JACARANDA
CHEMISTRY 2
VCE UNITS 3 AND 4 | SECOND EDITION

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JACARANDA

CHEMISTRY 2

VCE UNITS 3 AND 4 | SECOND EDITION

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AREA OF STUDY 2 REVIEW

ABOUT THIS RESOURCE

Jacaranda Chemistry has been reimagined to provide students and teachers with the most comprehensive resource on the market. This engaging and purposeful suite of resources is fully aligned to the VCE Chemistry Study Design (2017–2021).

Formats

Jacaranda Chemistry is now available in print and a range of digital formats, including:

Print	**learnON**	**eBookPLUS**	**PDF**	**eGuidePLUS**
Printed textbook with free digital access code inside	learnON is our immersive and flexible digital learning platform	The eBookPLUS is an electronic version of the student text	Downloadable PDFs available with eBookPLUS	The eGuidePLUS includes everything from the eBookPLUS with additional resources designed for teachers

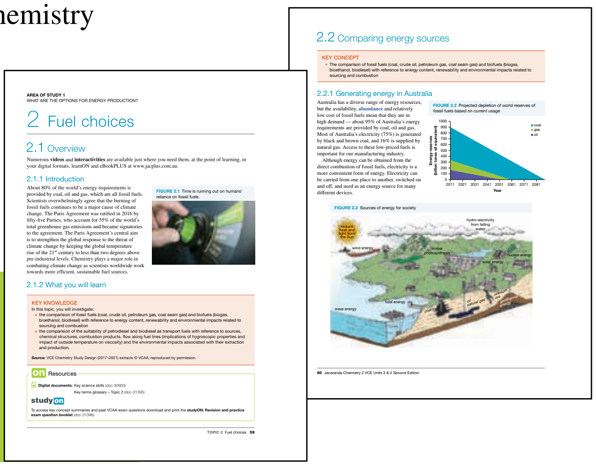
Fully aligned to the VCE Chemistry Study Design

Have confidence that you are covering the entire VCE Chemistry Study Design (2017–2021), with:

- tailored exercise sets at the end of each sub-topic
- additional background information easily distinguished from curriculum content
- practice SACs clearly linked to each outcome
- practice exams for each area of study.

Key concepts approach

Students can easily understand which aspect of the Study Design they are studying with Key Knowledge dot points highlighted at the start of each topic and broken down into Key Concepts in each sub-topic.



AREA OF STUDY 1
WHAT ARE THE OPTIONS FOR ENERGY PRODUCTION?

2 Fuel choices

2.1 Overview

Numerous **videos** and **interactivities** are available just where you need them, at the point of learning, in your digital formats, learnON and eBookPLUS at www.jacplus.com.au.

2.1.1 Introduction

About 80% of the world's energy requirements is provided by coal, oil and gas, which are all fossil fuels. Scientists overwhelmingly agree that the burning of fossil fuels continues to be a major cause of climate change. The Paris Agreement was ratified in 2016 by fifty-five Parties, who account for 55% of the world's total greenhouse gas emissions and became signatories to the agreement. The Paris Agreement's central aim is to strengthen the global response to the threat of climate change by keeping the global temperature rise of the 21st century to less than two degrees above pre-industrial levels. Chemistry plays a major role in combating climate change as scientists worldwide work towards more efficient, sustainable fuel sources.

FIGURE 2.1 Time is running out on humans' reliance on fossil fuels.

2.1.2 What you will learn

KEY KNOWLEDGE
In this topic, you will investigate:
- the comparision 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 comparision 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.

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on Resources
Digital documents: Key science skills (doc-30903)
Key terms glossary – Topic 2 (doc-31395)
studyon
To access key concept summaries and past VCAA exam questions download and print the **studyON: Revision and practice exam question booklet** (doc-31396).

TOPIC 2 Fuel choices 59

2.2 Comparing energy sources

KEY CONCEPT
- 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

2.2.1 Generating energy in Australia

Australia has a diverse range of energy resources, but the availability, **abundance** and relatively low cost of fossil fuels mean that they are in high demand — about 95% of Australia's energy requirements are provided by coal, oil and gas. Most of Australia's electricity (75%) is generated by black and brown coal, and 16% is supplied by natural gas. Access to these low-priced fuels is important for our manufacturing industry.

Although energy can be obtained from the direct combustion of fossil fuels, electricity is a more convenient form of energy. Electricity can be carried from one place to another, switched on and off, and used as an energy source for many different devices.

