life.

Proteins are organic biopolymers that have many important functions in living things. These include:

- enzymes that catalyse specific biochemical reactions
- hormones that control biological processes
- structural components in cell membranes, muscles, hair, feathers and spider silk (Figure 15.1.1)
- transport of substances across cell membranes or around the body; for example, haemoglobin is found in red blood cells (Figure 15.1.2) and binds to oxygen
- antibody molecules of the immune system.

The prefix 'mono' means one, only or single. Therefore, the term 'monomer' means one unit. When monomers join other monomers, a polymer is formed (the prefix 'poly' means many).

FIGURE 15.1.1 A spider's web is formed from threads of spider silk, spun from a strong fibrous protein called fibroin.

FIGURE 15.1.2 Red blood cells are biconcave disc-shaped cells that transport oxygen from the lungs to body cells. They contain the protein haemoglobin, which is able to bond reversibly to oxygen molecules.

Plants can manufacture all of the **amino acids** required to make proteins. They create amino acids from simple inorganic ingredients—such as carbon dioxide, water and nitrates—obtained from the atmosphere and soil. However, animals cannot do this. Animals obtain the amino acids they need to sustain their body functions from the plant and animal proteins in the food they eat.

STRUCTURE OF AMINO ACIDS

There are 20 different amino acids that make up all of the proteins in the human body. Every amino acid has an amino **functional group** (–NH_2), a carboxyl functional group (–COOH), and a hydrogen atom attached to a central carbon, called the α-carbon (alpha-carbon).

Two of the simplest amino acids are glycine and alanine. The structures of these two molecules are shown in Figure 15.1.3.

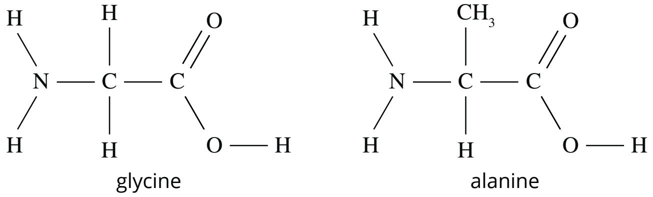


FIGURE 15.1.3 The structures of amino acids glycine and alanine.

General formula of amino acids

The amino acids used to produce the proteins in the human body have the general formula $H_2N–CH(R)–COOH$. The general structural formula of an amino acid is shown in Figure 15.1.4.

Amino acids such as those shown in Figure 15.1.4 are known as **2-amino acids**. This is because the carbon atom of the carboxyl group is numbered as the first carbon in the chain (according to IUPAC rules) and the amino group is bonded to the carbon atom adjacent to it, numbered '2' in the chain. 2-Amino acids are also called α-amino acids.

The twenty 2-amino acids used to make human proteins are listed in Table 15.1.1 on page 464, along with the three-letter abbreviations commonly used for them by biochemists.

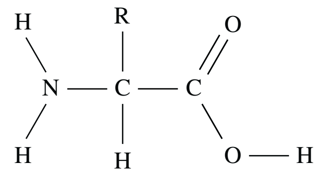


FIGURE 15.1.4 General structural formula of an amino acid. Different amino acids have different groups of atoms as the R group.

Properties of R groups in amino acids

The major difference between one amino acid and another is the group of atoms that make up the **side chain**. This side chain is represented in the general structure as an **R group**. The side chain may be:

- non-polar (e.g. $–CH_3$ in alanine and $–CH(CH_3)_2$ in valine)
- polar (e.g. $–CH_2COOH$ in aspartic acid and $–CH_2OH$ in serine).

The side chain may also include functional groups that can behave as:

- proton donors (e.g. $–CH_2COOH$ in aspartic acid contains an acidic carboxyl group)
- proton acceptors (e.g. $–CH_2CH_2CH_2CH_2NH_2$ in lysine contains a basic amino group).

Amino acids are commonly given three-letter abbreviations. For example, alanine is represented by Ala and glycine is represented by Gly.

ESSENTIAL AND NON-ESSENTIAL AMINO ACIDS

Within the cells in their bodies, humans can synthesise 11 of the 20 amino acids required to make proteins. These proteins sustain our bodily functions. However, the other nine amino acids (isoleucine, leucine, lysine, methionine, phenylalanine, threonine, tryptophan, valine and histidine, in the case of infants) must be provided directly through the proteins we eat. This is because human cells do not have the capacity to produce them.

These nine amino acids are known as **essential amino acids**. A healthy diet should include proteins that contain these essential amino acids. The human body does not store amino acids, so a balanced intake of protein is required each day. Lack of amino acids in the diet can cause serious diseases, such as kwashiorkor, which you can see in Figure 15.1.5. 'Kwashiorkor' means 'rejected one' in the Ga language of coastal Ghana where the disease is common. It reflects the incidence of the disease in children who have been weaned from breast milk to a diet that is high in carbohydrates and lacking in protein.

FIGURE 15.1.5 This child is suffering from kwashiorkor, which is a form of malnutrition caused by a protein-deficient diet.

TABLE 15.1.1 Amino acids found in the human body, with their three-letter abbreviations and R groups

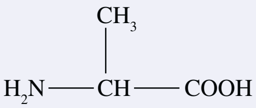
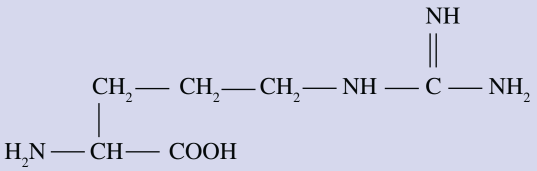
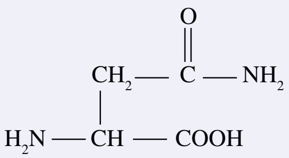
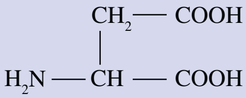
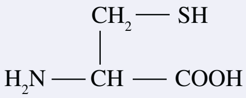
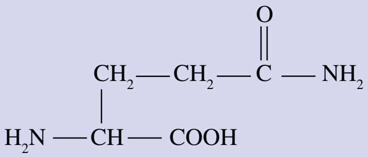
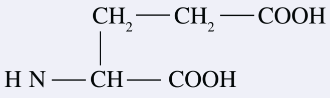
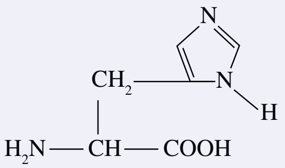
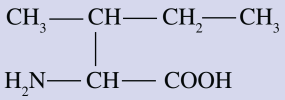
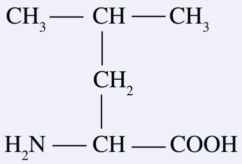
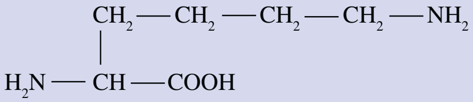
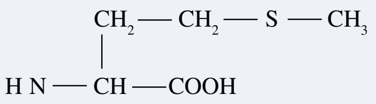
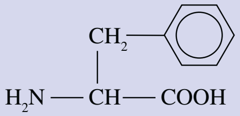
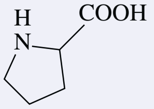
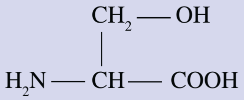
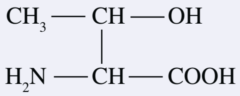
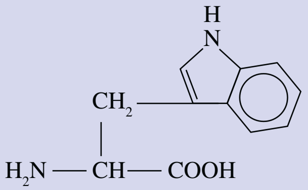
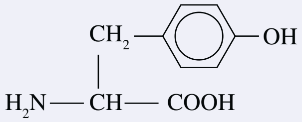
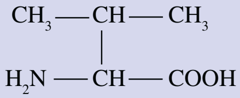
Name	Symbol	Structure
Alanine	Ala	 $H_2N-\overset{CH_3}{\overset{\vert}{CH}}-COOH$
Arginine	Arg	 $H_2N-\overset{CH_2-CH_2-CH_2-NH-\overset{NH}{\overset{\Vert}{C}}-NH_2}{\overset{\vert}{CH}}-COOH$
Asparagine	Asn	 $H_2N-\overset{CH_2-\overset{O}{\overset{\Vert}{C}}-NH_2}{\overset{\vert}{CH}}-COOH$
Aspartic acid	Asp	 $H_2N-\overset{CH_2-COOH}{\overset{\vert}{CH}}-COOH$
Cysteine	Cys	 $H_2N-\overset{CH_2-SH}{\overset{\vert}{CH}}-COOH$
Glutamine	Gln	 $H_2N-\overset{CH_2-CH_2-\overset{O}{\overset{\Vert}{C}}-NH_2}{\overset{\vert}{CH}}-COOH$
Glutamic acid	Glu	 $H\ N-\overset{CH_2-CH_2-COOH}{\overset{\vert}{CH}}-COOH$
Glycine	Gly	H_2N-CH_2-COOH
Histidine	His	
Isoleucine	Ile	 $\begin{array}{c}CH_3-CH-CH_2-CH_3\\ \vert\\ H_2N-CH-COOH\end{array}$
Leucine	Leu	 $H_2N-\overset{CH_3-CH-CH_3}{\overset{\vert}{\overset{CH_2}{\overset{\vert}{CH}}}}-COOH$
Lysine	Lys	 $H_2N-\overset{CH_2-CH_2-CH_2-CH_2-NH_2}{\overset{\vert}{CH}}-COOH$

TABLE 15.1.1 continued

Name	Symbol	Structure
Methionine	Met	 $\begin{array}{lll} & \mathrm{CH_2} & \mathrm{-CH_2-S-CH_3} \\ & \vert & \\ \mathrm{H\ N-} & \mathrm{CH} & \mathrm{-COOH} \end{array}$
Phenylalanine	Phe	
Proline	Pro	
Serine	Ser	 $\begin{array}{lll} & \mathrm{CH_2} & \mathrm{-OH} \\ & \vert & \\ \mathrm{H_2N-} & \mathrm{CH} & \mathrm{-COOH} \end{array}$
Threonine	Thr	 $\begin{array}{lll} \mathrm{CH_3-} & \mathrm{CH} & \mathrm{-OH} \\ & \vert & \\ \mathrm{H_2N-} & \mathrm{CH} & \mathrm{-COOH} \end{array}$
Tryptophan	Trp	
Tyrosine	Tyr	
Valine	Val	 $\begin{array}{lll} \mathrm{CH_3-} & \mathrm{CH} & \mathrm{-CH_3} \\ & \vert & \\ \mathrm{H_2N-} & \mathrm{CH} & \mathrm{-COOH} \end{array}$

A balanced diet

Proteins from animal sources contain all the essential amino acids. As Table 15.1.2 shows, vegetable proteins are often deficient in one or more essential amino acids. For example, corn is too low in lysine and tryptophan to support normal growth in young children.

TABLE 15.1.2 Foods deficient in one or more of the nine essential amino acids

Food	Amino acid deficiency
Legumes	Methionine
Soybeans	Methionine
Corn	Lysine, tryptophan
Nuts	Methionine
Wheat	Lysine

For this reason, vegetarians must ensure that their diets contain **complementary proteins**. This means that instead of eating plant protein from a single source, vegetarians should eat a variety of plant foods. Deficiencies of amino acids in one plant can then be supplemented by the amino acids present in another. For example, rice and lentils contain complementary proteins. In Asia, rice and lentils have been part of the staple diet for thousands of years. In developed countries, people usually get all the amino acids they require by eating complementary proteins.

THE ACID–BASE PROPERTIES OF AMINO ACIDS

Amino acids as zwitterions

Amino acids contain polar amino and carboxyl functional groups. Therefore, amino acids can form hydrogen bonds with water molecules and are soluble in water. In solution, the:

- $–NH_2$ group can act as a base, accepting a proton to become a $–NH_3^+$ group
- –COOH group can act as an acid, donating a proton to become a $–COO^-$ group.

As a result, an amino acid molecule in an aqueous solution may be in the form $^+H_3N–CH(R)–COO^-$. Such a molecule is shown in Figure 15.1.6 and is called a **zwitterion** or **dipolar ion**.

The relatively high melting point of pure crystalline amino acids is due to the zwitterion being present in the solid state.

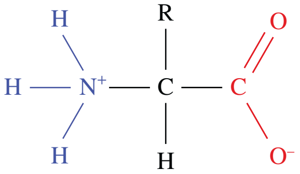


FIGURE 15.1.6 Structure of a zwitterion of an amino acid molecule. A zwitterion is a molecule that contains positive and negative charges but has no charge overall.

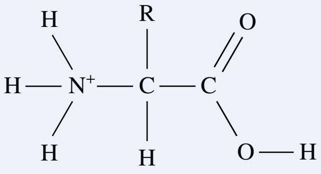
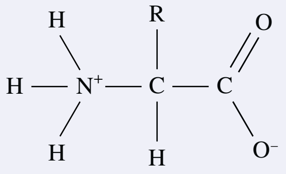
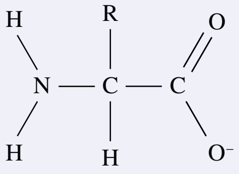
Acid–base properties

The dual acidic and basic nature of amino acids means that different chemical forms of an amino acid can be in equilibrium in a solution. The predominant form depends on the pH of the solution and the particular amino acid concerned.

- At intermediate pH (typically pH 5–7), the zwitterion $^+H_3N–CH(R)–COO^-$ is most abundant.
- At low pH, the cation $^+H_3N–CH(R)–COOH$ is most abundant. The H_3O^+ ions in solution can react with the amino acid according to the equation:
  $$^+H_3N–CH(R)–COO^-(aq) + H_3O^+(aq) \rightleftharpoons {}^+H_3N–CH(R)–COOH(aq) + H_2O(l)$$
  If the concentration of $H_3O^+(aq)$ is very high (as it is in a solution of low pH), the position of this equilibrium lies well to the right.
- At high pH, the anion $H_2N–CH(R)–COO^-$ is most abundant. The OH^- ions in solution can react with the amino acid according to the equation:
  $$^+H_3N–CH(R)–COO^-(aq) + OH^-(aq) \rightleftharpoons H_2N–CH(R)–COO^-(aq) + H_2O(l)$$
  If the concentration of $OH^-(aq)$ is very high (as it is in a solution of high pH), the position of this equilibrium lies well to the right.

As you can see in Table 15.1.3, the charge on the predominant form of the amino acid depends on the pH of the solution.

TABLE 15.1.3 Formation of cations, anions and zwitterions when amino acids are in solutions of various pH

Low pH	Intermediate pH	High pH
 Cation	 Zwitterion (no overall charge)	 Anion

Effect of the R group on the acid–base properties of amino acids

If the R group contains a functional group with acid–base properties, it is possible for other charged forms of the amino acid to form. For example, at a pH of 12, the predominant form of aspartic acid is an ion with a charge of 2– (see Figure 15.1.7). On the other hand, at a pH of 2, lysine exists predominantly as an ion with a charge of 2+ (see Figure 15.1.8).

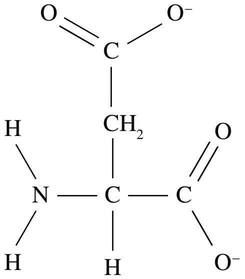


FIGURE 15.1.7 The structure of aspartic acid at pH 12 showing that it has a charge of 2–.

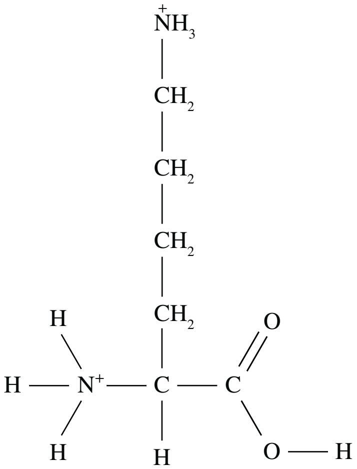


FIGURE 15.1.8 The structure of lysine at pH 2 showing that it has a charge of 2+.

15.1 Review

SUMMARY

- 2-Amino acids have the structure shown in Figure 15.1.9.

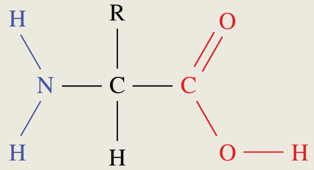


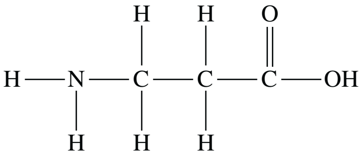
FIGURE 15.1.9 General structure of an amino acid.

- Amino acids contain a carboxyl group (highlighted in red in Figure 15.1.9), an amino group (highlighted in blue in Figure 15.1.9), a hydrogen atom and a side chain called the R group, all bonded to the same carbon atom.
- There are 20 different amino acids found in human proteins.
- Essential amino acids must be provided directly through the proteins in the diet, as human cells cannot produce them.
- Non-essential amino acids can be manufactured in the body from other dietary components.
- Three-letter abbreviations are commonly used to represent an amino acid.
- The R group, also known as the side chain, may be a non-polar group of atoms or a group of atoms that includes a polar functional group. The R group may also exhibit acid–base properties.
- Zwitterions are present in crystalline salts of amino acids and also in amino acid solutions of intermediate pH.
- An amino acid is present in cationic form in solutions of low pH and in anionic form in solutions of high pH.

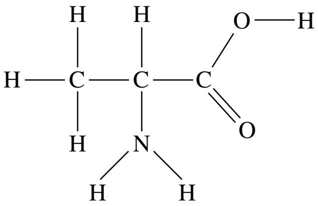
KEY QUESTIONS

1 Which one of these molecules is not a 2-amino acid?

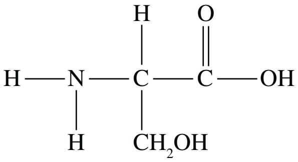
A



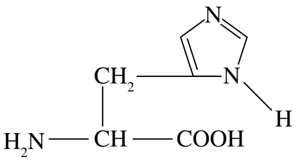
B



C



D



2 Use Table 15.1.1 (on page 465) to find the names of the amino acids with the following three-letter abbreviations.

a Asn
b Tyr
c Asp
d Met

3 Why must vegetarians ensure that their diet contains complementary proteins?

4 Why should essential amino acids be included in a healthy diet?

5 Use your understanding of bond polarity and the acid–base properties of functional groups to complete the following table that categorises properties of an amino acid's R group.

Structure of R group	Is the R group polar or non-polar?	Is the R group acidic, basic or neutral?
$-CH(CH_3)_2$		
$-CH_2COOH$		
$-CH_2C_6H_5$		
$-(CH_2)_4NH_2$		

15.2 The formation of proteins

In this section, you will learn about the chemical reactions of amino acids that produce larger molecules called polypeptides and proteins. These reactions are examples of **condensation polymerisation** reactions.

The monomers that make a polymer by a condensation polymerisation reaction have a pair of functional groups that can react together. When they react, a new functional group is produced that links the monomers. At the same time, a small molecule, such as water, is also produced.

Many biologically important molecules are produced by this type of reaction. These molecules include proteins, DNA, cellulose and starch. Insulin (see Figure 15.2.1) is a small protein that is made from 51 amino acids. It allows your body to use **glucose** from carbohydrates in your food, either for energy or for storing glucose for future use.

FIGURE 15.2.1 This young girl is injecting herself with insulin to control diabetes. Diabetes is a group of diseases associated with abnormally high levels of sugar in the blood.

DIPEPTIDES

As you learned in Chapter 10, a **condensation reaction** can occur between a molecule that contains a carboxyl group (–COOH) and a molecule that contains an amino group (–NH_2). An **amide** functional group (–CONH–) is formed that links the two molecules. A molecule of water is also produced as shown in Figure 15.2.2.

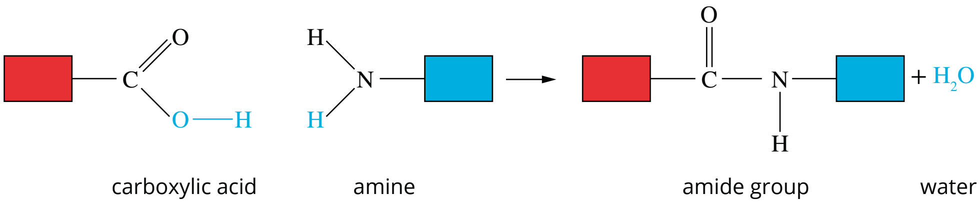


FIGURE 15.2.2 An amide group forms when a carboxyl group reacts with an amino group. A water molecule is also produced. The red and blue boxes represent the remaining atoms in the amino acids involved in this reaction.

Because 2-amino acids contain both an amino functional group and a carboxyl functional group, they can undergo condensation reactions with each other. When two amino acids react, an amide group, called a **peptide link** (also called a peptide group or peptide bond) is formed that links the molecules together.

Molecules made from amino acids are often called peptides. When two amino acid molecules react together as shown in Figure 15.2.3, the product is referred to as a **dipeptide**.

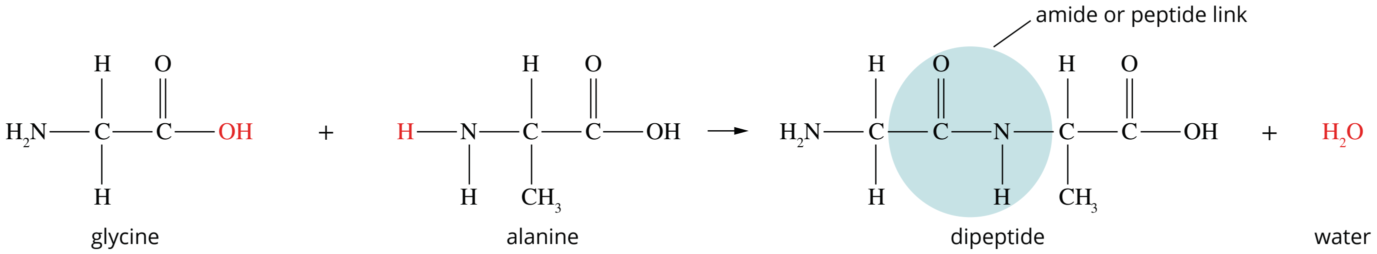


FIGURE 15.2.3 A condensation reaction between two amino acids, glycine and alanine. Note how the carboxyl and amino groups react to form the dipeptide and water.

Each time a pair of different amino acids react in this way, there are two possible product molecules, depending on which ends of each molecule react together.

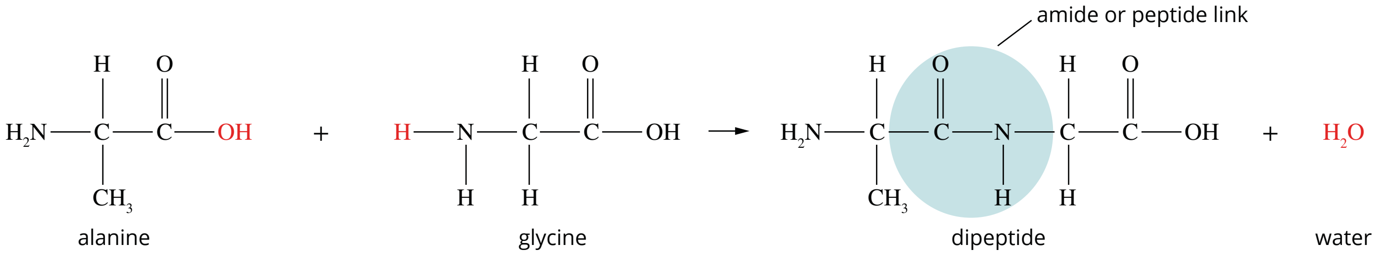


FIGURE 15.2.4 Another dipeptide molecule formed from the reaction between glycine and alanine.

POLYPEPTIDES

Polypeptides are polymers formed by condensation polymerisation of amino acids. During these reactions, the amino acids can form long chains. When three amino acid molecules react together, a **tripeptide** is formed. A polymer made from many amino acids is known as a **polypeptide**.

Naming polypeptides

A shorthand notation is often used to describe the amino acid sequence in a polypeptide, using the three-letter abbreviations listed in the table of 2-amino acid structures (Table 15.1.1 on page 464). By convention, the structure is drawn so the free amino group is on the left and the free carboxyl group is on the right. A reaction between six amino acids to form part of a polypeptide is shown in Figure 15.2.5. The polypeptide would be named as Ala–Glu–Gly–Cys–Val–Lys.

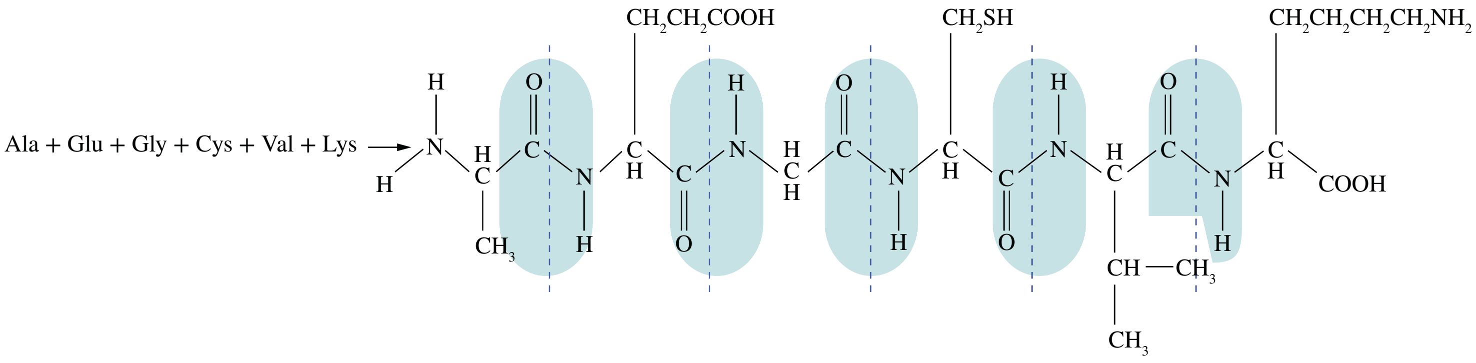


FIGURE 15.2.5 A condensation reaction between many amino acids produces a polypeptide. Peptide links are shaded in blue.

A polypeptide constructed from more than 50 amino acids is usually called a protein.

The hormone insulin is a protein that regulates the metabolism of sugars and fats in the human body. Insulin is one of the smallest proteins in the human body. It is made up of two linked chains, with a total of 51 **amino acid residues**. The sequence of amino acids in the two chains is shown in Figure 15.2.6. You can also see that the chains are linked by covalent bonds between sulfur atoms from the R group of cysteine residues. At the start of the longer chain is a free amino group on the phenylalanine (Phe). This is known as the **N-terminal** amino acid of that chain. At the end of the longer chain is threonine (Thr), which has a free carboxyl group and is therefore called the **C-terminal** amino acid.

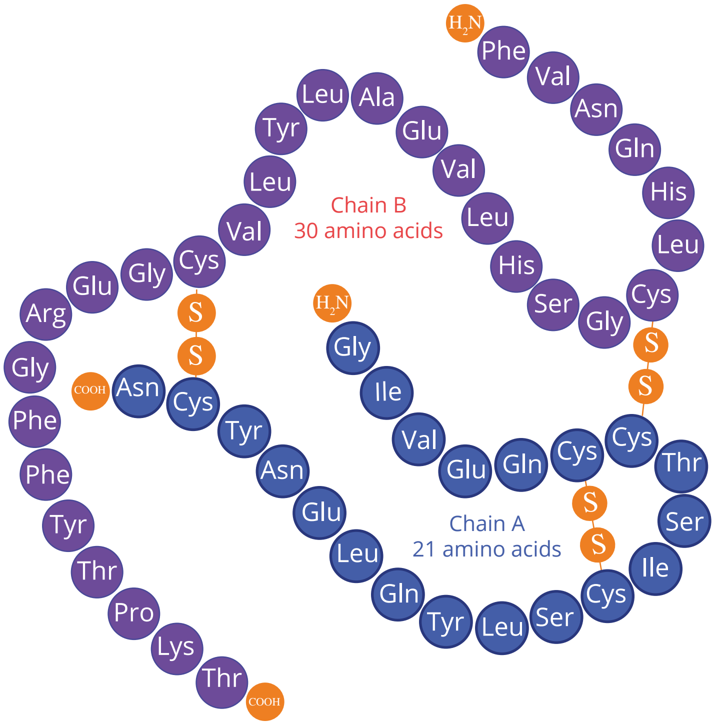


FIGURE 15.2.6 The amino acid sequence in the human insulin molecule. The polymer contains 51 amino acid units.

When amino acids react with each other, peptide bonds form. Small molecules, such as water, are also released in this process, making this a condensation polymerisation reaction.

You have seen that when polypeptides are formed, water is produced as a by-product. When proteins are broken down in the body (through digestion), water molecules are required to break the peptide bonds. This type of reaction is known as **hydrolysis** and, in this case, hydrolysis can be regarded as the reverse reaction to the condensation reactions that formed the protein.

CHEMFILE

Fred Sanger, a pioneer of protein sequencing

Fred Sanger (Figure 15.2.7) was awarded two Nobel Prizes in Chemistry. The first was for his work on **protein sequencing**. Sanger determined the order of different amino acids in the two chains of the insulin protein. Sanger's second Nobel Prize was for his work on DNA sequencing.

FIGURE 15.2.7 Fred Sanger (1918–2013).

Born in England in 1918, Sanger grew up very interested in nature and science. Sanger decided not to follow in his father's footsteps and study medicine because he felt that a career in science would give him a better chance to become a problem solver.

Sanger completed his science degree at the University of Cambridge in England in 1939. He then studied amino acid metabolism for his PhD before starting work on identifying the amino acid sequence of (bovine) insulin extracted from cattle (Figure 15.2.8). Sanger was the first person to determine a protein sequence and was awarded his first Nobel Prize in 1958, in recognition of his important discovery.

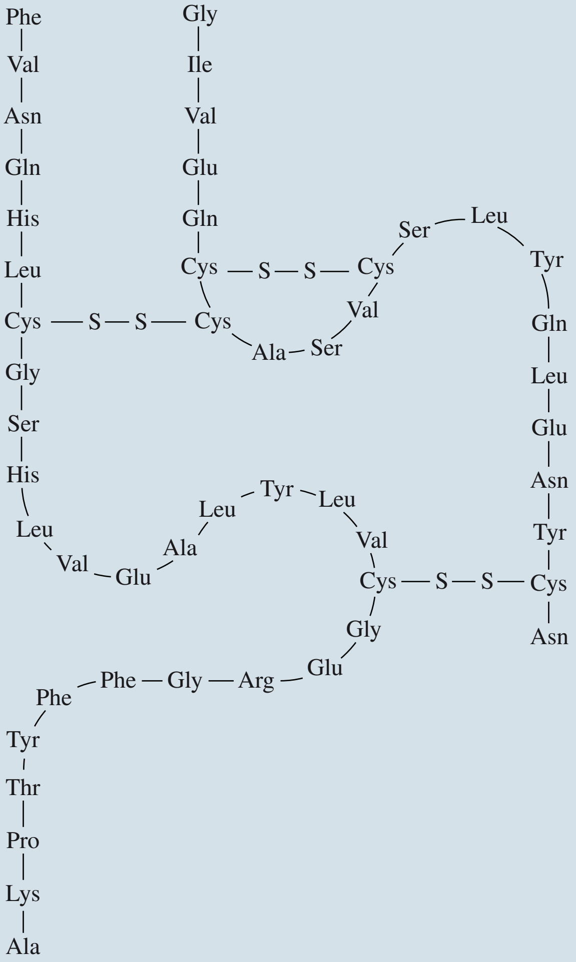


FIGURE 15.2.8 The amino acid sequence of bovine insulin. Its sequence of amino acids differs from human insulin by just three amino acids.

By this stage, Sanger had moved on to study DNA-related problems, in collaboration with other eminent scientists, including Francis Crick and John Kendrew. Solving the problem of DNA sequencing became a natural extension of his work in protein sequencing. In 1980, Sanger shared the Nobel Prize with Paul Berg and Walter Gilbert for his contribution to the determination of the nucleotide sequence in DNA.

15.2 Review

SUMMARY

- The carboxyl group and amino group of two 2-amino acids can take part in a condensation reaction that links them through a peptide group.
- Water is also produced as a by-product, making this reaction an example of a condensation polymerisation reaction (see Figure 15.2.9).
- In a similar manner, several amino acids combine to produce a polypeptide.
- Proteins are large polypeptide chains containing approximately 50 or more amino acids.

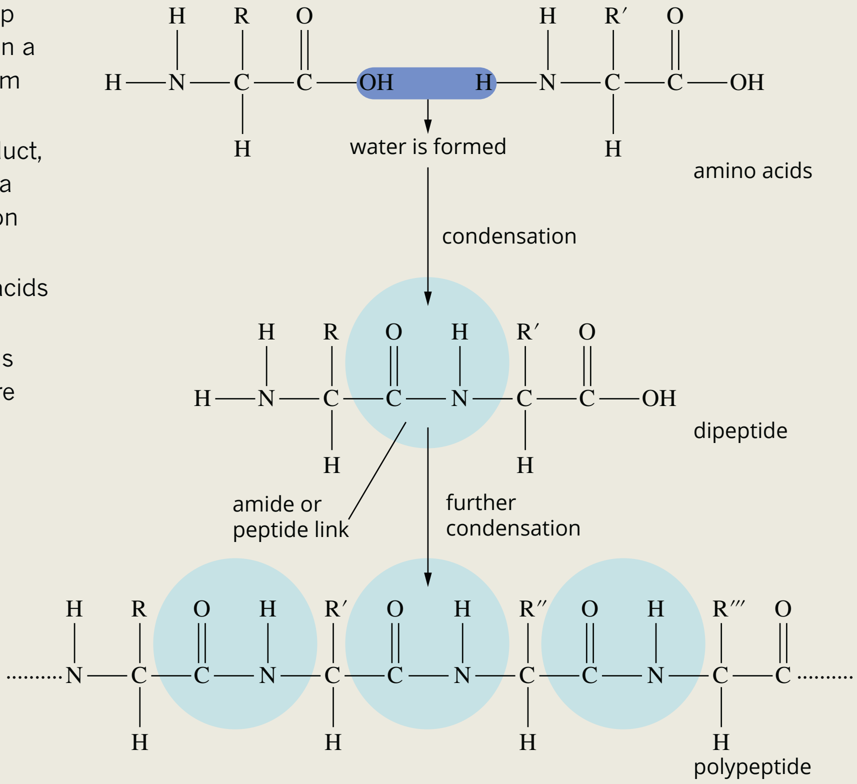


FIGURE 15.2.9 Condensation polymerisation of amino acids.

KEY QUESTIONS

1 Match the terms on the left with their descriptions on the right.

Tripeptide	By-product of the reaction that produces polypeptides
R group	Three amino acids joined by peptide links in a polypeptide chain
Polypeptide	Variable part of an amino acid
Amino group	Several amino acids that are joined by peptide links
Water	Functional group present in all amino acids

2 Figure 15.2.10 shows a tripeptide molecule.

a Identify the parts labelled A–D.

b Give the names of the three amino acids in the tripeptide molecule.

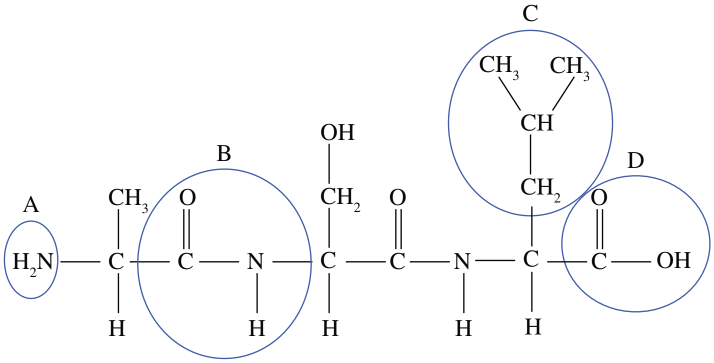


FIGURE 15.2.10 A tripeptide molecule.

3 Figure 15.2.11 shows a polypeptide. Which one of the following statements about this polypeptide is correct?

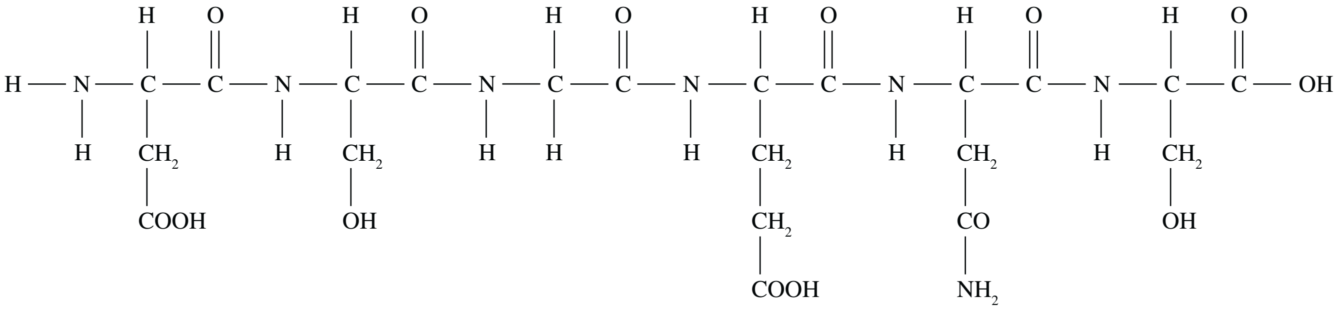


FIGURE 15.2.11 A polypeptide.

A This polypeptide contains only two carboxyl groups.

B Six water molecules were produced in this reaction.

C Six different amino acids were used to make this polypeptide.

D This polypeptide was produced by an additional polymerisation reaction.

4 **a** Draw structural formulas of serine and cysteine.

b Write an equation to show the formation of a dipeptide from these amino acids.

c Write the formula of another dipeptide that could be formed from these two amino acids.

d Name the type of reaction in part **b**.

15.3 Primary and secondary structures of proteins

Proteins differ from one another in the number, type and sequence of their constituent amino acids. Each protein has a precise chemical composition and amino acid sequence, which leads to it having a unique three-dimensional shape. There may be more than 500 amino acid units in a large protein. Determining the structure of these complex materials has proved challenging for chemists. Myoglobin (see Figure 15.3.1) was one of the first proteins to have its amino acid structure determined. It is made up of 153 amino acids.

The role of any protein in an organism depends on the protein's shape. The structure of a protein is usually considered at several levels of organisation within the molecule. All proteins are regarded as being made up of a primary, secondary and tertiary structure, while some of them also display a quaternary level of organisation.

In this section, you will investigate the primary and secondary structures of proteins.

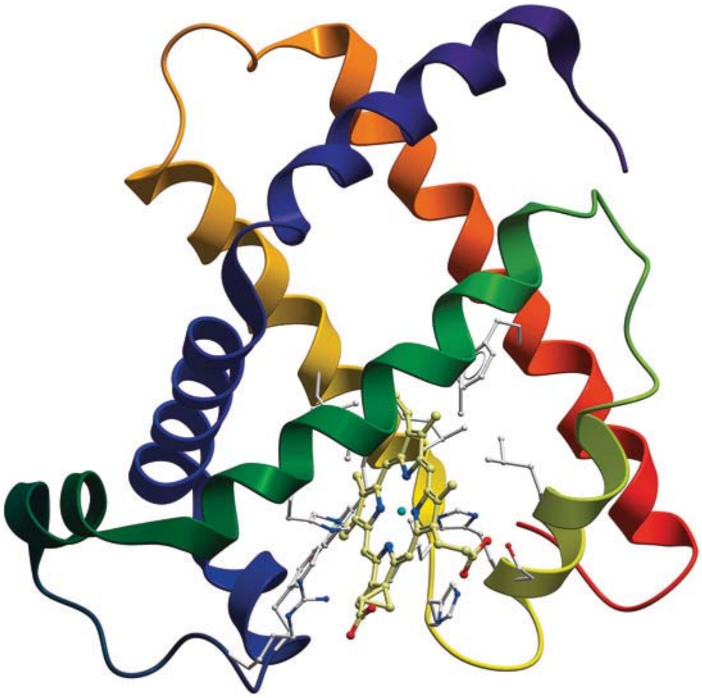


FIGURE 15.3.1 A representation of myoglobin. Myoglobin is a protein consisting of 153 amino acids in one polypeptide chain. This protein is found in muscle tissue where it binds to oxygen.

PRIMARY STRUCTURE OF PROTEINS

The number, type and sequence of the amino acid units in a protein is known as the protein's **primary structure**. As you can see in Figure 15.3.2, the primary structure may be represented by the three-letter abbreviations for the amino acids or by a structural formula of the protein. By convention, the sequence is written from left to right, starting from the N-terminal amino acid and ending with the C-terminal amino acid.

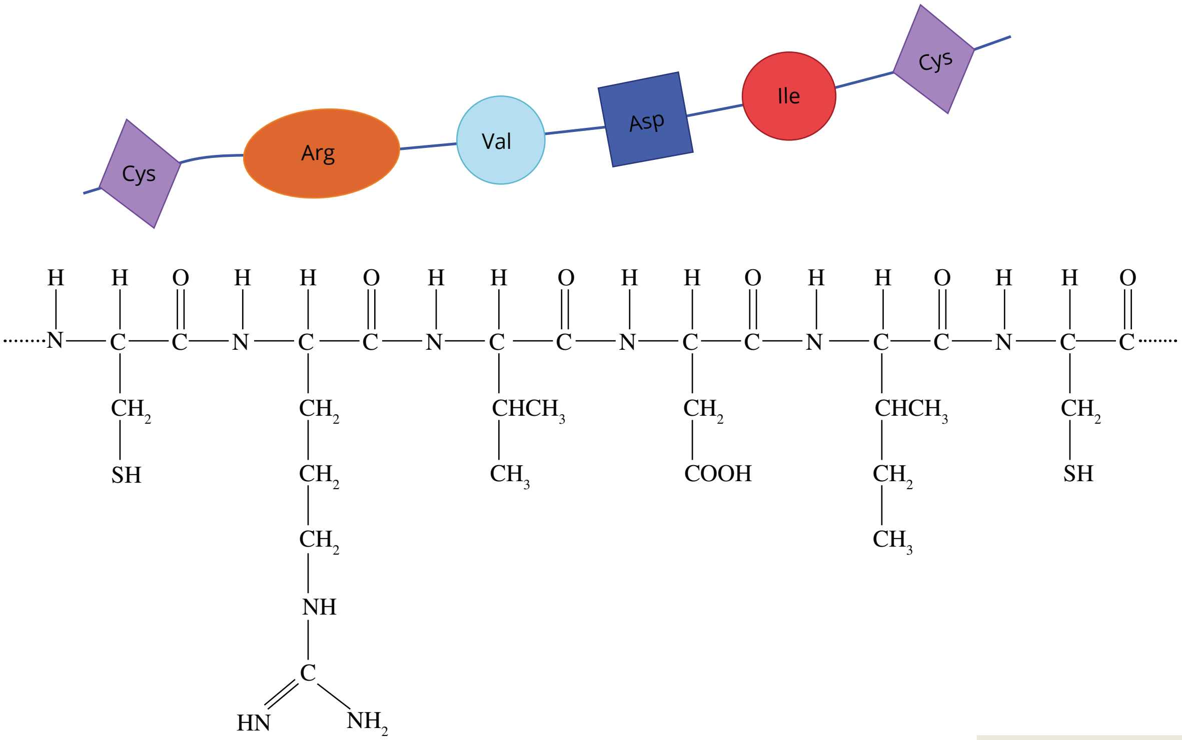


FIGURE 15.3.2 A small section of a protein molecule showing the primary structure represented by three-letter abbreviations and its structural formula.

The entire shape of a protein is determined by the precise order in which its amino acids are joined together. One of the smallest proteins in the human body, insulin, has a specific sequence of 51 amino acids. Many proteins contain hundreds of amino acids in a specific sequence.

The function of a protein is a consequence of its shape. Therefore, the order of amino acids is extremely important in determining the function of a protein.

CHEMISTRY IN ACTION

Protein sequencing

The primary structure of a protein is found experimentally by the process of protein sequencing (Figure 15.3.3).

The identity of the amino acids in a polypeptide can be determined by heating it in 6 M HCl. The polypeptide undergoes hydrolysis, forming the individual amino acid monomers. The amino acid mixture is separated by column chromatography, and then each amino acid is identified by its retention time. However, this technique does not give any indication of the sequence of amino acid units in a polypeptide.

One method of determining the sequence of a polypeptide begins with using different enzymes to hydrolyse specific peptide links within the molecule. For example, trypsin is an enzyme that hydrolyses the peptide link at the carboxyl side of arginine and lysine. This process is repeated with different enzymes to produce shorter peptides of varying lengths. These peptides can then be sequenced through a process called Edman degradation or by mass spectrometry. Careful analysis of how the sequences of the peptides overlap allows the overall sequence of the polypeptide to be determined.

FIGURE 15.3.3 This scientist is preparing to use an automated microsequencer machine to analyse the amino acid sequence of samples of protein.

SECONDARY STRUCTURE OF PROTEINS

Coiling and **pleating** of sections of a protein molecule produce a secondary level of structure in a protein. Hydrogen bonds between the polar –NH group in one peptide link and the polar –C=O group in another peptide link can form at regular intervals (see Figure 15.3.4).

This creates regions in which the molecule coils into a spiral shape called an **α-helix**, or where sections line up parallel to each other, forming a **β-pleated sheet**.

Such highly ordered segments, stabilised by hydrogen bonds, are referred to as the **secondary structure** of the protein.

α-helices

Keratin is a protein found in the fibres of hair and wool. The helical structure of keratin results from extensive hydrogen bonding between peptide links in the polypeptide chain. In this case, the hydrogen bonds result from the attraction between the partial positive charge on the H of a –NH group in a peptide link with the partial negative charge on the O of a –C=O group of a peptide link four amino acid units along the chain.

The hydrogen bonds make the molecule coil into the shape of an α-helix, the same shape as a spring (see Figure 15.3.5).

β-pleated sheets

Hydrogen bonds can also form between peptide links to produce regions where two or more parts of the polypeptide chains line up parallel to each other. The repeating structure of the backbone of the protein chain (–N–C–C–N–C–C–N–C–C–) allows these hydrogen bonds to form at regular intervals. This stabilises the protein structure. This type of secondary structure in the protein is called a β-pleated sheet (Figure 15.3.6).

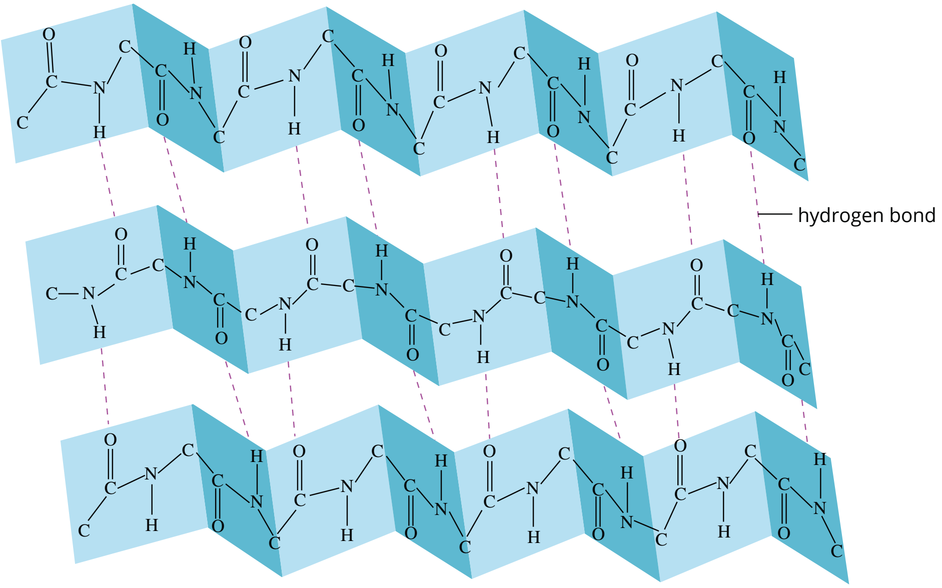


FIGURE 15.3.6 β-pleated sheet. Hydrogen bonds between the sheet are shown as dashed lines. The R groups (side chains) and hydrogen atoms on the α-carbons have been omitted for clarity.

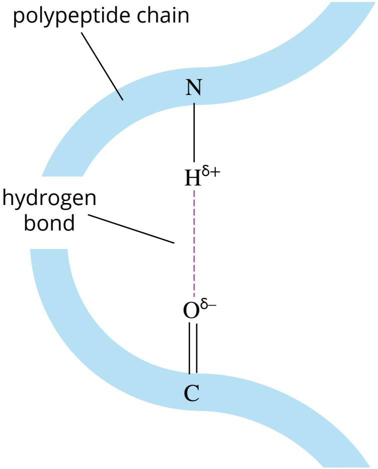


FIGURE 15.3.4 Hydrogen bonds can form between the polar –NH group in one peptide link and the polar –C=O group in another peptide link further along the polypeptide chain.

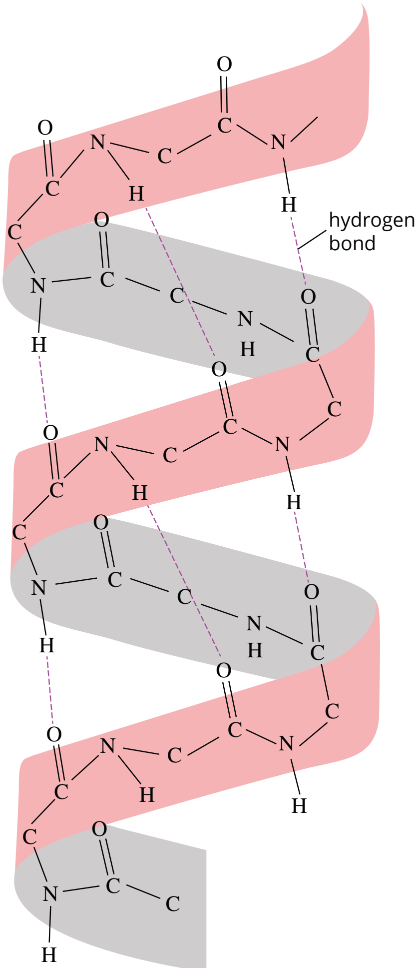


FIGURE 15.3.5 A polypeptide chain coils in an α-helix due to hydrogen bonds. The R groups (side chains) and hydrogen atoms on the α-carbons have been omitted for clarity.

Silk is a protein with a β-pleated sheet structure. The polypeptide chains mainly contain the amino acids glycine, alanine and serine as shown in Figure 15.3.7. Notice that every second R group is H.

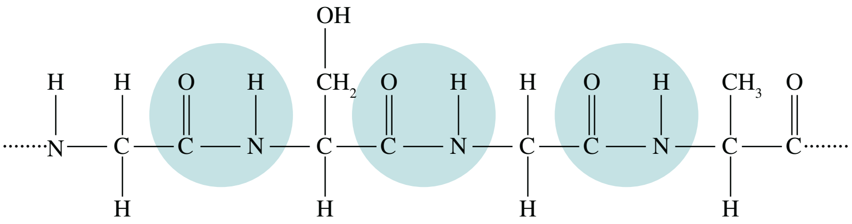


FIGURE 15.3.7 The amino acid sequence that is found in large parts of the polypeptide of silk. Peptide bonds are shaded blue.

With only these small side groups, sections of the protein molecule in silk can line up closely, enabling hydrogen bonds to form between these adjacent sections and producing β-pleated sheets.

The secondary structure of a protein results from hydrogen bonding within different regions of the amino acid sequence. This leads to the formation of α-helices or β-pleated sheets.

EXTENSION

Modelling protein structure

In computer models of protein structure, a segment twisted into an α-helix is often represented as a twisted ribbon and sections of β-pleated sheets are represented by a set of wide parallel ribbons with arrows.

A computer model of a protein is shown in Figure 15.3.8.

There are wide variations in the relative amounts of α-helix and β-sheet structures in individual proteins, with many proteins containing several regions of both.

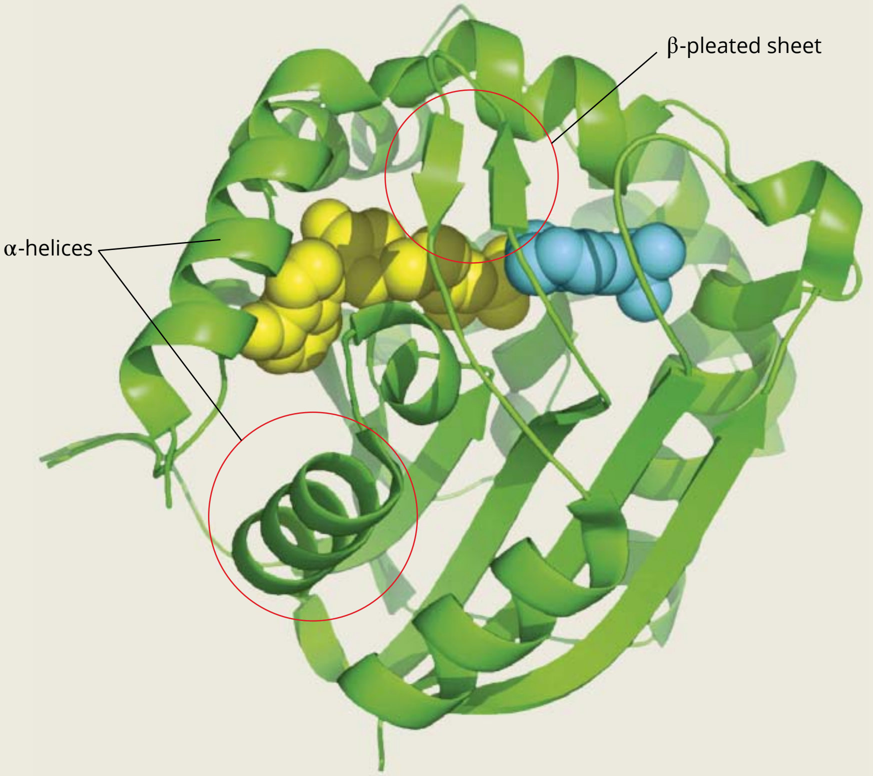


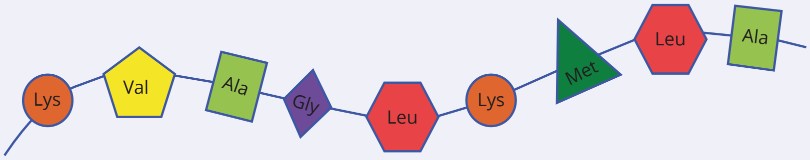
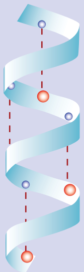
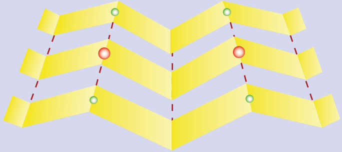
FIGURE 15.3.8 Computer model of a protein (green and yellow) in which several regions of α-helices and β-pleated sheets are seen. The blue part shows drug-like molecules interacting with the protein.

15.3 Review

SUMMARY

- There are 20 different 2-amino acids from which tens of thousands of different protein molecules are synthesised by cells. Each protein has a unique structure and function in the organism.
- The complex structure of these large molecules is often considered in distinct levels. The primary and secondary levels are summarised in Table 15.3.1.

TABLE 15.3.1 Primary and secondary structures of proteins

Structural level	Description	Bonds involved
Primary	The sequence of amino acids in the polypeptide chain  	Only covalent bonds are responsible for joining the monomer units together in the polymer. Monomers are linked by –CONH– groups, known as peptide links in proteins.
Secondary	The shape of the polypeptide as it is either twisted into an α-helix or bent back on itself to produce regions of β-pleated sheets  α–helix  β–pleated sheet	Hydrogen bonding between –NH and –C=O bonds in peptide links introduces a secondary structure to protein molecules, producing regions of α-helices or β-pleated sheets.

KEY QUESTIONS

1 Figure 15.3.9 shows a section of a protein.

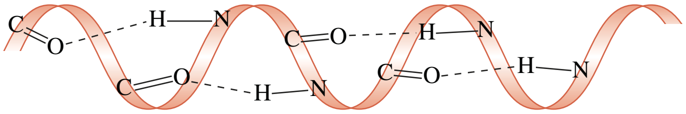


FIGURE 15.3.9 A section of a protein.

a What secondary structure is represented by the diagram?

b How does this type of secondary structure form? Refer to particular atoms and functional groups associated with the bonding that forms this structure.

2 Why is it important to be able to determine the specific sequence of amino acids in a protein?

3 Figure 15.3.10 represents a section of a polypeptide molecule. Complete the paragraph by filling in the blanks. You may need to refer to the Table 15.1.1 on pages 464–5 to answer this question.

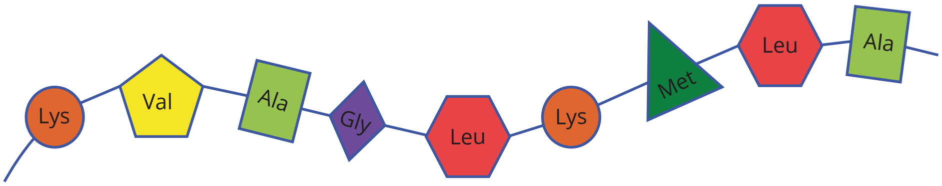


FIGURE 15.3.10 A section of a polypeptide molecule.

The image shows a section of the primary structure of part of a polypeptide. It consists of __________ amino acid units that are linked together by ______________ groups. It was produced by a __________________ ______________ reaction. In this polypeptide there are two units of leucine, two units of ______________, two units of __________________ and one unit each of ___________________, __________________, __________________.

4 How do α-helices and β-pleated sheets differ?

15.4 Tertiary and quaternary structures of proteins

In the previous section, you learned that the sequence and order of amino acid units in a protein chain is called the primary structure of the protein. As a consequence of hydrogen bonding between –C=O and –N–H groups along the chain, the protein chain can be twisted and folded into arrangements such as α-helices and β-pleated sheets, which are described as the secondary structure of the protein.

In this section, you will examine the overall three-dimensional shapes of proteins and the types of bonds that cause proteins to adopt their different shapes. These bonds are due to forces between the different functional groups in the R group or side chain of amino acid units.

OVERALL SHAPE OF A PROTEIN

The overall three-dimensional shape adopted by a protein molecule is called its **tertiary structure**. A tertiary structure is produced by the three-dimensional folding of its secondary structures (α-helices and β-pleated sheets). The protein can twist back over itself to create a unique shape, which is responsible for the protein's function (see Figure 15.4.1).

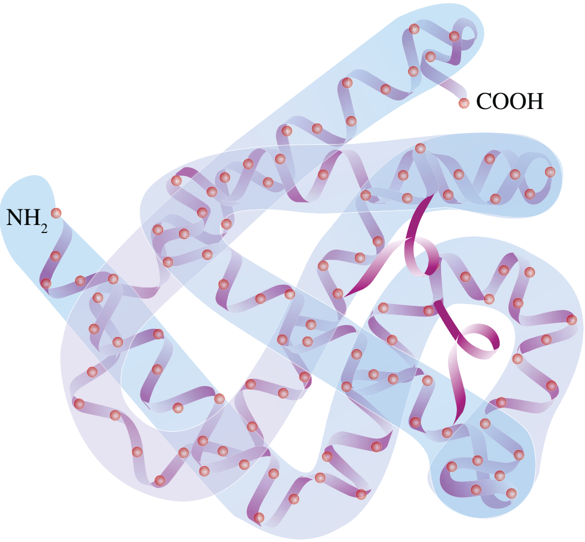


FIGURE 15.4.1 A model representing the tertiary structure of the protein myoglobin.

The side chains (R groups) of the amino acid units making up the polypeptide chain influence the overall three-dimensional shape of the molecule. Not only are some side chains relatively large (such as in phenylalanine), but others also contain polar functional groups, or can become charged depending on the pH of their surroundings. In addition, some amino acids have **hydrophobic** (non-polar) chains, which tend to fold towards the interior of protein molecules, away from contact with water molecules.

ℹ R groups of amino acids influence the properties of the amino acid. There are four main groups of amino acids, which can be classified as polar, non-polar, acidic or basic. These were discussed in section 15.1 (page 462).

Bonding in the tertiary structure of proteins

Five types of attractions that are important in chain folding are summarised in Table 15.4.1, which also identifies the features of the side chains that are involved.

TABLE 15.4.1 Types of bonds formed from interactions of specific R groups in different regions of the protein

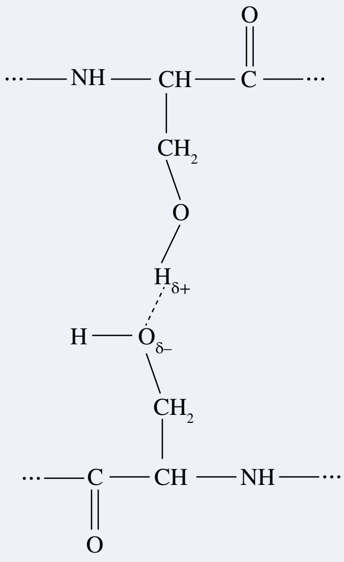
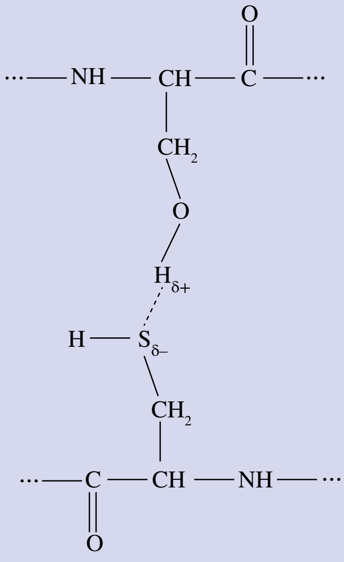
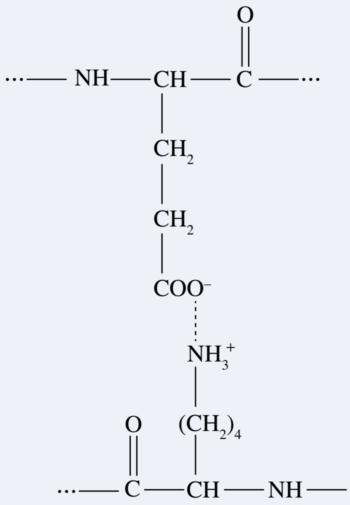
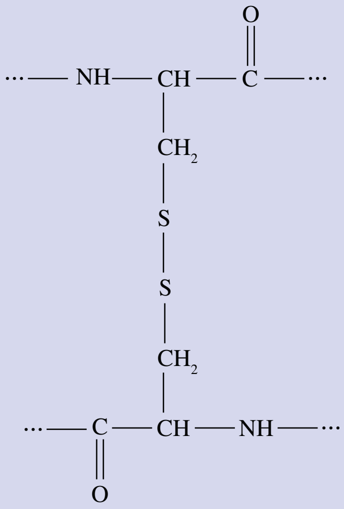
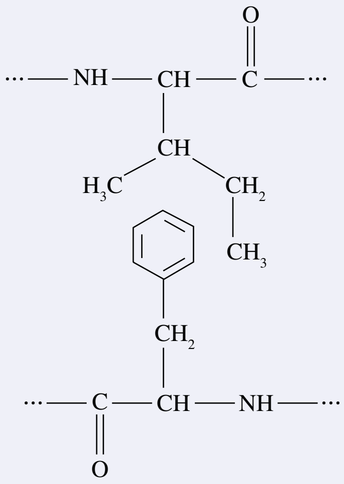
Bond type	Required components in R group	Visual representation
Hydrogen bonds	Contains –O–H, –N–H or –C=O	 A hydrogen bond linking two parts of a polypeptide chain.
Dipole–dipole interactions	Any polar group such as those containing –S–H, –O–H or –N–H	 A dipole–dipole interaction linking two parts of a polypeptide chain.

TABLE 15.4.1 continued

Bond type	Required components in R group	Visual representation
Ionic interactions	Contains $-NH_3^+$ and another group that contains $-COO^-$	 An ionic interaction linking two parts of a polypeptide chain.
Covalent cross-links	Cysteine side groups react to form a **disulfide bridge** (–S–S–).	 A disulfide bridge linking two parts of a polypeptide chain.
Dispersion forces	Any non-polar group	 Dispersion forces can link two parts of a polypeptide chain.

As a consequence of the different types of bonds that can fold a polypeptide into a three-dimensional shape, an enormous variety of protein shapes exist. Some proteins resemble flat sheets, others are long and helical, and others are compact and globular.

QUATERNARY STRUCTURE

Some proteins are composed of two or more polypeptide chains, and may even interact with non-protein molecules to produce a larger, more complex functional unit, known as the **quaternary structure**. Haemoglobin is an example of a protein with a quaternary structure.

Haemoglobin—the oxygen-transporting protein

Red blood cells are manufactured by the bone marrow at a rate of about 2 million per second. Red blood cells are functional for about 3 months in the human body. Each red blood cell contains approximately 250 million molecules of haemoglobin.

Figure 15.4.2 is a diagrammatic representation of haemoglobin. The four distinct subunits that make up its quaternary structure are highlighted in colour. Each subunit contains a polypeptide chain (collectively called globin) that is coiled into α-helices and then folded into a tertiary structure. Within each subunit, there is also an oxygen binding site, or haem group (light blue). Each haem group contains one atom of iron (green). Haemoglobin transports oxygen around the body by binding one oxygen molecule to each haem group.

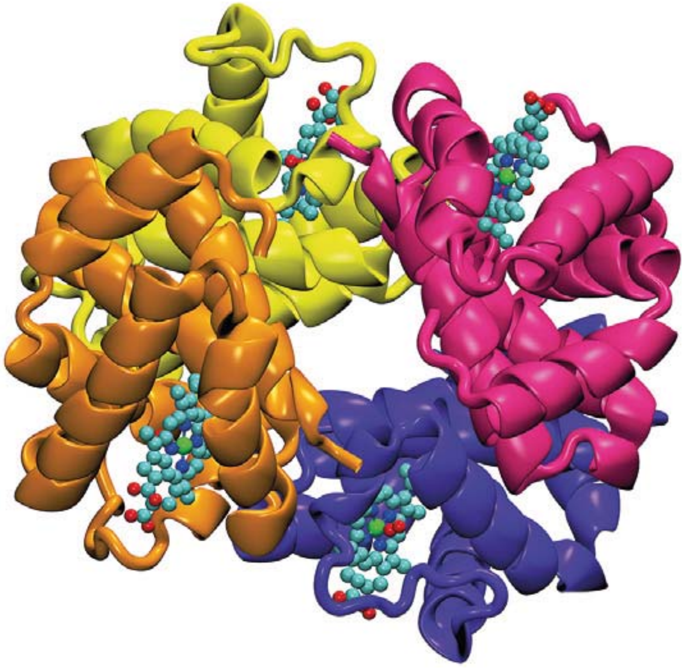


FIGURE 15.4.2 A representation of the structure of haemoglobin. Within each subunit is a haem group (light blue). Each group contains one atom of iron (green). In this model, the haem groups are oxygenated and the oxygen molecules are shown as paired red spheres.

The iron of the haem group can bond to one oxygen molecule, so each haemoglobin molecule is able to carry four oxygen molecules. In this form, the molecule causes the characteristic bright red colour of oxygenated blood and it is called oxyhaemoglobin.

Proteins that function in water, such as haemoglobin, tend to fold so that their hydrophobic non-polar R groups are least exposed to water molecules. The polar R groups are hydrophilic and are therefore located near the outer surface.

Two or more separate polypeptide chains can assemble together so that hydrophobic sections in the chains are in contact with each other, which minimises the contact of these sections of the chains with water. Haemoglobin has four chains that join together in this way. Dispersion forces are the major force of attraction holding the separate polypeptide chains together. However, hydrogen bonding, dipole–dipole attractions and ionic interactions may also be present between the chains.

15.4 Review

SUMMARY

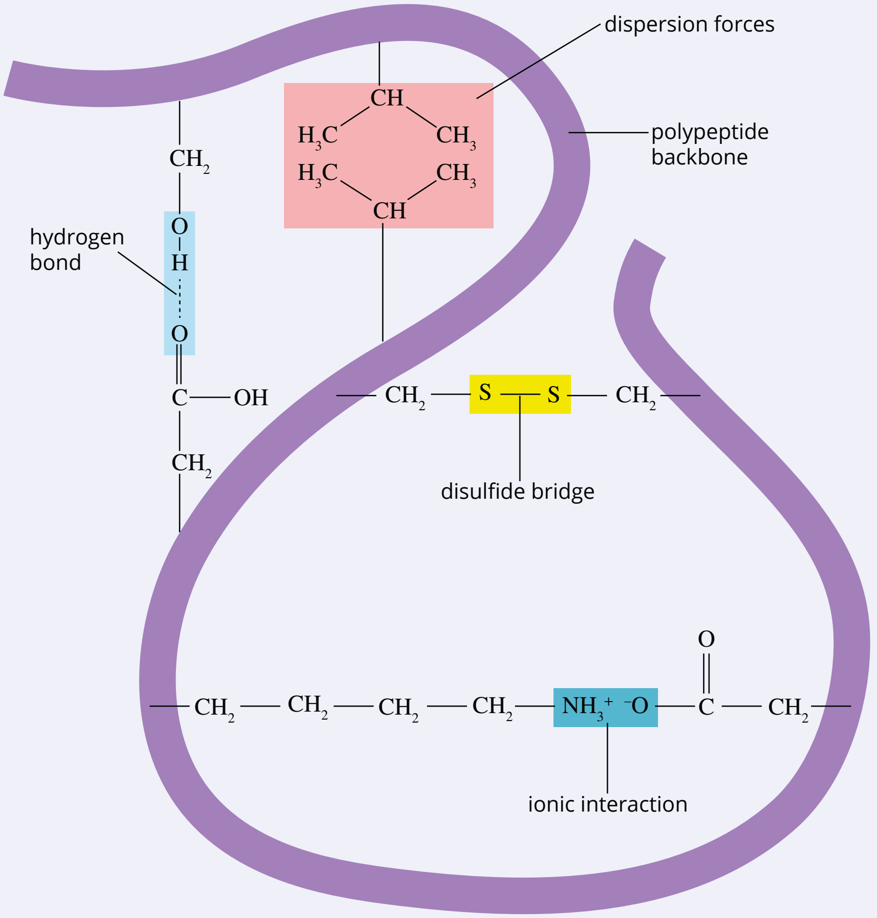
- The complex structure of large molecules such as proteins is often considered in distinct levels. The tertiary and quaternary levels of proteins are summarised in Table 15.4.2.

TABLE 15.4.2 Summary of the tertiary and quaternary structure of proteins

<table>
<tr><th>Structural level</th><th>Bonds involved</th></tr>
<tr><td>

Tertiary

The overall three-dimensional shape adopted by a protein molecule is called its tertiary structure.



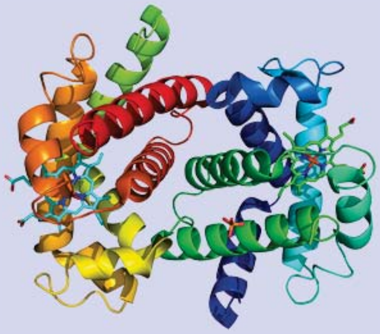
</td><td>

Hydrogen bonding can occur between polar functional groups in side chains, such as –OH and –C=O. Only dispersion forces are present between two non-polar R groups such as $–CH(CH_3)_2$. Cysteine’s R groups are able to form a covalent link, known as a disulfide bridge. Charged R groups are attracted by ionic interactions.

</td></tr>
<tr><td>

Quaternary

Some proteins consist of several associated polypeptide chains.



</td><td>

Dispersion forces between non-polar R groups are the major reason for the attraction between adjacent parts of the chains. Dipole–dipole attractions, hydrogen bonds, ionic interactions and disulfide bonds involving R groups may also occur.

</td></tr>
</table>

SUMMARY *continued*

- Many bond types produce the three-dimensional shape of proteins:
  - dispersion forces
  - dipole–dipole attractions
  - hydrogen bonds
  - covalent bonds in disulfide bridges
  - ionic interactions.

KEY QUESTIONS

1 Identify the levels of protein structure in which hydrogen bonds may contribute to the structure. More than one option may be correct.

A Primary structure
B Secondary structure
C Tertiary structure
D Quaternary structure

2 List the five main bond interactions that form when R groups in different regions of a polypeptide chain interact with each other. Give examples of the required components in R groups involved in such interactions, and an example of an amino acid that has an R group of this type.

3 Insulin is a protein involved in the control of blood glucose levels. A person with type I diabetes has a damaged pancreas, so they do not produce their own insulin. Instead they require daily injections of insulin. Explain why when not in use, the insulin should be stored in a refrigerator.

15.5 Fats and oils

Fats and oils are present in meat, fish, dairy products, eggs, all fried foods and vegetable oil. Canola (Figure 15.5.1) is one of the sources of oils used in food production. It is an excellent source of the unsaturated fatty acids used in margarine, cooking and salad oils. It is also the source of a by-product used as a livestock feed. There has been an increased demand for canola oil in recent years, which has led to many Australian farmers planting this crop.

FIGURE 15.5.1 A paddock of canola growing near Creswick in central Victoria.

Fats and oils are a major energy source in your diet. Fats are used by animals to store chemical energy. In this section, you will learn about the reactions that produce fats and oils. You will see the differences in the structure of fats and oils of animal and vegetable origin, and the way this affects their melting points. You will also learn about the place of fats and oils in a healthy, balanced diet.

TRIGLYCERIDES

Fat is a name used to describe a large number of organic compounds belonging to an even larger class of biological molecules called **lipids**. Fats and oils are the best known types of lipids. Compounds such as waxes and steroids (which include cholesterol) are also members of the lipid family.

Fats and oils contain large non-polar molecules known as **triglycerides**. Fats and oils have very similar chemical structures and are distinguished simply on the basis of their physical state at room temperature. At room temperature:

- fats are solids
- oils are liquids.

Being non-polar, triglycerides are unable to form hydrogen bonds with water, so fats are insoluble in water and oils are immiscible (cannot mix) with water. On the other hand, non-polar organic compounds such as **vitamins** A, D, E and K can dissolve in triglycerides. (You will learn more about vitamins later in this chapter.)

Fats and oils belong to the class of biological molecules called lipids. Fats are solids at room temperature and oils are liquids at room temperature.

General structure of a fatty acid and glycerol

Triglycerides are made by condensation reactions between a glycerol molecule and three **fatty acid** molecules. Glycerol (propane-1,2,3-triol) is a relatively small molecule with three hydroxyl functional groups (see Figure 15.5.2). Fatty acids have a carboxyl functional group attached to a long unbranched hydrocarbon chain, or 'tail'. This tail makes up the bulk of the molecule. Most have an even number of carbon atoms, usually between eight and 20 (see Figure 15.5.2).

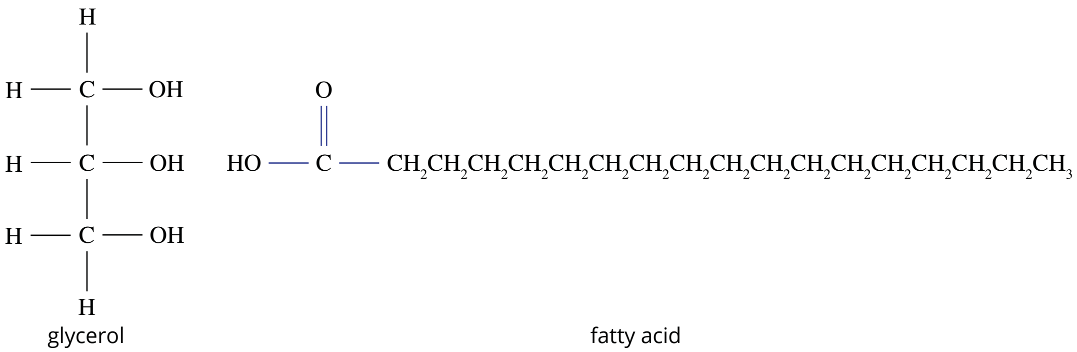


FIGURE 15.5.2 A glycerol molecule and a fatty acid molecule.

Condensation reactions to form triglycerides

As you learned in Chapter 10, a condensation reaction can occur between a molecule that contains a carboxyl group (–COOH), and a molecule that contains a hydroxyl group (–OH). An **ester functional group** (–COO–) is formed, linking the two molecules. A molecule of water is also produced.

When a small molecule, such as water, is produced in a reaction as a by-product, the reaction is said to be a condensation reaction.

A triglyceride is produced by a condensation reaction that involves the carboxyl group of a fatty acid and a hydroxyl group of glycerol, forming an **ester link**. During a condensation reaction involving one glycerol molecule and three fatty acids, three ester links form and three molecules of water are released. This process is shown in Figure 15.5.3.

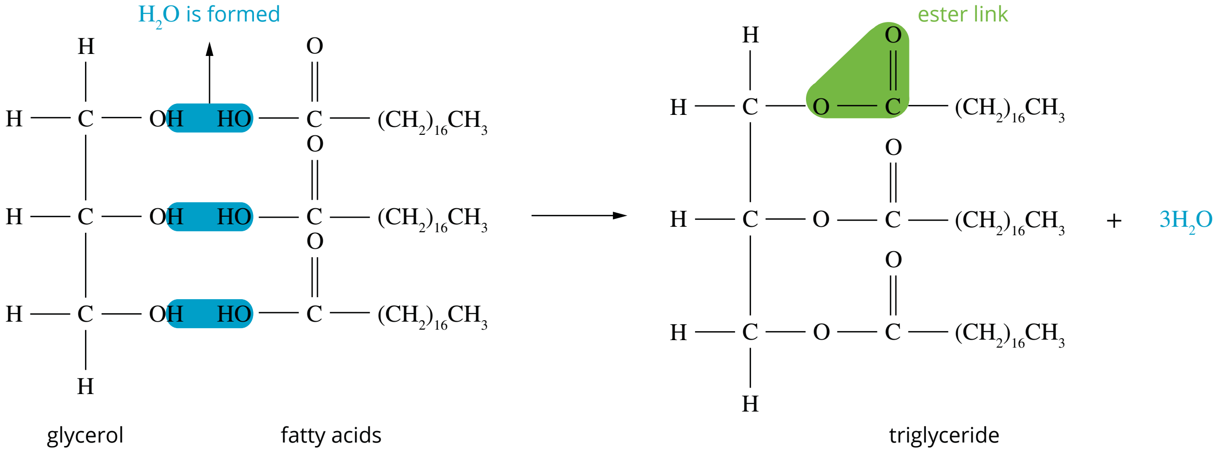


FIGURE 15.5.3 Equation showing a reaction between glycerol and fatty acids to produce a triglyceride and water.

Most triglycerides have two or three different fatty acid hydrocarbon chains. The hydrocarbon chains may differ in length. Some hydrocarbon chains may also contain one or more carbon–carbon double bonds.

SATURATED AND UNSATURATED FATTY ACIDS

Fats are classified on the basis of the structural features of the hydrocarbon chains of their fatty acid components.

- **Saturated fatty acids** have hydrocarbon chains that contain only single carbon–carbon bonds. Stearic acid, which occurs widely in meats, has a semistructural formula of $CH_3(CH_2)_{16}COOH$ and a molecular formula of $C_{17}H_{35}COOH$. Saturated fatty acids have the general formula $C_nH_{2n+1}COOH$.
- **Monounsaturated fatty acids** contain one carbon–carbon double bond in their hydrocarbon chain. The main dietary example is oleic acid, which is found in a number of vegetable oils. Its semistructural formula is $CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH$ and its molecular formula is $C_{17}H_{33}COOH$. Monounsaturated fatty acids have the general formula $C_nH_{2n-1}COOH$.
- **Polyunsaturated fatty acids** contain more than one carbon–carbon double bond in their hydrocarbon chain. Fish and vegetable oils are the main dietary source of polyunsaturated fatty acids. For example, sunflower oil is a good source of linoleic acid. Linoleic acid has the semistructural formula $CH_3(CH_2)_4CH{=}CHCH_2CH{=}CH(CH_2)_7COOH$ and its molecular formula is $C_{17}H_{31}COOH$.

The structure and general formula of stearic acid, oleic acid and linoleic acid are shown in Figure 15.5.4.

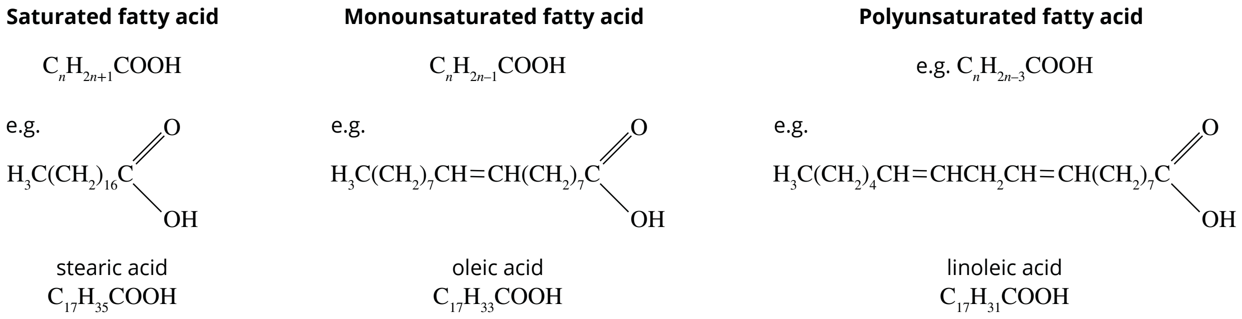


FIGURE 15.5.4 The general formula and semistructural formula of a representative saturated fatty acid, monounsaturated fatty acid and polyunsaturated fatty acid.

Table 15.5.1 lists further examples of saturated and unsaturated fatty acids as well as some dietary sources of these fatty acids.

TABLE 15.5.1 Examples of fatty acids and their sources

	Name	Semistructural formula	Molecular formula	Food sources
Saturated fatty acids	Lauric acid	$CH_3(CH_2)_{10}COOH$	$C_{11}H_{23}COOH$	Laurel oil, coconut oil, dairy products
	Myristic acid	$CH_3(CH_2)_{12}COOH$	$C_{13}H_{27}COOH$	Butter, coconut oil, nutmeg
	Palmitic acid	$CH_3(CH_2)_{14}COOH$	$C_{15}H_{31}COOH$	Dairy products, beef, palm oil
	Stearic acid	$CH_3(CH_2)_{16}COOH$	$C_{17}H_{35}COOH$	Beef, dairy products
Unsaturated fatty acids	Palmitoleic acid (monounsaturated)	$CH_3(CH_2)_5CH{=}CH(CH_2)_7COOH$	$C_{15}H_{29}COOH$	Cheese, macadamia nuts
	Oleic acid (monounsaturated)	$CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH$	$C_{17}H_{33}COOH$	Olive oil, canola oil, peanuts
	Linoleic acid	$CH_3(CH_2)_4(CH{=}CHCH_2)_2(CH_2)_6COOH$	$C_{17}H_{31}COOH$	Corn, peanuts, soybean oil
	Linolenic acid	$CH_3CH_2(CH{=}CHCH_2)_3(CH_2)_6COOH$	$C_{17}H_{29}COOH$	Walnuts, linseed oil, legumes
	Arachidonic acid	$CH_3(CH_2)_4(CH{=}CHCH_2)_4(CH_2)_2COOH$	$C_{19}H_{31}COOH$	Peanut oil
	Eicosapentaenoic acid (EPA)	$CH_3(CH_2CH{=}CH)_5(CH_2)_3COOH$	$C_{19}H_{29}COOH$	Salmon, tuna, seaweed

Saturated fats

Saturated fats are made from saturated fatty acids only. They are generally unreactive and exist as waxy solids at room temperature. Saturated fats occur in higher proportions in animal fats (such as those shown in Figure 15.5.5).

FIGURE 15.5.5 These foods are all sources of saturated fatty acids.

Unsaturated fats: omega-3 fatty acids and omega-6 fatty acids

Unsaturated fatty acids are classified according to the position of the first double bond from the end of the hydrocarbon chain. As shown in Figure 15.5.6, the **omega carbon** of an unsaturated fatty acid is the carbon in the methyl group at the end of the hydrocarbon chain. An **omega-3 fatty acid** has a carbon–carbon double bond on the third carbon from the omega carbon. For example, linolenic acid, which is obtained from linseed oil, walnut oil and peanut oil, is an omega-3 (ω-3) fatty acid.

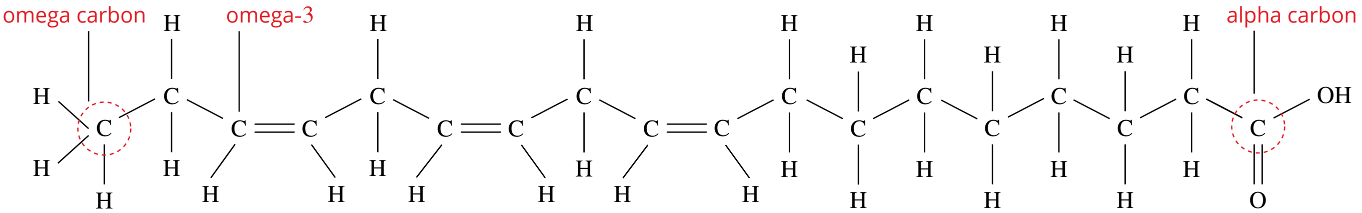


FIGURE 15.5.6 Molecular structure of linolenic acid, an omega-3 (ω-3) fatty acid.

In fatty acids, the carboxylic acid end is regarded as the start of the fatty acid chain (the α-carbon). The methyl end is considered the ω-carbon.

Similarly, the **omega-6 fatty acids** have a carbon–carbon double bond on the sixth carbon from the omega carbon (Figure 15.5.7). Sunflower oil, soya bean oils and corn are sources of omega-6 fatty acids.

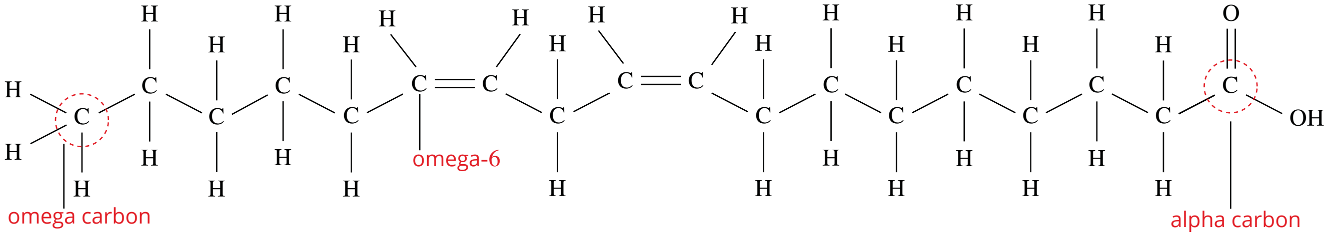


FIGURE 15.5.7 Molecular structure of linoleic acid, an omega-6 (ω-6) fatty acid.

Algae produce oils containing omega-3 fatty acids such as eicosapentaenoic acid (EPA). The algae are consumed by prawns and fish such as salmon (see Figure 15.5.8 on page 490). Eating these foods provides you with an excellent supply of omega-3 fatty acids.

Numerous claims have been made about the health benefits of omega-3 fatty acids, such as reduced incidence of heart disease, inflammation of the skin and arthritis. However, much of the supporting evidence has not been based on scientifically rigorous data. The optimum ratio of omega-3 fatty acids to omega-6 fatty acids in a healthy diet is also an area of contention. It may be that the actual ratio of omega-3 to omega-6 fatty acids is a far more significant factor than the intake of either.

FIGURE 15.5.8 Foods that are rich in omega-3 fatty acids include salmon, prawns, nuts and broccoli.

MELTING POINTS OF FATS AND OILS

Fats, which are solids at room temperature and occur widely in foods of animal origin, have higher melting points than oils. Oils are liquids that often originate from vegetable sources.

The melting points of triglycerides are often an important factor to consider when preparing or processing foods. For example, cocoa butter, which melts at close to body temperature, is ideal for making chocolate (Figure 15.5.9). It is extracted from cocoa beans and contains a higher proportion of saturated fatty acids (stearic and palmitic) than most other vegetable oils.

FIGURE 15.5.9 Chocolate makers take advantage of the melting point of cocoa butter to produce intricate structures, such as this gorilla.

The different melting points of triglycerides can be explained in terms of the length and degree of saturation of their fatty acid hydrocarbon chains.

As Table 15.5.2 shows, as the hydrocarbon chain increases in length, the melting point of a fatty acid increases. This is due to the increasing strength of dispersion forces between fatty acid molecules as molecular mass increases. The fatty acid tails can pack closely and so these intermolecular forces become stronger.

TABLE 15.5.2 Effect of hydrocarbon chain length on the melting points of fatty acids

Fatty acid	Number of carbon atoms	Number of C=C bonds	Melting point (°C)	Source
Lauric acid	12	0	44	Coconut oil
Palmitic acid	16	0	63	Cocoa beans
Stearic acid	18	0	70	Beef tallow

Furthermore, as Table 15.5.3 shows, when the number of carbon–carbon double bonds increases, the melting point of the fatty acid decreases. Most naturally occurring unsaturated fatty acids have a ***cis* arrangement** of the alkyl groups around the double bond. This produces a permanent bend or ‘kink’ in the hydrocarbon chain, as shown in Figure 15.5.10. As a result, the fatty acid tails are unable to line up and pack closely. The intermolecular dispersion forces are much weaker than those formed between saturated fatty acid tails.

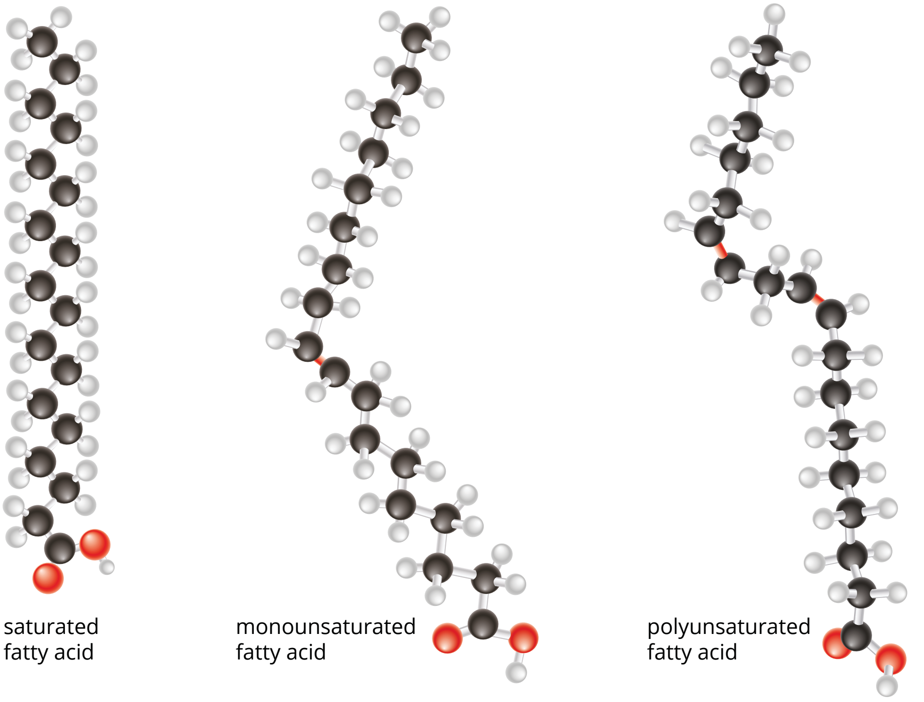


FIGURE 15.5.10 The different shapes of the hydrocarbon chains of these three fatty acids are produced by the double bonds in unsaturated fatty acids. Notice also the *cis* arrangement across the double bonds (highlighted in red).

ℹ A *cis* arrangement occurs when the longest hydrocarbon chains attached to the carbons of a double bond are on the same side of the double bond.

TABLE 15.5.3 Effect of number of double bonds on the melting point of unsaturated fatty acids

Fatty aid	Number of carbon atoms	Number of C=C bonds	Melting point (°C)	Source
Stearic acid	18	0	70	Beef tallow
Oleic acid	18	1	13	Olive oil
Linoleic acid	18	2	–5	Safflower oil
Linolenic acid	18	3	–11	Fish oil

CHEMFILE

Margarine

Unlike butter, which is made from saturated animal fats, margarine is usually made from vegetable oils that contain more polyunsaturated fats (Figure 15.5.11). Vegetable oils from plants such as sunflower, palm, soya and coconut are blended together to make margarine. In order to convert the unsaturated oils to solid form, they are partially saturated by reacting them with hydrogen in the presence of a nickel catalyst.

Antioxidants and stabilisers are added to margarine because the carbon–carbon double bonds in polyunsaturated fats are reactive. These additives prevent the polyunsaturated fats from reacting with oxygen in the air and producing substances with unpleasant odours whose presence leads to a condition known as rancidity.

FIGURE 15.5.11 Margarine contains additives that slow the oxidation of the double bonds present in its molecular structure.

ESSENTIAL AND NON-ESSENTIAL FATTY ACIDS

Most Western diets include more than enough fat to provide the fatty acids needed for the human body. In addition, fats can be converted into other fatty acids. Therefore, most fats are classified as containing **non-essential fatty acids**. For example, stearic acid can be converted into oleic acid if oleic acid is in short supply from dietary sources.

Several fatty acids are classified as **essential fatty acids** because humans are unable to produce them. These are all polyunsaturated fatty acids:

- linolenic acid, an omega-3 fatty acid
- linoleic acid, an omega-6 fatty acid
- arachidonic acid, an omega-6 fatty acid.

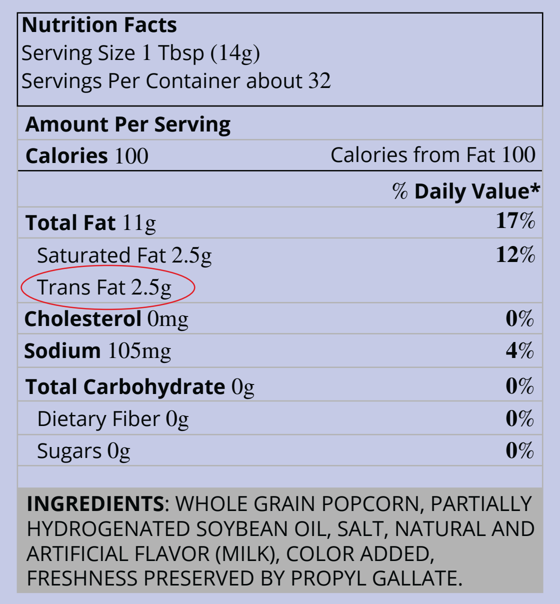
These fatty acids are required in small amounts to produce a number of compounds with a wide range of functions. These compounds include a group of hormones called prostaglandins and thromboxane, which is needed for blood clotting and also to form cell membranes.

Essential fatty acids are in high concentrations in fish oil and soybean oil, but a balanced diet that includes plenty of fruit and vegetables provides them in adequate amounts. Sunflower oil, which is used to produce margarine, is particularly rich in linoleic acid. It can be found in the sunflower seeds used in muesli, health bars and animal feedstocks.

CHEMFILE

trans fatty acids

You may have noticed the amount of *trans* fats listed on a food label, such as the popcorn label in Figure 15.5.12.