FIGURE 2.2 Projected depletion of world reserves of fossil fuels based on current usage

FIGURE 2.3 Sources of energy for society

60 Jacaranda Chemistry 2 VCE Units 3 & 4 Second Edition

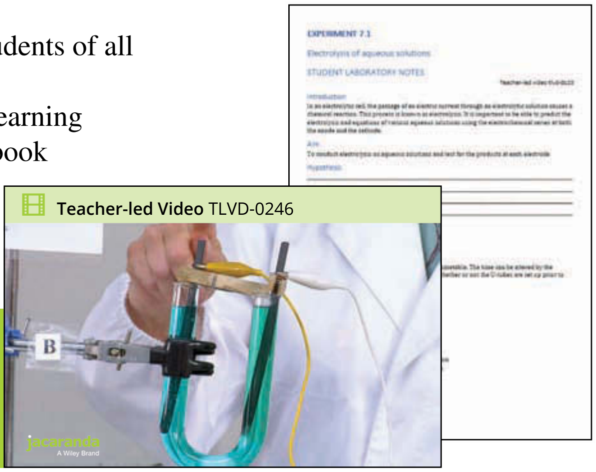
Engaging resources and rich media

A variety of online and offline resources to encourage students of all learning styles, including:

- videos and interactivities embedded at the point of learning
- practical investigations complete with printable logbook
- a variety of worksheets and activities allow students to apply their knowledge of the content.

Teacher-led videos

Videos of various sample problems and practical investigations led by experienced teachers allow students to better consolidate their learning.



EXPERIMENT 7.1

Electrolysis of aqueous solutions

STUDENT LABORATORY NOTES

Introduction

Aim

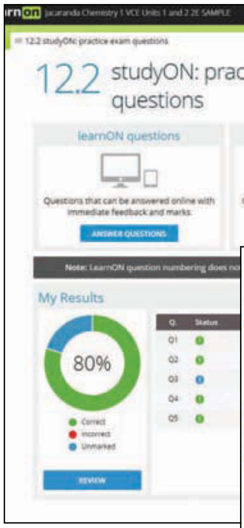
Hypothesis

Teacher-led Video TLVD-0246

Inspiring students to become independent learners

This resource, on the immersive digital platform learnON, encourages self-driven student learning through:

- fully worked solutions for every question providing students with immediate feedback
- progress tracked automatically in learnON allowing students to reflect on their learning, and enabling students to highlight areas of strength and weakness
- topic summary, key terms and practice questions at the end of every topic
- sample problems with fully worked solutions set out in the THINK–WRITE format.



12.2 studyON: practice exam questions

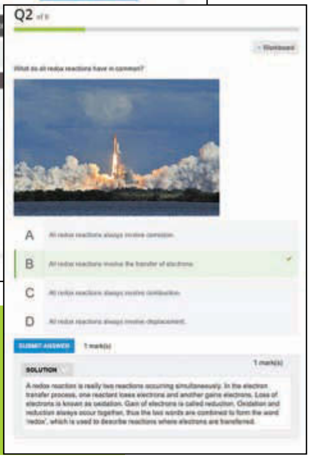
learnON questions

Questions that can be answered online with immediate feedback and marks

Textbook questions

Questions from your print or PDF textbook and eBookPLUS for this subtopic

Q.	Status
Q1	●
Q2	●
Q3	●
Q4	●
Q5	●



What do all redox reactions have in common?

A All redox reactions always involve corrosion.

B All redox reactions involve the transfer of electrons.

C All redox reactions always involve combustion.

D All redox reactions always involve displacement.

SOLUTION

A redox reaction is really two reactions occurring simultaneously. In the electron transfer process, one reactant loses electrons and another gains electrons. Loss of electrons is known as oxidation. Gain of electrons is called reduction. Oxidation and reduction always occur together, thus the two words are combined to form the word 'redox', which is used to describe reactions where electrons are transferred.

studyon

Prepare for exams with every past exam question since 2006! studyON is now included in learnON and as a printable exam revision booklet

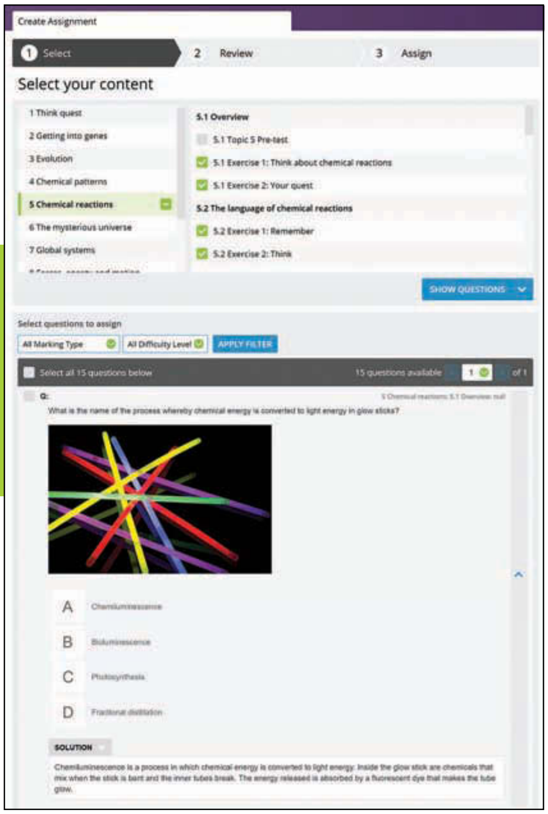
A wealth of teacher resources

Jacaranda Chemistry empowers teachers to teach their class their way with the extensive range of teacher resources including:

- quarantined topic tests and SACs that are easily customisable
- practical investigation support with demonstrative videos, laboratory information, expected results and risk assessments
- work programs
- curriculum grids.

Test Maker

Create custom tests for your class from the entire question pool — including all subtopic, topic review and past VCAA exam questions



Select your content

- 1 Think quest
- 2 Getting into genes
- 3 Evolution
- 4 Chemical patterns
- 5 Chemical reactions
- 6 The mysterious universe
- 7 Global systems

5.1 Overview

- ☐ 5.1 Topic 5 Pre-test
- ☑ 5.1 Exercise 1: Think about chemical reactions
- ☑ 5.1 Exercise 2: Your quest

5.2 The language of chemical reactions

- ☑ 5.2 Exercise 1: Remember
- ☑ 5.2 Exercise 2: Think

Select questions to assign

☐ Select all 15 questions below

15 questions available 1 of 1

Q:

What is the name of the process whereby chemical energy is converted to light energy in glow sticks?

A Chemiluminescence

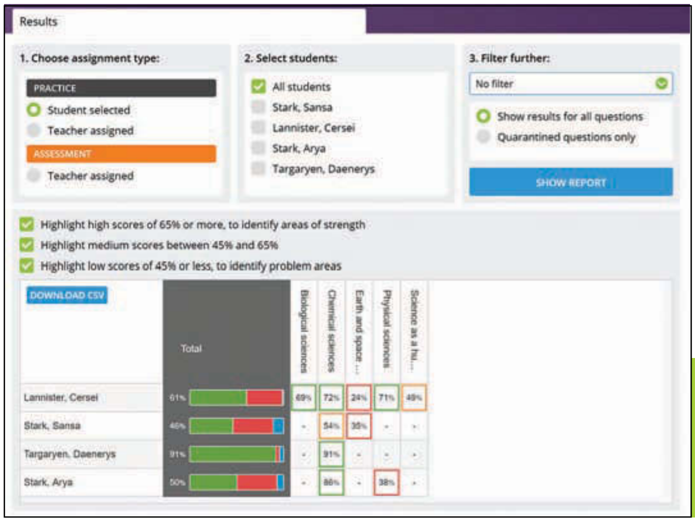
B Bioluminescence

C Photosynthesis

D Fractional distillation

SOLUTION

Chemiluminescence is a process in which chemical energy is converted to light energy. Inside the glow stick are chemicals that mix when the stick is bent and the inner tubes break. The energy released is absorbed by a fluorescent dye that makes the tube glow.



1. Choose assignment type:

PRACTICE
- ● Student selected
- ○ Teacher assigned

ASSESSMENT
- ○ Teacher assigned

2. Select students:

- ☑ All students
- ☐ Stark, Sansa
- ☐ Lannister, Cersei
- ☐ Stark, Arya
- ☐ Targaryen, Daenerys

3. Filter further:

No filter

- ● Show results for all questions
- ○ Quarantined questions only

- ☑ Highlight high scores of 65% or more, to identify areas of strength
- ☑ Highlight medium scores between 45% and 65%
- ☑ Highlight low scores of 45% or less, to identify problem areas

	Total	Biological sciences	Chemical sciences	Earth and space ...	Physical sciences	Science as a hu...
Lannister, Cersei	61%	69%	72%	24%	71%	49%
Stark, Sansa	46%	-	54%	35%	-	-
Targaryen, Daenerys	91%	-	91%	-	-	-
Stark, Arya	50%	-	86%	-	38%	-

Visibility of student results

Detailed breakdown of student results allows you to identify strengths and weaknesses across various topics and sub-topics.

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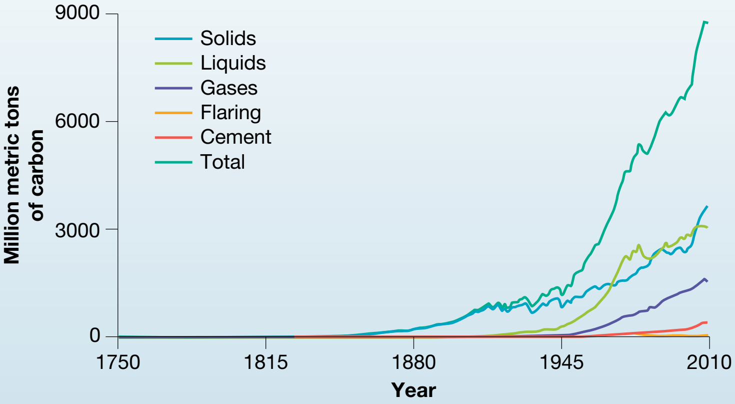
UNIT 3

HOW CAN CHEMICAL PROCESSES BE DESIGNED TO OPTIMISE EFFICIENCY?

FIGURE 1 Carbon emissions, pre-Industrial revolution to 2010.



When the Industrial Revolution began in the 1760s, the world's total population was approximately 750 million people. Today, the world's population stands at more than 7 billion people. New technologies and the growing population have created a demand for energy that has experienced near exponential growth. This growth is reflected in carbon emissions as shown in figure 1. While the quality of human life has undoubtedly increased since the Industrial Revolution, the size of the earth and its resources required to sustain life, has not.

With our growing population and demand for resources, it is imperative we understand and evaluate different chemical energy resources and manufacturing processes. We must ensure the efficient use of resources to create the products we need.

This unit examines chemical energy sources including fossil fuels, biofuels, galvanic cells and fuel cells. By investigating the combustion of fuels, including the energy transformations involved, stoichiometry can be applied to calculate the amount of resources required to produce the energy released. Galvanic cells, fuel cells and electrolytic cells are examined as a portable source of energy. The nature of their energy production is explained utilising the electrochemical series to predict and write half- and overall redox equations, and Faraday's laws are applied to calculate quantities in electrolytic reactions.

Finally, the efficiency of manufacturing processes are compared by understanding reaction rates and extent, equilibrium law and Le Châtelier's principle. This allows predictions of conditions that will improve the efficiency and percentage yield of chemical processes.

AREA OF STUDY	OUTCOME	CHAPTERS
1. What are the options for energy production?	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.	1. Obtaining energy from fuels 2. Fuel choices 3. Galvanic cells as a source of energy 4. Fuel cells as a source of energy
2. How can the yield of a chemical product be optimised?	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.	5. Rate of chemical reactions 6. Extent of chemical reactions 7. Production of chemicals by electrolysis, and rechargeable batteries

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AREA OF STUDY 1
WHAT ARE THE OPTIONS FOR ENERGY PRODUCTION?

1 Obtaining energy from fuels

1.1 Overview

Numerous **videos** and **interactivities** are available just where you need them, at the point of learning, in your digital formats, learnON and eBookPLUS at www.jacplus.com.au.

1.1.1 Introduction

Fuels are burned to produce heat energy. This energy is used to heat our homes, and for transport and industrial processes. It can also be converted into electrical energy, which can be conveniently transported over long distances and used to power many machines and appliances. The challenge for our society is to meet its increasing energy demands with a reliable supply of energy from clean, efficient and sustainable sources.

FIGURE 1.1 Fossil fuels will not last indefinitely — can biofuels provide the energy for all future transportation modes?

1.1.2 What you will learn

KEY KNOWLEDGE

In this topic, you will investigate:

- the definition of a fuel, including the distinction between fossil fuels and biofuels with reference to origin and renewability (the 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 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 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
- the use of specific heat capacity of water to determine the approximate amount of heat energy released in the combustion of a fuel.

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PRACTICAL WORK AND INVESTIGATIONS

Practical work is a central component of learning and assessment. Experiments and investigations, supported by a **Practical investigation logbook** and **Teacher-led videos**, are included in this topic to provide opportunities to undertake investigations and communicate findings.

on Resources

Digital documents Key science skills (doc-30903)
Key terms glossary — Topic 1 (doc-31392)
Practical investigation logbook (doc-31393)

studyon

To access key concept summaries and past VCAA exam questions download and print the **studyON: Revision and practice exam question booklet** (doc-31394).

1.2 Fossil fuels and biofuels

KEY CONCEPT

- 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)

1.2.1 What is a fuel?

A **fuel** is a substance that is exothermic, which means that it releases energy in the form of heat. Some fuels, such as uranium, release energy from nuclear reactions, but most fuels release heat energy when they react with oxygen. This is called combustion.

FIGURE 1.2 Explosives are an example of an exothermic fuel.

1.2.2 Distinction between a fossil fuel and a biofuel

Fossil fuels are carbon-based energy sources that were formed extremely slowly from the decaying remains of plants and animals that accumulated millions of years ago.

Biofuels are carbon-based energy sources that are primarily formed from plant matter. This biomass was created in a much shorter period of time (for example, 12 months for sugarcane) and can be used in its natural state or converted into a more easily usable form. In particular, **biogas**, **bioethanol** and **biodiesel** are used in Australia as energy sources, although research into improving the sustainability of biofuel production is ongoing. See topic 2 for more about Australia's energy sources.