Nutrition Facts
Serving Size 1 Tbsp (14g)
Servings Per Container about 32

Amount Per Serving	
Calories 100	Calories from Fat 100
	% **Daily Value***
Total Fat 11g	**17%**
Saturated Fat 2.5g	**12%**
Trans Fat 2.5g	
Cholesterol 0mg	**0%**
Sodium 105mg	**4%**
Total Carbohydrate 0g	**0%**
Dietary Fiber 0g	**0%**
Sugars 0g	**0%**

INGREDIENTS: WHOLE GRAIN POPCORN, PARTIALLY HYDROGENATED SOYBEAN OIL, SALT, NATURAL AND ARTIFICIAL FLAVOR (MILK), COLOR ADDED, FRESHNESS PRESERVED BY PROPYL GALLATE.

FIGURE 15.5.12 Nutrition data shown on a pack of popcorn.

As you learned in Chapter 10, unsaturated molecules can have geometric isomers described as ***cis* isomers** and ***trans* isomers**. Most unsaturated fats occurring naturally have the *cis* orientation of hydrocarbon chains. *trans* fats are unsaturated fats with a *trans* orientation of hydrocarbon chains across the double bond.

You can see this difference in orientation in Figure 15.5.13. These models also illustrate another significant structural difference between the isomers. Notice that only the *cis* isomer has a noticeable 'kink' in the hydrocarbon chain.

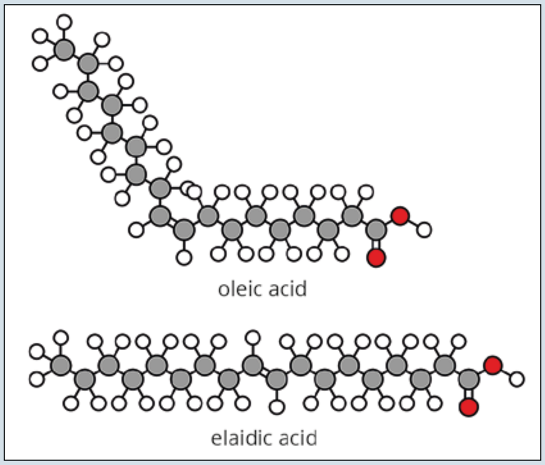


FIGURE 15.5.13 Two isomers of the fatty acid *cis*-oleic acid and its *trans* isomer.

Partial reaction of the polyunsaturated fats in vegetable oils with hydrogen reduces the number of double bonds present. Hydrogenation is used commercially to increase melting point, to improve shelf life and to make cooking fats for commercial deep-frying. However, it can also lead to double bond isomerism reactions producing *trans* fats.

In recent years, there has been considerable evidence to show that consumption of *trans* fats leads to increased risk of heart disease because of higher LDL cholesterol levels. Many countries have moved to ban or minimise their intake, or at least to require amounts of *trans* fats to be stated on food packaging.

According to the World Health Organization, 'Industrial *trans* fats (found in fast foods, snack foods, fried foods, frozen foods) are not part of a healthy diet …' and should be reduced 'to less than 1% of total energy intake'.

EXTENSION

Fats and good health

Coronary heart disease is a major cause of death in Australia. It is a disease of the arteries that supply blood to the heart and begins with the build-up of fatty deposits on the inner walls of the arteries. This leads to a condition called atherosclerosis, or 'hardening of the arteries'. As the deposits increase, arteries become narrowed and the flow of blood is restricted (Figure 15.5.14).

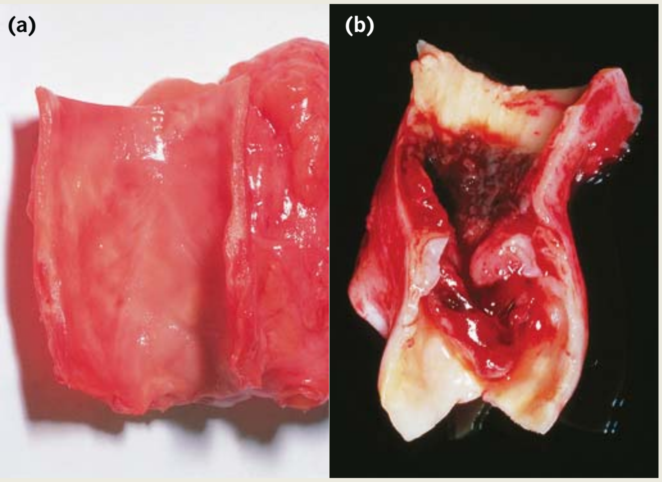


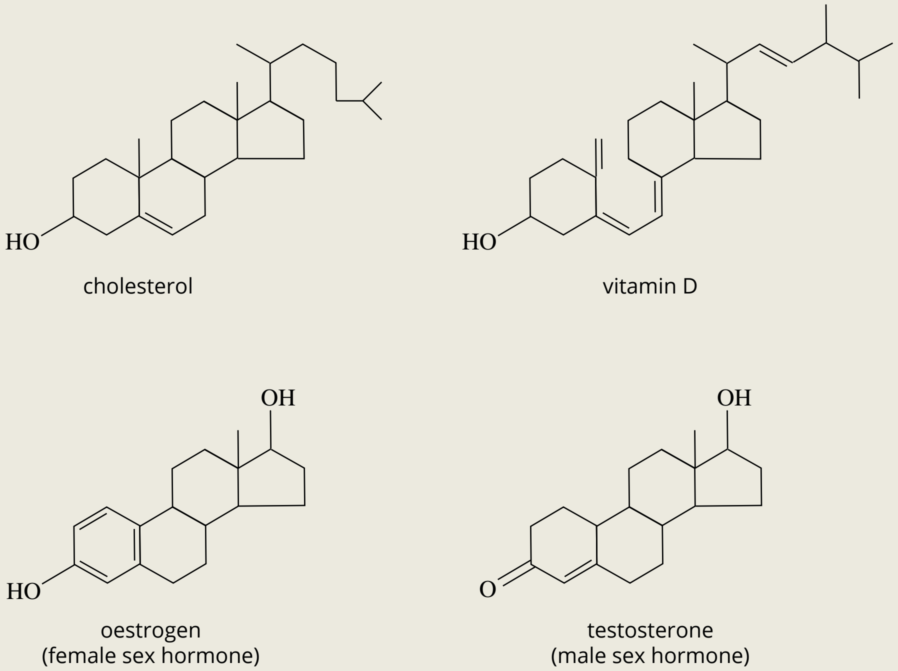
FIGURE 15.5.14 (a) A healthy artery and (b) an artery showing the effect of atherosclerosis, or hardening of the artery.

Eventually, if hardening of the arteries continues, an artery supplying blood to some part of the heart may become completely blocked. Without oxygen, that part of the heart muscle cannot function and a heart attack results.

One indication of possible danger is the amount of cholesterol in the blood. For all Australians, the National Heart Foundation has the following advice. To avoid coronary heart disease:

- exercise regularly
- maintain a balanced diet
- do not smoke.

Cholesterol is a lipid that occurs naturally in all animals. It is a white, fatty substance that is used by the body in the manufacture of hormones, bile and vitamin D (Figure 15.5.15). Its role in the body is therefore important. As it is made only by animals, cholesterol is not found in fruit, vegetables or other plant products. The small amount of cholesterol available from the animal products in a balanced diet is not enough to meet our daily requirements. The body synthesises most of its own cholesterol (3–5 grams per day) in the liver. High blood cholesterol is caused by the body making more than it needs.



cholesterol

vitamin D

oestrogen
(female sex hormone)

testosterone
(male sex hormone)

FIGURE 15.5.15 Cholesterol and three substances made from it. The substances have very similar molecular structures. Carbon and hydrogen atoms in the molecules have been omitted for clarity. The lines represent carbon–carbon bonds; there are carbon atoms at the end of each line.

15.5 Review

SUMMARY

- Fats and oils are composed of molecules called triglycerides.
- Triglycerides have a number of important roles in the human body, including as energy storage and insulation, and as a source of fatty acids from which other important compounds are produced.
- Triglycerides are formed in a condensation reaction between glycerol and fatty acids.
- Three ester links are formed in the condensation reaction between a glycerol molecule and three fatty acids to form a triglyceride molecule.
- Fatty acids are carboxylic acids with a long hydrocarbon chain.
- Saturated fatty acids have only carbon–carbon single bonds.
- Unsaturated fatty acids have one or more carbon–carbon double bonds.
- Unsaturated fatty acids with a double bond on the third last carbon atom in the hydrocarbon chain are classified as omega-3 fatty acids; unsaturated fatty acids with a double bond on the sixth last carbon atom are classified as omega-6 fatty acids.
- The most significant intermolecular forces between triglyceride molecules or fatty acid molecules are dispersion forces.
- Saturated fatty acids pack together more closely and can form stronger intermolecular bonds than unsaturated fatty acids. Saturated fatty acids, therefore, have higher melting points and are more likely to be solids at room temperature.
- In a similar way, unsaturated triglycerides, which are common in vegetable oils, have lower melting points than the saturated triglycerides common in animal fats.
- The essential fatty acids, linoleic acid, linolenic acid and arachidonic acid, must be included in the diet as they cannot be manufactured by humans from other organic compounds via biochemical pathways.

KEY QUESTIONS

1 Select the molecule that would have the lowest melting point.

A $CH_3(CH_2)_{16}COOH$
B $C_{17}H_{31}COOH$
C $CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH$
D $C_{19}H_{39}COOH$

2 Which two functional groups are directly involved in the formation of a triglyceride?

3 **a** Write an equation for the formation of the triglyceride glyceryl trioleate from the reaction of glycerol and oleic acid, $CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH$.

b Draw the structure of glyceryl trioleate, showing the ester bonds.

4 A fat present in a vegetable oil has the structure shown in Figure 15.5.16.

a Circle an ester functional group.

b Is this triglyceride saturated or unsaturated? Explain your answer.

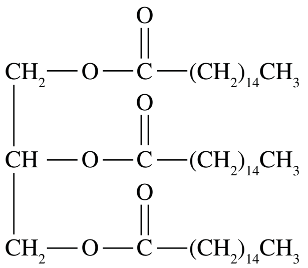


FIGURE 15.5.16 A triglyceride in a vegetable oil.

5 Refer to Table 15.5.1 on page 488 to classify the following fatty acids obtained from various food sources as being saturated, monounsaturated or polyunsaturated.

a Stearic acid
b $CH_3(CH_2)_5CH{=}CH(CH_2)_7COOH$
c $C_{13}H_{27}COOH$
d Arachidonic acid
e $C_{17}H_{31}COOH$
f $CH_3(CH_2)_{14}COOH$
g $C_{11}H_{23}COOH$
h $C_{17}H_{33}COOH$

15.6 Carbohydrates

There are millions of organic chemicals on Earth, and you do not need to look further than the plants and trees around you to find them. Figure 15.6.1 shows the sago palm, which is a common plant in the rainforest areas of Asia. Like many trees, the sago palm is a source of timber but, unlike most trees, its centre forms the basis of a popular dessert—sago pudding.

FIGURE 15.6.1 (a) The sago palm is found in rainforest areas of Asia. (b) As the sago palm ages, the centre softens and forms a product that is harvested. These women are beating the soft centre into a pulp. (c) The soft centre of the sago palm is the main ingredient in many desserts such as sago pudding.

The main structural component of all plants, including the sago palm, is the polymer **cellulose**. Over half the world's organic carbon is bound up in trees and other plants in the form of cellulose.

The soft centre of the sago palm tree is a form of **starch**. Starch is the main component of flour, an essential ingredient of foods such as bread, cakes, sauces and pastry.

Cellulose and starch belong to a class of compounds called **carbohydrates**. In this section, you will learn about the chemical structure of common carbohydrates and their importance to nature and society.

CARBOHYDRATES

Carbohydrates are made from the elements carbon, hydrogen and oxygen. Carbohydrates usually have the general formula $C_x(H_2O)_y$, where x and y are whole numbers. Carbohydrates range in size from small molecules, with relative molecular masses between 100 and 200, to very large polymers, with molecular masses greater than one million.

One of the simplest carbohydrates, glucose ($C_6H_{12}O_6$), is formed in the cells of green plants through the process of **photosynthesis**. Photosynthesis takes place in the presence of light and the process can be represented by the equation:

$$6CO_2(g) + 6H_2O(l) \xrightarrow{\text{light}} C_6H_{12}O_6(aq) + 6O_2(g)$$

Photosynthesis is an **endothermic** reaction, in which the Sun's energy is transformed into chemical potential energy in glucose. Living organisms use glucose as a source of energy. Animals cannot perform photosynthesis so they need to consume plants or animals in their diet to meet their energy needs.

MONOSACCHARIDES

The smallest carbohydrates are the **monosaccharides**. They are white, sweet-tasting solids that are highly soluble in water. The structures of the three most common monosaccharides, fructose, glucose and galactose, are shown in Figure 15.6.2. Note that these monosaccharides all have the same molecular formula of $C_6H_{12}O_6$, which means that they are isomers.

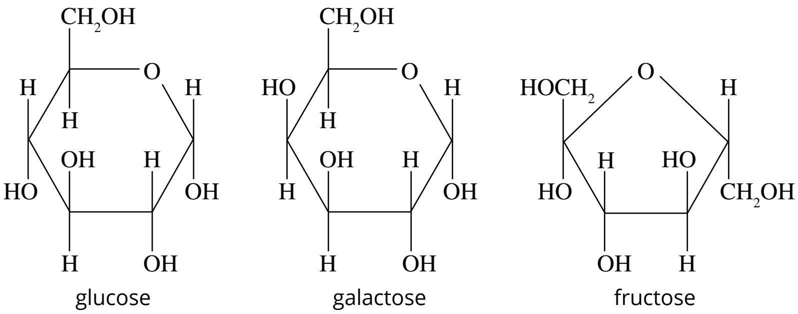


FIGURE 15.6.2 Structural formulas of glucose, galactose and fructose. Carbon atoms in the rings have been omitted for simplicity. There is a carbon atom at each corner of the ring structures except where an oxygen atom is shown.

The structures of the monosaccharides look very similar, particularly glucose and galactose. However, the positions of the hydroxyl (–OH) groups in glucose and galactose are different. These slight variations in structure lead to significant differences in their functions in living organisms.

When there are four different groups around a carbon atom, the molecule has a chiral centre. Glucose and galactose have five chiral centres. Although all the atoms in these molecules are connected in the same way, the groups are arranged differently around one of the chiral centres. It is this difference that causes the molecules to behave differently in living organisms.

All three monosaccharides contain a number of polar hydroxyl groups, which means they can form hydrogen bonds with water. As a result, monosaccharides are highly soluble.

Glucose is found in all living things, especially in the juice of fruits, the sap of plants and the blood and tissue of animals. As a product of photosynthesis, glucose functions as a key energy source in most forms of life.

Fructose is found in many fruit juices and honey. Its main role in the body is as an energy source, where it is used in much the same way as glucose. Figure 15.6.3 shows some fruits with high fructose contents.

Galactose is not found free in nature. However, it occurs as a component of larger carbohydrates like lactose, the main sugar found in milk.

FIGURE 15.6.3 Fructose is the most common sugar in fruit, especially berries.

Glucose, fructose and galactose are structural isomers. They have the same molecular formula but different molecular structures. The differences in their structures appear slight but they are of great importance to living organisms.

DISACCHARIDES

Disaccharides are carbohydrates formed from the reaction between two monosaccharide molecules. A condensation reaction occurs between the hydroxyl functional groups on neighbouring molecules and a water molecule is formed as a by-product.

The two monosaccharides are joined by an oxygen atom. The connection between the monosaccharide units is called an **ether link** (or **glycosidic link** in carbohydrates). Figure 15.6.4 shows the formation of two important disaccharides, maltose and sucrose.

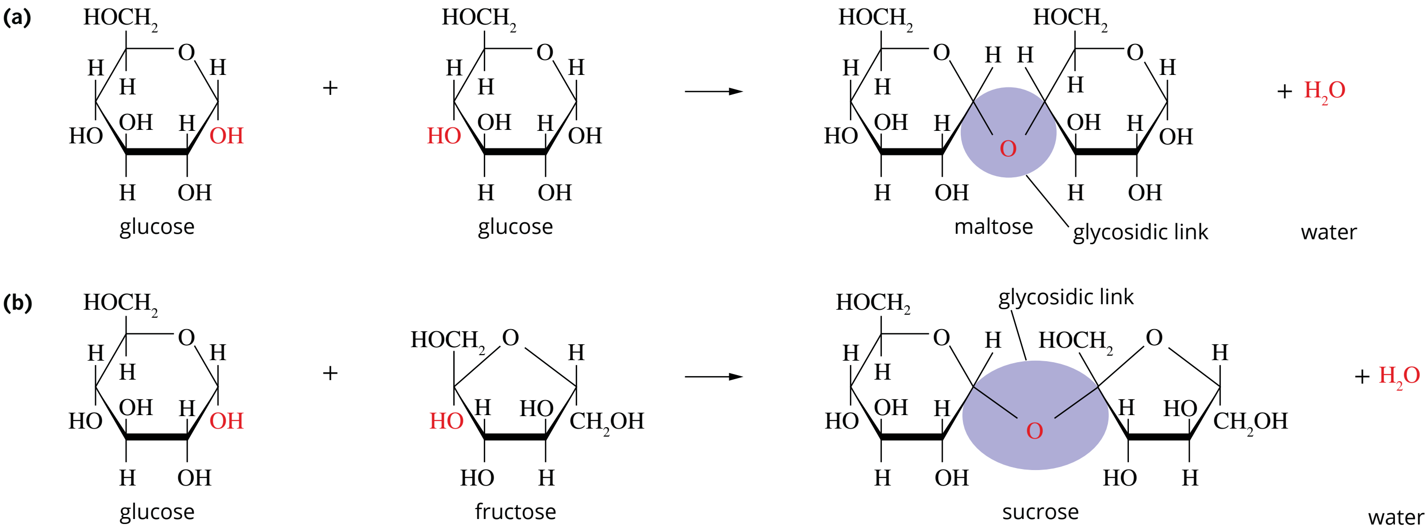


FIGURE 15.6.4 (a) The condensation of two glucose molecules forms maltose. (b) The condensation of glucose and fructose molecules forms sucrose. The glycosidic links are highlighted.

Maltose is added to foods as a sweetener and is used in the brewing industry as a raw material for fermentation into beer.

Sucrose is commonly referred to as table sugar. It is the most popular sweetener among the simple sugars. Sucrose is found in high concentrations in crops such as sugar beet and sugar cane shown in Figure 15.6.5.

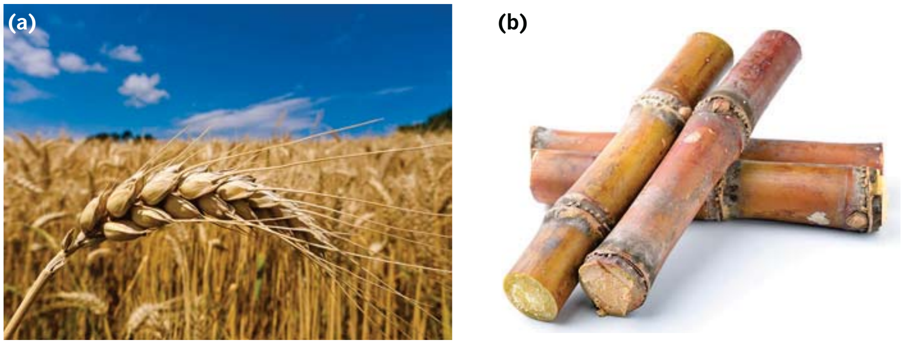


FIGURE 15.6.5 (a) Germinating barley seeds are a source of maltose. (b) The juice of sugar cane has a high sucrose content.

When two monosaccharides react, a disaccharide is formed. This is another example of a condensation reaction because a small molecule, such as water, is produced as a by-product. The bond formed between the two monosaccharides is called either an ether or a glycosidic link.

SWEETNESS

The smaller carbohydrates are often referred to as sugars because of their sweet taste. It is this sweetness that is often blamed for the dietary issues of many Australians. The lure of a sweet taste can lead people to eat more food than they require. The excess chemical energy consumed can end up being stored as fat in the body.

Monosaccharides and disaccharides are not the only substances to impart a sweet taste to foods. A range of artificial sweeteners such as cyclamates, sugar alcohols and aspartame are available to the food industry. These products are significantly sweeter than sugars.

Concerns about the intake of sugars by humans have seen an increase in the use of artificial sweeteners. Table 15.6.1 compares 'diet' versions of a popular soft drink with the regular version.

TABLE 15.6.1 Comparisons of the energy content of Coke® and its 'diet' versions

Product	Main ingredients	Energy (kJ/100 mL)
Diet Coke®	Carbonated water, caramel, aspartame, phosphoric acid, potassium benzoate, caffeine	1.5
Coke Zero®	Carbonated water, caramel, aspartame, phosphoric acid, potassium benzoate, caffeine	1.4
Coke®	Carbonated water, cane sugar, caramel, food acid, phosphoric acid, caffeine	180

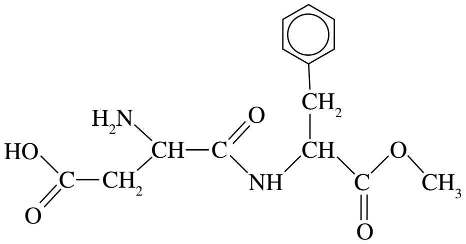


FIGURE 15.6.6 Aspartame, also known as food additive 951, is used as an artificial sweetener in diet soft drinks and as sugar-substitute tablets. It has different functional groups and a different structure from carbohydrates.

The use of artificial sweeteners has proved a popular way of reducing the amount of sugar added to foods. One of the most common sweeteners is aspartame, which is sold under the trade names NutraSweet® and Equal®. Although aspartame contains about the same amount of energy as an equal mass of sucrose (about 17 kJ g^{-1}), it can be used in much smaller quantities than sugar because it is nearly 200 times sweeter (Figure 15.6.6). Neotame, another artificial sweetener, is over 50 times sweeter than aspartame!

CHEMFILE

Too many names for sugar

Nutritionists are critical of the levels of sugars that most Australians consume. However, food manufacturers know that a high sugar content helps their products sell. Therefore, sugars are often labelled in ways other than 'sucrose' and 'fructose'.

In 2015, consumer group Choice published a list of the 43 forms of sugar present in Australian foods (Figure 15.6.7). When they released their findings, Choice asked for better labelling of foods to help consumers be more informed.

SUGAR COATING

43 DIFFERENT NAMES FOR 'ADDED SUGAR'

1. AGAVE NECTAR/SYRUP
2. BARLEY MALT
3. BEET SUGAR
4. BLACKSTRAP MOLASSES
5. BROWN SUGAR
6. CANE SUGAR
7. CAROB SYRUP
8. CASTER SUGAR
9. COCONUT SUGAR
10. COFFEE SUGAR CRYSTALS
11. CONFECTIONER'S SUGAR
12. CORN SYRUP
13. DATE SUGAR/SYRUP
14. DEMERARA
15. DEXTROSE
16. EVAPORATED CANE JUICE
17. FRUCTOSE
18. FRUIT JUICE
19. FRUIT JUICE CONCENTRATE
20. GLUCOSE
21. GOLDEN SYRUP
22. GRAPE SUGAR/SYRUP
23. HONEY
24. HIGH-FRUCTOSE CORN SYRUP
25. ICING SUGAR
26. INVERT SUGAR
27. LACTOSE
28. MALT
29. WHITE SUGAR
30. MALTOSE
31. MAPLE SYRUP
32. MOLASSES
33. MUSCOVADO
34. PALM SUGAR
35. PANELA
36. POWDERED SUGAR
37. RAPADURA
38. RAW SUGAR
39. RICE SYRUP
40. SUCROSE
41. SUGAR
42. TREACLE
43. TURBINADO

choice
CHOICE.COM.AU

FIGURE 15.6.7 The 43 forms of sugar in Australian foods as identified by Choice.

CHEMISTRY IN ACTION

Why are sugars sweet?

The sweetness of some substances is thought to be due to the shape of their molecules. To taste sweet, molecules seem to need three sites that can form bonds with taste buds on the surface of the tongue. Provided the bonds are of the correct type and the sites are certain distances apart, your brain recognises a substance as tasting sweet.

Two of these bonds to the taste buds are hydrogen bonds, and the third is formed with a non-polar site. The so-called 'triangle of sweetness' that must be present in the molecule is shown in Figure 15.6.8.

Some molecules have many such triangles that can 'lock on to' the taste buds for long periods. Substances that are several thousand times sweeter than glucose exist. Table sugar (sucrose) is twice as sweet as glucose.

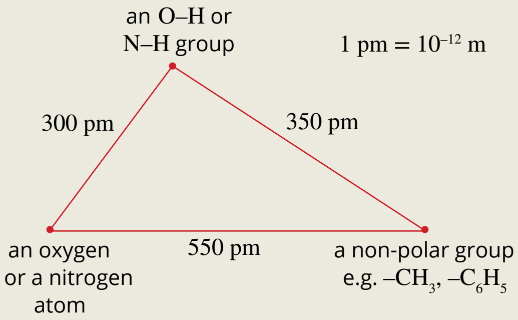


FIGURE 15.6.8 It is thought that this 'triangle of sweetness' must be present in a molecule for it to taste sweet.

Sweetness is commonly measured through comparison with sucrose. Sucrose is assigned an arbitrary value of 1 for sweetness. Table 15.6.2 lists other common sugars and sweeteners for comparison.

Table 15.6.2 shows that, despite the similar structures of sugars, their sweetness varies. Lactose has about one-sixth the sweetness of sucrose. Presumably the bonds in sucrose match the triangle of sweetness better than those of lactose. The table also shows why smaller proportions of artificial sweeteners are needed in processed foods to achieve the same sweetness as sugars.

TABLE 15.6.2 Comparison of common sugars and their sources

Sweetener	Sweetness value	Source
Lactose	0.16	Milk, sugar
Galactose	0.32	Component of lactose
Glucose	0.74	Formed in photosynthesis
Sucrose	1.00	Table sugar
Fructose	1.74	Fruit sugar
Cyclamate	30	Artificial sweetener
Aspartame	100–150	Artificial sweetener
Saccharin	450	Artificial sweetener
Neotame	7000–13 000	Artificial sweetener

POLYSACCHARIDES

A condensation reaction between monosaccharides does not necessarily stop with the formation of a disaccharide. Reactions with other monosaccharides can continue to produce a polymer, a **polysaccharide**. A polysaccharide can contain thousands of glucose units.

Polysaccharides are generally insoluble in water and have no taste. The three most important biological polysaccharides are starch, cellulose and glycogen. Simplified models of these polysaccharides can be seen in Figure 15.6.9.

The properties of starch, cellulose and glycogen are very different from each other, yet they are all polymers of the same monomer, glucose. How can three different substances be formed from the one monomer? The answer to this is found from a closer inspection of the structure of glucose. There are two forms of glucose. These are α-glucose and β-glucose, as shown in Figure 15.6.10 (page 500). The orientation of the hydroxyl groups is different in the two forms.

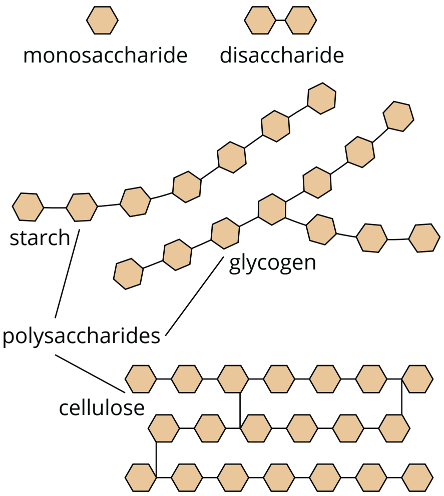


FIGURE 15.6.9 Representations of different carbohydrate molecules.

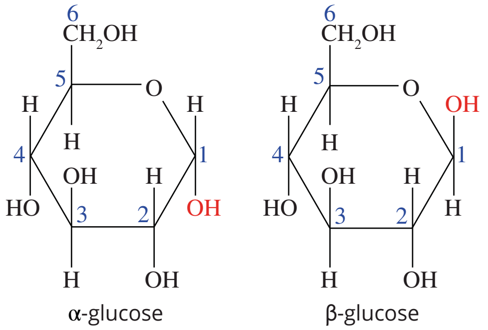


FIGURE 15.6.10 In α-glucose the –OH group on carbon number 1 points ‘downwards’ while in β-glucose it points ‘upwards’. The carbon atoms in the ring are numbered from 1 to 6 as shown.

Starch

Plants are able to produce and polymerise α-glucose molecules to form **starch**. Polymerisation is a condensation reaction, forming glycosidic links between each glucose molecule. This also produces many water molecules as a by-product. Plants use starch for storage of energy. When energy is needed, the plant can break down the starch back into glucose and utilise the glucose as an energy source to maintain its functions.

Foods such as potato and sago have a high starch content. If the starch forms a linear polymer, it is known as **amylose** (see Figure 15.6.11).

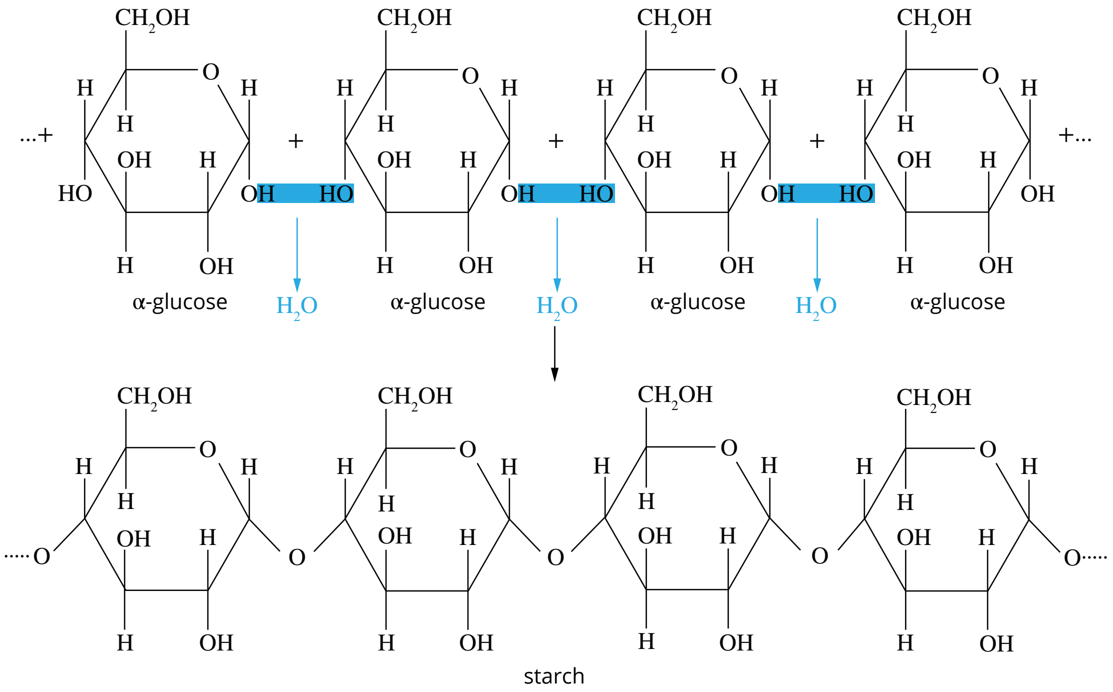


FIGURE 15.6.11 The condensation polymerisation of α-glucose to produce amylose, which is a form of starch.

A second form of starch, known as **amylopectin**, can form if some of the α-glucose molecules undergo condensation reactions between hydroxyl groups at different positions around the glucose rings. In this way, occasional branches occur in the structure. Figure 15.6.12 shows that the branches along the polysaccharide chains occur after about 20–24 glucose units.

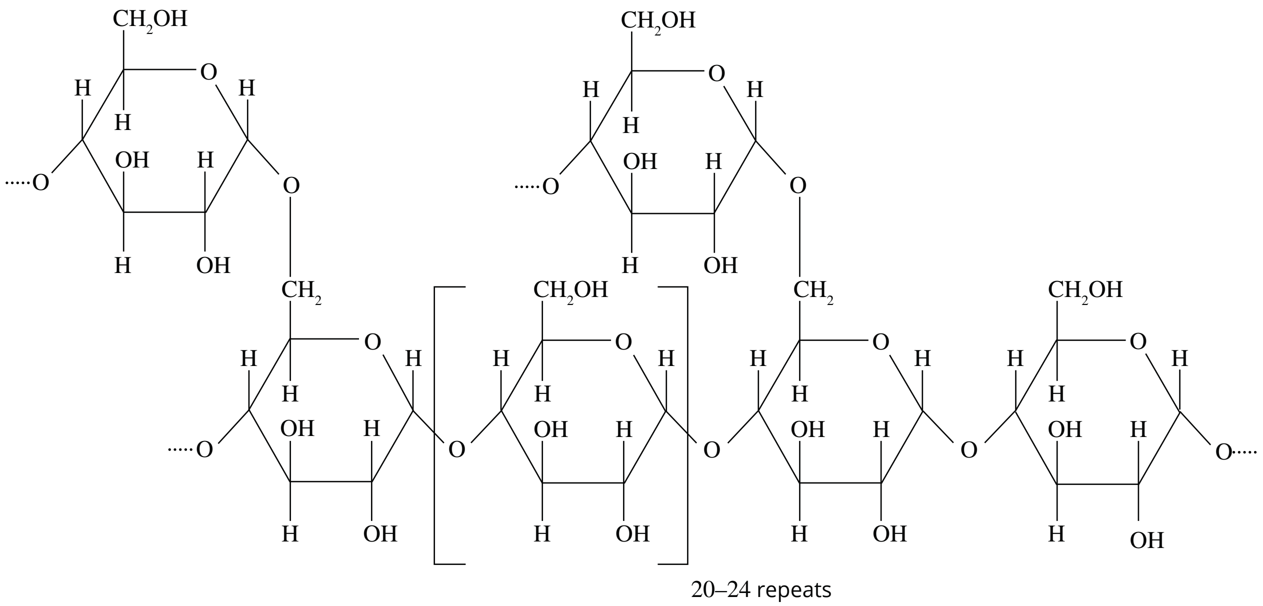


FIGURE 15.6.12 Amylopectin is a form of starch that has occasional branches along the glucose chains.

Amylose and amylopectin have different solubilities in water. The long molecules of amylose coil into spiral-like helices and pack together tightly, with many –OH groups inside the helices and away from contact with water. Therefore, amylose is largely insoluble in cold water. However, in the case of amylopectin, the branching of its molecules restricts the coiling of the polymer, leaving many more –OH groups exposed so that it dissolves in water.

Cellulose

Cellulose is the main structural material in plants. It is the most abundant molecule in living tissue and is found in the walls of plant cells. Cotton is almost pure cellulose, while wood is around 50% cellulose. Wood also contains other polysaccharides and a significant percentage of lignin, another type of complex organic polymer.

Cellulose is a very large, straight-chain polymer formed from the polymerisation of β-glucose. The chain of glucose molecules in cellulose looks similar to that of starch. However, as Figure 15.6.13 shows, there is a different arrangement of the glucose units.

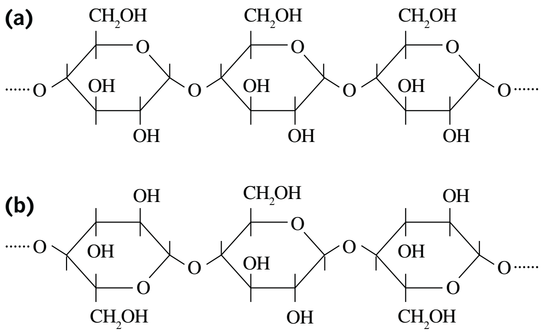


FIGURE 15.6.13 Sections of (a) starch and (b) cellulose polymers. Note the different orientations of the $-CH_2OH$ groups on adjacent glucose monomers.

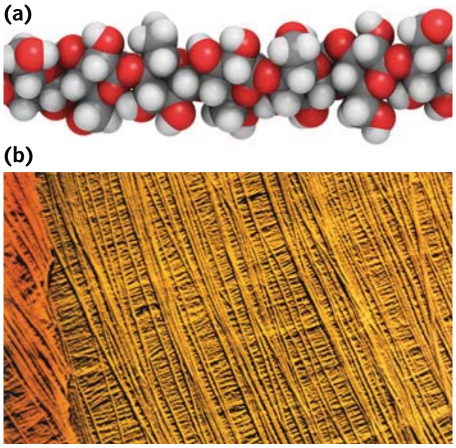


FIGURE 15.6.14 (a) This model shows the linear nature of a cellulose molecule. The oxygen atoms in the hydroxyl groups are coloured red. (b) A scanning electron microscope image shows the cellulose fibres in the walls of algae cells.

The alternating nature of the $-CH_2OH$ group in cellulose allows for good alignment of hydroxyl groups between neighbouring cellulose molecules. The result is hydrogen bonding between the molecules, resulting in a strong material that gives the plant support and rigidity. The linear nature of cellulose fibres is shown in Figure 15.6.14.

Glycogen

The third polysaccharide formed from polymerisation of glucose is **glycogen**. Glycogen is a polymer of α-glucose but is highly branched in a similar fashion to amylopectin (see Figure 15.6.15).

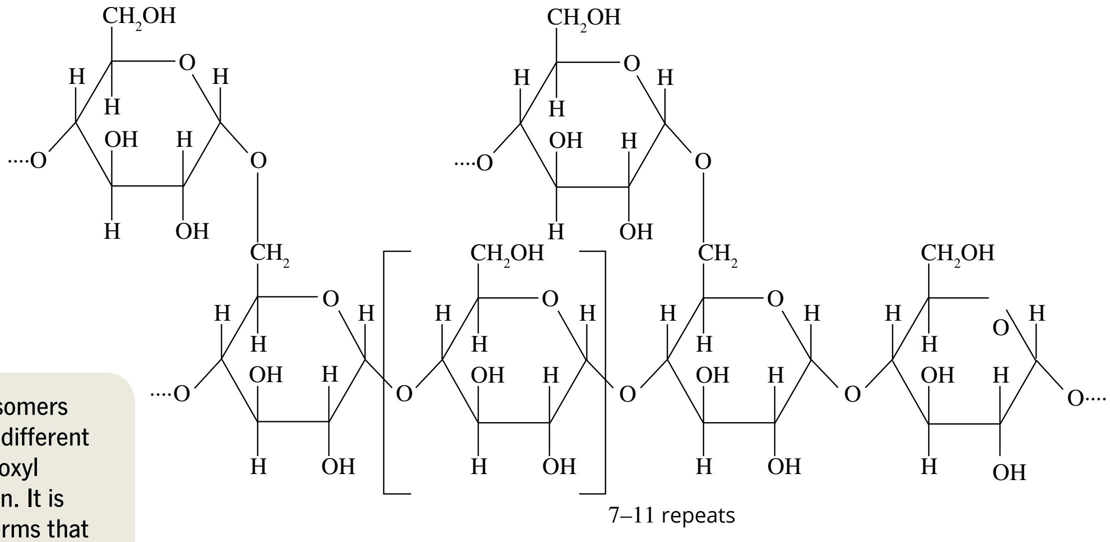


FIGURE 15.6.15 Glycogen is a highly branched polymer of α-glucose.

Glucose can form two isomers (α- and β-glucose) with different orientations of the hydroxyl group on the first carbon. It is because of these two forms that three of the most important polysaccharides found in living organisms exist—starch, cellulose and glycogen.

Animals use glycogen for energy storage. Glycogen is formed from excess glucose and stored in the liver or muscle tissue. If energy is needed, the glycogen can be broken down to glucose, which can then be used in cellular respiration.

EXTENSION

Carbohydrates in solution

The behaviour of some carbohydrates when they are dissolved in water can be quite complex. For example, monosaccharides can exist as isomers in equilibrium. Glucose isomers are shown in Figure 15.6.16.

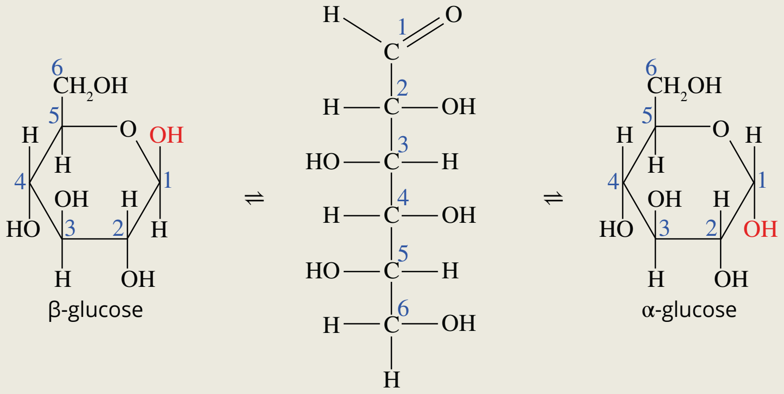


FIGURE 15.6.16 Glucose exists in solution in equilibrium between three isomers.

The existence of these three isomers of glucose in solution allows scientists to understand why two different forms of glucose can be found in many organisms. Figure 15.6.16 shows that β-glucose can be converted to α-glucose, and vice-versa, via the straight-chain form.

When the straight chain closes to make a ring, the –OH group bonded to carbon 1 can be above the ring or below the ring.

15.6 Review

SUMMARY

- Carbohydrates are made from the elements carbon, hydrogen and oxygen and usually have the formula $C_x(H_2O)_y$, where *x* and *y* are whole numbers.
- The main role of carbohydrates is as a source of energy for living things. Energy from the sun is transformed to chemical potential energy in carbohydrates.
- The smallest carbohydrates are monosaccharides.
- Glucose is an important monosaccharide. It is synthesised in plants through the process of photosynthesis.
- Monosaccharides are highly soluble in water as they contain several polar hydroxyl groups, allowing them to form hydrogen bonds with water molecules.
- Disaccharides are formed from condensation reactions between two monosaccharide molecules. The links formed between monosaccharides are known as ether or glycosidic links.
- Monosaccharides and disaccharides are often referred to as sugars because of their sweet taste.
- Aspartame is an example of an artificial sweetener. The energy content of aspartame is almost the same as that of sugar but aspartame is used in lower proportions because of its greater sweetness. Many 'diet' or 'light' products contain aspartame.
- Glucose can undergo condensation reactions to form a range of important polymers known as polysaccharides. The polysaccharides have different properties owing to the different orientations of the hydroxyl groups on the glucose units and the extent of branching in the polymer chain.
- Cellulose is a structural material in plants, starch is an energy storage material in plants and glycogen is an energy storage material in animals.
- Important carbohydrates are listed in Table 15.6.3.

TABLE 15.6.3 Important carbohydrates and their sources

Carbohydrate		Composition	Source
Monosaccharides	Glucose	$C_6H_{12}O_6$	Fruit juices
	Fructose	$C_6H_{12}O_6$	Fruit juices, honey
	Galactose	$C_6H_{12}O_6$	Not found naturally in its free form
Disaccharides	Maltose	Formed from glucose + glucose	Germinating grain
	Sucrose	Formed from glucose + fructose	Sugar cane, sugar beet
	Lactose	Formed from glucose + galactose	Milk
Polysaccharides	Glycogen	Polymer of glucose	Energy store in animals—in the liver and muscles
	Starch	Polymer of glucose	Energy store in plants—abundant in wheat, corn, potatoes etc.
	Cellulose	Polymer of glucose	Plant fibre—in plant cell walls

KEY QUESTIONS

1. Select the correct statements about starch (there may be more than one answer).
   - **A** Starch is a disaccharide.
   - **B** There are two common forms of starch.
   - **C** All forms of starch are highly soluble in water owing to the large number of hydroxyl groups.
   - **D** Starch is an energy storage molecule in plants.
   - **E** Starch is a polymer of sucrose.
   - **F** Many glycosidic links are formed when glucose reacts to form starch.
   - **G** Starch is composed of relatively large molecules.
2. Glucose is the most abundant monosaccharide. Draw a structural formula for glucose and use it to explain why it is highly soluble in water.
3. Glucose is described as a monosaccharide, maltose as a disaccharide and glycogen as a polysaccharide.
   - **a** What is the difference between these three types of carbohydrates?
   - **b** What type of reaction is involved in converting glucose to maltose and then to glycogen?
   - **c** Which functional group in the molecule is involved in these reactions?
4. The structure of lactose is shown in Figure 15.6.17. Lactose undergoes hydrolysis during digestion.

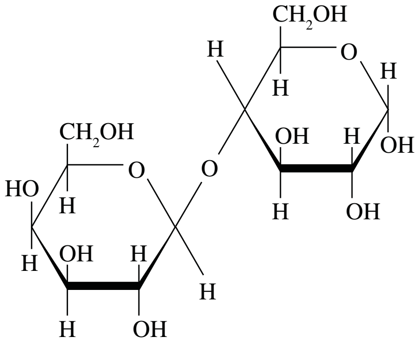


FIGURE 15.6.17 Structure of lactose.

   - **a** What is meant by the term 'hydrolysis'?
   - **b** Circle a hydroxyl and a glycosidic functional group in the molecule.
5. Name the carbohydrate that is a:
   - **a** structural material in plants
   - **b** energy storage material in animals
   - **c** energy storage material in plants
   - **d** disaccharide found in milk.
6. What is the difference between α-glucose and β-glucose?

15.7 Vitamins

The Australian government's National Health and Medical Research Council recommends that all babies receive a dose of vitamin K, as shown in Figure 15.7.1. Vitamin K aids the clotting of blood. Babies do not get enough vitamin K from their mothers during pregnancy or from breastfeeding. An injection or oral dose of the vitamin soon after birth helps to ensure that a baby does not suffer from serious bleeding if involved in an accident.

FIGURE 15.7.1 A newborn baby receiving a dose of vitamin K.

Up to this point, you have looked at the chemical substances in your diet that are required in large amounts. Proteins, fats and carbohydrates are all classed as **macronutrients**. Other substances, such as **vitamins**, are essential to your diet but in much lower concentrations than these macronutrients.

In this section, you will look at the structure and function of some of the most important vitamins.

BIOLOGICAL SIGNIFICANCE AND STRUCTURE

In 1912, Casimir Funk, a Polish biochemist, coined the word *vitamine* to describe the substances he was investigating that he felt were essential to life. 'Vita' is Latin for life. Funk thought each of the substances contained an **amine** group, and so used the term *vitamine* to name the substances he was investigating. Once it was discovered that some of them did not contain an amine group, the name was shortened to 'vitamin'.

Vitamins are organic compounds that are required in the diet (in addition to proteins, fats and carbohydrates) for the body to function properly. Vitamins also help to prevent specific diseases. For example, a deficiency of vitamin C leads to scurvy, and a deficiency of vitamin K can lead to uncontrolled bleeding. The roles of some important vitamins are listed in Table 15.7.1.

TABLE 15.7.1 The roles of some significant vitamins in the human body

Vitamin	Role in the human body
Vitamin D	Needed for absorption of calcium
Vitamin A	Needed for vision, healthy skin, bones and teeth
Vitamin B_1 (thiamine)	A coenzyme needed for the metabolism of energy in the body. Important vitamin needed for nerve functioning
Vitamin B_{12}	Supports the enzyme needed for making new cells

CHEMFILE

'Limeys'

British sailors are sometimes referred to as 'limeys'. The origin of the term dates back to the times when sailors on long voyages suffered a form of malnutrition known as scurvy. Someone with scurvy suffers from fatigue, swollen and bleeding gums and open sores (Figure 15.7.2).

In 1747, Scottish naval surgeon James Lind showed that the disease could be prevented by including fresh fruit and vegetables in the diet. On board the HMS *Salisbury*, he fed sailors suffering from scurvy different foods. He found the sailors fed limes and lemons recovered, the sailors fed boiled apple juice improved slightly and sailors on other diets did not improve.

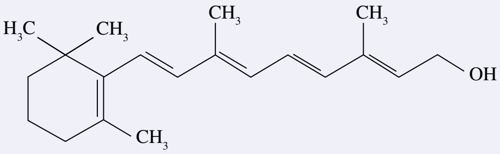
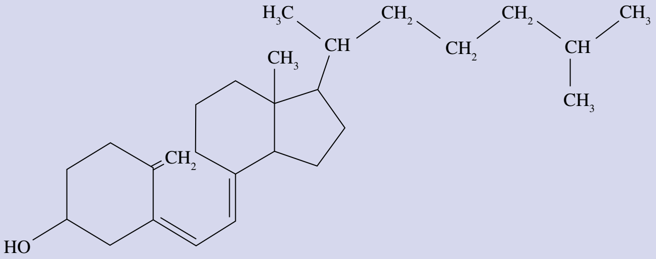
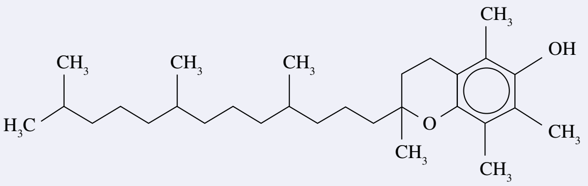
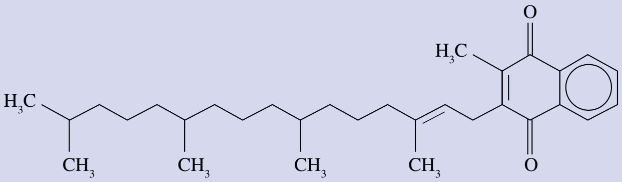
There was no refrigeration at the time so limes (hence the term 'limeys') and lemons were popular because they remain edible longer than most other fruits. It is now known that the ascorbic acid or vitamin C in citrus fruit is the reason limes prevent scurvy.

Scurvy is not necessarily a disease of the past. Students attending the University of Arizona in the 1990s were diagnosed with scurvy, as a consequence of very little fruit or vegetables in their diet!

FIGURE 15.7.2 Swollen gums are characteristic of scurvy.

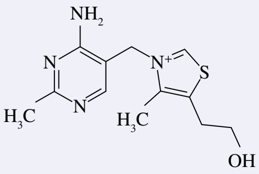
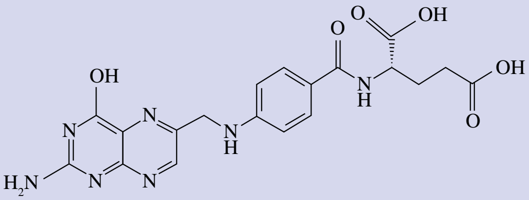
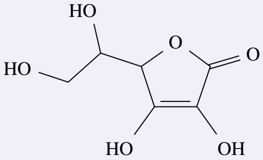
Unlike the macronutrients studied earlier in this chapter, vitamins do not share a common structure. Instead, vitamins are classified as fat soluble or water soluble. The four fat-soluble vitamins are described in Table 15.7.2

TABLE 15.7.2 Fat-soluble vitamins

Vitamin	Role and source
 Vitamin A (retinol)	Needed for maintaining good sight and healthy skin. Aids repair of body tissue. Source: dairy products, yellow vegetables, apricots and cantaloupes
 Vitamin D (calciferol)	Needed for making bones and absorption of calcium. Source: cod liver oil, egg yolks and dairy products
 Vitamin E (tocopherol)	Assists in maintaining cell membranes and guards fatty acids against oxidation (antioxidant). Source: plant oils and leafy green vegetables
 Vitamin K (phylloquinone)	Helps produce factors that support proper blood clotting. Source: leafy green vegetables and milk

There are nine water-soluble vitamins, some of which are shown in Table 15.7.3.

TABLE 15.7.3 Examples of water-soluble vitamins

Vitamin	Role and source
 Vitamin B_1 (thiamine)	Crucial for functioning of the nervous system. Aids in the digestion of carbohydrates. Source: nuts, seeds and whole-grain cereals
 Folic acid	Needed in the making of red blood cells. Helps prevent neural defects in a baby when taken during pregnancy. Source: leafy vegetables and legumes
 Vitamin C (ascorbic acid)	Important for the immune system and enhances the absorption of iron. Also acts as an antioxidant. Source: fresh fruit, particularly citrus

From the information in Tables 15.7.2 and 15.7.3, it should be evident that vitamins:

- do not have a common chemical structure
- are either fat soluble or water soluble
- are vital to the normal functioning of animals.

Most vitamins are considered essential because humans cannot synthesise them. The two exceptions are biotin and vitamin D. Biotin can be manufactured in the intestines, whereas vitamin D is synthesised in the skin after exposure to UV radiation.

Vitamins are essential because most vitamins cannot be synthesised in the human body. Vitamins are classified according to their solubility in water or fats.

SOLUBILITY OF VITAMINS

The solubility of vitamins is important because vitamins need to be transported and stored in the body. Water-soluble vitamins are likely to be found in the aqueous environment of the blood. Fat-soluble vitamins are found in fatty tissues.

The differences in solubility relate to the number of functional groups in the molecule that can form hydrogen bonds with water. The more of these groups there are in a vitamin molecule, the higher its solubility in water. One such group is the hydroxyl group (–OH). Figure 15.7.3 contrasts the number of hydroxyl groups on a water-soluble vitamin with those on a fat-soluble vitamin.

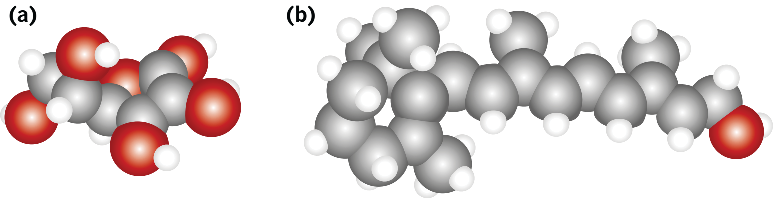


FIGURE 15.7.3 Models of a (a) water-soluble vitamin, vitamin C, and (b) fat-soluble vitamin, vitamin A. The oxygen atoms in hydroxyl groups are shown in red.

Fat-soluble vitamins have proportionally fewer groups that can form hydrogen bonds, making the molecules relatively non-polar. These non-polar vitamins can form dispersion forces with the lipids in the fat tissue of your body. This is another example of the 'like dissolves like' solubility rule.

Figure 15.7.4 shows that fat-soluble vitamins A and D have only one hydroxyl group in each molecule, whereas water-soluble vitamin C has four.

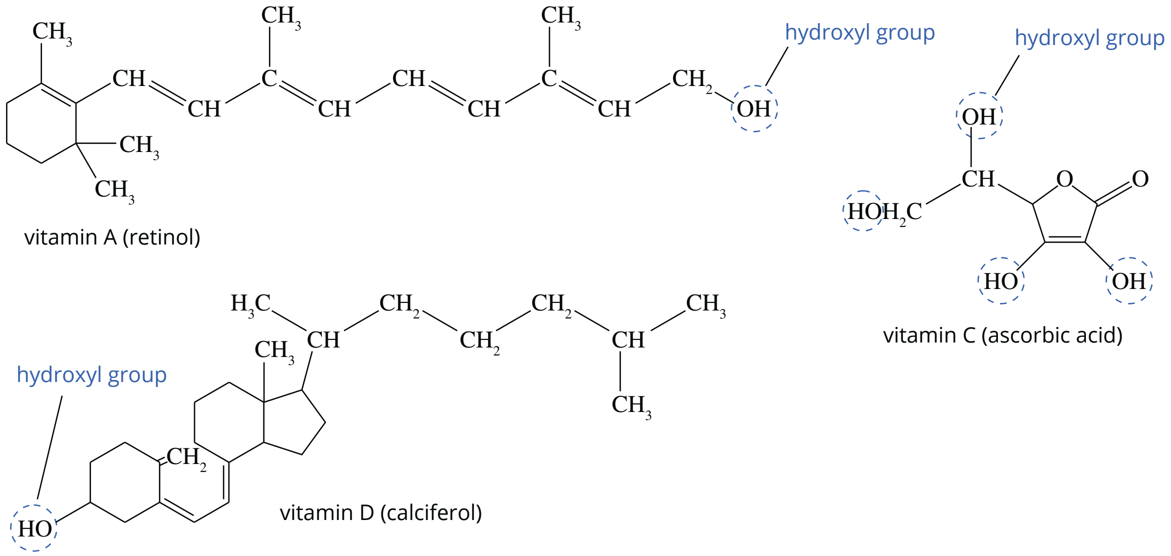


FIGURE 15.7.4 Chemical structures of vitamins A, C and D. The hydroxyl groups are circled. Vitamins A and D are fat soluble and vitamin C is water soluble.

The solubility of vitamins has implications for humans. For example, water-soluble vitamins:

- are excreted by the body if not used, so they must be consumed as a regular part of the diet
- should not be taken in large irregular doses as the extra amounts are not stored
- are removed from foods if they are cooked in water.

By contrast, fat-soluble vitamins can be stored in the body, in fatty tissue, for long periods of time. For example, an adult can store several years' supply of vitamin A. If the diet is deficient in vitamin A, these reserves are mobilised. However, a person taking excessive quantities of vitamin supplements is in danger of overdosing on fat-soluble vitamins because the body does not easily dispose of them. **Hypervitaminosis** is the term used for dangerously high vitamin levels.

The impact on the body of a vitamin deficiency varies with each vitamin. Figure 15.7.5 shows a person suffering from rickets, which results from a lack of vitamin D. Figures 15.7.6 and 15.7.7 show the effects of deficiencies in vitamin B_1 and vitamin B_3 respectively.

FIGURE 15.7.5 A deficiency of vitamin D can cause rickets. Rickets leads to irregular bone growth.

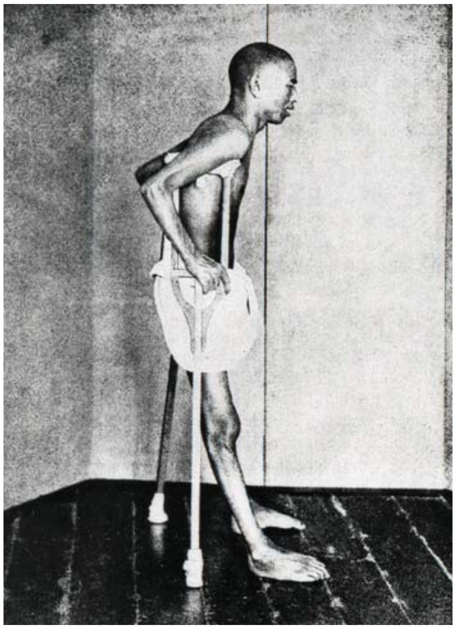


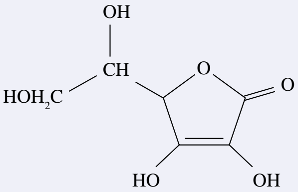
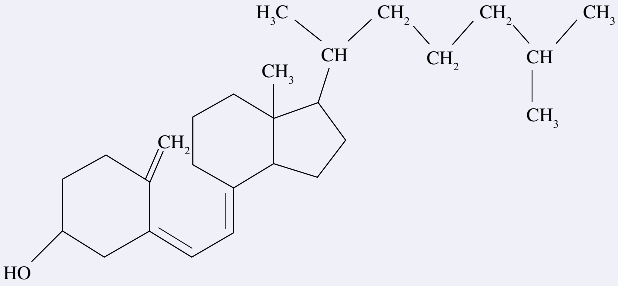
FIGURE 15.7.6 A deficiency in vitamin B_1 (thiamine) can lead to malnutrition in the form of beriberi. This disease was prevalent during World War I when many staple foods were unavailable.

FIGURE 15.7.7 A deficiency in vitamin B_3 (niacin) can lead to a skin condition known as pellagra.

A case study—vitamins C and D

As you have seen in this section, vitamins are either water soluble or fat soluble. Table 15.7.4 compares vitamins C and D. It includes some of the sources of these two types of vitamins and it outlines the significance of their different solubilities for humans.

TABLE 15.7.4 Comparison of water-soluble vitamin C with fat-soluble vitamin D

	Vitamin C	Vitamin D
Structure		
Bonding	Four hydroxyl groups Forms hydrogen bonds with polar molecules	One hydroxyl group Forms dispersion forces with non-polar molecules
Properties	Polar, soluble in water	Non-polar, soluble in fat
Significance of properties	Transported in the blood Passed from the body in urine Not stored in the body	Stored in fatty tissue
Essential or non-essential in diet	Essential	Non-essential (synthesised in skin after expose to UV radiation)
Sources	Cantaloupe, kiwi fruit, mango, pineapple, broccoli	Fish liver oil, fatty fish, mushrooms, egg yolks, milk

15.7 Review

SUMMARY

- Vitamins are organic compounds that are required in the diet for the body to function properly and to prevent specific diseases.
- Vitamins do not share a common molecular structure.
- Vitamins are classified as water soluble or fat soluble.
- Vitamins are water soluble if their molecules contain several functional groups that can form hydrogen bonds with water. Water-soluble vitamins are not stored in the body. Vitamin C is a water-soluble vitamin.
- Fat-soluble vitamins are insoluble in water because a large proportion of their molecules are non-polar. They can be stored in fatty tissue in the body for long periods of time, where they form dispersion forces with the lipids in fatty tissue. Vitamin D is a fat-soluble vitamin.
- Deficiencies in vitamins lead to diseases or conditions such as scurvy, dermatitis and beriberi.

KEY QUESTIONS

1 Select the statements that are correct for vitamins.

A Vitamins are required in the diet in similar amounts to proteins.
B A range of foods must be consumed to meet your vitamin needs.
C All vitamins have similar structures, just different molecule lengths.
D Fat-soluble vitamins do not contain any hydroxyl groups.
E All fat-soluble vitamins perform the same function in the body.
F Humans cannot synthesise most vitamins.
G Vitamins can be harmful if taken in excess.

2 Figure 15.7.8 is a structural diagram of a vitamin found in the human body. Fill in the gaps in the following paragraph related to this vitamin.

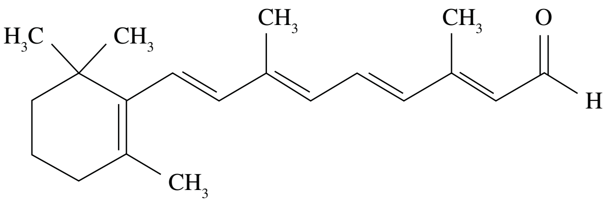


FIGURE 15.7.8 Structure of a vitamin.

This molecule is __________ in water because a large proportion of the molecule is ______________. It is ______________ in fat because ______________ ______________ are formed between the molecule and lipids in fatty tissue.

3 Warfarin is a medication given to people after surgery to prevent blood clotting.

a Warfarin interferes with the production of which vitamin in the liver involved in blood clotting?

b What property of this vitamin allows it to be stored in the body, making warfarin treatment necessary?

Chapter review

KEY TERMS

α-helix
amide
amine
amino acid
2-amino acid
amino acid residue
amylopectin
amylose
β-pleated sheet
C-terminal
carbohydrate
cellulose
cis arrangement
cis isomer
coiling
complementary proteins
condensation polymerisation
condensation reaction
dipeptide
dipolar ion
disaccharide
disulfide bridge
endothermic
essential amino acid
essential fatty acid
ester link
ether link
fatty acid
functional group
glucose
glycogen
glycosidic link
hydrolysis
hydrophobic
hypervitaminosis
lipid
macronutrient
monomer
monosaccharide
monounsaturated fatty acid
N-terminal
non-essential fatty acid
omega carbon
omega-3 fatty acid
omega-6 fatty acid
peptide link
photosynthesis
pleating
polypeptide
polysaccharide
polyunsaturated fatty acid
primary structure
protein
protein sequencing
quaternary structure
R group
saturated fatty acid
secondary structure
side chain
starch
steroid
tertiary structure
trans isomer
triglyceride
tripeptide
vitamin
zwitterion

Amino acids

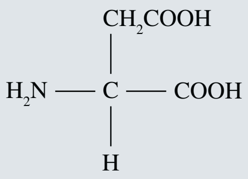
1 Select the correct statement about amino acids.

- **A** Amino acids contain only the elements C, H, O and N.
- **B** All 20 amino acids needed by humans are known as essential amino acids.
- **C** Amino acids may contain more than one nitrogen atom.
- **D** The functional group on an amino acid side chain is always non-polar.

2 What two functional groups are present in all amino acids?

3 Draw the general structure of an amino acid. Colour the amino group in blue and the carboxyl group in red.

4 Aspartic acid is one of the non-essential amino acids shown in Figure 5.8.1. It exists mainly as a zwitterion at pH 2.8.



$$H_2N-\overset{\displaystyle CH_2COOH}{\underset{\displaystyle H}{C}}-COOH$$

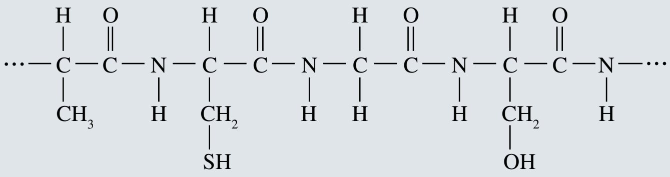
FIGURE 15.8.1 Structure of aspartic acid.

- **a** Name the:
  - **i** acidic functional group
  - **ii** basic functional group.
- **b** Explain what is meant by the term ‘zwitterion’.
- **c** Draw the structure of the molecule as it is most likely to exist in a solution at:
  - **i** pH much greater than 2.8
  - **ii** pH much less than 2.8
  - **iii** pH 2.8.

The formation of proteins

5 When alanine and glycine react, two different dipeptides can be formed.

- **a** Write the condensed structural formula of each dipeptide.
- **b** How many tripeptides can be formed from three amino acids?
- **c** Proteins are formed using 20 different amino acids and can be hundreds of amino acid units in length. On the basis of your answers to parts **a** and **b**, what can you say about the number of different proteins possible?
- **d** Circle the peptide links in the section of a protein chain shown in Figure 15.8.2.



$$\cdots-\overset{\displaystyle H}{\underset{\displaystyle CH_3}{C}}-\overset{\displaystyle O}{\overset{\|}{C}}-\underset{\displaystyle H}{N}-\overset{\displaystyle H}{\underset{\displaystyle CH_2SH}{C}}-\overset{\displaystyle O}{\overset{\|}{C}}-\underset{\displaystyle H}{N}-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-\overset{\displaystyle O}{\overset{\|}{C}}-\underset{\displaystyle H}{N}-\overset{\displaystyle H}{\underset{\displaystyle CH_2OH}{C}}-\overset{\displaystyle O}{\overset{\|}{C}}-\underset{\displaystyle H}{N}-\cdots$$

FIGURE 15.8.2 A section of a protein chain.

- **e** Write the formulas of the amino acids that make up this section of the chain.

Primary and secondary structures of proteins

6 Identify the type of bonding represented by labels **a** and **b** of the diagram in Figure 15.8.3. Identify the type of secondary structure in **c**.

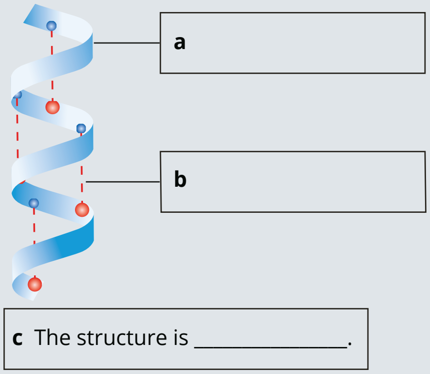


FIGURE 15.8.3 Bonding and structure.

7 How does a β-pleated sheet structure form in a protein?

Tertiary and quaternary structures of proteins

8 Some proteins exhibit quaternary structure. Which of the following statements describes this level of structure?

A A single polypeptide chain twisted into a series of helices by hydrogen bonding between peptide links

B The sequence (number, order and type) of amino acids in a polypeptide chain

C An association of two or more polypeptide chains joined by peptide links between the chains

D An association of two or more polypeptide chains held together by dispersion forces and other bonds

9 Circle the parts of the polypeptide segment in Figure 15.8.4 that might be involved in forming bonds responsible for the tertiary or quaternary structures of the protein molecule.

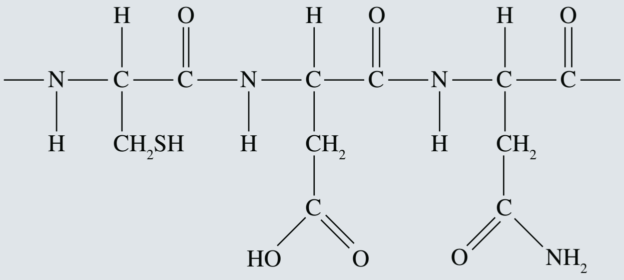


FIGURE 15.8.4 A polypeptide segment.

10 Mutations can cause the wrong amino acid to be inserted into a protein chain when it is being assembled. In some instances such a mistake has no effect on the function of the protein but in others it disables the protein. Explain how a single change in a protein's primary structure could cause such dramatically different results.

11 Explain what is meant by the primary, secondary and tertiary structures of a protein.

Fats and oils

12 Select the best reason for ensuring that you include omega-3 fatty acids and omega-6 fatty acids in your diet.

A They are needed as an energy source.

B They are the best form of energy storage.

C Some cannot be made in the body from other organic compounds.

D They are oils, rather than solid fats.

13 Describe the bonding between carbon atoms in the hydrocarbon tails in the following types of fatty acids.

a Saturated

b Monounsaturated

c Polyunsaturated

14 The structure of the fatty acid linoleic acid is:

$$CH_3(CH_2)_4CH{=}CHCH_2CH{=}CH(CH_2)_7COOH$$

a Name the chemical needed to react with linoleic acid to form a triglyceride.

b Draw the structure of the triglyceride made from linoleic acid.

c Name and circle the functional groups in the triglyceride molecule.

d Classify the triglyceride as saturated, monounsaturated or polyunsaturated.

e Is this triglyceride likely to be a solid or liquid at room temperature? Explain.

15 Sunflower oil is a liquid that can be used to make margarine. How are polyunsaturated oils, such as sunflower oil, converted to a solid form?

16 What is the difference between an omega-3 fatty acid and an omega-6 fatty acid?

Carbohydrates

17 Select the best explanation for why aspartame is used in diet foods in place of sugar.

A Aspartame molecules do not release energy in the human body.

B Aspartame is many times sweeter than sugar so less can be used.

C A given mass of aspartame releases less energy than an equivalent mass of sugar.

D Aspartame molecules absorb energy in the human body.

18 By referring to Figure 15.6.4 (on page 497), draw structural formulas to show the hydrolysis of maltose.

19 Why is glycogen sometimes referred to as animal starch?

20 The human brain relies almost exclusively on glucose as an energy source. Normal functioning of the brain depends on a constant supply of glucose from the blood. Explain how your body maintains a fairly constant concentration of glucose in the blood even though you don't eat foods that supply glucose constantly throughout the day.

21 Use the following terms to complete labels a–e in Figure 15.8.5, which shows the formation of a polysaccharide: polysaccharide, disaccharide, carbon dioxide, glycosidic link, glucose.

Vitamins

22 Vitamins C and E are both essential vitamins. While you need to consume regular doses of vitamin C, you can consume vitamin E less frequently. Select a likely reason for this difference.

- **A** Vitamin C is essential but vitamin E can be produced by humans.
- **B** Vitamin C is water soluble, whereas vitamin E is fat soluble.
- **C** Vitamin C is often stored in fat and is unavailable to the human body.
- **D** Vitamin E can be stored in the blood due to its solubility in water.

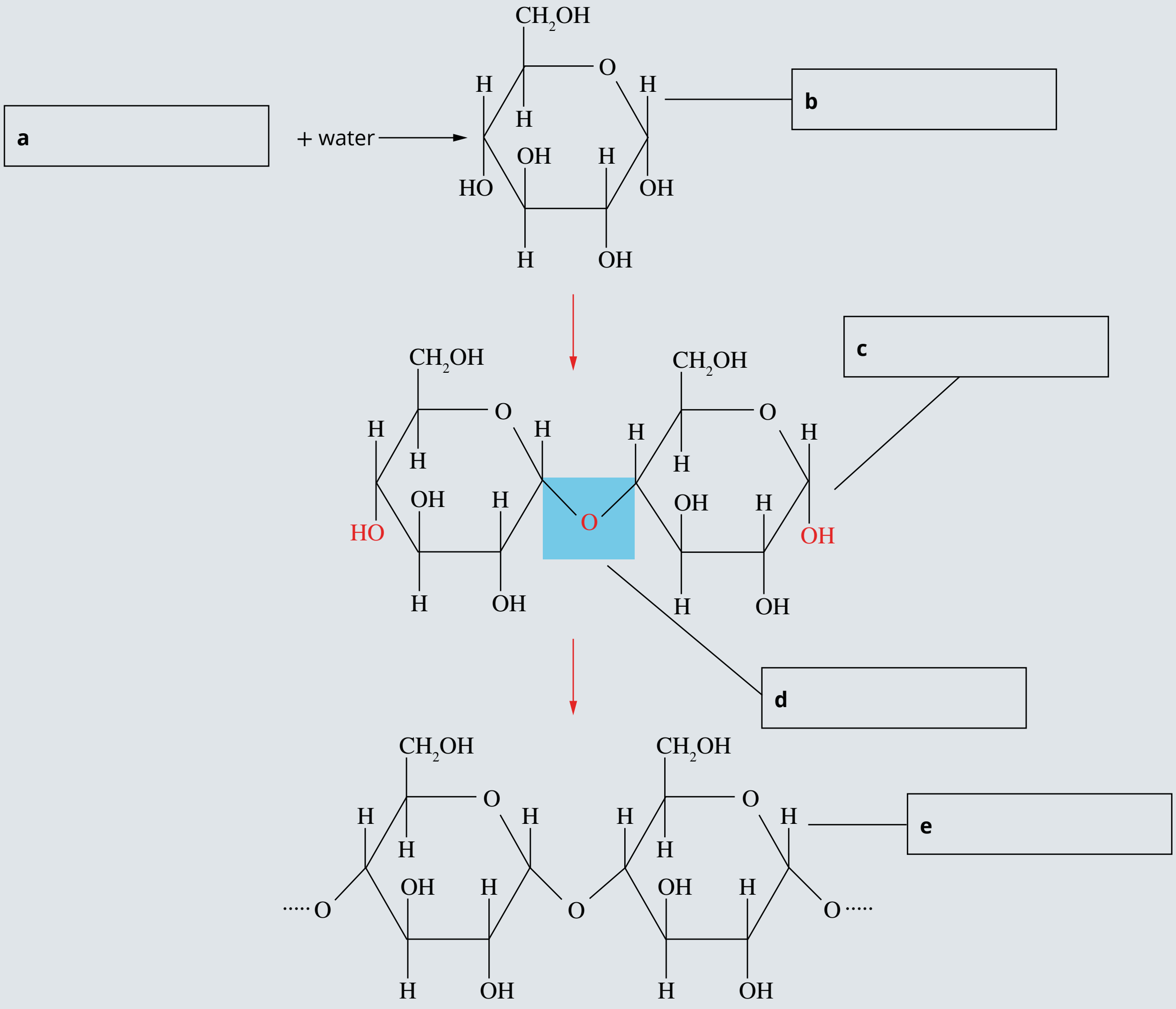


FIGURE 15.8.5 The formation of a polysaccharide.

23 Classify the following as properties of vitamin C or vitamin D.

- **a** Water soluble
- **b** Can be stored in the body
- **c** Can be made in the body
- **d** Fat soluble
- **e** Contains one hydroxyl group
- **f** Contains several hydroxyl groups
- **g** Found in fruit
- **h** Forms extensive hydrogen bonds with water
- **I** Mainly forms dispersion forces with other molecules
- **j** Found in fatty fish
- **k** Soluble in blood
- **l** Cannot be stored in the body

Connecting the main ideas

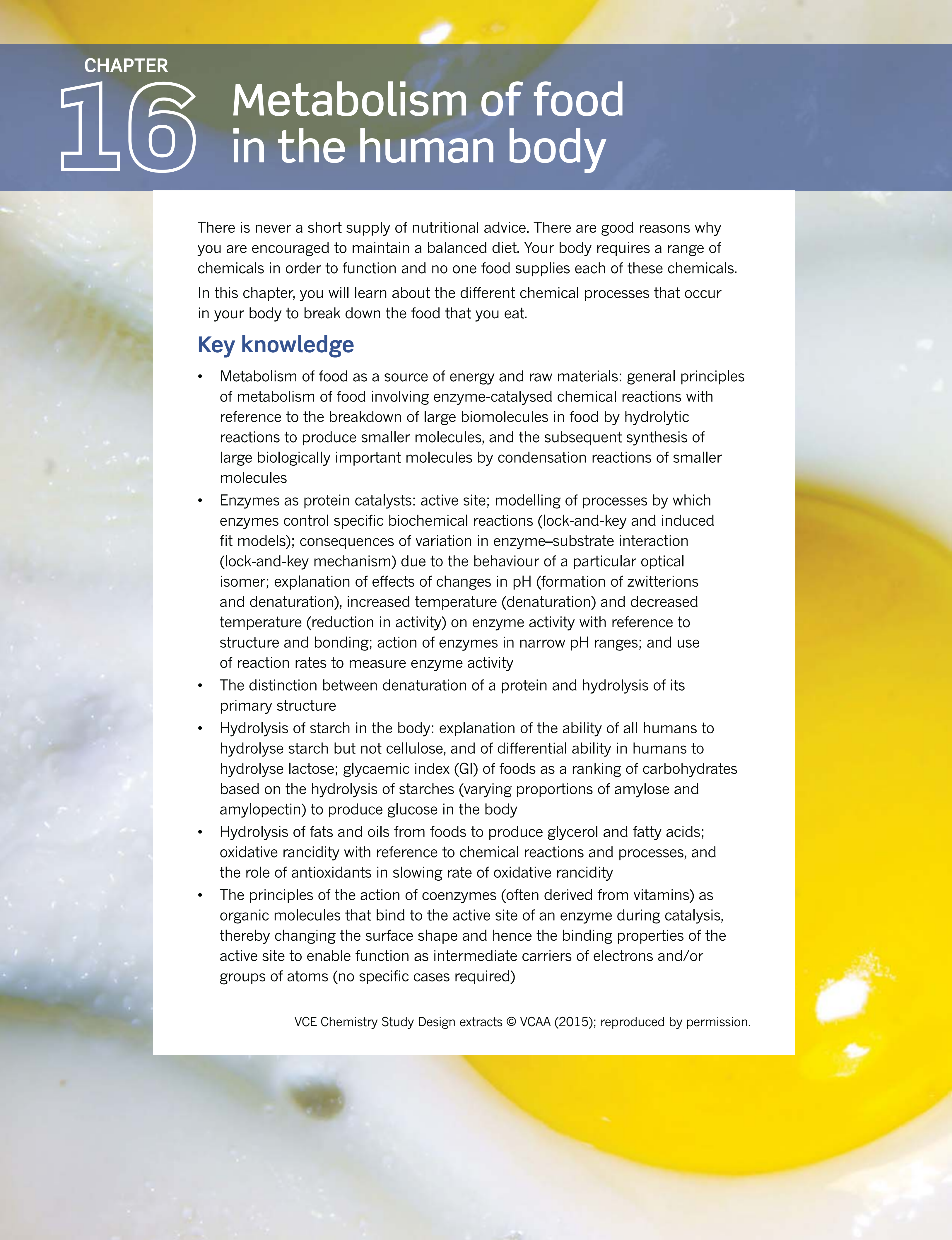
24 Classify each of the following substances obtained from food as soluble or insoluble in water.

- **a** Glycerol
- **b** Canola oil
- **c** Lactose
- **d** Cellulose
- **e** Glycine
- **f** Palmitic acid

25 What functional groups react to form each of the following, and with which biological polymers are each of the links associated?

- **a** An ester link
- **b** A glycosidic link
- **c** A peptide link

26
- **a** Explain the difference between condensation reactions and hydrolysis reactions.
- **b** What is the importance of these reactions in the human body?
- **c** Write equations for condensation reactions between:
  - **i** two glucose molecules
  - **ii** a glycerol molecule and three palmitic acid molecules
  - **iii** two alanine molecules.



CHAPTER 16

Metabolism of food in the human body

There is never a short supply of nutritional advice. There are good reasons why you are encouraged to maintain a balanced diet. Your body requires a range of chemicals in order to function and no one food supplies each of these chemicals.

In this chapter, you will learn about the different chemical processes that occur in your body to break down the food that you eat.

Key knowledge

- Metabolism of food as a source of energy and raw materials: general principles of metabolism of food involving enzyme-catalysed chemical reactions with reference to the breakdown of large biomolecules in food by hydrolytic reactions to produce smaller molecules, and the subsequent synthesis of large biologically important molecules by condensation reactions of smaller molecules
- Enzymes as protein catalysts: active site; modelling of processes by which enzymes control specific biochemical reactions (lock-and-key and induced fit models); consequences of variation in enzyme–substrate interaction (lock-and-key mechanism) due to the behaviour of a particular optical isomer; explanation of effects of changes in pH (formation of zwitterions and denaturation), increased temperature (denaturation) and decreased temperature (reduction in activity) on enzyme activity with reference to structure and bonding; action of enzymes in narrow pH ranges; and use of reaction rates to measure enzyme activity
- The distinction between denaturation of a protein and hydrolysis of its primary structure
- Hydrolysis of starch in the body: explanation of the ability of all humans to hydrolyse starch but not cellulose, and of differential ability in humans to hydrolyse lactose; glycaemic index (GI) of foods as a ranking of carbohydrates based on the hydrolysis of starches (varying proportions of amylose and amylopectin) to produce glucose in the body
- Hydrolysis of fats and oils from foods to produce glycerol and fatty acids; oxidative rancidity with reference to chemical reactions and processes, and the role of antioxidants in slowing rate of oxidative rancidity
- The principles of the action of coenzymes (often derived from vitamins) as organic molecules that bind to the active site of an enzyme during catalysis, thereby changing the surface shape and hence the binding properties of the active site to enable function as intermediate carriers of electrons and/or groups of atoms (no specific cases required)

16.1 Metabolism of food

Some industries take in raw materials and modify or redevelop these materials to make different products. The manufacturing of latex rubber products illustrated in Figure 16.1.1 is an example of such a process. Latex is harvested from a rubber tree and taken to a factory where it is processed into products such as balloons and latex gloves.

FIGURE 16.1.1 Latex is collected from rubber trees and processed in a factory like the one shown to produce latex gloves and other products.

In many ways the human body can be regarded as a natural factory. The food you consume contains the raw materials that are processed and modified in your body (Figure 16.1.2). Chemical bonds are broken and new bonds are formed as the molecules you need to survive are produced or extracted.

In this chapter, you will investigate a complex process that is easy to take for granted: the operation of your digestive system.

FIGURE 16.1.2 Your body takes in food as raw materials and processes it into molecules that you require. These molecules can then be used to synthesise more complex structures such as the enzyme shown here that breaks down glycogen, releasing glucose for energy.

NUTRIENTS

Food supplies **nutrients** for the human body. Nutrients are large **biomolecules** that are used by the body to provide energy, regulate growth and maintain and repair body tissue. Proteins, **triglycerides** (fats and oils), carbohydrates, minerals, vitamins and water are all nutrients.

Nutrients have a number of functions in the body, with different nutrients having different primary functions. Carbohydrates and triglycerides are the primary sources of energy for living systems. While proteins can also provide energy, their main role is in growth and tissue repair. The body requires each of these nutrients in relatively large quantities, so they are classed as **macronutrients**. Table 16.1.1 lists the different types of nutrients available through food.

TABLE 16.1.1 The nutrients in food and their sources

Nutrients	Function	Typical sources
Carbohydrates	Energy source Dietary fibre	Potatoes, bread, honey, celery
Triglycerides	Energy source	Margarine, butter, oils
Proteins	Growth and repair of tissues Control of reactions Energy source Other functions	Meat, fish, lentils, eggs
Mineral salts	Various specialised roles, e.g. a source of ions for cellular processes and muscle function	Meat, vegetables, dairy products
Vitamins	Various specialised roles, e.g. disease prevention	Milk, meat, vegetables, fruit
Water	Solvent Transport agent Reagent for hydrolytic reactions	Drinks, fruit, vegetables

Minerals such as sodium, potassium, magnesium, phosphorus, sulfur and chlorine are also considered macronutrients. There are also many other substances that you need in your diet in much smaller amounts. These **micronutrients** are essential for normal functioning of the body and include vitamins and trace minerals such as copper, fluorine, zinc, iodine, selenium, manganese, molybdenum, chromium, cobalt and boron. Common mineral nutrients are shown in Figure 16.1.3.

Micronutrients are essential for normal functioning of the body. Deficiencies can result in disease and developmental defects.

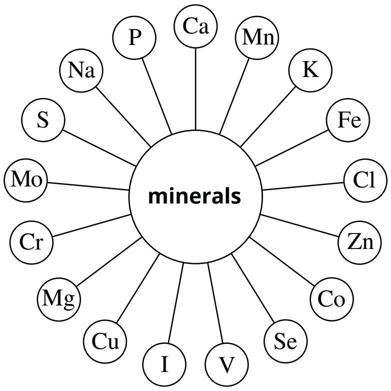


FIGURE 16.1.3 Micronutrients required by the human body.

CHEMISTRY IN ACTION

The importance of micronutrients

Although you only require small amounts of micronutrients in your diet, deficiencies can lead to severe health problems and disease.

The World Health Organization lists iron deficiency as the most common nutrient deficiency in the world, affecting people in both developing nations and in developed countries. Iron is usually obtained in the diet through the eating of red meat, so vegetarians and vegans are at high risk of developing an iron deficiency and may need to take iron supplements to remain healthy. Without sufficient iron, you can develop anaemia.

People suffering with anaemia don't have sufficient haemoglobin (the protein that transports oxygen in the blood). They can have symptoms such as lethargy and, in severe cases, trouble breathing. The structure of haemoglobin and its role in the body was discussed in Chapter 15 on page 483. The situation is more serious if growing children develop anaemia. Iron deficiency in the very young can lead to developmental problems, specifically in the spinal cord, and stunted growth.

Deficiencies in other micronutrients can also lead to serious diseases. A lack of vitamin D when you are very young can cause rickets. The structure of vitamin D and problems associated with rickets was discussed in Chapter 15 on page 508. The lack of vitamin D prevents proper absorption of calcium in bones. This stops the bones from hardening, causing malformations and bowing of the legs. In adults vitamin D deficiency can lead to osteomalacia, a condition that results in softening of the bones (Figure 16.1.5).

Skin lesions and severe weight loss can be signs of vitamin B_3 deficiency.

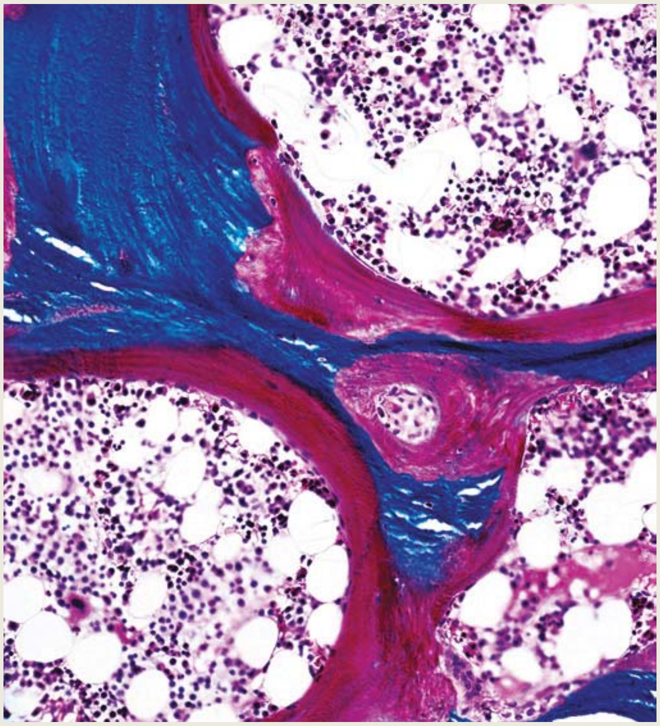


FIGURE 16.1.4 Light micrograph of a section through bone tissue in osteomalacia. The network of bone struts have a core (blue), surrounded by new but incomplete bone growth shown in pink. The spaces between the bone struts are white and filled with cells (dark nuclei). This abnormal bone growth leads to bone deformities. The condition can also lead to calcium being released from the bones, increasing blood calcium levels.

In Australia, people are very lucky to have access to fresh fruit and vegetables and healthy foods that are needed to prevent malnutrition and the diseases that are related to insufficient consumption of essential micronutrients.

METABOLISM

Metabolism refers to the chemical processes occurring within a living cell or organism that are necessary for the maintenance of life. A simplified version of metabolism is represented in Figure 16.1.5. Metabolism involves the breakdown of substances, usually the nutrients you obtain from food, to yield energy for vital processes. Another aspect of metabolism involves the synthesis of larger molecules that are necessary for life from smaller molecules.

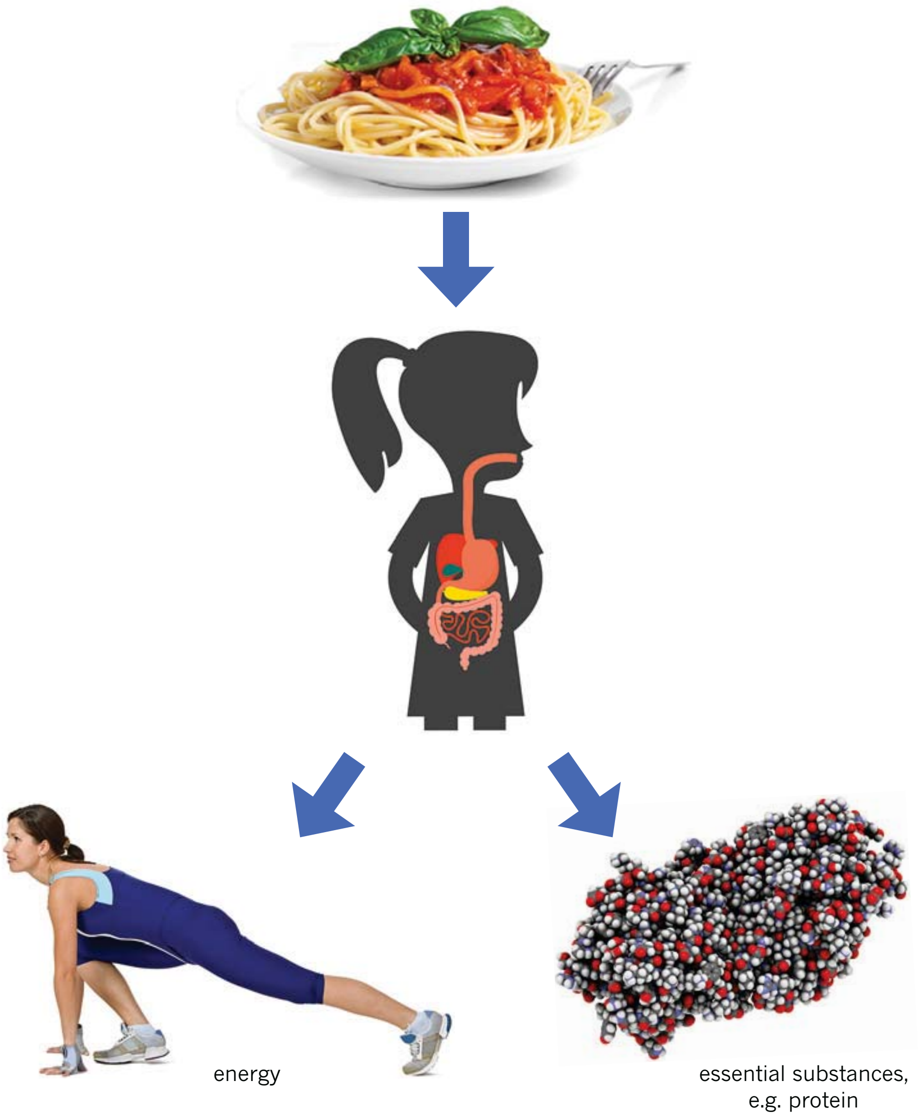


FIGURE 16.1.5 Through the process of metabolism, foods provide energy and the raw materials needed to construct essential substances like protein.

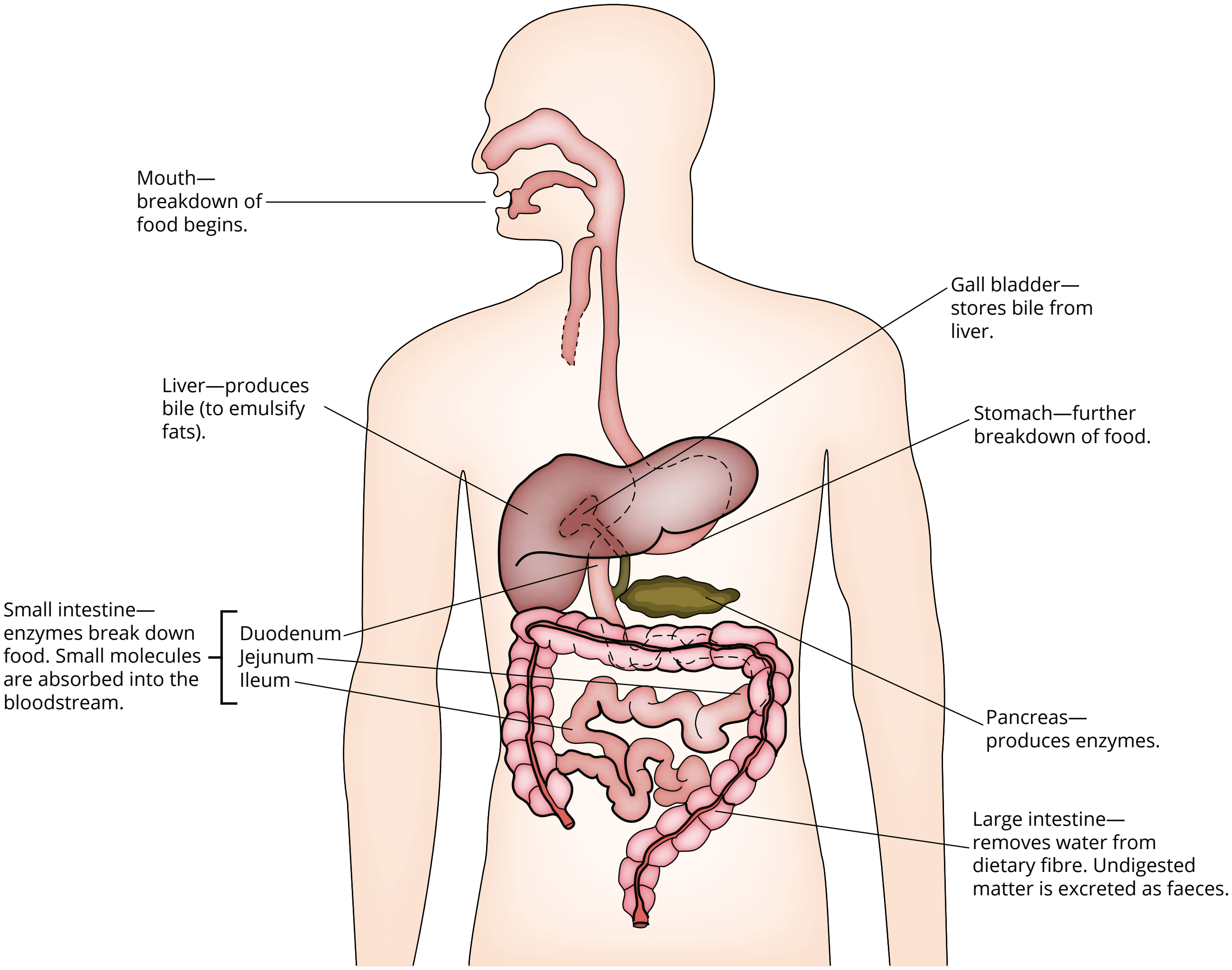
Metabolism is all the chemical reactions that occur within a living organism to maintain life.