1.2.3 Renewable and non-renewable resources

A fuel's renewability is based on the ability of a resource to be replaced by natural processes within a relatively short period of time. This means the amount of time it takes to produce the fuel by natural processes when compared to the rate at which the fuel is consumed. If the fuel can be replaced by natural processes at a rate that is greater than its consumption, then it is considered **renewable**. Biofuels, and solar, hydro-electric, tidal, geothermal and wave energy are all examples of renewable resources. Fossil and nuclear fuels cannot be replaced by natural processes at a rate that is greater than their consumption and so are **non-renewable**.

FIGURE 1.3 Renewable and non-renewable energy sources.

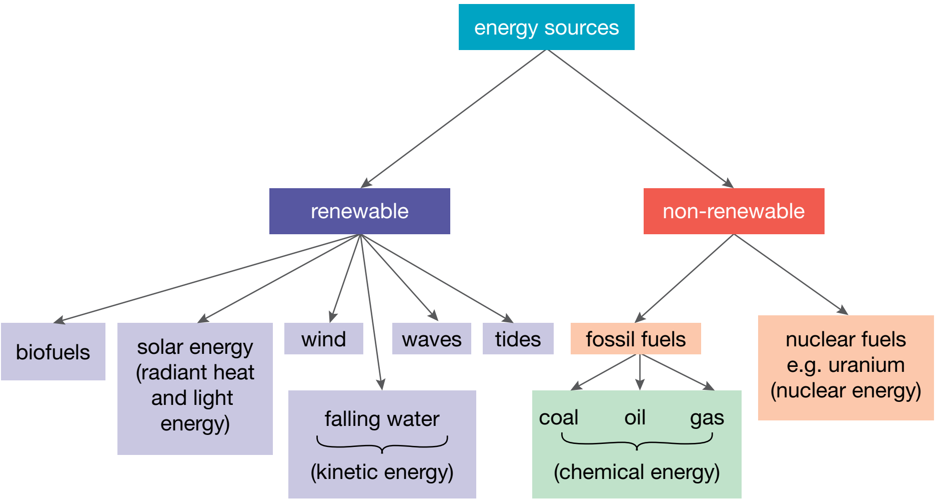


FIGURE 1.4 Uranium is a non-renewable, very high energy source. When refined from ore, 1 kg of Uranium-235 contains 2–3 million times the energy equivalent of 1 kg of coal.

1.2.4 Origin of fossil fuels

Fossil fuels are the most widely used fuel sources in the world. The most common fossil fuels are **coal**, **petroleum** and **liquefied petroleum gas (LPG)**, and **natural gas**.

Coal

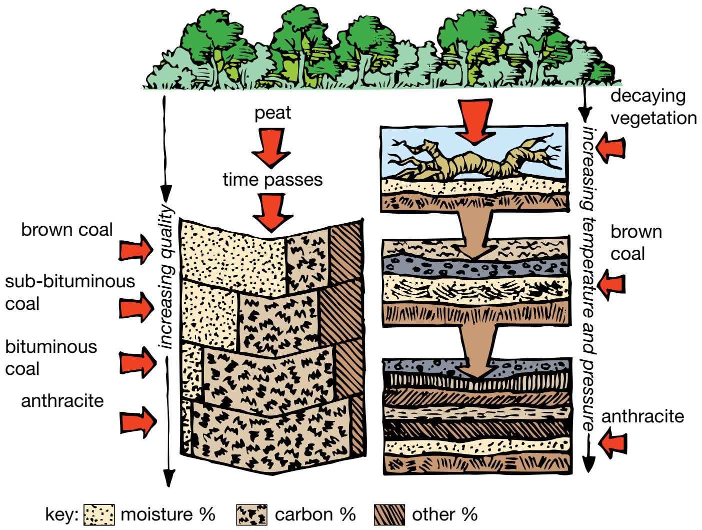
Coal is the world's most plentiful fossil fuel. It was formed from the combined effects of pressure, temperature, moisture and bacterial decay on vegetable matter over several hundred million years. Decaying vegetation progressively became peat (like soil and very soft), lignite (crumbly brown coal), bituminous coal (hard black coal) and anthracite (very hard black coal). As this progression occurred over time, the moisture content dropped and the carbon content increased as shown in figure 1.5. These changes in composition made it a more efficient fuel, so anthracite is the highest quality coal.

The main elements in coal are carbon (50–98%), hydrogen (3–13%), oxygen and very small amounts of nitrogen and sulfur. It also contains moisture and inorganic material that remains as ash when coal is burned. Traditionally, coal was burned in lumps, but ground coal powder is now used to improve the rate and efficiency of combustion.

Victoria generates most of its electricity from brown coal, which has about a quarter of the heat content of black coal. Brown coal can have up to 30% oxygen content, a relatively low carbon content of 60 to 75% when dried, and a high moisture content of 30 to 70%.

Through a process called destructive distillation, coal can be converted into many useful products, such as briquettes for heating, coal gas, sulfur, ammonia, benzene, coal tar and coke. Coal may be converted into electricity, gas or liquid fuels, all of which can be transported and used more cheaply and conveniently than solid coal.

FIGURE 1.5 Many different types of coal exist and their energy content varies. Anthracite (black) coal has more than twice the energy content of brown coal.

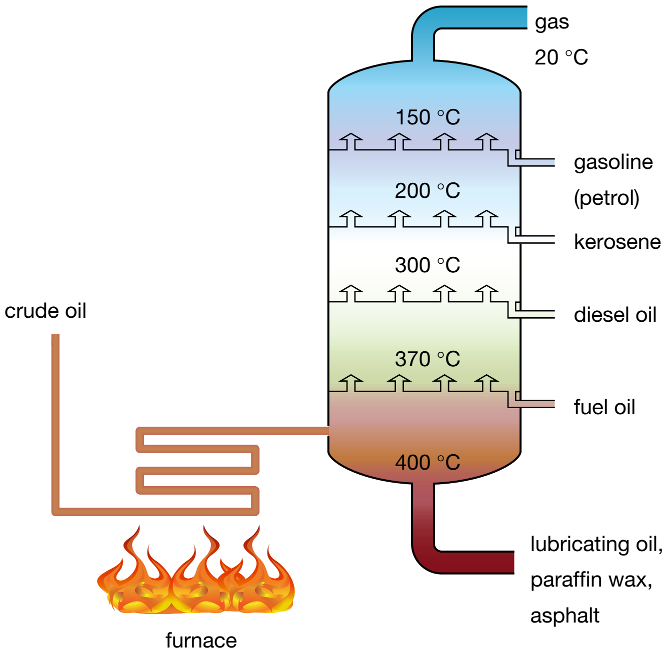


Petroleum and LPG

Petroleum (also called crude oil) is typically a viscous mixture composed of many different hydrocarbon compounds. It was formed from the remains of marine organisms, such as bacteria, algae and plankton. These marine organisms were altered, in a process similar to coal formation, from the combined effects of pressure, temperature, moisture and decay.

Petroleum is refined by **fractional distillation**, which separates out the component fuels based on their different boiling points. This process is performed in tall towers that are cooler at the top than at the bottom. The crude oil is heated and then introduced to the base of the tower. At this point, many of its components vaporise and these vapours rise up the tower, being cooled as they do so. When the vapours reach a point at which the tower's temperature equals their boiling temperature, condensation occurs. Specially designed trays containing bubble caps are placed inside the tower at strategic intervals. These are designed to allow the vapours to continue rising but stop condensed fractions from dripping back down to lower levels in the tower. The condensed fractions may then be removed from these trays to undergo further processing. Figure 1.6 shows a simplified outline of this process.

FIGURE 1.6 Schematic of fractional distillation of crude oil showing levels of the fractionating column



Fuels obtained from petroleum include petrol, liquefied petroleum gas, diesel fuel, heating oil and kerosene. Petroleum is also the raw material for a number of useful materials, including plastics, paints, synthetic fibres, medicines and pesticides.

Liquefied petroleum gas (LPG) is a hydrocarbon fuel that consists mainly of propane and butane. It is non-toxic, non-corrosive, lead-free and denser than air. LPG is liquefied under pressure but, when allowed to vaporise, it expands to nearly 300 times its liquefied volume. This means that LPG can be stored as a compact liquid but burns as a dry, gaseous vapour. LPG is popular with motorists, such as fleet-vehicle owners or taxi drivers, because it is considered to be a more economical energy source. Although LPG conversion costs for cars running on petrol are quite high, more people is considered to make the conversion (or buy new cars designed to run on LPG) because LPG prices are less variable, and potentially lower over the long term, than petrol prices.

on Resources

Digital document Experiment 1.1 Fractional distillation of an ethanol/water mixture (doc-31250)
Teacher-led video Experiment 1.1 Fractional distillation of an ethanol/water mixture (tlvd-0735)

Natural gas and coal seam gas

Natural gas is formed with oil in muds that are low in oxygen and rich in organic matter (typically ancient marine organisms). Natural gas is the lightest of the hydrocarbons produced, and is primarily composed of methane (CH_4). It is an important source of alkanes of low molecular mass. Victoria has large reserves of natural gas in the Gippsland basin. Typically, natural gas is composed of about 80% methane, 10% ethane, 4% propane and 2% butane. The remaining 4% consists of nitrogen and hydrocarbons of higher molecular mass. Natural gas also contains a small amount of helium and is one of its major sources.