DIGESTION

In animals, the metabolism of food starts in the digestive system. As soon as food enters the mouth, it begins to be broken down into smaller molecules in a process called **digestion**. Digestion is a complex process that involves large numbers of separate **enzymes** throughout the digestive system, which break down different components of the food.

Enzymes are highly specific biological catalysts. Each enzyme increases the rate of particular biochemical reactions. You will learn more about the action of enzymes and their specificity in sections 16.2 and 16.3.

A general outline of the metabolism of food through digestion in the body is shown in Figure 16.1.6 (on page 520).



Mouth
- Food is chewed into small pieces.
- Enzymes present in saliva react with components of food

→

Stomach

Food is broken down further by the combined action of hydrochloric acid and enzymes.

→

Small intestine
- Enzymes from the pancreas and the wall of the duodenum act on complex food molecules to produce smaller molecules.
- The smaller molecules are absorbed into the blood and transported around the body.

→

Large intestine
- Water is absorbed from the food.
- Bacteria in the colon ferment some of the fibre to produce useful small molecules.
- Remaining undigested fibre is excreted from the body as faeces.

FIGURE 16.1.6 Digestion starts as soon as food enters the mouth. As the food progresses down the gastrointestinal tract, different processes break down different components of the food. These reactions are catalysed by specific enzymes.

ℹ Digestion is one aspect of your metabolism. It breaks down food into the essential nutrients required by your body.

Digestion of carbohydrates

The digestion of carbohydrates starts in your mouth. Chewing increases the surface area of the food. It also mixes the food with your saliva, which contains the digestive enzyme amylase. Carbohydrates in your food (usually in the form of starch) are broken down into smaller **disaccharides**. The breakdown of carbohydrates continues in the first two areas of your small intestine—the duodenum (Figure 16.1.7) and the jejunum, which contain a number of digestive enzymes. These digestive enzymes are produced in the pancreas.

In the small intestine, disaccharides such as maltose are broken down by specific enzymes into glucose and other monosaccharides (Figure 16.1.8). The breakdown of carbohydrates is covered in more detail in section 16.4.

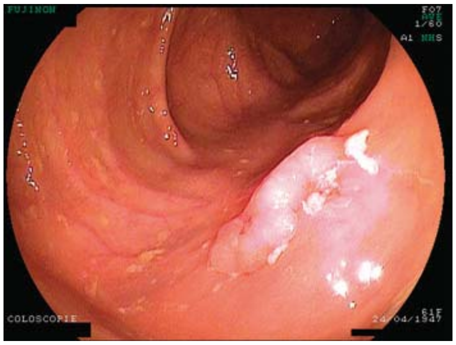


FIGURE 16.1.7 Interior of the duodenum. The duodenum receives food from the stomach and mixes it with a range of enzymes. This duodenum has polyps, a series of benign tumours.

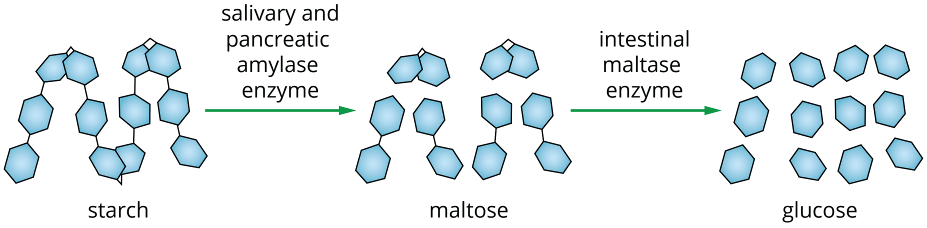


FIGURE 16.1.8 The digestion of carbohydrates requires specific enzymes found in the mouth and small intestine.

DIGESTION OF PROTEINS

The digestion of proteins produces individual amino acids, which are used by the body to synthesise enzymes and other essential proteins. Proteins are initially broken down by the enzyme pepsin, which is found in the stomach. This produces shorter polypeptide chains that move into the duodenum. Once in the small intestine, the polypeptides are broken down into smaller dipeptides. Further along in the intestine dipeptides are broken down into amino acids (Figure 16.1.9).

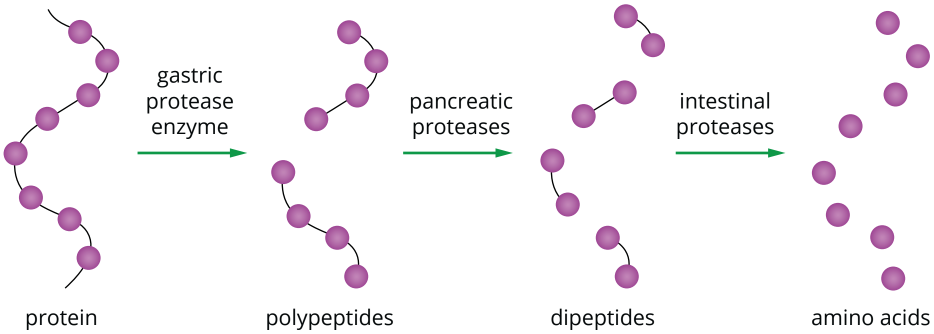


FIGURE 16.1.9 The digestion of proteins starts in the acidic environment of the stomach with the enzyme pepsin. At each stage of digestion, the peptide chains are broken into smaller units until eventually individual amino acids are released.

There are nine essential amino acids that, like vitamins and other micronutrients, must be consumed in your food.

Digestion of triglycerides

Triglycerides are fats and oils. The digestion of these large molecules is catalysed by the enzyme lipase. Lipase is found in the duodenum in the small intestine and hydrolyses the ester links in triglycerides, producing glycerol and fatty acids (Figure 16.1.10).

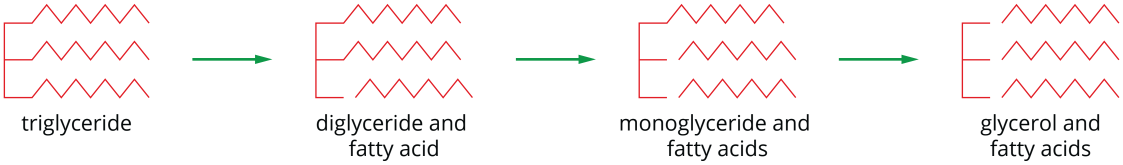


FIGURE 16.1.10 The digestion of triglycerides is catalysed by the enzyme lipase in the duodenum.

The breakdown of fats and oils is covered in more detail in section 16.5.

The process of digestion brings together many of the chemical concepts you have studied so far. A few examples are:

- reaction rates: chewing food increases its surface area, speeding up digestion
- solubility: food consists of polar and non-polar substances. Polar substances are digested in aqueous acid solutions in the stomach, but non-polar molecules pass through the stomach and are digested in the non-polar environment of the intestines
- enzyme action: each body cell contains as many as 2000 enzymes, each with special functions
- polymerisation: proteins and polysaccharides are built up from monomers in condensation polymerisation reactions.

ℹ Enzymes catalyse the hydrolysis of nutrients in the body. Different enzymes are found at different stages of the digestive system.

HYDROLYSIS AND CONDENSATION REACTIONS

The human body does not break down molecules to individual atoms; rather it reduces compounds to smaller soluble molecules that form the building blocks for new substances. These molecules are then transported to different parts of the body where they are reassembled.

The breakdown and subsequent rebuilding of nutrients such as proteins, carbohydrates and triglycerides involves two main types of chemical reactions that you are already familiar with.

- **Hydrolysis**: reactions involving hydrolysis are also referred to as **hydrolytic reactions**. They involve splitting large molecules by their reaction with water molecules.
- **Condensation**: condensation reactions (see Chapter 11) involve joining two smaller molecules to form a larger molecule with the elimination of a small molecule (water).

Enzymes are crucial for both types of reactions to occur in biological systems. Each step uses a particular enzyme that increases the reaction rate. Some enzymes catalyse only one particular reaction, whereas other enzymes are specific for a reaction involving a particular type of chemical bond or functional group.

Hydrolysis and condensation reactions can be regarded as the opposite of each other. Figure 16.1.11 shows a number of important reactions involved in digestion. The forward reaction in these examples shows the formation of larger biomolecules. The reverse reaction illustrates their breakdown through hydrolysis.

ℹ Condensation reactions and hydrolysis are reversible. They can be considered as the opposite of each other.

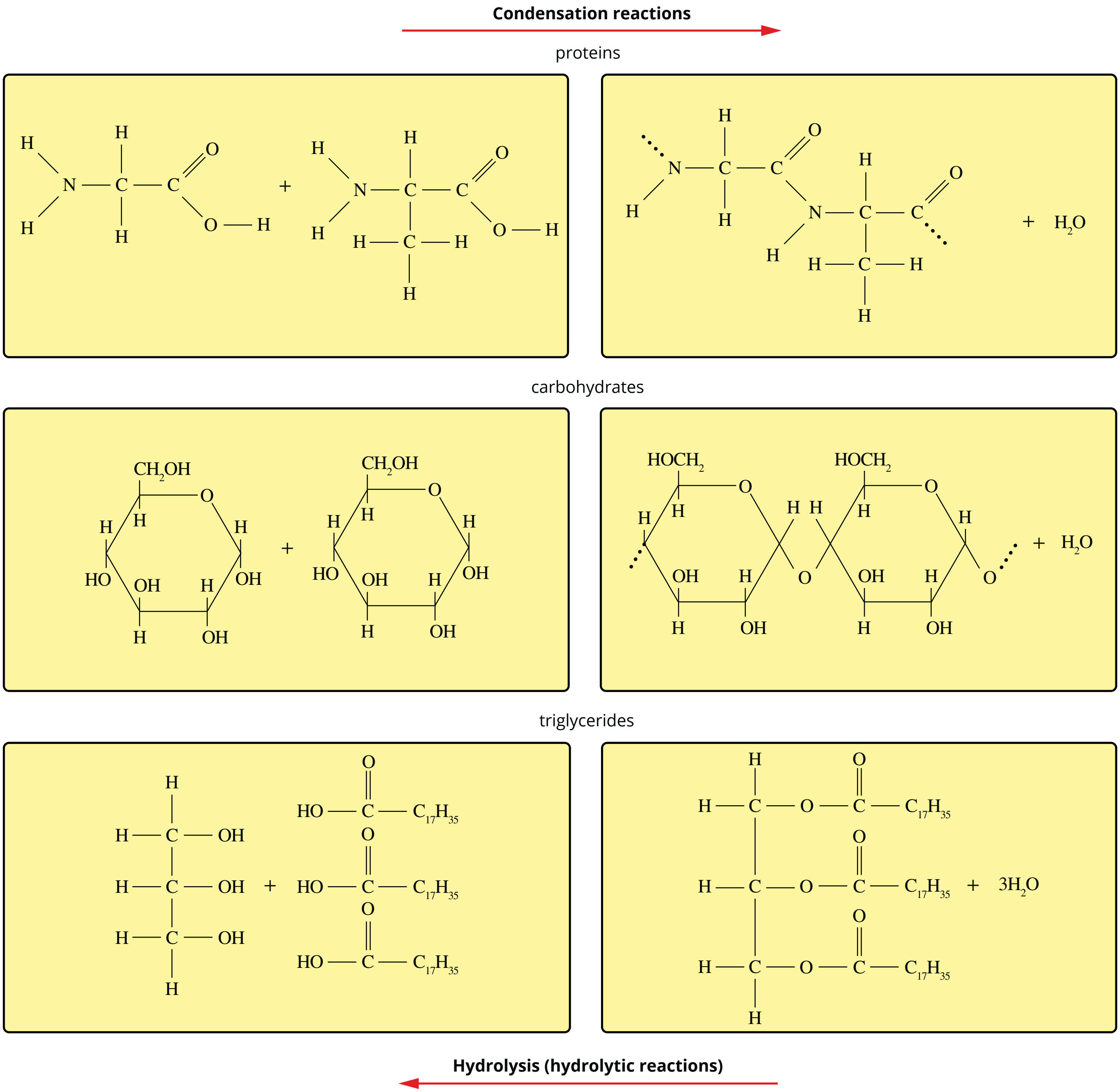


FIGURE 16.1.11 Condensation and hydrolytic reactions involving proteins, carbohydrates and triglycerides.

Figure 16.1.12 (page 524) illustrates the cycle of hydrolysis and condensation for proteins, carbohydrates and fats.

- Proteins are hydrolysed to soluble amino acids that are transported through the body to cells. Once inside cells, amino acids can be reassembled in condensation reactions to form new proteins.
- Polysaccharides are hydrolysed to soluble monosaccharides and disaccharides, which are transported through the body to be used for the production of energy. Monosaccharides can also be converted back to polysaccharides such as glycogen for use as energy stores.
- Triglycerides are hydrolysed to fatty acids and glycerol, which are transported through the body. Fatty acids and glycerol can be converted back to triglycerides or used to produce energy.

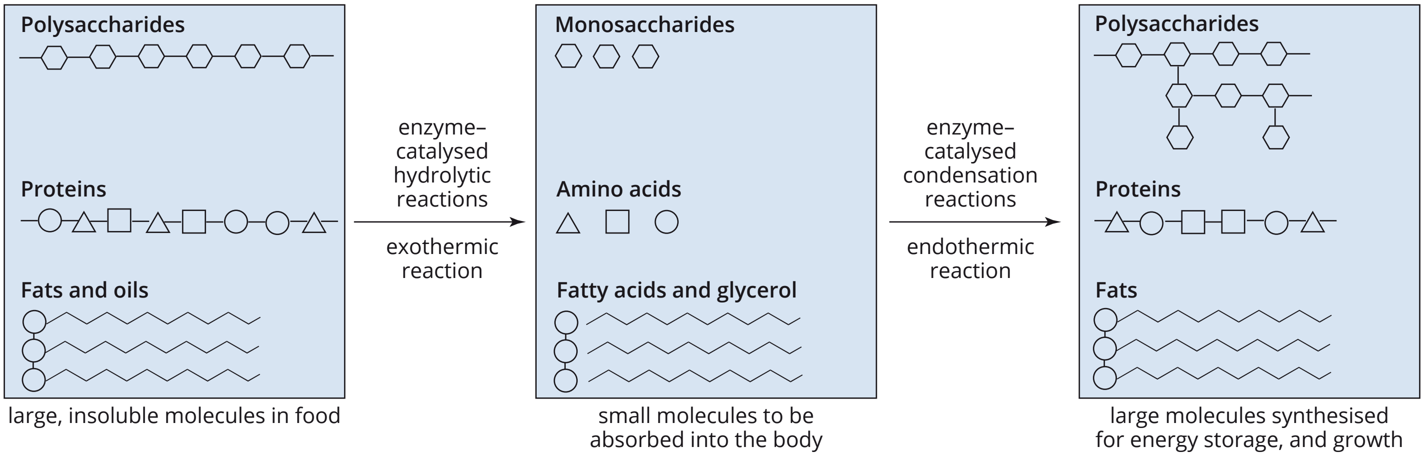


FIGURE 16.1.12 The breakdown and use of nutrients in the body involves numerous condensation and hydrolysis reactions.

In general, for the processes that occur during metabolism:

- macronutrients are relatively insoluble in water but smaller molecules are more soluble. The smaller molecules can be transported throughout the body in the blood
- condensation reactions tend to be endothermic, requiring energy to form larger molecules
- hydrolytic reactions tend to be exothermic, releasing energy as bonds are broken in the formation of smaller molecules.

CHEMFILE

Throw another locust on the barbie!

FIGURE 16.1.13 Many insects are edible and a source of nutrients.

As the world's population grows, concerns increase regarding the capacity to feed everyone on the planet. Recently, nutritionists have been suggesting a surprising solution—insects!

Over 200 species of insects have been declared edible (Figure 16.1.13) and they are accepted items on the menu in many countries. Insects are easy and fast to breed, placing little demand upon Earth's limited resources such as land.

However, the main advantage of consuming insects is their nutritional value. They are generally high in protein but low in total fat. The fat that they have is mainly monounsaturated fat. They are rich in micronutrients such as copper, iron, manganese, selenium and zinc as well as vitamins. The nutrient level varies with the body part so consumption of the whole insect is recommended.

Figure 16.1.14 shows a chef developing some special insect recipes.

FIGURE 16.1.14 A chef experimenting with different insect recipes.

16.1 Review

SUMMARY

- Food supplies nutrients to the body. Nutrients are a source of energy and they are also required to maintain normal body functions.
- Proteins, carbohydrates and triglycerides are examples of macronutrients. Substantial amounts of these three substances are needed in the diet.
- Vitamins and some minerals are examples of micronutrients. They are essential but are needed in smaller amounts.
- The metabolism of food involves the breakdown of food molecules in the digestive system and the synthesis of biologically important molecules in other parts of the body.
- Large biomolecules are often broken down in the body to smaller soluble molecules for ease of transport in the body. They can then be rebuilt in a different part of the body.
- The breakdown of large molecules in food occurs through hydrolytic reactions (hydrolysis).
- The synthesis of large, biologically important molecules occurs by condensation reactions.
- Figure 16.1.15 summarises the breakdown and synthesis reactions for the key nutrient families of carbohydrates, triglycerides and proteins.

Carbohydrates: polysaccharide $\xrightarrow{\text{hydrolysis}}$ monosaccharides $\xrightarrow{\text{condensation}}$ polysaccharide

Triglycerides: triglyceride $\xrightarrow{\text{hydrolysis}}$ glycerol and fatty acids $\xrightarrow{\text{condensation}}$ triglyceride

Proteins: protein $\xrightarrow{\text{hydrolysis}}$ amino acids $\xrightarrow{\text{condensation}}$ protein

FIGURE 16.1.15 Summary of the metabolism of the major nutrients obtained from food.

KEY QUESTIONS

1 Use the following words to complete the sentences about the cycle of breaking down and rebuilding nutrients obtained from food: hydrolytic, glycerol, water, proteins, triglyceride, condensation, monosaccharides.
Amino acids can combine to form _________ in _________ reactions.
___________ is also formed in this reaction. The reverse of this reaction is a __________reaction.
Polysaccharides are formed in condensation reactions involving ____________.
Fatty acids and __________ can combine in a condensation reaction to form a ____________.

2 Classify each of the following components of food as either a macronutrient or micronutrient.
- **a** Selenium
- **b** Carbohydrate
- **c** Protein
- **d** Vitamin C
- **e** Manganese
- **f** Triglyceride

3 Which one of the following statements correctly describes how the body obtains the energy it needs for movement?

A The body obtains all of its energy needs from the hydrolysis of carbohydrates.

B Energy is released by the oxidation of carbohydrates, proteins and triglycerides.

C Energy is released when large molecules are formed from the small molecules obtained during digestion.

D Energy is released by condensation reactions involving monosaccharides, amino acids, glycerol and fatty acids.

4 What role do enzymes play in digestion?

5 Why are larger nutrients such as triglycerides, polysaccharides and proteins broken down into smaller molecules in the early stages of digestion?

6 Sort the following steps in digestion into the order in which they occur.

- Action of bacteria in the large intestine
- Action of saliva in the mouth
- Action of enzymes in the small intestine
- Action of hydrochloric acid in the stomach

7 Complete the metabolism of food reaction sequences below by providing the appropriate reactants and products as required.

polysaccharide $\xrightarrow{\text{hydrolysis}}$ monosaccharides $\xrightarrow{\text{condensation}}$ ________________

________________ $\xrightarrow{\text{hydrolysis}}$ glycerol and fatty acids $\xrightarrow{\text{condensation}}$ ________________

________________ $\xrightarrow{\text{hydrolysis}}$ amino acids $\xrightarrow{\text{condensation}}$ ________________

16.2 Action of enzymes

Thousands of chemical reactions are involved in sustaining life. These reactions occur in a highly organised, sequential fashion. The biological catalysts that accelerate the rate of chemical reactions in cells are a particular type of protein called enzymes.

In this section, you will learn about several models that biochemists use to describe enzyme catalysis. Enzymes are highly efficient catalysts that can increase reaction rates by as much as a factor of 10^{10}. This is like taking 1 second to complete a task that normally takes 300 years!

ROLE OF ENZYMES

You have already learned about inorganic catalysts in Chapter 7, page 184. Just like inorganic catalysts, enzymes:

- are only needed in relatively small amounts
- are not used up or changed at the end of the reaction
- do not alter a reaction's equilibrium position
- provide an alternative reaction pathway that lowers the activation energy for a reaction (Figure 16.2.1).

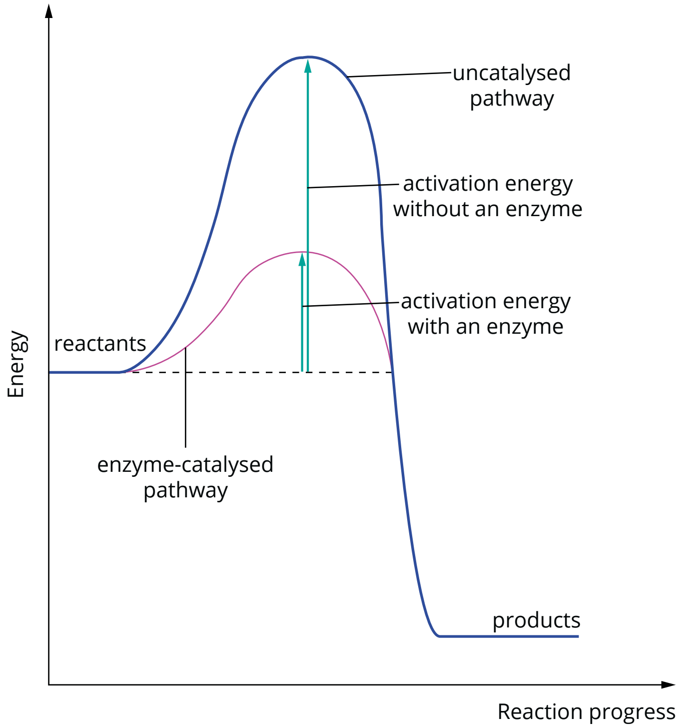


FIGURE 16.2.1 Both inorganic catalysts and enzymes lower the activation energy of a reaction by providing an alternative pathway by which the reaction can occur.

However, there is a significant difference between the behaviour of enzymes and inorganic catalysts. An inorganic catalyst, such as metallic platinum, can be used to catalyse many different reactions often using a variety of reactants. Enzymes may only catalyse one specific reaction or a reaction that involves a particular chemical bond or functional group. This characteristic is often referred to as the 'specificity of enzymes'. For example, the hydrolysis of the disaccharides sucrose and lactose to their constituent monosaccharides are catalysed by different enzymes. The models of enzyme action developed by scientists must account for this key difference.

Enzymes are also more sensitive than inorganic catalysts to changes in reaction conditions. You will investigate this in more detail in section 16.3.

The catalytic action of enzymes is specific for a single reaction or type of reaction.

Enzymes are sensitive to changes in environment, such as temperature and pH.

Living organisms are very complex systems. With so many reactions required to sustain each living organism, thousands of different enzymes are needed. It is important that chemists understand the role of enzymes and their action when they develop new medications. It is also important to investigate the potential of these complex catalysts for use in greener industrial processes.

LOCK-AND-KEY MODEL OF ENZYME ACTION

The catalytic activity of an enzyme is highly specific and depends on its overall three-dimensional structure. Because enzymes are proteins, their overall three-dimensional structure is dictated by their tertiary and quaternary structure. The specific part of the enzyme molecule with which a reactant can interact is known as its **active site**. The active site is usually a uniquely shaped flexible hollow or cavity within the protein where the reaction occurs. The reactant molecule that binds with the active site is referred to as the **substrate**.

One early model for the catalytic action of an enzyme is the 'lock-and-key' model. This model provides an explanation for the critical importance of the three-dimensional shape of the enzyme. In the lock-and-key model, the substrate molecule fits into the enzyme like a key in a lock, forming an **enzyme–substrate complex**, allowing the enzyme to break the bonds in the substrate. Figure 16.2.2 shows the steps involved in an enzyme-catalysed reaction according to the lock-and-key model. The enzyme is specific for a particular substrate, so binding of a different molecule will not result in a reaction.

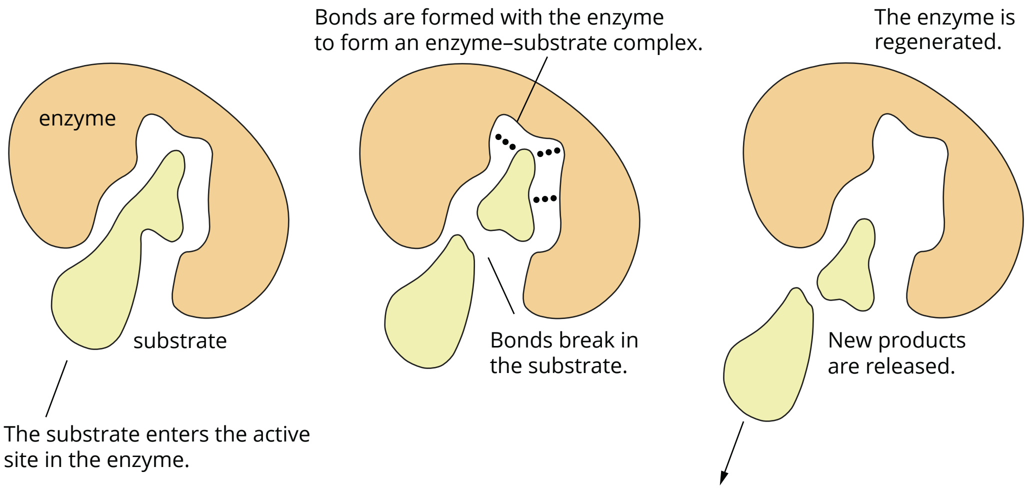


FIGURE 16.2.2 Steps in the action of an enzyme, according to the lock-and-key model.

The shape of the substrate molecule must match the shape of the active site. Only reactant molecules that have a suitable 'key' shape can enter and form the necessary intermolecular interactions with the active site ('lock') of the enzyme.

Optical isomers and enzymes

In Chapter 10 you learned about **optical isomers**; organic molecules containing a carbon atom bonded to four different substituents that can have two non-superimposable mirror images called **enantiomers**. These carbon atoms are described as being **chiral centres**. The diagrams in Figure 16.2.3 illustrate this property in one of the simplest of biochemical molecules, alanine. All the amino acids in your body, except glycine, are chiral. In fact, only one enantiomer of each amino acid is utilised in the body to build proteins. Consequently, all the enzymes in your body are also chiral.

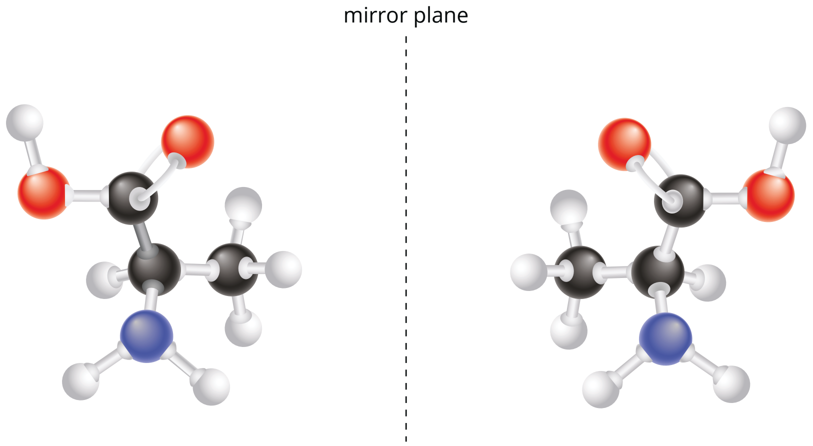


FIGURE 16.2.3 Two optical isomers of the amino acid alanine shown as a pair of mirror images. These two molecules are optical isomers (enantiomers) and cannot be superimposed.

You should recall from Chapter 10 that enantiomers only differ from each other in two ways:

- how they interact with plane polarised light
- how they interact with other chiral molecules.

A good example of the different properties of enantiomers is the amino acid phenylalanine. In the chiral environment of the taste buds of the tongue, one enantiomer (Figure 16.2.4), tastes sweet but the other enantiomer is tasteless.

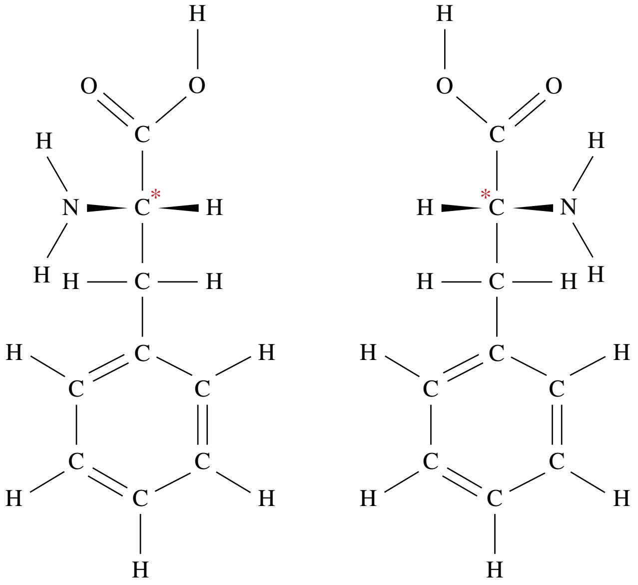


FIGURE 16.2.4 The two enantiomers of phenylalanine interact differently with taste receptors in your body. The enantiomer on the left tastes sweet, while the enantiomer on the right is tasteless. The chiral carbon is highlighted with an asterisk and the wedges represents bonds to atoms above the plane of the page.

Many substrate molecules have more than one chiral centre. Therefore, the way they interact with the chiral enzymes is specific. Enzymes can distinguish between the enantiomers of a chiral substrate. Because enantiomers have different three-dimensional shapes, they may interact with an active site differently. Only one enantiomer might fit the active site and participate in the reaction, so that enantiomer is the only one that is biologically active.

Enzymes can distinguish between enantiomers of a chiral substrate. Typically only one enantiomer is biologically active.

Example—catalysis of polypeptide hydrolysis

Figure 16.2.5 shows how a section of a larger polypeptide molecule might enter the active site of an enzyme that catalyses its hydrolysis. Intermolecular bonds are formed with groups on the enzyme surface, which weaken the peptide bond and make it easier to break. As a result, the activation energy barrier for the hydrolytic reaction is lowered.

The same enzyme–substrate interactions are impossible for optical isomers of this substrate molecule because their shape and the active site will not match up. The hydrolysis of the other isomers could not be catalysed by the same enzyme.

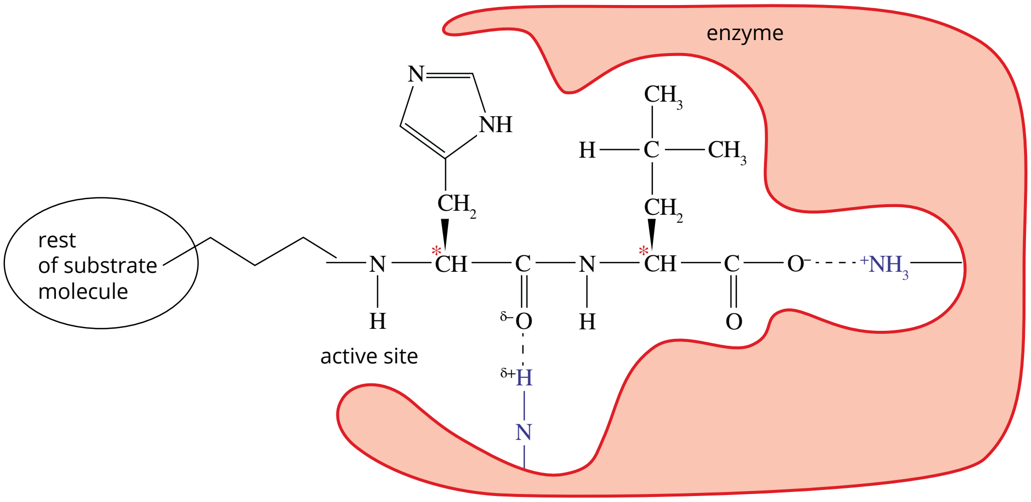


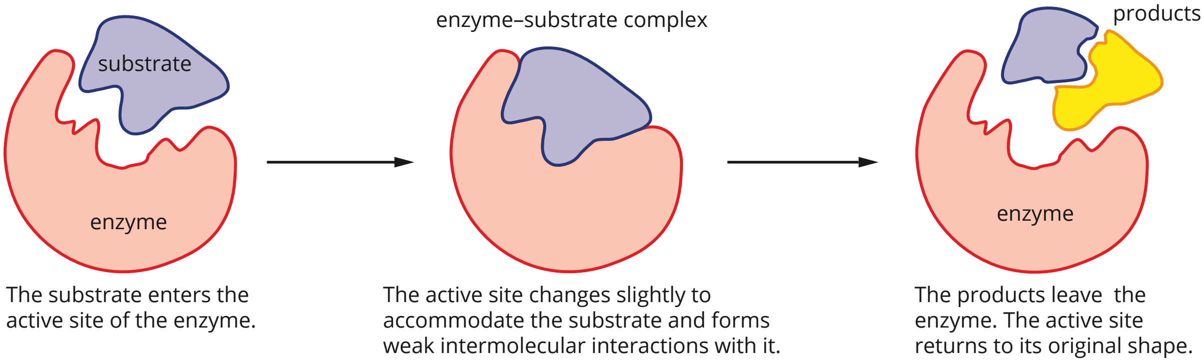
FIGURE 16.2.5 The active site of a protease enzyme, with a polypeptide molecule held by hydrogen bonds, ionic interactions and dispersion forces. The asterisks indicate chiral carbon atoms.

The types of intermolecular bonds formed between an enzyme and a substrate are the same as those that dictate the tertiary structure of proteins. The intermolecular forces are determined by the side chains of the amino acids in the peptide sequence and can include hydrogen bonds, ionic interactions, dipole–dipole attractions and dispersion forces.

INDUCED FIT MODEL OF ENZYME ACTION

Since the lock-and-key model for enzyme action was proposed, chemists have realised that enzymes have flexible structures. The shape of an enzyme's active site can be modified markedly by the binding of a substrate. This discovery led to a modification of the lock-and-key model and the development of the 'induced fit' model. The induced fit model for enzymes can be applied to a large number of chemical reactions.

As Figure 16.2.6 shows, the flexible active site can mould itself to achieve a better fit for substrate molecules. After the reaction, the products are released from the active site and the active site returns to its initial shape.



The substrate enters the active site of the enzyme.

The active site changes slightly to accommodate the substrate and forms weak intermolecular interactions with it.

The products leave the enzyme. The active site returns to its original shape.

FIGURE 16.2.6 Steps in the action of an enzyme, according to the induced fit model.

CHEMFILE

From lock-and-key to induced fit

The development of the lock-and-key model and the induced fit model of enzymes is a good example of how scientific ideas change over time as new evidence becomes available.

Emil Herman Fischer (Figure 16.2.7) was a remarkable chemist. He was awarded the Nobel Prize in Chemistry in 1902 for his work on identifying the 16 enantiomers of the aldo-hexoses, the family of sugars that glucose belongs to. His work on biomolecules and the precise stereochemistry of their different forms led him to propose the lock-and-key model of enzyme–substrate interactions.

This model formed the main explanation for the interactions in enzyme active sites and receptor sites until the American chemist Daniel Koshland (Figure 16.2.8) proposed the induced fit model of enzyme interactions.

Koshland described his model as more like a hand in glove, where the enzyme is flexible, not rigid, and can change shape slightly on binding of the substrate. Figure 16.2.9 shows a simplified version of the Fischer's lock-and-key model and Koshland's induced fit model. Koshland was able to build on the hypothesis put forward by Fischer to develop what is now considered to be a more accurate representation of enzyme interactions.

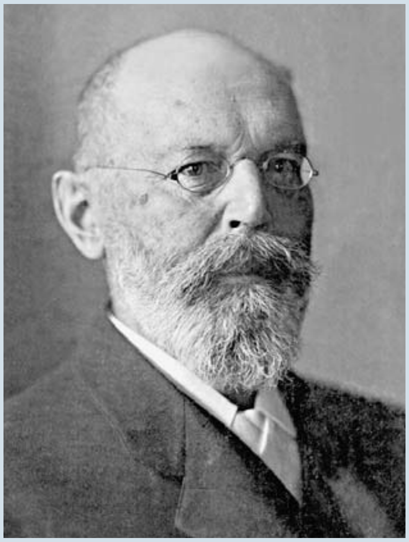


FIGURE 16.2.7 Emil Hermann Fischer (1852–1919) proposed the lock-and-key model of enzyme–substrate interactions.

FIGURE 16.2.8 Daniel Koshland (1920–2007) further developed Fischer's lock-and-key model by proposing the revised induced fit model for enzyme interactions.

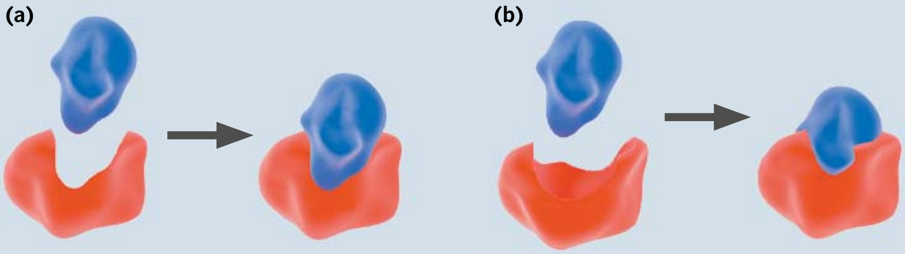


FIGURE 16.2.9 The two models of enzyme interaction proposed by (a) Fischer and (b) Koshland. The development of these models is an example of how scientific ideas change over time, being refined and adapted as new insights and discoveries are made.

COENZYMES

Many enzymes cannot function without the presence of a **cofactor**. A cofactor may be a metal ion or another non-protein organic compound, called a **coenzyme**. Coenzymes are small molecules compared to protein molecules (see Figure 16.2.10).

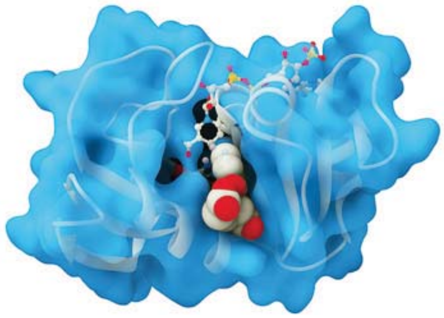


FIGURE 16.2.10 Folic acid acts as a coenzyme, binding to the dihydrofolate reductase enzyme.

Many coenzymes are derived from vitamins. As you learned in section 16.1, these vitamins are essential micronutrients that are required to be consumed in small amounts as part of a balanced diet. Figure 16.2.10 shows the coenzme folic acid bound into dihydrofolate reductase, an enzyme found in *Escherichia coli* bacteria in the human gut.

Coenzymes interact with the enzyme during catalysis and their role is often to act as carriers of electrons or specific groups of atoms. They change the surface shape of the enzyme and hence the binding properties of the active site, allowing the enzyme to better interact with the substrate.

Before binding to the coenzyme, the enzyme is inactive. You can see this in Figure 16.2.11. Once the coenzyme is bound, the newly formed enzyme–coenzyme complex can interact fully with the substrate and the catalytic process can occur.

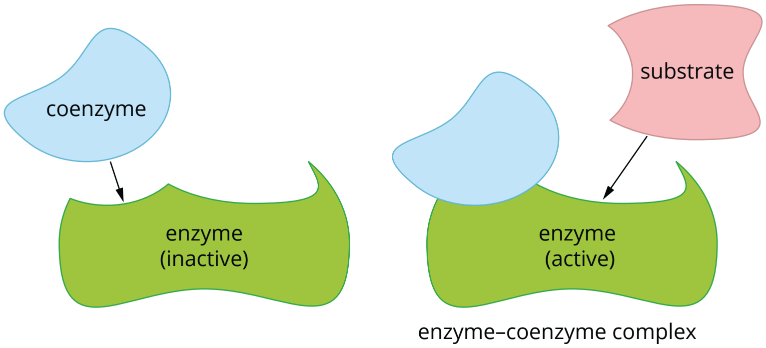


FIGURE 16.2.11 Coenzymes work by binding to particular enzymes. The newly formed complex can bind to the substrate, allowing the reaction to be catalysed.

Unlike an enzyme, a coenzyme may be changed as a result of the reaction as it accepts or donates an electron or group of atoms. If it accepts a particular group of atoms in one biochemical reaction it helps catalyse, there will be other reactions in which it is restored to its original form by the loss of the group.

Table 16.2.1 provides examples of coenzymes and their function.

TABLE 16.2.1 Examples of coenzymes and their role in enzyme catalysis

Coenzyme	Acts as a carrier of
NAD^+ (from niacin, vitamin B_3)	Electrons
FAD (from riboflavin, vitamin B_2)	Electrons
Coenzyme A (from pantothenic acid, vitamin B_5)	Acetyl group, $–COCH_3$
Coenzyme Q	Electrons
Thiamine pyrophosphate (from thiamine, vitamin B_1)	Aldehyde group, –CHO
Biotin	CO_2
Cobalamin (from vitamin B_{12})	Methyl group, $–CH_3$

Unlike enzymes, coenzymes can be changed after the reaction between the enzyme complex and the substrate.

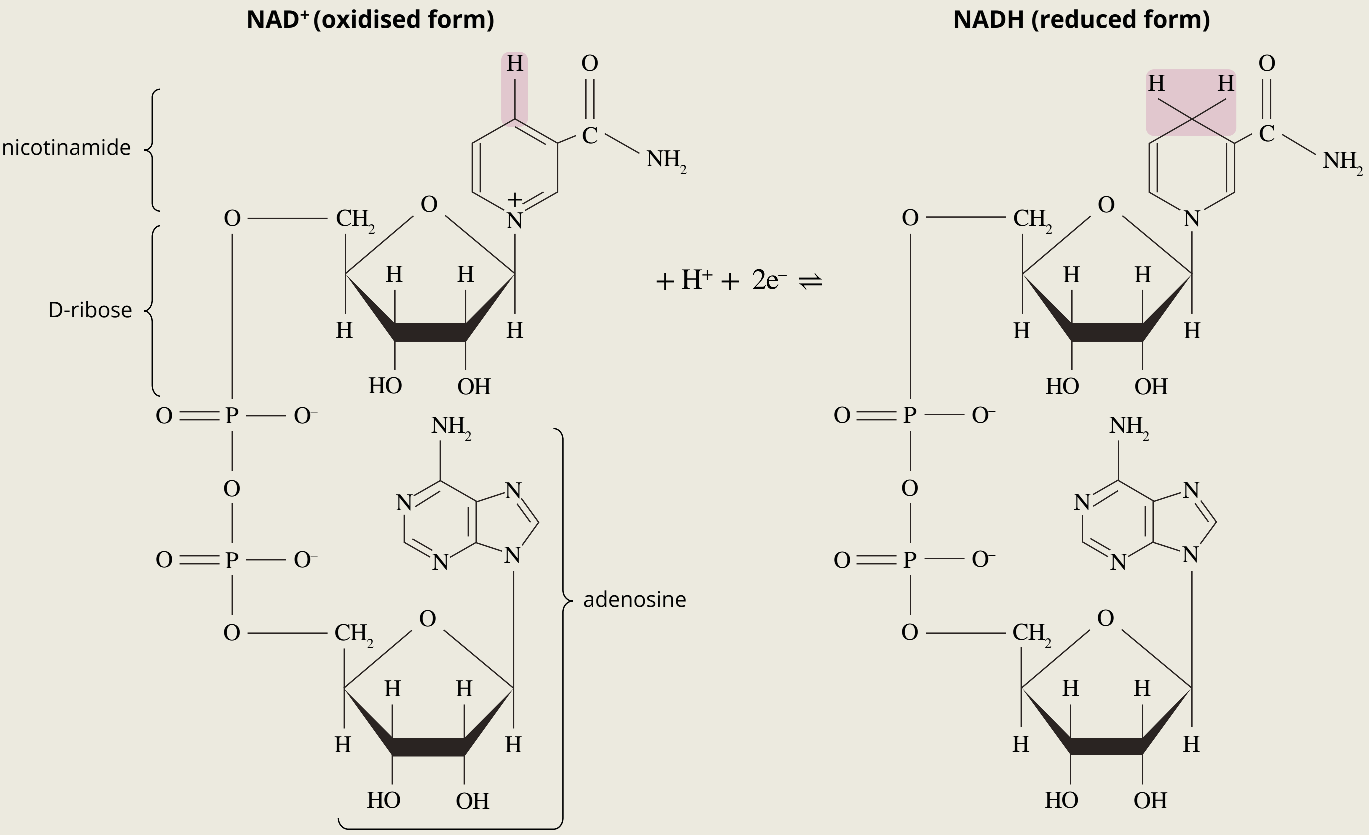
EXTENSION

An example of a coenzyme—nicotinamide adenine dinucleotide (NAD^+)

Niacin is one of the B vitamins found in meat, seafood, fruits, mushrooms and potatoes. It is a source of the coenzyme known as NAD^+, which is required in reactions in the body involving carbohydrates and fats.

As the structures shown in Figure 16.2.12 show, an equilibrium exists between the oxidised form of this coenzyme, NAD^+, and reduced form, NADH:

$$NAD^+(aq) + H^+(aq) + 2e^- \rightleftharpoons NADH(aq)$$



NAD^+ (oxidised form)

NADH (reduced form)

FIGURE 16.2.12 The structures of NAD^+ and NADH exist in an equilibrium between the oxidised and reduced forms. The two forms of this coenzyme are used by the body for electron transfer reactions.

The coenzyme can act as a carrier of electrons from one enzyme-controlled reaction to another. NAD^+ can accept electrons from one substrate, forming NADH, which is subsequently converted to NAD^+ by donating electrons to another substrate. It enables many enzymes to catalyse redox reactions, such as those involving the oxidation of hydroxyl functional groups to aldehydes or ketones.

The presence of NAD^+ modifies the binding properties of the active site of the enzyme alcohol dehydrogenase. The enzyme is then able to catalyse the oxidation of ethanol to ethanal:

$$CH_3CH_2OH(aq) \rightarrow CH_3CHO(aq) + 2H^+(aq) + 2e^-$$

Following this reaction, the ethanal and NADH leave the active site.

NADH is then oxidised back to NAD^+ in other biochemical reactions in which it also acts as a coenzyme and carrier of electrons.

16.2 Review

SUMMARY

- Enzymes are proteins that catalyse biochemical reactions by providing an alternative reaction pathway with a lower activation energy.
- Enzymes are not changed as a result of the process of catalysis.
- Enzymes are highly specific; enzymes may only catalyse one specific reaction or a reaction with a particular chemical bond or functional group.
- There are hundreds of enzymes in the human body to catalyse different biochemical reactions.
- Enzyme molecules have uniquely shaped active sites that interact with specific reactant molecules (substrates), weakening or breaking the bonds in the reactant molecules.
- Because of the difference in the three-dimensional shape of the two enantiomers of an optically active substrate, only one enantiomer may be able to interact with an enzyme's active site. As a consequence, only a reaction with that enantiomer may be catalysed.
- The earliest model to account for enzyme action was the lock-and-key model; its features are summarised in Figure 16.2.2 on page 528.
- A newer model for enzyme action is the induced fit model, summarised in Figure 16.2.6 on page 530. This model accounts for the flexibility of many enzymes' active sites.
- Many enzymes require the presence of an additional non-protein molecule called a coenzyme in order to function.
- Coenzymes are often made from vitamins.
- Coenzymes can act as carriers of electrons or groups of atoms in biochemical pathways.

KEY QUESTIONS

1 The enzyme glucokinase catalyses the first step in the oxidation of sugar in human liver cells, in a process called glycolysis. Which one of these statements about this process is correct?

A Many other enzymes can also catalyse this reaction.
B Glucokinase increases the activation energy of this reaction.
C Glucokinase is able to catalyse many other reactions.
D Glucokinase is a protein.

2 **a** The steps in the action of an enzyme involve, in particular, an active site and a substrate. Use a diagram to describe in detail the action of an enzyme (according to the lock-and-key model of enzyme action).

b The forces of attraction that enable a substrate to bind to an active site can vary. Describe four such forces.

3 Sugars are chiral molecules. One of the chiral centres in the form of glucose shown in Figure 16.2.13 is indicated by the asterisk. What is the total number of chiral centres in this form of glucose?

4 Identify whether each of the statements about the induced fit model of enzyme catalysis is true or false.

a This model explains why enzymes do not catalyse a wide range of reactions.
b The enzyme molecule has an active site.
c The active site does not change shape as the substrate enters.
d An enzyme–substrate complex forms.
e The active site is able to form relatively strong intermolecular bonds with both enantiomers of a substrate.

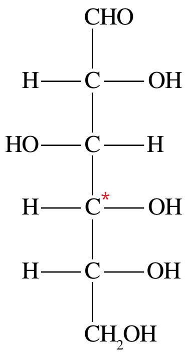


FIGURE 16.2.13 Chiral centre in glucose.

5 Identify the type of catalyst (inorganic, enzyme or both) that displays each of these properties.

- **a** Lowers the activation energy
- **b** Is highly specific
- **c** Is made of proteins
- **d** Is not changed by the reaction
- **e** Increases reaction rate

6 Provide definitions for each of the following terms.

- **a** Enantiomers
- **b** Cofactor
- **c** Substrate
- **d** Lock-and-key model
- **e** Coenzyme
- **f** Active site

7 The substrate of a particular metabolic reaction contains one chiral centre. The reaction is catalysed by an enzyme–coenzyme system. Which one of the following statements about the reaction is correct?

- **A** After the reaction, the enzyme and coenzyme will be changed.
- **B** The coenzyme consists of a long polypeptide chain.
- **C** Only one enantiomer of the substrate may be able to react at the enzyme's active site.
- **D** After the reaction, neither the enzyme nor the coenzyme will be changed.

16.3 Enzymes—dependence on pH and temperature

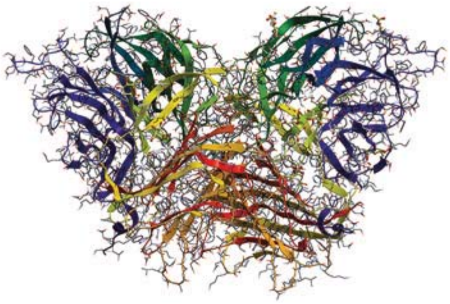


FIGURE 16.3.1 A ribbon model of the enzyme invertase (also called sucrase), which catalyses the hydrolysis of sucrose. It operates under mild conditions but is sensitive to changes in temperature and pH.

As you learned in the previous section, enzymes share many characteristics with inorganic catalysts. By lowering a reaction's activation energy barrier, both enzymes and inorganic catalysts increase reaction rate without altering the equilibrium position or being changed themselves by the process. However, an enzyme's ability to catalyse only a specific reaction or small group of reactions is markedly different from the versatility displayed by many inorganic catalysts.

In this section, you will learn about this significant difference between the two types of catalysts: their sensitivity to reaction conditions, such as temperature and pH (Figure 16.3.1).

MONITORING ENZYME ACTIVITY

The rate of conversion of a substrate into product by an enzyme is measured by a quantity called **enzyme activity**. Enzyme activity is the amount of substrate that is converted to products per unit time. Enzyme activity depends on the quantity of active enzyme that is present as well as reaction conditions. Enzyme activity can be monitored experimentally by following the rate of the reaction in solutions of equal concentration.

Measurements of enzyme activity may involve sampling the reaction mixture at fixed time intervals to measure the concentration of a reactant or product by UV–visible spectroscopy. Enzyme activity may also make use of an analytical technique such as volumetric analysis.

Any condition that affects the frequency at which substrate molecules enter the enzyme's active site or the effectiveness of the enzyme as a catalyst will affect enzyme activity. Enzyme activity can be influenced by a number of reaction conditions, including solution pH, temperature and the concentrations of the enzyme and the substrate.

EXTENSION

Investigating enzyme activity in sucrose hydrolysis

The enzyme-catalysed hydrolysis of sucrose using invertase enzyme can be monitored with the Fehling's test. Fehling's reagent contains copper ions that react to produce a reddish-brown precipitate when heated in the presence of some simple sugars, such as glucose. Fehling's reagent does not react with sucrose. As sucrose is hydrolysed, the Fehling's reagent reacts with the glucose that is produced. Figure 16.3.2 shows a student conducting the Fehling's test on a sample of glucose; the reddish brown colour of the precipitate can be clearly seen.

A simple experiment for testing the rate of hydrolysis by an enzyme at different temperatures is shown in Figure 16.3.3. As long as the concentrations of the sucrose and the invertase are kept constant at each temperature, the amount of precipitate formed after 5 minutes will indicate the optimum temperature at which the enzyme activity is greatest (the enzyme's optimum temperature). A similar set-up can be used to test the effect of changing pH.

FIGURE 16.3.2 A student conducts the Fehling's test on a solution containing glucose. On heating the reaction mixture it produces a reddish-brown colour. The amount of reddish-brown precipitate formed is proportional to the amount of glucose in the solution.

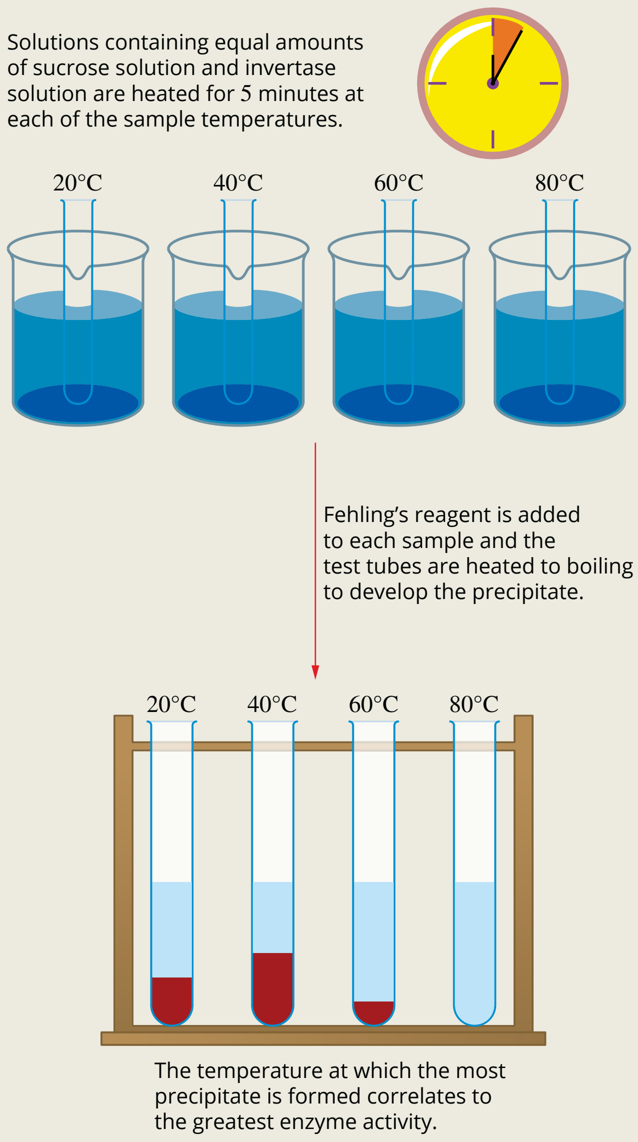


FIGURE 16.3.3 A simple experiment using Fehling's reagent for testing the rate of sucrose hydrolysis after 5 minutes at different temperatures.

DEPENDENCE ON pH

Enzymes operate effectively only within a narrow pH range, as the in Figure 16.3.4 show. Salivary amylase catalyses the breakdown of starch to a disaccharide, maltose, in the relatively neutral environment of the mouth. Pepsin catalyses the breakdown of proteins to amino acids in the acidic conditions of the stomach. Activity of these enzymes drops off drastically outside their normal conditions.

Pepsin is active only at pH values below 3 and amylase is active between pH 5 and 9. The pH at which the enzyme activity is greatest is known as the enzyme's **optimum pH**. The optimum pH of pepsin is 1.5, while the optimum pH of salivary amylase is 7.2.

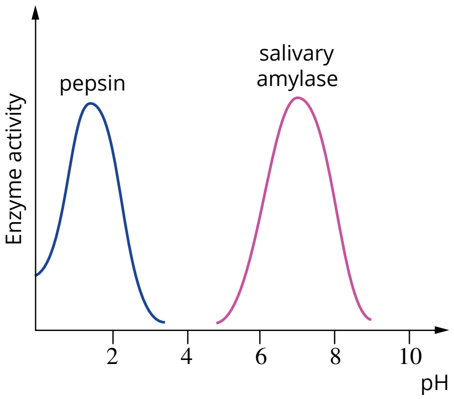


FIGURE 16.3.4 Enzymes are only effective in a narrow pH range. Pepsin is a protein-digesting enzyme secreted into the stomach. Salivary amylase is the enzyme in human saliva. These enzymes are most effective at very different pH values.

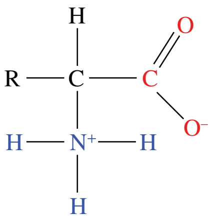


FIGURE 16.3.5 The general structure of a zwitterion of an amino acid. Different amino acids have different side chains, represented by the R group.

Acid–base properties of enzymes

You will recall that **2-amino acids** (those found in living systems) can form **zwitterions**, with the general structure shown in Figure 16.3.5. A zwitterion has both a positive and negative charge within the molecule.

Amino acids have different charges depending on the pH of the surrounding environment.

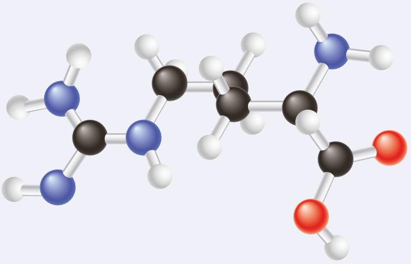
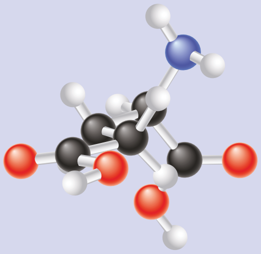
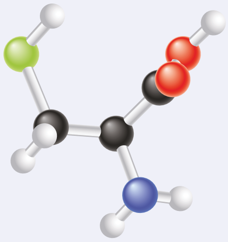
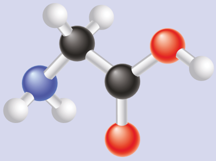
- At high pH, the $-NH_3^+$ group can act as an acid, donating a proton to become an $-NH_2$ group
- At low pH the $-COO^-$ group can act as a base, accepting a proton to become a $-COOH$ group.

As the following equation shows, the charge on the predominant form of the amino acid present in a solution depends on the pH of the solution.

$$\begin{array}{ccccc} \text{Low pH} & & \text{Intermediate pH} & & \text{High pH} \\ {}^{+}H_3N\text{–}CH(R)\text{–}COOH & \rightleftharpoons & {}^{+}H_3N\text{–}CH(R)\text{–}COO^- & \rightleftharpoons & H_2N\text{–}CH(R)\text{–}COO^- \\ \text{cation} & & \text{uncharged zwitterion} & & \text{anion} \end{array}$$

Just as the ionisation of the amino and carboxyl groups in amino acids depends on pH, some of the **R groups** of the amino acids may also be affected by changing pH. ‘Ball and stick’ computer models for a representative selection of amino acids and the properties of their corresponding R group are shown in Table 16.3.1.

TABLE 16.3.1 Properties of the R groups of some amino acids dependent on pH

Amino acid	R group	Properties of R group	‘Ball and stick’ model
Arginine	$-(CH_2)_3NHC(NH)NH_2$	Polar Positively charged at intermediate and lower pH	
Glutamic acid	$-(CH_2)_2COOH$	Polar Negatively charged at intermediate and higher pH	
Cysteine	$-CH_2SH$	Polar Not influenced by changing pH	
Glycine	$-H$	Non-polar Not influenced by changing pH	

Intermolecular bonds between the R groups (**side chains**) of a polypeptide maintain a protein's overall three-dimensional structure. Some bonds that determine the **tertiary structure** of an enzyme may be disrupted as changes in pH alter the ionisation of some R groups.

For example, the ionic interactions shown in Figure 16.3.6 might occur at pH 7 between side chains of the amino acid units along the protein chain, but not at pH 3 or 10. The change from neutral pH to an acidic pH of 3 would mean the carboxylic acid on the R group is not likely to ionise and will therefore not carry the negative charge required for the ionic interaction to occur. The opposite situation would be true with a change from neutral pH to the basic pH 10. At the higher pH, the amino group in the other side chain would not act as a base, remaining uncharged and unable to participate in the ionic interaction.

In this way, changes in pH can have a large impact on the stability of enzyme structure. As the tertiary structure of the enzyme is disrupted, the enzyme's active site changes shape and enzyme activity decreases. Extremely high or low pH values generally cause complete loss of activity for most enzymes. Drastic changes to pH can result in a permanent change to the shape of an enzyme through a process called denaturation (see below).

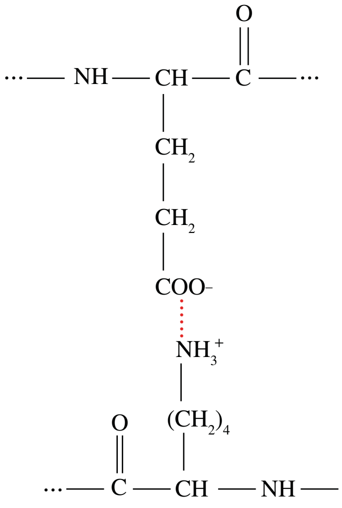


FIGURE 16.3.6 An ionic interaction linking two parts of a polypeptide chain. Ionic interactions between R groups of amino acids in proteins are dependent on pH. One R group contains $-NH_3^+$ and another R group contains $-COO^-$.

Changes in pH alter the charge of side chains containing amino and carboxyl functional groups.

DEPENDENCE ON TEMPERATURE

Enzyme activity is also affected by temperature. The graph in Figure 16.3.7 shows the effect of temperature on the rate of a reaction involved in carbohydrate metabolism. You can see from the steep sides of the curve that the rate of reaction drops off quickly either side of a narrow temperature range (30–40°C).

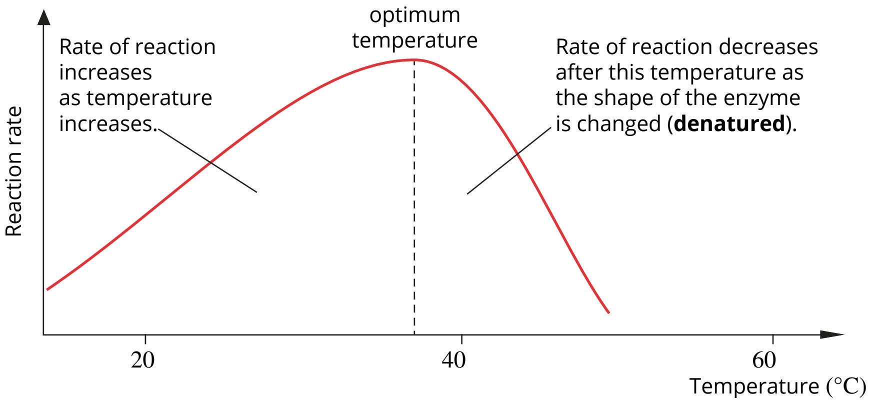


FIGURE 16.3.7 Effect of temperature on rate of reaction for an enzyme-catalysed reaction. Enzymes are only effective in a relatively narrow range of temperatures. Reaction rate is highest at the optimum temperature.

The temperature at which the enzyme activity is greatest is known as the enzyme's **optimum temperature**. Enzymes that operate inside human cells have an optimum temperature of about 37°C.

At temperatures above and below the optimum temperature, enzyme function is impaired. This is one of the reasons why conditions such as hypothermia and fever (when you have an abnormally low or high temperature) are life threatening.

An increase above or decrease below the optimum temperature have different effects on an enzyme.

- As the temperature increases above the optimum temperature, the increased kinetic energy of the molecules disrupts the structure of the enzyme. The increased movement throughout the enzyme breaks some of the intermolecular forces responsible for the tertiary and quaternary structure. This change in three-dimensional shape of the enzyme means the active site can no longer effectively catalyse the reaction so the reaction rate decreases rapidly.
- As the temperature decreases below the optimum temperature, the enzyme and substrate molecules have lower kinetic energies, resulting in less frequent and less energetic collisions between the molecules.

Denaturation

Once the temperature becomes too high, the increased kinetic energy of the polypeptide chains of the enzyme breaks some of the bonds between side chains of the amino acid units and new bonds are formed. A change in the enzyme's tertiary structure causes a change in the shape of the active site and the enzyme loses its catalytic activity. It is said to be denatured. This change to the protein structure is sometimes irreversible (Figure 16.3.8).

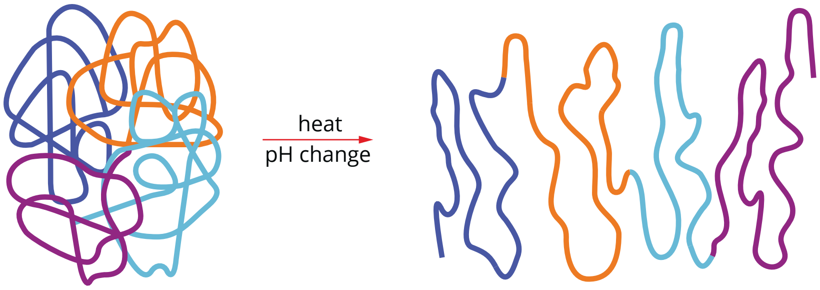


FIGURE 16.3.8 The specific three-dimensional shape of enzymes is lost when denaturation occurs.

Enzymes can also be denatured by a change in pH. As discussed earlier, when the pH is above or below the enzyme's optimum pH, the enzyme's overall three-dimensional shape can also be disrupted. Substantial changes in pH can change an enzyme's structure permanently.

CHEMFILE

Denaturing egg white

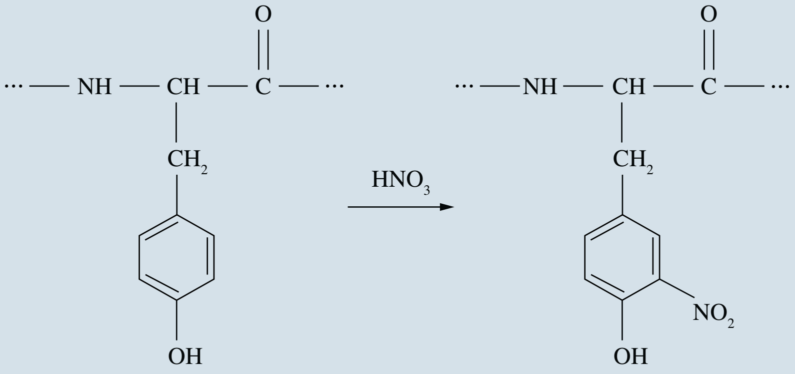
When egg white is heated, the clear liquid turns into an opaque solid. This is an everyday example of the denaturing of a protein. Egg white contains a protein called albumin. The denatured protein has very different chemical and physical properties from the original protein.

The protein in egg white can be denatured in a variety of ways. Some are irreversible, such as the cooking of an egg; others are reversible.

If you add salts such as ammonium sulfate to egg white, the water that surrounds the proteins is drawn away and forms ion–dipole bonds with the ions of the salt. Without the protective layer of water stabilising its tertiary structure, the protein denatures and precipitates out of solution. If you add enough water to hydrate the ions and the protein strands, the protein refolds and dissolves back into solution. In this instance, the denaturation of the protein is reversible.

When denaturation occurs because the hydrogen bonds in the protein molecules are disrupted, the process is irreversible. This can happen when the protein is heated (such as when you boil or fry an egg) or when protein is mixed with strong mineral acids such as nitric acid.

The reaction of nitric acid with proteins produces an identifiable yellow solid that is often used as a test for the presence of proteins. The yellow precipitate forms as a result of the nitration (addition of a nitro group) of the aromatic side chains (side chains containing a benzene ring) of amino acids such as phenylalanine (Figure 16.3.9).



Section of a protein chain containing an aromatic side chain.

The nitration product is yellow.

FIGURE 16.3.9 The reaction of aromatic side chains of proteins with nitric acid forms a yellow precipitate. This denatures the protein irreversibly.

Comparing denaturation with hydrolysis

Even though increased temperature and variations in pH can permanently change the tertiary structure of an enzyme, the primary structure of the protein, the covalently bonded sequence of amino acids, remains intact.

As you saw in section 16.1, the primary structure of enzymes and other proteins is broken down when food is digested. You will recall that the breakdown of proteins occurs through a process called hydrolysis. The hydrolysis of a protein molecule involves breaking covalent bonds in the **peptide link**. This is shown in Figure 16.3.10.

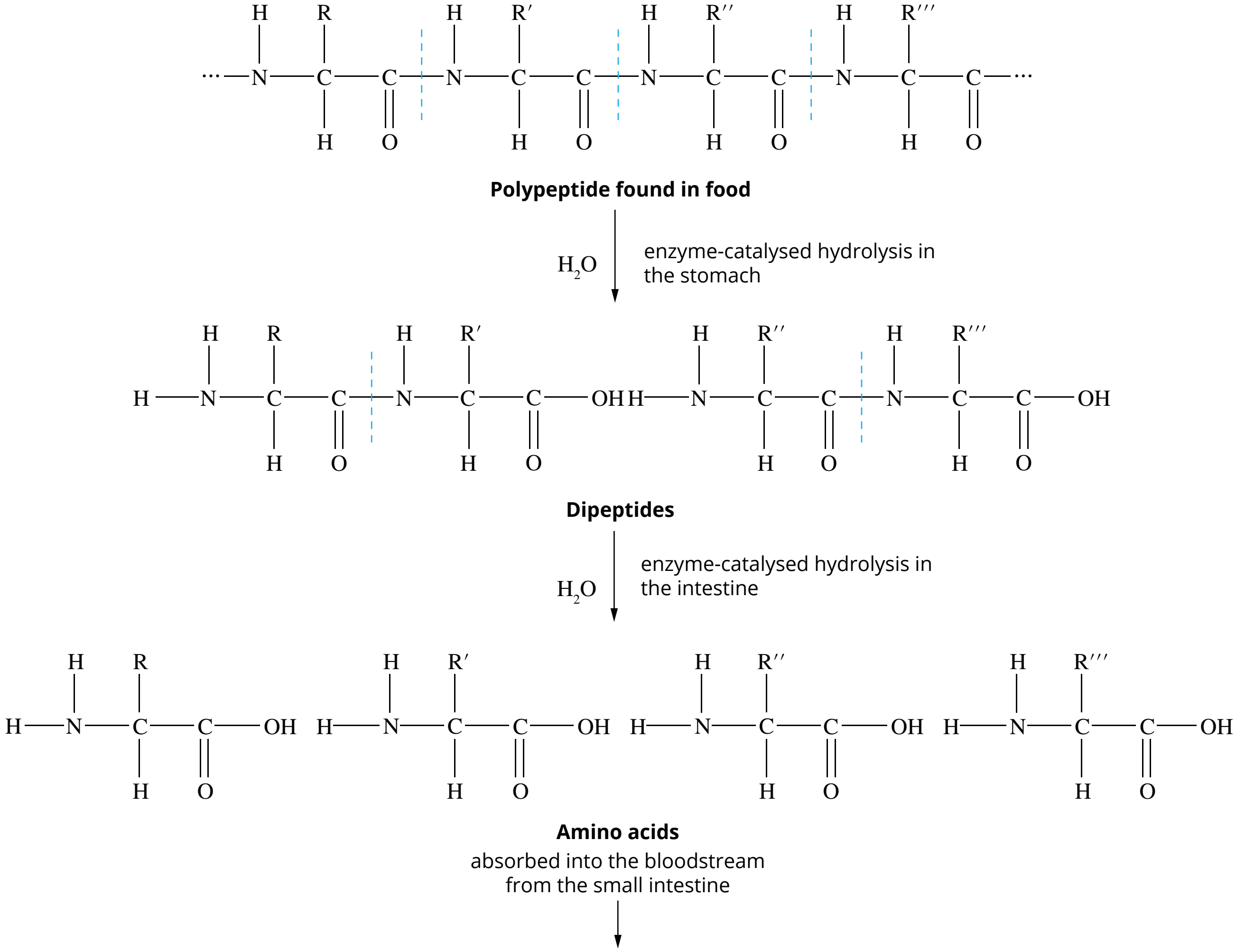


FIGURE 16.3.10 Digestion of protein in food. The blue dashed lines indicate where peptide links are broken during hydrolysis of the polypeptide.

The products of hydrolysis are shorter polypeptide chains or individual amino acids. As this is a hydrolytic reaction, water must be present as a reactant. One water molecule is consumed for each peptide bond broken.

In the laboratory, extreme conditions are required to hydrolyse a protein. Typically, the protein sample is heated in 6 M hydrochloric acid for 24–72 hours.

CHEMFILE

Chocolate-covered cherries

Chemist H.S. Paine invented liquid-centred chocolates by exploiting the differences in solubility of the disaccharide sucrose and the monosaccharides glucose and fructose. In the presence of very little water, sucrose forms a paste-like solid, whereas glucose and fructose are very soluble. Paine also knew that the enzyme invertase was produced by yeast to hydrolyse sucrose to glucose and fructose according to the reaction:

$$\underset{\text{sucrose}}{C_{12}H_{22}O_{11}(aq)} + H_2O(l) \xrightarrow{\text{invertase}} \underset{\text{glucose}}{C_6H_{12}O_6(aq)} + \underset{\text{fructose}}{C_6H_{12}O_6(aq)}$$

He added a small amount of invertase (from yeast) to a sucrose paste and moulded it around a cherry. This was then dipped in molten chocolate. The enzyme remains active inside the chocolate and hydrolyses sucrose into the more soluble sugars. Eventually, the cherry is surrounded by a sweet liquid like the one seen in Figure 16.3.11.

It takes several weeks for the paste to turn into a syrup because the chocolates are kept at 18°C. At this temperature, enzyme activity is low, slowing down the reaction rate. However, it is well worth the wait because chocolate-covered cherries are as delicious as they are messy.

FIGURE 16.3.11 The enzyme invertase is used to break down a paste of sucrose into a solution containing the more soluble fructose and glucose sugars to make the sweet liquid in chocolate-covered cherries.

16.3 Review

SUMMARY

- The effectiveness of an enzyme can be experimentally determined by measuring the change in concentration of a reactant or product of the reaction per unit time.
- Enzyme activity measures the ability of an enzyme to convert a substrate into products.
- Enzymes operate over an extremely mild and narrow set of conditions when compared with catalysis by inorganic catalysts.
- Enzymes are very sensitive to changes in pH and temperature.
- An enzyme is said to be denatured if its tertiary and quaternary structures are disrupted; for example, by high temperatures or pH changes.
- When an enzyme is denatured, the shape of its active site is changed and its catalytic activity is lost.
- During the hydrolysis of a protein, the primary structure is broken down as peptide links are broken. This occurs during digestion of food.
- The temperature at which the enzyme activity is greatest is the enzyme's optimum temperature.
- High temperature denatures an enzyme because the increased kinetic energy of the polypeptide chain disrupts the bonds that maintain the enzyme's tertiary and quaternary structure.
- Low temperature does not alter the tertiary structure but fewer, less energetic collisions occur per unit time between the enzyme and substrate so the rate of reactions is slower.
- The pH at which the enzyme activity is greatest is the enzyme's optimum pH.
- The charges on some R groups in the polypeptide chain of an enzyme depend on the pH of the solution.
- Changes to the charges on the R groups that occur as pH changes can result in a new tertiary structure for an enzyme, as intermolecular bonds are broken and new bonds are formed. The enzyme can become denatured.
- The optimum pH and temperature of an enzyme usually matches the conditions in which the enzyme operates.

KEY QUESTIONS

1 The structure of proteins can be disrupted by denaturation or hydrolysis. Describe each process and the bonding that is disrupted for each.

2 Enzyme activity is influenced by changes in pH. Changing pH can alter the charge on some functional groups because they act as weak acids or bases. The R groups of a polypeptide chain are important in maintaining the enzyme's tertiary structure. Complete the following table for each of the R groups listed.

Structure of R group	Is the R group acidic or basic or neither?	Is the R group positively charged, negatively charged or neutral?	
		In a solution of pH 2	In a solution of pH 11
$-CH_2COOH$			
$-CH_2CH(CH_3)_2$			
$-CH_2OH$			
$-(CH_2)_4NH_2$			

3 The enzyme carbonic anhydrase catalyses the decomposition of carbonic acid molecules to carbon dioxide and water in the lungs. When heated above 60°C, the enzyme becomes denatured.

- **a** What is meant by 'denatured'?
- **b** Describe what usually occurs to the structure of an enzyme when the enzyme is denatured.
- **c** Does the primary structure of the carbonic anhydrase enzyme change during the process?
- **d** Why is the function of the enzyme closely related to its tertiary structure?

4 One of the key differences between enzymes and inorganic catalysts is how they are affected by their environment.

- **a** Define 'enzyme activity'.
- **b** How can a change in pH effect enzyme activity?
- **c** What effect does decreasing the temperature have on enzyme activity?

16.4 Hydrolysis of carbohydrates

Figure 16.4.1 shows two different athletes. One is running a marathon and will run 42 km over 3 hours while the other is spending 45 seconds cutting through a log of wood. Both athletes require energy, but is this energy best provided by the same energy source—for example, a bowl of porridge?

FIGURE 16.4.1 A marathon runner and a woodchopper both require energy for their activities. Is a bowl of porridge a suitable energy source for one or both athletes?

Carbohydrates are one source of energy for living organisms. In this section, you will examine the digestion processes involved in the metabolism of carbohydrates and the dietary implications of the foods you choose to eat.

HYDROLYSIS OF CARBOHYDRATES IN THE BODY

Starch and **glycogen** are **polysaccharides**, which plants and animals use as a way of storing energy. Both starch and glycogen are polymers of the same **monosaccharide**, glucose. During digestion, these polysaccharides are hydrolysed to smaller carbohydrates and eventually to glucose.

Hydrolysis refers to the breaking of chemical bonds through the addition of water.

Starch hydrolysis

The enzyme amylase in saliva hydrolyses starch in the food you eat to maltose, a disaccharide. If you chew a piece of bread and then leave it in your mouth for a few minutes, you will notice a sweet taste. The sweet taste is the result of hydrolysis of starch to maltose.

Digestion can continue in the small intestine where the enzyme maltase is produced in the intestine lining. Maltase hydrolyses maltose to glucose. Figure 16.4.2 shows the structure of the starch polymer. Each glucose monomer is joined by a **glycosidic link**, formed as a result of condensation polymerisation of the glucose monosaccharides. It is the glycosidic links between each monosaccharide unit that are broken during digestion.

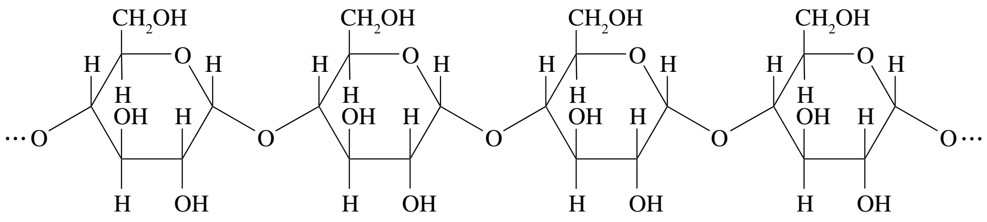


FIGURE 16.4.2 Starch consists of glucose molecules connected through glycosidic linkages. The glycosidic links are the carbon–oxygen–carbon bonds joining the ring units of each glucose to each other. The carbons of the glycosidic link are chiral. The enzyme amylase acts on these links.

Glucose molecules are highly soluble because hydrogen bonds can form between the numerous hydroxyl groups in the molecule and water. As a result, glucose dissolves in the blood and is transported to different parts of the body. Some glucose molecules are used to produce energy through respiration while others are used to synthesise energy storage molecules such as glycogen.

During respiration, glucose is oxidised to carbon dioxide and water and energy is produced. The equation for the oxidation of glucose is:

$$C_6H_{12}O_6(aq) + 6O_2(g) \rightarrow 6CO_2(g) + 6H_2O(l)$$

The digestion of starch is summarised in Figure 16.4.3. It is catalysed by two different enzymes—amylase and maltase.

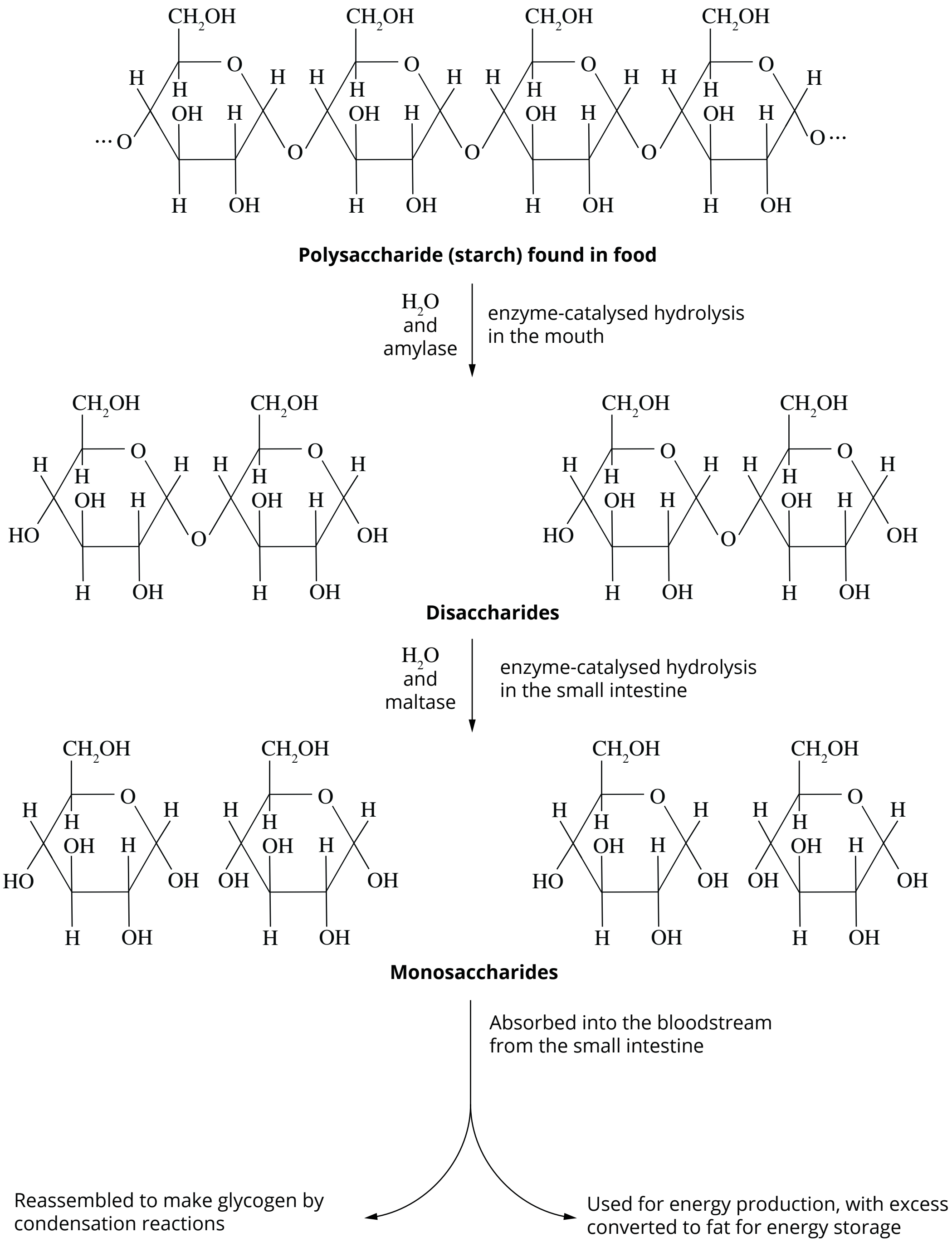


FIGURE 16.4.3 The digestion of starch.

Cellulose hydrolysis

The polysaccharide cellulose is present in large amounts in cereals, fruits and vegetables. It is better known as dietary fibre or roughage. Cellulose is rapidly hydrolysed by the enzyme cellulase.

Most animals, including humans, do not have the enzyme cellulase. Cellulose passes through your digestive system relatively unchanged but a small percentage can be hydrolysed by bacteria in the gut. A diet high in cellulose or fibre provides bulk to help food pass through the digestive system. Fibre helps prevent constipation, haemorrhoids and colon cancer.

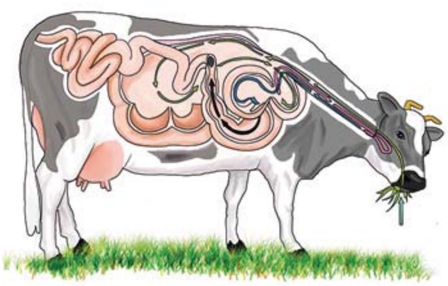


FIGURE 16.4.4 A cow's digestive system is more complex than a human's. This allows the cow to break down cellulose.

Cows and sheep can digest large amounts of cellulose because bacteria living in their gut produce the enzyme cellulase. A cow's stomach has four compartments and grass spends a considerable time in the first two compartments being broken down before moving through the rest of the digestive system. When a cow first eats, it chews the food just enough for it to travel to the first compartment. Later the cow will regurgitate the food as 'cud' and chew it thoroughly before the food moves progressively to the other compartments. Figure 16.4.4 shows the complexity of a cow's stomach.

Koalas eat an even higher fibre diet than cows do. Koalas have a large caecum (a bag of microorganisms) in their gut at the junction between the small and large intestine. **Microbial** digestion of cellulose occurs there; bacteria break down cellulose into smaller molecules that can be absorbed. Baby koalas build up levels of these microbes by eating their mother's faeces. Baby elephants (Figure 16.4.5) also feed on the dung of their mothers to build up the level of microbes in their gut.

FIGURE 16.4.5 Baby elephants feed on the dung of their parent to build up levels of microorganisms in their own stomach. These microrganisms break down cellulose into smaller molecules.

Lactose hydrolysis

Lactose is a disaccharide formed from the reaction between glucose and galactose. It has a sweet taste and is the predominant carbohydrate in the milk of mammals. The structure of lactose is shown in Figure 16.4.6. As with all other carbohydrates, the glucose and galactose sugars of the disaccharide are joined by a glycosidic linkage.

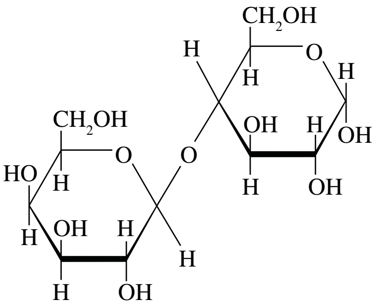


FIGURE 16.4.6 Lactose is a disaccharide made from glucose and galactose.

Usually when people drink milk, the enzyme lactase, found in the small intestine, hydrolyses lactose back to glucose and galactose. However, in some people milk and milk-based products such as ice cream can cause flatulence and stomach cramps. This is known as **lactose intolerance** and is commonly due to a lack of the enzyme lactase. If the body does not produce enough lactase, the lactose does not undergo hydrolysis and ferments in the gut, producing gas and cramping.

Lactose intolerance cannot be cured but its effects can be reduced by:

- adding lactase tablets to milk or taking lactase tablets before consumption. The added lactase hydrolyses the lactose
- consuming milk and milk-derived products such as cheese that have been processed to remove the lactose, such as those shown in Figure 16.4.7
- using a milk substitute, such as rice milk or soy milk. These plant-based products do not contain lactose.

FIGURE 16.4.7 The milk and cheeses shown here have had the lactose removed or fermented into lactic acid. The cheeses are ricotta, feta and mozzarella.

Lactose intolerance is not necessarily a problem when consuming butter and cheese. Lactose, like other disaccharides, is water soluble and more likely to be in the whey of milk than the fatty curds. Cheese and butter are made from the curds and contain very low levels of lactose. The harder the cheese and the longer it is aged, the lower the lactose content is.

GLYCAEMIC INDEX

Carbohydrates are a good source of energy for humans because when digested they produce glucose. The glucose is transported in the bloodstream for use by the cells of the body. The term **blood sugar** refers to the glucose that is present in the blood.

Carbohydrate-containing foods can be rated on a scale called the **glycaemic index** (GI). This scale ranks foods according to their effect on blood sugar levels over a period of time, usually 2 hours. It is therefore related to how quickly foods release the energy they contain. Another way of looking at a GI value is that it is a measure of the rate of hydrolysis of the carbohydrates present in a food.

Foods containing carbohydrates are compared with pure glucose, which is given a GI score of 100. Foods such as starchy potatoes with a GI value of more than 70 are considered to have a high GI. This means they release energy quickly.

The oats in porridge have a low GI of 55 or less and are slow to digest. They release energy slowly. When you consume low-GI foods, you are less likely to feel hungry in the short term after eating. The GI values for some foods are shown in Figure 16.4.8.

The glycaemic index of a food can be thought of as a measure of the rate of hydrolysis of the carbohydrates in food.





Snacks	GI	Starch	GI	Vegetables	GI	Fruits	GI	Dairy	GI
Pizza	33	White rice	38	Broccoli	10	Cherries	22	Yogurt, plain	14
Chocolate bar	49	White spaghetti	38	Pepper	10	Apple	38	Yogurt, low fat	14
Pound cake	54	Sweet potato	44	Lettuce	10	Orange	43	Whole milk	30
Popcorn	55	White bread	71	Mushrooms	10	Grapes	46	Soy milk	31
Energy bar	58	Porridge, rolled oats	55	Onions	10	Kiwi	52	Skim milk	32
Cola	72	Brown rice	55	Green peas	48	Banana	56	Chocolate milk	35
Doughnut	76	Pancakes	67	Carrots	49	Pineapple	66	Yogurt, fruit	36
Jelly beans	80	Wholemeal bread	59	Beets	64	Watermelon	72	Custard	43
Pretzels	83	Baked potato	85	Pumpkin	75	Dates	103	Ice cream	60

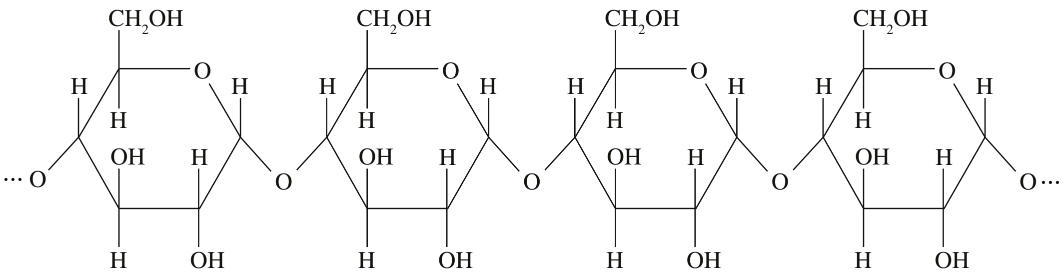
FIGURE 16.4.8 GI chart for different food groups.

An understanding of chemistry and the digestion process allows you to predict the GI values of many foods. The grains in wholemeal products still contain the husks, which are mainly composed of cellulose, and their particles are large. The rate of hydrolysis (digestion) is slowed because of the small surface area that is exposed and the lack of cellulase enzyme. On the other hand, the grains in finely ground white flour have had the outer husks removed. The increase in surface area and easier access to the starch inside the grains allows processed flours, such as that shown in Figure 16.4.9, to be easily digested.

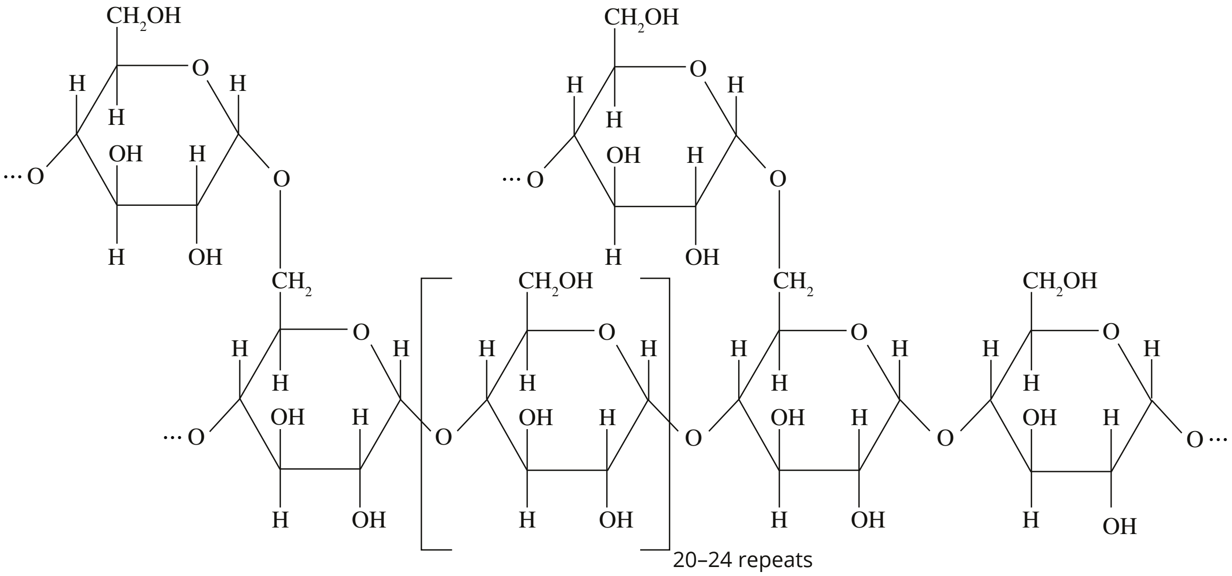
Fruit sugar has a low GI because it contains mainly fructose, which needs to be first converted to glucose in the liver before being released into the bloodstream.

The main reason for the varying rates of hydrolysis of carbohydrates is the type of starch present in the food. Figure 16.4.10 (page 548) shows the difference between linear and branched forms of starch. The linear structure of amylose allows its molecules to pack together tightly, making it less soluble in water than the branched polymer amylopectin. On the other hand, the branched structure of amylopectin makes it more soluble in water than amylose and there is greater access for enzymes to hydrolyse its glycosidic links. As a consequence, amylopectin is digested more rapidly than amylose.

FIGURE 16.4.9 Grains of wheat are slow to be digested because enzymes cannot contact the starch until the husk has softened and cracked. Milled wheat produces flour that is digested very quickly.



amylose



amylopectin

FIGURE 16.4.10 Amylose is a straight chain polymer while amylopectin is a polymer with branches along the chain of glucose units.

Foods with a high percentage of amylopectin tend to have a high GI. Foods with a low GI value often have a high proportion of amylose, where the molecules are more tightly packed together and more resistant to the penetration of enzymes. Depending on the plant, starch usually contains 20–25% amylose and 75–80% amylopectin.

In general, starches from grains, such as wheat and rice, have a higher amylose content (are slower to be digested) than starches from tubers, such as potatoes. Figure 16.4.11 compares what happens to blood sugar levels when you consume low-GI foods and high-GI foods.

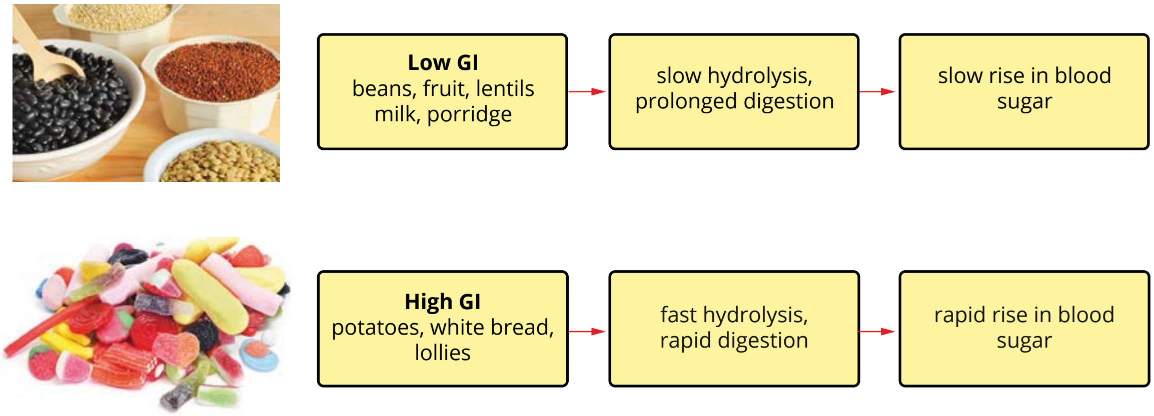


FIGURE 16.4.11 Comparison of low-GI with high-GI foods.

Dietary implications

While the GI levels of food are a consideration when choosing a good diet, there are too many complicating factors to simply say that you should only consume low-GI foods. A good diet must be balanced and contain a variety of different food types to ensure that you receive the required levels of macronutrients and micronutrients.

Often, low-GI foods are healthy because of the other nutrients that they contain, rather than their low GI rating. Fruits containing vitamins and antioxidants are an example of this, as are foods made from whole grains and vegetables, such as beans and broccoli, which provide you with the benefit of dietary fibre.

Figure 16.4.1 (on page 544) posed the question of whether a bowl of porridge is a good source of energy for all athletes. With your understanding now of how carbohydrates are digested in the body you should realise that porridge would be a suitable food for a distance runner because it releases energy slowly and steadily, matching the efforts of the athlete. However, a woodcutter might prefer a few jelly beans before competing as he needs his energy released very quickly for a short burst of high-intensity effort.

CHEMFILE

Diabetes

Blood sugar levels are particularly important for people with type 2 diabetes. Glucose and fat storage in the body is regulated by the hormone insulin. People with type 2 diabetes are resistant to the action of insulin or cannot produce insulin quickly enough to match the release of glucose into the blood (Figure 16.4.12). This means their blood glucose levels are not regulated efficiently and may rise above or fall below normal levels.

Low-GI foods such as porridge can be good for people with diabetes because these foods release glucose very slowly. However, if a person with diabetes experiences a 'hypo', where their blood glucose level falls below the normal range of 4–8 mmol L^{-1}, they need to eat a high-GI food such as jelly beans to quickly raise their blood sugar. People with type 2 diabetes are not always dependent on insulin injections, because type 2 diabetes can often be controlled by diet and exercise.

People with juvenile onset diabetes—type 1 diabetes—are insulin dependent and must have regular insulin injections in order to control their blood sugar levels within a safe range.

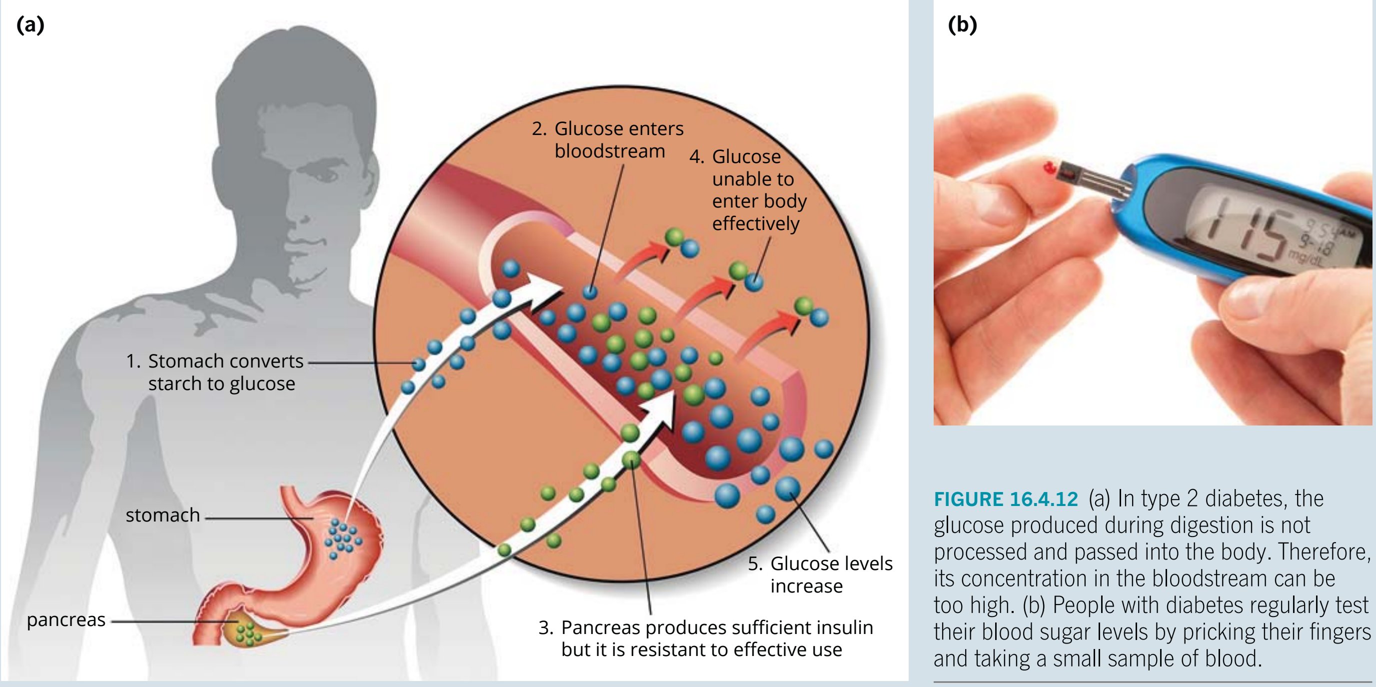


FIGURE 16.4.12 (a) In type 2 diabetes, the glucose produced during digestion is not processed and passed into the body. Therefore, its concentration in the bloodstream can be too high. (b) People with diabetes regularly test their blood sugar levels by pricking their fingers and taking a small sample of blood.

16.4 Review

SUMMARY

- Carbohydrates are hydrolysed during digestion to smaller carbohydrates, often glucose.
- Polysaccharides are hydrolysed to disaccharides and then to monosaccharides. The monosaccharides can be transported in the bloodstream to cells for the production of energy or storage as glycogen (Figure 16.4.13).
- Enzymes play an important role in hydrolysis. Amylase and maltase hydrolyse glycosidic links in starch and maltose in the digestive process.
- Humans cannot digest cellulose. However, some animals, such as cows and koalas, have bacteria in their digestive tracts that digest cellulose using the enzyme cellulase. The glucose produced from this process is a source of energy for the animal.
- Lactose intolerance is often the result of a human not being able to produce the enzyme lactase to hydrolyse lactose in milk.
- The branches in the amylopectin component of starch make it easier to hydrolyse than the amylose component.
- The glycaemic index (GI) of a food is a measure of its impact upon blood sugar levels. High-GI foods are digested easily and can cause a spike in sugar levels. Low-GI foods are slow to digest and they have a smaller effect upon blood sugar levels, providing energy over a longer period of time.

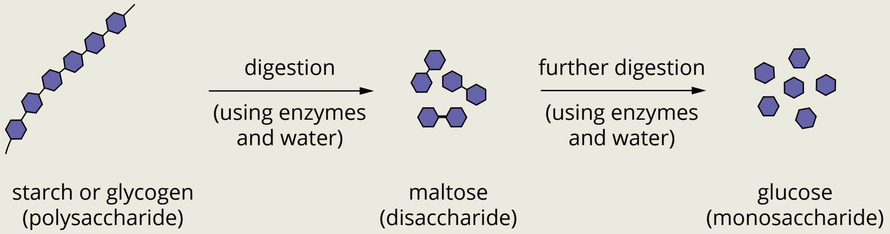


FIGURE 16.4.13 Hydrolysis of polysaccharides.

KEY QUESTIONS

1 Sucrose is a disaccharide with a molecular formula of $C_{11}H_{22}O_{11}$.

  - **a** What is the molecular formula of the monosaccharides from which it is formed?
  - **b** What is the name of the link between the monosaccharide units that breaks when sucrose is hydrolysed?

2 Sort the following carbohydrates in order of ease of digestion in humans (easiest to hardest): cellulose, amylopectin, maltose, amylose.

3 For each carbohydrate, identify where in the digestive system hydrolysis occurs and by which enzyme.

  - **a** Maltose
  - **b** Cellulose
  - **c** Starch
  - **d** Lactose

4 Examine each pair of substances and decide which member of the pair has the lower GI.

  - **a** Amylose and amylopectin
  - **b** Ground flour and wheat grain
  - **c** Broccoli and potato
  - **d** Strawberry and jelly bean
  - **e** Skim milk and whole milk

5 Fill in the blanks to complete the sentences about porridge.

Porridge is an example of a __________ GI food. It digests __________ due to the relatively __________ surface area of its components. It releases energy ___________ and its impact upon blood sugar levels will be ____________.

16.5 Hydrolysis of fats and oils

Nutritionists generally agree that you should only consume a meal of fish and chips like the one shown in Figure 16.5.1 on an occasional basis. Although some fats and oils are essential in the diet, foods such as fish and chips, pizzas, hot dogs, pies and snacks often contain a high proportion of fats and oils (triglycerides), which are thought to increase the risk of cardiovascular disease.

In this section, you will examine how the digestive system hydrolyses triglycerides into smaller, more soluble molecules that can be transported around the body.

You will also consider the factors that cause fats and oils to 'go off', developing an unpleasant taste or offensive odours.

FIGURE 16.5.1 A meal of fish and chips contains a relatively high amount of fat or oil.

HYDROLYSIS OF TRIGLYCERIDES

A triglyceride is a large molecule formed from the reaction between glycerol and three fatty acid molecules. Figure 16.5.2 shows the structure of a typical triglyceride. The ester links joining the glycerol to each fatty acid molecule have been highlighted.

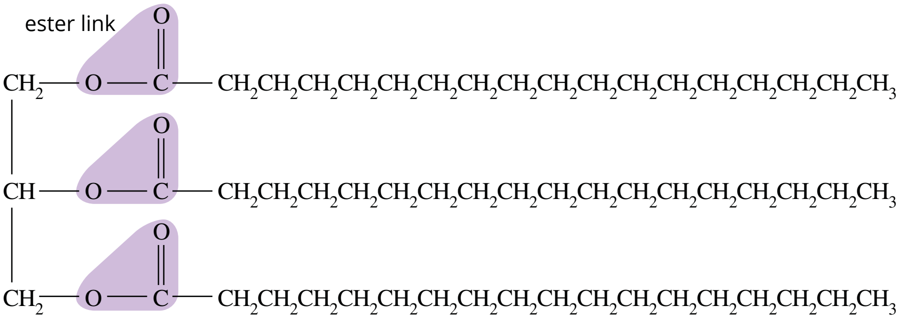


FIGURE 16.5.2 Structure of a triglyceride showing the three ester links in the molecule.

Like proteins and carbohydrates, triglycerides undergo enzyme-catalysed hydrolysis during digestion. However, unlike proteins and carbohydrates, triglycerides are insoluble in water so their molecules remain intact as they pass through the digestive tract until they reach the small intestine. In the small intestine, **bile** is used to process the triglycerides.

Bile is produced in the liver but is stored in the gall bladder, where it is concentrated. It enters the duodenum, or upper part of the small intestine, via the bile duct. The relationship between these organs is shown in Figure 16.5.3.

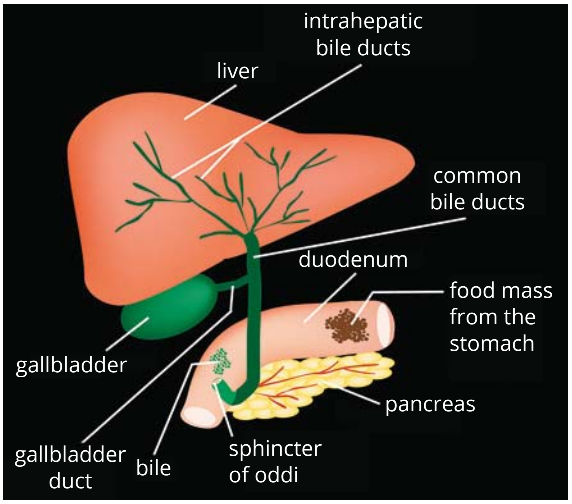


FIGURE 16.5.3 A section of the small intestine is shown in the lower part of the diagram. Bile is produced in the liver and stored in the gall bladder. It moves into the small intestine when needed.

Bile emulsifies fats, breaking them down into smaller particles and dispersing them as small droplets. This process of creating an **emulsion** is similar to how detergents work on the fat left in a frying pan after cooking fatty food. The effect of emulsification on fats in the small intestine is shown in Figure 16.5.4.

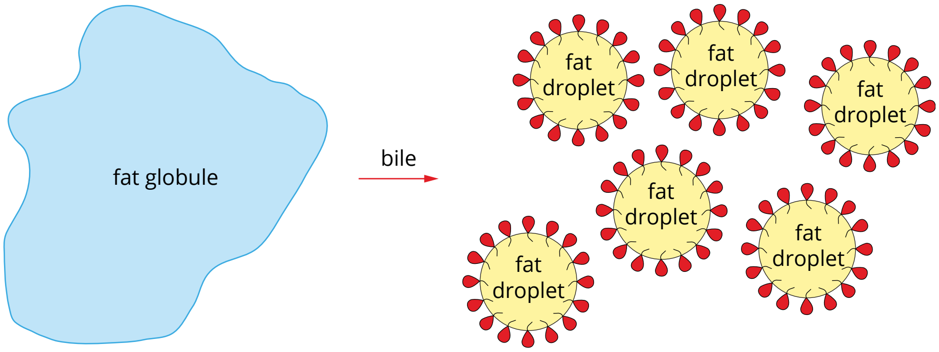


FIGURE 16.5.4 A triglyceride enters the small intestine as a fat globule or an oil globule. The bile turns this globule into an emulsion, consisting of much smaller fat droplets with bile particles embedded in the surface. The surface area of the fat exposed for hydrolysis by the water-soluble lipase enzyme is now much greater.

Emulsification of fats increases their surface area, so that more triglyceride molecules are exposed to the aqueous environment.

In your body, the enzyme lipase breaks down triglycerides. However, lipase is a water-soluble protein so it can only interact at the surface of the hydrophobic fat globules. Emulsification of fats by bile increases the surface area of the fats, which means that lipase can access more triglyceride molecules, which increases the rate of hydrolysis.

Lipase enters the intestine from the pancreas. The enzyme catalyses the hydrolysis of the three ester bonds in the triglyceride molecules. You can see in Figure 16.5.5 how the triglyceride molecules undergo hydrolysis to form glycerol and fatty acids.

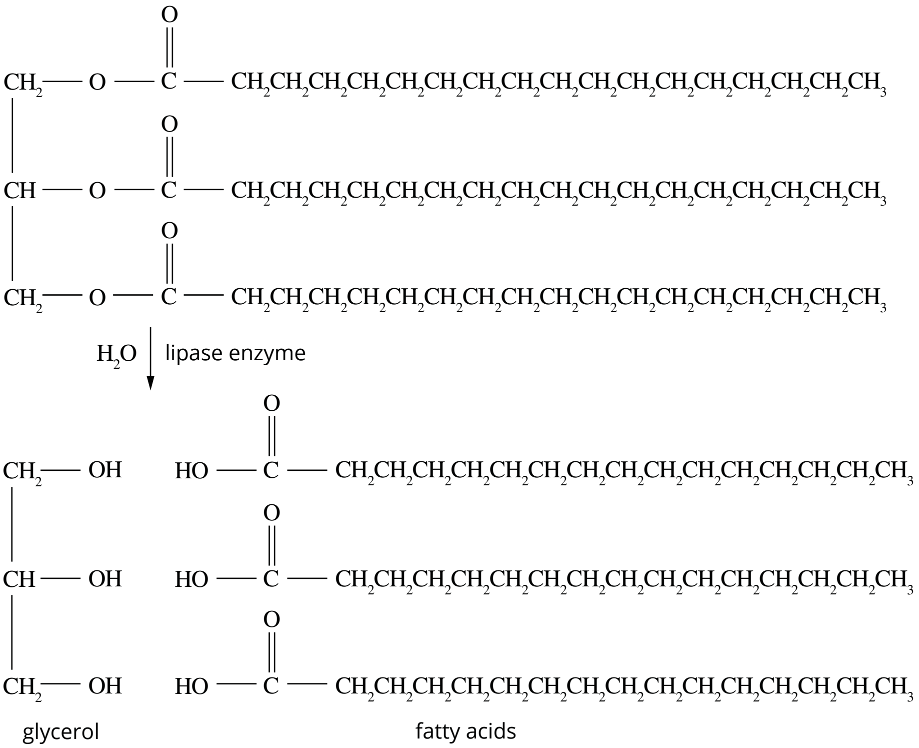


FIGURE 16.5.5 Hydrolysis of a triglyceride to glycerol and three fatty acid units.

The three fatty acids will not necessarily have the same structure. Figure 16.5.6 shows a general equation for the hydrolysis of a triglyceride where the letter R is used to represent each fatty acid hydrocarbon chain.

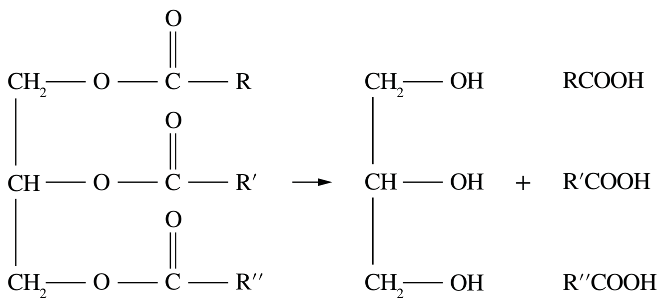


FIGURE 16.5.6 General equation for the hydrolysis of a triglyceride. R, R′ and R″ represent different hydrocarbon chains.

The glycerol and fatty acids that are produced pass into the bloodstream to the liver, where they are re-formed into triglycerides.

When the amount of fat and carbohydrate eaten is more than required to meet the body's energy needs, triglycerides are stored in **adipose tissue** as an energy reserve. Adipose tissue, or fatty tissue, is connective tissue consisting mainly of fat cells. It is found under the skin or in deposits around muscles or organs and serves as long-term energy storage in the body. A simplified version of the digestion of fat and its eventual storage in adipose tissue is shown in Figure 16.5.7.

Triglyceride hydrolysis produces four molecules: one glycerol molecule and three fatty acid molecules.

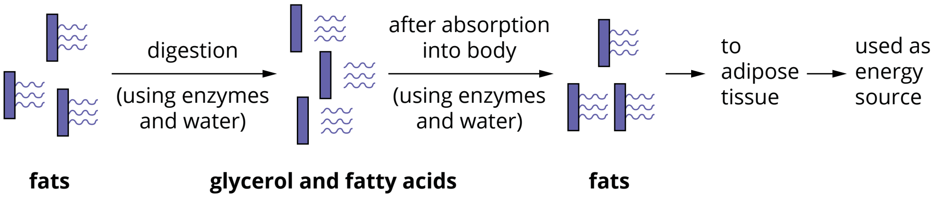


FIGURE 16.5.7 When fats are digested, they are first hydrolysed then re-formed for transport to the adipose tissue. They can be stored in fat cells in the adipose tissue.

The diagram in Figure 16.5.8 represents the storage of fat globules in adipose tissue under the skin. High levels of adipose tissue are associated with bad health. The build-up of adipose tissue around organs is particularly dangerous.

When the body requires energy, triglycerides are hydrolysed and transported to muscle cells. At the muscle cells, the fatty acids are oxidised. The eventual products of this complex process are carbon dioxide and water. A typical equation is:

$$CH_3(CH_2)_{14}COOH(aq) + 23O_2(g) \rightarrow 16CO_2(g) + 16H_2O(l) \quad \Delta H = -9770\ kJ\ mol^{-1}$$

Excess glycerol is transported to the liver where it may be converted into glucose.

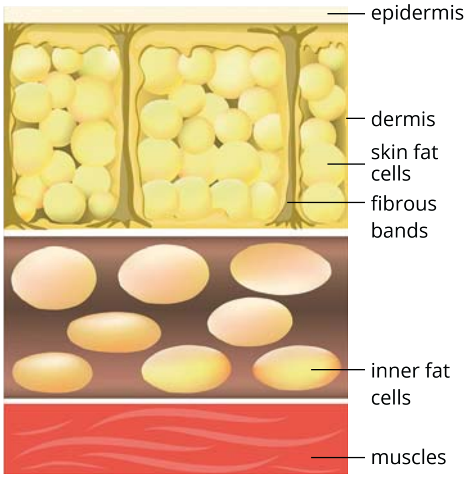


FIGURE 16.5.8 Fat deposits are often found under the skin as globules of fat stored in connective fatty tissue. High levels of fat deposits are not good for health.

RANCIDITY

Like all food components, fats and oils deteriorate over time and so they cannot be stored indefinitely. In particular, unsaturated fats are less stable than saturated ones.

The carbon–carbon double bonds in unsaturated fats are more reactive than single bonds and can react in a number of ways with enzymes, heat, water, oxygen or light. These reactions can lead to the formation of extra functional groups, such as hydroxyl groups, on the fat. In some cases, the hydrocarbon chain itself can break apart to form smaller molecules with noxious odours or flavours. When this happens, the oxidised fat is described as **rancid**. Rancidity is a notable deterioration in taste or smell.

Fats and oils can become rancid by different processes, depending on conditions and their chemical structure. One of these processes, **oxidative rancidity**, leads to the formation of unpleasant smelling and potentially harmful short-chain aldehydes and ketones. The higher the degree of unsaturation of a triglyceride, the more susceptible it is to oxidation. Foods such as fish contain high levels of unsaturated triglycerides that are susceptible to rancidity (Figure 16.5.9).

FIGURE 16.5.9 Fish and many other foods need to be stored in the refrigerator. The oils from fish such as tuna and mackerel are examples of highly unsaturated triglycerides.

These foods should be stored in the refrigerator, where the lower temperatures reduce the rate of oxidation and delay the formation of oxidative by-products that cause bad odours.

The most important type of oxidative rancidity is **autoxidation**, which involves a **free radical** chain reaction.

Free radicals are molecules or atoms with unpaired outer-shell electrons. They are unstable and highly reactive. The formulas of free radicals are often written with a dot to represent the unpaired electron. Two examples of free radicals are shown in Figure 16.5.10.

$\bullet CH_3$ $\bullet OH$

FIGURE 16.5.10 Two examples of free radicals, a methyl radical and a hydroxyl radical. They both have a single unpaired electron, represented as a dot.

EXTENSION

Autoxidation of fats

Autoxidation is a complex process. There are three main steps in the free radical chain reaction.

1 Initiation: formation of free radicals

A bond in an unsaturated fatty acid is broken in the presence of sunlight or a metal catalyst and free radicals are formed. The reaction for the formation of the radical species can be represented as:

$RH \xrightarrow{\text{sunlight}} R\bullet + H\bullet$

2 Propagation: the continued formation of free radicals (the chain reaction)

The fatty acid radical reacts with oxygen to form a fatty acid peroxyl radical, ROO•, which in turn reacts with another fatty acid to form a fatty acid hydroperoxide, ROOH:

$R\bullet + O_2 \rightarrow ROO\bullet$

$ROO\bullet + RH \rightarrow ROOH + R\bullet$

The hydroperoxide molecule is unstable and can break up into aldehydes and ketones, which cause the unpleasant smell and taste of rancid food.

For example:

$ROOH \rightarrow R'CHO + R''\bullet + OH\bullet$

(where R, R´ and R´´ are hydrocarbon chains of different lengths)

3 Termination: the reaction ends when two radicals combine

For example:

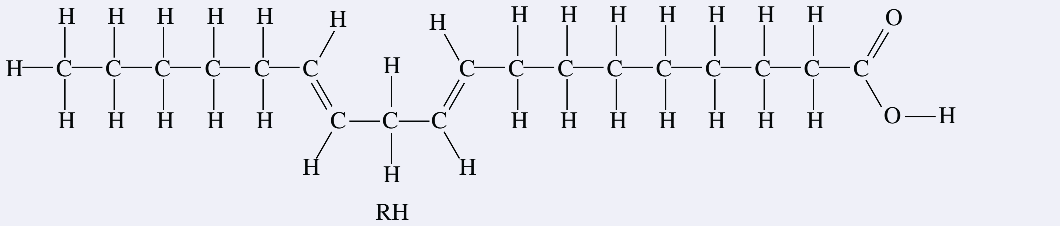
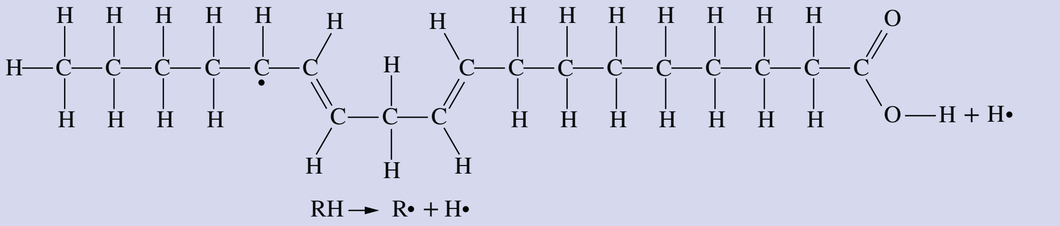
$R\bullet + ROO\bullet \rightarrow ROOR$

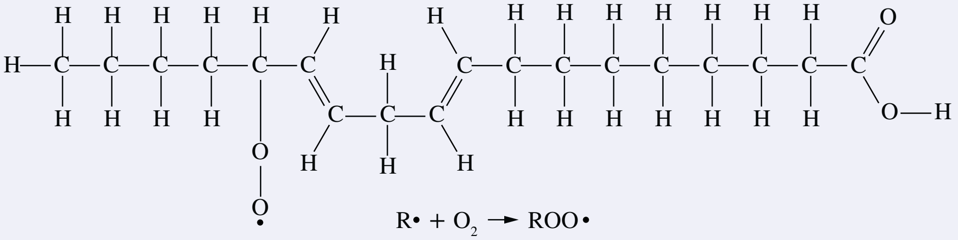
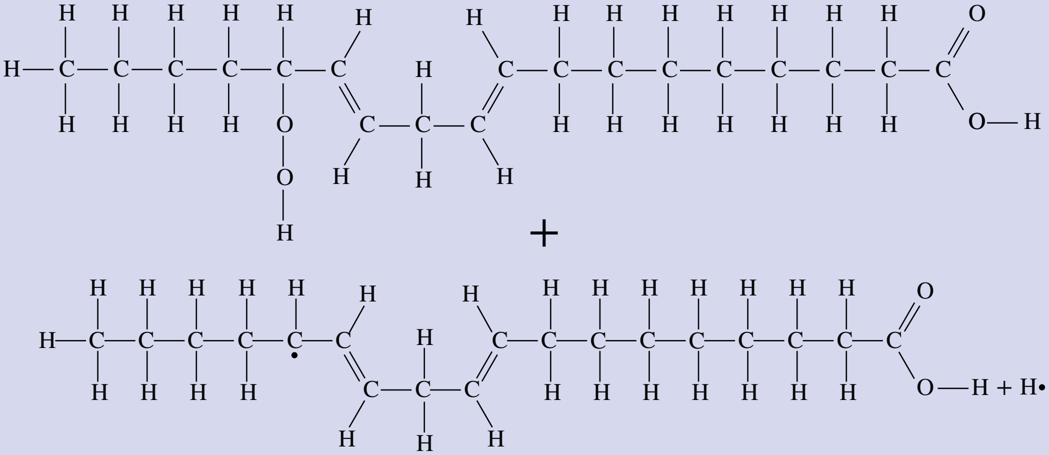
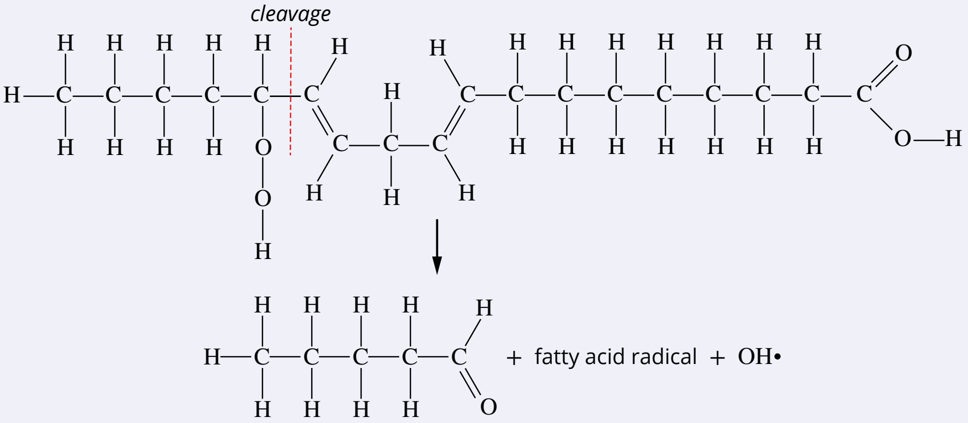
$R\bullet + R\bullet \rightarrow R\text{–}R$

$ROO\bullet + ROO\bullet \rightarrow ROOR + O_2$

The reactions in the initiation and propagation steps for linoleic acid are outlined in Table 16.5.1.

TABLE 16.5.1 Autoxidation of linoleic acid.

Description	Diagram
Linoleic acid, general formula RH, is shown at right. The carbon atoms adjacent to the double bonds are susceptible to oxidation.	
Initiation A carbon–hydrogen bond is broken at the fifth carbon in the chain next to the carbon–carbon double bond. The hydrogen and carbon atoms retain one electron each, producing a free radical hydrogen and a free radical fatty acid.	

Propagation An oxygen molecule bonds to the carbon from where the hydrogen was removed, to form a new free radical, called a fatty acid peroxyl radical.	 $R\bullet + O_2 \rightarrow ROO\bullet$
Propagation The fatty acid peroxyl radical reacts with a nearby fatty acid molecule to form a fatty acid hydroperoxide and to create a new free radical. This is also a propagation step, where one free radical creates a chain reaction of more free radicals.	 $ROO\bullet + RH \rightarrow ROOH + R\bullet$
The hydroperoxide undergoes several different reactions, one of which is to cleave the molecule at the carbon atom to which the peroxide is attached. It is this reaction that often forms products, such as pentanal, considered to be rancid.	 pentanal (unpleasant smell and taste) formation of aldehyde: $ROOH \rightarrow R'CHO + R''\bullet + OH\bullet$

A relatively small amount of oxygen can lead to a significant degree of rancidity. During the propagation steps, a fatty acid free radical converts another fatty acid to a free radical and a chain reaction occurs. The steps for the radical-initiated oxidation of fatty acids is outlined in the flowchart in Figure 16.5.11.

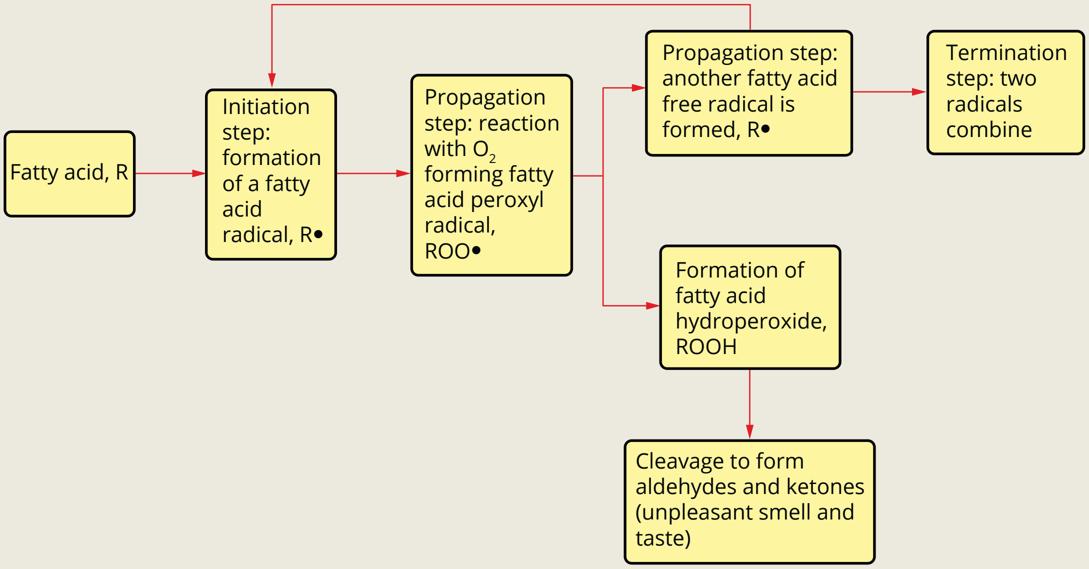
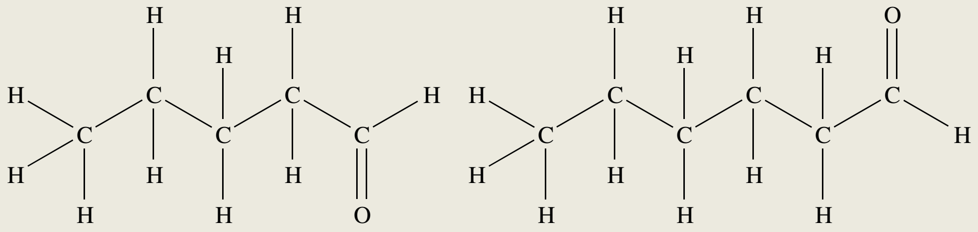


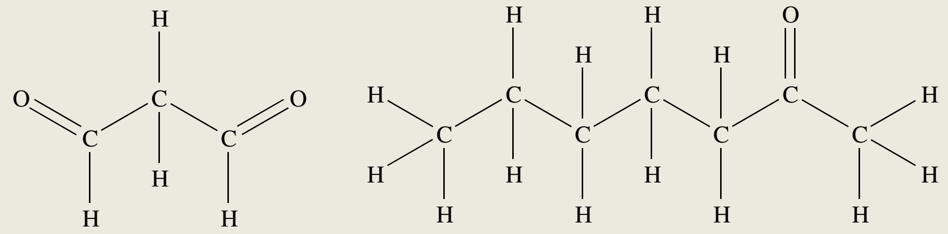
FIGURE 16.5.11 Flowchart for oxidative rancidity for an unsaturated fatty acid or triglyceride. The end result is the molecule breaking at the carbon–carbon double bond.

This sequence of reactions is one of many possible autoxidation reactions for linoleic acid. A variety of different products can form during the oxidation. Some of the products have no effect on taste and flavour, while others are unpleasant or even toxic. Examples of unpleasant compounds formed from oxidation of triglycerides are shown in Figure 16.5.12.



pentanal (musty smell)

hexanal (grassy smell)



malonaldehyde (pungent smell)

heptan-2-one (cheesy smell)

FIGURE 16.5.12 Four examples of products of meat or fish rancidity that have unpleasant smells.

Antioxidants

Methods for slowing the rate of deterioration of food include:

- dehydration
- refrigeration
- use of preservatives
- use of **antioxidants**.

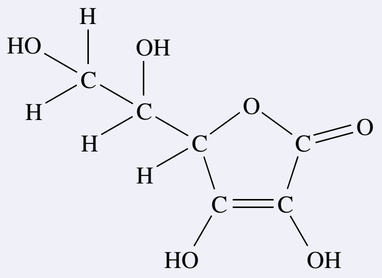
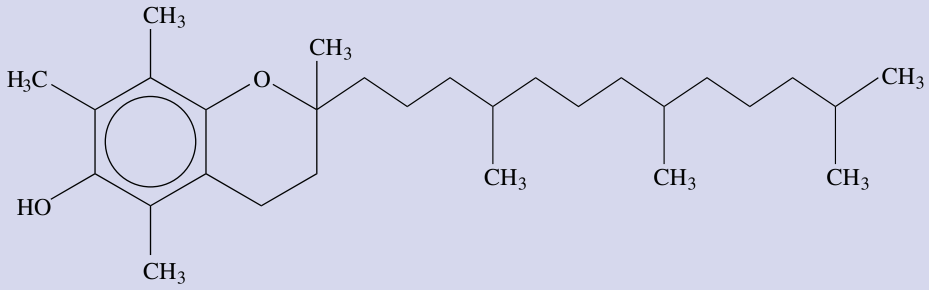
An antioxidant is a substance that slows the rate of oxidation of another substance, or simply delays its oxidation. Antioxidants do not stop the formation of free radicals, but they do interrupt the propagation of free radicals.

Antioxidants can interrupt the propagation of free radicals once they are formed.

Some antioxidants, such as vitamin C, are oxidised in preference to fats and oils. However, most antioxidants work by donating a hydrogen atom to peroxide radicals, preventing them from reacting with nearby molecules. These hydrogen atoms often come from hydroxyl groups in the antioxidant molecules.

Antioxidants are naturally present in some foods while synthetic antioxidants are added to other foods to aid in preservation. Table 16.5.2 lists some naturally occurring antioxidants and the foods in which they can be found.

TABLE 16.5.2 Some natural antioxidants and their sources

Antioxidant	Food sources
Selenium	Fish, red meat, eggs, chicken, shellfish, whole grains, brazil nuts, garlic
α-Carotene	Carrots, sweet potatoes, broccoli, palm oil, peaches, tomatoes, apricots, mangoes, rockmelons.
Ascorbic acid (vitamin C) 	Citrus fruits, green leafy vegetables, green capsicums, strawberries, kiwi fruit
Vitamin E (some carbon and hydrogen atoms are omitted in the formula below for clarity) 	Soybeans, sunflowers, canola, wheat germ, nuts, seeds, whole grains

A diet that includes a range of different-coloured fruit and vegetables is likely to contain a significant proportion of antioxidants. Blueberries, citrus fruit, leafy vegetables and whole grains are all good examples. You can see some of these foods in Figure 16.5.13.

FIGURE 16.5.13 These foods are high in naturally occurring antioxidants.

Some common synthetic antioxidants, along with their structures, are listed in Table 16.5.3.

TABLE 16.5.3 Synthetic antioxidants

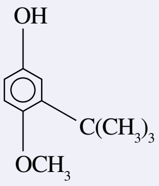
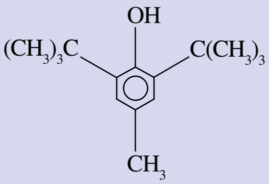
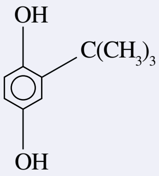
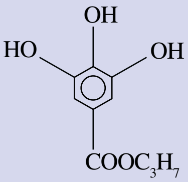
Abbreviation and formula	Name	Comments
BHA 	Butylated hydroxyanisole, which consists of two isomers, 2-tert-butyl-4-hydroxyanisole and 3-tert-butyl-4-hydroxyanisole	Fat-soluble and helps delay oxidative fat rancidity
BHT 	Butylated hydroxytoluene	Fat-soluble and helps delay oxidative fat rancidity
TBHQ 	Mono-tert-butylhydroquinone	Moderately soluble in both oil and water It acts as a preservative for unsaturated oils
PG 	Propyl gallate	Used in foods, cosmetics, hair products, adhesives, and lubricants

Figure 16.5.14 compares the structure of the natural antioxidant vitamin C with the structures of the synthetic antioxidants BHA and BHT. Note the hydroxyl groups on each molecule. These hydroxyl groups provide hydrogen atoms to react with fatty acid free radicals to prevent their propagation.

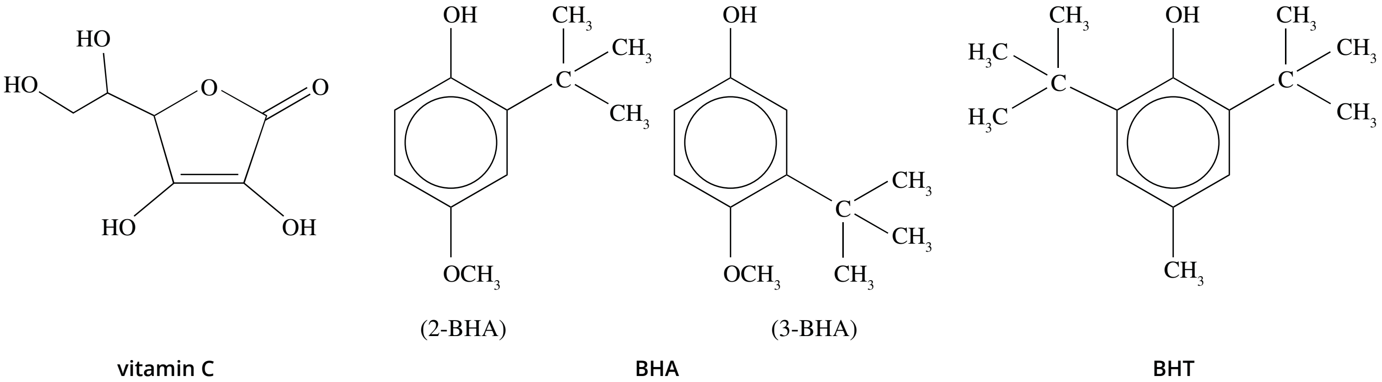


FIGURE 16.5.14 The structures of the natural antioxidant vitamin C and the synthetic antioxidants BHA and BHT.

Regulations govern the levels of synthetic antioxidants in packaged foods. Some synthetic antioxidants can be detrimental to health unless their levels are limited to accepted guidelines. The maximum permitted levels vary with the specific antioxidant. For example, levels of propyl gallate are controlled by Australian food code E310 to low levels of 100 mg kg^{-1} because of concerns about its toxicity, while levels of vitamin C are much higher.

CHEMFILE

What's in your olive oil?

There is continuing frustration among Australian olive oil producers at the lack of regulation of olive oil sold in Australia (Figure 16.5.15). In 2010, the University of California and the Australian Oils Research Laboratory both found extensive issues with olive oil imported from Europe.

These issues included:

- evidence of rancidity in 86% of samples
- oils labelled extra virgin were not extra virgin (69% of samples tested failed). Extra virgin means the oil is extracted by pressing rather than through solvents
- substitution of cheaper oils for olive oil.

In contrast, Australian oils performed very well in these tests.

The presence of rancidity in oils from overseas could be explained if the oils were stored before being transported over long distances. Unfortunately, it is difficult to take legal action over the substitution of inferior oils.

FIGURE 16.5.15 Testing of olive oils has indicated issues with oil quality and freshness.

16.5 Review

SUMMARY

- Triglycerides are hydrolysed by enzymes during digestion. The products are glycerol and the fatty acids from which the triglyceride was originally made.
- Digestion of triglycerides occurs in the small intestine where bile emulsifies the fat, which is then hydrolysed by the enzyme lipase.
- Once hydrolysed, the glycerol and fatty acids pass into the bloodstream to the liver where triglycerides are re-formed. The triglyceride can be stored in adipose tissue or it can be oxidised in muscle cells to release energy (Figure 16.5.16).
- Triglycerides can deteriorate with time, especially unsaturated triglycerides. When the flavour or aroma is spoilt, the triglyceride is described as rancid.
- Oxidative rancidity occurs as a consequence of the reaction of oxygen with unsaturated fats or fatty acids.
- Antioxidants improve the shelf life of foods, usually by reacting with free radicals and restricting their propagation.
- Some foods contain natural antioxidants. Other foods have synthetic antioxidants added to prolong shelf life. Synthetic antioxidants usually contain hydroxyl groups.

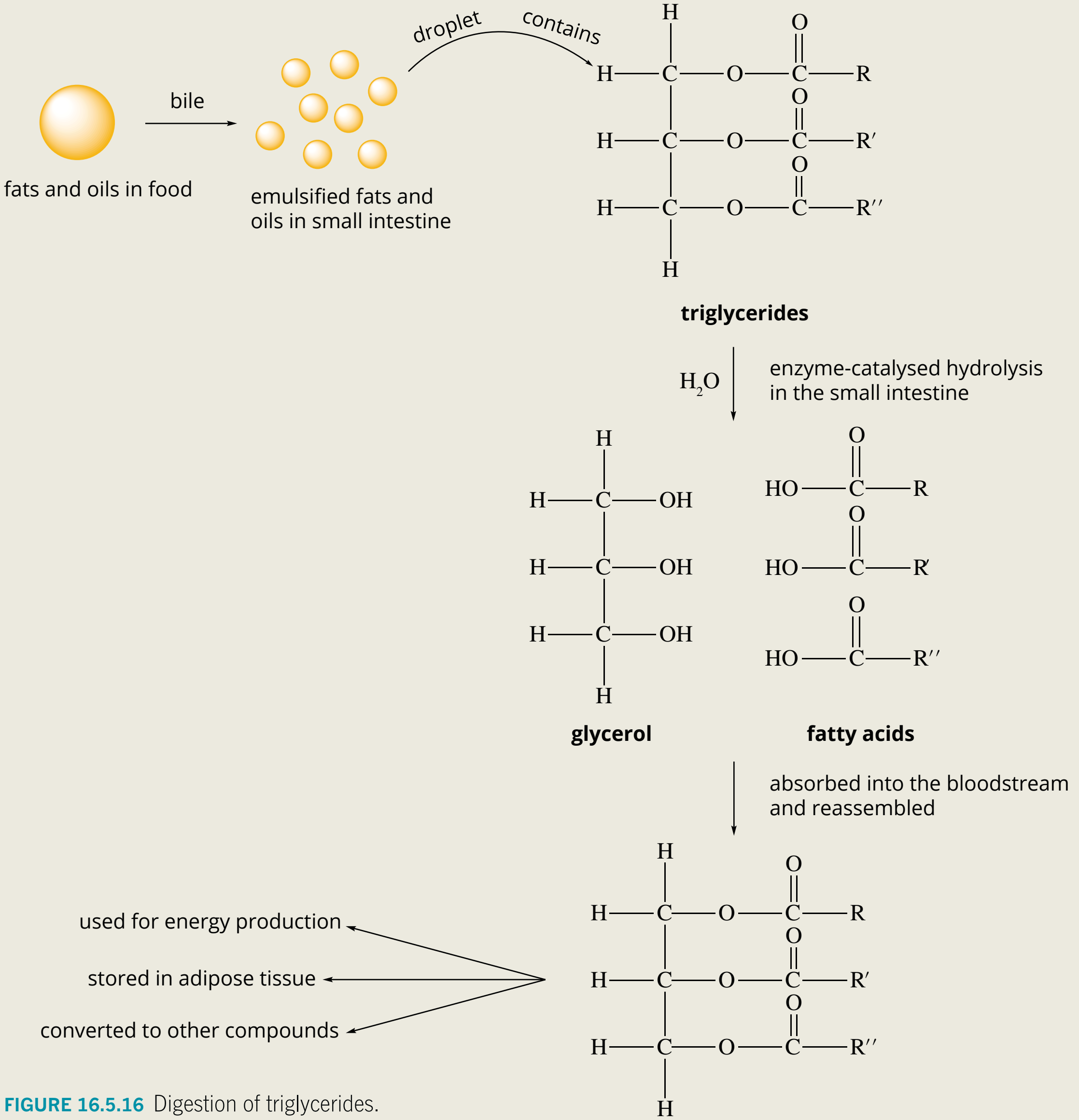


FIGURE 16.5.16 Digestion of triglycerides.

KEY QUESTIONS

1 Label the parts of the diagram in Figure 16.5.17 showing the hydrolysis of a triglyceride.

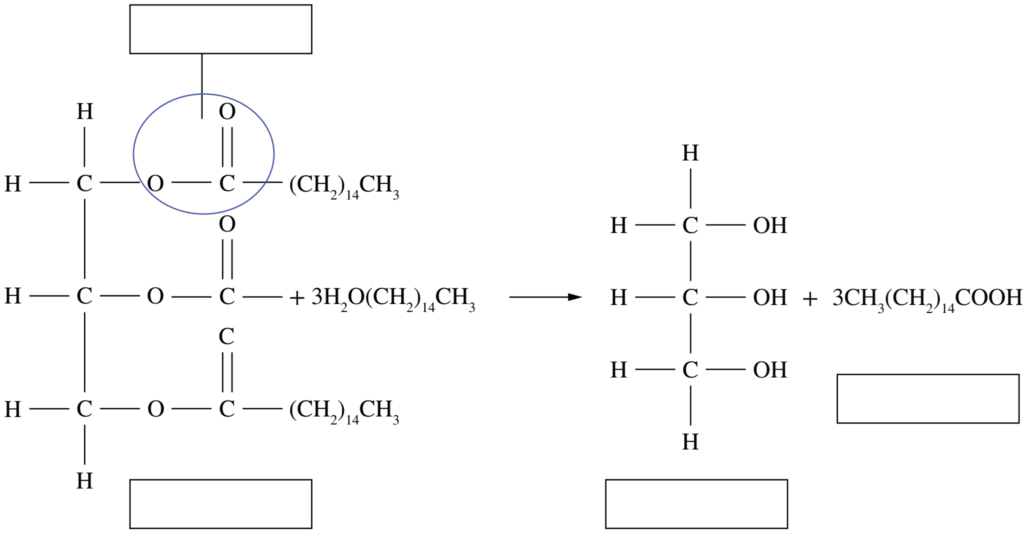


FIGURE 16.5.17 Hydrolysis of a triglyceride.

2 Define:

a hydrolysis

b oxidative rancidity

c emulsification

d condensation.

3 Complete the following sentences to produce a summary about the digestion of fats.

Digestion of fats occurs in the _________ _________. Bile _________ the fats and the enzyme lipase _________ them to fatty acids and __________. The products pass into the bloodstream to cells, where they can be re-formed and stored in _____________ _____________.

4 State whether each of the following statements about oxidative rancidity and antioxidants are true or false. Rewrite each false statement to make it true.

a Rancidity is more likely to occur when a triglyceride is saturated.

b Antioxidants often contain hydroxyl groups.

c Antioxidants react with the carbon–carbon double bonds in triglycerides before oxygen can.

d Rancidity can be the result of oxygen reacting near a carbon–carbon double bond in a fatty acid.

e Rancidity can only occur from the reaction between a triglyceride and water.

f Some vitamins are antioxidants.

Chapter review

16

KEY TERMS

active site
adipose tissue
2-amino acid
antioxidant
autoxidation
bile
biomolecule
blood sugar
cellulose
chiral centre
coenzyme
cofactor
condensation
denatured
digestion
disaccharide
emulsion
enantiomer
enzyme
enzyme activity
enzyme–substrate complex
free radical
glycaemic index
glycogen
glycosidic link
hydrolysis
hydrolytic reaction
lactose intolerance
macronutrient
metabolism
microbial
micronutrient
monosaccharide
nutrient
optical isomer
optimum pH
optimum temperature
oxidative rancidity
peptide link
polysaccharide
prosthetic group
quaternary structure
R group
rancid
side chain
starch
substrate
triglyceride
zwitterion

Metabolism of food

1 Determine whether each statement applies to a polysaccharide, triglyceride, protein or all of them.

- **a** Hydrolysis involves enzymes
- **b** Is not a polymer
- **c** Digestion starts with saliva
- **d** Can be stored in adipose tissue
- **e** Made in plants
- **f** Contains nitrogen
- **g** Prone to rancidity
- **h** Digestion involves the action of bile

2 Medicinal proteins such as insulin are administered by injection. Suggest why insulin cannot be given orally as tablets or capsules.

3 Complete the following table about the molecular structure of the major components of food.

	Names of links between units	Functional groups formed when links break	Monomer or smallest components
Carbohydrate		hydroxyl	
Fat		hydroxyl and …	… and glycerol
Protein		… and carboxyl	

Action of enzymes

4 **a** Name and describe the functions of two enzymes in the body.

- **b** Explain why the action of enzymes justifies the statement ‘Enzymes make life possible’.
- **c** Why is the action of an enzyme often described as operating like a lock and key?

5 Indicate whether the following statements summarising the properties of enzymes are true or false.

- **a** Enzymes are made of proteins.
- **b** Enzymes do not change the position of equilibrium.
- **c** Enzymes are consumed by the reaction.
- **d** Enzymes increase the activation energy of a reaction.
- **e** Enzymes increase the rate of reaction.
- **f** Enzymes are sensitive to conditions such as pH changes or temperature increase which denatures the enzyme.
- **g** Enzymes are highly specific for the biochemical reactions they catalyse because of the shapes of their active site.

6 On the diagram shown in Figure 16.6.1:

- **a** identify the model of enzyme action shown
- **b** label the parts of the diagram as indicated to show the first two steps of enzyme action
- **c** draw and label a diagram to show the next step in this process.

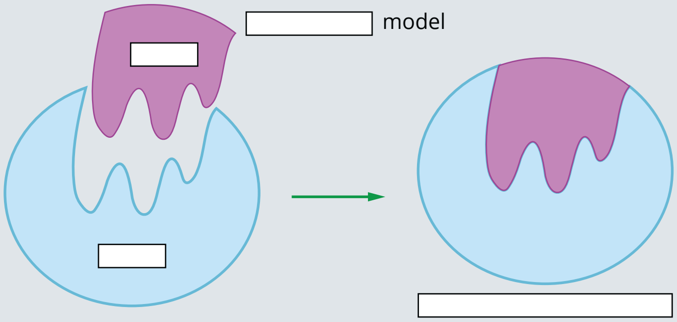


FIGURE 16.6.1 Model of enzyme action.

7 **a** The steps in the action of an enzyme involve, in particular, an active site and a substrate. With the use of a diagram, describe the action of an enzyme according to the induced fit model.

b The forces of attraction that enable a substrate to bind to an active site can vary. Describe four such forces.

Enzymes—dependence on pH and temperature

8 Jellied pineapple dessert cannot be made by using gelatine and fresh pineapple because an enzyme in the pineapple causes molecules in the gelatine to break down instead of setting. Suggest how jellied pineapple might be prepared.

9 Which one of these formulas gives the correct structure of tyrosine, $NH_2CH(C_6H_4OH)COOH$, in the highly acidic conditions present in the human stomach?

A $^{+}NH_3CH(C_6H_4OH)COOH$

B $NH_2CH(C_6H_4OH)COO^-$

C $^{+}NH_3CH(C_6H_4OH)COO^-$

D $NH_2CH(C_6H_4OH)COOH$

10 Draw the structure of the zwitterion form of the amino acid valine (Figure 16.6.2).

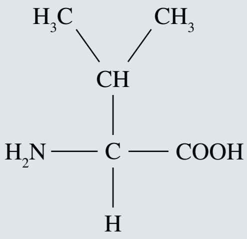


FIGURE 16.6.2 Valine.

11 The enzyme carbonic anhydrase catalyses the decomposition of carbonic acid molecules to carbon dioxide and water in the lungs. When heated to more than 60°C, the enzyme becomes denatured.

a What is meant by the term 'denatured'?

b Describe the events that usually occur to the structure of an enzyme when it is denatured.

c Does the primary structure of the carbonic anhydrase enzyme change during the process?

d Why is the functioning of the enzyme closely related to its tertiary structure?

12 The graph in Figure 16.6.3 shows the effect of temperature on the enzyme activity for a metabolic reaction. For each of the parts of the graph labelled A, B and C, explain the variation in enzyme activity with temperature.

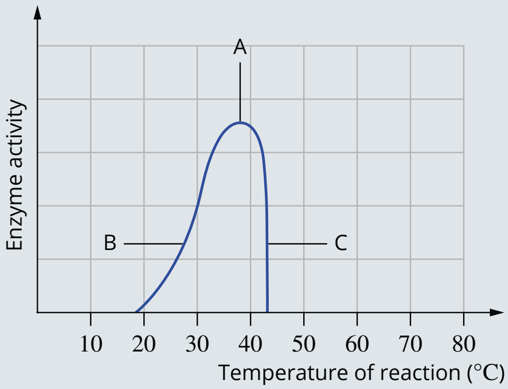


FIGURE 16.6.3 Graph of enzyme activity with temperature for a metabolic process in the body.

Hydrolysis of carbohydrates

13 Outline the steps of digestion of carbohydrates in the order in which they occur.

14 Lactose intolerance can cause bloating and discomfort in some people when they consume milk and milk products. Explain why this can occur.

15 Starch, glycogen and cellulose are all polymers that contain glucose monomers. Explain why the human body can completely digest starch and glycogen but cannot digest cellulose to any great extent.

16 Oats are a grain crop grown in Australia for cereals and other food products. They contain a high proportion of both starch and cellulose. Oats require very little processing before being added to foods. Explain why oats are considered a low-GI food.

Hydrolysis of fats and oils

17 Sort the following steps in the autoxidation of a fatty acid (RH) into the correct sequence.

$ROO\bullet \rightarrow ROOH$

$ROOH \rightarrow$ unpleasant products

$RH \rightarrow R\bullet + H\bullet$

$R\bullet + O_2 \rightarrow ROO\bullet$

Connecting the main ideas

18 Classify the following reactions as condensation or hydrolysis.

a Formation of protein from amino acid

b Formation of starch from the polymerisation of glucose

c Formation of triglyceride in the blood

d Breakdown of glycogen to glucose

e Formation of glycerol and palmitic acid from a fat

f Splitting of maltose into two molecules of glucose

19 Name the functional group that is formed in the reactions of:

- **a** stearic acid + glycerol →
- **b** glucose + fructose →
- **c** glycine + glycine →
- **d** glucose + glucose →
- **e** linoleic acid + glycerol →

20 Vitamin C ($C_6H_8O_6$) is an essential nutrient required in small amounts in the diet. Among its important functions, vitamin C acts as a coenzyme for a number of enzymes involved in the reaction pathways that produce collagen. Collagen is the main structural protein in the various connective tissues in animals.

Select from the following words to fill in the blanks in the following sentences to complete the summary about vitamin C: decreased, only one, lower, water-soluble.

With four hydroxyl groups, vitamin C is a __________ vitamin. Like many organic biomolecules, it contains chiral carbon atoms. It is likely that ____________ enantiomer(s) can act as a coenzyme for particular biochemical reactions.

In the absence of vitamin C, the activity of these enzymes will be ___________ and the amount of collagen produced will be__________.

21 **a** Vitamin C acts as an antioxidant in the human body. Explain how vitamin C does this and which functional groups are important for this action.

b Vitamin C is considered a natural antioxidant. What does this term mean?

CHAPTER 17

The energy content of food

Food is essential to your enjoyment of life and your very existence. The composition of different foods governs how they taste, their appearance, and the amount of nutrients and energy they supply when you eat them. Many people need to monitor their diet carefully, so it is important for this information to be reflected accurately on packaging.

In this chapter, you will compare the energy content of proteins, carbohydrates and fats. You will observe how the relative amounts of these in different foods influence the energy available from foods. You will learn how the energy content of foods is determined experimentally by burning them in a bomb calorimeter and how calorimeters can be calibrated to make the results obtained more accurate. Finally, you will look at how solution and bomb calorimetry can be used to determine the enthalpy change in a range of chemical reactions.

Key knowledge

- The comparison of energy values of carbohydrates, proteins and fats and oils
- Glucose as the primary energy source, including a balanced thermochemical equation for cellular respiration
- The principles of calorimetry; solution and bomb calorimetry, including determination of calibration factor and consideration of the effects of heat loss; and analysis of temperature–time graphs obtained from solution calorimetry

17.1 Food—an energy source

Food supplies the energy required for the millions of chemical reactions that occur in your body. Energy is needed for physical activity and functions such as breathing, as well as for the production of materials for growth and repair.

The balance between the energy supplied by the food you eat and the energy you use in everyday activities is a frequent topic of discussion. While thin fashion models are portrayed as having the 'perfect' body shape, studies reveal that obesity is on the rise and people are heavier than they used to be. In contrast, in some parts of the world, people can only dream of the opportunity to eat as much as their bodies need every day.

If you take in more energy from food than you use, you will gain weight. Similarly, if you use more energy than is supplied to your body, you will lose weight. It is important to know how much energy is available from particular foods, so processed foods are labelled with their energy content, as well as percentages of carbohydrates, fats and protein.

Table 17.1.1 summarises the nutrient and energy content of some common foods.

The unit of energy is the joule (J). Larger amounts of energy are commonly expressed in kilojoules (kJ). 1 kJ = 1000 J.

TABLE 17.1.1 The nutrient and energy content of some common foods (per 100 g)

Food	Carbohydrates (g/100 g)	Fat (g/100 g)	Protein (g/100 g)	Energy (kJ/100 g)
 Milk chocolate	52	30	8	2130
 Donut	51	23	5	1803
 Hot chips	40	19	3	1434
 Apples	13.8	0.2	0.3	247

ENERGY FROM GLUCOSE

You may remember from Chapter 15 that glucose is a **monosaccharide**, one of the simplest **carbohydrates**. Fructose, found in fruits and honey, is also a monosaccharide. All monosaccharides are white, crystalline solids with a sweet taste, and all have the formula $C_6H_{12}O_6$.

Molecules of the monosaccharides contain a number of polar hydroxyl groups, enabling them to form hydrogen bonds with water. As a result, monosaccharides are highly soluble in water. The structure of glucose is shown in Figure 17.1.1.

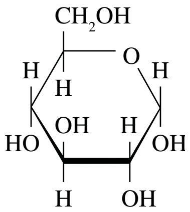


FIGURE 17.1.1 Structural formula of glucose. Carbon atoms in the ring have been omitted for clarity.

The smallest carbohydrates are the monosaccharides. With the molecular formula $C_6H_{12}O_6$, glucose, fructose and galactose are isomers. Starch, cellulose and glycogen are polysaccharides—polymers of glucose molecules linked together in different ways by condensation reactions.

Glucose is found in all living things, especially in the juice of fruits, the sap of plants and the blood and tissue of animals. Both glucose and its polymer starch are more rapidly digested than other forms of food. They are the main sources of energy in most diets and the human body uses them for energy in preference to fats and proteins.

The process by which polysaccharides are broken down to form monosaccharides such as glucose is called **hydrolysis**. This process was described in detail in Chapter 15 on page 470.

Cellular respiration

Glucose is the primary energy source for the cells of plants and animals and is used to obtain energy by a process known as **cellular respiration**. There are two main types of cellular respiration.

- **Aerobic respiration** requires oxygen and is the main source of energy for the human body.
- **Anaerobic respiration** does not require oxygen and yields less energy.

In aerobic respiration, glucose is oxidised to carbon dioxide and water through a sequence of reactions. The overall equation for aerobic respiration is:

$$C_6H_{12}O_6(aq) + 6O_2(g) \rightarrow 6CO_2(g) + 6H_2O(l) \qquad \Delta H = -2860 \text{ kJ mol}^{-1}$$

In humans, an alternative form of respiration, called anaerobic respiration, can occur in muscles during prolonged and vigorous exercise, when the supply of oxygen is limited. It can result in the build-up of lactate ions, $CH_3CH(OH)COO^-$, which can cause painful muscular cramping. The overall equation for anaerobic respiration in humans is:

$$C_6H_{12}O_6(aq) \rightarrow 2CH_3CH(OH)COO^-(aq) + 2H^+(aq) \qquad \Delta H = -120 \text{ kJ mol}^{-1}$$

In yeast, anaerobic respiration produces ethanol and carbon dioxide—this process is widely used to produce alcoholic beverages. The equation for this process is:

$$C_6H_{12}O_6(aq) \rightarrow 2C_2H_5OH(aq) + 2CO_2(g) \qquad \Delta H = -69 \text{ kJ mol}^{-1}$$

These reactions for anaerobic and aerobic respiration are all exothermic. Although anaerobic respiration yields less energy per mole of glucose, it is often a faster process than aerobic respiration. Short bursts of exercise, such as sprinting, rely on anaerobic processes for energy because the individual steps in the reactions involved in anaerobic respiration occur more rapidly.

EXTENSION

Exercise and lactate ions

As athletes turn the final bend in a 400-metre race, they strive to maintain or increase their speed. They gasp for breath, their hearts race, and their legs feel like lead. Then when they finish, the athletes experience severe cramping pain in their muscles.

The experience of these athletes is a consequence of their muscles running out of oxygen to oxidise glucose. Despite the accelerated beating of their hearts and their rapid breathing, the athletes reach a point during the race when they experience 'oxygen debt': their blood can no longer provide oxygen at a sufficiently fast rate. From this stage onwards their bodies obtain energy anaerobically.

Unlike aerobic energy production, in which the products of glucose oxidation are water and carbon dioxide, anaerobic energy production involves the breakdown of glucose molecules into the lactate ion ('lactic acid'), shown in Figure 17.1.2. Lactate production yields much less energy.

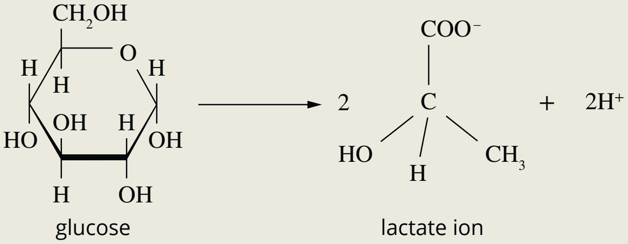


FIGURE 17.1.2 The anaerobic production of energy involves formation of two lactate ions from each glucose molecule.

The accumulation of lactate ions in the muscles causes much of the pain and fatigue that the athlete experiences (Figure 17.1.3). Once the race is over the discomfort eventually disappears as the lactate ions are oxidised to carbon dioxide and water. The training of elite athletes involves conditioning their bodies to use energy supplies as efficiently as possible.

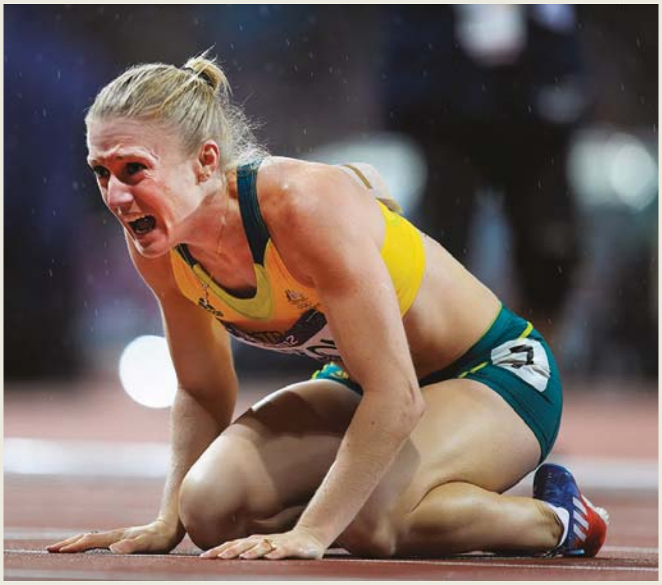


FIGURE 17.1.3 The fatigue experienced by an athlete is partly due to the formation of lactate ions produced by the anaerobic breakdown of glucose molecules in muscle cells.

ENERGY VALUES OF CARBOHYDRATES, PROTEINS AND FATS

A balanced diet is made up of a variety of foods containing carbohydrates, proteins and fats. Each of these three major nutrients provides a different quantity of energy per gram.

The **energy content** of foods is measured in kJ g^{-1}, kJ/100 g or even kJ mol^{-1} if the food is a pure substance such as glucose. For most foods, the energy released on combustion is similar to the energy released when the food is oxidised during respiration.

For convenience, each of the major food nutrients—carbohydrates, fats and proteins—are considered to have a particular heat of combustion, although there is a range of values for different members of these food groups. For example, carbohydrates are considered to have a heat of combustion of 17 kJ g^{-1}, whereas the heat of combustion of monosaccharides is 15.7 kJ g^{-1} and that of polysaccharides is 17.6 kJ g^{-1}.

Table 17.1.2 compares the heats of combustion (energy content) and energy available to the body for each of the nutrients in food. The energy available to the body from a nutrient or food is called its **energy value**.

TABLE 17.1.2 Comparison of the heat of combustion and energy available to the human body of the three main nutrients

Nutrient	Energy content (heat of combustion) ($kJ\ g^{-1}$)	Energy value (energy available for the body) ($kJ\ g^{-1}$)
Carbohydrates	17	17
Fats and oils	39	37
Proteins	24	17

Note that fats and oils have a significantly higher energy value than carbohydrates and proteins. This is essentially due to the degree to which these molecules can be oxidised.

Carbohydrates tend to contain more oxygen atoms than fats and oils do. At a simple level, the carbon atoms in carbohydrate molecules have a higher 'degree of oxidation'. Therefore, fats and oils have greater potential for oxidation and release more energy on combustion.

The following equations compare the combustion of a trisaccharide made up of three glucose units, $C_{18}H_{32}O_{16}$, and the combustion of linoleic acid, $C_{18}H_{32}O_2$, a fatty acid with the same number of carbons and hydrogens. As more oxygen is required to oxidise the fatty acid than the trisaccharide, more energy will be produced. This can be seen in the enthalpy values shown in the equations.

$$C_{18}H_{32}O_{16}(s) + 18O_2(g) \rightarrow 18CO_2(g) + 16H_2O(l) \qquad \Delta H = -6111\ kJ\ mol^{-1}$$
trisaccharide

$$C_{18}H_{32}O_2(s) + 25O_2(g) \rightarrow 18CO_2(g) + 16H_2O(l) \qquad \Delta H = -8382\ kJ\ mol^{-1}$$
linoleic acid

Energy available to the body

Table 17.1.2 shows that the energy released when food is burned is often greater than the energy that is available for the human body to use after the food has been digested. This can be due to:

- incomplete absorption of nutrients by the body after digestion of the food
- incomplete oxidation of nutrients, such as proteins and insoluble fibre
- heat loss; not all of the energy released by the oxidation of glucose is available for use in cells as some is lost as waste heat.

Even within a particular nutrient class, such as the carbohydrates, the energy available to the body can vary. Starch is readily digested by humans and is the primary source of glucose, so most of the energy from starch is absorbed during digestion. On the other hand, humans lack the enzyme cellulase, which is required to hydrolyse cellulose. Cellulose in foods such as vegetables is often referred to as **dietary fibre** and provides little energy.

CHEMFILE

The importance of cellulose

Even though humans are unable to digest cellulose, a diet high in cellulose provides 'bulk' to aid the passage of food through the digestive system. Such 'bulk' helps prevent constipation and reduce the risk of bowel cancer, also known as colorectal cancer. Bowel cancer is the second most common cancer in men and women in Australia and is more common in people over the age of 50. High red meat consumption, especially processed meats, increases the risk of developing bowel cancer. This risk can be reduced by eating a healthy diet with plenty of fresh fruit and vegetables.

Calculating the energy value of foods

When the percentage composition of a food is known, its energy value can be calculated using the percentages and the energy available to the body for each nutrient. The composition and energy value of a range of foods are given in Table 17.1.3.

TABLE 17.1.3 The composition and energy value of a range of foods

Food	Carbohydrate (%)	Protein (%)	Fats and oils (%)	Energy value (kJ g^{-1})
White rice	79	7	Negligible	15.2
Wholemeal bread	39	11	4	9.7
Avocados	6	2	17	7.2
Roasted peanuts	18	26	50	24.3
Pizza (with cheese)	31	11	8	10.0
Apples	53	4	8	11.7
Almonds	19	19	54	25.4

Experimental methods for determining the energy value of foods are discussed in section 17.2.

Worked example 17.1.1

CALCULATING THE ENERGY VALUE OF FOODS

Labelling on a sample of unsalted cashews indicates they contain 29.0% carbohydrates, 18.0% protein and 46.0% fat. The remaining 7.0% is water, which does not supply energy.

Calculate the energy value of the cashews, in kJ g^{-1}.

Thinking	Working
Use Table 17.1.2 (on page 569) to determine the available energy for each nutrient type.	Carbohydrate: 17 kJ g^{-1} Protein: 17 kJ g^{-1} Fat: 37 kJ g^{-1}
Assuming that there is 100 g of the sample, multiply each percentage of the nutrient by the available energy per gram for the nutrient type.	Carbohydrate: 29.0 g × 17 kJ g^{-1} = 493 kJ Protein: 18.0 g × 17 kJ g^{-1} = 306 kJ Fat: 46.0 g × 37 kJ g^{-1} = 1702 kJ
Find the sum of the energies for the three nutrient types and divide by 100 to find the energy value in kJ g^{-1}.	$\text{Energy value} = \frac{493 + 306 + 1702}{100}$ $= 25\ \text{kJ g}^{-1}$ (2 significant figures)

Worked example: Try yourself 17.1.1

CALCULATING THE ENERGY VALUE OF FOODS

Labelling on a sample of white bread indicates it contains 53.0% carbohydrates, 8.0% protein and 4.0% fat. The remaining 35.0% is water, which does not supply energy.

Calculate the energy value of the bread, in kJ g^{-1}.

17.1 Review

SUMMARY

- Glucose is a monosaccharide, one of the simplest types of carbohydrates, with the formula $C_6H_{12}O_6$.
- Glucose is the primary energy source for humans.
- Cellular respiration is an exothermic process. There are two forms of cellular respiration: aerobic respiration and anaerobic respiration.
- In aerobic respiration, oxygen oxidises glucose according to the equation:

$$C_6H_{12}O_6(aq) + 6O_2(g) \rightarrow 6CO_2(g) + 6H_2O(l) \qquad \Delta H = -2860 \text{ kJ mol}^{-1}$$

- Anaerobic respiration does not require oxygen and yields less energy than aerobic respiration.
- The energy value of foods is measured in kJ g^{-1}.
- The energy value of a food can be calculated using data for the available energy of the various components of the food and the percentages of each component of the food.

KEY QUESTIONS

1 Match each quantity of energy in joules to the equal quantity in kilojoules.

Energy in joules (J)	Energy in kilojoules (kJ)
100	1.00
1.0×10^4	1.0×10^{-4}
10.0	0.100
1.00×10^3	1.00×10^{-2}
0.10	10

2 Which one of the following is not a monosaccharide?

A Starch
B Glucose
C Fructose
D Galactose

3 Use the following terms to complete the sentences about respiration in humans: cellular/intramuscular, endothermic/exothermic, oxidised/reduced, carbon dioxide/oxygen, released/absorbed, aerobic/anaerobic, less/more / the same.

In ______________________ respiration, glucose is used by cells to obtain energy. Aerobic respiration is an ______________________ process in which the glucose is ______________________ by ______________________. A relatively large amount of energy is ______________________ during aerobic respiration and can be used by the cells of the body. Another type of respiration, known as ____________________ respiration, occurs less frequently in human cells and releases ___________________ energy per mole of glucose than aerobic respiration.

4 The heat of combustion of a food is often larger than the energy that is available for the human body to use. Which one of the following reasons does not explain this observation?

A The food is not completely absorbed by the body after digestion.
B Energy is lost to the surroundings during combustion reactions.
C Proteins may not be completely oxidised.
D Dietary fibre (cellulose from plant material) is not digested.

5 Labelling on a sample of cheddar cheese indicates it contains 2.0% carbohydrates, 26.7% protein and 33.3% fat. The remaining 38.0% is water. Calculate the energy value of the cheese, in kJ g^{-1}.

17.2 Introducing calorimetry

One of the simplest ways to measure the energy in a sample of food is to burn it. The energy released when the food is burned can be transferred to water and the change in the temperature of the water is measured.

If the food is burned in an enclosed space with an ample supply of oxygen, this energy determination can be very accurate, with little energy lost to the surroundings. For most foods, the energy released during combustion is slightly more than the energy released when the food is oxidised during respiration.

In this section, you will learn the principles of the techniques used to determine the energy content of food.

CALORIMETRY

Calorimetry is the experimental method of measuring the heat energy released or absorbed by a chemical reaction or physical process, such as by the combustion of a fuel or a food.

In the simplest form of calorimetry, the heat energy released by a chemical reaction can be transferred to water in a separate container. The quantity of energy transferred can be calculated from the increase in temperature of the water in the calorimeter.

Transferring heat energy to water

When an exothermic chemical reaction, such as the combustion of food, is carried out underneath a container of water, such as a test tube, some of the heat released by the combustion reaction is transferred to the water. This can be seen in Figure 17.2.1. (A similar experimental arrangement was described in Chapter 2, on page 56, for determining the approximate amount of heat energy released by the combustion of fuels.)

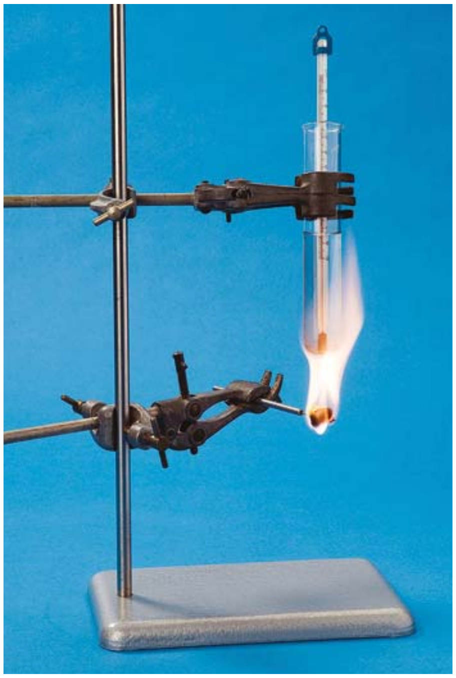


FIGURE 17.2.1 Heat energy from a burning biscuit can be transferred to a measured volume of water in a test tube.

The heat energy transferred to the volume of water can be calculated by measuring the:

- initial temperature of the water
- highest temperature of the water
- volume of water.

The relationship used to calculate the energy that has been transferred to the water is:

$$q = m \times C \times \Delta T$$

where q is the energy that is transferred to the water (in J), m is the mass of the water (in g), C is the **specific heat capacity** of the water (4.18 J °C^{-1} g^{-1}), and ΔT is the change in temperature of the water (in °C or K):

$$\Delta T = \Delta T_{\text{final}} - \Delta T_{\text{initial}}$$

Recall that the density of water is 1.0 g mL^{-1}, so 1 mL of water has a mass of 1 g.

Water is distinguished by its very high heat capacity, which is a consequence of the hydrogen bonding between its molecules. See *Heinemann Chemistry 1*, section 12.2, for more detail on the specific heat capacity of water and calculations using specific heat capacity.

Worked example 17.2.1

CALCULATING THE HEAT ENERGY TRANSFERRED TO WATER FROM BURNING FOOD

A sample of burning food is used to heat 100 mL of water. Calculate the heat energy, in kilojoules, that has been transferred if the temperature of the water increases from 18.5°C to 44.0°C.

Thinking	Working
Change the volume of water in millilitres to mass of water in grams. Remember that the density of water is 1.00 g mL^{-1}.	1 mL of water has a mass of 1 g, so 100 mL of water has a mass of 100 g.
Calculate the change in temperature, ΔT, by subtracting the initial temperature from the final temperature: $\Delta T = \Delta T_{\text{final}} - \Delta T_{\text{initial}}$	$\Delta T = \Delta T_{\text{final}} - \Delta T_{\text{initial}}$ $= 44.0 - 18.5$ $= 25.5°\text{C}$
Calculate the heat energy transferred to the water, in joules, using the formula: $q = m \times C \times \Delta T$	$q = m \times C \times \Delta T$ $= 100 \times 4.18 \times 25.5$ $= 10\,659$ J
Express the quantity of energy, in kJ, to the appropriate number of significant figures. Remember that to convert from joules to kilojoules, you divide by 10^3.	$q = \frac{10\,659}{1000}$ $= 10.7$ kJ (3 significant figures)

Worked example: Try yourself 17.2.1

CALCULATING THE HEAT ENERGY TRANSFERRED TO WATER FROM BURNING FOOD

A sample of burning food is used to heat 200 mL of water. Calculate the heat energy, in kilojoules, that has been transferred if the temperature of the water increases from 15.5°C to 30.0°C.

CHEMFILE

‘Calorie’ or ‘calorie’

A unit called the **calorie** (cal) was used in the old imperial system of measurement to measure the energy present in food. A calorie is the amount of heat required to raise the temperature of 1 g of water by 1°C. 1 cal is equal to 4.18 J.

To make matters more complicated, a unit called the Calorie (with a capital ‘C’) was also used. 1 Cal is equal to 1000 cal.

Although imperial units were withdrawn from general use in Australia between 1970 and 1988 and replaced with metric units, such as the joule, it is still common to find references to calories, or Calories, in dietary advice, as shown in Figure 17.2.2, especially when weight loss is a targeted aim for the use of a food product.

Important facts and figures

Nutrition information

Servings per package: 11 serving size: 11.4 g (2 Biscuits)

	Quantity per serving	% daily intake* (per serving)	Quantity per 100 g
Energy	181 kJ (43 Cal)	2.1%	1590 kJ (380 Cal)
Protein	1.3 g	2.6%	11.3 g
Fat, Total	0.1 g	0.2%	1.2 g
- Saturated	0.0 g	0.1%	0.3 g
- Trans	0.0 g		0.0 g
- Polyunsaturated	0.1 g		0.6 g
- Monounsaturated	0.0 g		0.2 g
Carbohydrate	8.8 g	2.8%	77.5 g
- Sugars	0.4 g	0.5%	3.7 g
Dietary fibre	0.5 g	1.7%	4.1 g
Sodium	97 mg	4.2%	849 mg

* Percentage daily intakes are based on an average adult diet of 8700 kJ. Your daily intakes may be higher or lower depending on your energy needs. All values considered averages unless otherwise indicated.

FIGURE 17.2.2 Nutrition information from a packet of crispbread biscuits. Notice the energy values in kilojoules are also converted to calories.

Heat loss

When energy is transferred from a burning piece of food, or another fuel, across an open space, heat is lost to the surroundings such as the air around the burning food. Similarly if there is no lid on a container of water, heat will be lost from the surface of the water. This heat loss is illustrated in Figure 17.2.3.

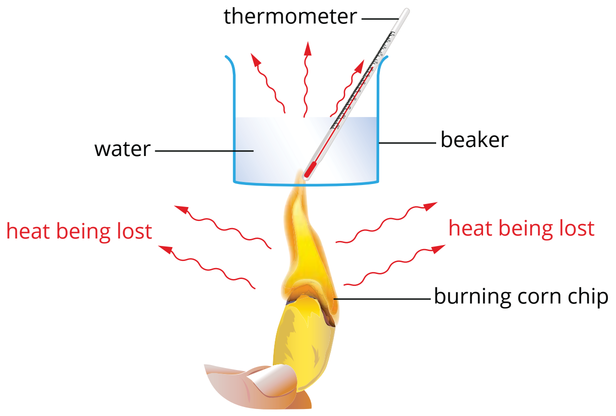


FIGURE 17.2.3 Heat is lost to the surroundings when a piece of food is burned to heat some water.

When some heat energy from the burning food is transferred to the surrounding air, the temperature of the water does not increase as much as it would if all the energy was used to heat the water. A lower change in temperature, ΔT, of the water results in a lower energy value, q.

There are a number of ways to reduce heat loss during the calorimetry experiment shown in Figure 17.2.3, including:

- putting a lid on the calorimeter
- insulating the beaker of water (with flameproof material)
- placing insulation around the burning food, although sufficient oxygen must reach the food for combustion to be complete.

ESTIMATING THE ENERGY CONTENT OF FOOD

The amount of energy transferred to a fixed volume of water when a sample of food is burned can be calculated using the relationship:

$$q = m \times C \times \Delta T$$

If the mass of food burned to produce this energy is measured, the energy content of the food (energy released per gram of food) can be calculated as follows:

$$\text{Energy content} = \frac{\text{energy transferred to the water}}{\text{change in mass of the food during combustion}} = \frac{q}{\Delta m}$$

The mass of food burned is determined by measuring the initial mass of food, and then subtracting the final mass. It is not necessary to burn all the food sample, as long as the mass that is burned is measured.

This calculation of energy content assumes that all the energy is transferred from the burning food to the volume of water. Substantial heat losses occur when the experiment described above is performed, so the values calculated for the energy content will be less than the actual values. At best, this experiment could only be used to obtain an estimate of a food's energy content or perhaps to compare the energy released by two or more foods.

As you will see shortly, modifications to the experimental equipment allow much more accurate measurements. However, before looking at these modifications, Worked Example 17.2.2 gives you practice at calculating energy content from simple experimental data.

Worked example 17.2.2

ESTIMATING THE ENERGY CONTENT OF A SAMPLE OF FOOD

A 0.850 g plain biscuit was burned under a steel can containing 150 mL of water. After the flame went out, the mass of the biscuit was 0.300 g and the temperature of the water had risen by 22.5°C. Calculate the energy content of the biscuit in kJ g^{-1}.

Thinking	**Working**
Calculate the heat energy absorbed by the water in joules, using the formula: $q = m \times C \times \Delta T$	$q = m \times C \times \Delta T$ $= 150 \times 4.18 \times 22.5$ $= 14\,108$ J
Express the quantity of energy in kJ. Remember that to convert from joules to kilojoules, you divide by 10^3.	$q \text{ (in kJ)} = \frac{14\,108}{1000}$ $= 14.108$ kJ
Calculate the mass of the food that was burned by subtracting the final mass from the initial mass: $\Delta m = \Delta m_{\text{inital}} - \Delta m_{\text{final}}$	$\Delta m = \Delta m_{\text{inital}} - \Delta m_{\text{final}}$ $= 0.850 - 0.300$ $= 0.550$ g
Calculate the energy content of the food by dividing the energy transferred to the water by the change in mass during combustion: $\text{Energy content} = \frac{q}{\Delta m}$	$\text{Energy content} = \frac{q}{\Delta m}$ $= \frac{14.108}{0.550}$ $= 25.7$ kJ g^{-1} (3 significant figures)

Worked example: Try yourself 17.2.2

ESTIMATING THE ENERGY CONTENT OF A SAMPLE OF FOOD

A 2.500 g corn chip was burned under a steel can containing 200 mL of water. After the flame went out, the mass of the corn chip was 1.160 g and the temperature of the water had risen by 35.0°C. Calculate the energy content of the corn chip in $kJ\ g^{-1}$.

CALORIMETERS

Energy changes that occur during chemical and physical changes are measured with a device called a **calorimeter**. Calorimeters are constructed in such a way that the energy losses that occur in the simple experimental apparatus described earlier are minimised, enabling more accurate results. In a calorimeter, almost all of the heat energy released or absorbed is transferred directly to or from a measured volume of water.

Two types of calorimeters are designed for measuring the energy changes in different types of reactions.

- In **solution calorimeters**, the reaction takes place in a solution.
- In **bomb calorimeters**, the reaction takes place in a sealed bomb vessel.

Solution calorimetry

Energy changes that occur in reactions can be measured with a solution calorimeter. A solution calorimeter may be as simple as a polystyrene foam coffee cup with a lid, as shown in Figure 17.2.4.

The insulation provided by the polystyrene foam prevents the transfer of heat to or from the surroundings of the calorimeter. The reaction is carried out in the calorimeter with an accurately known volume of water. The initial and final temperatures are measured and recorded, as are the amounts of reactants used.

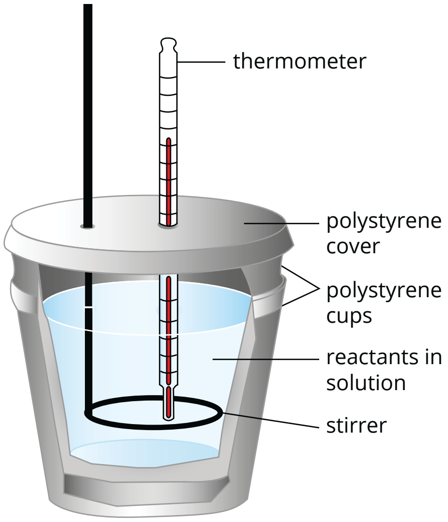


FIGURE 17.2.4 A simple 'coffee-cup' calorimeter.

Measurement of enthalpy change, ΔH, was explained in detail in Chapter 2, page 57. Reactions that involve the release of energy are exothermic (ΔH is negative); reactions that involve the absorption of energy are endothermic (ΔH is positive).

If the temperature of the water in the calorimeter increases, the reaction occurring in the calorimeter is an **exothermic** reaction. The reaction has released heat energy, the water in the calorimeter has absorbed that energy and the temperature of the water has increased.

Similarly, if the temperature of the water in the calorimeter decreases, the reaction occurring in the calorimeter has absorbed energy from the water. In this case, the reaction is an **endothermic** reaction.

A coffee cup calorimeter has some limitations. The polystyrene container absorbs some heat, so the temperature change is lower than it would otherwise be and the calculated value for the heat released or absorbed by the reaction is lower than it should be.

A solution calorimeter cannot be used to measure the energy content of food because the reaction in this case is a combustion reaction in which the food burns in oxygen. However, a solution calorimeter can be used to determine the energy change that occurs when a food such as glucose dissolves in water. Solution calorimetry is used in the laboratory to determine the enthalpy changes that occur when acids react with bases and solids dissolve in water.

The construction of a laboratory solution calorimeter is shown in Figure 17.2.5. The stirrer is used to ensure the temperature of the water is uniform. The use of the electrical heater for calibrating the calorimeter is described in the next section.

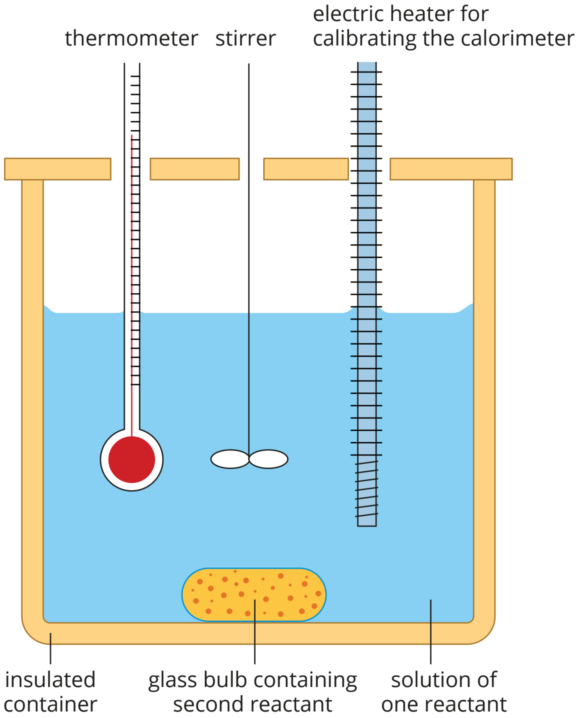


FIGURE 17.2.5 A solution calorimeter; breaking the glass bulb starts the reaction.

Bomb calorimetry

Figure 17.2.6 shows the components of a bomb calorimeter, which is used for reactions that involve gaseous reactants or products. The reaction vessel in a bomb calorimeter is designed to withstand the high pressures that may build up during reactions.

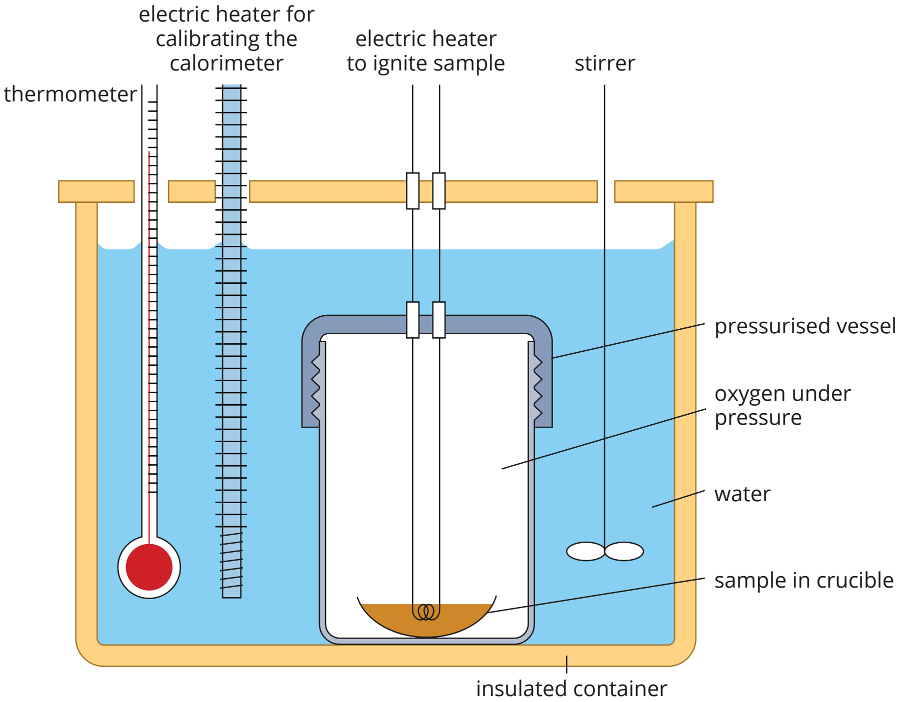


FIGURE 17.2.6 A bomb calorimeter used for reactions that involve gases, such as the combustion of foods.

Food scientists measure the energy content of food by burning the food in a bomb calorimeter. Sufficient oxygen is required to completely combust the food so that all the available energy is released. Insulation around the calorimeter prevents heat escaping and the change in temperature is measured with a thermometer. The stirrer ensures that the temperature of the water is uniform.

Calorimetry calculations for both bomb and solution calorimeters are explained in more detail in section 17.3.

CHEMISTRY IN ACTION

Food processing and calorimetry

A walk down the supermarket aisles reveals the seemingly endless variety of processed foods available to the consumer. Preventing the growth of microorganisms and slowing the oxidation of fats that cause rancidity are two reasons why food requires preserving. Traditional methods of food preservation available to home cooks include drying, heating, freezing, salting, pickling and smoking.

Modern, commercial processing techniques involve heat treatment for preservation of the food product or to develop texture, flavours and colours. Instruments that can simulate the conditions found in food processing enable food scientists to improve processing techniques and ensure a high-quality product.

Calorimetry can be used to establish a connection between temperature and specific physical properties of substances. Differential scanning calorimetry (DSC) is a thermal analysis technique that measures how physical properties of a sample change, along with temperature, against time. Such measurements can provide both quantitative and qualitative information about physical and chemical changes that involve endothermic and exothermic processes.

A typical differential scanning calorimeter is shown in Figure 17.2.7.

Food processing involves either heating or cooling materials so DSC is particularly suitable for analysis of food systems. The energy information from DSC can be used directly to understand the thermal changes that food may undergo during processing or storage.

DSC can be used to study the effects of temperature changes on proteins, carbohydrates, fats and oils.

- Fats, oils and spreads: oxidation stability, melting and crystallisation behaviour
- Protein: denaturation and thermal stability
- Pastes and gels containing polysaccharides: specific heat capacity, melting and crystallisation behaviour
- Flour and rice starch: changes in the granules of starch due to gelatinisation

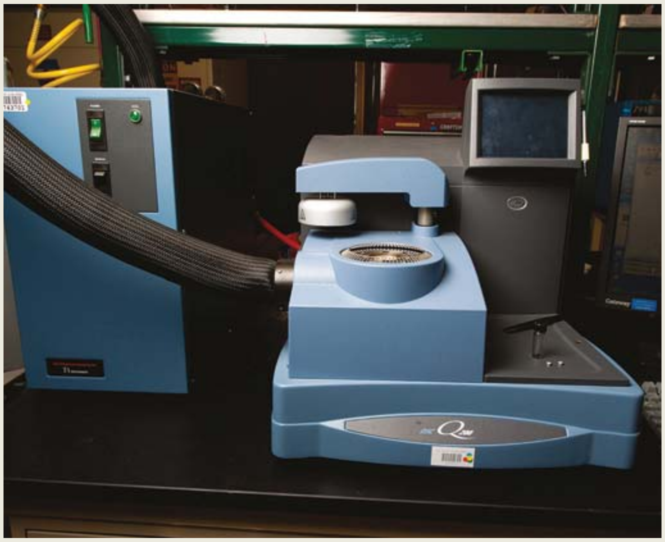


FIGURE 17.2.7 A differential scanning calorimeter is used to measure the effects of temperature on substances.