FIGURE 1.7 Methane gas is used in homes because it readily undergoes complete combustion.

Natural gas is less dense than air, which means that it disperses in air. However, it is explosive in certain concentrations, so a safety measure incorporated by gas companies is to add an odour to natural gas so that leaks may be readily detected. Natural gas itself is odourless.

Methane is the major constituent of natural gas and it burns with a hot, clean flame.

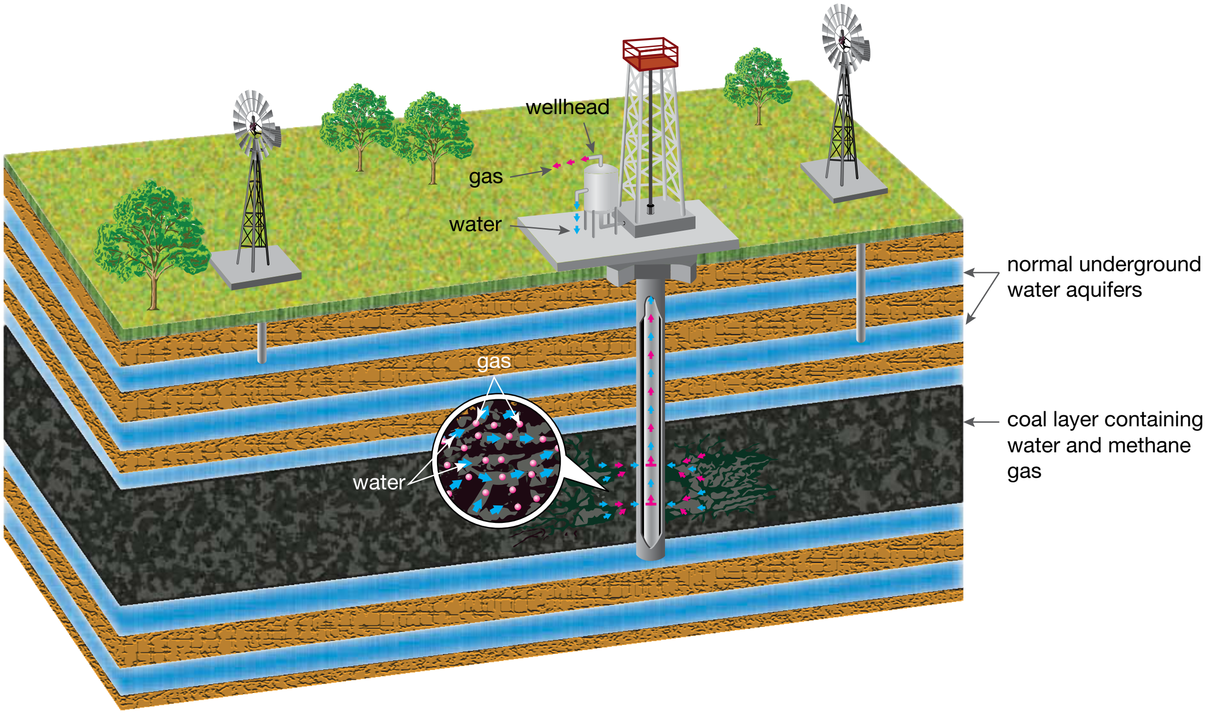
$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$$

Coal miners have long been aware of the dangers of methane gas. Released from coal seams during underground mining operations, methane gas has been responsible for many explosions and subsequent tragedies. Methane gas, besides being found in association with petroleum deposits, is also a by-product of coal formation. It is often **absorbed** onto the surface of coal deposits deep underground.

Coal seam gas (CSG), also called coal bed methane, is extracted by drilling deep wells into underground coal deposits. Such wells are typically 100 to 1500 m deep and are below the level of **aquifers** used for bore water supplies in inland Australia. The coal seams, which are nearly always filled with water, are further injected with water or chemicals to increase the pressure and crack the rocks. The accompanying decrease in pressure in the coal seam below allows the methane to desorb from the coal. It is then brought to the surface through the drilled well, along with more of the underground water. This process is called **fracking**.

Australia has large deposits of coal seam gas, which are now being extracted from the Bowen and Surat Basins in eastern Queensland and northern New South Wales. The methane produced is relatively free from impurities, often containing only small amounts of ethane, nitrogen and carbon dioxide, and so requires minimal processing. It is used in the same way as natural gas and also contributes to a growing export industry for liquefied natural gas.

FIGURE 1.8 Coal seam gas is produced from coal deposits that lie deep underground.