17.2 Review

SUMMARY

- Calorimetry is the experimental method by which the heat energy released or absorbed in a chemical reaction or physical process is measured.
- During calorimetry, energy is transferred to a fixed volume of water and the temperature change is measured. The quantity of energy that is transferred can be calculated using the equation: $q = m \times C \times \Delta T$.
- A calorimeter is an instrument that measures energy changes in a reaction. It is made up of an insulated container of water in which the reaction occurs, with a stirrer and thermometer to measure the temperature change during the reaction. A lid is an important part of the insulation.
- If the insulation around a calorimeter is insufficient, or missing, or if there is no lid, heat will be lost from the water to the surroundings and the calculated value measured for ΔT will be lower.
- A solution calorimeter is an insulated container that holds a known volume of water and in which a reaction in solution, such as dissolution of a solid, or a neutralisation reaction, can be carried out.
- A bomb calorimeter is an insulated container in which a sealed, oxygen filled reaction vessel is surrounded by a known volume of water. Combustion reactions are carried out in the reaction vessel and the heat from the reaction is transferred to the surrounding water.

KEY QUESTIONS

1 Match each definition on the left to a symbol on the right.

Final temperature – initial temperature	t
Specific heat capacity	q
Initial mass – final mass	ΔT
Heat energy	C
Time	Δm

2 Calculate the energy required to increase the temperature of:

a 100 mL of water by 15.2°C

b 500 mL of water from 16.0°C to 28.0°C

c 1.50 kg of water from 20.0°C to 30.0°C.

3 Calculate the final temperature of 250 g of water which is initially at 18.0°C if the amount of energy transferred to the water is 4.50 kJ.

4 Calculate the energy content, in kJ g^{-1}, of a wafer biscuit if combustion of 5.00 g of biscuit heats 500 mL of water by 38.3°C.

5 If the energy content of corn chips is 22.0 kJ g^{-1}, what is the mass of corn chips that is burned when 34.7 kJ of energy is transferred to 200 mL of water, assuming all the energy from the burning chips is absorbed by the water?

6 Classify the following investigations according to whether they would be best carried out in a bomb calorimeter or a solution calorimeter.

a Determining the energy content of a corn chip

b Determining the enthalpy of neutralisation of hydrochloric acid

c Determining the enthalpy of the reaction between magnesium and hydrochloric acid

d Determining the enthalpy of combustion of sucrose

e Determining the enthalpy of solution of glucose

f Determining the energy content of dried bread

7 Use the following terms to complete the statements about calorimeters: absorbed, decreases, endothermic, exothermic, increases, insulating, lid, lost, released, required, stays the same, thermometer.

_______________ a calorimeter improves the accuracy of measurement of the amount of energy _______________ or absorbed by a chemical reaction.

Heat energy can be _______________ from a calorimeter, so a(an) _______________ is a useful form of insulation.

If the reaction occurring in a calorimeter is exothermic, the temperature of the water _______________. If the reaction occurring is _______________ the temperature of the water in a calorimeter decreases.

FIGURE 17.3.1 Bomb calorimeter temperature changes being observed by a laboratory technician. Bomb calorimeters are used to measure the heat released by combustion reactions. The rise in temperature is used to calculate the energy released.

17.3 Calibration of calorimeters

A calorimeter is useful for determining how much energy is released or absorbed by chemical reactions. A bomb calorimeter, such as the one shown in Figure 17.3.1, is used to determine the energy released by combustion reactions, including the combustion of foods. Calorimeters can also be used for reactions in solution, including neutralisation reactions and the dissolution of solids in water.

Heat energy is often lost to the surroundings when it is transferred, so it is useful to be able to allow for losses that occur within a calorimeter when measuring the energy change associated with a reaction. A relationship has to be established between the heat energy being transferred and the temperature change that occurs within the calorimeter.

In this section, you will learn how calorimeters can be calibrated, so that the data they supply is more accurate and the effect of heat loss is minimised. You will also learn how a calibrated bomb calorimeter can be used to determine the energy content of food in kJ g^{-1} or the enthalpy of combustion of a pure food, such as glucose, in kJ mol^{-1}.

FIGURE 17.3.2 Berthelot's bomb calorimeter. The reaction vessel was lined with platinum to avoid corrosion from acidic vapours and solutions.

CHEMFILE

Pierre Berthelot

Pierre Berthelot (1827–1907) was a French pharmacist and professor of organic chemistry. He was one of the first scientists to use the word 'synthesis' to describe the production of organic compounds from their elements. Berthelot is also known for the development of new experimental techniques in the field of thermochemistry. He introduced the terms 'exothermic' to describe a reaction that releases heat and 'endothermic' for a reaction that absorbs heat.

Berthelot also devised methods for conducting chemical reactions within a closed chamber surrounded by water at a known temperature. The quantity of heat produced by the reaction could then be determined by measuring the rise in temperature of the water at the completion of the reaction.

From these experiments, Berthelot introduced the bomb calorimeter, shown in Figure 17.3.2. For the combustion reactions of gases, the gas under test was mixed with excess oxygen, compressed and then sparked. Using a bomb calorimeter, Berthelot could determine heats of combustion more accurately than previously known. Berthelot, his students and other collaborators compiled reliable data for heats of combustion, solution and neutralisation.

CALIBRATION OF CALORIMETERS

When a reaction takes place in a calorimeter, the heat change causes a rise or fall in the temperature of the contents of the calorimeter. Although the formula $q = m \times C \times \Delta T$ can be used to determine the relationship between heat energy and temperature change, the heat losses that occur can lead to inaccurate results.

For more accurate measurements of the heat produced in a reaction, you have to determine first how much energy is required to change the temperature of the water by 1°C for the particular calorimeter in use. This is known as the **calibration factor** (CF) of the calorimeter. For energy measured in joules, the calibration factor has the unit J $°C^{-1}$. Once the calibration factor of a calorimeter is known, it is said to be **calibrated**.

Both the solution and bomb calorimeters described in section 17.2 have electric heaters, which can be used for calibration (see Figures 17.2.5 and 17.2.6 on page 577).

Electrical calibration of calorimeters

A calorimeter can be calibrated by using the electric heater to release a known quantity of thermal energy and measuring the resultant rise in temperature of the water in the calorimeter.

The thermal energy released when an electric current passes through the heater can be calculated from the formula:

energy (in joules) = voltage (volts) × current (amps) × time (seconds), or

$$E = V \times I \times t$$

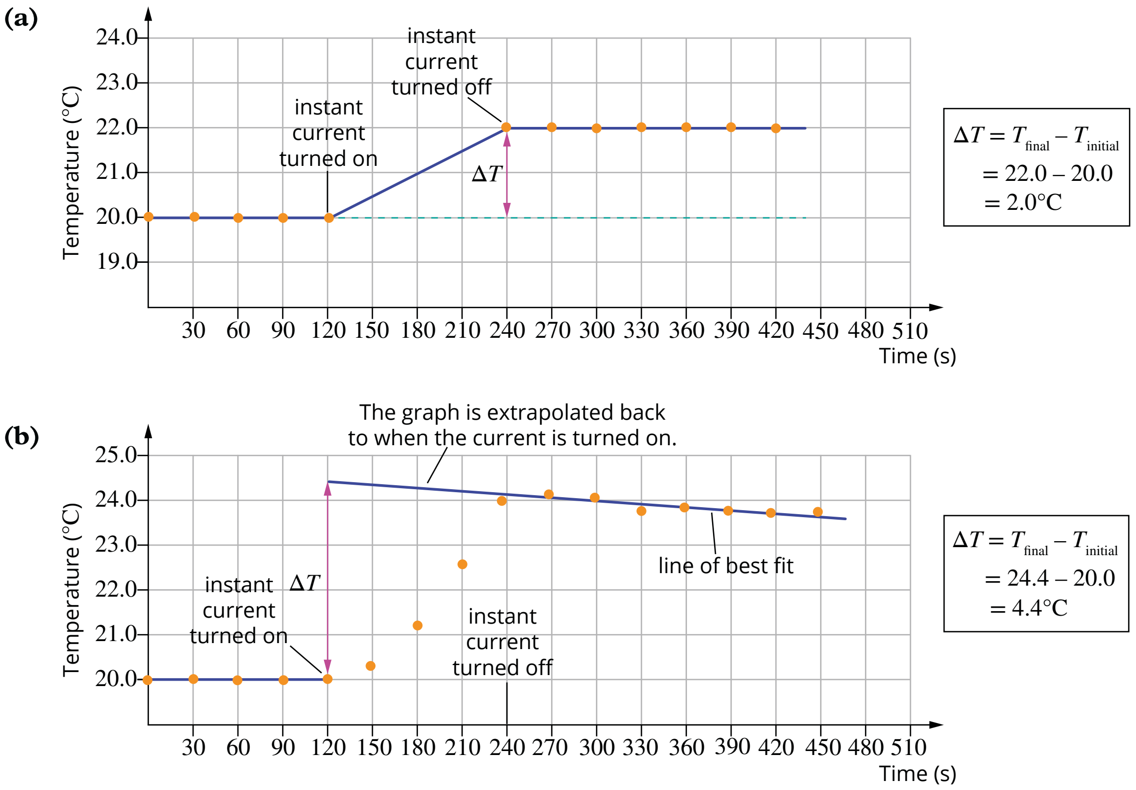
If the temperature change, ΔT, caused by the addition of the known amount of energy is measured, the calibration factor for the calorimeter can be calculated from the expression:

$$CF = \frac{E}{\Delta T} = \frac{VIt}{\Delta T}$$

Temperature–time graphs in calorimetry

Measuring the temperature change, ΔT, that occurs during a calorimetry experiment is not always as simple as calculating the difference between the final temperature and the initial temperature of the water in the calorimeter. Because a calorimeter is not perfectly insulated, it slowly loses heat during and after the heater is operating. A more accurate determination of the temperature change (ΔT) can be achieved by plotting a graph of temperature against time before, during and after the calibration.

Two temperature–time graphs for the calibration of different calorimeters are shown in Figure 17.3.3. Figure 17.3.3a shows the results for a calorimeter with ‘perfect’ insulation and no heat loss. Figure 17.3.3b is typical of the results obtained using school laboratory calorimeters.



$$\Delta T = T_{\text{final}} - T_{\text{initial}} = 22.0 - 20.0 = 2.0°\text{C}$$

$$\Delta T = T_{\text{final}} - T_{\text{initial}} = 24.4 - 20.0 = 4.4°\text{C}$$

FIGURE 17.3.3 Graphs of temperature in a solution calorimeter before, during and after calibration.
(a) These results would be obtained when a perfectly insulated calorimeter is calibrated.
(b) These results might be obtained when the temperature readings are affected by heat loss and non-instantaneous heat transfer.

In Figure 17.3.3b, heat loss causes a negative slope to the line of the graph after the heater has been turned off. A more accurate estimate of the value of ΔT can be found by **extrapolating** the line back to the time when heating commenced. The temperature change between this value and the initial temperature can be measured. A delay in the transfer of heat through the water can be observed by the continuing increase in temperature after the heater has been turned off. This can also be accounted for by the extrapolation method, although it is important to understand that the accuracy of this approach is limited.

Worked example 17.3.1

CALCULATING THE CALIBRATION FACTOR OF A CALORIMETER BY ELECTRICAL CALIBRATION

A bomb calorimeter was calibrated by passing 1.50 A through the electric heater for 50.5 s at a potential difference of 6.05 V. The temperature of the water in the calorimeter was initially 18.05°C and rose to 19.38°C during the calibration. Determine the calibration factor of the calorimeter.

Thinking	**Working**
Calculate the thermal energy released by the heater in the calorimeter when the electric current was passed through it. Use the equation: $E = V \times I \times t$	$E = V \times I \times t$ $= 6.05 \times 1.50 \times 50.5$ $= 458$ J
Calculate the temperature change during the calibration. Use the equation: $\Delta T = \Delta T_{\text{final}} - \Delta T_{\text{initial}}$	$\Delta T = \Delta T_{\text{final}} - \Delta T_{\text{initial}}$ $= 19.38 - 18.05$ $= 1.33$°C
Calculate the calibration factor by dividing the energy by the change in temperature. Use the equation: $CF = \frac{E}{\Delta T} = \frac{VIt}{\Delta T}$	$CF = \frac{E}{\Delta T}$ $= \frac{458}{1.33}$ $= 344$ J °C^{-1}

Worked example: Try yourself 17.3.1

CALCULATING THE CALIBRATION FACTOR OF A CALORIMETER BY ELECTRICAL CALIBRATION

A bomb calorimeter was calibrated by passing 1.05 A through the electric heater for 120 s at a potential difference of 5.90 V. The temperature of the water in the calorimeter was initially 15.20°C and rose to 17.50°C during the calibration. Determine the calibration factor of the calorimeter.

If you know the calibration factor for a calorimeter, you can use it to determine the energy change that is responsible for a temperature change during a reaction in the calorimeter. These calculations are discussed later in this section.

Chemical calibration of calorimeters

A calorimeter may also be calibrated by performing a chemical reaction in the calorimeter that releases a known quantity of thermal energy and then measuring the resultant rise in temperature.

Solid benzoic acid (C_6H_5COOH) is commonly used to calibrate bomb calorimeters. The **enthalpy of combustion**, ΔH_c, of benzoic acid is –3227 kJ mol^{-1}.

Enthalpy of combustion was discussed in Chapter 2 on page 40 and is defined as the enthalpy change that occurs when one mole of the compound is burned completely in oxygen. It has the symbol ΔH_c and is measured in kJ mol^{-1}.

Calibration is achieved by burning a known amount (in moles) of benzoic acid in the calorimeter. The change in temperature (ΔT) is measured and used to calculate the calibration factor, as shown in Worked Example 17.3.2.

The energy released during calibration is calculated using ΔH_c for the reaction and the amount of reactant (n):

$$E = n \times \Delta H_c$$

The calibration factor is then calculated using:

$$CF = \frac{E}{\Delta T}$$

Worked example 17.3.2

CALCULATING THE CALIBRATION FACTOR OF A CALORIMETER BY CHEMICAL CALIBRATION

A bomb calorimeter was calibrated by the complete combustion of 1.000 g of benzoic acid ($M(C_6H_5COOH) = 122.0$ g mol^{-1}; $\Delta H_c = -3227$ kJ mol^{-1}). The temperature of the water in the calorimeter rose from 17.50°C to 21.67°C during the calibration. Determine the calibration factor of the calorimeter.

Thinking	Working
Determine the amount, in moles, of benzoic acid that undergoes complete combustion. Use the equation: $n = \frac{m}{M}$	$n = \frac{m}{M}$ $= \frac{1.000}{122.0}$ $= 0.008\,197$ mol
Calculate the thermal energy released by the complete combustion of the benzoic acid in the calorimeter. Use the equation $E = n \times \Delta H_c$, noting that the energy will be in kJ.	$E = n \times \Delta H_c$ $= 0.008\,197 \times 3227$ $= 26.35$ kJ
Calculate the temperature change during the calibration. Use the equation: $\Delta T = \Delta T_{\text{final}} - \Delta T_{\text{initial}}$	$\Delta T = \Delta T_{\text{final}} - \Delta T_{\text{initial}}$ $= 21.67 - 17.50$ $= 4.17$°C
Calculate the calibration factor by dividing the energy by the change in temperature. Use the equation: $CF = \frac{E}{\Delta T}$	$CF = \frac{E}{\Delta T}$ $= \frac{26.45}{4.17}$ $= 6.34$ kJ °C^{-1}

Worked example: Try yourself 17.3.2

CALCULATING THE CALIBRATION FACTOR OF A CALORIMETER BY CHEMICAL CALIBRATION

A bomb calorimeter was calibrated by the complete combustion of 1.245 g of benzoic acid ($M(C_6H_5COOH) = 122.0$ g mol^{-1}; $\Delta H_c = -3227$ kJ mol^{-1}). The temperature of the water in the calorimeter rose from 17.50°C to 24.70°C during the calibration. Determine the calibration factor of the calorimeter.

USING A CALORIMETER TO DETERMINE THE ENERGY CONTENT OF FOOD

A bomb calorimeter may be calibrated by either the electrical or the chemical calibration methods described earlier in this section.

When an accurately weighed food sample is burned in a bomb calorimeter as shown in Figure 17.3.4, the heat released by the combustion is transferred into the water surrounding the reaction vessel and the change in temperature is measured. This is a very accurate method of determining the energy content of a food sample.

The calibration factor is used to determine the energy (E) that is responsible for the temperature change that occurs during the combustion reaction:

$$E = CF \times \Delta T$$

Note that the value of ΔT is the change in temperature that occurs when the reaction is carried out in the calorimeter, not when the calorimeter is calibrated.

The energy content of the food, in kJ g^{-1}, is calculated by dividing the energy change, in kJ, by the mass of the food that was combusted.

$$\text{Energy content of food} = \frac{E}{m}$$

FIGURE 17.3.4 A food scientist inserts a food sample into a bomb calorimeter.

Worked example 17.3.3

CALCULATING THE ENERGY CONTENT OF A SAMPLE OF FOOD USING A BOMB CALORIMETER

A 1.670 g cheese snack was burned in a bomb calorimeter. The calibration factor of the bomb calorimeter was 6.34 kJ °C^{-1}. During the combustion of the snack, the temperature of the water rose by 5.85°C. The mass of the ash left over at the end of the experiment was negligible. Calculate the energy content of the snack in kJ g^{-1}.

Thinking	Working
Calculate the heat energy released by the food, in kJ, using the equation: $E = CF \times \Delta T$	$E = CF \times \Delta T$ $= 6.34 \times 5.85$ $= 37.089$ kJ
Calculate the energy content of the food using the equation: Energy content = $\frac{E}{m}$ Express your answer to the correct number of significant figures.	There was a negligible mass left over after combustion, so the mass reacting was 1.670 g. Energy content = $\frac{E}{m}$ $= \frac{37.089}{1.670}$ = 22.2 kJ g^{-1} (3 significant figures)

Worked example: Try yourself 17.3.3

CALCULATING THE ENERGY CONTENT OF A SAMPLE OF FOOD USING A BOMB CALORIMETER

7.00 g of pizza biscuits were burned in a bomb calorimeter. The calibration factor of the bomb calorimeter was 8.45 kJ °C^{-1}. During the combustion of the biscuits, the temperature of the water rose by 17.75°C. The mass of the ash left over at the end of the experiment was negligible. Calculate the energy content of the biscuits in kJ g^{-1}.

CALORIMETRY INVOLVING PURE SUBSTANCES

Solution and bomb calorimeters can be used to determine the enthalpy changes, ΔH, for different chemical reactions. Worked Example 17.3.4 shows how the enthalpy of combustion of glucose, ΔH_c in kJ mol^{-1}, can be determined.

Worked example 17.3.4

CALCULATING THE ENTHALPY OF COMBUSTION OF A PURE COMPOUND USING A BOMB CALORIMETER

9.396 g of glucose (molar mass 180.0 g mol^{-1}) is completely burned in a bomb calorimeter. The calibration factor of the calorimeter was 9.56 kJ °C^{-1}. During the combustion of the glucose, the temperature of the water rose by 15.27°C. Calculate the enthalpy of combustion of glucose in kJ mol^{-1}.

Thinking	Working
Calculate the amount of reactant in moles, using the equation: $n = \frac{m}{M}$	$n = \frac{m}{M}$ $= \frac{9.396}{180.0}$ $= 0.052\,20$ mol
Calculate the heat energy released, in kJ, using the equation: $E = CF \times \Delta T$	$E = CF \times \Delta T$ $= 9.56 \times 15.27$ $= 1463$ kJ
Calculate the energy released per mole.	Energy released per mole $= \frac{E}{n}$ $= \frac{1463}{0.052\,20}$ $= 2797$ $= 2.80 \times 10^3$ kJ mol^{-1}
State the enthalpy of combustion with the correct sign, remembering that combustion is an exothermic process.	ΔH_c(glucose) $= -2.80 \times 10^3$ kJ mol^{-1} (3 significant figures)

Worked example: Try yourself 17.3.4

CALCULATING THE ENTHALPY OF COMBUSTION OF A PURE COMPOUND USING A BOMB CALORIMETER

1.164 g of oleic acid (molar mass 284.0 g mol^{-1}) was completely burned in a bomb calorimeter. The calibration factor of the calorimeter was 10.20 kJ °C^{-1}. During the combustion of the oleic acid, the temperature of the water rose by 4.51°C. Calculate the enthalpy of combustion of oleic acid in kJ mol^{-1}.

A solution calorimeter can be used to determine energy changes that occur for reactions in solution. Worked Example 17.3.5 shows how the **heat of solution** of glucose can be determined. The heat of solution of glucose is the ΔH when one mole of glucose dissolves in water.

Worked example 17.3.5

CALCULATING THE HEAT OF SOLUTION

A solution calorimeter has a calibration factor of 400 J °C^{-1}. If the temperature decreases by 1.375°C when 9.00 g of glucose (M = 180.0 g mol^{-1}) is dissolved in the water of the calorimeter, calculate the enthalpy of solution of glucose.

Thinking	Working
Calculate the amount of reactant in moles, using the equation: $n = \frac{m}{M}$	$n = \frac{m}{M}$ $= \frac{9.00}{180.0}$ = 0.0500 mol
Calculate the heat energy released or absorbed, in kJ, using the equation: $E = CF \times \Delta T$	$E = CF \times \Delta T$ = 400 × 1.375 = 550 J = 0.550 kJ
Calculate the energy released per mole.	Energy change per mole = $\frac{E}{n}$ $= \frac{0.550}{0.0500}$ = 11.0 kJ mol^{-1}
State the heat of solution with the correct sign, remembering that a temperature increase indicates an exothermic process and a temperature decrease indicates an endothermic process.	ΔH(glucose) = +11.0 kJ mol^{-1} (3 significant figures)

Worked example: Try yourself 17.3.5

CALCULATING THE HEAT OF SOLUTION

The heat of solution of sucrose, $C_{12}H_{22}O_{11}$ (M = 342.0 g mol^{-1}) can be determined using solution calorimetry. When 41.587 g of sucrose was dissolved in 200 mL of water in a calorimeter, the temperature decreased by 1.65°C. The calibration factor of the calorimeter was 396.4 J °C^{-1}. Calculate the heat of solution of sucrose.

17.3 Review

SUMMARY

- Solution and bomb calorimeters can be calibrated to establish the relationship between the energy transferred to the water and the temperature change in the calorimeter.
- Calibration involves adding a known quantity of heat energy from an electrical source or from a chemical source.
- A calibration factor tells you how much energy is required to change the temperature of the water in a calorimeter by 1°C.
- Electrical energy may be calculated using the equation $E = V \times I \times t$, where V is the voltage, in volts, I is the current, in amps, and t is the time, in seconds.
- For electrical calibration of a calorimeter, the calibration factor is calculated using the equation $CF = \frac{E}{\Delta T}$ where $E = VIt$.
- During electrical calibration, the value of the temperature change, ΔT, may be affected by heat loss from the calorimeter, so a temperature–time graph is used to determine a more accurate value of ΔT.
- For the chemical calibration of a bomb calorimeter using the combustion of benzoic acid, the calibration factor is calculated using the equation $CF = \frac{E}{\Delta T}$, where $E = n \times \Delta H_c$. ΔH_c is the heat of combustion of benzoic acid.
- When a reaction is carried out in a calibrated calorimeter, the energy released by the reaction is determined using the equation $E = CF \times \Delta T$.
- The energy content of food, in kJ g^{-1}, is determined using the equation energy content $= \frac{E}{m}$, where energy is measured in kJ.
- The enthalpy of combustion, in kJ mol^{-1}, of pure nutrients such as glucose and fatty acids can be determined using a calibrated bomb calorimeter. In this case the enthalpy of combustion is determined using the equation $\Delta H_c = \frac{E}{n}$.

KEY QUESTIONS

1 Identify whether the following features of calorimeters apply to bomb calorimeters, solution calorimeters or both.
   - **a** The calorimeter contains water that is heated up by the reaction.
   - **b** The reaction occurs in the water.
   - **c** The initial and final temperatures of water must be known.
   - **d** Energy changes for gaseous reactions can be measured.
   - **e** Food can be burned in the calorimeter to find energy content.
   - **f** A calibration factor can be found for the calorimeter.

2 The temperature of a calorimeter increases by 8.5°C when 4.5 A of current is passed through it at a potential of 5.2 V for 4 minutes. Which one of the following is the calibration factor of the calorimeter?

A 110 J $°C^{-1}$ **B** 661 J $°C^{-1}$ **C** 796 J $°C^{-1}$ **D** 5616 J $°C^{-1}$

3 A bomb calorimeter was calibrated by passing 1.25 A through the electric heater for 90.5 s at a potential difference of 4.40 V. The temperature of the water in the calorimeter was initially 16.600°C and rose to 17.500°C during the calibration. Calculate the calibration factor of the calorimeter.

4 A bomb calorimeter containing 100 mL of water is calibrated by passing a 3.00 A current through the instrument for 240 s at a potential difference of 3.50 V. The temperature of the water in the calorimeter rises by 1.80°C.
   - **a** Calculate the calibration factor for the calorimeter and water.
   - **b** A piece of fish finger of mass 5.00 g was burned in the calibrated bomb calorimeter. If the temperature of the water increased by 14.8°C, calculate the energy content of the fish finger in kJ g^{-1}.

5 A solution calorimeter was calibrated by the electrical method, using a current of 3.80 A for 150 s with a voltage of 6.50 V. The temperature–time graph for the calibration is shown in Figure 17.3.5. The heater was turned on at t = 120 s and was turned off at t = 270 s. Calculate the calibration factor for this calorimeter.

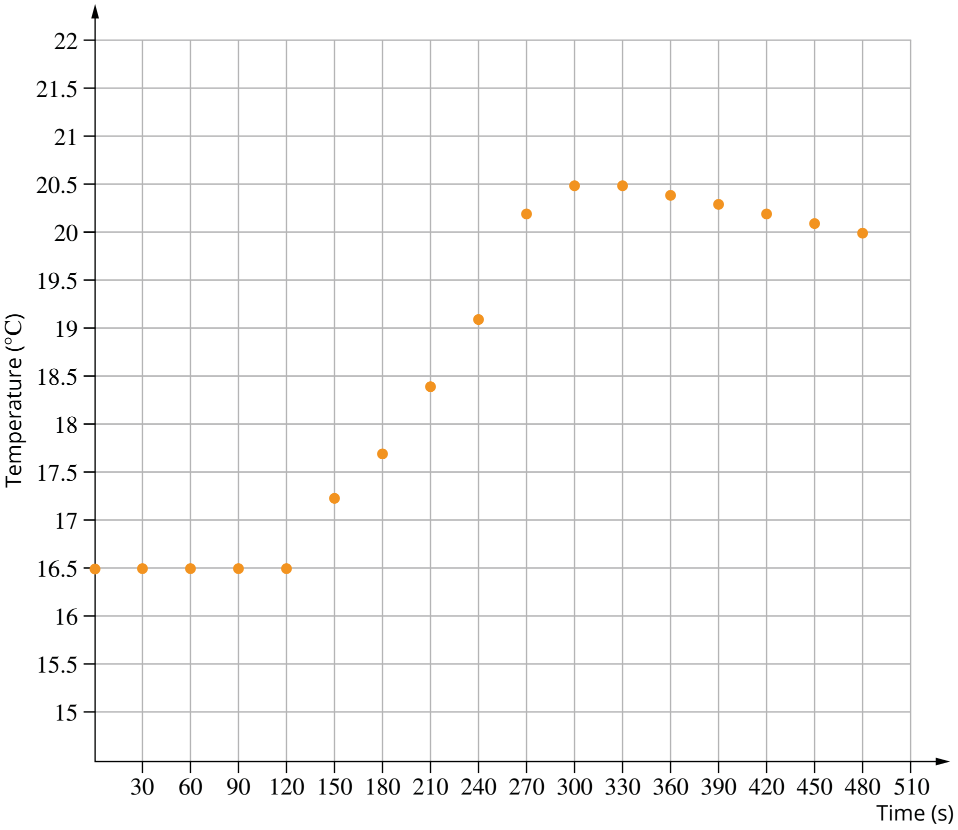


FIGURE 17.3.5 Graph of temperature against time during electrical calibration of a solution calorimeter.

6 During the chemical calibration of a bomb calorimeter by the complete combustion of 0.153 g of benzoic acid ($M(C_6H_5COOH)$ = 122.0 g mol^{-1}; ΔH_c = –3227 kJ mol^{-1}), the temperature of the water in the calorimeter increased by 5.80°C. Calculate the calibration factor for this calorimeter.

7 Which one of the following quantities could be expressed in kJ mol^{-1}?

A Heat of combustion of a chicken-flavoured biscuit
B Heat of combustion of ascorbic acid
C Energy content of an apple
D Energy value of a chocolate biscuit

8 1.45 g of citric acid ($C_6H_8O_7$: molar mass = 192.0 g mol^{-1}) was completely burned in a bomb calorimeter. The calibration factor of the bomb calorimeter was 601 J °C^{-1}. During the combustion of the citric acid, the temperature of the water rose by 24.63°C. Calculate the enthalpy of combustion of citric acid in kJ mol^{-1}.

9 The heat of solution of sucrose, $C_{12}H_{22}O_{11}$ (M = 342.0 g mol^{-1}) can be determined using solution calorimetry. When 39.94 g of sucrose was dissolved in 200 mL of water in a calibrated calorimeter, the temperature decreased by 1.50°C. The calibration factor of the calorimeter was 420.1 J °C^{-1}. Calculate the heat of solution of sucrose, including the sign to indicate whether it is exothermic or endothermic.

Chapter review

17

KEY TERMS

aerobic respiration
anaerobic respiration
bomb calorimeter
calibrated
calibration factor
calorie
calorimeter
calorimetry
carbohydrate
cellular respiration
dietary fibre
endothermic
energy content
energy value
enthalpy of combustion
exothermic
extrapolate
heat of combustion
heat of solution
hydrolysis
monosaccharide
solution calorimeter
specific heat capacity

Food—an energy source

1 Aerobic cellular respiration involves the oxidation of glucose by oxygen. Which one of the following alternatives lists the products of aerobic respiration?

A Water and glycogen
B Water and carbon dioxide
C Oxygen and carbon dioxide
D Lactic acid and ethanol

2 Which one of the following nutrients will produce the most energy when consumed?

A 15 g protein
B 8 g fat
C 20 g carbohydrate
D 5 g fat and 10 g protein

3 The composition of roasted peanuts and of almonds is given in Table 17.1.3 on page 570. Consider this information as you complete the statements by selecting from the following terms: almonds, roasted peanuts, lower, higher, 1998, 1.998, 1850, 850.

________________ have the greater fat content and this results in these nuts having a significantly ________________ energy value. The energy obtained from the fat in almonds would be ________kJ per 100 g of nuts whereas the fat in roasted peanuts would only yield _________ kJ per 100 g of nuts.

4 Labelling for a stuffed pepper indicates it contains 16% carbohydrates, 13% protein and 6.0% fat. The rest of the pepper is water.
Calculate the energy value of the stuffed pepper, in kJ g^{-1}.

Introducing calorimetry

5 Calculate the amount of energy that has been transferred to 50.0 mL of water in a test tube when the temperature of the water increases from 18.5°C to 29.8°C.

6 The equation $q = m \times C \times \Delta T$ describes the relationship between heat energy and the temperature change of a substance being heated. It is used to determine how much energy has been absorbed by a material, such as a mass of water, when its temperature increases by a measured amount.

Which one of the following statements about this equation is correct?

A The specific heat capacity, C, depends on the material that is generating the heat energy.
B The mass, m, represents the mass of the material that is being heated.
C q is measured in kJ °C^{-1}.
D ΔT refers to the change in temperature of the fuel generating the heat.

7 A 500 mL volume of water in an electric kettle was heated using 136 kJ of electrical energy. If the water was initially at 15.0°C, calculate its final temperature.

8 A peanut with a mass of 1.200 g was burned under a steel can containing 200 mL of water. After the flame went out the mass of the peanut was 0.750 g and the temperature of the water had risen by 13.2°C. Calculate the energy content of the peanut in kJ g^{-1}, assuming all the energy from the burning peanut is transferred to the water.

9 A biscuit has an energy content of 12.8 kJ g^{-1}. What volume of water, in litres, would be heated from 20.0°C to 60.0°C by the transfer of all of the energy from the combustion of one biscuit with a mass of 17.0 g?

Calibration of calorimeters

10 A bomb calorimeter can be used to determine the energy content of a food such as popcorn.

a Rearrange the following steps to describe how a bomb calorimeter can be electrically calibrated.

- Measure and record the highest temperature reached of the water.
- Turn off and disconnect the electrical circuit.
- Connect the heater of the bomb calorimeter into an electirc circuit with a voltmeter and an ammeter in the circuit.
- Add an accurately measured and recorded volume of water to a calorimeter and measure and record the temperature of the water.
- Turn on the power supply and read the current and voltage for a predetermined time, such as 120 s. Record these values.

b Rearrange the following steps to describe how a calibrated bomb calorimeter is used to determine the energy content of a food such as popcorn.

- Record the highest temperature reached in the calorimeter.
- Add the pre-weighed food to be burned into the calorimeter and connect the oxygen supply and ignition device.
- Monitor the temperature of the water until the temperature no longer increases.
- Add the same volume of fresh water as used for the calibration.
- Record the initial temperature of the water in the calorimeter.
- Ignite the food using the ignition device.

11 A calorimeter is calibrated by the passage of 2.75 A through an electric heater for 150 s at a potential difference of 4.05 V. A temperature increase of 3.40°C occurs during the calibration. Determine the calibration factor.

12 A temperature rise of 1.78°C was observed when 1.00×10^{-3} mol of propane gas was burned in a calorimeter. The calibration factor of the calorimeter was previously determined to be 1250 J $°C^{-1}$.

a Write an equation for the combustion of propane.

b Calculate the energy change during the reaction.

c Calculate the heat of combustion for propane in kJ mol^{-1}.

d Write a thermochemical equation for the combustion of propane.

13 When 1.01 g of solid potassium nitrate was dissolved in a calorimeter, the temperature dropped by 0.672°C. When the calorimeter was calibrated, a current of 1.50 A applied at a potential difference of 5.90 V for 60.0 s caused a temperature rise of 0.456°C.

a Write an equation for the dissolution of potassium nitrate.

b Determine the calibration factor of the calorimeter.

c Calculate the energy change during the reaction.

d Write the thermochemical equation for the reaction.

14 A bomb calorimeter was calibrated by the complete combustion of 2.405 g of benzoic acid ($M(C_6H_5COOH) = 122.0$ g mol^{-1}; $\Delta H_c = -3227$ kJ mol^{-1}). The temperature of the water in the calorimeter rose from 17.50°C to 26.35°C during the calibration. Determine the calibration factor of the calorimeter.

15 20.0 g of snack food was completely burned in a bomb calorimeter with a calibration factor of 14.32 kJ $°C^{-1}$. During the combustion of the snack food, the temperature of the water rose by 28.98°C. Calculate the energy content of the snack food in kJ g^{-1}.

16 A bomb calorimeter was calibrated electrically. A potential of 8.20 V was applied for 120 s with a current of 4.25 A and the temperature increased by 1.02°C.

4.50 g of glucose (molar mass 180.0 g mol^{-1}) was burned completely in the same calibrated bomb calorimeter. During the combustion of the glucose, the temperature of the water rose by 16.74°C. What is the enthalpy of combustion of glucose in kJ mol^{-1}?

17 A bomb calorimeter has a calibration factor of 15.40 kJ $°C^{-1}$. Calculate the temperature increase if 25.0 g of caramel popcorn (energy content 18.0 kJ g^{-1}) was completely burned in the calorimeter.

18 A bomb calorimeter was found to have a calibration factor of 7.89 kJ $°C^{-1}$. It was calibrated by the complete combustion of 1.375 g of benzoic acid ($M(C_6H_5COOH) = 122.0$ g mol^{-1}; $\Delta H_c = -3227$ kJ mol^{-1}). The temperature of the water in the calorimeter was initially 16.70°C. Determine the final temperature reached by the calorimeter during the calibration.

19 Palmitic acid ($C_{16}H_{32}O_2$) ($M = 256.0$ g mol^{-1}; $\Delta H_c = -10031$ kJ mol^{-1}) was burned in a bomb calorimeter. Calculate the mass that would cause the temperature of the water in the calorimeter, with calibration factor of 25.3 kJ $°C^{-1}$, to increase by 10.0°C.

Connecting the main ideas

20 Use the following terms to complete the sentences about calorimeters and their calibration: absorbed, calibrating, combustion, decrease, electrical, energy, heat, increase, neutralisation, released, temperature, water.

A bomb calorimeter is suitable for determining the energy released by a ________________ reaction. The heat energy released by the reaction is transferred to a fixed volume of ________________ and the temperature ________________ is measured using a thermometer.

________________ a calorimeter is important because it allows us to relate the change in ________________ of the water in the calorimeter with a specific amount of ________________ that is released into or absorbed from the water.

21 Which one of the following is most likely to be the temperature change in 100.0 mL of water in a beaker with no insulation and no lid, when 2.10 kJ of energy is produced by a burning biscuit under the beaker?

A 3.20°C

B 5.02°C

C 5.50°C

D 6.30°C

22 A bomb calorimeter was calibrated by the passage of 4.50 A for 4.00 minutes at a voltage of 6.15 V. The temperature of the water in the calorimeter increased by 2.00°C during the calibration.

This calorimeter was then used to determine the heat content of a sample of potato crisps. 5.00 g of potato crisps was burned in the calorimeter and the temperature of the water in the calorimeter rose by 33.9°C.

Calculate the energy content of the potato crisps in $kJ\ g^{-1}$.

23 A food van serves cinnamon donuts from the side of the road.

a A 70.0 g cinnamon donut was described as containing 14.0 g fat, 28.0 g carbohydrate and 4.5 g protein.

Calculate the theoretical energy value in $kJ\ g^{-1}$ of this donut.

b 10.0 g of cinnamon donut was combusted in a calibrated bomb calorimeter. The temperature of the water in the calorimeter increased by 11.2°C. The calibration factor of this calorimeter was $13.2\ kJ\ °C^{-1}$. Calculate the energy content in $kJ\ g^{-1}$ of this donut using this experimental data.

24 A calorimeter is calibrated by the electrical calibration method. The temperature rise was measured as the difference between the highest temperature reached and the initial temperature.

Which one of the following would be the most likely outcome if the insulation surrounding the calorimeter was not adequate?

A Heat would escape from the calorimeter, but the calibration factor would not change.

B Heat would escape from the calorimeter and the calibration factor would be measured as being smaller than it should be.

C Heat would escape from the calorimeter and the calibration factor would be measured as being larger than it should be.

D Heat would transfer into the calorimeter and the calibration factor would be measured as being larger than it should be.

25 A student is having difficulty with the calculations for the calibration of a solution calorimeter and the calculations that follow. The student wants to determine the heat energy per gram required to dissolve honey in water. The student's data for the calibration are shown in Tables 17.4.1 and 17.4.2.

TABLE 17.4.1 Calibration data

Volume of water in calorimeter (mL)	100
Voltage (V)	5.40
Current (amps)	2.60
Time (s)	180
Initial temperature (°C)	15.5
Final temperature (°C)	17.8

TABLE 17.4.2 Data from experiment in which honey is dissolved in water

Volume of water in calorimeter (mL)	100
Mass of honey (g)	19.80
Initial temperature (°C)	17.8
Final temperature (°C)	16.1

The student's calculations are as follows:

$$CF = 5.40 \times 2.60 \times 180$$
$$= 2527.2\ J$$

Heat energy per gram to dissolve the honey:

$$E = CF \times \Delta T$$
$$= 2527.2 \times 1.7$$
$$= 4296.24\ J$$

$$\text{Energy per gram} = \frac{4296.24}{100}$$
$$= 42.96\ J\ g^{-1}$$

0.430 kJ of energy is given out when 1 gram of honey dissolves. This is an exothermic reaction.

Describe any errors that the student has made in the calculations, and then complete the calculation correctly.

26 Figure 17.4.1 shows the temperature–time graph plotted by the data logging equipment used by a student to determine the change in temperature during the calibration of a solution calorimeter. The heater was turned on at t = 120 s and it was turned off at t = 300 s.

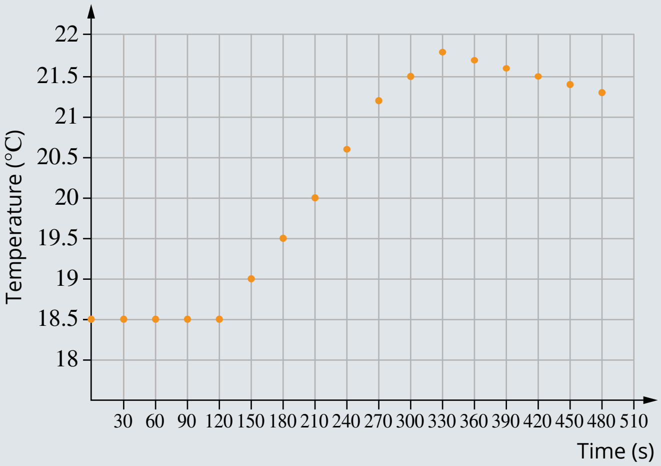


FIGURE 17.4.1 Temperature–time graph used for calibration of a calorimeter.

The student ignored the graph and instead used the formula $\Delta T = T_{\text{final}} - T_{\text{initial}}$ to determine ΔT and hence the calibration factor.

The student then correctly made the additional measurements needed to determine the enthalpy change of a reaction.

Which of the following statements would best describe the student's results?

A The value of ΔT will be too high.

B The calibration factor calculated for the calorimeter will be too high.

C The value of the enthalpy change measured by the calorimeter will be too low.

D The effect on the experimental results would cancel out when the calibration factor was used to calculate energy changes.

27 Several mistakes or errors that could occur when calibrating a calorimeter are listed in the following table. For each mistake or error, indicate the likely effect on the calculated calibration factor by placing a tick in the appropriate column.

Mistake or error	Calibration factor is too small	Calibration factor would be correct	Calibration factor is too large
The lid is left off during calibration.			
Less water is used in the calorimeter for the calibration than for subsequent measurements.			
During electrical calibration, the voltmeter had a systematic error making it read too low.			
During chemical calibration, the mass of benzoic acid was recorded as less than its actual value.			

28 A student conducted an experiment to determine the energy content of jelly babies. A bomb calorimeter was electrically calibrated by passing a current of 4.05 A at a potential difference of 6.10 V for 240 s. The temperature increased by 13.90°C. Approximately half a jelly baby of mass 5.147 g was placed into the combustion chamber of the calorimeter. The combustion chamber was then filled with oxygen and the jelly baby ignited. The temperature of the water surrounding the combustion chamber increased from 18.50°C to 48.20°C. The remains of the jelly baby weighed 4.207 g.

a Determine the calibration factor of the calorimeter.

b Calculate the energy content of the jelly baby in kJ g^{-1}.

c State the major sources of error that may have affected the student's result.

UNIT 4 • Area of Study 2

REVIEW QUESTIONS

What is the chemistry of food?

Multiple-choice questions

Questions 1 and 2 refer to the following information.

The following list gives the formulas of a number of important biochemical molecules.

I	$C_6H_{12}O_6$	**II**	$CO(NH_2)_2$
III	$C_2H_5NO_2$	**IV**	$C_3H_7NO_2$
V	$C_{17}H_{33}COOH$	**VI**	$C_3H_8O_3$
VII	CO_2	**VIII**	$C_{17}H_{35}COOH$

1 From the list, identify two molecules that would react together to form a dipeptide.

A II and III
B III and IV
C IV and VI
D IV and II

2 When a saturated fat undergoes hydrolysis, two products that might be formed are:

A VI and VIII
B I and III
C V and VI
D II and VIII.

3 When starch is formed from glucose, the condensation reaction that occurs involves:

A a carboxyl functional group and an amino functional group
B two hydroxyl functional groups
C a hydroxyl functional group and a carboxyl functional group
D a hydroxyl functional group and an amino functional group.

4 Olive oil contains a high proportion of oils made from a fatty acid called oleic acid. The formula of oleic acid is $C_{18}H_{34}O_2$. How many carbon-to-carbon *double* covalent bonds are in oleic acid?

A 0
B 1
C 2
D 3

5 When a protein such as insulin is formed, the condensation reaction that occurs involves:

A a carboxyl functional group and an amino functional group
B two hydroxyl functional groups
C a hydroxyl functional group and a carboxyl functional group
D a hydroxyl functional group and an amino functional group.

6 The secondary structure of many proteins includes helical regions. The type of chemical bond responsible for maintaining this shape is the:

A hydrogen bonds
B ion–dipole bonds
C ionic bonds
D covalent bonds.

7 When hydrochloric acid was added to some clear uncooked egg white in a test tube, a white gelatinous precipitate formed. When the mixture was boiled gently, the precipitate slowly dissolved. Which of the following lists the likely changes in the contents of the test tube?

A Protein $\xrightarrow{\text{acid added}}$ denatured and coagulated protein $\xrightarrow{\text{heat}}$ free amino acids
B Protein $\xrightarrow{\text{acid added}}$ free amino acids $\xrightarrow{\text{heat}}$ carbon dioxide and water
C Glucose $\xrightarrow{\text{acid added}}$ starch $\xrightarrow{\text{heat}}$ glucose
D Free amino acids $\xrightarrow{\text{acid added}}$ denatured and coagulated protein $\xrightarrow{\text{heat}}$ free amino acids

8 The body can obtain energy from glucose by aerobic or anaerobic respiration. Which of the following correctly compares these two processes?

A Aerobic respiration generates less energy and produces carbon dioxide, and the product of anaerobic respiration is lactic acid.
B Aerobic respiration generates less energy and produces lactic acid, and the product of anaerobic respiration is carbon dioxide.
C Aerobic respiration generates more energy and produces carbon dioxide, and the product of anaerobic respiration is lactic acid.
D Aerobic respiration generates more energy and produces lactic acid, and the product of anaerobic respiration is carbon dioxide.

9 What will be the molar mass of a tripeptide formed from the condensation of the amino acids phenylalanine (M = 165 g mol^{-1}), isoleucine (M = 131 g mol^{-1}) and methionine (M = 149 g mol^{-1})?

A 391 g mol^{-1}
B 409 g mol^{-1}
C 445 g mol^{-1}
D It will depend on the sequence in which they are connected.

10 A triglyceride molecule with $M = 878$ g mol^{-1}, when fully hydrolysed, yields a single fatty acid molecule. What will the molar mass of this fatty acid be closest to?

A 262 g mol^{-1}
B 280 g mol^{-1}
C 292 g mol^{-1}
D 310 g mol^{-1}

11 The linkages by which monosaccharides are joined to form disaccharides and polysaccharides are called:

A carbohydrate links
B peptide links
C ester links
D glycosidic links.

12 The polysaccharides starch, cellulose and glycogen have significantly different properties primarily because:

A each is formed from a different monosaccharide monomer
B the monosaccharide monomer from which they are formed is linked together in different ways
C they are composed of different amounts of glucose and fructose
D each is produced by a different type of organism.

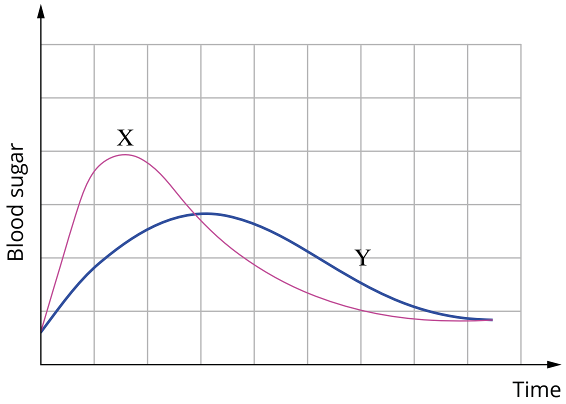
13 An essential fatty acid is one that:

A is necessary for health but cannot be synthesised by the body
B is necessary for the proper function of an enzyme in the body
C cannot be obtained from food and must be synthesised in the body
D is needed by all living things for good health.

14 Antioxidants prevent the rapid degradation of food by:

A preferentially reacting with oxidising species before they attack food molecules
B forming a protective barrier around food particles
C reversing the reactions in which food molecules are attacked by oxidants
D reacting with food molecules to form less reactive products.

15 The blood sugar levels of a group of test subjects were monitored for the 2 hours after they had eaten 10.0 g of one of two different starchy foods (X or Y). The averaged results are shown on the graph below. From these results it is reasonable to make the following conclusion.



A X has the higher glycemic index and a higher amylose/amylopectin ratio.
B X has the higher glycemic index and a lower amylose/amylopectin ratio.
C X has the lower glycemic index and a higher amylose/amylopectin ratio.
D X has the lower glycemic index and a lower amylose/amylopectin ratio.

16 Which of the following best distinguishes the roles of carbohydrates and fats as metabolic energy sources?

A Carbohydrates have a higher energy content but fats are the primary energy source.
B Fats have a higher energy content but carbohydrates are the primary energy source.
C Carbohydrates have a higher energy content and are the primary energy source.
D Fats have a higher energy content and are the primary energy source.

17 A vitamin is:

A an organic compound (or group), required in small quantities and typically only obtainable from the diet
B any essential nutrient that cannot be synthesised by the body
C any essential source of energy for the body
D a chemical that does not occur in nature but that improves health when consumed.

18 Artificial sweeteners, such as aspartame, taste sweet because they share some common features with naturally sweet compounds like sugars. In particular, like sugars, they possess:

A a similar ratio of C:H:O atoms
B a large number of hydroxyl groups
C a similar spatial arrangement of certain functional groups
D the ability to link together in long chains by forming glycosidic links.

19 Artificial sweeteners, such as aspartame, are perceived to have which of the following dietary advantages over natural sugars?

A They have a much lower energy content than sugars.

B They have antioxidant properties in addition to their sweetness.

C They have similar energy content to sugar but their higher sweetness means smaller amounts are required.

D They have a much longer shelf life and can be obtained in much higher purity.

20 A temperature rise of 2.0°C occurred when 1.50×10^{-3} mol of ethane gas burnt in a bomb calorimeter.

$$2C_2H_6(g) + 7O_2(g) \rightarrow 4CO_2(g) + 6H_2O(l) \qquad \Delta H = -3120 \text{ kJ mol}^{-1}$$

The calibration constant of the calorimeter, in J °C^{-1}, is:

A 1170

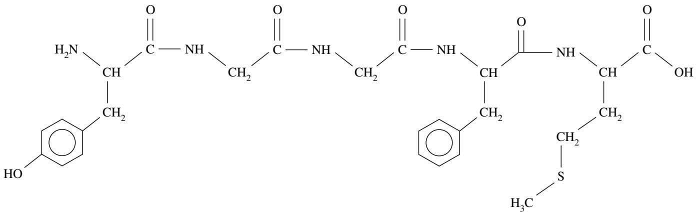
B 3120

C 2340

D 4680

Short-answer questions

21 Enkephalins are short polypeptides involved in the nervous system's detection of pain and harm. The structure of met-enkephalin, so-called because it contains a methionine residue, is shown. Another important example is leu-enkephalin, which has a leucine (side chain Z = $CH_2CH(CH_3)_2$) residue in place of methionine.



a Draw the structure of leu-enkephalin.

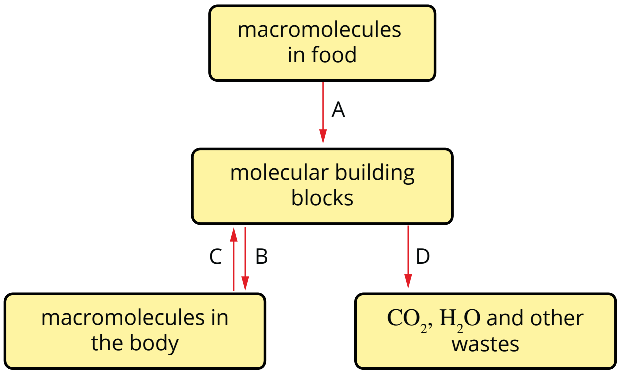
b Refer to a table of amino acids and use it to name the other amino acids present in leu-enkephalin.

c On your structure circle and label:

- **i** peptide linkages
- **ii** terminal carboxyl and amino groups
- **iii** aromatic (benzene) rings.

d Mark with an asterisk (*) all of the chiral centres in your structure.

22 Digestion and absorption of nutrients in humans tends to follow the general scheme shown here.



a For which of the processes (A–D) in this scheme is the key change that is occurring:

- **i** hydrolysis?
- **ii** condensation?
- **iii** respiration?

b Which of the processes involve reactions catalysed by enzymes?

c What (apart from chemical products) is usually produced in process D, which is very useful to the body?

d Describe the connections between starch (in food), glucose and glycogen, and explain how the scheme above applies in this case.

e Cellulose in food does not follow this pathway for humans. Explain why cellulose and starch undergo different processes.

f Name the molecular building blocks obtained from:

- **i** fats and oils
- **ii** proteins.

23 Valine is an essential amino acid while aspartic acid is not.

a What does this distinction mean?

b Name three other essential amino acids.

c Draw the structures of valine and aspartic acid.

d Circle the side (Z) groups on each structure.

e At very low pH, both amino acids exist in solution as cations with a charge of +1. At very high pH, valine exists as a −1 anion but aspartic acid exists as a −2 anion. Explain these observations and draw the structures of the ions described.

f Draw the structure of the two possible dipeptides that can form when a molecule of valine reacts with a molecule of aspartic acid (excluding reactions involving side groups).

24 Give explanations for the following facts relating to protein structure and function.

a Formation of the primary structure of proteins produces water as a by-product but formation of secondary, tertiary and quaternary structures do not.

b Despite having unique and very different amino acid sequences, almost all proteins are able to form α-helical and β-pleated regions.

c The secondary and tertiary structures of proteins are generally much more easily disrupted than is the primary structure.

d The tertiary structures of some proteins are more easily disrupted by an increase in temperature than are those of others.

e All proteins are denatured by extreme pH changes, but some enzymes can lose their activity as a result of even relatively small pH changes without being fully denatured.

25 **a** Draw the structure of β-glucose (ring form), showing all bonds and accurately representing the relative arrangement of atoms.

b Add the following to your diagram:

- **i** two water molecules, each hydrogen bonded through a H atom to O atoms on the glucose molecule
- **ii** two water molecules, each hydrogen bonded through its O atom to appropriate H atoms on the glucose molecule.

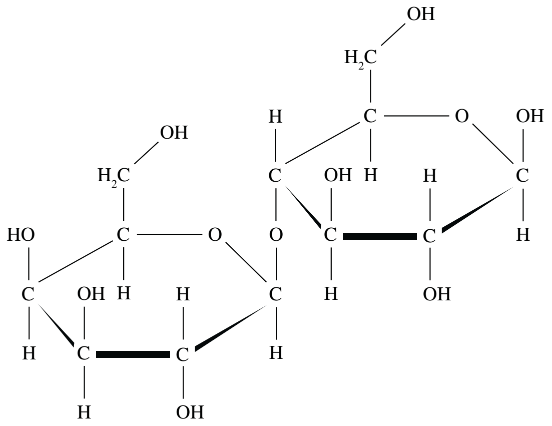
26 The reaction of glucose with oxygen, whether by direct combustion or through cellular respiration, is usually represented by the same equation. Reaction of 1 mol of glucose generates 2.83 MJ of energy.

a Write the complete thermochemical equation for cellular respiration.

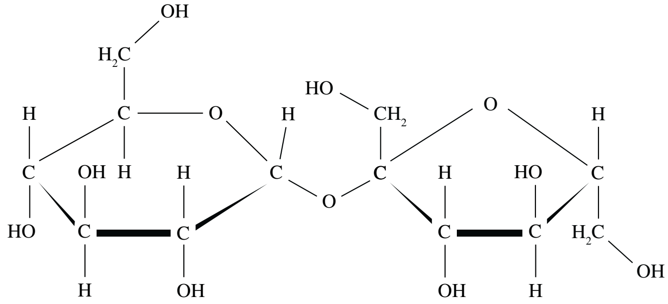
b How much energy is released by the reaction of 10.0 g of glucose?

c What volume of oxygen, measured at SLC, is consumed in reacting enough glucose to produce 500 kJ of energy?

27 **a** To which class of carbohydrates do the molecules shown below belong?



lactose



sucrose

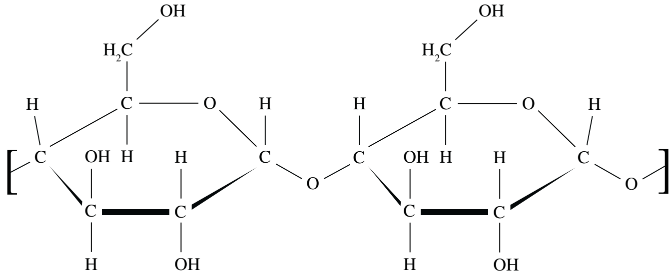
b Are these two structural isomers? Explain.

The enzymes that catalyse the hydrolysis of these molecules are called lactase and sucrase respectively.

c What are the hydrolysis products of sucrose?

d What is the cause of lactose intolerance and why do only some humans suffer from this condition?

28 Part of the structure of a molecule of amylose (a type of starch) is shown below.



a Circle and label the glycosidic link on the diagram above.

b Changing the stereochemistry on one of the carbon atoms in each ring unit gives the basic structure of cellulose instead. Mark this carbon atom on your structure with an asterisk (*).

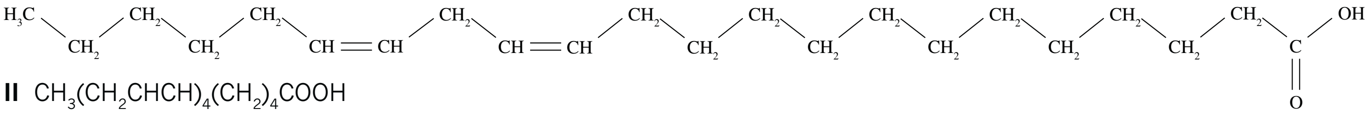
c Why does such a relatively small structural change turn a polysaccharide that is readily digested by human enzymes (starch) into one that is almost indigestible to humans (cellulose)?

d Amylopectin and glycogen have similar basic structures but with more branching. How do branched polysaccharides form and how is branching different from 'normal' chain formation?

e Describe the different functions of starch, cellulose and glycogen.

Refer to the fatty acid structures represented by I–IV when answering Questions 29 and 30.

I



II $CH_3(CH_2CHCH)_4(CH_2)_4COOH$

III $CH_3(CH_2)_{18}COOH$

IV $CH_3(CH_2)_8CHCH(CH_2)_4COOH$

29 Answer the following questions for each of the fatty acids shown in **I–IV**.

- **a** Write its molecular formula in the form $C_xH_yO_z$ and also in the form C_nH_mCOOH.
- **b** Identify it as saturated, monounsaturated or polyunsaturated.
- **c** Identify it as omega-3, omega-6 or neither.

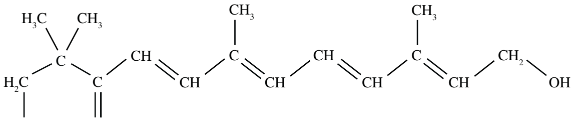
30 **a** Draw the structure of the triglyceride molecule resulting from condensation of glycerol with three molecules of IV.

- **b** On the structure drawn for part **a**, clearly circle the ester linkages.
- **c** Which of the fatty acids is most likely to produce the triglyceride with the highest melting temperature? Explain.
- **d** Which of the fatty acids will produce the triglyceride that is **least** likely to become rancid through oxidative attack on exposure to air? Explain.

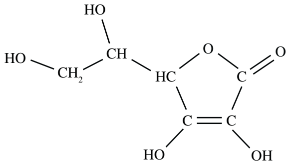
31 Write balanced chemical equations for the:

- **a** oxidation of glucose in respiration
- **b** hydrolysis of sucrose to form glucose and fructose
- **c** formation of a triglyceride (write it in the form $C_xH_yO_z$) by condensation of glycerol with the fatty acid lauric acid ($C_{11}H_{23}COOH$)
- **d** complete oxidation of the fatty acid lauric acid to carbon dioxide and water by reaction with oxygen.

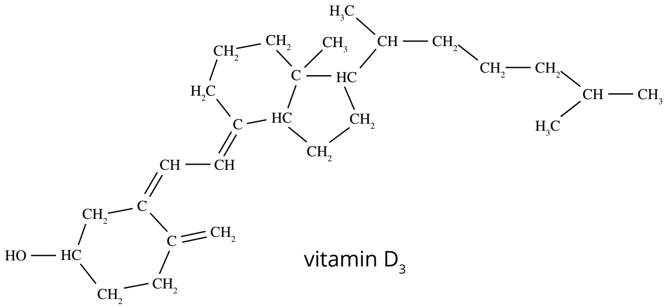
32 The structures of three vitamins are shown below.



vitamin A



vitamin C



vitamin D_3

- **a** On the structure of vitamin C add hydrogen-bonded water molecules to the four hydrogen atoms capable of forming them.
- **b** Explain why, unlike vitamin C, vitamins A and D are almost insoluble in water but dissolve well in oil.

33 Vitamin C is necessary for the correct function of some enzymes involved in formation of connective tissue in the body. A deficiency can result in a disease called scurvy.

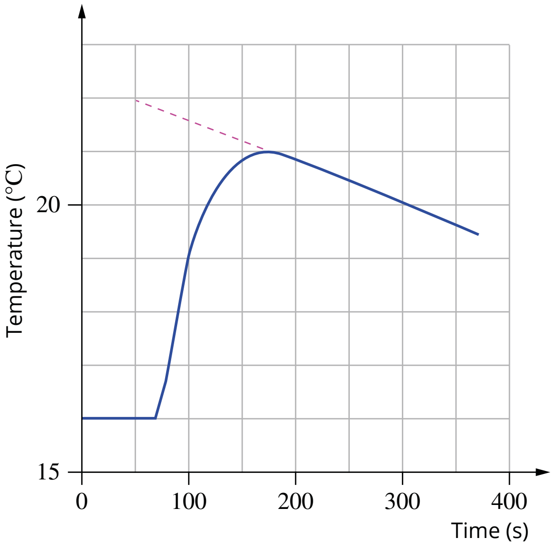
- **a** What is the name of small molecules like vitamin C that are necessary for the correct function of an enzyme?
- **b** What do the terms ‘active site’ and ‘substrate’ mean with respect to enzyme function?
- **c** Given that enzymes are essential for the normal progress of chemical reactions in the body, why are they described as ‘catalysts’ rather than as ‘reactants’?
- **d** What are the key differences between the ‘lock-and-key’ model and the ‘induced fit’ model of enzyme function?
- **e** What role do molecules like vitamin C usually play when involved in enzyme activity?

34 An experiment was performed to measure the enthalpy change for the displacement reaction between zinc metal and copper sulfate solution:

$$Zn(s) + CuSO_4(aq) \rightarrow ZnSO_4(aq) + Cu(s)$$

A calorimeter containing an excess of copper sulfate in solution was allowed to reach temperature equilibrium and then 0.833 g of zinc powder were added.

The temperature was monitored for several minutes. The graph of the temperature changes is shown below.



- **a** At what time was the zinc metal added?
- **b** Is the reaction endothermic or exothermic?
- **c** Why does the temperature decrease after 170 s? How could the calorimeter be modified to reduce this?
- **d** Use the dotted extrapolation line to estimate the true temperature change for the experiment.
- **e** The calorimeter constant for the calorimeter used is 486 J °C^{-1}. Calculate the enthalpy change for the reaction.

35 The energy content of a food sample was measured in a bomb calorimeter that had been calibrated by passing a current of 3.00 amperes at 5.00 volts through the electrical heater for 2.00 minutes. The temperature rose by 1.85°C. When a 0.220 g sample of the food was completely burned in the calorimeter, the temperature rose by 2.68°C.

- **a** Calculate the value of the calorimeter constant.
- **b** Determine the energy content of the food in kJ g^{-1}.
- **c** How does the energy content of food as measured by bomb calorimetry usually compare to the energy available from metabolism of food in living things?

APPENDIX 1 Symbols, units and fundamental constants

TABLE 1 Units and symbols based on the SI system. Units listed in red are the arbitrarily defined fundamental units of the SI system

Quantity	Symbol for physical quantity	Corresponding SI unit	Symbol for SI unit	Definition of SI unit
Mechanics				
Length	l	metre		fundamental unit
Area	A	square metre	m^2	
Volume	V	cubic metre	m^3	
Mass	m	kilogram	kg	fundamental unit
Density	d	—	$kg\ m^{-3}$	
Time	t	second	s	fundamental unit
Force	F	newton	N	$kg\ m\ s^{-2}$
Pressure	P	pascal	Pa	$N\ m^{-2}$
Energy	E	joule	J	N m
Electricity				
Electric current	I	ampere	A	fundamental unit
Electric charge	Q	coulomb	C	A s
Electric potential difference	V	volt	V	$J\ A^{-1}\ s^{-1}$
Nuclear and chemical quantities				
Atomic number	Z	—	—	—
Neutron number	N	—	—	—
Mass number	A	—	—	$Z + N$
Amount of substance	n	mole	mol	fundamental unit
Relative atomic mass	A_r	—	—	—
Relative molecular mass	M_r	—	—	—
Molar mass	M	—	—	$kg\ mol^{-1}$
Molar volume	V_m	—	—	$m^3\ mol^{-1}$
Concentration	c	—	—	$mol\ m^{-3}$
Thermal quantities				
Temperature	T	kelvin	K	fundamental unit
Specific heat capacity	C	—	—	$J\ K^{-1}\ kg^{-1}$

TABLE 2 SI prefixes, their symbols and values

SI prefix	Symbol	Value
pico	p	10^{-12}
nano	n	10^{-9}
micro	μ	10^{-6}
milli	m	10^{-3}
centi	c	10^{-2}
deci	d	10^{-1}
kilo	k	10^{3}
mega	M	10^{6}
giga	G	10^{9}
tera	T	10^{12}

TABLE 3 Some physical constants

Description	Symbol	Value
Avogadro's constant	N_A	$6.02 \times 10^{23}\ mol^{-1}$
Charge of an electron	e	-1.60×10^{-19} C
Mass of electron	m_e	9.109×10^{-31} kg
Mass of proton	m_p	1.673×10^{-27} kg
Mass of neutron	m_n	1.675×10^{-27} kg
Gas constant	R	$8.31\ J\ K^{-1}\ mol^{-1}$
Ionic product for water	K_w	$1.00 \times 10^{-14}\ mol^2\ L^{-2}$ at 298 K
Molar volume of an ideal gas	V_m	
at 273 K, 100 kPa		$22.7\ L\ mol^{-1}$
at 298 K, 100 kPa		$24.8\ L\ mol^{-1}$
Specific heat capacity of water	c	$4.18\ J^{-1}\ g^{-1}\ K^{-1}$
Density of water	d	$1.00\ g\ mL^{-1}$ at 298 K

APPENDIX 2 Significant figures and standard form

SIGNIFICANT FIGURES

The number of significant figures a piece of data has indicates the precision of a measurement. For example, compare the following data:

- A jogger takes 20 minutes to cover 4 kilometres.
- A sprinter takes 10.21 seconds to cover 100.0 metres.

The sprinter's data has been measured more precisely than that of the jogger. This is indicated by the greater number of significant figures in the second set of data.

Which figures are significant?

A significant figure is an integer or a zero that follows an integer.

In the data above, the:

- distance '4 kilometres' has one significant figure
- time '20 minutes' has two significant figures (the zero follows the integer 2)
- 10.21 seconds and 100.0 metres each have four significant figures.

A zero that comes before any integers, however, is not significant. For example:

- the value 0.0004 has only one significant figure, whereas the value 0.0400 has three significant figures. The zeros that come before the integer 4 are not significant, whereas those that follow the integer are significant.

Using significant figures

In chemistry you will often need to calculate a value from a set of data. It is important to remember that the final value you calculate is only as precise as your *least precise piece of data*.

Addition and subtraction

When adding or subtracting values, the answer should have no more digits to the right of the decimal place than the value with the least number of digits to the right of the decimal place.

Example

12.78 mL of water was added to 10.0 mL of water. What is the total volume of water?

12.78 mL + 10.0 mL = 22.78 = 22.8 mL

Because one of the values (10.0 mL) has only one digit to the right of the decimal place, the answer will need to be adjusted so that it too has only one digit to the right of the decimal place.

Multiplication and division

When multiplying and dividing values, the answer should have no more significant figures than the value with the least number of significant figures.

Example

An athlete takes 3.5 minutes to complete four laps of an oval. What is the average time taken for one lap?

$$\text{Average time} = \frac{3.5 \text{ minutes}}{4} = 0.875 = 0.88 \text{ minutes}$$

Because the data (3.5 minutes) has only two significant figures, the answer will need to be adjusted to two significant figures so that it has the same degree of precision as the data. (Note: The 'four' is taken to indicate a precise number of laps and so is considered to have as many significant figures as the calculation requires. This applies to values that describe *quantities* rather than *measurements*.)

Rounding off

When adjusting the number of significant figures, if the integer after the last significant figure is equal to or greater than '5', then the last significant integer is rounded up. Otherwise, it is rounded down.

STANDARD FORM

A value written in standard form is expressed as a number equal to or greater than 1 and less than 10 multiplied by 10^x, where x is an integer. For example, when written in standard form:

- 360 becomes 3.6×10^2
- 0.360 becomes 3.60×10^{-1}
- 0.000456 becomes 4.56×10^{-5}.

Sometimes you will need to use standard form to indicate the precision of a value.

APPENDIX 3 Table of relative atomic masses*

TABLE 1 Table of relative atomic masses*

Element name	Symbol	Atomic number	Relative atomic mass	Element name	Symbol	Atomic number	Relative atomic mass	Element name	Symbol	Atomic number	Relative atomic mass
Actinium	Ac	89	—	Germanium	Ge	32	72.63	Potassium	K	19	39.098
Aluminium	Al	13	26.9815	Gold	Au	79	196.9666	Praseodymium	Pr	59	140.9077
Americium	Am	95	—	Hafnium	Hf	72	178.49	Promethium	Pm	61	—
Antimony	Sb	51	121.76	Hassium	Hs	108	—	Protactinium	Pa	91	231.0359
Argon	Ar	18	39.948	Helium	He	2	4.00260	Radium	Ra	88	—
Arsenic	As	33	74.9216	Holmium	Ho	67	164.9303	Radon	Rn	86	—
Astatine	At	85	—	Hydrogen	H	1	1.0080	Rhenium	Re	75	186.21
Barium	Ba	56	137.33	Indium	In	49	114.82	Rhodium	Rh	45	102.9055
Berkelium	Bk	97	—	Iodine	I	53	126.9045	Roentgenium	Rg	111	—
Beryllium	Be	4	9.01218	Iridium	Ir	77	192.22	Rubidium	Rb	37	85.468
Bismuth	Bi	83	208.9804	Iron	Fe	26	55.845	Ruthenium	Ru	44	101.07
Bohrium	Bh	107	—	Krypton	Kr	36	83.80	Rutherfordium	Rf	104	—
Boron	B	5	10.81	Lanthanum	La	57	138.9055	Samarium	Sm	62	150.4
Bromine	Br	35	79.904	Lawrencium	Lr	103	—	Scandium	Sc	21	44.9559
Cadmium	Cd	48	112.41	Lead	Pb	82	207.2	Seaborgium	Sg	106	—
Caesium	Cs	55	132.9055	Lithium	Li	3	6.94	Selenium	Se	34	78.97
Calcium	Ca	20	40.08	Livermorium	Lv	116	—	Silicon	Si	14	28.086
Californium	Cf	98	—	Lutetium	Lu	71	174.967	Silver	Ag	47	107.868
Carbon	C	6	12.011	Magnesium	Mg	12	24.305	Sodium	Na	11	22.9898
Cerium	Ce	58	140.12	Manganese	Mn	25	54.9380	Strontium	Sr	38	87.62
Chlorine	Cl	17	35.453	Meitnerium	Mt	109	—	Sulfur	S	16	32.06
Chromium	Cr	24	51.996	Mendelevium	Md	101	—	Tantalum	Ta	73	180.9479
Cobalt	Co	27	58.9332	Mercury	Hg	80	200.59	Technetium	Tc	43	—
Copernicium	Cn	112	—	Molybdenum	Mo	42	95.95	Tellurium	Te	52	127.60
Copper	Cu	29	63.55	Neodymium	Nd	60	144.24	Terbium	Tb	65	158.9254
Curium	Cm	96	—	Neon	Ne	10	20.180	Thallium	Tl	81	204.384
Darmstadtium	Ds	110	—	Neptunium	Np	93	—	Thorium	Th	90	232.038
Dubnium	Db	105	—	Nickel	Ni	28	58.693	Thulium	Tm	69	168.9342
Dysprosium	Dy	66	162.50	Niobium	Nb	41	92.9064	Tin	Sn	50	118.71
Einsteinium	Es	99	—	Nitrogen	N	7	14.0067	Titanium	Ti	22	47.87
Erbium	Er	68	167.26	Nobelium	No	102	—	Tungsten	W	74	183.84
Europium	Eu	63	151.96	Osmium	Os	76	190.2	Uranium	U	92	238.0289
Fermium	Fm	100	—	Oxygen	O	8	15.9994	Vanadium	V	23	50.942
Flerovium	Fl	114	—	Palladium	Pd	46	106.4	Xenon	Xe	54	131.29
Fluorine	F	9	18.9984	Phosphorus	P	15	30.9738	Ytterbium	Yb	70	173.05
Francium	Fr	87	—	Platinum	Pt	78	195.08	Yttrium	Y	39	88.9058
Gadolinium	Gd	64	157.25	Plutonium	Pu	94	—	Zinc	Zn	30	65.38
Gallium	Ga	31	69.72	Polonium	Po	84	—	Zirconium	Zr	40	91.22

* Based on the atomic mass of $^{12}C = 12$.
The values for relative atomic masses given in the table apply to elements as they exist in nature, without artificial alteration of their isotopic composition, and, further, to natural mixtures that do not include isotopes of radiogenic origin.

Answers

Comprehensive answers and fully worked solutions for all section review questions, Try yourself: Worked examples, chapter review questions and Area of Study review questions are available via Heinemann Chemistry 5th edition ProductLink.

Chapter 1 Fuels

1.1 Types of fuels

1 A non-renewable fuel cannot be replenished at the rate at which it is consumed. A renewable fuel can be replenished at a rate at which it is consumed.

2 Renewable: bioethanol, biogas, biodiesel. Non-renewable: coal, oil, LPG, natural gas, coal seam gas.

3 Coal has the longest expected lifespan based on reserves and current rates of use. Carbon dioxide emission issues may reduce long-term dependence on coal.

4 **a** The rate of global energy use is more than can be supplied by wood.
  b Using a non-renewable energy source cannot be sustained indefinitely but moderate and careful use now can increase the likelihood that it will meet the needs of future generations.

5 Crude oil consists of a range of hydrocarbons with different boiling temperatures. Fractional distillation is needed to separate them.

1.2 Fossil fuels and biofuels

1 Coal is excavated, crushed and dried. Coal is added to a furnace. Energy released from coal is transferred to water. Steam is produced. Steam turns a turbine. Electricity is generated.

2 **a** Advantage **b** Disadvantage **c** Advantage
  d Advantage **e** Disadvantage

3

Source	Composition of source	Extraction process
Crude oil	Mixture of alkanes	Fractional distillation
Coal seam gas	Gas adsorbed on solid	Fracking
Sewage	Organic matter	Anaerobic digester
Gas well	Mainly small alkanes	Drilling

4 **a** Energy will be absorbed by the evaporation of the water. The energy content per gram will be less than that for coal with a lower water content.
  b Removal of some water by drying and/or crushing
  c Use of off-peak (e.g. night time) electricity to dry the coal would reduce the cost.
  d Potential atmospheric pollution from oxides of sulfur require either pre-treatment and/or post-treatment to remove or reduce sulfur from the brown coal and post-treatment to remove or reduce it from exhaust gases.

1.3 Petrodiesel and biodiesel

1 D

2 Transesterification

3 **a** True **b** True **c** False
  d True **e** False **f** True

4 Some CO_2 is consumed in the production of the triglycerides that biodiesel is made from.

Chapter 1 review

1 Apart from the difficulties in daily travel, lack of crude oil and natural gas will make transport of manufactured goods difficult and costly. It will also stop the production of all the products that are derived from crude oil—plastics, synthetic fibres, dyes, paints, solvents, detergents and pharmaceuticals.

2 **a** Coal
  b Coal, oil, natural gas, nuclear energy, hydraulic power, new technologies, hydroelectricity

3 The formation of fossil fuels occurs over millions of years. Once the current reserves of fossil fuels have been used, they will not be replaced in the foreseeable future.

4 **a** Black coal **b** Peat **c** Black coal

5 **a** Methane and carbon dioxide
  b The composition of biogas depends on the original material from which it is sourced and the method of decomposition.

6 Soybean, canola and palm oil

7 When coal is burnt, energy is used to vaporise this water, reducing the amount of heat released.

8 Natural gas

9 The percentage of energy from a source that is converted to the form of energy desired.

10 Heat losses to the surroundings, friction, release of light and sound.

11 **a** Petrol, bioethanol, biogas **b** B

12 Photosynthesis uses six molecules of carbon dioxide to produce one molecule of glucose:
$6CO_2(g) + 6H_2O(l) \rightarrow C_6H_{12}O_6(aq) + 6O_2(g)$
Fermentation of glucose produces ethanol and two molecules of CO_2:
$C_6H_{12}O_6(aq) \rightarrow 2CO_2(g) + 2CH_3CH_2OH(aq)$
Combustion of ethanol releases heat and four molecules of CO_2:
$2CH_3CH_2OH(l) + 3O_2(g) \rightarrow 3H_2O(g) + 2CO_2(g)$
Therefore, all of the carbon dioxide released into the atmosphere by the fermentation and combustion of ethanol has been taken in by plants in the process of photosynthesis.

13 Biogas is formed through the action of anaerobic bacteria on organic matter. Anaerobic bacteria operate in the absence of oxygen. Methane is the most abundant component of biogas, followed by carbon dioxide and then a mix of other gases in low percentages.

14 **a** A mixture of 10% ethanol and 90% conventional petrol.
  b Use of E10 petrol will extend the availability of petrol as a fuel and will allow more of the larger fractions from crude oil to be used as a feedstock for other uses rather than being burnt as a fuel.

15 All of the points are inter-related. Many other valid responses are possible.
  a Polar ice caps are shrinking, causing sea levels to rise worldwide. Local effects on the wildlife adapted to polar conditions. Melting ice adds cold, fresh water to the ocean with the possibility of altering the major ocean currents, resulting in climate changes, e.g. to Western Europe.
  b Changed weather patterns causing droughts, floods, hurricanes and resulting in changed growth patterns in plants that might lead to both plant and animal extinctions.
  c The changed weather patterns can result in crops failing, affecting the economy and driving some people to starvation.
  d Some plants and animals that are dependent on particular weather conditions for propagation or for key parts of their life cycle may become extinct.

16 C

17 Advantages = a, b, c, e, f, g; disadvantages = d, h

18 **a** Biodiesel **b** Petrodiesel **c** Biodiesel **d** Biodiesel

19 **a** Biochemical fuels are derived from renewable resources such as plants. Ethene, the feedstock used for the industrial production of ethanol, is derived from the distillation and cracking of crude oil, a non-renewable resource.
  b Ethanol can be produced from the fermentation of sugar by yeasts. Sugar may be derived from sugar cane or by the hydrolysis of starch from grains such as maize.

20 Individual student response required.

21 **a** Burning coal to generate electricity produces greenhouse gas emissions, which would not help Australia meet its Paris Agreement obligations. However, the cost of electricity could rise if other energy sources are required to replace coal, which is relatively abundant and cheap.

b Biofuels could potentially be carbon neutral. This would help Australia meet its Paris Agreement obligations.

Chapter 2 Energy from fuels

2.1 Exothermic and endothermic reactions

1 D

2 **a** 180 kJ **b** 1.5×10^3 kJ **c** 0.0100 kJ or 1.00×10^{-2} kJ **d** 2.0×10^{-6} kJ

3 In chemistry, the system is usually the chemical reaction, whereas the surroundings refer to everything else; for example, the beaker or test tube in which the reaction takes place.

4 In any reaction, the total amount of chemical energy of the reactants is made up of the bonds between atoms within the reactants. If the total amount of chemical energy within the reactants is less than the total amount of chemical energy within the products, energy must be supplied to the system, the reaction is said to be endothermic.

2.2 Thermochemical equations and energy profile diagrams

WE 2.2.1 –147 kJ mol^{-1}

1 A negative ΔH value indicates a reaction is *exothermic*. This is because the enthalpy of the reactants is *greater than* the enthalpy of the products. Energy is being *released to* the surroundings.

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

3 It would be lower because the change of state of the H_2O from liquid to gas will require energy to be absorbed.

4 **a** Endothermic

b The total enthalpy of the product (HI) is greater than that of the reactants (hydrogen gas and iodine gas)

c The activation energy is greater than the ΔH value.

5 $6CO_2(g) + 6H_2O(l) \rightarrow C_6H_{12}O_6(aq) + 6O_2(g) \quad \Delta H = +2803 \text{ kJ mol}^{-1}$

2.3 Energy from combustion

WE 2.3.1 $2C_6H_{14}(l) + 19O_2(g) \rightarrow 12CO_2(g) + 14H_2O(l)$

WE 2.3.2 $CH_3OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 4H_2O(l)$

WE 2.3.3 $CH_3OH(l) + O_2(g) \rightarrow CO(g) + 2H_2O(l)$

WE 2.3.4 2.72×10^5 kJ

1 $2C_6H_6(l) + 15O_2(g) \rightarrow 12CO_2(g) + 6H_2O(l)$

2 Propane: –50.5 kJ g^{-1} Octane: –47.68 kJ g^{-1}

Octane releases more energy per gram; therefore, octane releases more energy per kilogram.

3 $C_2H_5OH(l) + 2O_2(g) \rightarrow 2CO(g) + 3H_2O(l)$

4 **a** 1.39×10^4 kJ **b** 4.86×10^5 kJ **c** 1.20×10^7 kJ **d** 1.7×10^{10} kJ

2.4 Determining the heat of combustion of fuels

WE 2.4.1 70.5 kJ **WE 2.4.2** -1.26×10^3 kJ mol^{-1}

WE 2.4.3 $2C_2H_6(g) + 7O_2(g) \rightarrow 4CO_2(g) + 6H_2O(l) \quad \Delta H = -3120 \text{ kJ mol}^{-1}$

1 1.05×10^2 kJ

2 It is assumed that all of the energy released by the combustion of the fuel is used to heat the water. In reality, some of the energy will be used to heat the steel can as well as being lost to the surroundings.

3 -2.23×10^3 kJ mol^{-1} **4** –48.1 kJ g^{-1}

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

b 3.01 g

Chapter 2 review

1 **a** 2.21 kJ **b** 152 J **c** 1.89 MJ **d** 12.5 kJ

2 **a** Exothermic, because heat and light energy are released to the surrounding environment by the combustion of wood.

b Endothermic, because thermal energy is absorbed from the surrounding environment to melt the ice.

c Endothermic, because electrical energy is consumed from a power supply as the battery is recharged.

d Exothermic, because heat energy is released to the surrounding environment as organisms in the compost heap decompose the plant material. The temperature of the heap rises as a consequence.

3 Luminescence is the ability of chemicals to give off light, or glow. Chemiluminescence results from exothermic reactions where the energy given off to the surroundings is in the form of light energy. Glow sticks are produced when two chemicals are mixed together once a reaction vessel is broken, allowing them to mix. When they mix, the energy is released to the surroundings as light energy. Bioluminescence describes living things that are luminescent. Glow-worms are able to control the amount of luminescence they give off by taking in more or less oxygen for the reaction system in which light energy is released.

4 C

5 **a** True **b** False **c** False **d** True

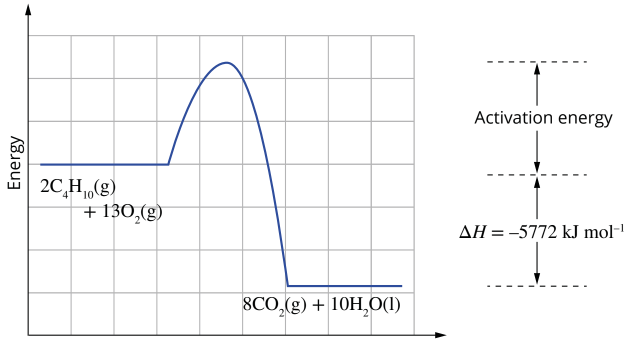
6 **a** Exothermic **b** –5238 kJ mol^{-1}

7 If a chemical equation is written for an endothermic reaction, ΔH is positive, telling you that energy is absorbed as the reaction proceeds. The enthalpy of the products must be higher than the enthalpy of the reactants.

If this reaction is reversed, the enthalpy of the reactants is now higher than the enthalpy of the products. The reaction releases energy as the reaction proceeds, so is exothermic. ΔH becomes negative.

8 **a** Higher energy in bonds of reactants

b



9 $C_4H_9OH(g) + 6O_2(g) \rightarrow 4CO_2(g) + 5H_2O(l)$

10 $2C_4H_{10}(g) + 9O_2(g) \rightarrow 8CO(g) + 10H_2O(l)$

11 278 MJ

12 **a** **i** 4.781×10^4 kJ **ii** 4.98×10^4 kJ **iii** 1.43×10^5 kJ

b H_2, C_4H_{10}, C_8H_{18}

13 **a** 25.1 kJ **b** 78.5 kJ **c** 62.8 kJ **d** 789 kJ **e** 54.1 kJ

14 33.0°C **15** –32.9 kJ g^{-1}

16 $H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l) \quad \Delta H = -286 \text{ kJ mol}^{-1}$

Or

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

17 **a** 1 mol of CO(g) and 0.5 mol of $O_2(g)$

b **i** –566 kJ mol^{-1} **ii** +566 kJ mol^{-1}

18 $C_2H_6(g) + 3\frac{1}{2}O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l) \quad \Delta H = -1.54 \times 10^3 \text{ kJ mol}^{-1}$

Or

$2C_2H_6(g) + 7O_2(g) \rightarrow 4CO_2(g) + 6H_2O(l) \quad \Delta H = -3.08 \times 10^3 \text{ kJ mol}^{-1}$

19 **a** -16.0×10^3 kJ g^{-1} = -16.0×10^6 MJ t^{-1}

b Lower. Some of the heat released by the burning wood would be used to heat the beaker holding the water and to heat the air surrounding the beaker. Not all of the energy will be used to heat the water so the temperature rise will be lower than it should be, making the heat of combustion of the fuel seem lower than the actual value.

Also, the combustion of the wood may have been incomplete, with some carbon and carbon monoxide formed instead of carbon dioxide. As a consequence, less energy would have been released and the temperature rise would be lower.

Chapter 3 Combustion of fuels

3.1 Introducing gases

WE 3.1.1 **a** 700 cm^3 **b** 0.700 L **c** 0.000700 m^3

WE 3.1.2 **a** 90.2 kPa **b** 0.891 atm **c** 90.2 kPa **d** 0.902 bar

1 **a** Molecules of gases are in constant, rapid, random motion and the forces between molecules are negligible. They continue to move outwards until stopped by the walls of the container, filling all the space available.

b Most of the volume occupied by a gas is space, so compression can be achieved by reducing the space between the particles.

c The molecules in a gas are spread much further apart than those of a liquid. A given mass of gas would occupy a much greater volume than the same mass of the liquid phase. Therefore, the density of the gas is less.

d Gases mix easily together because of the large amount of space between the molecules.

e The pressure exerted by a gas depends on the number of collisions of gas particles and the wall of the container. The pressure is independent of the type of gas involved. The total pressure exerted by a mixture of gases will depend on the total number of collisions each gas has with the container.

2 **a** Tyres have a recommended maximum pressure to give a comfortable ride as well as good traction on the road. If the pressure in a tyre is too high, the gas inside cannot be compressed as easily and passengers will be more aware of bumps on the road.

b During a long journey on a hot day, the air in a tyre warms up. This means the air molecules have increased kinetic energy, and collisions with the walls of the tyres will increase in frequency and exert more force, and so the pressure will increase.

c Particles from the cooking food escape the pot and move randomly through the house. If the food has an odour, and if there are enough particles in the air, you will detect the odour as you enter the house.

d As air is pumped into a balloon, air molecules collide with the rubber of the balloon, forcing it to expand. If too much air is pumped in, the balloon reaches a stage where it cannot stretch any further. If the number of collisions by molecules per given surface area is increased still further, the rubber will break.

3 **a** As temperature increases, the average kinetic energy of gas molecules in the can will increase. This will lead to an increase in the frequency and force of collisions of gas molecules with the inside walls of the aerosol cans. This will cause an increase in pressure.

b As the syringe is compressed, the inside surface area of the syringe will decrease. The number of collisions of molecules per unit area per second with the inside walls of the syringe will increase. This will cause a pressure increase.

4 **a** 1.40×10^5 Pa **b** 92 kPa
c 3.22×10^3 mmHg 4.30×10^5 Pa
d 900 mmHg 1.18 atm 1.20 bar
e 1.84 atm 1.87×10^5 Pa 1.87 bar
f 0.790 atm 600 mmHg 0.800 bar

5 **a** 2×10^3 mL **b** 4.5×10^{-3} m^3
c 2.25 L **d** 0.120 L
e 5.6×10^{-3} L **f** 3.7×10^3 L
g 2.85×10^{-4} m^3 **h** 4.70 L 4.70×10^3 cm^3

3.2 Universal gas equation

WE 3.2.1 373 K **WE 3.2.2** 87 L **WE 3.2.3** 150 L

1 **a** 373 K **b** 448 K **c** 128 K
2 **a** 34 L **b** 25 mL **c** 1.2 L
3 **a** 2.28 g **b** 64.5 g **c** 0.248 g
4 1.2×10^2 kPa
5 **a** 4.5 L **b** 86.8 L **c** 6.21 L
6 17 g **7** 304 K = 31°C
8 There is a greater amount of nitrogen.

3.3 Calculations involving combustion of fuels—Part 1

WE 3.3.1 2.0 mol **WE 3.3.2** 10.9 kg

1 **a** $\frac{n(CH_3OH)}{n(O_2)} = \frac{2}{3}$ **b** $\frac{n(O_2)}{n(H_2O)} = \frac{3}{4}$ **c** $\frac{n(CH_3OH)}{n(CO_2)} = \frac{2}{2} = 1$

2
- Write a balanced equation for the reaction.
- Identify the known and unknown substances in the question.
- Calculate the amount, in mol, of the known substance using $n = \frac{m}{M}$.
- Use mole ratios from the equation to calculate the amount of the unknown.
- Calculate the mass of the unknown substance using $m = n \times M$.

3 **a** 702 g **b** 618 g
4 **a** 20.1 g **b** 24.4 g **c** 11.0 g
5 **a** 3.59 kg **b** 3.03 kg

3.4 Calculations involving combustion of fuels—Part 2

WE 3.4.1 513 L **WE 3.4.2** 2.24×10^3 L **WE 3.4.3** 50 mL
WE 3.4.4 **a** C_4H_{10} **b** 111 L

1 **a** **i** 62 L **ii** 37 L
b **i** 46.5 L **ii** 27.9 L
c **i** 9.58×10^3 L **ii** 5.75×10^3 L
2 24.3 g **3** 4.07 L **4** 0.5 L **5** 75 mL

3.5 Calculations involving energy changes

WE 3.5.1 520 MJ **WE 3.5.2** 139 L

1 A
2 **a** $2C_8H_{18}(g) + 25O_2(g) \rightarrow 16CO_2(g) + 18H_2O(g)$
b $2C_8H_{18}(g) + 17O_2(g) \rightarrow 16CO(g) + 18H_2O(g)$
3 **a** 4.68 MJ
b 5.20 MJ
c 629 kJ
4 1.59 L **5** 11.95 MJ
6 **a** 498 kJ **b** 11.6 kJ **c** 7.68 mL

7 **a** The first experiment using 1 mole of methane releases the most energy.

b The combustion of methanol will release more carbon dioxide to produce the same amount of energy as methane.

Chapter 3 review

1 B
2 A
3 smaller, straight-line, weak, elastic, directly, K

4 **a** As volume is reduced, there is an increase in the frequency of molecular collisions per unit wall area. This is measured as an increase in pressure.

b When the temperature of a gas is lowered, the average kinetic energy of the particles decreases. The rate of collisions between particles and the walls of the container decreases and particles collide with less force. As pressure is a measure of the force of molecular collisions per unit wall area of the container, pressure is found to decrease.

c In a mixture of gases, the particles of each gas are moving and colliding with the walls of the container, independently of each other. Each gas therefore exerts a pressure. As the gases behave independently of each other, total pressure is simply the sum of the individual gas (or partial) pressures.

d When more gas is added to a container, the total number of particles in the container increases. Provided that the volume of the container and the temperature have not changed, the collisions of these additional particles means that the total pressure in the container has increased.

5 **a** The pressure inside the container is reduced.
b There are fewer gas molecules to collide with each other and the walls of the container. Pressure is the force exerted by the molecules over a defined area, so this will decrease.
6 64.5 g
7 **a** 6.2 L **b** 19 g
8 B **9** 5.56 L **10** 13.8 g **11** 497°C
12 **a** 44.0 g **b** 24.8 L **c** $1.77\ g\ L^{-1}$ **d** Greater
13 **a** 0.22 mol **b** $46\ g\ mol^{-1}$
14 Container A
15 **a** 8.94×10^3 mol **b** 257 kg
16 **a** 20.1 g **b** 24.4 g **c** 11.0 g
17 40.9 g **18** 3.7 tonne
19 **a** **i** 62 L **ii** 37 L
b **i** 14 L **ii** 8.5 L
c **i** 0.409 L **ii** 0.245 L
d **i** 46.5 L **ii** 27.9 L
e **i** 9.6×10^3 L **ii** 5.7×10^3 L
20 24.3 g **21** 35.0 L
22 **a** 5 L **b** 10 L **c** 5 g
23 **a** 100 mL of oxygen in excess
b $V(CO_2)$ = 240 mL $V(H_2O)$ = 320 mL
c There was an increase in volume of 80 mL.
24 **a** 25 L **b** 44.7 g
25 46.2 g **26** 6.72×10^{12} L **27** 29.2 MJ
28 **a** 2.09 g **b** 1.67×10^3 MJ
29 1.68×10^4 MJ **30** 31.8 L
31 **a** $m(CH_4)$ = 1.80 kg $m(C_3H_8)$ = 1.98 kg
b For CH_4: $m(CO_2)$ = 4.95 kg
For C_3H_8: $m(CO_2)$ = 5.95 kg
c For CH_4: $2.02 \times 10^4\ MJ\ tonne^{-1}$
For C_3H_8: $1.68 \times 10^4\ MJ\ tonne^{-1}$
d A lower mass of methane is required to produce 100 MJ of energy, so methane has the higher energy content. A lower mass of carbon dioxide is released in generating this amount of energy. This means methane has a higher amount of heat energy produced per tonne of carbon dioxide released.
32 **a** Equal. With pressure, volume and temperature the same, *n* will be the same.
b Carbon dioxide. Each CO_2 molecule contains 3 atoms and each O_2 molecule contains 2 atoms. As there are an equal amount of molecules of each gas, there are more atoms in the CO_2 sample.
c Carbon dioxide. Density = mass ÷ volume. The volume is the same for each gas, but the mass of CO_2 is greater, so it has the greater density.
33 $-2.22 \times 10^3\ kJ\ mol^{-1}$
34 **a** $C_2H_5OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(g)$
b **i** 1.91 kg **ii** 1.08×10^3 L
c **i** 39.3 kg **ii** 1.17×10^3 MJ
d 0.0644 g

Chapter 4 Redox reactions

4.1 Oxidation and reduction

1 I_2, loses, oxidised, gains, reduced, I^-
2 **a** Oxidation **b** Oxidation **c** Reduction
d Oxidation **e** Reduction **f** Reduction
3 $Ni(s) \rightarrow Ni^{2+}(aq) + 2e^-$
4 $Al(s) \rightarrow Al^{3+}(l) + 3e^-$: oxidation $S(l) + 2e^- \rightarrow S^{2-}(l)$: reduction
5 **a** Zn(s) **b** Ca(s) **c** Br^- ions in AgBr
6 **a** Oxidant O_2, reductant Zn **b** Oxidant Cl_2, reductant Ca
c Oxidant Ag^+ in AgBr, reductant Br^- in AgBr
7 **a** $Ag^+(aq) + e^- \rightarrow Ag(s)$
$M(s) \rightarrow M^{3+}(aq) + 3e^-$
$M(s) + 3Ag^+(aq) \rightarrow M^{3+}(aq) + 3Ag(s)$
b The silver half-equation is reduction, the unknown metal half-equation is oxidation.
c M(s) is the reducing agent, $Ag^+(aq)$ is the oxidising agent.

4.2 Oxidation numbers

WE 4.2.1 $\overset{+1}{Na}\overset{+5}{N}\overset{-2}{O_3}$
WE 4.2.2 The oxidation number of copper decreased from +2 to 0, so the copper in CuO has been reduced.
The oxidation number of H has increased from 0 to +1, so H_2 has been oxidised.
The oxidation number of O has not changed.
1 **a** +2 **b** +4 **c** –4 **d** 0 **e** +4
2 K_2MnO the oxidation state of K is +1, O is –2
$2 \times +1 + x + 4 \times -2 = 0$; hence $x = +6$
3 **a** Ca: +2; O: –2 **b** Ca: +2; Cl: –1
c H: +1; S: +6; O: –2 **d** Mn: +7; O: –2
e F: 0 **f** S: +4; O: –2
g Na: +1; N: +5; O: –2 **h** K: +1; Cr: +6; O: –2
4 **a** Oxidant Cl_2; reductant Mg
b Oxidant O_2; reductant SO_2
c Oxidant Fe_2O_3; reductant CO
d Oxidant H_2O_2; reductant Fe^{2+}
5

Redox reaction	Conjugate redox pair (oxidation process)	Conjugate redox pair (reduction process)
$Na(s) + Ag^+(aq) \rightarrow Na^+(aq) + Ag(s)$	$Na(s)/Na^+(aq)$	$Ag^+(aq)/Ag(s)$
$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$	$Zn(s)/Zn^{2+}(aq)$	$Cu^{2+}(aq)/Cu(s)$
$2K(s) + Cl_2(g) \rightarrow 2K^+(s) + 2Cl^-(s)$	$K(s)/K^+(s)$	$Cl_2(g)/Cl^-(s)$

4.3 Writing complex redox equations

WE 4.3.1 $MnO_4^-(aq) + 4H^+(aq) + 3e^- \rightarrow MnO_2(s) + 2H_2O(l)$
WE 4.3.2
$2SO_3^{2-}(aq) + \overset{4H^+}{\cancel{16H^+(aq)}} + 12e^- \rightarrow 2H_2S(g) + \cancel{6H_2O(l)}$
$3ClO^-(aq) + \cancel{6H_2O(l)} \rightarrow 3ClO_3^-(aq) + \cancel{12H^+(aq)} + 12e^-$
$2SO_3^{2-}(aq) + 4H^+(aq) + 3ClO^-(aq) \rightarrow 2H_2S(g) + 3ClO_3^-(aq)$
1 **a** $MnO_2(s) + 4H^+(aq) + 2e^- \rightarrow Mn^{2+}(aq) + 2H_2O(l)$
b $MnO_4^-(aq) + 4H^+(aq) + 3e^- \rightarrow MnO_2(s) + 2H_2O(l)$
c $SO_4^{2-}(aq) + 10H^+(aq) + 8e^- \rightarrow H_2S(g) + 4H_2O(l)$
d $SO_2(g) + 2H_2O(l) \rightarrow SO_4^{2-}(aq) + 4H^+(aq) + 2e^-$
e $H_2S(g) \rightarrow S(s) + 2H^+(aq) + 2e^-$
f $SO_3^{2-}(aq) + H_2O(l) \rightarrow SO_4^{2-}(aq) + 2H^+(aq) + 2e^-$
2 **a** $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$
b $Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$
c $3Zn(s) + Cr_2O_7^{2-}(aq) + 14H^+(aq) \rightarrow$
$3Zn^{2+}(aq) + 2Cr^{3+}(aq) + 7H_2O(l)$
3 **a** $Fe^{2+}(aq) \rightarrow Fe^{3+}(aq) + e^-$
$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$
$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6Fe^{2+}(aq) \rightarrow$
$2Cr^{3+}(aq) + 7H_2O(l) + 6Fe^{3+}(aq)$
b $SO_3^{2-}(aq) + H_2O(l) \rightarrow SO_4^{2-}(aq) + 2H^+(aq) + 2e^-$
$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l)$
$5SO_3^{2-}(aq) + 2MnO_4^-(aq) + 6H^+(aq) \rightarrow$
$5SO_4^{2-}(aq) + 2Mn^{2+}(aq) + 3H_2O(l)$
c $MnO_2(s) + 4H^+(aq) + 2e^- \rightarrow Mn^{2+}(aq) + 2H_2O(l)$
$2Cl^-(aq) \rightarrow Cl_2(g) + 2e^-$
$MnO_2(s) + 4H^+(aq) + 2Cl^-(aq) \rightarrow Mn^{2+}(aq) + 2H_2O(l) + Cl_2(g)$
4 **a** **i** Ce^{4+} is reduced to Ce^{3+} and H_2S is oxidised to S.
ii $Ce^{4+}(aq) + e^- \rightarrow Ce^{3+}(aq)$
$H_2S(aq) \rightarrow S(s) + 2H^+(aq) + 2e^-$
iii $2Ce^{4+}(aq) + H_2S(aq) \rightarrow 2Ce^{3+}(aq) + S(s) + 2H^+(aq)$
b **i** NO_3^- is reduced to NO and Cu is oxidised to Cu^{2+}.
ii $NO_3^-(aq) + 4H^+(aq) + 3e^- \rightarrow NO(g) + 2H_2O(l)$
$Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$
iii $2NO_3^-(aq) + 8H^+(aq) + 3Cu \rightarrow 2NO(g) + 4H_2O(l) + 3Cu^{2+}(aq)$
c **i** H_2O_2 is reduced to H_2O and Br^- is oxidised to Br_2.
ii $H_2O_2(aq) + 2H^+(aq) + 2e^- \rightarrow 2H_2O(l)$
$2Br^-(aq) \rightarrow Br_2(l) + 2e^-$
iii $H_2O_2(aq) + 2H^+(aq) + 2Br^-(aq) \rightarrow 2H_2O(l) + Br_2(l)$
d **i** MnO_2 is reduced to Mn^{2+} and S is oxidised to SO_2.

ii $MnO_2(s) + 4H^+(aq) + 2e^- \rightarrow Mn^{2+}(aq) + 2H_2O(l)$
$S(s) + 2H_2O(l) \rightarrow SO_2(g) + 4H^+(aq) + 4e^-$
iii $2MnO_2(s) + 4H^+(aq) + S(s) \rightarrow 2Mn^{2+} + 2H_2O(l) + SO_2(g)$

Chapter 4 review

1 **a** False **b** False **c** True **d** False

2 loses, positive, loses, gains, negative, gains, 7, gains, bromide

3 Oxidation half-equation: $Pb(s) \rightarrow Pb^{2+}(aq) + 2e^-$
Reduction half-equation: $Ag^+(aq) + e^- \rightarrow Ag(s)$
Overall: $Pb(s) + 2Ag^+(aq) \rightarrow Pb^{2+}(aq) + 2\ Ag(s)$

4 **a** Oxidation **b** Oxidation **c** Reduction
d Oxidation **e** Reduction **f** Reduction

5 **a** Charges are not balanced: $Ag(s) \rightarrow Ag^+(aq) + e^-$
b Electrons appear on both sides of the equation:
$Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$
c State symbols are incorrect: $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$
d Atoms are not balanced: $I_2(aq) + 2e^- \rightarrow 2I^-(aq)$
e Electrons are being subtracted: $Na^+(aq) + e^- \rightarrow Na(s)$

6 **a** Cu(s) **b** Mg(s) **c** Zn(s) **d** Ni(s)

7 **a** +4 **b** –2 **c** +6 **d** +6 **e** +4 **f** +2

8

Compound	Element	Oxidation number
$CaCO_3$	Ca	+2
HNO_3	O	–2
H_2O_2	O	–1
HCO_3^-	C	+4
HNO_3	N	+5
$KMnO_4$	Mn	+7
H_2S	S	–2
Cr_2O_3	Cr	+3
N_2O_4	N	+4

9 K_3N, N_2, N_2O, NO, N_2O_3, N_2O_4, $Ca(NO_3)_2$
Oxidation states for nitrogen are as follows:
K_3N: –3 N_2: 0 N_2O: +1 NO: +2
N_2O_3: +3 N_2O_4: +4 $Ca(NO_3)_2$: +5

10 b, c, e, f and h are redox reactions because the elements in the reactions undergo changes in oxidation number

11

	Species	Oxidation number of the underlined atom
a	<u>Cu</u>O	+2
b	<u>Fe</u>$(OH)_3$	+3
c	H<u>Cl</u>O_2	+3
d	<u>Mn</u>O_4^-	+7
e	<u>Cr_2</u>O_7^{2-}	+6

12 **a** **i** 0 **ii** +2
b **i** +5 **ii** +4
c oxidant HNO_3; reductant Cu

13

Equation	Conjugate redox pair (oxidation)	Conjugate redox pair (reduction)
$Fe(s) + I_2(aq) \rightarrow FeI_2(aq)$	$Fe(s)/Fe^{2+}(aq)$	$I_2(aq)/I^-(aq)$
$Mg(s) + FeCl_2(aq) \rightarrow MgCl_2(aq) + Fe(s)$	$Mg(s)/Mg^{2+}(aq)$	$Fe^{2+}(aq)/Fe(s)$
$10Br^-(aq) + 2MnO_4^-(aq) + 16H^+(aq) \rightarrow 2Mn^{2+}(aq) + 8H_2O(l) + 5Br_2(aq)$	$Br^-(aq)/Br_2(aq)$	$MnO_4^-(aq)/Mn^{2+}(aq)$
$Cu(s) + 2NO_3^-(aq) + 4H^+(aq) \rightarrow Cu^{2+}(aq) + 2NO_2(g) + 2H_2O(l)$	$Cu(s)/Cu^{2+}(aq)$	$NO_3^-(aq)/NO_2(g)$

14

Step	Task	How it's done	Half-equation
1	Balance nitrogens.	Already balanced	$NO_3^- \rightarrow NO_2$
2	Balance oxygens by adding H_2O.	Add one H_2O molecule(s) to right-hand side of the equation.	$NO_3^- \rightarrow NO_2 + H_2O$
3	Balance hydrogens by adding H^+.	Add $2H^+$ ion(s) to the left-hand side of the equation.	$NO_3^- + 2H^+ \rightarrow NO_2 + H_2O$
4	Balance charge by adding electrons.	Charge on left-hand side = –1 + 2 = +1 Charge on right-hand side = 0 Add one e^- to the left-hand side of the equation.	$NO_3^- + 2H^+ + e^- \rightarrow NO_2 + H_2O$
5	Add state symbols to give the final half equation.	Give the appropriate states for each reactant and product in the equation.	$NO_3^-(aq) + 2H^+(aq) + e^- \rightarrow NO_2(g) + H_2O(l)$

15 $2IO_3^-(aq) + 12H^+(aq) + 10e^- \rightarrow I_2(aq) + 6H_2O(l)$

16 Oxidation half-equation:
$SO_2(g) + 2H_2O(l) \rightarrow SO_4^{2-}(aq) + 4H^+(aq) + 2e^-$
Reduction half-equation:
$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$
Overall equation: $3SO_2(g) + Cr_2O_7^{2-}(aq) + 2H^+(aq) \rightarrow$
$3SO_4^{2-}(aq) + 2Cr^{3+}(aq) + H_2O(l)$

17 **a** $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$
$Pb^{2+}(aq) + 2e^- \rightarrow Pb(s)$
$Zn(s) + Pb^{2+}(aq) \rightarrow Zn^{2+}(aq) + Pb(s)$
b $Fe^{2+}(aq) \rightarrow Fe^{3+}(aq) + e^-$
$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l)$
$5Fe^{2+}(aq) + MnO_4^-(aq) + 8H^+(aq) \rightarrow$
$5Fe^{3+}(aq) + Mn^{2+}(aq) + 4H_2O(l)$
c $SO_2(aq) + 2H_2O(l) \rightarrow SO_4^{2-}(aq) + 4H^+(aq) + 2e^-$
$I_2(aq) + 2e^- \rightarrow 2I^-(aq)$
$SO_2(aq) + 2H_2O(l) + I_2(aq) \rightarrow SO_4^{2-}(aq) + 4H^+(aq) + 2I^-(aq)$
d $OCl^-(aq) + 2H^+(aq) + 2e^- \rightarrow Cl^-(aq) + H_2O(l)$
$2I^-(aq) \rightarrow I_2(aq) + 2e^-$
$OCl^-(aq) + 2H^+(aq) + 2I^-(aq) \rightarrow Cl^-(aq) + H_2O(l) + I_2(aq)$

18 Half-equations:
$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$
$2MnO_2(s) + 2H^+(aq) + 2e^- \rightarrow Mn_2O_3(s) + H_2O(l)$
Overall equation:
$Zn(s) + 2MnO_2(s) + 2H^+(aq) \rightarrow Zn^{2+}(aq) + Mn_2O_3(s) + H_2O(l)$

19 **a** Half-equations:
$C_6H_8O_6(aq) \rightarrow C_6H_6O_6(aq) + 2H^+(aq) + 2e^-$
$I_2(aq) + 2e^- \rightarrow 2I^-(aq)$
b The oxidation reaction is:
$C_6H_8O_6(aq) \rightarrow C_6H_6O_6(aq) + 2H^+(aq) + 2e^-$
The reduction reaction is: $I_2(aq) + 2e^- \rightarrow 2I^-(aq)$

20 **a** $2H_3AsO_4(aq) + 4H^+(aq) + 4e^- \rightarrow As_2O_3(s) + 5H_2O(l)$
$I^-(aq) + 3H_2O(l) \rightarrow IO_3^-(aq) + 6H^+(aq) + 6e^-$
b $6H_3AsO_4(aq) + 2I^-(aq) \rightarrow 3As_2O_3(s) + 2IO_3^-(aq) + 9H_2O(l)$

21 **a** **i** +3 **ii** +2 **iii** +4
b $S_2O_4^{2-}(aq) + 2H_2O(l) \rightarrow 2HSO_3^-(aq) + 2H^+(aq) + 2e^-$
$S_2O_4^{2-}(aq) + 2H^+(aq) + 2e^- \rightarrow S_2O_3^{2-}(aq) + H_2O(l)$

22 **a** Oxidation number of nitrogen in $(NH_4)_2Cr_2O_7$ is –3 and in N_2 it is 0.
Oxidation number of chromium in $(NH_4)_2Cr_2O_7$ is +6 and in Cr_2O_3 it is +3.
Nitrogen has been oxidised and chromium has been reduced.
b **i** $2NH_4^+(s) \rightarrow N_2(g) + 8H^+(aq) + 6e^-$
ii $Cr_2O_7^{2-}(s) + 8H^+(aq) + 6e^- \rightarrow Cr_2O_3(s) + 4H_2O(g)$
c Reaction **i** is oxidation, reaction **ii** is reduction
d $(NH_4)_2Cr_2O_7(s) \rightarrow N_2(g) + Cr_2O_3(s) + 4H_2O(g)$
e $NH_4^+(s)/N_2(g)$ and $Cr_2O_7^{2-}(aq)/Cr_2O_3(s)$

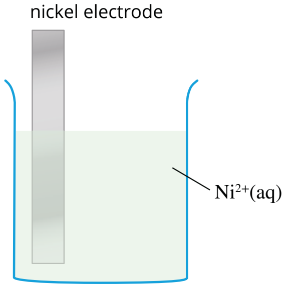
23 **a** $Fe_2O_3(s) + 6e^- \rightarrow 2Fe(l) + 3O_2^-(s)$
b reduction
c $Fe_2O_3(s) + 2Al(s) \rightarrow 2Fe(l) + Al_2O_3(s)$
d 5.29 g (3 significant figures)

Chapter 5 Galvanic cells as a source of energy

5.1 Galvanic cells

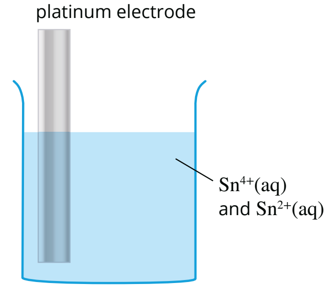
1 D

2 **a**



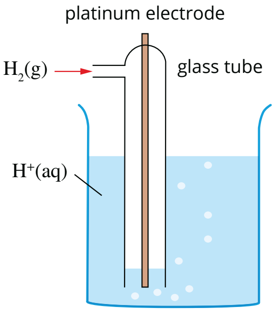
$Ni^{2+}(aq)/Ni(s)$ half-cell

b



$Sn^{4+}(aq)/Sn^{2+}(aq)$ half-cell

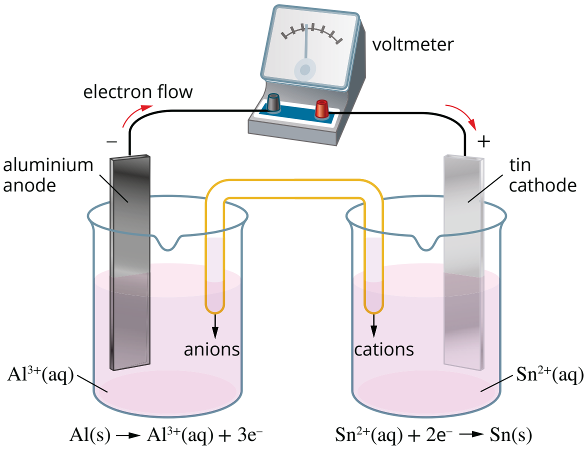
c



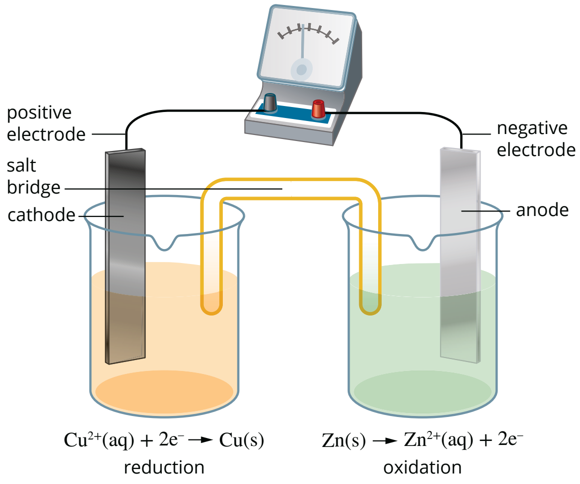
$H^+(aq)/H_2(g)$ half-cell

3 **a** $Sn^{2+}(aq) + 2e^- \rightarrow Sn(s)$ **b** $Al(s) \rightarrow Al^{3+}(aq) + 3e^-$

4



5 $Zn(s) + Cu^{2+}(aq) \longrightarrow Cu(s) + Zn^{2+}(aq)$

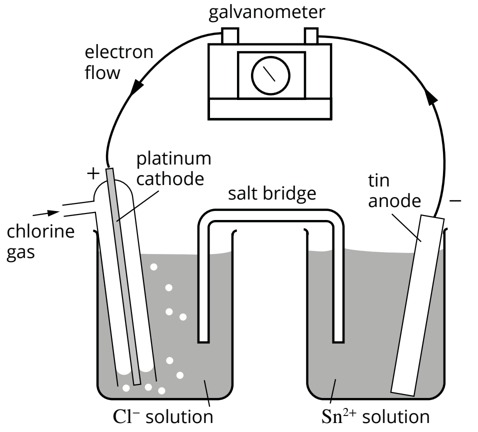


5.2 The electrochemical series

WE 5.2.1 The nickel electrode will be the anode and the tin electrode will be the cathode.
Electrons flow from the negative electrode (anode) to the positive electrode (cathode).

1 **a** Reduction: $Pb^{2+}(aq) + 2e^- \rightarrow Pb(s)$
Oxidation: $Al(s) \rightarrow Al^{3+}(aq) + 3e^-$
b $3Pb^{2+}(aq) + 2Al(s) \rightarrow 3Pb(s) + 2Al^{3+}(aq)$
c The lead electrode will be the cathode and the aluminium electrode will be the anode.

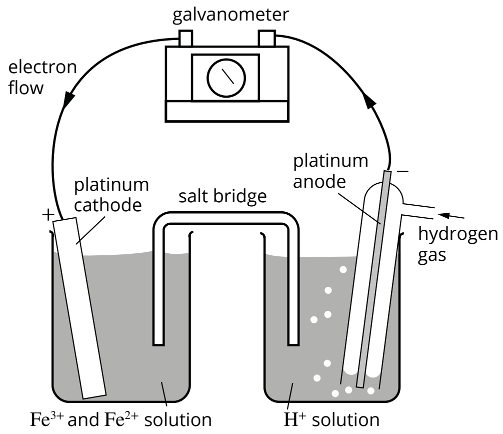
2



$Cl_2(g) + 2e^- \longrightarrow 2Cl^-(aq)$ $Sn(s) \longrightarrow Sn^{2+}(aq) + 2e^-$

Overall reaction: $Cl_2(g) + Sn(s) \longrightarrow 2Cl^-(aq)Sn^{2+}(aq)$

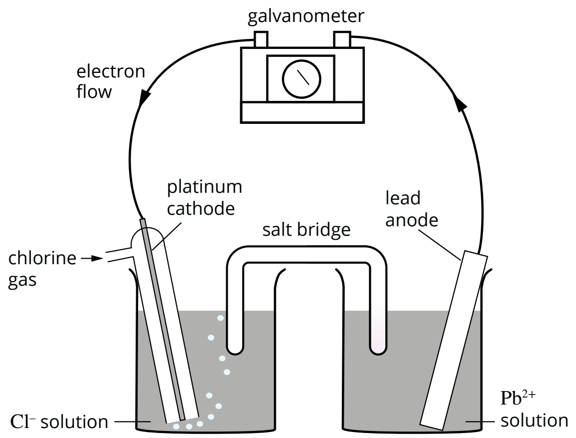
3 **a**



$Fe^{3+}(aq) + e^- \longrightarrow Fe^{2+}(aq)$ $H_2(g) \longrightarrow 2H^+(aq) + 2e^-$

Overall reaction: $2Fe^{3+}(aq) + H_2(g) \longrightarrow 2Fe^{2+}(aq) + 2H^+(aq)$

b



$Cl_2(g) + 2e^- \rightarrow 2Cl^-(aq)$ $Pb(s) \rightarrow Pb^{2+}(aq) + 2e^-$

Overall reaction: $Cl_2(g) + Pb(s) \rightarrow Pb^{2+}(aq) + 2Cl^-(aq)$

4 Question 1 cell: 1.54 V Question 2 cell: 1.50 V
Question 3a cell: 0.77 V Question 3b cell: 1.49 V

5.3 Predicting direct redox reactions

WE 5.3.1 **a** No reaction occurs because both I_2 and Pb^{2+} are oxidising agents.
b No reaction because the oxidising agent, I_2, is below the reducing agent, Cl^-, in the electrochemical series.
c No reaction occurs because both Cl^- and Pb are reducing agents.

1 B **2** C
3 **a** $Cl_2(g) + 2Br^-(aq) \rightarrow 2Cl^-(aq) + Br_2(l)$
b $Cl_2(g) + 2I^-(aq) \rightarrow 2Cl^-(aq) + I_2(s)$
c No reaction
d $Br_2(l) + 2I^-(aq) \rightarrow 2Br^-(aq) + I_2(s)$
4 **a** $Zn(s) + 2Ag^+(aq) \rightarrow Zn^{2+}(aq) + 2Ag(s)$
b Chemical energy is transformed into heat energy.
5 $CuSO_4$: A reaction occurs $MgCl_2$: No reaction occurs
$Pb(NO_3)_2$: A reaction occurs $ZnCl_2$: No reaction occurs

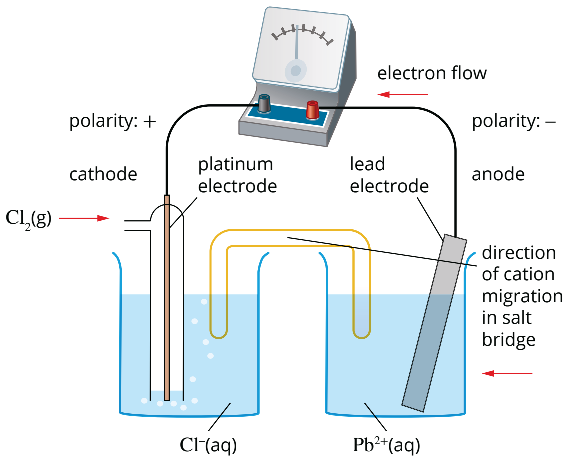
5.4 Everyday sources of power

1 Secondary cells can be recharged whereas primary cells cannot.
2 D **3** A
4 **a** True **b** True **c** False **d** True **e** False **f** False
5 **a** $Zn(s) + 2OH^-(aq) \rightarrow Zn(OH)_2(s) + 2e^-$
b $Ag_2O(s) + H_2O(l) + 2e^- \rightarrow 2Ag(s) + 2OH^-(aq)$

Chapter 5 review

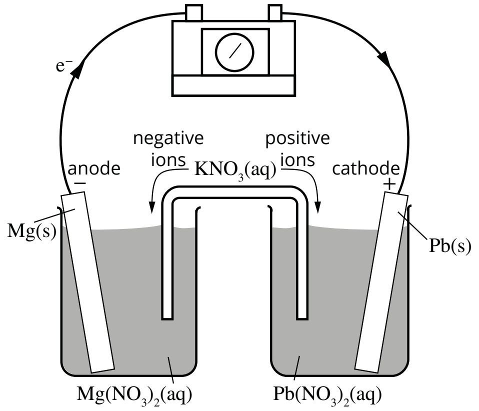
1 D **2** A
3 **a** Oxidant: a substance that causes another substance to be oxidised and is reduced in the process. Reductant: a substance that causes another substance to be reduced and is oxidised in the process.
b Anode: electrode at which oxidation occurs. Cathode: electrode at which reduction occurs.
c Conjugate redox pair: an oxidant and its corresponding reduced form, e.g. Cu^{2+}/Cu. The reduced form has gained electrons. Conjugate acid–base pair: A conjugate acid contains one more hydrogen ion or proton than the base.
d External circuit: section of a circuit where the electrons flow, e.g. through wires. Internal circuit: part of cell where the current is due to the movement of ions, e.g. in the salt bridge.

4

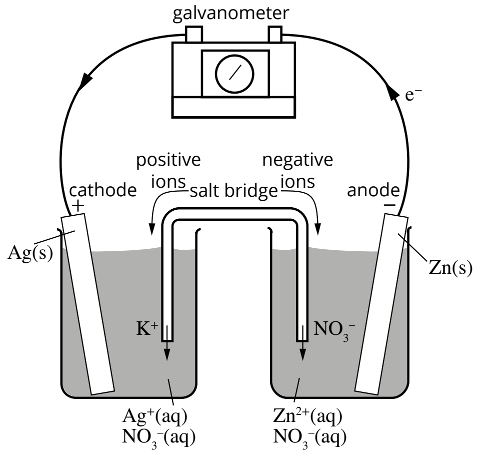


half-equation: $Cl_2(g) + 2e^- \rightarrow 2Cl^-(aq)$ half-equation: $Pb(s) \rightarrow Pb^{2+}(aq) + 2e$

5 **a**

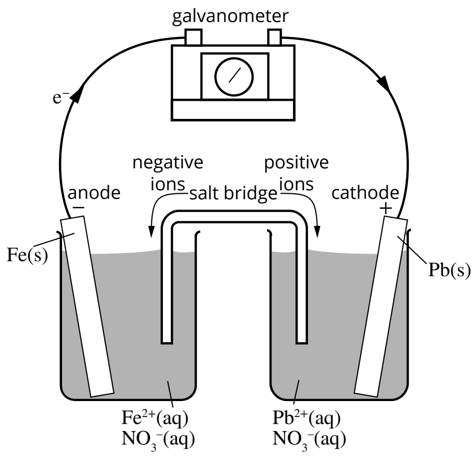


b $Mg(s) \rightarrow Mg^{2+}(aq) + 2e^-$
$Pb^{2+}(aq) + 2e^- \rightarrow Pb(s)$
Overall: $Mg(s) + Pb^{2+}(aq) \rightarrow Mg^{2+}(aq) + Pb(s)$
c Lead electrode is the cathode; magnesium electrode is the anode
d Anions will migrate to the $Mg^{2+}(aq)/Mg(s)$ half-cell, cations to the $Pb^{2+}(aq)/Pb(s)$ half-cell.
6 cell potential difference = higher half-cell $E°$ – lower half-cell $E°$
$= E° (Cu^{2+}(aq)/Cu(s)) - E° (Zn^{2+}(aq)/Zn(s))$
$= 0.34 - (-0.76) = 1.10$ V
7 $Sn^{2+} > Fe^{2+} > Br^-$
8 $Ni^{2+}(aq)/Ni(s)$ and $Br_2(l)/Br^-(aq)$, $Fe^{2+}(aq)/Fe(s)$ and $Fe^{3+}(aq)/Fe^{2+}(aq)$, $Ni^{2+}(aq)/Ni(s)$ and $Fe^{3+}(aq)/Fe^{2+}(aq)$, $Ni^{2+}(aq)/Ni(s)$ and $Fe^{2+}(aq)/Fe(s)$
9 **i**



Cathode (+): $Ag^+(aq) + e^- \longrightarrow Ag(s)$
Anode (–): $Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^-$
Overall: $Zn(s) + 2Ag^+(aq) \longrightarrow Zn^{2+}(aq) + 2Ag(s)$

ii

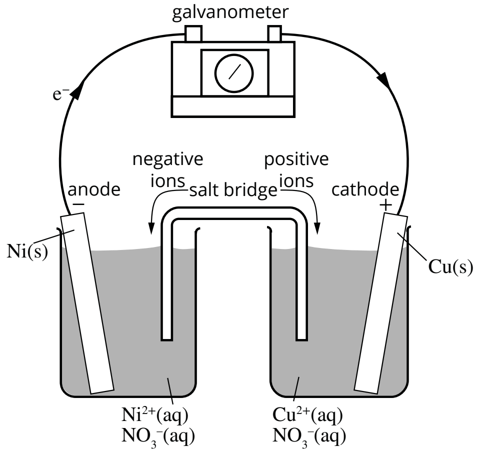


Cathode (+): $Pb^{2+}(aq) + 2e^- \longrightarrow Pb(s)$

Anode (–): $Fe(s) \longrightarrow Fe^{2+}(aq) + 2e^-$

Overall: $Fe(s) + Pb^{2+}(aq) \longrightarrow Fe^{2+}(aq) + Pb(s)$

iii



Cathode (+): $Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$

Anode (–): $Ni(s) \longrightarrow Ni^{2+}(aq) + 2e^-$

Overall: $Ni(s) + Cu^{2+}(aq) \longrightarrow Ni^{2+}(aq) + Cu(s)$

10 $B^{2+} > A^{2+} > C^{2+} > D^{2+}$

11 **a** **i** Reaction will occur.
- **ii** $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$ (oxidation); $Cl_2(g) + 2e^- \rightarrow 2Cl^-(aq)$ (reduction)
- **iii** $Zn(s) + Cl_2(g) \rightarrow Zn^{2+}(aq) + 2Cl^-(aq)$

b **i** No reaction

c **i** Reaction will occur.
- **ii** $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$ (oxidation); $Ag^+(aq) + e^- \rightarrow Ag(s)$ (reduction)
- **iii** $2Ag^+(aq) + Zn(s) \rightarrow 2Ag(s) + Zn^{2+}(aq)$

d **i** No reaction

12 **a** $3Cu^{2+}(aq) + 2Al(s) \rightarrow 3Cu(s) + 2Al^{3+}(aq)$

b No reaction

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

d $2H^+(aq) + Fe(s) \rightarrow H_2(g) + Fe^{2+}(aq)$

e No reaction

13 **a** $Ag^+(aq)$; $Mg^{2+}(aq)$

b Mg(s); Ag(s)

c A coating of silver will form on the lead when it is placed in silver nitrate solution because Ag^+ ions are stronger oxidants than Pb^{2+} ions.

d Zinc and magnesium

14 **a** Oxidising agent

b Strong reducing agent

c True

d False

e True

15 **a** Predict $Fe^{2+}(aq)$ and $H^+(aq)$ are formed

b $2Fe^{3+}(aq) + H_2(g) \rightarrow 2Fe^{2+}(aq) + 2H^+(aq)$

c If significant reaction had occurred, the yellow solution containing Fe^{3+} ions would have become pale green as Fe^{2+} ions formed. Because no reaction was observed, the rate of the reaction may have been slow. Alternatively, it must be remembered that the electrochemical series is only valid for certain conditions. It is possible that under the conditions in which the experiment was performed, little reaction would occur.

16 Galvanic cell: Device that converts chemical energy into electrical energy

Primary cell: A non-rechargeable galvanic cell

Secondary cell: A rechargeable galvanic cell

17 **a** Electrons flow away from the negative electrode (anode), through the external circuit, to the positive electrode (cathode).

b A battery consists of a number of cells connected together in series.

c When a cell discharges, chemical energy is converted to electrical energy. When it is recharged, electrical energy is converted to chemical energy.

18 The products of cell reaction remain in contact with the electrodes and are in forms that can be converted back to reactants.

19 When a cell discharges, oxidation occurs at the anode which has a negative polarity. Reduction occurs at the cathode, which has positive polarity. The oxidation and reduction reactions in the cell generate electricity. When the cell is recharged, the direction of the electron flow is reversed. An external supply of electricity is required to reverse these reactions. Oxidation now occurs at the positive electrode while reduction occurs at the negative electrode.

20 Convenience and flexibility of the portable equipment powered by these cells. Furthermore, the price of individual cells is regarded as relatively low.

21 half-cells, anode, cathode, negative, positive

cannot, can

increases, side reactions

22 The student could construct an electrochemical cell from an Mn^{2+}/Mn half-cell and a Zn^{2+}/Zn half-cell. If the manganese electrode was found to be the positive electrode, then Mn^{2+} would be a stronger oxidant than Zn^{2+} and the Mn^{2+}/Mn pair should be placed between the Zn^{2+}/Zn pair and the Fe^{2+}/Fe pair in the series.

If the manganese electrode were negative, then Mn^{2+} would be a weaker oxidant than Zn^{2+} and the Mn^{2+}/Mn pair should be placed below the Zn^{2+}/Zn pair. In this case, the student could determine whether to place the manganese pair above or below the H_2O/H_2, OH^- pair by constructing a cell from an Mn^{2+}/Mn half-cell and an H_2O/H_2, OH^- half-cell and finding the polarity of the manganese electrode.

23 **a** Bromine is a stronger oxidant than iodine, so it reacts with iodide ions. Because bromine is a weaker oxidant than chlorine, bromine does not react with chloride ions.

b Hydrogen peroxide acts as both a strong oxidant and as a weak reductant. (It appears in the electrochemical series on the left side of one half reaction and the right side of another.) Hydrogen peroxide therefore reacts with itself. The reaction is very slow unless a catalyst such as manganese dioxide is added.

c Sn^{2+} ions can be oxidised to Sn^{4+} ions by a suitable oxidant. Tin metal can reduce Sn^{4+} ions so that they re-form Sn^{2+} ions.

d Zinc is a stronger reductant than iron and, if the two metals are in contact, the zinc is oxidised preferentially. For this reason, the presence of a zinc block on the iron hull of a ship protects the hull from corrosion.

24 The brown stain contains iodine (I_2). A reductant stronger than I^- ions would react with iodine. A solution containing Sn^{2+} ions might react and cause the stain to be removed.

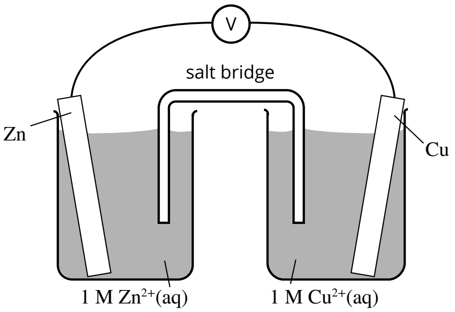
25 The electrochemical series is based on reactions occurring under standard conditions of 25°C (298 K), 1 bar (100 kPa) pressure and 1 M concentration and can only be used to predict the possibility of reaction occurring under these conditions. The series gives no information about the rate of reactions so even if a reaction is predicted it may be so slow that no reaction is apparent.

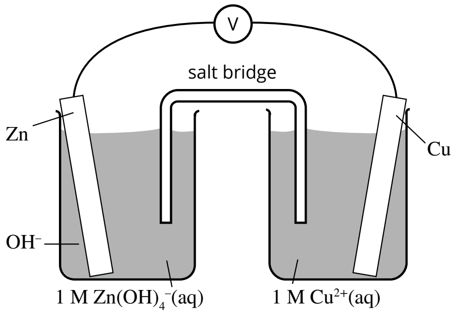
26 **a** $Zn(s) + 4OH^-(aq) + Cu^{2+}(aq) \rightarrow Zn(OH)_4^{2-}(aq) + 2Cu(s)$

b The student should make two electrochemical cells consisting of the:

- Cu^{2+}/Cu half-cell and the 'alkaline zinc half-cell'
- Cu^{2+}/Cu half-cell and the Zn^{2+}/Zn half-cell as shown in the diagrams.

The cell voltages should be measured and if they are identical then the two half-cells have the same *E*° values (they would not be expected to have the same *E*° values).





Chapter 6 Fuel cells as a source of energy

6.1 Continuous sources of electrical energy

1 A **2** B, C, G

3 **a** Anode: $H_2(g) \rightarrow 2H^+(aq) + 2e^-$; cathode: $O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$

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

4 **a** $2CH_3OH(g) + 3O_2(g) \rightarrow 2CO_2(g) + 4H_2O(l)$

b Reduction of $O_2(g)$

c NaOH(aq) or KOH(aq)

d Oxygen is reduced, forming OH^- ions at the cathode of the fuel cell, so an increase in pH occurs at this electrode initially. The OH^- ions migrate to the anode where they are consumed. Once the rate of production of OH^- ions at the cathode becomes equal to the rate at which they depart, the pH near the electrode will be constant.

e A fuel cell converts chemical energy into electrical energy directly, with relatively little energy being converted into thermal energy. If electrical energy were obtained by burning methanol (in a process similar to that used to obtain electrical energy from coal in coal-fired power stations), the energy 'losses' of the various energy transformations involved would be greater. In particular, large losses occur when thermal energy is converted into mechanical energy.

5 Fuel cells are about twice as efficient as coal-fired power stations. Consequently, fuel cells produce the same quantity of energy from about half as much fuel. Less fuel means less carbon dioxide gas is produced. As carbon dioxide is a major greenhouse gas, the use of fuel cells has the potential to reduce the greenhouse effect.

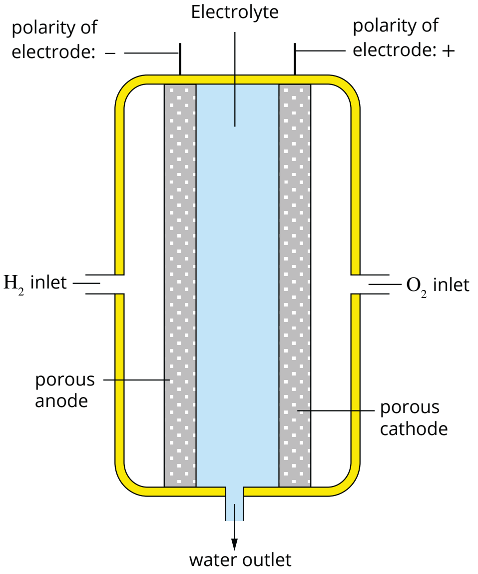
Chapter 6 review

1 A **2** C **3** B **4** B

5 **a** True **b** False **c** True **d** False **e** False

6 Chemical, electrical, fuel, oxidation, oxidising agent, reduced, reactants, electrolyte, electrolyte, no direct contact, more, much less, energy and water, hydrogen

7



8 **a** All types of cells

b All types of cells

c All types of cells

d Secondary cells only

e All types of cells

f Primary and secondary cells only

g Fuel cells only

9 **a** $CH_3CH_2OH(g) + H_2O(l) \rightarrow CH_3COOH(aq) + 4H^+(aq) + 4e^-$

b $O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$

c Cathode

d Yes. The net cell reaction in the fuel cell is the oxidation of ethanol to form carbon dioxide and water. Like ethanol, methane in natural gas can be oxidised to carbon dioxide and water. Provided the electrode materials used in the cell act as effective catalysts for both reactions, it is likely that the use of natural gas would produce a voltage.

10 **a** $CH_4(g) + H_2O(l) \rightarrow CO_2(g) + 8H^+(aq) + 8e^-$

b 1.06 V

11 **a** $HCHO(g) + O_2(g) \rightarrow CO_2(g) + H_2O(l)$

b $O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq)$

12 **a** $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$

b X is the anode and Y is the cathode.

c Because fuel cells are more efficient at converting chemical energy to electrical energy, there will be less CO_2 emitted to the atmosphere per joule of energy generated.

13 **a**
- Both cells are designed to convert chemical energy into electrical energy at relatively high efficiencies.
- Oxidation and reduction reactions take place in different places within the cells.
- Both have an anode, which is negative, at which an oxidation half-reaction occurs.
- Both have a cathode, which is positive, at which a reduction half-reaction occurs.
- Both have an electrolyte, which provides ions to balance charges formed at the electrodes; cations flow towards the cathode and anions flow towards the anode.

b
- A fuel cell produces electrical energy continuously when reactants are provided; primary cells can produce power for only a limited time until their reactants are depleted.

  - A fuel cell uses a combustible fuel and air or oxygen; primary cells can be made from different combinations of two conjugate redox pairs.
  - The reactants in fuel cells are usually gaseous; a range of solids, liquids and gases can be used as the reactants in primary cells.
  - Electrodes in fuel cells must be porous to allow contact between reactant gases and the electrolyte; electrodes in primary cells need not be porous.
  - Catalysts are used in fuel cells to increase cell efficiency; catalysts are not required in primary cells.

14 Advantages:
- Much more efficient than power stations and fossil-fuel-driven vehicles
- Almost the only product apart from electricity is water, so fewer carbon emissions
- Generate power continuously as they are supplied with gaseous fuel, which is ideal for commercial power generation
- Operate more quietly than internal combustion engines
- Hydrogen can be generated using renewable energy or from biogas
- Heat produced as a by-product can be used for other purposes, including electricity generation

Disadvantages:
- Costly to produce
- Rate of the cell reaction is slow, so expensive catalytic material is needed
- Most hydrogen is produced from fossil fuels, in a process that creates greenhouse gases and consumes energy
- Lack of a hydrogen distribution network and the costs associated with the construction of pipelines, filling stations etc.
- Storage issues caused by hydrogen's low energy content per unit volume
- Safety issues due to the explosive nature of hydrogen

Area of study 1 What are the options for energy production?

Multiple-choice questions

1	B	**2**	C	**3**	D	**4**	B	**5**	A	**6**	D
7	A	**8**	C	**9**	C	**10**	C	**11**	B	**12**	B
13	D	**14**	A	**15**	D	**16**	C	**17**	A	**18**	C
19	D	**20**	D	**21**	A						

Short-answer questions

22 **a** A chemical that undergoes reaction in a way that provides useful energy.

b The methane found in natural gas, like all fossil fuels, derives from the decomposition of ancient biomass largely as a result of the action of heat and pressure in the Earth's crust and is tapped from underground reserves where it is normally associated with coal and oil. It is non-renewable. Since its carbon comes from underground reserves, its combustion adds to current levels of atmospheric carbon dioxide.

The methane found in biogas derives from the anaerobic digestion of biomass by microorganisms. It is renewable because the carbon in the source biomass is absorbed from the atmosphere during photosynthesis, its re-release upon combustion of the biogas has relatively little net effect of atmospheric carbon dioxide levels.

23 **a** Petrol, petrodiesel, LNG, LPG

b Methanol, ethanol, biodiesel

c Generally, the higher the proportion of oxygen in a fuel, the lower the available energy. The presence of oxygen means that the fuel is already partially oxidised.

d Methanol and ethanol are renewable fuels that are relatively easy to produce, store and transport in large quantities. As fossil fuel reserves diminish, they are becoming increasingly cost-effective.

e Air transport

f For most forms of ground-based transport, the storage volume is more limiting than mass considerations.

24 **a** 742 MJ

b Heat loss in the boiler. Heat loss through friction in moving parts within the turbines and generator.

c One that cannot be replaced or regenerated as fast as it is consumed.

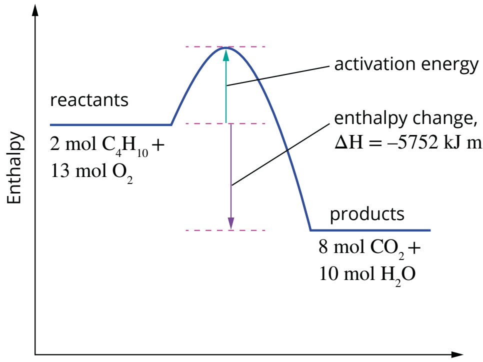
d Biogas is a renewable energy source, whereas existing coal supplies (which remain large) are non-renewable and would eventually be consumed. Because biogas carbon is derived from absorption of atmospheric CO_2 in photosynthesis, its use as a fuel has relatively little effect on net levels of atmospheric CO_2. Biogas can be produced from waste biomass that would otherwise require disposal.

25 **a** +362 kJ mol^{-1} **b** –181 kJ mol^{-1}

c +57 kJ mol^{-1} **d** +67 kJ mol^{-1}

26 **a** The equation has combustion of 2 mol of butane, hence $\Delta H = 2 \times (-2876) = -5752$ kJ mol^{-1}

b



c Some initial input of energy is required to allow some reactants to overcome the activation energy barrier (associated with breaking bonds in reactants) to initiate the rapid reaction.

d 49.6 kJ g^{-1} **e** 91.2°C

27 **a** 50.1 MJ **b** 30.9 L

c $2CH_4(g) + 3O_2(g) \rightarrow 2CO(g) + 4H_2O(g)$ $\Delta H = -1042$ kJ mol^{-1}

or

$CH_4(g) + \frac{3}{2}O_2(g) \rightarrow CO(g) + 2H_2O(g)$ $\Delta H = -521$ kJ mol^{-1}

d **i** 802 kJ **ii** 746 kJ **iii** 521 kJ

28 **a** 41.9 MJ kg^{-1}

b Imperfect insulation may allow some heat losses;
some of the energy released is absorbed by the container;
incomplete combustion of the fuel will reduce energy released

29 **a** **i** 163 atm **ii** 1.24×10^5 mmHg

b 689 g **c** 4.27 m^3 **d** 618

30 **a** Advantages: very high energy per unit mass; water is the only product of combustion; renewable

Disadvantages: hydrogen is difficult and dangerous to transport and store; requires energy for production; relatively expensive

b Advantages: no recharge time; range is potentially greater; one of the reactants (oxygen/air) doesn't need to be carried with the cell; doesn't incorporate toxic materials such as heavy metals

Disadvantages: hydrogen is difficult and dangerous to transport and store; relatively expensive; lower power output

c Advantages: greater efficiency of energy conversion so potentially longer range; quieter

Disadvantages: lower power output; expensive

31 **a** Anode: $CH_3OH(g) + H_2O(l) \rightarrow CO_2(g) + 6H^+(aq) + 6e^-$

Cathode: $O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$

b 22.7 kJ **c** 5.1 kJ **d** 22%

e Incomplete reaction of the fuel (methanol). Some may be incompletely oxidised or pass into the electrolyte waste without reacting at all. Generation of heat.

32 **a** Oxidation number changes: I (+5 → −1) and S (+4 → +6).
Oxidant HIO_3. Reductant SO_2.
b Not redox
c Oxidation number changes: Fe (+2 → +3) and O (0 → −2).
Oxident O_2. Reductant $Fe(OH)_2$ (or Fe^{2+}).
d Oxidation number changes: H (−1 → 0) and H (+1 → 0).
Oxident H_2O. Reductant NaH.

33 **a** Oxidation: $Al(s) \rightarrow Al^{3+}(aq) + 3e^-$
Reduction: $Br_2(aq) + 2e^- \rightarrow 2Br^-(aq)$
Overall: $2Al(s) + 3Br_2(aq) \rightarrow 2Al^{3+}(aq) + 6Br^-(aq)$
b Oxidation:
$S_2O_3^{2-}(aq) + 5H_2O(l) \rightarrow 2SO_4^{2-}(aq) + 10H^+(aq) + 8e^-$
Reduction: $ClO^-(aq) + 2H^+(aq) + 2e^- \rightarrow Cl^-(aq) + H_2O(l)$
Overall: $4ClO^-(aq) + S_2O_3^{2-}(aq) + H_2O(l) \rightarrow 2SO_4^{2-}(aq) + 4Cl^-(aq) + 2H^+(aq)$
c Oxidation: $H_2O_2(aq) \rightarrow O_2(aq) + 2H^+(aq) + 2e^-$
Reduction: $MnO_4^-(aq) + 4H^+(aq) + 3e^- \rightarrow MnO_2(s) + 2H_2O(l)$
Overall: $3H_2O_2(aq) + 2MnO_4^-(aq) + 2H^+(aq) \rightarrow 3O_2(aq) + 2MnO_2(s) + 4H_2O(l)$

34 **a** Cadmium **b** KOH or NaOH
c For effective recharging of a cell, the discharge products must remain in electrical contact with the electrodes. Because the products in this cell are solids, they remain on the respective electrode surfaces allowing the cell reactions to be reversed.
d At the positive electrode (the anode during recharging):
$Ni(OH)_2(s) + OH^-(aq) \rightarrow NiOOH(s) + H_2O(l) + e^-$
At the negative electrode (the cathode during recharging):
$Cd(OH)_2(s) + 2e^-(aq) \rightarrow Cd(s) + 2OH^-(aq)$
Overall:
$2Ni(OH)_2(s) + Cd(OH)_2(s) \rightarrow 2NiOOH(s) + Cd(s) + 2H_2O(l)$
e Enthalpy (chemical energy) → electrical energy

35 **a** $E°(Sn^{2+}/Sn) = -0.14$ V and $E°(Fe^{2+}/Fe) = -0.41$ V
i 0.27 V **ii** Fe^{2+}/Fe
iii $Sn^{2+}(aq) + Fe(s) \rightarrow Sn(s) + Fe^{2+}(aq)$
b $E°(Fe^{3+}/Fe^{2+}) = +0.77$ V and $E°(Al^{3+}/Al) = -1.71$ V
i 2.48 V **ii** Al^{3+}/Al
iii $3Fe^{3+}(aq) + Al(s) \rightarrow 3Fe^{2+}(s) + Al^{3+}(aq)$
c $E°(H^+/H_2) = 0$ V and $E°(I_2/I^-) = +0.54$ V
i 0.54 V **ii** H^+/H_2
iii $I_2(aq) + H_2(g) \rightarrow 2I^-(aq) + 2H^+(aq)$

36 **a** A **b** O_2
c $4Al(s) + 3O_2(g) + 6H_2O(l) \rightarrow 4Al^{3+}(aq) + 12OH^-(aq)$
d The cathode is the site of the reduction reaction involving oxygen/air, which must be in contact with the electrolyte.
A porous electrode will allow a large surface area for this reaction and thereby maximise the rate of reaction and hence the current/power output of the cell.
e $E°(Zn^{2+}/Zn) < E°(O_2,H_2O/OH^-)$ so a spontaneous cell reaction will occur.
$E°(Ag^+/Ag) > E°(O_2,H_2O/OH^-)$ so a spontaneous cell reaction will not occur.
f Smaller because $E°(Zn^{2+}/Zn) > E°(Al^{3+}/Al)$.
g With an acidic electrolyte the cathode reaction becomes:
cathode reaction:
$O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l) \quad E° = +1.23$ V
anode reactions:
$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^- \quad E° = -0.76$ V
$Ag(s) \rightarrow Ag^+(aq) + e^- \quad E° = +0.80$ V
$E°(Zn^{2+}/Zn) < E°(O_2,H^+/H_2O)$ so a spontaneous cell reaction will occur.
$E°(Ag^+/Ag) < E°(O_2,H^+/H_2O)$ so a spontaneous cell reaction will occur.
Essentially, O_2 becomes a stronger oxidant in acidic conditions, and is capable of spontaneous reaction with the relatively weak reductant, Ag.

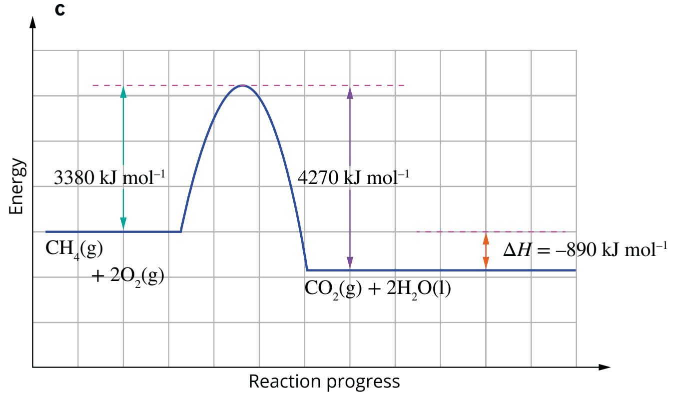
Chapter 7 Rate of chemical reactions

7.1 Investigating the rate of chemical reactions

1 C
2 **a** Increasing **b** Increasing **c** Increasing
d Increasing **e** Adding
3 **a** $CaCO_3(s) + 2HNO_3(aq) \rightarrow Ca(NO_3)_2(aq) + CO_2(g) + H_2O(l)$
b Decreasing because the gradient of the graph is decreasing.
4 **a** Using smaller pieces of wood with a larger surface area
b Using a brick cleaner with a higher concentration
c Increasing the temperature of the oven

7.2 Collision theory

1 D **2** A
3 **a** $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$
b –890 kJ mol^{-1}
c



4 139 kJ mol^{-1}

7.3 Effect of temperature on rate of reaction

WE 7.3.1 Surface area of iron anchor is relatively small so frequency of collisions with reacting particles would be low. Concentration of oxygen at greater depths is also low so frequency of collisions is further reduced. Therefore, rate of corrosion is reduced.

1 D **2** A, B and C **3** D, F, B, E, C, A
4 **a** At higher temperatures the molecules that react to form fibreglass plastics have greater energy. They collide more frequently and are more likely to have a total energy exceeding the activation energy of the reaction involved, increasing the rate of reaction.
b Fine particles have a large surface area, resulting in a high frequency of collisions of aluminium particles with gas molecules (such as oxygen) in the air and hence rapid reaction rate. The aluminium can burn vigorously and release a large quantity of heat.
c At high altitude, air pressure is considerably lower than at any location in the Australian bush so water boils at a lower temperature (up to 30°C lower). Thus, the average kinetic energy of the molecules in the potato is lower, so they are less likely to have a total energy exceeding the activation energy of the reactions involved in cooking a potato, so the potato cooks slower.

7.4 Catalysts

1 D
2 **a** A substance that increases the rate of a chemical reaction without itself undergoing permanent change.
b The minimum amount of energy required by the reactants in order to form products in a reaction.
3 When salt is mixed with sugar, the salt acts as a catalyst and lowers the activation energy of the combustion reaction between sugar and oxygen.
4 **a** Reactions involving a heterogeneous catalyst take place at the surface of the catalyst. Reactants form bonds with the catalyst, lowering the activation energy of reactions and allowing them to proceed more rapidly.

b A porous pellet has a much larger surface area than a solid lump. More reactants may be in contact with the surface of a porous pellet at any instant, producing a faster rate of reaction.

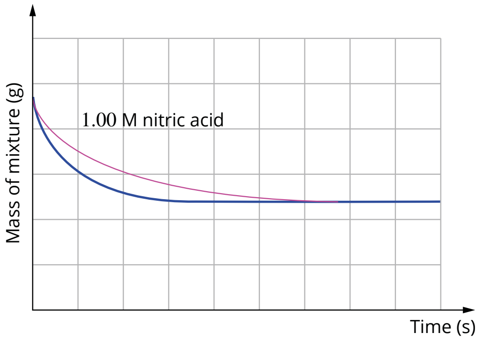
Chapter 7 review

1 D **2** C **3** B **4** B

5 **a** A gas is produced so mass is lost from the mixture.

b Cu is limiting.

c

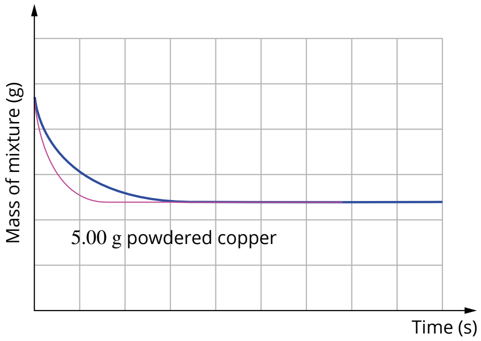


Decreased rate of mass loss due to lower nitric acid concentration.

($n(HNO_3) = cV = 1.00 \times 0.500 = 0.500$ mol)

Copper is still limiting, so final mass remains the same.

d

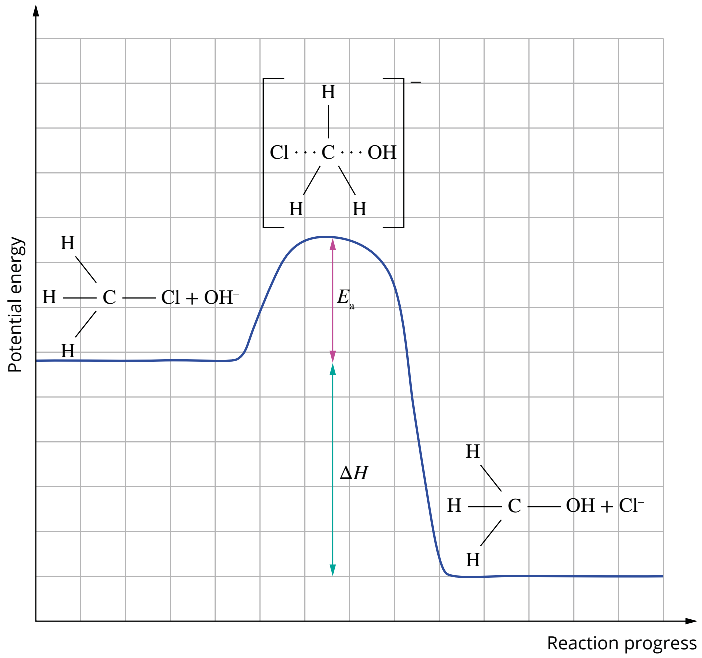


Increased rate of mass loss due to increased copper surface area. Copper is still limiting, so final mass remains the same.

6 Reactant particles must: collide with each other, collide with sufficient energy to break the bonds within the reactants, collide with the correct orientation to break the bonds within the reactants and so allow the formation of new products.

7 Collision 1 has the correct orientation, allowing bonds to break within the reactants and bonds to form within the products.

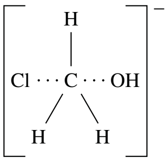
8 **a**



b Minimum amount of energy required by the reactants in order to form products in a reaction. It is related to the energy required to break bonds in the reactants.

c Exothermic

d



e C–Cl bond being broken in chloromethane. C–O bond beginning to form between chloromethane and hydroxide ion.

9 **a** The single H–H bond in each hydrogen molecule and the double O=O bond in each oxygen molecule.

b Two H–O bonds in each new water molecule.

c The energy change for the reaction is the difference between the energy absorbed to break the bonds in the H_2 and O_2 reactants, and the energy released when the bonds in the H_2O product are made.

d No reaction occurs until sufficient energy is supplied to overcome the activation energy.

10 B **11** D

12 **a** At lower temperatures the molecules that react to cause the apple to brown have less energy. They collide less frequently and are less likely to have a total energy exceeding the activation energy of the reaction involved, decreasing the rate of reaction.

b Using pure oxygen gas instead of air increases the concentration of oxygen. This results in a higher frequency of collisions between hydrogen and oxygen molecules and hence an increased reaction rate.

13 A **14** C

15 **a** Surface area of a solid reactant, concentration of reactants in a solution, pressure of any gaseous reactants, temperature of the reaction, presence of a catalyst.

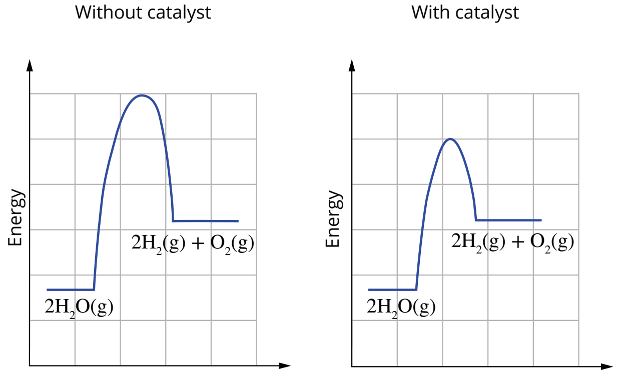
b **i** Surface area of a solid reactant, concentration of reactants in a solution, pressure of any gaseous reactants

ii Temperature of the reaction (also increases collision frequency), presence of a catalyst

16
1. Increasing the pressure of the gases increases the number of collisions between the reactant molecules in a given time, so more collisions occur with the correct orientation to react and with energy that is greater than or equal to the activation energy. As a result, the rate of reaction would increase.
2. Adding a catalyst allows the reaction to occur by a different pathway with a lower activation energy. The proportion of collisions with energy greater than the activation energy would thus be increased. As a result, the rate of reaction would increase.

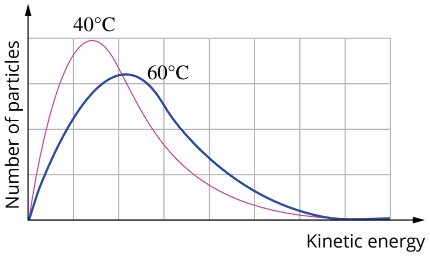
17 **a** 1370 kJ mol^{-1} **b** –572 kJ mol^{-1}

c

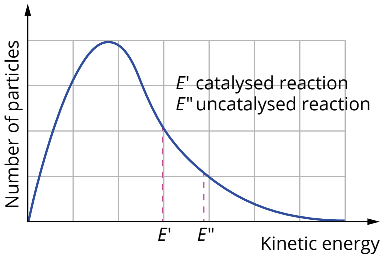


d +572 kJ mol^{-1}

18 a



b



c When a catalyst is present, the reaction proceeds by an alternative reaction pathway with a lower activation energy (*E´*) than in the uncatalysed reaction (*E´´*). At a given temperature, there will be a greater proportion of reacting particles that have a kinetic energy equal to or greater than the activation energies (*E´* than *E´´*). As more reactants have sufficient energy to react, the rate of reaction increases.

19 a $CaCO_3(s) + 2HCl(aq) \rightarrow CaCl_2(aq) + CO_2(g) + H_2O(l)$

b $n(CaCO) = 10.0\text{ g}/100.1\text{ g mol}^{-1} = 0.0999\text{ mol}$

$n(HCl) = 0.1\text{ M} \times 0.1\text{ L} = 0.01\text{ mol}$

$\therefore CaCO_3$ is in excess

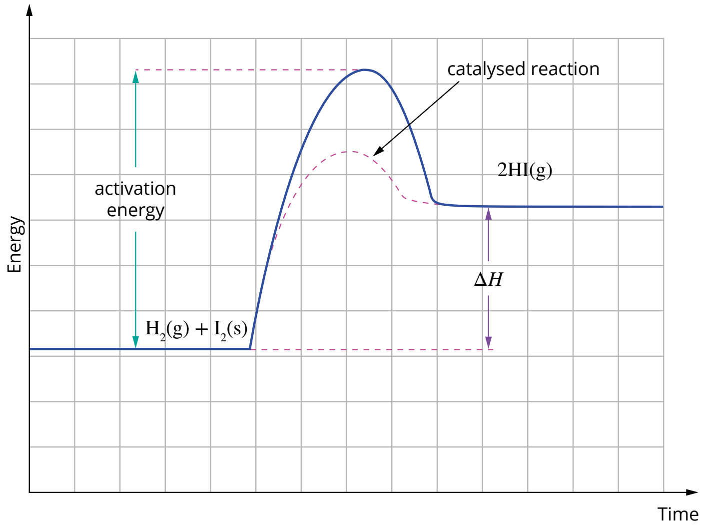
c The rate of reaction can be measured by:

- a decrease in mass of reaction mixture as $CO_2(g)$ escapes to the atmosphere
- an increase in pH with a pH probe as acid is consumed.

d The rate of reaction with the smaller lumps will be faster. The smaller lumps have a larger surface area so more collisions can occur per second.

e Increase temperature; increase concentration of hydrochloric acid.

20 a, c



b The reaction is endothermic.

21 a The temperature of the new process (550°C) is much lower than the temperature of 1800°C in the blast furnace.

b $2Fe(s) + O_2(g) \rightarrow 2FeO(s)$

$4Fe(s) + 3O_2(g) \rightarrow 2Fe_2O_3(s)$

c No. The reaction of iron with water is different to the reaction of iron with dry oxygen and proceeds at a different rate.

d Exothermic

e High surface area of iron pellets, high temperature caused by trapped heat that was unable to escape rapidly.

f Water would have caused the production of more hydrogen and increased the fire. The method used by the firefighters to extinguish the fire was to flood the hold with liquid nitrogen, which extinguished the surface fire but did not stop the deeper burning. A crane and clamshell bucket was then used to unload the iron into piles less than 1 m deep so the heat could escape.

22 a Higher body temperature increases the rate of reactions. Increased pulse and breathing rate increases the concentration of reactants.

b Lower body temperature decreases rate of metabolic reactions in the body.

23 To increase the rate of dissolution without ruining the toffee, you could:

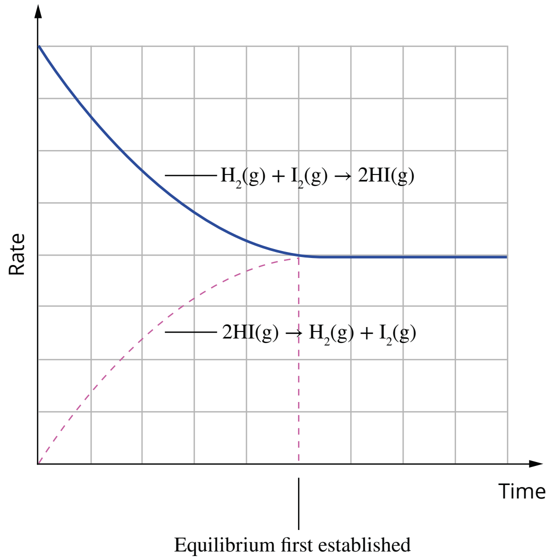
- grind up the sugar crystals or use caster sugar
- use a cup of hot water to dissolve the sugar
- gently heat the sugar and water mixture while the sugar was dissolving
- stir the sugar and water mixture while the sugar was dissolving.

Chapter 8 Extent of chemical reactions

8.1 Dynamic equilibrium

1 C

2



3 closed, decreases, less, backward, increases, equal

4 a 0.07 M **b** 0 M **c** 0.03 M **d** 0.08 M **e** 0.04 mol

f There is no change in concentration of NO_2 or N_2O_4. This is when the system is at equilibrium and both the forward and reverse reactions are occurring at the same rate.

g 6 s

h The intensity of the brown colour will increase as the concentration of NO_2 increases until equilibrium is reached. Once equilibrium is reached, the colour of the reaction mixture will remain constant.

8.2 The equilibrium law

WE 8.2.1 $\frac{M^2}{M^2 \times M} = \frac{1}{M} = L\text{ mol}^{-1}$

1 $Q_c = \frac{[HCl]^2}{[H_2][Cl_2]}$ **2** Right

3 a A system in which all the species are in the same state

b $Q_c = \frac{[\text{products}]^{\text{coefficient}}}{[\text{reactants}]^{\text{coefficient}}}$ and is equal to K_c at equilibrium

c The ratio of the equilibrium concentrations of the products over the equilibrium concentrations of the reactants raised to the power of their coefficients. It is given the symbol K_c and the value for the equilibrium constant changes with temperature.

4 $\frac{[[Cu(NH_3)_4]^{2+}]}{[Cu^{2+}][NH_3]^4}$

As $Q_c > K_c$, in order to reach equilibrium $[[Cu(NH_3)_4]^{2+}]$ must decrease and the concentration of the reactants increase. This will occur if the reaction moves backwards in the direction of producing more reactants.

8.3 Working with equilibrium constants

1 **a** $K_c = \frac{[NH_3]^2}{[N_2][H_2]^3}$ **b** 0.01 M^{-2}

c $K_c = \frac{[N_2]^{\frac{1}{2}}[H_2]^{\frac{3}{2}}}{[NH_3]}$ **d** 10 M

e **i** The value of the equilibrium constant is the reciprocal of the original constant.

ii The new equilibrium constant has a value equal to the square root of the original constant.

2 **a** 0.020 $M^{\frac{1}{2}}$ **b** 50 $M^{\frac{1}{2}}$

3 **a** 8.35 M^4 **b** 0.767 $M^{-\frac{1}{2}}$ **c** 1.30 $M^{\frac{1}{2}}$ **d** 0.346 M^{-2}

4 B

5 **a** Increased **b** Decreased **c** Increased **d** Decreased

8.4 Calculations involving equilibrium

WE 8.4.1 K_c = 0.694 M **WE 8.4.2** 0.17 M **WE 8.4.3** 0.0248 M

1 0.10 M

2 1.1×10^2 M^{-1}

3 0.127 M

4 0.033 M^{-1}

5 2.41×10^{-3} M^{-2}

6 **a** 0.011 M **b** 0.020

c The system is not at equilibrium. A net backwards reaction will occur. As the reaction moves towards equilibrium, the concentrations of H_2 and I_2 will decrease and the concentration of HI will increase until the value of the reaction quotient is equal to the equilibrium constant.

7 5.5 M^{-1}

8.5 Le Châtelier's principle

1 **a** Net forward reaction **b** Net back reaction

c Net forward reaction

2 **a** Net back reaction **b** Net forward reaction

3 For the reaction $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$ the equilibrium law is:

$$K_c = \frac{[SO_3]^2}{[SO_2]^2[O_2]}$$

When SO_3 is added to the system, it increases the concentration of the products. The concentration fraction, $Q_{c,}$ will increase. Because $Q_c > K_c$, the system will favour the back reaction in order to decrease the value of Q_c until equilibrium is re-established ($Q_c = K_c$).

For the reaction $CH_3COOH(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3COO^-(aq)$ the equilibrium law is:

$$K_c = \frac{[CH_3COO^-][H_3O]^+}{[CH_3COOH^-]^2[H_2O]}$$

When CH_3COO^- is removed from the system, it decreases the concentration of the products. The concentration fraction, Q_c, will decrease. As $Q_c < K_c$, the system will favour the forward reaction in order to increase the value of Q_c until equilibrium is re-established ($Q_c = K_c$).

4 C

5 incomplete, haemoglobin, oxygen, CO–haemoglobin, O_2–haemoglobin, oxygen, O_2, O_2–haemoglobin

8.6 Further applications of Le Châtelier's principle

WE 8.6.1 The system will shift to the left. This increases the amount of the reactants, including Cl_2.

1 B

2 **a** Net forward reaction **b** No effect

c Net forward reaction

3 **a** **i** Increase **ii** Increase **iii** Decrease

b **i** Cannot cause forward reaction

ii Increase

iii Cannot cause forward reaction

4 **a** Decrease **b** Higher

5 **a** Decrease the temperature **b** Decrease the volume

8.7 Optimising the yield of industrial processes

1 high, temperature, catalyst, reaction rate

2 High temperature and low pressure

3 58.1%

4 **a** Low temperatures, high pressures, excess of reactant

b Increased pressure, high temperatures and the use of a catalyst.

c The use of high pressure is expensive and can be dangerous so the reaction is run at 1 atm to reduce costs. The moderate temperature is used to ensure a reasonable rate of reaction without impacting too highly on the equilibrium yield. The decrease in reaction rate due to the lower temperature is offset by the addition of a catalyst. This compromise ensures the most efficient yield and rate for the plant.

5 Temperatures higher than 200°C are required to obtain an acceptably fast rate of reaction.

6 **a** The reaction is exothermic.

b As the reaction is an exothermic process, the gases are cooled before being pumped back into the reaction system to maximise equilibrium yield. Pumping hot gases into the reaction mixture would cause the temperature to rise and favour the back reaction, reducing the yield of ammonia.

Chapter 8 review

1 For a reaction to be homogeneous, the reactants and products must all be in the same state. For a reaction to be at equilibrium, the reaction must be reversible and have reached a state where the rate of the forward reaction is equal to the rate of the reverse reaction. There will be no observable change in concentration of the reactants or the products.

2 **a** Chemical equilibrium is 'dynamic' because both forward and reverse reactions occur at the same rate. An equilibrium develops between water vapour and water when wet clothes are in a sealed bag, with water evaporating as rapidly as water vapour condenses, so the clothes remain wet.

b When the bag is opened, water vapour escapes and the rate of evaporation exceeds the rate of condensation. The system is not in equilibrium and the clothes dry.

3 $K_c = \frac{[Fe^{2+}]^2[Sn^{4+}]}{[Fe^{3+}][Sn^{2+}]}$

4 **a** $CH_3OH(g) \rightleftharpoons 2H_2(g) + CO(g)$ **b** $S_2(g) + 2H_2(g) \rightleftharpoons 2H_2S(g)$

c $NO_2(g) \rightleftharpoons \frac{1}{2}N_2O_4(g)$

5 The reaction quotient is the ratio of the concentrations of the products to the concentration of the reactants, with the index of each concentration the same as the coefficient of the substance in the reaction equation. The value of the reaction quotient becomes equal to the equilibrium constant at equilibrium.

6 As Q_c for the reaction is larger than K_c, the reaction must move to decrease Q_c. This will happen with a decrease in the concentration of the products. There will be a net backwards reaction, decreasing the concentration of ethyl ethanoate as the mixture reaches equilibrium.

7 **a** less than **b** $\frac{[H_2O]^2[N_2]}{[H_2]^2[NO]^2}$ **c** moves to the right

8 **a** No; K_c is very small. **b** 10^{10}

c Yes; K_c is very large (provided the rate is sufficiently fast).

9 **a** $K_c = \frac{[Br_2][Cl_2]}{[BrCl]^2}$

b **i** $K_c = \sqrt{32} = 5.7$ ii $K_c = \frac{1}{32} = 0.031$

iii $K_c = 32^2 = 1.0 \times 10^3$ iv $K_c = \frac{1}{\sqrt{32}} = 0.18$

10 No, left **11** 0.53

12 3.6 (no units) **13** 0.019 M

14 **a** $K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]}$ **b** 0.400 M

c 0.80 M (2 significant figures) **d** 2.5 M^{-1}

15 0.0980 M

16 **a** [A] = 1.0 M, [B] = 0.25 M, [D] = 1.5 M

b 0.016 M **c** 0.032 mol

17 **a** Increase **b** Increase

18 **a** Net back reaction **b** Net forward reaction

c No effect

19 If Ca^{2+} ions were inefficiently absorbed from food, decreased concentrations of these ions could occur in body fluids. As a consequence, a net forward reaction would occur, raising the concentration of dissolved Ca^{2+} ions and resulting in decreased amounts of calcium phosphate in bones.

20 **a** **i** Net forward reaction **ii** No change

iii Net forward reaction

b **i** Increase **ii** No change

iii No change

c Likely to be large

21 **a** Exothermic reaction, so K_c will decrease as temperature increases, so a net back reaction occurs

b As volume increases the colour of the gas mixture will decrease. (A net back reaction will also occur, further lightening the colour.)

c Addition of a catalyst would have not changed the colour because the rate of the forward and back reactions are increased equally.

d Addition of oxygen will cause a net forward reaction to occur.

22 The patient is treated with excess oxygen. This is done to drive the equilibrium towards the formation of oxyhaemoglobin.

23 B

24 **a** **i** Decrease **ii** Decrease **iii** increase

iv No change **v** No change

b **i** Increase **ii** Increase **iii** Increase

iv Increase **v** No change

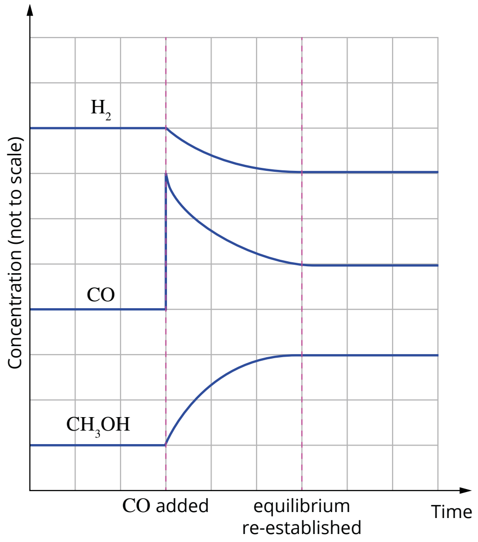
25 **a** **i** High temperature; high pressure

ii Low temperature; high pressure

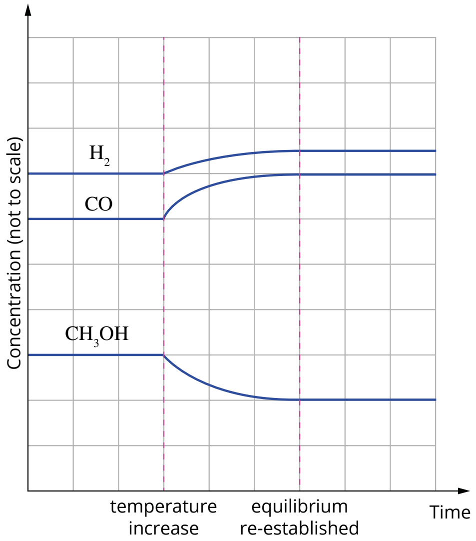
b Temperature

c Use a catalyst.

d **i**



ii



26 **a** **i** Increase **ii** Increase

b In practice, satisfactorily high equilibrium yields of sulfur trioxide can be obtained without needing to use high pressures, which would involve more expensive equipment.

c To increase the yield of sulfur trioxide and to minimise emissions of sulfur oxides, which act as pollutants.

d The rate of reaction and the magnitude of K_c.

27 **a** Left **b** Right

28 **a** **i** Increase **ii** Increase

iii Decrease **iv** Decrease

b Endothermic

29 **a** $2SO_3(g) + CO_2(g) \rightleftharpoons CS_2(g) + 4O_2(g)$

b $K_c = \frac{[CS_2][O_2]^4}{[SO_3][CO_2]}$

c **i** 0.112 mol **ii** 1.6×10^{-3} M^{-2}

d **i** Increase **ii** Increase **iii** No effect

iv Decrease **v** No effect

30 **a** $K_c = \frac{[SO_3]^2}{[SO_2]^2[O_2]}$

b 15–20 minutes; 25–30 minutes, 35–40 minutes

c 1.56 M^{-1}

d 10 minutes; before 10 minutes the concentrations were changing slowly but the catalyst caused equilibrium to be reached more rapidly.

e 3.50 M^{-1}

f Increased pressure by reducing volume. Also, because the value of K_c at 25–30 minutes is larger than at 15–20 minutes and this is an exothermic reaction, a decrease in temperature must have occurred.

Chapter 9 Production of chemicals by electrolysis

9.1 Electrolytic cells

WE 9.1.1 $Zn(s) + Cu^{2+}(aq)$

1 A **2** B

3 non-spontaneous, electrical energy, chemical energy, positive, negative, oxidation, reduction

4 **a** Nickel

b Carbon rod (positive): $2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$
Nickel rod (negative): $Ni^{2+}(aq) + 2e^- \rightarrow Ni(s)$

c $2H_2O(l) + 2Ni^{2+}(aq) \rightarrow O_2(g) + 4H^+(aq) + 2Ni(s)$

5 **a** $O_2(g) + 4H^+(aq) + 4e^- \rightleftharpoons 2H_2O(l)$ 1.23 V
$Pb^{2+}(aq) + 2e^- \rightleftharpoons Pb(s)$ –0.13 V
$Fe^{2+}(aq) + 2e^- \rightleftharpoons Fe(s)$ –0.44 V
$2H_2O(l) + 2e^- \rightleftharpoons H_2(g) + 2OH^-(aq)$ –0.83 V
$Mg^{2+}(aq) + 2e^- \rightleftharpoons Mg(s)$ –2.34 V

Although NO_3^- ions are attracted to the anode, they cannot be ionised because nitrogen is already in its highest oxidation state (+5).

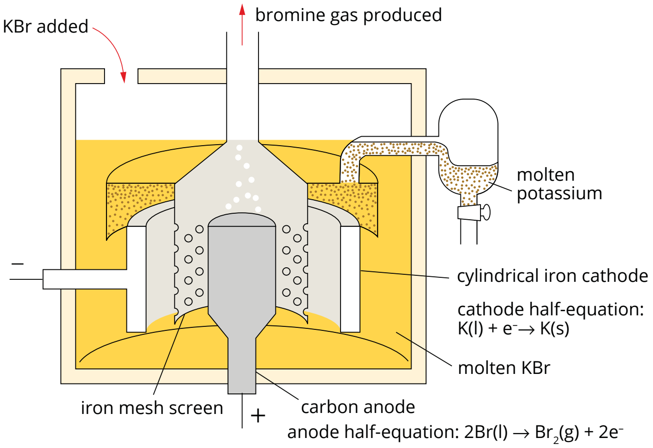
b Anode: $Pb(s) \rightarrow Pb^{2+}(aq) + 2e^-$. Pb(s) is oxidised instead of Fe(s), even though Fe(s) is the stronger reducing agent, because Fe(s) is at the cathode where there is a continuous supply of electrons.
Cathode: $2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$. As water is a stronger oxidising agent than Mg^{2+}, water will be reduced in preference to the Mg^{2+}.

c $Pb(s) + 2H_2O(l) \rightarrow Pb(OH)_2(s) + H_2(g)$

9.2 Commercial electrolytic cells

1 D

2



3 **a** An inert electrode would be suitable. A reactive electrode would be oxidised at the anode, releasing cations into the solution, thus contaminating the electrolyte. The only reactive electrode that would be suitable is a zinc electrode.

b Zinc ions are a stronger oxidising agent than water, so the zinc ions are preferentially reduced at the cathode. It is also cheaper than the molten electrolyte.

c Oxygen

4 **a** It is cheaper to obtain chlorine by electrolysis of concentrated sodium chloride solution than from molten sodium chloride because electrical energy is required in order to melt sodium chloride.

b Fluorine is the strongest oxidising agent known. Since a stronger oxidising agent than fluorine would be required to convert F^- ions into fluorine, the element cannot be made by direct reaction. However, it is generated at the anode during electrolysis of molten metal fluorides.

c Na^+ ions are stronger oxidising agents than Ca^{2+} ions, so sodium metal is formed at the cathode in preference to calcium.

9.3 Faraday's laws

WE 9.3.1 5.92 g
WE 9.3.2 0.764 h

1 **a** 1 F **b** 2 F **c** 2 F **d** 2 F
2 10.0 g **3** 3.36 h
4 **a** 0.12 A **5** +2

Chapter 9 review

1 **a** In galvanic cells the anode is negative and the cathode is positive; in electrolytic cells the anode is positive and the cathode is negative.

b In galvanic cells the direction of electron flow is determined by the cell reaction; in electrolytic cells the direction of electron flow is determined by the external power supply. Direction of electron flow is always from anode to cathode through the external circuit.

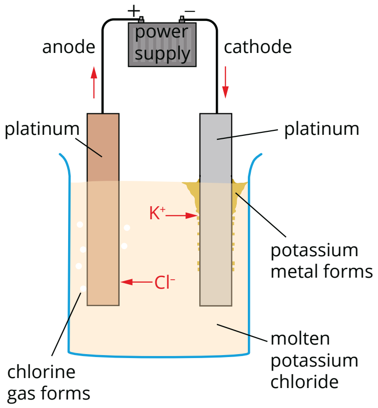
c In galvanic cells chemical energy is converted into electrical energy; in electrolytic cells electrical energy is converted into chemical energy.

d Galvanic cell reactions occur spontaneously; electrolytic cell reactions are non-spontaneous.

2 Anode: $2Cl^-(l) \rightarrow Cl_2(g) + 2e^-$
Cathode: $Zn^{2+}(l) + 2e^- \rightarrow Zn(l)$
Overall: $Zn^{2+}(l) + 2Cl^-(l) \rightarrow Zn(l) + Cl_2(g)$

3 In the cell with copper electrodes:
Anode: $Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$
Cathode: $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$
In the cell with the platinum electrodes:
Anode: $2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$
Cathode: $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$

4



5 The electrolyte solution contains water. As water is a stronger oxidising agent than Mg^{2+}, water will be reduced in preference to the Mg^{2+}. The reaction that did occur was:
$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$

6 **a** $O_2(g) + 4H^+(aq) + 4e^- \rightarrow H_2O(l)$ +1.23 V
$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$ 0.34 V
$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s)$ −0.76 V
$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$ −0.83 V
The SO_4^{2-} ions are not involved in the reaction.

b Anode: $Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$
Cathode: $Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$

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

7

Experiment	Cathode reaction	Anode reaction
a	$K^+(l) + e^- \rightarrow K(l)$	$2I^-(l) \rightarrow I_2(l) + 2e^-$
b	$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$	$2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$
c	$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$	$Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$
d	$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$	$2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$
e	$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$	$2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$

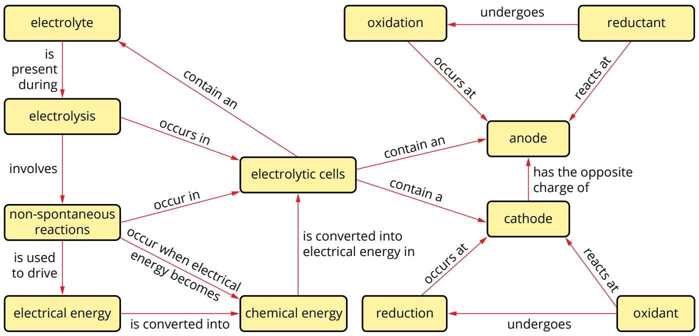
8 If an aqueous solution of sodium chloride was used instead of molten sodium chloride, water would be present. Water is a stronger oxidising agent and reducing reducing agent than $Na^+(aq)$ and $Cl^-(aq)$ respectively. This means water is preferentially oxidised and reduced instead of $Cl^-(aq)$ and $Na^+(aq)$ respectively. Therefore, neither sodium nor chlorine would be produced.
However, at higher sodium chloride concentrations, $Cl^-(aq)$ is reduced instead of water so chlorine is produced.

9 **a** Anode: $2Cl^-(aq) \rightarrow Cl_2(g) + 2e^-$
Cathode: $2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$

b The semipermeable membrane only allows Na^+ ions to move through from the anode compartment to the cathode compartment. This allows for a very pure sodium hydroxide product to be produced. The semipermeable membrane also prevents mixing between the reactive products.

10 The electrochemical series shows that the oxidising strength of H_2O is greater than that of Al^{3+}. If water is present in an electrolysis cell, it reacts preferentially at the cathode and electrolysis of aqueous aluminium salts does not yield aluminium metal.

11 **a** $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$ **b** 4.0 years
12 7.4 g
13 **a** 4+ **b** 4.00 F **c** 138 g
14 **a** Anode: $2H_2O(l) + 4H^+(aq) \rightarrow O_2(g) + 4e^-$
Cathode: $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$
b 0.800 M
15 **a** $Ag^+(aq) + e^- \rightarrow Ag(s)$ $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$
$Cr^{3+}(aq) + 3e^- \rightarrow Cr(s)$
b $m(Cu) = 2.94$ g $m(Cr) = 1.61$ g
16 **a** Cathode **b** Negative **c** 23.5 h
17 **a** 3.95 g **b** 1.00 M **c** $O_2(g)$ **d** 0.75 M
18 Magnesium
19 **a** 4500 C
b A: $2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$
B: $2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$
C: $Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$
D: $2H^+(aq) + 2e^- \rightarrow H_2(g)$
c 1.48 g **d** 0.522 L
e As the concentration of copper ions increases in the solution due to the anode reaction, the copper will be deposited on the cathode because Cu^{2+} is a stronger oxidant than H^+.
20 **a** 6.2×10^2 g **b** 3.0×10^5 L
21 **a** 19.9 h **b** 333 kg **c** 6.23×10^5 L
22 **a** 1.07×10^{10} C **b** 5.36×10^{10} J **c** $1790
23



24 The reaction in a galvanic cell is spontaneous and if the reactants in the cell were in the one container and in contact with each other, the reaction between them could occur directly, releasing energy as heat rather than as electricity.

In electrolysis cells, the reaction is non-spontaneous so that both the electrode reactions can occur within the same container. The products of the electrolysis reaction should not be allowed to come into contact with each other, however, or a reaction may occur.

25 **a** 0.300 mol **b** 1.2×10^5 C **c** 1.2 mol
d +4 **e** TiO_2

Area of study 2 How can the yield of a chemical product be optimised?

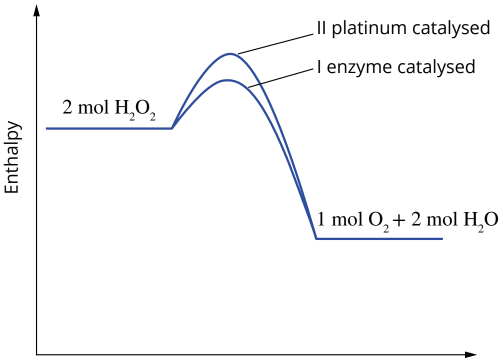
Multiple-choice questions

1	C	**2**	D	**3**	B	**4**	D	**5**	B	**6**	A
7	C	**8**	D	**9**	B	**10**	D	**11**	C	**12**	B
13	C	**14**	C	**15**	A	**16**	C	**17**	A	**18**	A
19	B	**20**	B								

Short-answer questions

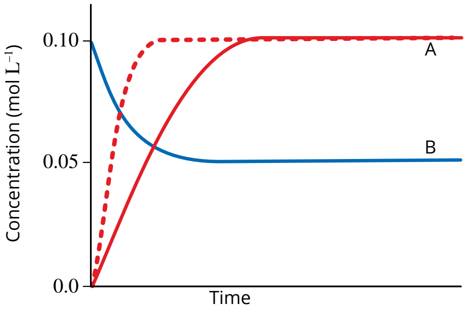
21 **a** Concentration of sodium thiosulfate is higher so there will be more frequent collisions between reactant particles and fruitful collisions and hence the rate of reaction.
b The higher temperature means the particles in the mixture will be moving faster and hence colliding more frequently. There will be a higher proportion of collisions that are fruitful, since there is a greater chance of a collision having energy greater than the activation energy.
c
- Changing reactant pressures for gases
- A catalyst
- Changing the available surface area for reactions involving solids or for non-homogenous mixtures

22 **a** To act as a catalyst and lower the activation energy, giving a higher reaction rate.
b



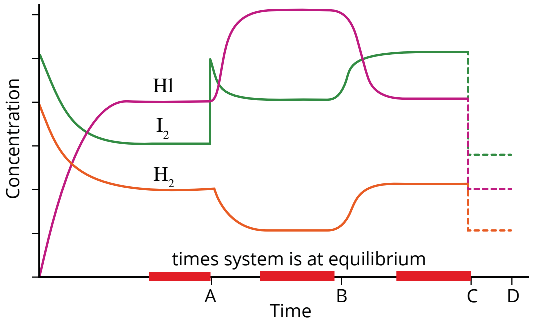
c System I. The lower activation energy requirement means that there is a greater probability of any given collision having sufficient energy to meet it, so fruitful collisions will occur more frequently.
23 **a** The rates are equal up until time *T*.
b The addition of reactant W increases the frequency of collisions between left-hand side particles so the rate of the forward reaction increases initially.

There will be a net forward reaction. This will consume the left-hand side particles so the forward reaction will slow down, and generate right-hand side particles so the reverse reaction speeds up. When the two rates become equal again, equilibrium has been re-established and no further change occurs.
c **i** Adding Y **ii** Adding a catalyst
iii Adding an inert gas
d The particles will be moving slower and hence colliding less frequently, and a lower proportion of collisions will meet the activation energy requirement and are fruitful. Hence, there will be a lower frequency of fruitful collisions and a lower rate. This is true for both forward and reverse reactions.
e Forward
f Exothermic. Lowering the temperature will always induce a shift in the exothermic direction.
24 **a** A is NO_2. B is N_2O_4. **b** $K = \frac{[NO_2]^2}{[N_2O_4]}$
c Final concentration will be unchanged but reached in less time.



d 0.20 M
25 **a** Decrease **b** Decrease **c** No change
d Decrease **e** Increase **f** Decrease
g Decrease **h** No change **i** No change
26 **a** Iodine (I_2) has been added, followed by a net forward reaction to re-establish equilibrium.
b The temperature has been increased, resulting in a net back reaction.
c Equilibrium exists when the concentrations are constant (see diagram).

d See diagram



27 **a** **I** $CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g)$

II $CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$

b **i** Catalyst **ii** Lower

iii Increase the reaction rate so products form faster. Favour the forward reaction and increase yield.

c **i** Exposure to CO will drive the first reaction to the right. This lowers the concentration of free haemoglobin, Hb_4, which drives the second reaction to the left, removing $Hb_4.O_2$.

ii High O_2 pressure will drive the second reaction to the right. This lowers the concentration of free haemoglobin, Hb_4, which drives the first reaction to the left, removing $Hb_4.CO$.

d $CH_3OH(g) + O_2(g) \rightarrow CO(g) + 2H_2O(g)$

28 **a** **i** Positive electrode (anode): $2I^-(aq) \rightarrow I_2(aq) + 2e^-$

Negative electrode (cathode):

$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$

ii Brown I_2 forming at the positive electrode; bubbles forming at the negative electrode and increasing pH of electrolyte if tested with indicator

b **i** Positive electrode (anode): $2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$

negative electrode (cathode): $Pb^{2+}(aq) + 2e^- \rightarrow Pb(s)$

ii Bubbles forming at the positive electrode and decreasing pH of electrolyte if tested with indicator; lead solid/crystals deposited at the negative electrode

c **i** Positive electrode (anode): $Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$

negative electrode (cathode):

$2H_2O(l) + 2e- \rightarrow H_2(g) + 2OH^-(aq)$

ii Copper positive electrode getting smaller, and appearance of blue colour (Cu^{2+}) in the electrolyte solution; bubbles forming at the negative electrode and increasing pH of electrolyte if tested with indicator

29 **a** **i** Anode: reductant strength is $H_2O > Cl^-$, so

$2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$

ii Cathode: oxidant strength is $Sn^{2+} > H_2O > Mg^{2+}$, so

$Sn^{2+}(aq) + 2e^- \rightarrow Sn(s)$

b $2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$.

c At high concentrations of Cl^- ions, chlorine gas is usually formed as it is able to effectively compete with water to react at the anode: $2Cl^-(aq) \rightarrow Cl_2(aq) + 2e^-$

30 **a** Spatula

b Positive electrode (anode): $2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$

Negative electrode (cathode): $Ni^{2+}(aq) + 2e^- \rightarrow Ni(s)$

c 0.68 g

31 **a** $Li^+(l) + e^- \rightarrow Li(l)$ **b** $2Cl^-(l) \rightarrow Cl_2(l) + 2e^-$

c Water (H_2O) is a stronger oxidant than Li^+ and would be preferentially reduced at the cathode, producing hydrogen gas rather than lithium metal.

d A mixed electrolyte will have a lower melting temperature, making the process safer and less expensive. Potassium chloride is appropriate because K^+ will not be reduced in preference to Li^+.

e It must not be allowed to come into contact with air because it will be spontaneously re-oxidised. And it must not be allowed to come in contact with water.

32 **a** A pair of electrodes (anode and cathode) and an electrolyte.

b In a galvanic cell, high-energy reactants undergo spontaneous reaction to generate electricity. The energy transformation is:

chemical energy → electrical energy.

Heat energy is also produced, reducing the efficiency of the cell.

In an electrolytic cell, electricity is used to drive non-spontaneous reactions to produce useful chemical products (often very reactive ones). The energy transformation is:

electrical energy → chemical energy.

Heat energy is also produced, reducing the efficiency of the cell.

c Electrons always flow from the site of oxidation (the anode) to the site of reduction (the cathode).

In a galvanic cell, the electrons flow spontaneously from the oxidation reaction at the anode, which is therefore designated negative.

In an electrolytic cell, the electrons are driven through the cell from the negative terminal of an external power source to its positive terminal. Thus, the electrode designated negative in the electrolytic cell receives electrons from the power source and is the site of reduction, making it the cathode.

d A galvanic cell employs a spontaneous redox reaction (favourable oxidant–reductant combination) to produce an electron flow. If the reactants come into direct contact, electrons flow directly between them and no current is produced.

In an electrolytic cell, there are no favourable oxidant–reductant combinations and instead non-spontaneous reactions occur by forcing a current through the cell, forming reactive products that would react spontaneously if allowed to come into contact.

33 **a** **i** For example, sodium (and other group 1 metals), magnesium, aluminium

ii For example, NaOH, H_2, Cl_2

b The following is an example of the answers for aluminium.

i $C(s) + 2O^{2-}(l) \rightarrow CO_2(g) + 4e^-$

ii $Al^{3+}(l) + 2e^- \rightarrow Al(l)$

iii For example, molten cryolite (Na_3AlF_6) is used as a solvent; graphite electrodes are used; anodes are consumed as cell operates; molten aluminium collects beneath the electrolyte

The following is an example of the answers for NaOH.

i $2Cl^-(aq) \rightarrow Cl_2(g) + 2e^-$

ii $2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$

iii For example, high NaCl(aq) concentration are used so $Cl^-(aq)$ oxidised at anode; semipermeable membrane prevents mixing of Cl^- and OH^- ions in electrolyte while still allowing Na^+ ions to migrate

c Water can act as an oxidant or a reductant. Electrolysis from an aqueous solution is only possible when the desired reaction involves a stronger oxidant or reductant than water, otherwise water will react preferentially. In that case, the desired reaction can only be achieved in the absence of water, either in an alternative solvent or in a molten electrolyte.

d A good electrical conductor, relatively inexpensive, relatively inert and has a high melting temperature.

e Metallic cathodes are always inert as the electrolytic process ensures only reduction can occur at their surface. However, the iron in a steel anode would likely be a better reductant than the target species so that the outcome would be the oxidation, and hence the consumption, of the electrode itself rather than the desired electrode reaction.

34 **a** Anode: $2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$

Cathode: $2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$

b Anode: $2Cl^-(aq) \rightarrow Cl_2(g) + 2e^-$

Cathode: $2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$

c Anode: $2Cl^-(l) \rightarrow Cl_2(g) + 2e^-$

Cathode: $Na^+(l) + e^- \rightarrow Na(l)$

35 **a** (+) electrode:

$2Ni(OH)_2(s) + 2OH^-(aq) \rightarrow 2H_2O(l) + 2NiOOH(s) + 2e^-$

(–) electrode: $Zn(OH)_2(s) + 2e^- \rightarrow 2OH^-(aq) + Zn(s)$

b External power source used to drive current through cell to force non-spontaneous reactions to occur. In a secondary cell, the non-spontaneous reactions are the reverse of the spontaneous reactions that occur during discharge.

c For recharging, the discharge products must remain in electrical contact with the electrodes. Any discharge products that migrate away from the electrode will not be available for reaction reversal during recharging, so less reactant will be available on the next discharge cycle.

d
- Discharge products are more soluble and mobile at higher temperatures, and hence more readily migrate away from the electrodes.
- At higher temperatures, side-reactions are more likely to occur, reducing the amount of active material.

e
- Some of the discharge products become coarse and resist current flow.
- Impurities may be present in electrodes or half-cell chemicals.
- Build-up of products may reduce contact between the electrolyte and the electrodes.
- Mechanical vibration can dislodge reactive materials from the electrodes over time.

Chapter 10 Structure and nomenclature of organic compounds

10.1 Diversity of carbon compounds

1 B

2 **a** A formula that represents the three-dimensional arrangement of atoms in a molecule.

b A formula that summarises the structural formula of a compound without showing the arrangement of atoms in space. The carbon atoms and the attached hydrogen atoms, as well as any functional groups, are listed on one line in the order in which they appear in the structural formula.

c An organic compound in which all the carbon atoms are joined by single bonds.

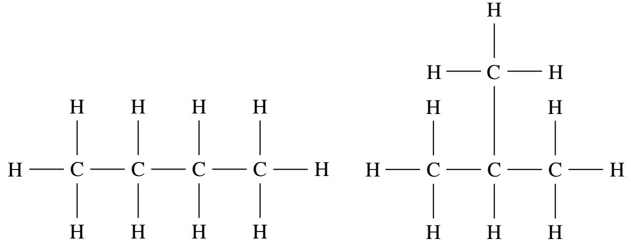
d An organic compound that contains one or more multiple bonds, such as carbon–carbon double or triple bonds.

e Isomers that arise from a functional group being in different locations on the carbon chain.

3 A and C

4 **a** Butane (C_4H_{10})

b



5 The carbon atoms in hydrocarbons have four bonds to other atoms. According to the valence shell electron repulsion theory, the angle around between each bond is 109.5° and the geometry around each carbon is tetrahedral. This means that carbon–carbon bonds are much less than 180° and so the chain is zig-zag shaped.

10.2 Stereoisomers

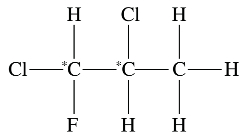
WE 10.2.1 The third carbon atom from the left

1 The screw does not have a plane of symmetry because of the spiralling thread. The thread in the mirror image is spiralling in the wrong direction to superimpose on the original. The screw is chiral. The nail has a vertical plane of symmetry and so it is superimposable on its mirror image. The nail is achiral.

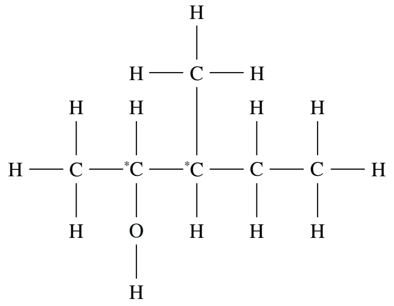
2 Carbon number 3

3 **a** 0

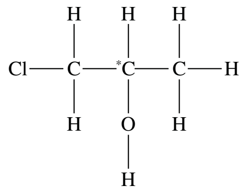
b 2



c 2



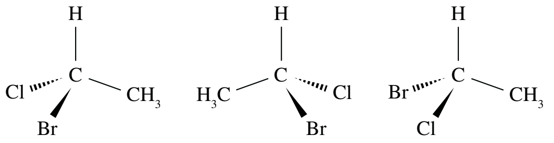
d 1



4 **a** Alkenes i, ii, iv and v **b** Alkenes i and iii

c Alkene ii does not have *cis–trans* isomerism because there must be two different groups attached to each of the carbon atoms in the double bond.

5



original

enantiomer as mirror image

rotated enantiomer

10.3 Hydrocarbons

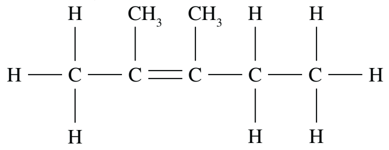
WE 10.3.1 3,6-Dimethyloctane

WE 10.3.2 *cis*-5-Methylhept-2-ene

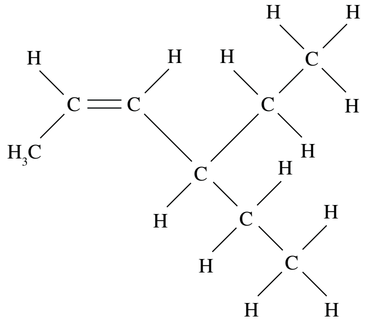
1 **a** 3,3-Dimethylhex-1-yne **b** Methylbut-2-ene

c *cis*-4-Ethylhex-2-ene

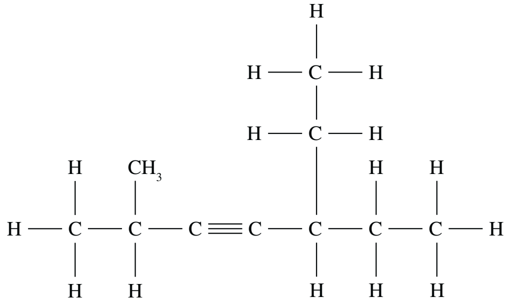
2 **a**



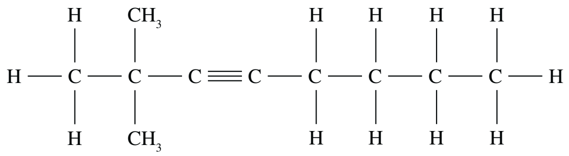
b



c

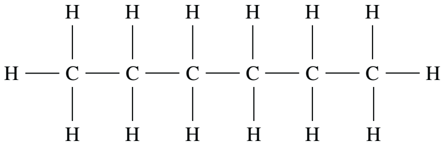


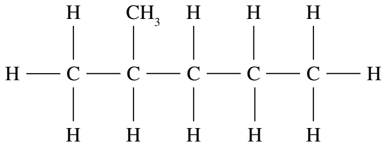
d

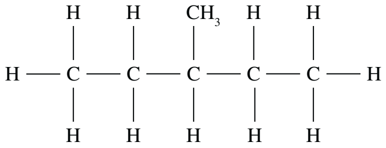


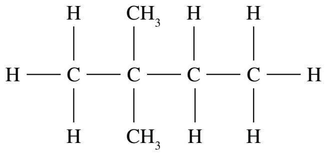
3 5-Ethyl-2-methylhept-3-yne and 2,2-dimethyloct-3-yne are structural isomers of the formula $C_{10}H_{18}$.

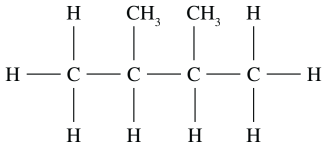
4 There are five possible isomers.







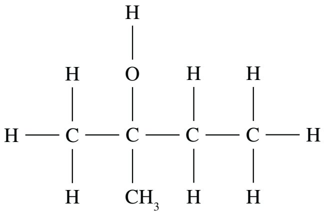




10.4 Functional groups—Part 1

1 2-Fluoro-3-bromopentane **2** $CH_3CFICHClCH_2CH_2CH_3$

3 2-Methylbutan-2-ol

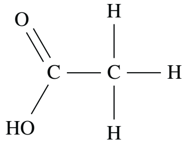


4 **a** 1-Bromopropane **b** 2-Chloro-4-methylpentane
c Pentan-1-ol **d** Octan-4-amine

5 Chloroethane has no isomers and so numbers are not needed. In propan-3-amine, the carbons should be numbered from the carbon atom closest to the amino functional group. Thus the amino group is located on the first carbon instead of the third carbon. Hence, the correct name is propan-1-amine.

10.5 Functional groups—Part 2

1 **a** Ketones **b** Aldehydes **c** Amides **d** Esters
2 **a** Methyl methanoate **b** Methanoic acid
c Propyl butanoate **d** Methyl ethanoate
e Ethyl hexanoate
3 Ethanoic acid

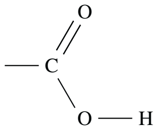


10.6 An overview of IUPAC nomenclature

WE 10.6.1 6-Chlorohexan-1-amine

1 **a** −C≡C−

b



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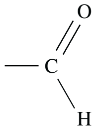

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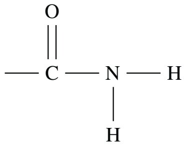
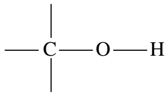


e



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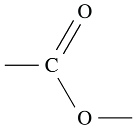
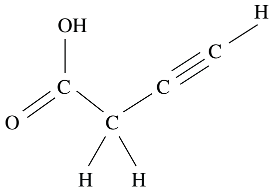


2 **a** 3-Hydroxybutanoic acid **b** 3-Methylpentan-2-amine
c 4-Chloro-3-ethylpenan-2-ol **d** 5-Fluoropent-2-yne

3 **a**



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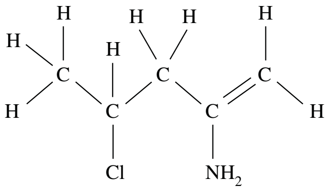

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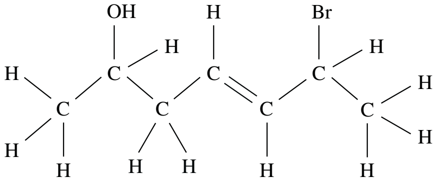

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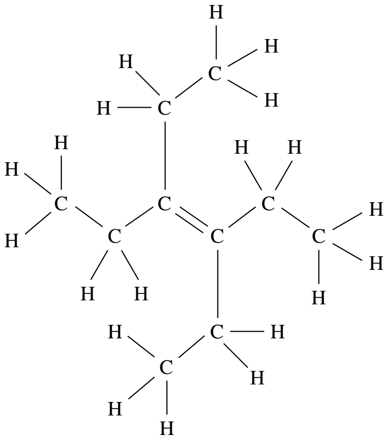


4 **a** **i** $CH_2{=}CHCH_2NH_2$ **ii** $CH_3CHClCH_2CH_2COOH$
iii $CH_2{=}CHCHOHCH_2CH_3$

b **i** Amino groups have priority over alkenes and so -amine should go at the end and have the lowest number. The correct name is prop-2-en-1-amine.

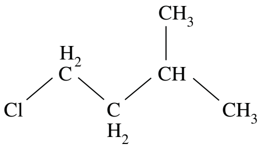
ii Carboxylic acid groups always go at the end of the chain and contain carbon 1. The correct name is 4-chloropentanoic acid.

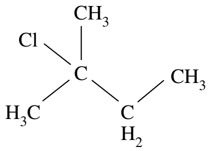
iii The ethyl chain is a part of the longest carbon chain. Hydroxyl groups have priority over alkenes and so –ol should go at the end. Numbering of the longest carbon chain should aim to minimise the number of the hydroxyl and alkene functional groups. Therefore the carbon-carbon double bond is at carbon number 1 and the hydroxyl group is at carbon number 3. The correct name is pent-1-en-3-ol.

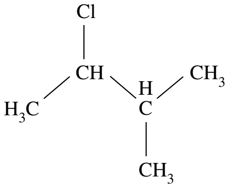
Chapter 10 review

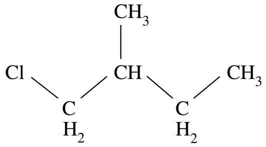
1 **a** 8

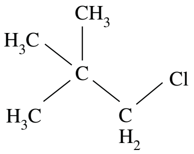
b

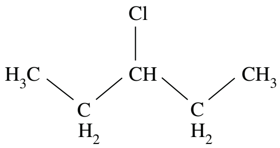

1-chloro-3-methylbutane

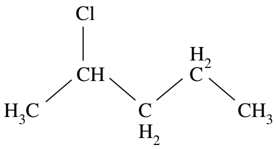

2-chloro-2-methylbutane

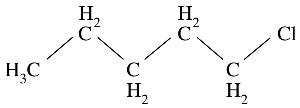

2-chloro-3-methylbutane


1-chloro-2-methylbutane


1-chloro-2,2-dimethylpropane


3-chloropentane

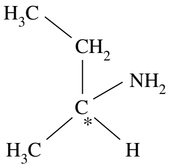

2-chloropentane


1-chloropentane

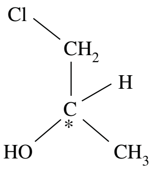
2 A positional isomer occurs when a functional group may be attached to more than one position in an organic molecule. A chain isomer occurs when the carbon chain of an organic molecule can be rearranged to form a new structure.

3 $CH_2{=}CHCH_2CH_3$ (but-1-ene) represents a straight chain positional isomer. The other straight chain positional isomer is $CH_3CH{=}CHCH_3$ (but-2-ene). A chain isomer of this structure is $(CH_3)_2C{=}CH_2$ (methylpropene) which has a different carbon backbone with a methyl branch at carbon 2.

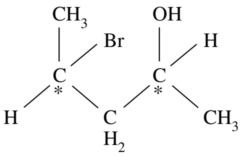
4 **a**



b



c



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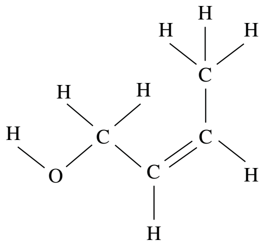


6 Positional and chain isomers. In addition, there may be *cis–trans* isomerism about the double bond.

7 **a** C_5H_{12} **b** C_6H_{12} **c** C_4H_6 **d** C_7H_{14}

8 3 (pentane, methylbutane, dimethylpropane)

9 If an ethyl group is on the second carbon, then the longest chain is 6 carbons long and the name would be 3-methylhexane.

10 **a** N and H **b** Cl **c** H and O

11 Propan-1-ol is a primary alcohol; the carbon to which the hydroxyl group is attached has only one alkyl group attached to it. Propan-2-ol is a secondary alcohol; the carbon to which the hydroxyl group is attached has two alkyl groups attached to it.

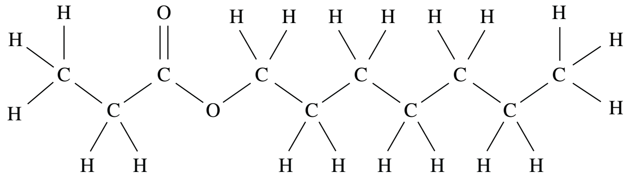
12 **a** 2-Aminopropan-1-ol **b** 8-Chlorooctan-2-ol
c 2-Iodoheptan-3-amine

13 Aldehydes contain a carbonyl group at the end of a carbon chain, ketones contain a carbonyl group within the chain, a carboxylic acid has a carbonyl group with a hydroxyl group attached to the carbon, an amide has a carbonyl group with an amino group attached to the carbon.

14 Carboxyl and amide carbons have three bonds within the functional group. They can only make one bond to connect to a carbon chain and so can never be within a chain.

15 **a** But-3-enoic acid **b** 4-Aminobutan-2-ol
c Butyl ethanoate **d** *trans*-2-Methylhex-3-ene
e 4-Fluorobut-1-yne **f** *cis*-1-Bromobut-2-ene

16 **a**



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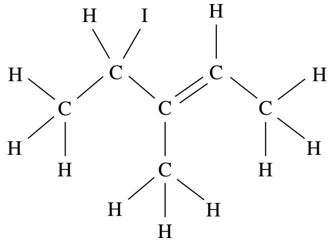

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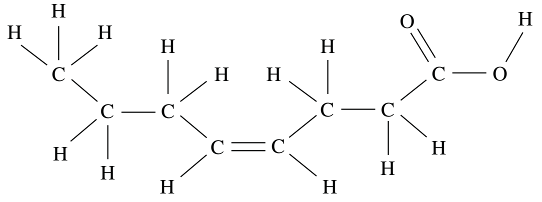

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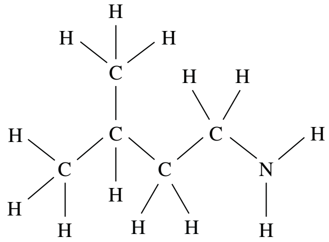


17 **a** $CH_3CH_2CH_2CH_2CH{=}CHCH_2COOH$
b $CH_3CH_2CH_2CH_2CH_2COOCH_3$
c $CH_2FCH_2CH_2OH$
d $CH_2OHCH_2CH_2COOH$
e $CH_3CH_2CH(CH_3)CH(CH_3)CH_2NH_2$

18 **a** $CH_3CH_2CH_2COCH_3$
b $CH_3CH(CH_3)CH_2CH_2OH$
c $CH_3CH_2CONH_2$
d $CH{\equiv}CCH_2CHClCH_3$
e $CH_3CH_2COOCH_2CH_3$

19 **a** The double bond cannot be in the '4' position as it must be between two carbon atoms. If the 4-carbon is involved in a double bond it should have priority in the name and so be called but-1-ene.

b Hydroxyl group has higher priority than amino group so the name should be 2-aminoethanol. No number is need for the hydroxyl as isomers are not possible with this group in this chain.

c The triple bond has higher priority than the chloro group so the name should be 3-chlorohex-1-yne.

d The longest chain in this arrangement is 5 carbons long, so the stem should be pent- and the branch should be methyl. The correct name is 2-chloro-3-methylpentane.

e The double bond has higher priority than the methyl groups so the name should be 4,4-dimethylpent-2-ene.

f The longest chain in this arrangement is 7 carbons long, so the stem should be hept- and there are no branches. The correct name is 4-bromoheptane.

20 **i** **a** Primary alcohol
b Chloroalkane
c Secondary alcohol
d Carboxylic acid
e Amine
f Alkane
g Alkene

ii **a** Heptan-1-ol
b 4-Chloroheptane
c Hexan-2-ol
d Pentanoic acid
e Butan-2-amine
f 2-Methyloctane
g 2-Methylpropene

21 Various answers possible.

Chapter 11 Properties and reactions of organic compounds

11.1 Boiling points and solubilities of organic compounds

1 alkane, dispersion forces, increase, insoluble, weaker, hydrogen bonding

2 $CH_3CH(CH_3)CH_3$, $CH_3CH_2CH_2CH_3$, $CH_3CH_2CH_2CH_2CH_2CH(CH_3)CH_3$, $CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_3$

Boiling point will increase with molecular size. The presence of branching within the molecule will produce a lower boiling point compared to a molecule of similar size with a straight chain structure.

3 $CHCH$, CH_3CHCH_2, $CH_3CH_2CH_2CH_3$, $CH_3CH_2CH_2CH_2Cl$, $CH_3CH_2CH_2CH_2OH$, $CH_3CH_2CH_2COOH$

4 **a** Miscible
b Miscible
c Immiscible
d Miscible

11.2 Viscosities and flashpoints of organic compounds

1 ii, iv, i, iii

2 Propan-1-ol, propan-1,2-diol, glycerol

3 A

4 A

5 **a** –39°C

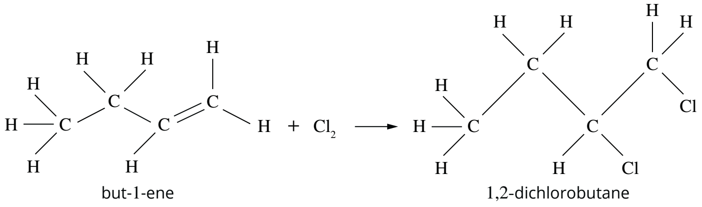
b Ethanal is an aldehyde, which contains a polar carbonyl group. The presence of the permanent dipole will result in dipole–dipole interactions between ethanal molecules. The greater intermolecular force will mean the flashpoint will be higher for ethanal than for the non-polar ethane. Both ethanol and ethanoic acid can form hydrogen bonds, which are stronger than the dipole–dipole interactions for ethanol. Therefore, the flashpoint of ethanal must be below 16.6°C.

11.3 Chemical properties of alkanes, haloalkanes and alkenes

1 $CH_4(g) + Cl_2(g) \rightarrow CH_3Cl(g) + HCl(g)$
$CH_3Cl(g) + Cl_2(g) \rightarrow CH_2Cl_2(g) + HCl(g)$
$CH_2Cl_2(g) + Cl_2(g) \rightarrow CHCl_3(g) + HCl(g)$
$CHCl_3(g) + Cl_2(g) \rightarrow CCl_4(g) + HCl(g)$

2 **a** Chloroethane
b 1,2-Dichloroethane
c Ethanol
d Ethane

3 **a**



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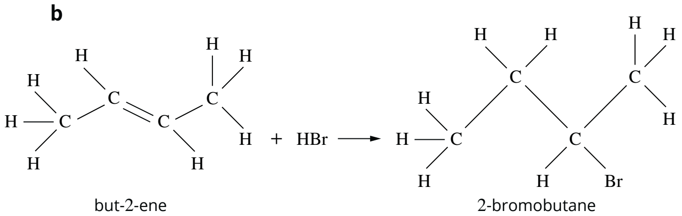


4 **a** Ethanamine
b Butan-2-ol
c Pentan-2-ol
d Butan-2,3-diol

5 **a** $CH_3Cl(g) \xrightarrow{OH^-} CH_3OH(aq)$
b $CH_3CH_2BrCH_3(l) \xrightarrow{NH_3} CH_3CH_2NH_2CH_3(l)$
c $CH_3CH_2CH_2Cl(l) \xrightarrow{OH^-} CH_3CH_2CH_2OH(l)$

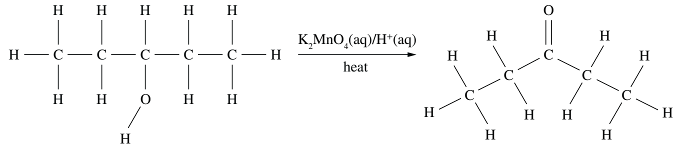
11.4 Reactions of alcohols, carboxylic acids and esters

1 **a** Tertiary **b** Secondary **c** Secondary

2 **a** $2C_5H_{12}O(g) + 15O_2(g) \rightarrow 10CO_2(g) + 12H_2O(g)$

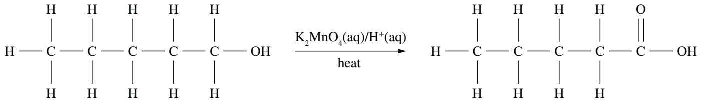
b Pentan-3-ol, secondary; 2-methylbutan-2-ol, tertiary; pentan-1-ol, primary.

c Pentan-3-ol will oxidise to pentan-3-one. The solution will change from deep purple to clear as the reaction proceeds.



2-Methylbutan-2-ol is a tertiary alcohol so will not react under the conditions described. No colour change will be observed; the solution will remain deep purple.

Pentan-1-ol will oxidise to the carboxylic acid. The solution will change from orange to green as the reaction proceeds.



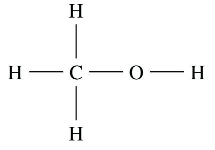
Reasoning: The aldehyde will be produced first but because there is no mention of how harsh the reaction conditions are it is assumed they oxidise completely to the carboxylic acid

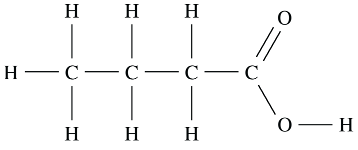
3 **a** Water must be present as a reagent and the reaction requires an alkali or dilute acid catalyst.

b **i** Methanol and butanoic acid
ii Propan-1-ol and ethanoic acid
iii Hexanol and propanoic acid

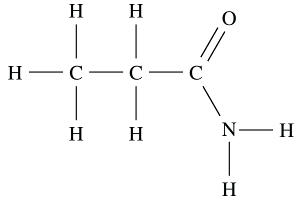
4 pentanamide, water, condensation

5 **a** Methanol and sodium butanoate; however, the addition of acid to the sodium butanoate will form butanoic acid

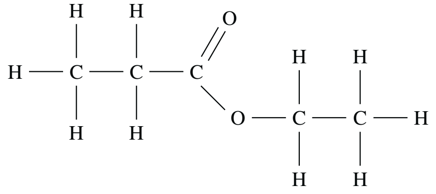

methanol


butanoic acid

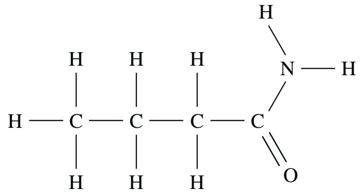
b


propanamide

c


ethyl propanoate

d


butanamide

11.5 Reaction pathways

1 **a** Ethene $\xrightarrow{H_2O}$ ethanol $\xrightarrow{NH_3}$ ethylamine

b Butane $\xrightarrow{Cl_2}$ 1-chlorobutane $\xrightarrow{OH^-}$ butan-1-ol

c 1-Chloropentane $\xrightarrow{OH^-}$ 1-pentanol $\xrightarrow{K_2Cr_2O_7/H^+}$ pentanoic acid

2 **a** Methane $\xrightarrow{Cl_2\text{, UV light}}$ chloromethane $\xrightarrow{OH^-}$ methanol $\xrightarrow{K_2Cr_2O_7/H^+}$ methanoic acid

b Ethene $\xrightarrow{H_2O}$ ethanol

c This synthesis can be carried out in three stages: (1) synthesis of propan-1-ol, (2) synthesis of methanoic acid and (3) synthesis of 1-propyl methanoate

1 Propane $\xrightarrow{Cl_2}$ 1-chloropropane $\xrightarrow{OH^-}$ propan-1-ol

2 Methane $\xrightarrow{Cl_2}$ chloromethane $\xrightarrow{OH^-}$ methanol $\xrightarrow{K_2Cr_2O_7/H^+}$ methanoic acid

3 Propan-1-ol + methanoic acid $\xrightarrow{H^+}$ 1-propyl methanoate + water

3 **a** Pentan-1-ol

b Sodium hydroxide

c Pentanoic acid

d Acidified potassium dichromate or potassium permanganate and heat

e Ammonia

4 This synthesis is carried out in three parts: (1) synthesis of 1-butanol, (2) synthesis of ethanoic acid and (3) synthesis of butyl ethanoate.

1 Butane $\xrightarrow{Cl_2}$ 1-chlorobutane $\xrightarrow{OH^-}$ butan-1-ol

2 Ethene $\xrightarrow{H_2O}$ ethanol $\xrightarrow{K_2Cr_2O_7/H^+}$ ethanoic acid

3 Ethanoic acid + butan-1-ol $\xrightarrow{H^+}$ butyl ethanoate + water

11.6 Yield and the chemical industry

WE 11.6.1 55.9% **WE 11.6.2** 43% **WE 11.6.3** 55.2%

1 82.4%

2 **a** 32% **b** 6.3%

3 247 g

4 Reaction 1: 32.3% Reaction 2: 100%

5 36.7%

6 2.61 kg

Chapter 11 review

1 Methylpropane and butane have the lowest boiling points because alkanes are non-polar, so dispersion forces are the only intermolecular forces. Dispersion forces are not as strong as other intermolecular forces so the boiling points of alkanes are low. Molecules of butane have a greater surface area and can fit more closely together than molecules of methylpropane, forming stronger intermolecular bonds. Dipole–dipole interactions exist between the polar regions of the molecules. Hydrogen bonds exist between the propan-1-ol molecules because of the electronegative nature of the oxygen atom. These bonds are stronger than the dispersion forces between methylpropane and butane molecules and dipole–dipole forces in methyl methanoate molecules.

2 Boiling points of compounds are determined by the strength of the intermolecular forces. Weak dispersion forces are present in all molecules, polar or non-polar, so must be kept as close to constant as possible when making comparisons on the effect of changing functional groups. Because dispersion forces increase with molecular size, it is important to select compounds of a similar molar mass.

3 **a** $CH_3CH(CH_3)CH(CH_3)CH_2CH_2OH$, $CH_3CH(CH_3)CH_2CH_2CH_2CH_2OH$, $CH_3(CH_2)_5CH_2OH$

b They would have greater solubility in hexane because hexane is a non-polar solvent. The presence of the single polar hydroxyl group would not be sufficient to overcome the non-polar characteristic of the large hydrocarbon chains.

4 **a** A measure of how well a liquid flows.

b The lowest temperature at which the fuel will ignite with an ignition source.

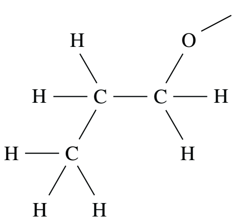
5 Octane

Intermolecular forces determine both the viscosity and flashpoint of organic compounds. This is because octane has the higher molar mass. Both octane and pentane are non-polar hydrocarbons so the only intermolecular forces between molecules are dispersion forces. As the size of the molecules increases so does the strength and number of dispersion forces between molecules.

6

Reactants	Type of reaction	Product
Alkene and hydrogen	Addition (hydrogenation)	Alkane
Alkene and hydrogen bromide	Addition	Bromoalkane
Alkene and water (with a catalyst)	Addition (hydrolysis)	Alcohol
Alkene and bromine	Addition	Dibromoalkane
Alkene in the presence of a catalyst	Addition polymerisation	Saturated hydrocarbon polymer

7 **a**



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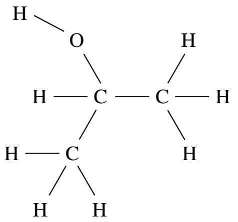
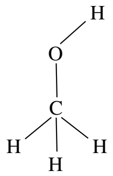


b



8 **a** $CH_3CH_2CH_2CH_3 \xrightarrow{Cl_2\text{, UV light}} CH_2CH_2Cl(l)$

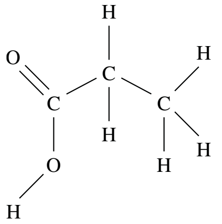
b $CH_3CH_2CH_2CH_2Cl(l) \xrightarrow{OH^-} CH_3CH_2CH_2CH_2OH(aq)$

c $C_2H_6(g) + O_2(g) \rightarrow CO_2(g) + H_2O(g)$

9 **a** Aldehyde, carboxylic acid **b** Ketone

c No reaction will occur.

10 **a**



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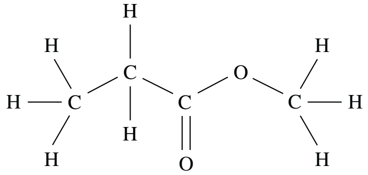

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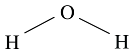


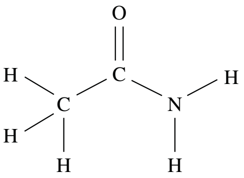
11 **a** $CH_3CH_2COOCH_3(l) + H_2O(l)$ **b** $CH_3COO(CH_2)_4CH_3(l) + H_2O(l)$

c $HCOOCH(CH_3)_2(l) + H_2O(l)$

12 **a** CH_3COOH **b** $CH_3CH_2CH_2OH$, CH_3COOH

c CH_3CH_2OH, $HCOOH$

13 **a**



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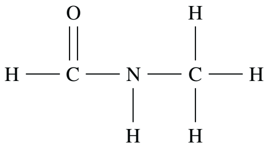
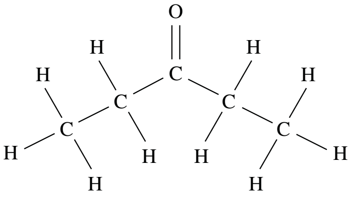
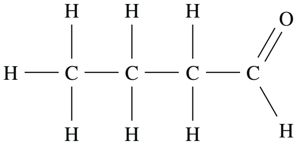


c

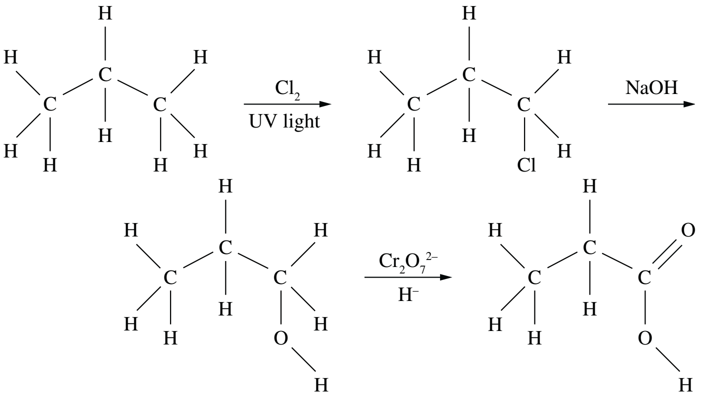


d

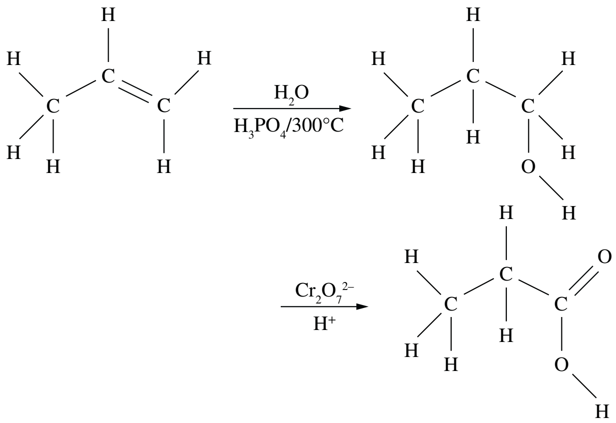


14 **a** Cl_2 and sunlight **b** Propan-2-ol **c** Propan-2-amine

15 **a**



b



16 **a** 1 Ethene $\xrightarrow{HCl}$ chloroethane $\xrightarrow{OH^-}$ ethanol

2 1-Chloropropane $\xrightarrow{OH^-}$ propan-1-ol $\xrightarrow{Cr_2O_7^{2-}/H^+}$ propanoic acid

Overall: ethanol + propanoic acid $\xrightarrow{H_2SO_4}$ ethyl propanoate

b Ethene $\xrightarrow{Cl_2}$ chloroethane $\xrightarrow{NaOH}$ ethanol $\xrightarrow{Cr_2O_7^{2-}/H^+}$ ethanoic acid $\xrightarrow{ROH/H_2SO_4}$ ethyl ethanoate

17 63.9%

18 **a** 3.26 g **b** 69.9%

19 **a** **i** $CH_3CH_3(g) \xrightarrow{Cl_2\text{, UV light}} CH_3CH_2Cl(g)$

ii $CH_2CH_2(g) \xrightarrow[H_3PO_4/300°\ C]{H_2O} CH_3CH_2OH(g)$

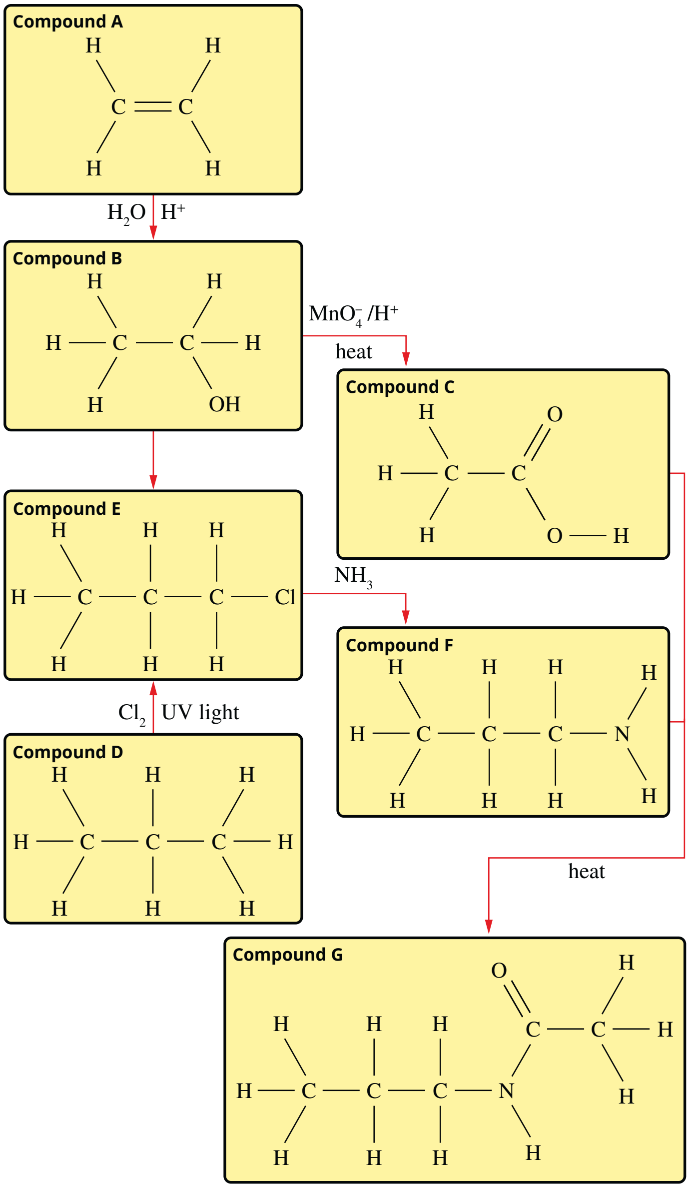
iii $CH_3CH_2Cl(g) \xrightarrow{OH^-} CH_3CH_2OH(aq)$

iv $CH_3CH_2OH(aq) \xrightarrow{K_2Cr_2O_7/H^+} CH_3COOH(aq)$

b **i** Substitution **ii** Addition

iii Substitution **iv** Oxidation

20 **a**



N-propylethanamide

b The bromine test for unsaturated hydrocarbons. When aqueous Br_2 is added to A, an addition reaction will occur and the solution will turn from orange to colourless. If $Br_2(aq)$ is added to D, no reaction will occur and the solution will remain orange.

c B. Although both compounds can form hydrogen bonds with water, the larger size (greater number of carbon atoms) of propanamine (F) will give it lower solubility.

Chapter 12 Analysis of organic compounds by spectroscopic techniques

12.1 Infrared spectroscopy

WE 12.1.1 C=O carbonyl group and C–H groups.

1 **a** Vibrational **b** Valence electron movement
c Valence electron movement

2 **a** Microwave **b** Infrared **c** Radio **d** Gamma rays

3 **a** O–H at 3200–3550 cm^{-1} and C–O at 1000–1300 cm^{-1}
b N–H at 3350–3500 cm^{-1} and C=O at 1670–1750 cm^{-1}
c N–H at 3350–3500 cm^{-1}
d O–H at 2500–3300 cm^{-1}, C=O at 1670–1750 cm^{-1} and C–O at 1000–1300 cm^{-1}
e C=O at 1670–1750 cm^{-1} and C–O at 1000–1300 cm^{-1}
f C=O at 1670–1750 cm^{-1}

4 The absorption bands from C–O and C–C bonds are located in the fingerprint region below 1400 cm^{-1}. Many molecules contain these bonds in various functional groups, and so they give few clues to the structure of a compound. The exact wavenumber of C–O and C–C absorption bands are highly specific to an individual molecule and can be used to compare the molecule to a reference standard for positive identification.

5 **a** O–H acids at approx. 3000 cm^{-1}, C=O at approx. 1700 cm^{-1}
b C–H at approx. 2800 cm^{-1}, C=O at approx. 1700 cm^{-1}
c O–H alcohols at approx. 3300 cm^{-1}, C–H at approx. 2800 cm^{-1}
d N–H at approx. 3400 cm^{-1}, C–H at approx. 2900 cm^{-1}

12.2 Nuclear magnetic resonance spectroscopy

WE 12.2.1 1,1,2-Trichloroethane

1 **a** The number of non-equivalent hydrogen environments.
b The type of hydrogen environment.
c The relative number of hydrogen atoms in each proton environment.
d The number of hydrogen atoms neighbouring a specific proton environment.

2 **a** **i** 2 **ii** 3 **iii** 4 **iv** 4
b **i** 2 **ii** 4 **iii** 4 **iv** 3
c A triplet (3-line pattern), a quartet (4-line pattern) and a singlet (1-line pattern).
d 3:2

3 The signal is likely to be caused by RCH=CHC**H**$_3$. This group has three hydrogen atoms, one neighbour and a typical chemical shift of 1.6–1.9 ppm.

4 **a** 3
b $-COCH_3$ 2.1–2.7 ppm
RCH_3 0.8–1.0 ppm
$-OCH_2R$ 3.3 ppm
c A:B:C = 2:3:3
d Proton NMR peaks are split because of interaction of the magnetic fields on adjacent atom. The number of peaks associated with each proton environment is shown in the figure in part b. Using the *n* + 1 rule:
- The quadruple peaks at A indicate that there are three hydrogens attached to an adjacent atom.
- The single peak at B indicates that there are no hydrogens attached to the adjacent atom.
- The triplet at B indicates that there are two hydrogens attached to the adjacent atom.

e A = CH_2 group
B = methyl group of ester
C = methyl group of CH_3CH_2
f 4

12.3 Mass spectrometry

WE 12.3.1 C_4H_{10}, butane

1 **a** 114 g mol^{-1} **b** 43
c $C_6H_{13}^+$ **d** Octane, C_8H_{18}

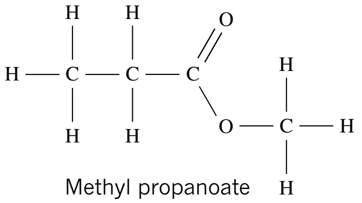
2 $C_2H_4{}^{79}Br_2{}^+$, $C_2H_4{}^{79}Br^{81}Br^+$, $C_2H_4{}^{81}Br_2{}^+$

3 **a** $CH_3CH_2CH_2Br$
b The peaks are due to the molecular ion containing Br but it might be the ^{79}Br or ^{81}Br isotopes.
c The two isotopes of bromine, ^{79}Br and ^{81}Br, are found in almost equal abundances so the peaks are almost equivalent in height.
d $CH_3CH_2CH_2{}^+$

4 **a** Butanone **b** Ethanamide

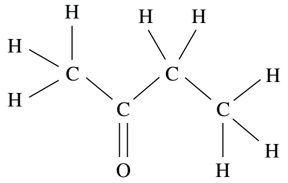
12.4 Determination of molecular structure by spectroscopy

WE 12.4.1



Methyl propanoate

1



2 Propanoic acid

Chapter 12 review

1 Lowest C–Br, C–O, C–H, O–H highest

2 **a** Both spectra contain broad, strong absorption bands at 3300 cm^{-1}, which corresponds to the expected absorbance by alcohol O–H bonds. The spectra do not contain peaks at 1700 cm^{-1} and so they cannot be acids.
  b The two spectra have different peaks in the fingerprint region and so cannot be of the same molecule.

3 **a** Broad absorption at 3200–3550 cm^{-1}
  b Absorption at 3500 cm^{-1} and 1670–1750 cm^{-1}
  c Absorption at 1670–1750 cm^{-1}
  d Absorption at 700–800 cm^{-1}

4 TMS is used as a reference in NMR spectroscopy. The location of a signal is compared to the TMS signal and called the chemical shift. The chemical shift is in units of ppm.

5 **a** Methyl ethanoate
  b Ethyl methanoate
  c Propanoic acid

6 Proton NMR spectra can give an indication of the number of different proton environments. The peak splitting indicates the environments of neighbouring protons. The peak areas provide information about the number of equivalent hydrogen atoms. For example, CH_2 splits signals from hydrogens to adjacent atoms into 3 peaks. Carbon NMR spectra give an indication of the number of different carbon environments. Two peaks indicate two different carbon environments. Chemical shift data can be used to indicate the type of carbon environment (e.g. C=O). For example, if C_3H_6O was propanone, all of the hydrogens would be found in a CH_3 bonded to a C=O environment; therefore, there would be only one peak in the proton NMR spectrum. The chemical shift data from the carbon NMR spectrum would show two peaks for the two carbon environments. One would correlate to a chemical shift indicating a CH_3 carbon environment and another to the C=O carbon environment.

7 **a**

Group	Shift (ppm)	Splitting	Peak area
$-CH_3$	0.9	triplet	6
$-CH_2-$	1.3	septet	2

b

Group	Shift (ppm)	Splitting	Peak area
$-CH_3$	0.9	triplet	3
$-CH_2-$	1.5	quartet	2

c

Group	Shift (ppm)	Splitting	Peak area
$-CH_3COO$	2.0	singlet	3
$-\mathbf{CH_2}OH$	3.3	quartet	2
$-CH_2O\mathbf{H}$	9	singlet	1

8 Molecular ion has *m/z* of 44, and is $C_3H_8^+$, base ion has *m/z* of 29, 15 less than the molecular ion and is $C_2H_5^+$

9 C_4H_6

10 **a** C_4H_{10} **b** C_3H_6O **c** $C_2H_6N_2$

11 **a** **i** 98 corresponds to the molecular ion made up of two ^{35}Cl isotopes.
  ii 100 corresponds to the molecular ion with one ^{35}Cl and one ^{37}Cl isotope.
  iii 102 corresponds to the molecular ion with two ^{37}Cl isotopes
  b The most abundant Cl isotope is ^{35}Cl therefore it has a higher peak.
  c $ClCCH_3^+$

12 Propanal

13 2,2-Dimethylpropane

14 The mass spectrum shows a molecular ion with *m/z* of 88, meaning that the molecular formula is twice the empirical formula: $C_4H_8O_2$. The IR spectrum shows strong absorption bands at 1700 and 3000 cm^{-1}, suggesting the presence of acid hydroxyl and carbonyl groups. The compound is likely to be a carboxylic acid. The proton spectrum shows three signals, and so three hydrogen environments. The sum of the relative peak areas is the same as the number of hydrogen atoms in the formula. The signal at 1.1 ppm is doublet with relative peak area of 6, and represents two equivalent $-CH_3$ groups with one hydrogen in a neighbouring environment. The signal at 2.6 ppm is a 7-line pattern with relative peak area of 1, and represents a –CH– neighbouring two methyl groups. The singlet at 11.8 ppm represents a single carboxylic acid proton. The carbon spectrum shows only three signals, giving three carbon environments. The carbon at 184 ppm is most likely a carboxyl carbon. The carbon signal at 19 ppm represents carbons in methyl groups. The carbon signal at 35 ppm represents a carbon with two or more alkyl groups attached. All the information gives a semistructural formula of $(CH_3)_2CHCOOH$ and name of 2-methylpropanoic acid.

15 NMR spectroscopy is used to identify types of atoms within the molecule and can give information about their chemical environment and connectivity. IR spectroscopy is usually used to identify general functional groups in a molecule but can also be used for positive identification by analysing the fingerprint region compared to a reference. Mass spectrometry gives information about the molecular mass and possible fragments within a molecule, which can lead to confirmation of a suspected structure.

16 **a** Proton NMR spectroscopy gives a large amount of information about organic molecules. It can be used to identify the number and types of hydrogen chemical environments, the relative amounts of hydrogen atoms in each environment and the connectivity of adjacent environments. It is fairly difficult to confirm which functional groups are present in a molecule by proton NMR spectroscopy alone.
  b IR spectroscopy is extremely useful for identifying functional groups. Many molecules have isolated or symmetrical hydrogen environments, which leads to simpler and less informative spectra. Carbon NMR spectroscopy can be used to identify sections of a molecule that contain no hydrogen environments. Mass spectrometry is useful to ensure that a proposed structure is correct. In many cases mass spectrometry is more powerful for the identification of molecules when the proton NMR spectroscopy is too complex to easily analyse.

17 The computer could look for specific ion peaks that would correspond to the molecular ions of illegal substances. It could then confirm the presence of these compounds by identifying the fragment ions of that compound.

Chapter 13 Analysis of organic compounds by chromatography

13.1 Principles of chromatography

WE 13.1.1 0.75

1 The component at the top has a greater rate of adsorption and desorption than components at the bottom.

2 $R_f = \dfrac{\text{distance the component travels from the origin}}{\text{distance the solvent front travels from the origin}}$

3 **a** **i** Solvent **ii** Water coated onto paper
b **i** Solvent **ii** Aluminium oxide or silica dioxide packed into column
c **i** Solvent **ii** Layer of fine powder such as aluminium oxide onto plate

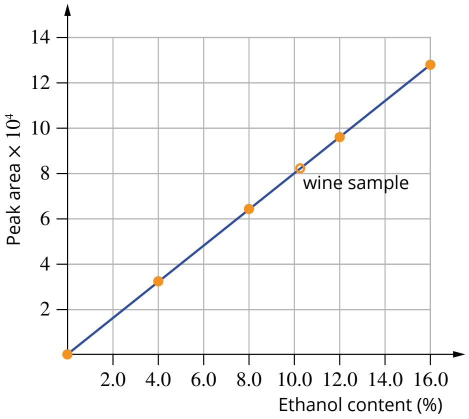
4 The sample would dissolve in the solvent rather than be carried along by the stationary phase.

13.2 High-performance liquid chromatography

WE 13.2.1 3.0 μg mL^{-1}

Extension question

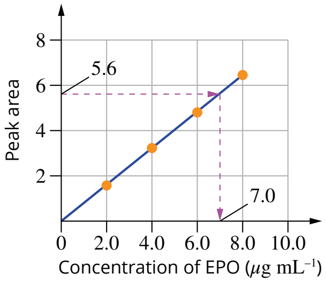
a



b 10.4%
c Techniques such as AA, GLC, HPLC, and UV spectroscopy do not directly measure concentration. Standards must be used. More than one standard should be used and the unknown sample should lie between these standards. This is because a zero standard may be contaminated with trace amounts of the chemical being tested. Calibration graphs are often non-linear and multiple standards increase the chance of detecting incorrectly prepared solutions.

1 C

2 **a**



b 7.0 μg mL^{-1}

3 An HPLC instrument does not directly produce measurements of concentration. R_t indicates the identity of components in a mixture. A calibration curve can then be used to determine the concentration of the component.

4 A, B, C, D

Chapter 13 review

1 **a** 2 **b** Purple **c** A and B only
d R_f(red spot) = 0.28; R_f(green spot) = 0.83

2 **a** A: 0.59; B: 0.49; C: 0.38; D: 0.20; E: 0.13
b A: leucine and/or isoleucine; B: β-phenylamine; C: proline and/or valine and/or tyrosine; D: threonine and/or hydroxyproline and/or serine and/or glycine; E: lysine and/or arginine and/or taurine
c A: leucine and/or isoleucine; B: β-phenylamine; C: proline; D: serine; E: arginine
d A two-way chromatogram produces better separation of components of complex mixtures, permitting easier isolation and identification.

3 **a** Stationary phase = powdered alumina (also accept powdered alumina on glass sheet). Mobile phase = water or ethanol.
b 7.5 cm
c The R_f values would not change. The movement of the component and solvent front both increase by the same proportion so there is no change in the R_f.
d Taurine and glycine

4 D

5 **a** Obtain chromatograms of blood sample and standard solutions of testosterone. Use R_t values to identify testosterone peak on chromatogram of blood. Measure testosterone peak areas. Construct a calibration curve and mark blood testosterone peak area on it. Determine testosterone concentration in blood sample.
b 48.0 ng L^{-1}

6 Serine, threonine, valine **7** 2.7%

8 HPLC is more sensitive, faster, resolves components better and it is able to detect colourless components readily.

9 **a** Retention time **b** Retention time **c** Peak area

10 Adsorption—the attraction of one substance to the surface of another.
Chromatography—a set of techniques used to separate and analyse the components in a mixture.
Desorption—the breaking of the bonds between a substance and the surface to which the substance is adsorbed.
Eluent—a liquid used as the mobile phase in chromatography.
Mobile phase—the phase that moves over the stationary phase in chromatography.
Stationary phase—a solid, or a solid that is coated in a viscous liquid, used in chromatography.
Retention time—the time taken for a component to pass through a chromatography column.

11 **a** Number of components and absorbance of components, from which concentration can be determined.
b 4
c Solid samples are dissolved in a suitable solvent. The liquid sample is injected into the top of an HPLC column. The stationary and mobile phases are chosen to achieve a good separation of the components in the sample. The sample components alternately adsorb onto the stationary phase and then desorb into the solvent as they are swept forward. The time taken to exit the column increases if the component strongly absorbs onto the stationary phase and has a low solubility in the mobile phase.

12 Paper chromatography identifies the components of a mixture whereas the thin-layer chromatography is more sensitive and is capable of greater resolution. A wider range of solvents can be used in thin-layer chromatography for further analysis.

Chapter 14 Analysis of organic compounds by volumetric analysis

14.1 Principles of volumetric analysis

1 B

2 **a** A standard solution is a solution of accurately known concentration. A primary standard is a substance that is readily obtained in a pure form, has a known formula and can be stored without deteriorating or reacting with the atmosphere. It should also be cheap and have a high molar mass.

b The equivalence point in a titration occurs when the reactants have been mixed in the mole ratio shown by the reaction equation. The end point occurs when the indicator changes colour.

c A burette is a piece of equipment capable of delivering different volumes of a liquid accurately (generally up to 50.00 mL). Pipettes usually deliver only a fixed volume of liquid (e.g. 20.00 mL).

d An aliquot is the volume of liquid delivered from a pipette. A titre is delivered by a burette and is the volume needed to reach the end point of a titration.

3 primary standard, volumetric flask, aliquot, pipette, indicator

4 **a** Methyl orange **b** Alizarin yellow
c Phenol red **d** Methyl red

5 Yellow

6 **a** The equivalence point occurs in the range pH 3–11. Both indicators will change colour over this pH range. Both indicators will provide a sharp end point, i.e. they will change colour at the equivalence point with the addition a small volume (1 drop) of acid.

b The equivalence point occurs in the pH range 3–7. Methyl orange provides a sharper end point over this pH range.

c The equivalence point occurs in the pH range 7–11. Phenolphthalein provides the sharper end point.

d Both indicators will provide a broad end point and neither would be suitable.

14.2 Acid–base titrations of organic compounds

WE 14.2.1 0.552 M **WE 14.2.2** 0.107 M

1 C

2 **a** $CH_3COOH(aq) + KOH(aq) \rightarrow CH_3COOK(aq) + H_2O(l)$
b 0.021 45 mol **c** 0.021 45 mol
d 0.858 M **e** 51.5 g L^{-1}

3 0.735 M

4 **a** 0.658 M
b 5.92%

14.3 Redox titrations of organic compounds

WE 14.3.1 0.201 M

1 $CH_3CHOHCH_3(aq) \rightarrow CH_3COCH_3(aq) + 2H^+(aq) + 2e^-$

2 2.38 g

3 0.0625 M

4 If the maximum concentration of vitamin C in fruit juice were 0.000 50 g mL^{-1}, titration of an aliquot of 50.00 mL of fruit juice with 0.0100 M iodine solution would give a maximum titre of 14.20 mL. The titration is a direct one using starch solution as the indicator. It involves the following steps.

1 Place the standard solution of iodine in a burette. Record the initial volume.
2 Place an aliquot of the juice in a conical flask.
3 Add 2 or 3 drops of indicator to the juice.
4 Titrate the juice with the iodine solution. Record the volume of solution used to reach the end point.
5 Repeat steps 1–4 to obtain three concordant titres (titres within 0.1 mL).

5 **a** 6.74 mol L^{-1} (3 significant figures) **b** 310 g L^{-1}

Chapter 14 review

1 **a** Primary standard: has a very high level of purity; has a known formula; is stable, e.g. will not react with atmospheric gases (e.g. carbon dioxide, water vapour); has a high molar mass to minimise errors in weighing; is readily available; is relatively inexpensive.

b Accurately weigh an empty weighing bottle, add the primary standard and reweigh. Transfer the weighed sample to a volumetric flask using a dry glass funnel. Rinse out the weighing bottle and glass funnel using a wash bottle. Half fill the volumetric flask with water and shake to dissolve the sample. When the sample has dissolved, add water to the calibration mark and shake the flask again. Determine the concentration of the primary standard.

2 **a** 24.22, 24.20 and 24.16 mL **b** 24.19 mL

3 The volumetric flask should be rinsed with deionised water, the pipette with hydrochloric acid, the burette with ethanamine ($CH_3CH_2NH_2$) solution and the conical flask with deionised water.

4 **a** Rinsing with water would dilute the standard solution.
b A smaller titre of the unknown solution would be required to react with the standard solution. This would then result in the concentration of the unknown solution being determined to be higher than it actually is.

5 Sodium hydroxide reacts with carbon dioxide and absorbs water from the atmosphere.

6 **a** 0.000 7884 mol **b** 0.001 577 mol **c** 0.0789 M

7 **a** Neither acidic nor basic **b** Acidic
c Basic **d** Acidic

8 **a** $CH_3COOH(aq) + NaOH(aq) \rightarrow CH_3COON_4(aq) + H_2O(l)$
b 0.020 24 mol **c** 0.020 24 mol **d** 1.012 M

9 $3CH_3CH_2CH_2CH_2OH(aq) + 2Cr_2O_7^{2-}(aq) + 16H^+(aq) \rightarrow 3CH_3CH_2CH_2COOH(aq) + 4Cr^{3+}(aq) + 11H_2O(l)$

10 **a** 0.250 g (3 significant figures)
b 19.1% (3 significant figures)
c Fillers, binders, sweeteners, flavours and colouring

11 **a** 0.000 460 mol (3 significant figures)
b 0.000 690 mol
c 0.008 62 mol (3 significant figures)
d 0.396 g (3 significant figures)
e 3.60% (3 significant figures) No; this product would not conform with the regulations for low-alcohol beer.

12 **a** 0.009 41 mol (3 significant figures)
b 0.009 41 mol (3 significant figures)
c 3.5% (2 significant figures)

13 **a** $Fe^{2+}(aq) \rightarrow Fe^{3+}(aq) + e^-$
b $MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l)$
c $5Fe^{2+}(aq) + MnO_4^-(aq) + 8H^+(aq) \rightarrow 5Fe^{3+}(aq) + Mn^{2+}(aq) + 4H_2O(l)$
d 0.001 30 mol
e 0.0162 mol (3 significant figures)
f 0.246 g (3 significant figures)
g Low results, due to loss of vitamin paste during transfer, or aliquots being less than the correct volume.

14 **a** $5Fe^{2+}(aq) + MnO_4^-(aq) + 8H^+(aq) \rightarrow 5Fe^{3+}(aq) + Mn^{2+}(aq) + 4H_2O(l)$
b 0.003 03 mol (3 significant figures)
c 84.7% (3 significant figures)
d The end point is readily recognised by the first permanent tinge of pink caused by excess permanganate ions.
e Wear safety glasses and a laboratory coat; hold pipette close to the top when fitting the pipette filler.

15 **a** $\frac{5}{4}$ **b** 59.98 g mol^{-1} **c** Propan-1-ol

16 **a** $MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l)$ multiply by 2
$C_2O_4^{2-}(aq) \rightarrow 2CO_2(g) + 2e^-$ multiply by 5,
then add the equations
$2MnO_4^-(aq) + 16H^+(aq) + 10e^- + 5C_2O_4^{2-}(aq) \rightarrow 2Mn^{2+}(aq) + 8H_2O(l) + 10CO_2(g) + 10e^-$
Simplify:
$2MnO_4^-(aq) + 16H^+(aq) + 5C_2O_4^{2-}(aq) \rightarrow 2Mn^{2+}(aq) + 8H_2O(l) + 10CO_2(g)$
b 0.0180 M

Area of study 1 How can the diversity of carbon compounds be explained and categorised?

Multiple-choice questions

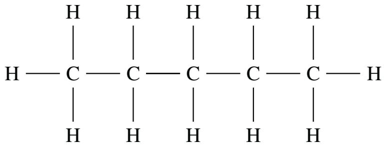
1	D	**2**	D	**3**	A	**4**	C	**5**	B	**6**	D
7	C	**8**	A	**9**	C	**10**	C	**11**	D	**12**	C
13	D	**14**	C	**15**	C	**16**	A	**17**	A	**18**	C
19	B	**20**	A								

Short-answer questions

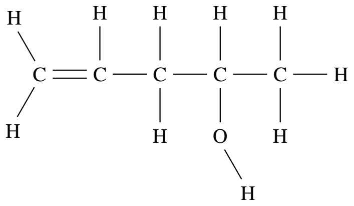
21 a i C_7H_{16} **ii** e.g. $CH_3CH_2CH_2CH(CH_3)CH_2CH_3$
b i $C_4H_{10}O$ **ii** e.g. $CH_3CH_2CHOHCH_3$
c i $C_3H_6O_2$ **ii** e.g. CH_3CH_2COOH
d i $C_5H_{11}OCl$ **ii** e.g. $CH_2Cl(CH_2)_4OH$
e i C_8H_{16} **ii** e.g. $CH_3CH_2CHCHCH_2CH(CH_3)_2$
f i $C_6H_{12}O$ **ii** e.g. $CH_3CH_2CH(CH_3)CH_2CHO$
g i C_8H_{12} **ii** e.g. $CH_3CCCH_2CH_2CHCHCH_3$
h i $C_6H_{12}O$ **ii** e.g. $CH_3CHCHC(OH)(CH_3)CH_3$
i i $C_4H_7NO_2$ **ii** e.g. $CH_3COCH_2CONH_2$

22 a Heptan-3-ol, 1 chiral centre
b 3-Fluorobutanoic acid, 1 chiral centre
c *trans*-Pent-2-ene, no chiral centres
d 4-Ethylhexan-3-amine, 1 chiral centre
e 1-Aminopropan-2-ol, 1 chiral centre
f 5-Chlorohexan-3-ol, 2 chiral centres
g 6-Hydroxyoctanoic acid, 1 chiral centre
h 2-Bromo-3-methylpentane, 2 chiral centres
i Methyl butanoate, no chiral centres

23 a



b



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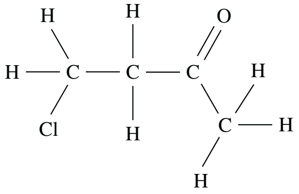

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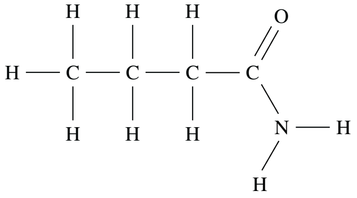

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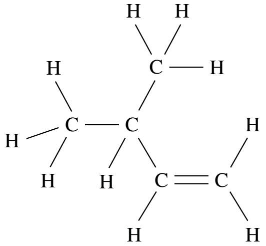

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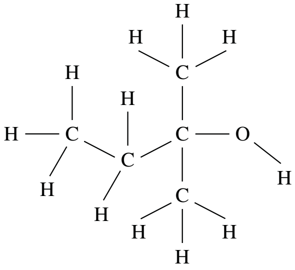

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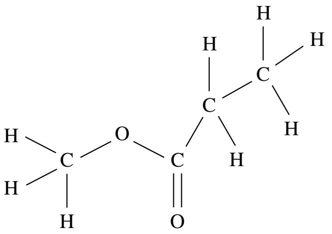

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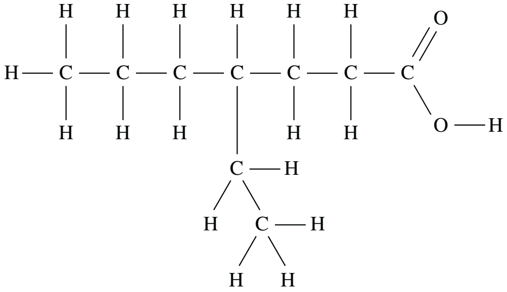
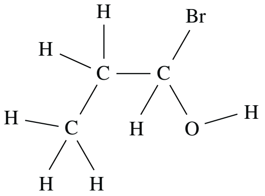


i



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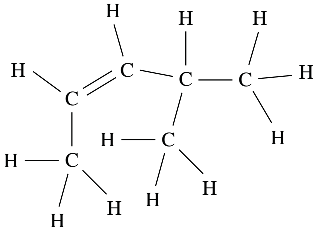

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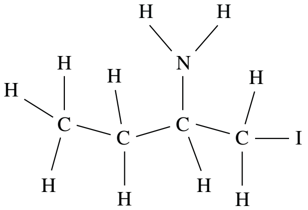
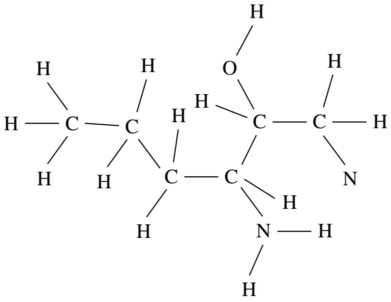
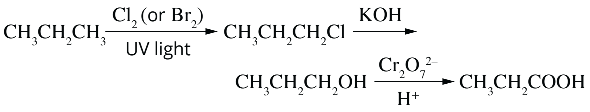


l

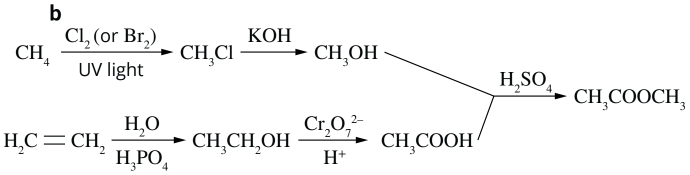


24 a Acidified dichromate ($Cr_2O_7^{2-}/H^+$) or acidified permanganate (MnO_4^-/H^+)
b Warm with hydroxide (eg KOH, NaOH), or H_2O/catalyst
c H_2O and acid catalyst (eg H_3PO_4)
d Acidified dichromate ($Cr_2O_7^{2-}/H^+$) or acidified permanganate (MnO_4^-/H^+)
e H_2 and Ni catalyst (other metals sometimes used)
f NH_3

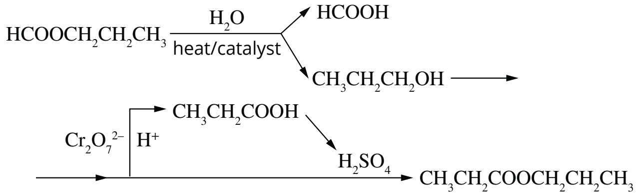
25 **a**



b



c



26 **a** $CH_3CH_2COOH + NaHCO_3 \rightarrow CH_3CH_2COONa + CO_2 + H_2O$

b $CH_3CH_2CH_2OH + H_2O \rightarrow CH_3CH_2COOH + 4H^+ + 4e^-$

c $CH_3CH_2COOH + CH_3CH_2OH \rightarrow CH_3CH_2COOCH_2CH_3 + H_2O$

d $CH_3CH_2COOH + CH_3CH_2NH_2 \rightarrow CH_3CH_2COO^- + CH_3CH_2NH_3^+$

e $2CH_3CH_2COOH + 7O_2 \rightarrow 6CO_2 + 6H_2O$

27 **a** Resistance to flow.

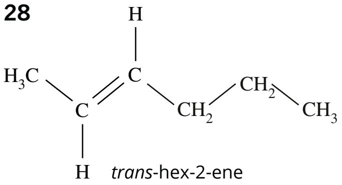
b **i** Viscosity increases from methanol to ethanol to propan-1-ol because larger molecules have stronger dispersion forces between them, tending to restrict movement.

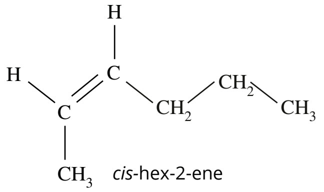
ii Water solubility decreases from butan-1-ol to hexan-1-ol because additional $-CH_2-$ groups reduce the polarity of the molecules, increasing the effect of the hydrophobic part that cannot form hydrogen bonds to water molecules.

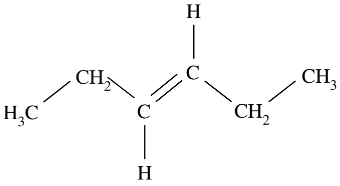
iii Ethane-1,2-diol has one more hydroxyl group than ethanol. The additional hydrogen bonding that this allows accounts for the higher viscosity and boiling point of ethane-1,2-diol.

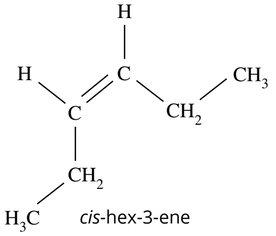
iv Benzene has a comparable molecular mass to butan-1-ol but is non-polar and can only form relatively weak intermolecular dispersion forces. Weak bonding between benzene molecules results in low viscosity, and the inability to form strong bonds to water molecules results in relatively low water solubility.

28


trans-hex-2-ene


cis-hex-2-ene


trans-hex-3-ene


cis-hex-3-ene

29 **a** Radiowaves (radio frequencies)

b Nuclear magnetic dipoles switching between low and high energy states corresponding to alignment with the external magnetic field.

c An internal standard for determination of chemical shifts.

d **i** B. High chemical shift characteristic of aldehyde and quartet results from three adjacent H atoms.

ii D. Singlet suggests no neighbouring H atoms. Chemical shift consistent with adjacent C=O group.

iii E. Quartet shows three neighbouring H atoms. Moderately high chemical shift consistent with adjacent O atom.

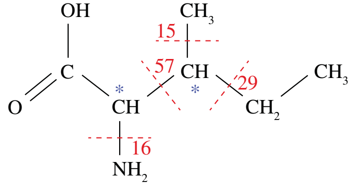
iv C. Singlet because all H atoms are equivalent so no splitting is observed. Chemical shift consistent with adjacent halogen (Cl) atom.

v F. Triplet shows two neighbouring H atoms and low chemical shift is consistent with no adjacent heteroatoms.

vi A. Doublet shows one neighbouring H atom and chemical shift is consistent with an adjacent C=O group.

30 **a** $C_6H_{13}NO_2$ **b** 131

c



d **i** CH_3^+ **ii** $C_2H_5^+$ **iii** $C_4H_9^+$

e **i** The strongest signal in the mass spectrum.

ii CO_2H

31 **a** 52.2% **b** 5.60 kg

c Sodium hydroxide and sodium ethanoate

d 42.4%; slightly lower

e Addition reactions of alkenes

32 **a** Spectrum A: ~3000 cm^{-1} is C–H, ~1700 cm^{-1} is C=O
Spectrum B: ~3000 cm^{-1} is C–H, ~3400 cm^{-1} is O–H

b Spectrum A is propanone; spectrum B is propan-2-ol.

c Because of the symmetry of the molecule.

d because of the symmetry of the molecule the two terminal carbon atoms are in identical environments.

e ^1H NMR: three peaks for three different H environments ($-C\underline{H}_3$, $-C\underline{H}(OH)-$and $-CH(O\underline{H})-$)
^{13}C NMR: two peaks for two different C environments ($-CH_3$, $-CH(OH)-$)

f **i** 58

ii Molecular mass, hence molecular formula.

iii $[CH_3CO]^+$

33 **a** Taurine, glycine

b Viewing under UV light or applying a stain

c 0.12

d Taurine

34 **a** Sorbic acid adsorbs most strongly. Its longer retention time indicates that it spends a relatively long time adsorbed onto the stationary phase.

b Benzoic acid

c 4.74 mg/100 mL

d 31.6 mg/100 g

35 96.6%

Chapter 15 Structure and bonding in food molecules

15.1 Amino acids

1 A

2 **a** Asparagine **b** Tyrosine
c Aspartic acid **d** Methionine

3 The human body only manufactures some of the required amino acids. The other amino acids, called essential amino acids, are provided in our food. Animal protein provides all these essential amino acids. Vegetable protein is often deficient in one or more essential amino acids.

4 Nine out the 20 amino acids required by the body cannot be manufactured in the body. They must be provided by the food we eat. These are called essential amino acids.

5

Structure of R group	Is the R group polar or non-polar?	Is the R group acidic, basic or neutral?
$-CH(CH_3)_2$	Non-polar	Neutral
$-CH_2COOH$	Polar	Acidic
$-CH_2C_6H_5$	Non-polar	Neutral
$-(CH_2)_4NH_2$	Polar	basic

15.2 The formation of proteins

1

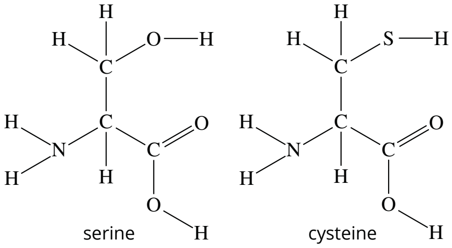
Tripeptide	Three amino acids joined by peptide links in a polypeptide chain
R group	Variable part of an amino acid.
Polypeptide	Several amino acids that are joined by peptide links
Amino group	Functional group present in all amino acids
Water	By-product of the reaction that produces polypeptides

2 **a** A, amino group; B, peptide or amide link or bond or group; C, R group; D, carboxyl group

b Alanine, serine, leucine

3 C

4 **a**



serine cysteine

b $H_2NCH(CH_2OH)COOH + H_2NCH(CH_2SH)COOH \rightarrow H_2NCH(CH_2OH)CONHCH(CH_2SH)COOH + H_2O$

c $H_2NCH(CH_2SH)CONHCH(CH_2OH)COOH$

d Condensation

15.3 Primary and secondary structures of proteins

1 **a** α-helix

b α-helices result from hydrogen bonding in different regions of the amino acid sequence. In this case, the hydrogen bonds arise due to attraction between the partial positive charge on the H of a –N–H bond in a peptide link with the partial negative charge on the O of a –C=O bond of a peptide link four amino acid units along the chain.

2 The sequence of amino acids gives proteins their unique shape based on interactions of functional groups in different regions of the sequence. As protein shape is related to function, determining this sequence allows scientists to understand more about the role of specific proteins.

3 9, peptide/amide, condensation polymerisation, alanine, lysine, glycine, valine, methionine

4 α-helices result from interaction between the hydrogen on the amino group and the oxygen of the carbonyl group of a peptide link specifically four amino acids along in the chain causing a hydrogen bond to form. This results in this section of the protein coiling into an α-helix. β-pleated sheets are also formed from hydrogen bonds between peptide links in regions where two or more parts of the polypeptide chain line up parallel to each other. The resulting structure is similar to a pleat.

15.4 Tertiary and quaternary structures of proteins

1 B, C, D

2

Bond type	Required components in R group	Amino acid examples
Hydrogen bonds	Contains –O–H, –N–H and –C=O	Serine, threonine, histidine
Dipole–dipole interactions	Any polar group such as those containing –S–H, –O–H or –N–H	Cysteine, asparagine
Ionic interactions	Contains $–NH_3^+$ and another group that contains $–COO^-$	Aspartic acid, glutamic acid, lysine, arginine
Covalent cross-links	Cysteine side groups react to form a disulfide bridge (–S–S–)	Cysteine
Dispersion forces	Any non-polar group	Alanine, leucine, phenylalanine

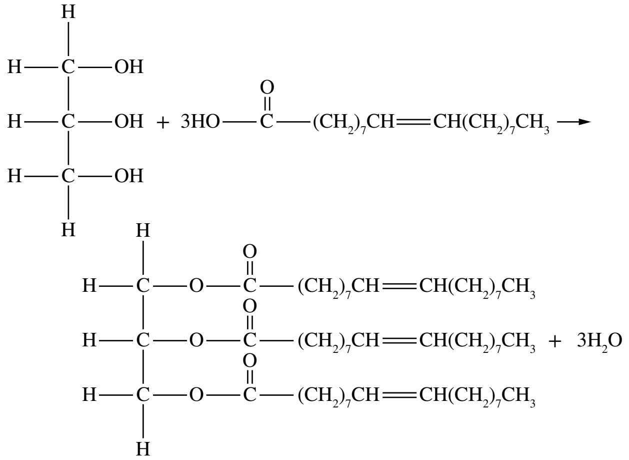
3 Bonds that hold together the secondary and tertiary structure of insulin are sensitive to excessive heat. An increase in temperature will cause these bonds to break, causing the insulin to lose its shape. When a protein loses its shape, it loses its function.

15.5 Fats and oils

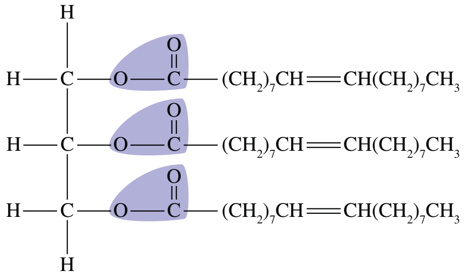
1 B

2 Hydroxyl and carboxyl

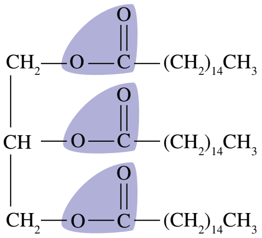
3 **a**



b



4 **a**



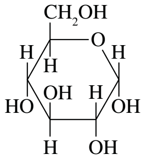
b The fat is saturated because the alkyl groups in the molecules $(CH_3(CH_2)_{14})$ contain only single carbon–carbon bonds. Alkyl groups with the general formula C_nH_{2n+1} are saturated.

5 **a** Saturated **b** Monounsaturated **c** Saturated
d Polyunsaturated **e** Polyunsaturated **f** Saturated
g Saturated **h** Monounsaturated

15.6 Carbohydrates

1 B, D, F, G

2 The glucose molecule has five polar OH groups that form hydrogen bonds with water. As a result, glucose is highly soluble in water.



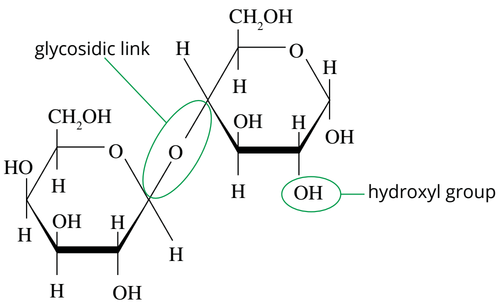
glucose

3 **a** Glucose is a monosaccharide. Maltose is made up of two monosaccharide molecules bonded together. Starch is a polymer of monosaccharide molecules.

b Condensation **c** Hydroxyl functional group

4 **a** A hydrolysis reaction is one in which water is a reactant.

b



5 **a** Cellulose **b** Glycogen **c** Starch **d** Lactose

6 The orientation of the hydroxyl group on the first carbon in α-glucose points 'downwards' and in β-glucose it points 'upwards'.

15.7 Vitamins

1 B, F, G

2 Insoluble, non-polar, soluble, dispersion forces

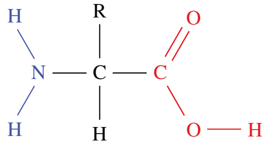
3 **a** Vitamin K
  b Vitamin K is fat soluble so is able to be stored in fatty tissue and used when necessary.

Chapter 15 review

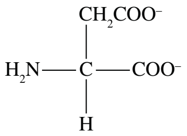
1 C

2 Carboxyl and amino functional groups

3



4 **a** **i** Carboxyl
  ii Amino
  b A molecule that contains positive and negative charges but has no charge overall.
  c **i**



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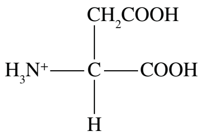

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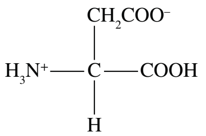
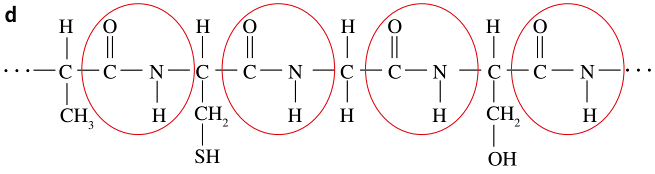


Either carboxyl protons may be lost.

5 **a** $H_2NCHCH_3CONHCH_2COOH$, $H_2NCH_2CONHCHCH_3COOH$
  b 6 (using each amino acid once in each peptide)
  c Very large numbers
  d



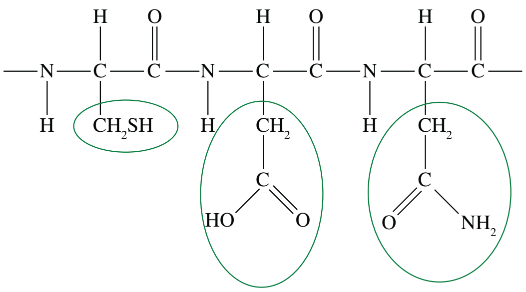
  e H_2NCHCH_3COOH, $H_2NCH(CH_2SH)COOH$, H_2NCH_2COOH, $H_2NCH(CH_2OH)COOH$

6 **a** Covalent bond/peptide bond/amide bond
  b Hydrogen bond **c** α-helix

7 β-sheets are formed when two adjacent strands of peptide lie in a plane and form hydrogen bonds between their respective backbones.

8 D

9



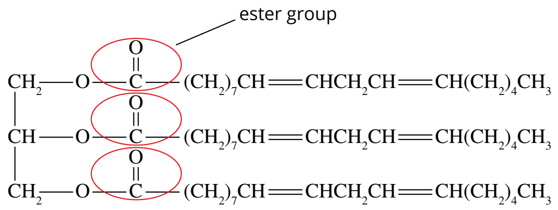
10 The activity of an enzyme, which is a type of protein, is dependent on its three-dimensional shape. The tertiary structure results from a combination of hydrogen bonding, electrostatic attraction between polar groups and disulfide linkages. If the wrong amino acid is introduced into the chain, these bonds may not form and the tertiary structure may be distorted. In some instances the enzyme becomes inactive, depending upon how the tertiary structure is altered.

11 Primary structure: the sequence of amino acids in a protein.
Secondary structure: the folding of a section due to, for example, hydrogen bonding between peptide links.
Tertiary structure: the overall three-dimensional shape of a protein.

12 C

13 **a** Saturated fatty acids have single bonds between carbon atoms.
  b Monounsaturated fatty acids have a single carbon to carbon double bond.
  c Polyunsaturated fatty acids have multiple double bonds.

14 **a** Glycerol
  b



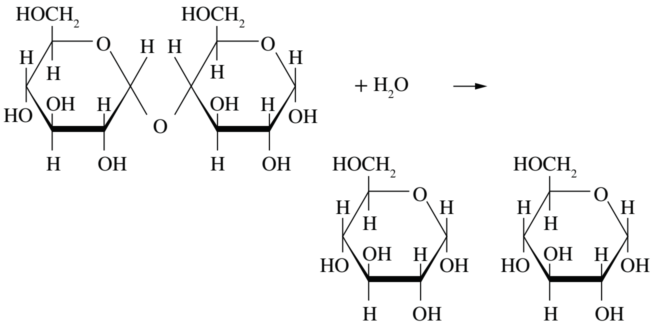
  c Ester group (circled in part **b**)
  d Polyunsaturated
  e The fat is likely to be a liquid at room temperature. Decreasing saturation results in relatively greater spacing between the hydrocarbon chains in the fatty acids and, therefore, reduced dispersion forces.

15 Some of the double bonds in sunflower oil are converted to single bonds via a catalysed addition reaction with hydrogen.

16 The term 'omega' refers to the last carbon in the fatty acid chain. The number 3 or 6 indicates the position of the double bond in the unsaturated fatty acid in relation to this carbon. That is, the double bone in omega-3 fatty acids is the on the third carbon along from the omega carbon.

17 B

18



19 Glycogen is the main storage polysaccharide in animals. Therefore, it fulfills the same role in animals that starch does in plants.

20 When the body digests food and absorbs glucose, the glucose is transported by the blood to the liver where it is converted to glycogen, a storage polysaccharide. The glycogen is slowly hydrolysed between meals to maintain a fairly constant concentration of glucose in the blood for use by tissues such as those in the brain.

21 **a** Carbon dioxide **b** Glucose **c** Disaccharide
d Glycosidic **e** Polysaccharide

22 B

23 **a** Vitamin C **b** Vitamin D **c** Vitamin D **d** Vitamin D
e Vitamin D **f** Vitamin C **g** Vitamin C **h** Vitamin C
i Vitamin D **j** Vitamin D **k** Vitamin C **l** Vitamin C

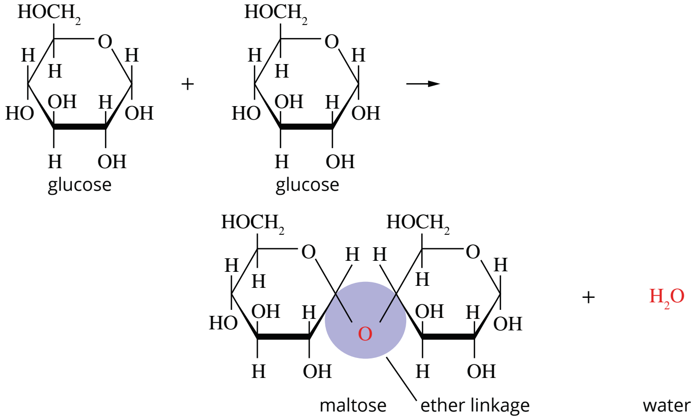
24 **a** Soluble **b** Insoluble **c** Soluble **d** Insoluble
e Soluble **f** Insoluble

25 **a** Carboxyl and hydroxyl groups; lipids
b Two hydroxyl groups; carbohydrates
c Carboxyl and amino groups; proteins

26 **a** Condensation reactions involve the linking together of two small molecules and the elimination of a small molecule, usually water. Hydrolysis reactions consume water and they can often be regarded as the reverse of condensation reactions.

b Vital biochemical processes include condensation reactions (e.g. synthesis of lipids, proteins and polysaccharides) and hydrolysis reactions (e.g. digestion).

c **i**



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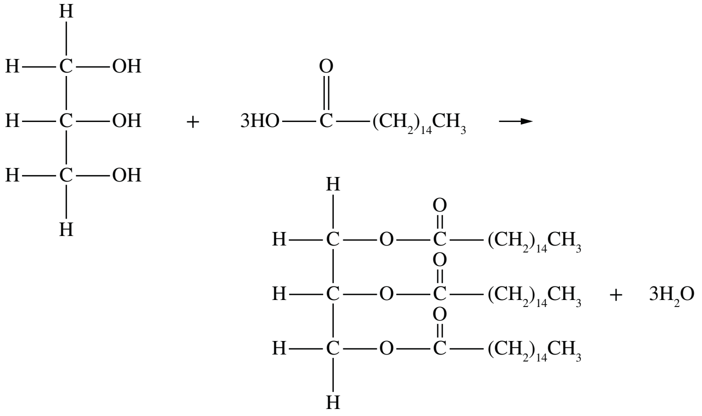

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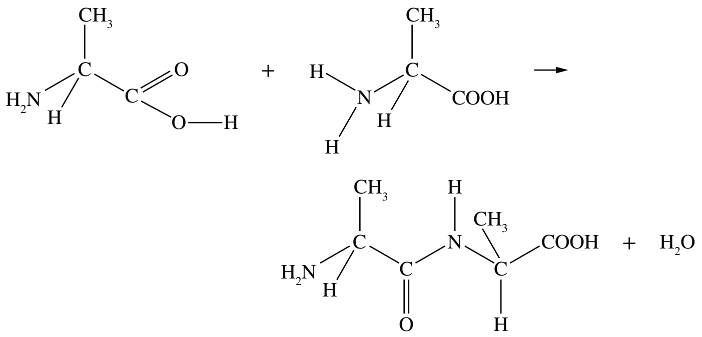


Chapter 16 Metabolism of food in the human body

16.1 Metabolism of food

1 proteins, condensation, water, hydrolytic, monosaccharides, glycerol, triglyceride

2 **a** Micronutrient **b** Macronutrient **c** Macronutrient
d Micronutrient **e** Micronutrient **f** Macronutrient

3 B

4 Enzymes catalyse many of the important digestion reactions. They are essential for the hydrolysis of large molecules obtained from food into smaller molecules.

5 The products of digestion are more water soluble so they can pass into the bloodstream more readily to be transported around the body.

6 Action of saliva in the mouth → action of hydrochloric acid in the stomach → action of enzymes in the small intestine → action of bacteria in the large intestine

7 Polysaccharide $\xrightarrow{\text{hydrolysis}}$ monosaccharides $\xrightarrow{\text{condensation}}$ polysaccharide

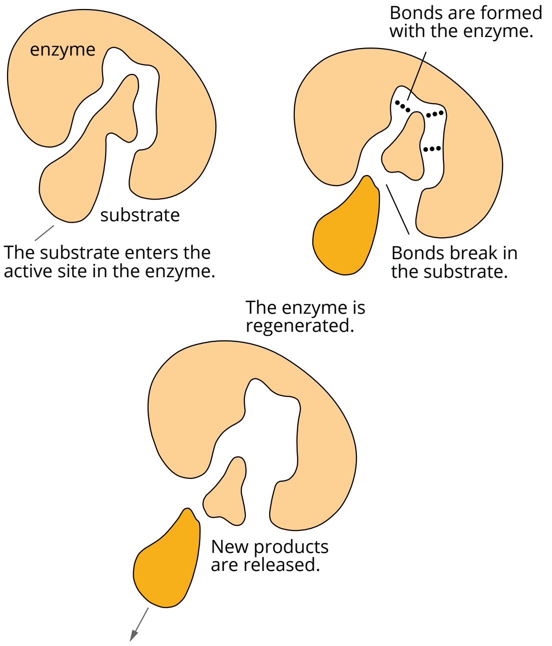
Triglyceride $\xrightarrow{\text{hydrolysis}}$ glycerol and fatty acids $\xrightarrow{\text{condensation}}$ triglyceride

Protein $\xrightarrow{\text{hydrolysis}}$ amino acids $\xrightarrow{\text{condensation}}$ protein

16.2 Action of enzymes

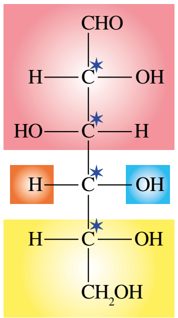
1 D

2 **a**



b Hydrogen bonds, ion–dipole interaction, dipole–dipole interactions, ionic interactions

3 4



4 **a** True **b** True **c** False **d** True **e** False

5 **a** Both **b** Enzymes **c** Enzymes **d** Both **e** Both

6 **a** A pair of molecules that are optical isomers of each other. Different structural arrangements that are non-superimposable mirror images.

b Either a metal ion or an organic molecule that binds to the enzyme to assist with the catalytic process.

c The reactant in an enzyme catalysed reaction.

d The earliest model used to describe how enzymes catalyse biochemical reactions. In the lock-and-key model a reactant (substrate) enters a hollow in an enzyme called its active site, producing the enzyme-substrate complex. Only substrates with specific three-dimensional shapes can interact at the active site, so only one enantiomer of a pair of optical isomers (mirror images) may be involved in catalysis.

e An organic molecule that must associate with an enzyme as well as the substrate for catalysis to occur.

f A flexible hollow or cavity in an enzyme that is able to form intermolecular bonds with a substrate molecule.

7 C

16.3 Enzymes—dependence on pH and temperature

1 During hydrolysis, covalent bonds between carbon atoms and nitrogen atoms are broken. This breaks the protein into its component amino acids. Denaturation is a result of the disruption of interactions between the side chains of the amino acids and the amide links that form the peptide chain. These interactions are responsible for the three-dimensional shape of the enzyme. When the shape is altered, the enzyme ceases to function but the primary structure remains intact.

2

Structure of R group	Is the R group acidic or basic or neither?	Is the R group positively charged, negatively charged or neutral?	
		In a solution of pH 2	In a solution of pH 11
$-CH_2COOH$	Acidic	Neutral	Negative
$-CH_2CH(CH_3)_2$	Neither	Neutral	Neutral
$-CH_2OH$	Neither	Neutral	Neutral
$-(CH_2)_4NH_2$	Basic	Positive	Neutral

3 **a** Denaturation occurs when there is a change to the structure and shape of an enzyme that prevents it from functioning. The enzyme is said to be 'denatured'.

b Denaturation usually involves disruption of the bonds that hold the enzyme's protein chain in a particular shape, followed by unfolding of the chain. The unfolded chains will often clump together, in a process called coagulation.

c No

d The overall three-dimensional shape of an enzyme is known as its tertiary structure. Since enzyme action depends upon the existence of a suitable hollow or cavity within the molecule, the tertiary structure is crucial to the enzyme's operations.

4 **a** Enzyme activity is an indication of the amount of substrate converted to product per unit time. Enzyme activity can be influenced by a number of reaction conditions, including solution pH, temperature and substrate concentration.

b Changes to the pH of the solution can change the charge of acidic or basic side groups on the amino acids of the protein. These changes can cause the protein to denature, disrupting the three-dimensional shape of the active site and reducing enzyme activity.

c A decrease in temperature reduces the frequency and energy of the collisions between reactants. This reduces the rate of reaction observed as a reduction in enzyme activity.

16.4 Hydrolysis of carbohydrates

1 **a** $C_6H_{12}O_6$ **b** Glycosidic links

2 Maltose, amylopectin, amylose, cellulose

3 **a** Small intestine by maltase

b Cellulose is not digested by humans and passes through the digestive tract unchanged. Only animals that have cellulase can digest cellulose.

c Mouth by amylase (in buccal cavity)

d Small intestine by lactase

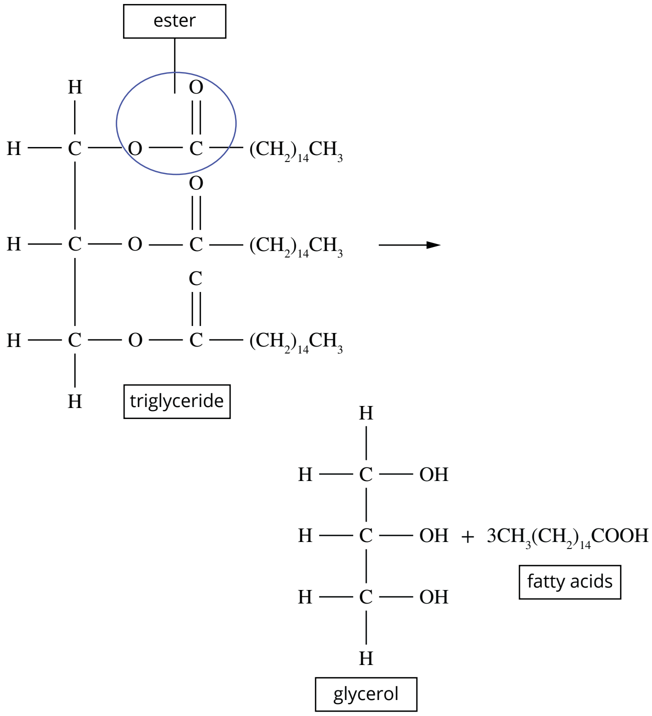
4 **a** Amylose **b** Wheat grain **c** Broccoli

d Strawberry **e** Whole milk

5 low, slowly, low, slowly, minimal

16.5 Hydrolysis of fats and oils

1



2 **a** The process by which a triglyceride is broken down to fatty acids and glycerol

b The process by which oxygen reacts with unsaturated triglycerides producing molecules that cause an unpleasant taste in oil and fats

c The process by which a fat globule is broken into many smaller particles that can be dispersed in an aqueous environment

d The process in which fatty acids and glycerol combine to form a triglyceride

3 small intestine, emulsifies, hydrolyses, glycerol, adipose

4 **a** False. Rancidity is more likely to occur when a triglyceride is unsaturated.
b True
c False. Antioxidants react with free radicals, preventing their further propagation
d True
e False. Rancidity occurs when a triglyceride reacts with oxygen in a process called autoxidation, which involves the formation of free radicals.
f True

Chapter 16 review

1 **a** All **b** Triglyceride **c** Polysaccharide
d Triglyceride **e** All **f** Protein
g Triglyceride **h** Triglyceride

2 The protein would be broken down in the process of digestion before it could be absorbed into the blood.

3

	Names of links between units	Functional groups formed when links break	Monomer or smallest components
Carbohydrate	glycosidic	hydroxyl	glucose
Fat	ester	hydroxyl and carboxyl	fatty acids and glycerol
Protein	peptide/ amide	amino and carboxyl	amino acid

4 **a** Enzymes in the body include:

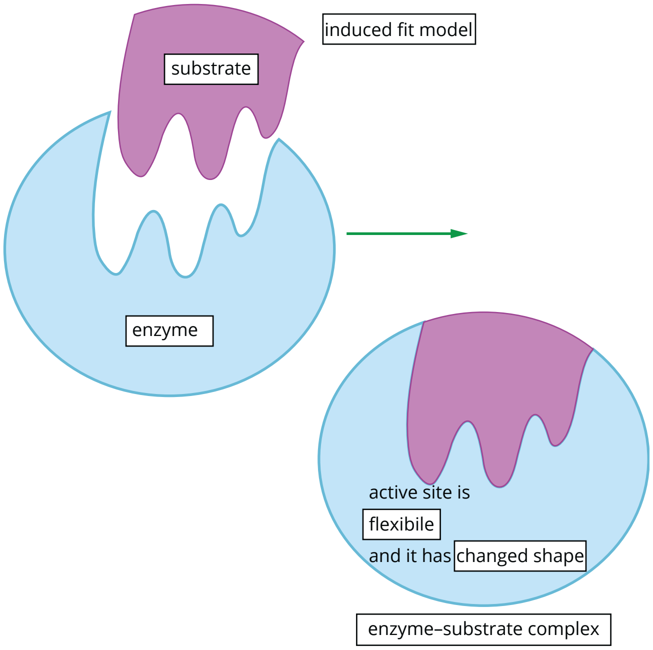
- pepsin, which hydrolyses peptide bonds of certain amino acids
- DNA polymerase, which replicates and repairs DNA
- lactase, which breaks down the sugar lactose in the small intestine
- salivary amylase, which breaks down polysaccharides in the mouth.

b Almost all the chemical reactions occurring in living organisms are controlled by enzymes. Enzymes speed up the reactions that are essential for life processes by as much as 10^{10} times; reactions that do not contribute to the functioning of a creature are not catalysed and occur at much slower rates.

c The shape and functional groups in the active site of the enzyme allow it to bind only with certain substrates so that only a specific reaction is catalysed. In a similar way, a lock will only open using a key of a certain shape.

5 **a** True **b** True **c** False **d** False
e True **f** True **g** True

6

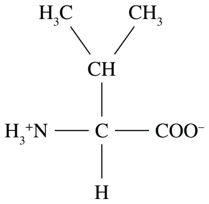


7 **a** The active site of an enzyme binds the substrate facilitating the catalysis of the substrate reaction. The active site is selective for binding only a specific substrate and catalysing a single reaction.
b The amino acid side chains of the active site bind the substrate via a combination of interactions including hydrogen bonds, ionic interactions, dispersion forces and covalent disulfide bonds.

8 The catalytic property of the enzyme can be destroyed by changing its shape—in a process called denaturation. This can be done by heating the pineapple. Alternatively, canned pineapple can be used to make this dessert because the fruit is heated during the canning process.

9 A

10



11 **a** Denaturation occurs when there is a change to the structure and shape of an enzyme that prevents it from functioning.
b Denaturation usually involves the disruption of the bonds that hold the enzyme's protein chain in a particular shape, by the unfolding of the chain. The unfolded chains will often clump together, in a process called coagulation.
c No
d The overall three-dimensional shape of an enzyme is known as its tertiary structure. Since enzyme action depends on the existence of a suitable hollow or cavity within the molecule, the tertiary structure is crucial to the enzyme's operations.

12 A, optimum temperature, fastest reaction rate. B, less frequent collisions, lower energy reactants. C, enzyme denatures, tertiary structure changes, three-dimensional shape of active site alters.

13 Enzymes in saliva act on starch. Hydrochloric acid and enzymes in the stomach act on food. Enzymes in the small intestine act on food. Bacteria in the large intestine act on dietary fibre.

14 Some people are unable to produce lactase so they cannot digest lactose. Instead, lactose sits and ferments in the digestive tract where the gas it produces can cause bloating and cramps.

15 Humans lack the enzyme (cellulase) that catalyses the hydrolysis of cellulose to form glucose.

16 The surface area of oats is relatively low. The husk of the oats has not been removed. The impact on blood sugar levels will be slow.

17 RH → R• + H• $\quad$ R• + O_2 → ROO•
ROO• → ROOH $\quad$ ROOH → unpleasant products

18 **a** Condensation **b** Condensation **c** Condensation
d Hydrolysis **e** Hydrolysis **f** Hydrolysis

19 **a** Ester **b** Glycosidic (ether) **c** Amide/peptide
d Glycosidic (ether) **e** Ester

20 water-soluble, only one, decreased, lower

21 **a** Vitamin C prevents the propagation of free radicals in the autoxidation process in the decomposition of lipids. It is the hydroxyl groups present in the molecule that facilitate this role.
b Vitamin C is found naturally in a number of fruits and vegetables such as citrus fruits and leafy green vegetables.

Chapter 17 The energy content of food

17.1 Food—an energy source

WE 17.1.1 12 kJ g^{-1} (2 significant figures)

1

Energy in joules (J)	Energy in kilojoules (kJ)
100	0.100
1.0×10^4	10
10.0	1.00×10^{-2}
1.00×10^3	1.00
0.10	1.0×10^{-4}

2 A

3 cellular respiration, exothermic, oxidised, oxygen, released, anaerobic respiration, less

4 B **5** 17 kJ g^{-1}

17.2 Introducing calorimetry

WE 17.2.1 12.1 kJ (3 significant figures)

WE 17.2.2 21.8 kJ g^{-1} (3 significant figures)

1

Final temperature – initial temperature	ΔT
Specific heat capacity	C
Initial mass – final mass	Δm
Heat energy	q
Time	t

2 **a** 6.35 kJ **b** 25.1 kJ **c** 62.7 kJ

3 22.3°C **4** 16.0 kJ g^{-1} **5** 1.58 g

6 **a** Bomb **b** Solution **c** Solution

d Bomb **e** Solution **f** Bomb

7 insulating, released, lost, lid, increases, endothermic

17.3 Calibration of calorimeters

WE 17.3.1 323 J °C^{-1} **WE 17.3.2** 4.57 kJ °C^{-1}

WE 17.3.3 21.4 kJ g^{-1} (3 significant figures)

WE 17.3.4 -1.12×10^4 kJ mol^{-1} (3 significant figures)

WE 17.3.5 +5.38 kJ mol^{-1} (3 significant figures)

1 **a** Bomb, solution **b** Solution **c** Bomb, solution

d Bomb **e** Bomb **f** Bomb, solution

2 B **3** 0.553 kJ °C^{-1}

4 **a** 1.40 kJ °C^{-1} **b** 4.14 kJ g^{-1}

5 823 J °C^{-1} **6** 698 J °C^{-1}

7 B **8** 1.96×10^3 kJ mol^{-1} **9** +5.40 kJ mol^{-1}

Chapter 17 review

1 B

2 D

3 almonds, higher, 1998, 1850

4 7.2 kJ g^{-1}

5 2.36 kJ **6** B **7** 80.1°C

8 24.5 kJ g^{-1} **9** 1.30 L

10 **a**
- Connect the heater of the bomb calorimeter into an electirc circuit with a voltmeter and an ammeter in the circuit.
- Add an accurately measured and recorded volume of water to a calorimeter and measure and record the temperature of the water.
- Turn on the power supply and read the current and voltage for a predetermined time, such as 120 s. Record these values.
- Measure and record the highest temperature reached of the water.
- Turn off and disconnect the electrical circuit.

b
- Add the same volume of fresh water as used for the calibration.
- Record the initial temperature of the water in the calorimeter.
- Add the preweighed food to be burnt into the calorimeter and connect the oxygen supply and ignition device.
- Ignite the food using the ignition device.
- Monitor the temperature of the water until the temperature no longer increases.
- Record the highest temperature reached in the calorimeter.

11 491 J °C^{-1}

12 **a** $C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(l)$

b 2.23 kJ is released by 1.00×10^{-3} mol

c −2.23 MJ mol^{-1}

d $C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(l)$ $\Delta H = -2.23$ MJ mol^{-1}

13 **a** $KNO_3(s) \xrightarrow{H_2O(l)} K^+(aq) + NO_3^-(aq)$

b 1.16 kJ °C^{-1}

c 783 J

d $KNO_3(s) \rightarrow K^+(aq) + NO_3^-(aq)$ $\Delta H = +78.3$ kJ mol^{-1}

14 7.19 kJ °C^{-1} **15** 20.8 kJ g^{-1} **16** -2.75×10^3 kJ mol^{-1}

17 29.2°C **18** 21.31°C **19** 6.46 g

20 combustion, water, increase, calibrating, temperature, energy.

21 A **22** 22.5 kJ g^{-1}

23 **a** 15 kJ g^{-1} **b** 14.8 kJ g^{-1}

24 C

25
1. The student has forgotten to divide the energy by the change in temperature when calculating the calibration factor.
2. The student has then multiplied the calibration factor by ΔT, which is correct, but the value is too large due to the earlier mistake.
3. The energy has been divided by the mass of the water, instead of the mass of the honey to calculate the energy content.
4. Conversion to kJ is incorrect. Energy content in J g^{-1} should be divided by 1000, not 100.
5. The final statement suggests that energy is given out when the honey dissolves when it is actually taken in as can be seen by the drop in temperature. Therefore dissolving honey in water is actually an endothermic reaction.

The student's calculations should be as follows:

$$CF = \frac{5.40 \times 2.60 \times 180}{2.3} = 1098.8\,J$$

Heat energy per gram to dissolve the honey:

$E = CF \times \Delta T = 1098.8 \times 1.7 = 1868\,J$

$$\text{Energy per gram} = \frac{1868}{19.80} = 94.3\,J\,g^{-1}$$

94.3 J of energy is taken in when 1 g of honey dissolves. This is an endothermic reaction.

26 B

27

Mistake or error	Calibration factor is too small	No effect on calibration factor	Calibration factor is too large
The lid is left off during calibration.			✓
Less water is used in the calorimeter for the calibration than for subsequent measurements.	✓		
During electrical calibration, the voltmeter had a systematic error making it read too low.	✓		
During chemical calibration, the mass of benzoic acid was recorded as less than its actual value.	✓		

28 **a** 427 J °C^{-1} **b** 13.5 kJ g^{-1}

c Major sources of error for any calorimetric analysis are loss of heat to the surroundings due to inefficient insulation, inaccurate temperature recording or inaccurate volume measurement.

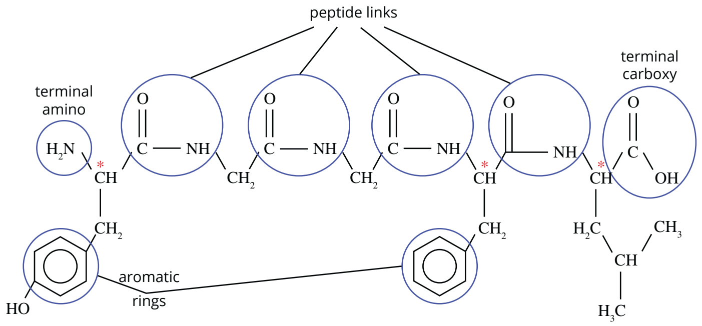
Area of study 2 What is the chemistry of food?

Multiple-choice questions

1	B	**2**	A	**3**	B	**4**	B	**5**	A	**6**	A
7	A	**8**	C	**9**	B	**10**	B	**11**	D	**12**	B
13	A	**14**	A	**15**	B	**16**	B	**17**	A	**18**	C
19	C	**20**	A								

Short-answer questions

21 a, c, d See diagram.



b Tyrosine, glycine (× 2), phenylalanine

22 a i A, C **i** B **ii** D

b All of them **c** Energy

d Starch in food undergoes hydrolysis (A) during digestion to form glucose, which is absorbed into the bloodstream. Some glucose is used to derive energy in cellular respiration (D). Some excess glucose undergoes condensation (B) to form glycogen for temporary storage, which is later hydrolysed (C) to release its stored glucose when needed.

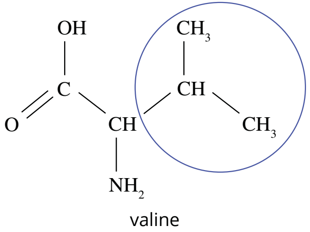
e Humans lack the enzyme necessary for hydrolysis of cellulose to glucose (cellulase), so cellulose passes though the digestive tract mostly unreacted. No strong interaction can form between the active site of amylase (the enzyme that catalyses starch hydrolysis) and cellulose.

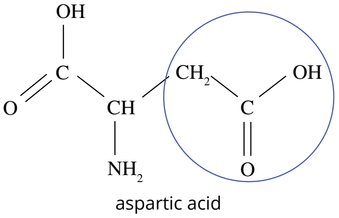
f i Fatty acids (and glycerol) **ii** Amino acids

23 a Essential amino acids cannot be synthesised in the body and must therefore be obtained from the diet.

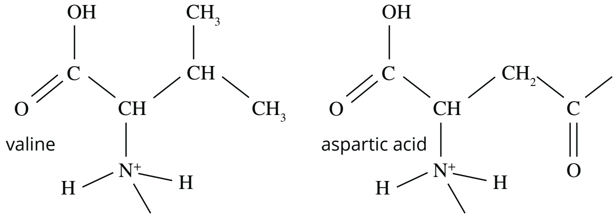
b Histidine, isoleucine, leucine, lysine, methionine, phenylalanine, threonine, tryptophan, valine

c, d

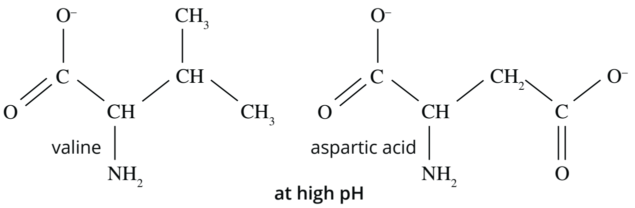




e At low pH (acidic) the amino group becomes protonated and hence positively charged. At high pH (basic) the acidic carboxyl groups become deprotonated and gain a negative charge. Aspartic acid possesses two carboxyl groups, and at sufficiently high pH both can become deprotonated.

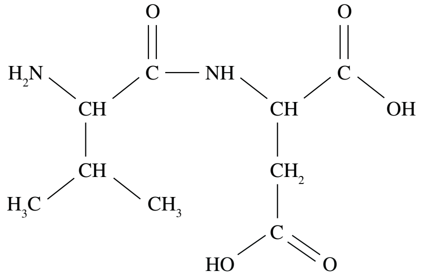


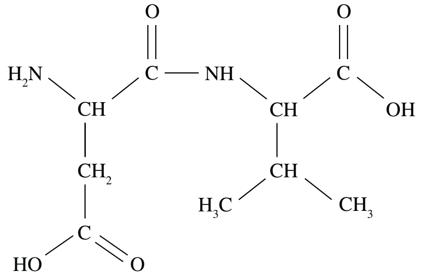
at low pH



at high pH

f





24 a The primary structure of a protein relates to the formation of peptide linkages in a condensation reaction between carboxyl and amino functional groups, and water is produced as a by-product. Secondary and tertiary structures do not involve condensation reactions.

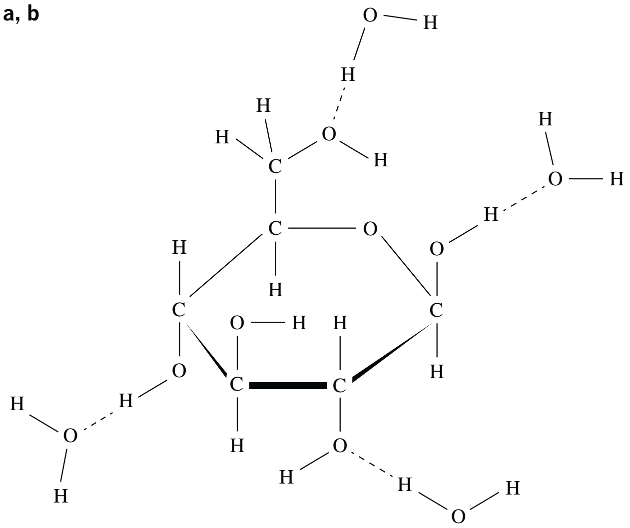
b These are features of the secondary structure of proteins, maintained by hydrogen bonding between the regularly spaced peptide linkages along the backbone of all protein chains.

c The secondary and tertiary structures of proteins are largely maintained by non-covalent bonding interactions, which are generally weaker than the covalent bonding in the peptide linkages maintaining the primary structure.

d The bonding in the tertiary structure of a protein includes types of widely varying strength. Proteins with higher proportions of the stronger bonding types involved in their tertiary structures will tend to be more stable.

e Even before the disruption to bonding becomes sufficient to permanently denature an enzyme, changes that affect the functional groups at the active site can significantly interfere with the substrate interactions and reduce activity.

25 a, b



26 **a** $C_6H_{12}O_6(aq) + 6O_2(g) \rightarrow 6CO_2(g) + 6H_2O(l)$

$\Delta H = -2.83$ MJ mol^{-1} = -2.83×10^3 KJ mol^{-1}

b 157 kJ **c** 26.3 L

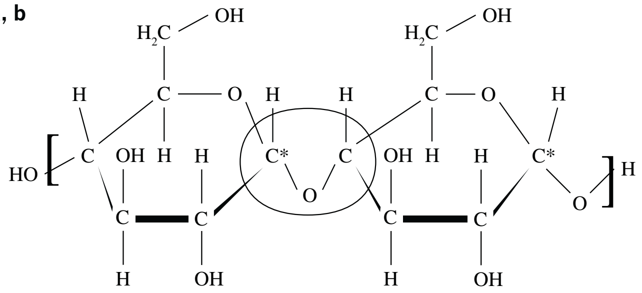
27 **a** Disaccharides

b Yes, both have the molecular formula $C_{12}H_{22}O_{11}$ but clearly have different structures.

c Glucose and fructose

d Some humans lose the ability to produce lactase and so are unable to digest/hydrolyse lactose, which results in irritation in the gut, among other symptoms.

28 **a, b**



c Altering the stereochemistry on even one atom changes the spatial configuration of key atoms and groups and prevents binding to the enzyme's active site.

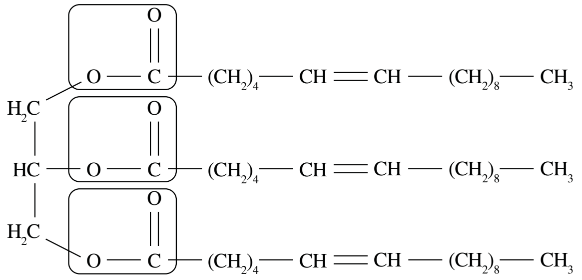
d Normal chain formation involves formation of glycosidic links at carbons 1 and 4. Branching results when glycosidic links form via hydroxyl groups at other centres on the glucose molecule.

e Starch is the primary form of storage of excess glucose in plants, while glycogen performs a similar function in animals. Cellulose is a structural material produced by plants for making cell walls.

29

I	**a** $C_{22}H_{40}O_2$; $C_{21}H_{39}COOH$	**b** Polyunsaturated	**c** Omega-6
II	**a** $C_{18}H_{28}O_2$; $C_{17}H_{27}COOH$	**b** Polyunsaturated	**c** Omega-3
III	**a** $C_{20}H_{42}O_2$; $C_{19}H_{39}COOH$	**b** Saturated	**c** Neither
IV	**a** $C_{16}H_{30}O_2$; $C_{15}H_{29}COOH$	**b** Monounsaturated	**c** Neither

30 **a, b**



c Fatty acid III. Saturated fats tend to have higher melting temperatures.

d Fatty acid III. It has no reactive double bonds.

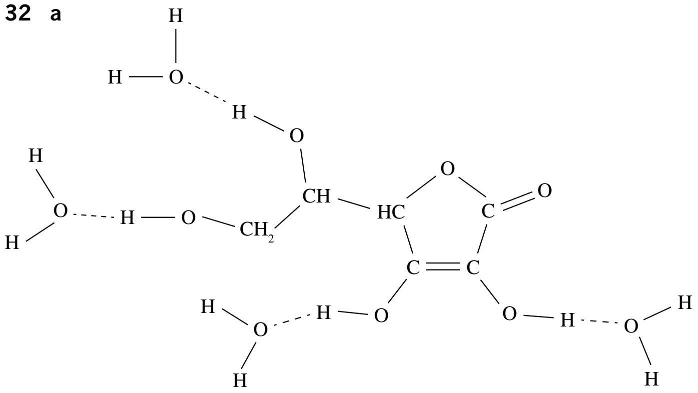
31 **a** $C_6H_{12}O_6(aq) + 6O_2(g) \rightarrow 6CO_2(g) + 6H_2O(l)$

b $C_{12}H_{22}O_{11}(aq) + H_2O(l) \rightarrow 2C_6O_{12}O_6(aq)$

c $3C_{11}H_{23}COOH(l) + C_3H_8O_3(aq) \rightarrow C_{39}H_{74}O_6(l) + 3H_2O(l)$

d $C_{11}H_{23}COOH(l) + 17O_2(g) \rightarrow 12CO_2(g) + 12H_2O(l)$

32 **a**



b Vitamin C has several polar hydroxyl groups that allow it to form strong hydrogen bonds to water molecules. Vitamins A and D lack these and are non-polar, allowing them to dissolve only in non-polar solvents such as oils.

33 **a** Coenzyme (or cofactor)

b The 'active site' of an enzyme is the region on its surface responsible for its catalytic activity. The 'substrate' binds to the active site of the enzyme and is altered in a way that lowers the activation energy of a reaction in which the substrate participates.

c Enzymes increase the rate of reaction but are unchanged after the reaction is complete.

d In the lock-and-key model the active site has a fixed shape that only the substrate, or a close mimic, can fit into and bind. The induced fit model holds that the enzyme and the substrate are altered by the binding process.

e Coenzymes usually attach to the active site of the enzyme (or sometimes the substrate) and are necessary for the 'fit' between substrate and active site that allows effective binding to occur.

34 **a** 70 s

b Exothermic (temperature increases)

c Loss of heat to the surroundings. Better insulation for the calorimeter.

d 5.7°C **e** –218 kJ mol^{-1}

35 **a** 973 J °C^{-1} **b** 11.9 kJ g^{-1} **c** Higher

Glossary

A

absolute temperature scale The absolute temperature scale is measured in kelvin (T (K) = T (°C) + 273). The scale starts at absolute zero, the temperature at which atoms and molecules have minimum kinetic energy.

absolute zero A temperature of –273°C or 0 K. Molecules and atoms have minimum kinetic energy at this temperature.

absorb The process of incorporating a substance into the interior of another substance or object as in the absorption of water into a sponge.

absorbance The proportion of incident electromagnetic radiation absorbed by a sample.

absorption band The inverted peaks in an infrared spectrum that represent the frequencies of infrared radiation absorbed by specific bonds.

accumulator A secondary, or rechargeable, electrochemical cell.

achiral Not chiral. An achiral object is superimposable on its mirror image. An achiral molecule does not have optical isomers. The molecule will usually have a plane of symmetry.

acid–base indicator A substance that changes colour depending on the concentration of H_3O^+ ions in solution.

acid rain Rainwater that has reacted with acidic emissions from industry and vehicles and has a pH less than 5.5.

activation energy The minimum energy required by reactants for a reaction to occur; symbol E_a. This energy is needed to break the bonds between atoms in the reactants to allow products to form.

active material A chemical that participates in the charge–discharge reactions in a cell or battery. These materials include the electrolyte and the electrode materials.

active site The location on an enzyme's structure at which a reaction is catalysed. It is usually a hollow or a cavity in the protein structure, where the enzyme binds and interacts with the substrate.

actual yield The mass of product actually obtained during a chemical reaction. This will be less than or equal to the theoretical yield.

addition polymerisation The process of forming a polymer by an addition reaction, where many monomers bond together by rearrangement of C=C double bonds without the loss of any atom or molecule. An addition polymer is made from unsaturated monomers.

addition reaction A reaction in which a molecule bonds to an unsaturated hydrocarbon, forming a single carbon–carbon bond. In this process two reactant molecules become one.

adipose tissue One of the main types of connective tissue in the body. It is mainly fat.

adsorb The process of sticking molecules onto the surface of a solid or liquid.

adsorption The attraction and binding of molecules or particles of one substance to the surface of another.

aerobic respiration In aerobic respiration, oxygen oxidises glucose to produce energy, according to the equation:

$$C_6H_{12}(aq) + 6O_2(g) \rightarrow 6CO_2(g) + 6H_2O(l) \qquad \Delta H = -2860 \text{ kJ mol}^{-1}$$

alcohol A homologous series of organic molecules that contains the hydroxyl (–OH) functional group.

aldehyde A homologous series of organic molecules which contains the carbonyl functional group, C=O, bonded to a hydrogen on one end of the molecule. Aldehydes can be recognised by the presence of a –CHO group at one end of a compound's condensed structural formula.

aliquot A fixed volume of liquid measured by a pipette.

alkaline cell A commercial electrochemical cell with an alkaline electrolyte that is a moist paste rather than a solution.

alkane A saturated hydrocarbon that contains only single bonds; general formula C_nH_{2n+2}.

alkene An unsaturated hydrocarbon containing one or more carbon–carbon double bonds. Alkenes with one double bond have the general formula C_nH_{2n}.

alkyl group A group obtained by removing a hydrogen atom from an alkane, with a general formula C_nH_{2n+1}; for example, methyl ($-CH_3$). Alkyl groups make up branches in organic compounds.

alkyne An unsaturated hydrocarbon containing one or more carbon–carbon triple bonds. Alkynes with one triple bond have the general formula C_nH_{2n-2}.

α-helix One type of secondary structure found in proteins. It has a spiral shape and it is maintained by hydrogen bonding between amino acid units in the chain.

amide A compound containing the –CONH– functional group. This group forms the link between amino acids in proteins, where it is also called a peptide link.

amide functional group A functional group found in the homologous series of amides consisting of an amine group attached to a carbonyl group $-CONH_2$.

amine A homologous series of organic molecules that contains the amino ($-NH_2$) functional group.

amino acid The monomer molecule used to make proteins.

2-amino acid An organic molecule that has an amino group, a carboxyl group, an H atom and an R group covalently bonded to the second carbon atom in the molecule's carbon chain. The R group consists of different sets of atoms.

amino acid residue A term used to refer to the section of a polypeptide chain that came from a particular amino acid.

amino functional group The functional group found in the homologous series of amines. It contains a nitrogen atom covalently bonded to two hydrogen atoms, $-NH_2$.

amount The number of particles of a substance present, usually measured in moles.

amylopectin A form of starch that has occasional cross-links between glucose chains.

amylose A linear form of starch.

anaerobic A process that can occur without the presence of oxygen.

anaerobic respiration A form of respiration in which oxygen is not required. The overall equation for anaerobic respiration in humans is:

$$C_6H_{12}O_6(aq) \rightarrow 2CH_3CH(OH)COO^-(aq) + 2H^+(aq) \qquad \Delta H = -120 \text{ kJ mol}^{-1}$$

anode An electrode at which an oxidation reaction occurs.

antioxidant A substance that reduces damage due to oxygen, such as that caused by free radicals. Most antioxidants protect fatty foods by reacting with free radicals, preventing a chain reaction that might cause rancidity.

aromatic hydrocarbon Unsaturated cyclic compound made from hydrogen and carbon atoms, often including benzene as a part of the structure. Benzene is a cyclic hydrocarbon with the formula C_6H_6.

atom economy A method of tracking the atoms in a reaction equation to calculate the mass of the atoms of reactants actually used to form products as a percentage of the total mass of the reactants. Atom economy can be calculated from the formula:

$$\text{atom economy} = \frac{\text{molar mass of desired product}}{\text{molar mass of all products}} \times 100$$

autoignition point The lowest temperature at which a fuel spontaneously ignites; also called self-ignition point or ignition point.

autoxidation Reaction with oxygen that occurs in the open air or in the presence of oxygen and forms peroxides or hydroperoxides. The browning of fruits like bananas is an example of auto-oxidation.

average titre The average of three concordant titres.

Avogadro's number The number of particles in one mole of any substance, equivalent to 6.02×10^{23} particles.

B

bar A unit of pressure. 1 bar = 100 kPa. It is about equal to atmospheric pressure at sea level.

base peak The highest intensity peak in a mass spectrum. It is assigned an intensity of 100.

battery A combination of cells connected in series.

battery capacity The maximum amount of energy available under certain specified conditions. It is determined by the amount of reactants contained in the battery.

battery life A measure of battery performance. It can be the time the battery operates in a device following a full charge or the number of charge–discharge cycles before a battery becomes unusable.

benzene A cyclic hydrocarbon of formula C_6H_6. The molecules contain a six-carbon ring with delocalised electrons. The carbon–carbon bonds are intermediate between single and double bonds.

β-pleated sheet One of the two types of secondary structure found in proteins. It consists of polypeptide strands bonded laterally. The parallel groups of a polypeptide chain are twisted back on themselves, forming a pleated sheet. It is maintained by hydrogen bonding.

bile Bile is a greenish-brown alkaline fluid that aids digestion. It is secreted by the liver and stored in the gall bladder.

biodegradation The breakdown of a substance by living organisms, such as bacteria and fungi.

biodiesel A fuel derived from vegetable oil or animal fat, consisting of long-chain alkyl esters. Biodiesel is typically made by reacting triglycerides with an alcohol.

bioethanol Ethanol that is made by fermenting the sugar and starch components of plants using yeast.

biofuel A fuel that can be produced from crops or other organic material. Examples of biofuels are ethanol from fermentation of sugars, methane from animals, and biogas produced from plant and animal waste materials.

biogas A mixture of gases produced by the breakdown of organic matter in the absence of oxygen.

bioluminescence The light that is emitted by a chemical reaction within a living organism.

biomolecule A molecule that is present in living organisms, including macronutrients such as proteins, carbohydrates and triglycerides.

blood sugar Blood sugar refers to glucose that is dissolved in blood. Glucose enters the bloodstream as a result of digestion of carbohydrates and other biomolecules.

bomb calorimeter An insulated container in which a sealed, oxygen-filled reaction vessel is surrounded by a known volume of water. Combustion reactions are carried out in the reaction vessel and the heat from the reaction is transferred to the surrounding water.

bond energy The amount of energy required to break a covalent bond.

bond strength The strength of a covalent bond. In general, higher energy bonds have greater bond strength.

brine A concentrated sodium chloride solution.

burette Glassware used for volumetric analysis to transfer a variable volume of solution accurately.

C

C-terminal The end of a protein or polypeptide with a free carboxyl group (–COOH).

calibrated In the context of calorimetry, calibration is the process used to establish the relationship between the temperature change of the water in a calorimeter and the amount of energy being added. The calorimeter is then described as having been calibrated.

calibration curve A plot of data involving two variables that is used to determine values for one of the variables. In spectroscopy and chromatography, it is a plot of absorbance versus concentration to determine the concentration of a solution of unknown concentration. The curve is constructed by measuring the absorbance of a set of standard solutions.

calibration factor The calibration factor of a calorimeter is the amount of energy that is required to change the temperature of the water within a calorimeter by 1°C.

calorie Imperial measurement used to measure the energy in food and is given the unit cal. A calorie is the amount of heat required to raise the temperature of 1 g of water by 1°C. 1 cal is equal to 4.18 J.

calorimeter An instrument designed to measure energy changes in a reaction. It is made up of an insulated container of water in which the reaction occurs, with a stirrer and thermometer to measure the temperature change during the reaction. A lid is an important part of the insulation.

calorimetry The experimental method by which the heat energy released by the combustion of a fuel or a food, or another chemical reaction such as a neutralisation reaction, is measured.

carbohydrate A naturally occurring condensation polymer containing carbon, hydrogen and oxygen, which has the general formula $C_x(H_2O)_y$.

carbon neutral A process that absorbs the same amount of carbon as it generates. The carbon dioxide absorbed from the atmosphere by a carbon neutral process compensates for the carbon dioxide produced by the process.

carbon-13 NMR spectroscopy Also called carbon NMR and ^{13}C NMR spectroscopy. A type of nuclear magnetic resonance spectroscopy that investigates the ^{13}C nucleus. It is used to determine the chemical environment of carbon atoms in compounds.

carbonyl functional group A functional group that consists of a carbon atom double bonded to an oxygen atom, –CO–. This group is present in aldehydes, ketones, carboxylic acids, amides and esters.

carboxyl functional group A functional group that consists of a hydroxyl group attached to the carbon of a carbonyl group, –COOH. This group is present in carboxylic acids.

carboxylic acid A homologous series of organic molecules that contain the carboxyl functional group (–COOH).

catalysis The increase in the rate of a chemical reaction due to the presence of a catalyst.

catalyst A substance that increases the rate of a reaction but is not consumed in the reaction. The catalyst provides an alternative reaction pathway with a lower activation energy.

cathode An electrode at which a reduction reaction occurs.

cellular respiration The process by which cells obtain energy using glucose as the primary energy source. Cellular respiration involves aerobic and, to a lesser extent, anaerobic respiration.

cellulose A carbohydrate that is a polymer of β-glucose and is the main component of the cell walls of plants.

chain isomer An isomer of an organic molecule caused by branching of the hydrocarbon chain.

chemical energy The sum of the chemical potential energy and kinetic energy in a substance. Chemical energy is stored in the bonds between atoms and molecules. The energy results from things such as attractions between electrons and protons in atoms, repulsions between nuclei, repulsions between electrons, movement of electrons, and vibrations and rotations around bonds.

chemical shift The position of a signal in the nuclear magnetic resonance (NMR) spectrum, relative to the signal produced by the tetramethylsilane (TMS) standard. Measured in parts per million, ppm.

chemiluminescence The light that is emitted by a chemical reaction that does not produce significant amounts of heat.

chemiluminescent Emitting light as the result of a chemical reaction.

chiral A chiral object is not superimposable on its mirror image. A chiral molecule has two optical isomers, called a pair of enantiomers. Chiral molecules do not have a plane of symmetry.

chiral centre A carbon atom that is attached to four different groups in a tetrahedral arrangement.

chromatogram The output of a chromatography procedure. In TLC and paper chromatography, it is the pattern of bands or spots formed on a plate or on paper. In high-performance liquid chromatography (HPLC), it is the graph produced.

chromatography A technique for separating the components of a mixture. The components are carried by a mobile phase (gas or liquid) over the adsorbent surface of a stationary phase, which can be solid or liquid.

***cis* arrangement** An arrangement of the alkyl groups at the double bond of most unsaturated fats, which produces a bend or 'kink' in the hydrocarbon chain.

***cis* isomer** An isomer in which the highest priority groups attached to the carbons of a double bond are on the same side of the double bond plane.

***cis–trans* isomers** Isomers that occur when two different groups are attached to each carbon in a carbon-carbon double bond. They occur because there is restricted around the carbon–carbon double bond.

closed system A system in which only energy is exchanged with the surroundings.

cloud point The temperature below which diesel or biodiesel appear cloudy owing to the formation of small crystals. The presence of these crystals thickens the fuel and clogs filters and injectors.

coal seam gas Natural gas trapped by pressure on the surface of a coal seam.

coenzyme An organic molecule that is required by an enzyme in order to catalyse a reaction.

cofactor A metal ion or small molecule that combines with an enzyme and is required for enzyme activity. It may be a metallic cation, a small organic molecule or an organometallic compounds.

coiling When sections of a protein form a spiral shape owing to hydrogen bonding.

collision theory A theoretical model that accounts for the rates of chemical reactions in terms of collisions between particles occurring during a chemical reaction.

column chromatography A chromatographic technique in which the stationary phase is in a column. Examples include gas chromatography and high-performance liquid chromatography.

combustion A rapid reaction with oxygen accompanied by the release of large amounts of energy.

competing equilibria Equilibria that have a common reactant; each equilibrium can be regarded as competing for this reactant. The equilibrium with the larger equilibrium constant has a significant effect on the position of equilibrium of the other reaction.

complementary proteins A combination of proteins that is able to provide the complete set of all the essential amino acids for the human diet.

complete combustion A combustion reaction that takes place with sufficient oxygen. The only carbon-containing product from complete combustion of hydrocarbons is carbon dioxide.

component The chemicals in a mixture. The components can be separated by chromatography.

concentration A measure of how much solute is dissolved in a specified volume of solution.

concentration fraction The ratio of concentrations of products to reactants in a reversible reaction, as expressed in the equilibrium law. It can also be called the reaction quotient.

concordant titres A set of titres that vary within a narrow range, usually within 0.10 mL from highest to lowest of one another.

condensation A chemical reaction in which two molecules combine to form a larger molecule, together with the loss of water.

condensation polymerisation Formation of a polymer by condensation reactions.

condensation reaction A reaction in which two molecules link together by eliminating a small molecule such as water.

conjugate redox pair An oxidising agent (a reactant) and the reducing agent (a product) that is formed when the oxidising agent gains electrons. In this case, the oxidation number of the oxidising agent decreases, e.g. Cu^{2+}/Cu. Alternatively, it may be a reducing agent (a reactant) and the oxidising agent (a product) that is formed when the reducing agent loses electrons. In this case, the oxidation number of the reducing agent increases.

coulomb The unit of charge; symbol C.

cyclic molecule A molecule in which the atoms are bonded to form a ring.

D

decomposition A reaction in which a compound is broken down into smaller parts.

delocalised electrons Electrons that are not restricted to a single atom or covalent bond. The electrons can be shared between several atoms.

denatured A term that describes an enzyme that has undergone a change in its three-dimensional shape so that it is unable to function as a catalyst. The shape of its active site is changed.

desorption The breaking of the bonds between a substance and the surface to which the substance is adsorbed.

dietary fibre The indigestible part of food from plants, such as vegetables, fruits, grains, beans and legumes. It is a mixture of different chemicals, including carbohydrates such as cellulose.

digestion Digestion involves the breakdown of large insoluble molecules into smaller, soluble molecules.

dilute Add more solvent to a solution to decrease the concentration of solute.

dimer A chemical structure formed from two similar sub units; for example, paired carboxylic acids that form hydrogen bonds with each other.

dipeptide An organic molecule that has been produced by the condensation reaction between two amino acids.

dipolar ion A particle carrying both a positive and negative charge; for example, $+H_3NCH_2COO-$.

dipole A molecule that has two oppositely charge ends.

dipole–dipole attraction A form of intermolecular force that occurs between polar molecules where the positively charged end of one molecule is attracted to the negatively charged end of another molecule.

dipole–dipole bond An intermolecular force that occurs between polar molecules in which the positively charged end of one molecule is attracted to the negatively charged end of another molecule.

disaccharide A carbohydrate consisting of two monosaccharides joined by a glycosidic (or ether) link.

dispersion force A very weak force of attraction between molecules due to temporary dipoles induced in the molecules. The temporary dipoles are the result of random fluctuations in the electron density.

disulfide bridge Also known as a disulfide bond (–S–S–). A covalently bonded set of two sulfur atoms (derived from the oxidation and joining of two nearby –SH groups in cysteine units) that can connect polypeptide chains together.

dynamic equilibrium A point in a chemical reaction when the rate of the forward reaction is equal to the rate of the reverse reaction.

E

elastic collision An elastic collision is one in which there is no loss of kinetic energy.

electrochemical cell A device that converts chemical energy into electrical energy, or vice versa.

electrochemical series A list of half-equations, written as reduction reactions, arranged in order so that the strongest oxidising agents are on the top left side of the list.

electrode A solid conductor in a half-cell at which oxidation or reduction reactions occur.

electrolysis A process that produces a non-spontaneous redox reaction by the passage of electrical energy from a power supply through a conducting liquid.

electrolyte A chemical substance that conducts electric current as a result of dissociation into positively and negatively charged ions, which migrate toward the negative and positive terminals of an electric circuit.

electrolytic cell A cell in which electrolysis can occur.

electromagnetic spectrum The range of electromagnetic radiation. It is often represented in order of wavelength, from low energy radio waves to high-energy gamma rays.

electromotive force The 'electrical pressure' between two points in a circuit, such as the electrodes of an electrochemical cell; a measure of the energy given to electrons in a circuit.

electronegative A measure of the ability of an atom of an element to attract electrons.

electronic configuration The arrangement of electrons in energy levels within an atom.

electroplating A process that uses electrolysis to deposit a layer of metal on the surface of another material. This process is also called deposition.

eluent The solvent that carries the components and passes through a chromatography column.

emulsion A suspension of small droplets of one liquid in another.

enantiomer One of a pair of molecules that are mirror images of each other that cannot be superimposed. Enantiomers are optical isomers.

end point The point during a titration when the indicator changes colour.

endothermic A reaction that absorbs energy from the surroundings; ΔH is positive.

energy content The amount of energy per gram or per 100 g, or per mole (if a nutrient is a pure substance), that a food can supply. Units can be $kJ\ g^{-1}$, kJ/100 g or $kJ\ mol^{-1}$.

energy density The energy released when 1 litre of fuel undergoes complete combustion.

energy efficiency The percentage of total energy that is converted into the desired form of energy.

energy profile diagram A diagram that shows the energy changes during the course of a reaction.

energy transformation The process of converting one form of energy into another form of energy.

energy value The amount of energy per gram or per 100 g, or per mole (if a nutrient is a pure substance), that a food can supply. Units can be $kJ\ g^{-1}$, kJ/100 g or $kJ\ mol^{-1}$.

enhanced greenhouse effect An increase in the temperature of Earth's surface due to an increased concentration of greenhouse gases, as a result of human activities.

enthalpy Heat content. The sum of the chemical potential and kinetic energies in a substance; symbol H.

enthalpy change The difference in the total enthalpy of the products and the total enthalpy of the reactants; symbol ΔH. Also known as heat of reaction.

enthalpy of combustion The enthalpy change that occurs when one mole of a compound is burned completely in oxygen; symbol ΔH_c.

enzyme A protein molecule that functions as a catalyst of a specific biochemical reaction. A catalyst increases the rate of a reaction.

enzyme activity The amount of substrate converted to products per unit time by an enzyme. It represents the ability of the enzyme molecules to catalyse the reaction.

enzyme–substrate complex The intermediate molecule that forms when a substrate molecule interacts with the active site of an enzyme, during the catalysis of a chemical reaction.

equilibrium When a chemical reaction reaches equilibrium, the quantities of reactants and products in the reaction remain unchanged. The rates of the forward and reverse reactions are equal.

equilibrium constant The value of the concentration fraction when equilibrium is reached; symbol K_c. The equilibrium constant for the chemical equation:

$$aW + bX \rightleftharpoons cY + dZ$$

is given by the expression:

$$K_c = \frac{[Y]^c[Z]^d}{[W]^a[X]^b}$$

equilibrium law The equilibrium law for the chemical equation:

$$aW + bX \rightleftharpoons cY + dZ$$

is given by the expression:

$$K_c = \frac{[Y]^c[Z]^d}{[W]^a[X]^b}$$

where K_c is a constant at a particular temperature.

equilibrium yield The amount of product obtained when a chemical reaction reaches equilibrium.

equivalence point The point during a titration when the reactants in solution are present in stoichiometric proportions, i.e. in the mole ratio shown by the reaction equation.

equivalent A term used in NMR spectroscopy to describe atoms that require the same amount of energy to change spin state, and hence have the same chemical shift.

essential amino acid An amino acid that must be included in the diet as it cannot be synthesised in the human body.

essential fatty acid A fatty acid that is needed by the body but not produced in the body.

ester The name of the homologous series of molecules that contain the ester (–COO–) functional group.

ester functional group The functional group that is the result of the reaction between an alcohol and a carboxylic acid. It consists of a carbonyl group bonded to an oxygen atom bonded to another carbon atom, –COO–.

ester link The link that is the result of the reaction between a hydroxyl and a carboxyl functional group. It consists of a carbonyl group bonded to an oxygen atom bonded to another carbon atom (–COO–).

esterification reaction The chemical reaction between an alcohol and a carboxylic acid to form an ester as the main product.

ether link A link that consists of the bond C–O–C. In carbohydrates, an ether link is also known as a glycosidic link.

exothermic An exothermic reaction releases energy to the surroundings; ΔH is negative.

extent of reaction The relative amounts of products compared with reactants. The extent of a reaction is indicated by the value of the equilibrium constant.

external circuit The section of an electrochemical cell in which electrons move. This section of the circuit will include the wires attached to the electrodes.

extrapolate To extend a line that has been constructed in response to a trend observed in a set of data to values beyond that data.

F

faraday The charge on one mole of electrons; symbol F. 1 F = 96 500 C mol^{-1}.

Faraday's first law of electrolysis The mass of metal produced at the cathode is directly proportional to the electrical charge passed through the cell. It may be written symbolically as: $m \propto Q$.

Faraday's second law of electrolysis In order to produce one mole of a metal, one, two, three, or another whole number of moles of electrons must be consumed.

fatty acid A carboxylic acid that has a relatively long hydrocarbon chain.

fatty acid ester A carboxylic acid with a long hydrocarbon tail, usually containing 12–20 carbon atoms, derived from the reaction of an alcohol with a triglyceride.

fermentation The breakdown of sugar solutions, by the action of enzymes in yeasts, into ethanol and carbon dioxide. The chemical equation for the fermentation of glucose is:

$$C_6H_{12}O_2(aq) \rightarrow 2CH_3CH_2OH(aq) + 2CO_2(g)$$

fingerprint region The part of the infrared (IR) spectrum below 1400 cm^{-1} that is unique to a particular molecule.

flashpoint The lowest temperature at which the vapour of a liquid fuel will ignite when an ignition source (such as a flame) is applied to it.

fossil fuel A fuel that that has been produced over a long time by the breakdown of organic material. This process can take many thousands of years. Examples are coal, crude oil and natural gas.

fracking The process of injecting sand, water or chemicals at high pressure into coal or rock to release trapped natural gas.

fractional distillation The separation of the components in a mixture on the basis of their boiling temperatures.

fragmentation The breaking-up of a molecular ion into a number of smaller parts in mass spectrometry.

free radical An atom or group of atoms that has at least one unpaired electron and is therefore unstable and highly reactive.

fuel A substance with stored energy that can be released relatively easily for use as heat or power. The stored energy can be in the form of chemical energy (e.g. coal) or nuclear energy (e.g. uranium).

fuel cell A type of electrochemical cell in which the reactants are supplied continuously, allowing continuous production of electrical energy.

functional group An atom or group of atoms in an organic molecule that largely determines the molecule's properties and reactions.

G

galvanic cell A type of electrochemical cell also known as a voltaic cell; a device that converts chemical energy into electrical energy.

galvanometer An instrument for detecting electric current.

gas constant The constant, R, in the universal gas equation $PV = nRT$. $R = 8.31\ \text{J K}^{-1}\ \text{mol}^{-1}$ when pressure is measured in kPa, volume in L and temperature in K.

geometric isomer A type of stereoisomer that can occur when there is restricted rotation in a molecule. Restricted rotation can occur about a carbon–carbon double bond or a ring. Stereoisomers of alkenes can be distinguished using the labels *cis*- and *trans*-.

glucose A monosaccharide that plants can form through the process of photosynthesis. Its molecular formula is $C_6H_{12}O_6$.

glycaemic index A means of measuring the effects of food on blood sugar levels. Glucose has a glycaemic index (GI) of 100.

glycogen A branched polysaccharide that is a polymer of α-glucose. Glycogen is the main form of carbohydrate storage in animals and is found primarily in the liver and muscle tissue.

glycosidic link The ether link (C–O–C) formed when monosaccharide units bond to each other. It is the result of the reaction between two hydroxyl groups on two monosaccharides. Glycosidic links are found in disaccharides, trisaccharides and polysaccharides.

greenhouse effect The process by which heat radiation from Earth's surface is absorbed and re-radiated by gases in the atmosphere. The greenhouse effect maintains the temperature of Earth at conditions suitable for life.

greenhouse gas A gas that is able to absorb and re-radiate heat radiation. These gases contribute to the greenhouse effect. Examples are carbon dioxide, methane and water vapour.

H

half-cell Half an electrochemical cell, which contains the oxidant and conjugate reductant. When two half-cells are combined, a galvanic cell is formed.

half-equation A balanced chemical equation which shows the loss or gain of electrons by a species during oxidation or reduction. For example, the oxidation of magnesium is written as the half-equation $Mg(s) \rightarrow Mg^{2+} + 2e^-$.

halo functional group A functional group that consists of a halogen atom bonded to the carbon chain. The halo functional groups are named fluoro-, chloro-, bromo- and iodo-.

haloalkane A molecule derived from alkanes that contain at least the one halogen functional group.

halogen An element in group 17 of the periodic table.

heat content At a simple level, the heat content, or enthalpy, can be regarded as the chemical energy of a substance; symbol H.

heat of combustion The energy released when a specified quantity (e.g. 1 mole or 1 gram) of a substance burns completely in oxygen.

heat of reaction The exchange of heat between a system and its surroundings during a chemical reaction under constant pressure; symbol ΔH. Also known as enthalpy change.

heat of solution The amount of heat energy that is released or absorbed when a substance dissolves forming a solution. Also referred to as the enthalpy of solution; expressed in kJ mol^{-1}.

heterogeneous catalyst A catalyst that has a different physical state (phase) from the reactants and products.

heterogeneous reaction A chemical reaction in which at least two of the species are in different state or phase.

high-performance liquid chromatography (HPLC) A very sensitive technique used to separate the components in a mixture, to identify each component, and to measure the concentrations of the components. It uses a pump to pass a pressurised liquid solvent containing the sample mixture through a column filled with solid adsorbent material. Also known as high-pressure liquid chromatography.

homogeneous catalyst A catalyst that has the same physical state (phase) as the reactants and products.

homogeneous reaction A chemical reaction in which all the species are in the same state or phase.

homologous series A series of organic compounds in which each member of the group differs from the previous member by a $-CH_2$ unit. Examples are alkanes, alkenes and alcohols.

hydration reaction A reaction that involves water as a reactant.

hydrocarbon A compound that contains carbon and hydrogen only. Examples include alkanes and alkenes.

hydrogen bond A type of intermolecular force that exists between molecules where a hydrogen atom is covalently bonded to an oxygen, nitrogen or fluorine atom within the molecule. The hydrogen develops a positive charge and bonds to lone pairs of electrons on the oxygen, nitrogen or fluorine atoms in a neighbouring molecule.

hydrogen economy A proposed system of delivering energy for society using hydrogen as the source of energy.

hydrogen halide Diatomic molecules consisting of a hydrogen atom and a halogen atom joined by a covalent bond. HF, HCl, HBr and HI are hydrogen halides.

hydrogenation reaction The reaction of an organic compound with hydrogen so that it becomes more saturated.

hydrolysis A reaction involving the breaking of a bond in a molecule using water as a reactant. Two smaller molecules are usually formed.

hydrolytic reaction A reaction involving the breaking of a bond in a molecule using water as a reactant. Two smaller molecules are usually formed.

hydrophobic Describes substances that tend to repel or fail to mix with water, and which are usually non-polar.

hydroxyl functional group A functional group that consists of an oxygen atom covalently bonded to a hydrogen atom, –OH. This functional group is present in alcohols.

hygroscopic The property of absorbing moisture from the air.

hypervitaminosis Refers to abnormally high storage levels of vitamins, which can lead to toxic symptoms.

I

ideal gas A gas that obeys the gas equations at all temperatures and pressures.

ignition point The lowest temperature at which a liquid or gas will spontaneously ignite without the application of an external ignition source.

immiscible Describes a liquid that will not mix with or dissolve in another liquid; for example, oil in water.

incomplete combustion A combustion reaction that takes place when oxygen is limited. Incomplete combustion of hydrocarbons produces carbon and carbon monoxide as well as carbon dioxide.

inert A substance that is unreactive, such as a platinum or graphite electrode.

inert electrode An electrode that is not consumed in the reaction that occurs at the electrode. The electrode serves only as a conductor of electrons. Precious metals and carbon are typically used as inert electrodes.

infrared (IR) spectroscopy An analytical technique that uses the infrared part of the electromagnetic spectrum to investigate the vibrational energy of molecular bonds.

inorganic Of a compound that consists of elements other than carbon. Although certain compounds of carbon, such as carbon dioxide and carbonates, are also classified as inorganic.

internal circuit The part of an electrochemical cell in which ions move, e.g. solutions and salt bridge.

irreversible reaction A reaction in which significant reaction can occur in one direction only.

isomers Molecules that have the same molecular formula but a different arrangement of atoms.

isotope Each of two or more forms of the same element that contain equal numbers of protons but different numbers of neutrons in their nuclei.

IUPAC nomenclature A set of rules for naming organic molecules. It is usually systematic and gives the number of carbon atoms and the location and type of functional groups present.

K

kelvin scale The absolute temperature scale is measured in kelvin (T (K) = T (°C) + 273).

ketone A homologous series of organic molecules that contains the carbonyl functional group (C=O) within the carbon chain.

kinetic energy The energy that a particle or body has due to its motion (KE = $\frac{1}{2}mv^2$).

kinetic energy distribution diagram A graph of kinetic energy against number of particles that shows the range of energies in a sample of a gas or a liquid at a given temperature. Also known as a Maxwell–Boltzmann distribution curve.

kinetic molecular theory A theory that aims to explain the behaviour of gases by assuming gases are composed of a large number of particles in random motion, these particles move in straight lines and have elastic collisions, the gas particles are very small and there is no attraction between the particles and the average kinetic energy of the gas particles is related to the temperature of the gas.

L

lactose intolerance The inability of the body to digest lactose, a disaccharide found in milk. It is usually due to a deficiency of the enzyme lactase.

law of conservation of energy A scientific law that states energy cannot be created or destroyed; it can only be transformed from one type of energy to another.

Le Châtelier's principle If an equilibrium system is subjected to a change, the system will adjust itself to partially oppose the effect of the change.

lead–acid battery A secondary cell or accumulator used to start most cars.

lipid A class of organic compounds that includes fats, oils, waxes and steroids. They are insoluble in water but soluble in non-polar solvents.

liquefied petroleum gas A mixture of propane and butane that is separated from natural gas or crude oil. It is stored under pressure to liquefy the propane and butane.

lithium-ion cell A galvanic cell that generates electricity from the oxidation of lithium embedded in the lattice structure of a graphite rod and the reduction of a metal oxide. The reduction product combines with the lithium ions.

M

macronutrient A component of food required in large amounts in the diet for growth, metabolism and other body functions. Proteins, carbohydrates and triglycerides are examples of macronutrients.

main group metal A metal in groups 1–3 such as lithium, sodium, potassium, magnesium, calcium, barium and aluminium.

mass spectrometer An instrument designed to measure the mass-to-charge ratio, m/z, of particles.

mass spectrometry An analytical technique that uses the mass-to-charge, m/z, ratio of atoms, molecules and fragments of molecules to identify substances.

mass spectrum A graph of data produced from a mass spectrometer which shows the abundance or relative intensity of each particle, and their mass-to-charge, m/z, ratios.

materials-based storage A general name given to methods of storing hydrogen that includes adsorption to the surface of materials such as metal hydrides, absorption into the lattice structure of some solid materials and reversible reactions with a range of different chemicals.

Maxwell–Boltzmann distribution curve A graph of kinetic energy against number of particles that shows the range of energies in a sample of a gas or a liquid at a given temperature. Also known as a kinetic energy distribution diagram.

metabolism Chemical processes occurring within a living cell or organism that are necessary for the maintenance of life.

microbial Relating to microbes or microorganisms, often bacteria.

micronutrient A component of food required in the diet in small amounts. Micronutrients have important roles to play in metabolism and preventing diseases. Vitamins and some minerals are examples.

miscible Describes a liquid that will mix with or dissolve in another liquid; for example, ethanol and water.

mobile phase In chromatography, the phase that moves over the stationary phase.

molar mass The mass of one mole or equivalent of a compound.

molar volume The volume occupied by one mole of gas at a specified set of conditions. At standard temperature (0°C or 273 K) and pressure (100 kPa), the molar volume of a gas is 22.7 L mol^{-1}.

mole The unit for the amount of substance (usually abbreviated to mol).

molecular formula A formula that gives the actual number and type of atoms present in a molecule.

molecular ion A whole molecule with an overall positive or negative charge. In this course positively charged molecular ions are investigated.

molecular ion peak A peak in a mass spectrum that is by the presence of a whole molecule ion. The peak with the greatest m/z value is likely to be due to the molecular ion in most cases.

monomer Small molecule that is able to react to form long chains of repeating units, called polymers.

monoprotic acid An acid that can donate only one hydrogen ion.

monosaccharide The simplest unit of carbohydrates. Monosaccharides are the building blocks of more complex carbohydrates and have the formula $C_6H_{12}O_6$. Examples are glucose, fructose and galactose.

monounsaturated fatty acid A fatty acid that contains one carbon-carbon double bond.

N

N-terminal The end of a protein or polypeptide with a free amine group ($-NH_2$).

natural gas A fossil fuel composed of hydrocarbons that are gases under the conditions they are extracted from the Earth. Natural gas consists mainly of methane (CH_4).

neighbour The ^1H atoms within three bonds of a hydrogen atom that can cause its signal to split into a lined pattern. Hydroxyl hydrogens do not cause splitting and are not included as neighbours.

nickel–metal hydride cell A rechargeable cell that generates an electric current by the oxidation of nickel metal hydride and the reduction of NiOOH.

non-essential fatty acid Fatty acid that can be produced in the body and so does not have to be included in the diet.

non-rechargeable cell A primary galvanic cell.

non-renewable Non-renewable energy resources are those that are being used at a faster rate than they can be replaced.

non-spontaneous reaction Reactions that would not normally occur without the application of electrical energy. They are the reverse of spontaneous reactions, which produce energy.

nuclear magnetic resonance (NMR) spectroscopy A technique used to analyse materials using the interaction of the nucleus of particular isotopes, most commonly usually ^1H or ^{13}C, with an external magnetic field and electromagnetic radiation.

nuclear magnetic resonance (NMR) spectrum The representation in graph form of the energy required to change a nucleus from a low energy spin state to a high-energy spin state.

nuclear shielding Modification of the magnetic field experienced by a nucleus in an external magnetic field caused by the magnetic field of surrounding atoms in the molecule.

nuclear spin A property of a nucleus with an odd number of protons or neutrons that causes it to interact with a magnetic field. The nuclear spin can be either with or against an external magnetic field.

nutrient A substance that provides nourishment for growth or metabolism.

O

omega carbon The carbon in the methyl group at the end of the hydrocarbon chain in an unsaturated fatty acid.

omega-3 fatty acid Essential fatty acid that contains a carbon–carbon double bond on the third carbon from the end of the hydrocarbon chain.

omega-6 fatty acid Essential fatty acid that contains a carbon–carbon double bond on the sixth carbon from the end of the hydrocarbon chain.

open system A system that allows matter and energy to be exchanged with the surroundings.

optical isomers Isomers in which there can be a different three-dimensional arrangement of groups around one or more atoms.

optimum pH The pH at which enzyme activity is greatest.

optimum temperature The temperature at which enzyme activity is greatest.

organic acid An organic compound that contains a functional group that can donate a proton. This is typically a carboxylic acid (containing a –COOH functional group).

organic base An organic compound that contains a functional group that can accept a proton. This is typically an amine (containing a $-NH_2$ functional group).

organic compound A compound composed of molecules based on a carbon backbone.

organic molecule A molecule that is based on a hydrocarbon skeleton. Organic molecules also commonly contain other non-metal elements, such as oxygen, nitrogen, sulfur and chlorine.

origin In paper or thin-layer chromatography, the point at which a small spot of a mixture is placed so that it can be separated.

oxidant A chemical species (element, compound or ion) that accepts one or more electrons in an oxidation–reduction reaction. An oxidant causes another substance to be oxidised, and in the process the oxidant is reduced. An oxidant is also called an oxidising agent.

oxidation (i) A reaction in which oxygen is a reactant. Oxidation can be defined as the addition of oxygen to form oxides, such as combustion reactions. (ii) The process by which a chemical species such as a metal atom or a non-metal ion loses electrons. An oxidation half-equation will show the electrons as products (on the right-hand side of the arrow). Oxidation is said to have occurred when there is an increase in an element's oxidation number during the reaction.

oxidation number A number assigned to an atom in a compound or as the free element, which represents the charge that atom would have if it was an ion. A series of oxidation number rules are used to determine the oxidation number of an element in a compound. Oxidation numbers are used to identify redox reactions.

oxidative rancidity The process by which lipids deteriorate and become rancid; potentially harmful compounds are produced in the food.

oxidised The loss of electrons or an increase in oxidation number. When a substance is oxidised, the electrons are written on the right-hand side of the arrow in the half-equation.

oxidising agent A reactant that causes another reactant to lose electrons during a redox reaction. This reactant is, itself, reduced and gains electrons. The oxidation number of the oxidising agent decreases during the reaction. For example, in the reaction between magnesium and oxygen, the oxygen is the oxidising agent, as it causes magnesium to lose electrons and form Mg^{2+}.

P

paper chromatography An analytical technique for separating and identifying mixtures that uses paper as the stationary phase.

parent molecule The alkane from which the name of a molecule is derived from.

partial pressure The pressure exerted by one component of a mixture of gases. The total pressure of a mixture of gases is equal to the sum of the individual partial pressures of each component in the mixture.

pascal Unit of pressure equal to 1 newton per square metre ($1\ N\ m^{-2}$), where:

$$\text{pressure} = \frac{\text{force}}{\text{area}}$$

peptide link or **peptide group** The –CONH– functional group between amino acid units in a polypeptide chain; also called amide link.

percentage yield A measure of the quantity of a product obtained from a chemical process compared to the maximum amount possible if the reaction were complete, expressed as a percentage:

$$\text{percentage yield} = \frac{\text{actual yield}}{\text{theoretical yield}} \times \frac{100}{1}$$

petrodiesel The most common form of diesel fuel. It is produced from crude oil by fractional distillation. The composition of petrodiesel varies, but is generally around 75% alkanes and 25% aromatic hydrocarbons. The alkanes range from $C_{10}H_{22}$ to $C_{15}H_{32}$.

pH curve A plot showing change in pH during a volumetric titration.

photochemical smog Atmospheric pollution produced through the action of sunlight on nitrogen oxides and unburned hydrocarbons to form ozone and other pollutants. The nitrogen oxides are formed in high temperature reactions such as those that occur in car engines and lightning strikes.

photosynthesis The chemical process by which oxygen and glucose are produced in plant cells in the presence of light. It can be represented by the equation:

$$6CO_2(g) + 6H_2O(l) \rightarrow C_6H_{12}O_2(aq) + 6O_2(g)$$

pipette Glassware used for volumetric analysis to transfer a fixed volume of solution accurately.

plane of symmetry A plane of symmetry divides a three-dimensional object into two equal halves that are mirror images of each other.

pleating When sections of a protein line up parallel to each other owing to hydrogen bonding.

polar bond A covalent bond in which the electrons are not shared equally between the two atoms in the bond.

polymer A natural or synthetic compound of high molar mass consisting of up to millions of repeated linked units known as monomers. There are many different types of polymers.

polypeptide An organic polymer molecule made from a condensation reaction between amino acids.

polyprotic acid An acid that can donate more than one hydrogen ion.

polysaccharide A long chain carbohydrate made up of smaller carbohydrates called monosaccharides. Each monosaccharide is connected by glycosidic links. Starch, glycogen and cellulose are polysaccharides.

polyunsaturated fatty acid Fatty acid that contains more than one carbon–carbon double bond.

position of equilibrium The relative amounts of reactants and products at equilibrium. The position of equilibrium varies depending on the extent of the reaction.

positional isomers Isomers that arise from a functional group being in different locations on the carbon chain.

potential difference The electromotive force between two points in a circuit, such as the electrodes of an electrochemical cell.

pressure The force exerted per unit area of a surface.

primary alcohol An alcohol in which the carbon that is bonded to the –OH group is only attached to one alkyl group.

primary amine An amine in which the nitrogen atom is bonded to one carbon and two hydrogen atoms.

primary cell A galvanic cell that is non-rechargeable because the products of the reaction migrate away from the electrodes.

primary standard A substance used to make a standard solution. It is so pure that its amount, in moles, can be accurately determined from its mass.

primary structure The sequence (number, order and type) of amino acids in a polypeptide chain.

protein An organic polymer molecule made from amino acids by condensation polymerisation. Approximately 50 or more amino acids form a protein.

protein sequencing A technique used to determine the amino acid sequence of a polypeptide.

proton NMR spectroscopy Also called ^1H NMR spectroscopy. A type of nuclear magnetic resonance spectroscopy that investigates the ^1H nucleus. It is used to determine the chemical environment of hydrogen atoms in compounds and gives information about the environments neighbouring each hydrogen atom.

Q

qualitative analysis An analysis based on apparent, non-measurable qualities that may be subjective. In chromatography, this type of analysis is used to determine the identity of the chemical(s) present in a substance.

quantitative analysis The determination of the quantities of particular components present in a substance.

quantum A discrete amount of electromagnetic radiation.

quaternary structure The highest level of organisation in protein structure. Proteins have a quaternary structure if they are composed of two or more polypeptide chains.

R

R group The side chain in an amino acid molecule or amino acid unit in a polypeptide chain. It can be composed of different sets of atoms. The amino acids used to make the proteins in the human body have 20 different R groups.

rancid Describes a lipid that has broken to produce smaller molecules with noxious odours and flavours.

rate of reaction The change in concentration of a reactant or product over a period of time (usually one second):

$$\text{rate of reaction} = \frac{\text{change in concentration}}{\text{time}}$$

reaction pathway A series of chemical reactions that converts a starting material into a product in a number of steps.

reaction quotient This is another name for the concentration fraction. It is the ratio of concentrations of products to reactants in a reversible reaction, as expressed in the equilibrium law.

reaction table A useful tool for solving equilibrium problems; sometimes referred to as a RICE table, where R stands for the chemical equation for the reaction, I stands for the initial amounts (or concentrations) for each species in the reaction mixture, C represents the change in the amounts (or concentrations) for each species as the system moves towards equilibrium, and E represents the equilibrium amounts (or concentrations) of each species when the system is in a state of equilibrium.

reactive electrode An electrode that is consumed in an electrochemical cell reaction.

rechargeable cell A type of cell in which the chemical energy can be replenished repeatedly through application of electrical energy.

redox reaction A reaction in which electron transfer occurs from the reducing agent to the oxidising agent. In a redox reaction, the oxidation number of one element will increase (be oxidised) and the oxidation number of another element will decrease (be reduced).

reduced The gain of electrons or a decrease in oxidation number. When a substance is reduced, the electrons are written on the left-hand side of the arrow (as reactants) in the half-equation.

reducing agent A reactant that causes another reactant to gain electrons during a redox reaction. This reactant is, itself, oxidised and loses electrons. For example, in the reaction between magnesium and oxygen, the magnesium is the reducing agent, as it causes oxygen to gain electrons and form O^{2-} ions:

$$2Mg(s) + O_2(g) \rightarrow 2MgO(s)$$

reductant A substance that causes another substance to be reduced; in the process the reductant is oxidised. A reductant is also called a reducing agent.

reduction The process by which a chemical species gains electrons or its oxidation number decreases. A reduction half-equation will show the electrons on the reactant side (left-hand side) of the equation.

renewable Resources are renewable if they are not finite (e.g. wind power) or can be replenished (e.g. biochemical fuels).

retardation factor In paper and thin-layer chromatography, the ratio of the distance a component has moved from the origin to the distance the solvent (mobile phase) has moved from the origin; symbol R_f.

retention time The time taken for a component to pass through a chromatography column; symbol R_t.

reversed-phase HPLC A form of HPLC that uses a non-polar stationary phase.

reversible reaction A reaction in which significant reaction can occur in the reverse direction because the products are present and can react with each other under suitable conditions.

S

salt bridge An electrical connection between the two half-cells in a galvanic cell; it is usually made from a material saturated in electrolyte solution.

saponification A process in which soap is produced by heating a fat or vegetable oil with alkali.

saturated Describes hydrocarbons composed of molecules with only carbon–carbon single bonds.

saturated ester An ester in which the hydrocarbon tail contains only carbon–carbon single bonds.

saturated fatty acid Fatty acid that contains carbon–carbon single bonds.

saturated molecule An organic compound in which all the atoms are joined by single bonds.

saturated solution A solution that cannot dissolve any more solute at the given temperature.

secondary alcohol An alcohol in which the carbon bonded to the –OH group is also bonded to two alkyl groups. The alkyl groups may be the same or different.

secondary cell An accumulator or rechargeable cell. Recharging can occur because the products formed in the cell during discharge remain in contact with the electrodes in a convertible form.

secondary structure Initial level of spatial arrangement of a polypeptide chain. There are two forms of secondary structure: α-helices and β-pleated sheets.

self-discharge A process in which batteries lose their stored charge without any external connection between their electrodes. This results from internal chemical reactions within the battery.

semipermeable membrane A a type of membrane that will only allow certain molecules or ions to pass through it.

semistructural formula A condensed formula that summarises the structural formula of a compound in a single line of text.

shale gas Natural gas that is trapped in shale rock, usually well below Earth's surface.

SI units An internationally accepted system of physical units. For example, the SI unit for energy is the joule, J.

side chain The R group in an amino acid molecule; there are 20 different side chains on the 2-amino acids used to make human proteins.

smelting The process where a metal ore is heated in order to separate the desirable components from the other parts of the ore.

solution calorimeter An insulated container that holds a known volume of water and in which a reaction in solution, such as dissolution of a solid or a neutralisation reaction, can be carried out.

solvent front Describes the movement of the solvent during chromatography. It is visible as the wet moving edge of the solvent as it travels along the stationary phase.

specific heat capacity The amount of energy required to increase the temperature of 1 g of a substance by1°C. The specific heat capacity of water is 4.18 $J\ °C^{-1}\ g^{-1}$.

spiking A procedure used to tentatively identify a component within a mixture by high-performance liquid chromatography. If a chemical is thought to be one of the components of a mixture, it can be added to the sample. If there are no extra peaks in the chromatogram, just a larger peak for one of the components, it is assumed that the added chemical is one of the components of the mixture.

splitting pattern The resultant multi-peaked signal that a proton gives in a ^1H NMR spectrum when it has hydrogens in neighbouring environments. The number of lines in the pattern is equal to the number of neighbouring hydrogen atoms plus one, or '$n + 1$'.

spontaneous reaction A reaction that occurs naturally, either in electrochemical cells or when chemicals are mixed directly. The reaction does not need to be driven by an external source of energy.

standard Chemical of known composition used for comparison.

standard atmosphere One standard atmosphere (1 atm) is the pressure required to support 760 millimetres of mercury (760 mmHg) in a mercury barometer at 25°C. One atmosphere pressure is approximately the pressure experienced at sea level.

standard conditions Established reference conditions to compare testing of experimental activities. Conditions at which gas pressure is 1 bar (100 kPa), the concentrations of dissolved species are 1.0 M and the temperature is 25°C (298 K).

standard electrode potential The electromotive force that is measured when a half-cell, at standard conditions (gas pressures 1 bar, solution concentrations of 1.0 M and temperature of 25°C), is connected to a standard hydrogen half-cell; symbol $E°$. Gives a numerical measure of the tendency of a half-cell reaction to occur as a reduction reaction.

standard hydrogen half-cell A $H^+(aq)/H_2(g)$ half-cell; made from a platinum electrode placed in acid solution with hydrogen gas bubbled over it. The pressure of the gas is 1 bar, the H^+ concentration is 1 M and the temperature is 25°C.

standard laboratory conditions (SLC) Conditions of temperature and pressure relevant to a gas, where the temperature is 298 K (25°C) and the pressure is 100 kPa.

standard reduction potential A numerical measure of the tendency of a half-cell reaction to occur as a reduction reaction. It is measured by connecting a half-cell, at standard conditions (gas pressures 1 bar, solution concentrations of 1.0 M and temperature of 25°C), to a standard hydrogen half-cell.

standard solution A solution of accurately known concentration.

standard temperature and pressure (STP) Conditions of temperature and pressure relevant to a gas, where the temperature is 0°C (273 K) and pressure is 100 kPa.

standardised The process by which the concentration of a solution is accurately determined, often through titration with a standard solution.

starch A polysaccharide formed from the polymerisation of α-glucose molecules. Starch is an odourless and tasteless white substance that occurs widely in plant tissue. It is used by plants to store energy.

stationary phase A solid, or a viscous liquid that is coated into a solid, used in chromatography. The components of a mixture undergo adsorption to this phase as they are carried along by the mobile phase.

steam reforming A process that produces hydrogen, carbon monoxide or other useful products from hydrocarbon fuels such as natural gas.

stem name The name of a molecule derived from the number of carbon atoms in the longest continuous carbon chain in a hydrocarbon and the highest priority functional group present. For example, the stem name of 2-chlorobutan-1-ol is butan-1-ol.

stereoisomer A type of isomer in which the atoms in two molecules are connected in the same order, but have different arrangements in space.

stock solution A high concentration solution which is diluted to a lower concentration before use.

stoichiometry The calculation of relative amounts of reactants and products in a chemical reaction. Chemical equations give the ratios of the amounts (moles) of the reactants and products.

structural formula A formula that represents the three-dimensional arrangement of atoms in a molecule.

structural isomers Isomers are molecules that have the same molecular formulas but their atoms are bonded together in different ways.

substitution reaction A reaction that involves the replacement of an atom or group of atoms with another atom or group of atoms.

substrate A reactant in a reaction that is catalysed by an enzyme.

surface area The area of all surfaces of the substance that are exposed to the other reactants. This is proportional to the amount of particles available at the surface to react.

surroundings The rest of the universe around a particular chemical reaction. The chemical reaction is the system. Energy moves between the system and surroundings in exothermic and endothermic reactions.

sustainable Able to support energy and resources into the future without depletion.

system In chemistry, a system is a chemical reaction. A system operates within its surroundings. Energy can move between the two. You always consider energy as being absorbed or released from the perspective of the system. For example, energy is absorbed into the system from the surroundings, or energy is released by the system to the surroundings.

T

tertiary alcohol An alcohol in which the carbon bonded to the –OH group is also bonded to three alkyl groups.

tertiary structure The overall three-dimensional shape of a polypeptide chain.

tetrahedral In the shape of a tetrahedron, where four points at equal distances are spread as far apart as possible in three dimensions.

theoretical yield The mass of product that would be formed if the limiting reagent reacted fully. The mass that is expected for a particular product in a chemical reaction, based on the mass of limiting reactant used.

thermochemical equation A chemical equation that includes the enthalpy change of the reaction, ΔH. For example:

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

thin-layer chromatography (TLC) A chromatography technique that uses a thin layer of fine powder spread on a glass or plastic plate as the stationary phase.

titration The process used to determine the concentration of a reactant where one solution is added from a burette to a known volume of another solution.

titration curve A graph obtained from a titration of pH against volume of reactant added from a burette.

titre A variable volume of liquid measured in a burette by subtracting the final burette reading of a titration from the initial burette reading.

***trans* isomer** An isomer in which the highest priority groups attached to the carbons of a double bond are on opposite sides of the double bond plane.

transesterification A process in which triglyceride reacts with an alcohol to form esters.

transition element An element, such as iron, copper, nickel or chromium, that is found in the middle block of the periodic table, in groups 3–12.

transition state An arrangement of atoms in a reaction that occurs when sufficient energy is absorbed for the activation energy to be reached. It represents the stage of maximum potential energy in the reaction. Bond breaking and bond forming are both occurring at this stage, and the arrangement of atoms is unstable.

transmittance The ratio of light that passes through a sample compared to the light given off by the source.

triglyceride An ester derived from a glycerol molecule and three fatty acids.

tripeptide An organic molecule made from three amino acid units linked by peptide bonds.

U

universal gas equation The equation that describes the behaviour of an ideal gas: $PV = nRT$

unsaturated Describes hydrocarbons composed of molecules containing one or more carbon–carbon double or triple bonds.

unsaturated ester An ester in which the hydrocarbon tail contains at least one carbon–carbon double bond.

unsaturated molecule An organic molecule that contains one or more carbon–carbon double or triple bonds.

V

valence number The number of valence electrons in an atom of an element.

valence shell electron pair repulsion (VSEPR) theory A model in chemistry used to predict the shape of molecules based on electrostatic repulsion between electron pairs.

velocity A measurement of the rate and direction of motion of an object. It has the symbol v, and the unit m s^{-1}.

vibrational energy levels Different fixed energies that molecules can have as a result of the bending and stretching of bonds.

viscosity A measure of a liquid's resistance to flow. Honey has a high viscosity and petrol has a low viscosity.

vitamin An organic compound required by the body to prevent a disease or medical condition. Most vitamins are substances not produced in the human body.

volt The unit of potential difference.

voltaic cell A type of electrochemical cell that is also known as a galvanic cell; a device that converts chemical energy into electrical energy.

voltmeter An instrument for measuring electrical potential difference between two points in a circuit.

volume The amount of space that a substance occupies. It can be calculated by multiplying length by width by depth of a regular solid. Otherwise it can be determined by finding the volume of water displaced by the substance.

volumetric analysis Quantitative analysis using measurement of solution volumes, usually involving titration.

W

wavenumber A unit of frequency used in infrared spectroscopy. It is equal to the inverse of the wavelength of the radiation, and is measured in cm^{-1}.

Z

zwitterion A dipolar ion formed when the amino and carboxyl groups in an amino acid or polypeptide are both charged.

Index

Page references in **bold** refer to the main discussion of key terms in the text.

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Notes

Notes

Groups

s BLOCK

p BLOCK

ATOMIC NUMBER → 12
SYMBOL → Mg
ELECTRON STRUCTURE → [Ne]$3s^{2}$
Magnesium
RELATIVE ATOMIC MASS ( ) indicates most stable isotope → 24.3
BOILING POINT °C → 1090
MELTING POINT °C → 650
ELECTRONEGATIVITY → 1.3

d BLOCK

Periods	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1									1 1.0 H -252.9 -259 2.2 $1s^{1}$ Hydrogen									2 4.0 He -268.9 -272 – $1s^{2}$ Helium
2	3 6.9 Li 1347 180 1.0 $1s^{2}2s^{1}$ Lithium	4 9.0 Be 2468 1287 1.6 $1s^{2}2s^{2}$ Beryllium											5 10.8 B 4000 2077 2.0 $1s^{2}2s^{2}2p^{1}$ Boron	6 12.0 C 4827 3500 2.6 $1s^{2}2s^{2}2p^{2}$ Carbon	7 14.0 N -195.8 -210 3.0 $1s^{2}2s^{2}2p^{3}$ Nitrogen	8 16.0 O -183 -219 3.4 $1s^{2}2s^{2}2p^{4}$ Oxygen	9 19.0 F -188.1 -220 4.0 $1s^{2}2s^{2}2p^{5}$ Fluorine	10 20.2 Ne -246 -249 – $1s^{2}2s^{2}2p^{6}$ Neon
3	11 23.0 Na 882.9 97.8 0.9 [Ne]$3s^{1}$ Sodium	12 24.3 Mg 1090 650 1.3 [Ne]$3s^{2}$ Magnesium											13 27.0 Al 2519 660.3 1.6 [Ne]$3s^{2}3p^{1}$ Aluminium	14 28.1 Si 3265 1414 1.9 [Ne]$3s^{2}3p^{2}$ Silicon	15 31.0 P 280.5 44.2 2.2 [Ne]$3s^{2}3p^{3}$ Phosphorus	16 32.1 S 444.6 115.2 2.6 [Ne]$3s^{2}3p^{4}$ Sulfur	17 35.5 Cl -34 -102 3.2 [Ne]$3s^{2}3p^{5}$ Chlorine	18 39.9 Ar -185.8 -189 – [Ne]$3s^{2}3p^{6}$ Argon
4	19 39.1 K 758.8 63.5 0.8 [Ar]$4s^{1}$ Potassium	20 40.1 Ca 1484 842 1.0 [Ar]$4s^{2}$ Calcium	21 45.0 Sc 2836 1541 1.4 [Ar]$3d^{1}4s^{2}$ Scandium	22 47.9 Ti 3287 1670 1.5 [Ar]$3d^{2}4s^{2}$ Titanium	23 50.9 V 3407 1910 1.6 [Ar]$3d^{3}4s^{2}$ Vanadium	24 52.0 Cr 2671 1907 1.7 [Ar]$3d^{5}4s^{1}$ Chromium	25 54.9 Mn 2061 1246 1.6 [Ar]$3d^{5}4s^{2}$ Manganese	26 55.8 Fe 2861 1538 1.8 [Ar]$3d^{6}4s^{2}$ Iron	27 58.9 Co 2927 1495 1.9 [Ar]$3d^{7}4s^{2}$ Cobalt	28 58.7 Ni 2913 1455 1.9 [Ar]$3d^{8}4s^{2}$ Nickel	29 63.5 Cu 2560 1085 1.9 [Ar]$3d^{10}4s^{1}$ Copper	30 65.4 Zn 907 419.5 1.6 [Ar]$3d^{10}4s^{2}$ Zinc	31 69.7 Ga 2229 27.8 1.8 [Ar]$3d^{10}4s^{2}4p^{1}$ Gallium	32 72.6 Ge 2833 938.2 2.0 [Ar]$3d^{10}4s^{2}4p^{2}$ Germanium	33 74.9 As 613 816.8 2.2 [Ar]$3d^{10}4s^{2}4p^{3}$ Arsenic	34 79.0 Se 684.8 220.8 2.6 [Ar]$3d^{10}4s^{2}4p^{4}$ Selenium	35 79.9 Br 58.8 -7.2 3.0 [Ar]$3d^{10}4s^{2}4p^{5}$ Bromine	36 83.8 Kr -153.4 -157 – [Ar]$3d^{10}4s^{2}4p^{6}$ Krypton
5	37 85.5 Rb 687.8 39 0.8 [Kr]$5s^{1}$ Rubidium	38 87.6 Sr 1377 777 1.0 [Kr]$5s^{2}$ Strontium	39 88.9 Y 3345 1522 1.2 [Kr]$4d^{1}5s^{2}$ Yttrium	40 91.2 Zr 4406 1854 1.3 [Kr]$4d^{2}5s^{2}$ Zirconium	41 92.9 Nb 4741 2477 1.6 [Kr]$4d^{4}5s^{1}$ Niobium	42 96.0 Mo 4639 2622 2.2 [Kr]$4d^{5}5s^{1}$ Molybdenum	43 (98) Tc 4262 2157 2.1 [Kr]$4d^{5}5s^{2}$ Technetium	44 101.1 Ru 4147 2333 2.2 [Kr]$4d^{7}5s^{1}$ Ruthenium	45 102.9 Rh 3695 1963 2.3 [Kr]$4d^{8}5s^{1}$ Rhodium	46 106.4 Pd 2963 1555 2.2 [Kr]$4d^{10}5s^{0}$ Palladium	47 107.9 Ag 2162 961.8 1.9 [Kr]$4d^{10}5s^{1}$ Silver	48 112.4 Cd 766.8 321.1 1.7 [Kr]$4d^{10}5s^{2}$ Cadmium	49 114.8 In 2072 156.6 1.8 [Kr]$4d^{10}5s^{2}5p^{1}$ Indium	50 118.7 Sn 2602 231.9 2.0 [Kr]$4d^{10}5s^{2}5p^{2}$ Tin	51 121.8 Sb 1587 630.6 2.0 [Kr]$4d^{10}5s^{2}5p^{3}$ Antimony	52 127.6 Te 987.8 449.5 2.1 [Kr]$4d^{10}5s^{2}5p^{4}$ Tellurium	53 126.9 I 184.4 113.7 2.7 [Kr]$4d^{10}5s^{2}5p^{5}$ Iodine	54 131.3 Xe -108.1 -112 2.6 [Kr]$4d^{10}5s^{2}5p^{6}$ Xenon
6	55 132.9 Cs 670.8 28.5 0.8 [Xe]$6s^{1}$ Caesium	56 137.3 Ba 1845 727 0.9 [Xe]$6s^{2}$ Barium	57 138.9 La 2464 920 1.1 [Xe]$5d^{1}6s^{2}$ Lanthanum	72 178.5 Hf 4600 2233 1.3 [Xe]$4f^{14}5d^{2}6s^{2}$ Hafnium	73 180.9 Ta 5455 3017 1.5 [Xe]$4f^{14}5d^{3}6s^{2}$ Tantalum	74 183.8 W 5555 3414 1.7 [Xe]$4f^{14}5d^{4}6s^{2}$ Tungsten	75 186.2 Re 5596 3454 1.9 [Xe]$4f^{14}5d^{5}6s^{2}$ Rhenium	76 190.2 Os 5008 3033 2.2 [Xe]$4f^{14}5d^{6}6s^{2}$ Osmium	77 192.2 Ir 4428 2446 2.2 [Xe]$4f^{14}5d^{7}6s^{2}$ Iridium	78 195.1 Pt 3825 1768 2.2 [Xe]$4f^{14}5d^{9}6s^{1}$ Platinum	79 197.0 Au 2836 1064 2.2 [Xe]$4f^{14}5d^{10}6s^{1}$ Gold	80 200.6 Hg 356.6 -38.8 1.9 [Xe]$4f^{14}5d^{10}6s^{2}$ Mercury	81 204.4 Tl 1473 303.8 1.8 [Xe]$4f^{14}5d^{10}6s^{2}6p^{1}$ Thallium	82 207.2 Pb 1749 327.5 1.8 [Xe]$4f^{14}5d^{10}6s^{2}6p^{2}$ Lead	83 209.0 Bi 1564 271.4 1.9 [Xe]$4f^{14}5d^{10}6s^{2}6p^{3}$ Bismuth	84 (210) Po 962 253.8 2.0 [Xe]$4f^{14}5d^{10}6s^{2}6p^{4}$ Polonium	85 (210) At 366.8 301.8 2.2 [Xe]$4f^{14}5d^{10}6s^{2}6p^{5}$ Astatine	86 (222) Rn -61.8 -71.2 – [Xe]$4f^{14}5d^{10}6s^{2}6p^{6}$ Radon
7	87 (223) Fr 676.8 27 0.7 [Rn]$7s^{1}$ Francium	88 (226) Ra 1140 699.8 0.9 [Rn]$7s^{2}$ Radium	89 (227) Ac 3200 1050 1.1 [Rn]$6d^{1}7s^{2}$ Actinium	104 (261) Rf – – – [Rn]$5f^{14}6d^{2}7s^{2}$ Rutherfordium	105 (262) Db – – – [Rn]$5f^{14}6d^{3}7s^{2}$ Dubnium	106 (266) Sg – – – [Rn]$5f^{14}6d^{4}7s^{2}$ Seaborgium	107 (264) Bh – – – [Rn]$5f^{14}6d^{5}7s^{2}$ Bohrium	108 (267) Hs – – – [Rn]$5f^{14}6d^{6}7s^{2}$ Hassium	109 (268) Mt – – – [Rn]$5f^{14}6d^{7}7s^{2}$ Meitnerium	110 (271) Ds – – – [Rn]$5f^{14}6d^{8}7s^{2}$ Darmstadtium	111 (272) Rg – – – [Rn]$5f^{14}6d^{9}7s^{2}$ Roentgenium	112 (285) Cn – – – [Rn]$5f^{14}6d^{10}7s^{2}$ Copernicium	113 (284) Uut* – – – [Rn]$5f^{14}6d^{10}7s^{1}7p^{1}$ Ununtrium	114 (289) Fl – – – [Rn]$5f^{14}6d^{10}7s^{2}7p^{2}$ Flerovium	115 (289) Uup* – – – [Rn]$5f^{14}6d^{10}7s^{2}7p^{3}$ Ununpentium	116 (292) Lv – – – [Rn]$5f^{14}6d^{10}7s^{2}7p^{4}$ Livermorium	117 (294) Uus* – – – [Rn]$5f^{14}6d^{10}7s^{2}7p^{5}$ Ununseptium	118 (294) Uuo* – – – [Rn]$5f^{14}6d^{10}7s^{2}7p^{6}$ Ununoctium

*temporary names

f BLOCK

58 140.1 Ce 3443 799 1.1 [Xe]$4f^{2}5d^{0}6s^{2}$ Cerium	59 140.9 Pr 3520 931 1.1 [Xe]$4f^{3}5d^{0}6s^{2}$ Praseodymium	60 144.2 Nd 3074 1016 1.1 [Xe]$4f^{4}5d^{0}6s^{2}$ Neodymium	61 (145) Pm 3000 1042 – [Xe]$4f^{5}5d^{0}6s^{2}$ Promethium	62 150.4 Sm 1794 1072 1.1 [Xe]$4f^{6}5d^{0}6s^{2}$ Samarium	63 152.0 Eu 1794 1072 – [Xe]$4f^{7}5d^{0}6s^{2}$ Europium	64 157.3 Gd 3273 1313 1.2 [Xe]$4f^{7}5d^{1}6s^{2}$ Gadolinium	65 158.9 Tb 3230 1359 – [Xe]$4f^{9}5d^{0}6s^{2}$ Terbium	66 162.5 Dy 2567 1412 1.2 [Xe]$4f^{10}5d^{0}6s^{2}$ Dysprosium	67 164.9 Ho 2700 1472 1.2 [Xe]$4f^{11}5d^{0}6s^{2}$ Holmium	68 167.3 Er 2868 1529 1.2 [Xe]$4f^{14}5d^{0}6s^{2}$ Erbium	69 168.9 Tm 1950 1545 1.2 [Xe]$4f^{12}5d^{0}6s^{2}$ Thulium	70 173.1 Yb 1196 824 – [Xe]$4f^{14}5d^{0}6s^{2}$ Ytterbium	71 175.0 Lu 3402 1663 1.0 [Xe]$4f^{14}5d^{1}6s^{2}$ Lutetium
90 232.0 Th 4875 1750 1.3 [Rn]$5f^{0}6d^{2}7s^{2}$ Thorium	91 231.0 Pa – 1572 1.5 [Rn]$5f^{2}6d^{1}7s^{2}$ Protactinium	92 238.0 U 4131 1135 1.7 [Rn]$5f^{3}6d^{1}7s^{2}$ Uranium	93 (237) Np 3902 644 1.3 [Rn]$5f^{4}6d^{1}7s^{2}$ Neptunium	94 (244) Pu 3228 640 1.3 [Rn]$5f^{6}6d^{0}7s^{2}$ Plutonium	95 (243) Am 2011 1176 – [Rn]$5f^{7}6d^{0}7s^{2}$ Americium	96 (247) Cm – 1345 – [Rn]$5f^{7}6d^{1}7s^{2}$ Curium	97 (247) Bk – 986 – [Rn]$5f^{9}6d^{0}7s^{2}$ Berkelium	98 (251) Cf – 900 – [Rn]$5f^{10}6d^{0}7s^{2}$ Californium	99 (252) Es – 860 – [Rn]$5f^{11}6d^{0}7s^{2}$ Einsteinium	100 (257) Fm – 1527 – [Rn]$5f^{12}6d^{0}7s^{2}$ Fermium	101 (258) Md – 827 – [Rn]$5f^{13}6d^{0}7s^{2}$ Mendelevium	102 (259) No – 827 – [Rn]$5f^{14}6d^{0}7s^{2}$ Nobelium	103 (262) Lr – 1627 – [Rn]$5f^{14}6d^{1}7s^{2}$ Lawrencium