Although the coal seam gas industry has shown enormous expansion since 1996, there are concerns from various groups about its environmental impact. These include farmers who worry that it might pollute aquifers that supply some of Australia's most economic farming land. Concerns have also been raised about the use of fracking to increase gas flow in wells. Fracking has been used around Australia, but current regulations are inconsistent in each state and territory. Victoria became the first state to permanently ban fracking on land. As fracking involves injecting very large amounts of water and other chemicals deep underground, environmental groups say drinking water and aquifers can become contaminated during this process.

FIGURE 1.9 Public opinion is divided over the environmental impact of fracking, and France, Germany, Scotland and some US states have banned its use.

1.2.5 Origin of biofuels

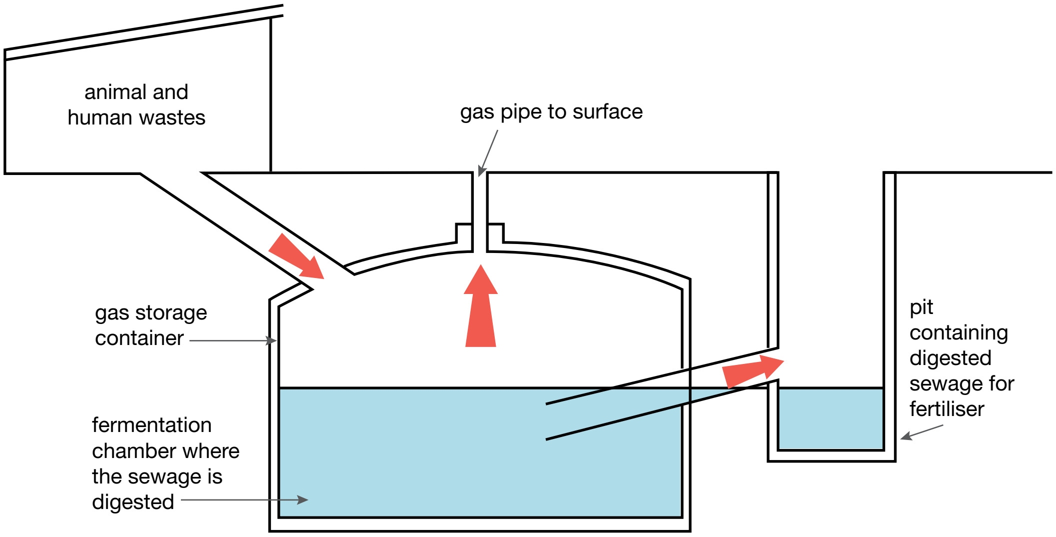
Biofuels are fuels made from waste plant and animal matter. They have been growing more popular in recent years due to the rise in oil prices and because of the impact fossil fuel combustion has on **global warming**. The three most common biofuels are biogas, bioethanol and biodiesel.

Biogas

Biogas is a combustible fuel used to generate electricity, light, heat, motion and fuels such as ethanol, and may contain up to 65% methane. It is produced when animal waste or other organic material rots in the absence of oxygen, such as when rubbish has been buried underground, or in digestive processes of mammals that involve the breakdown of food by bacteria in the gut. The most common material used for biogas production is livestock manure. The manure is fed into an airtight digester where it is allowed to ferment. The biogas produced is then collected and stored in a tank (see figure 1.10).

Biogas is commonly used to power furnaces, heaters and engines, and to generate electricity. Compressed biogas can also be used to fuel vehicles, and the residue from a biogas digester can be used as a fertiliser.

FIGURE 1.10 Biogas is a useful energy source.

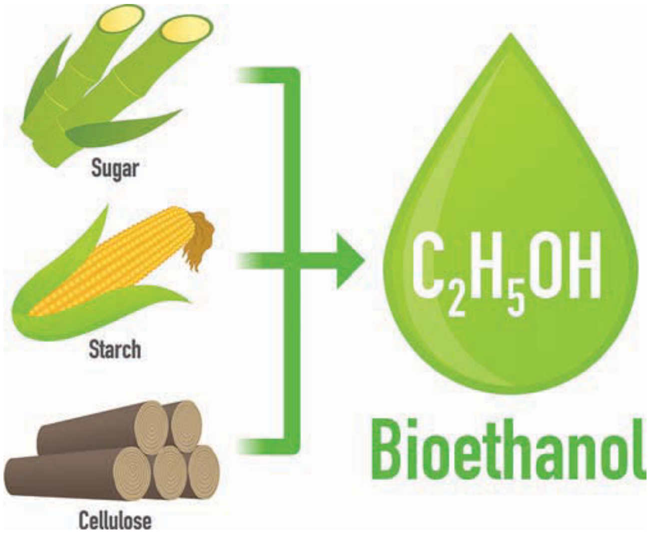


Bioethanol

Bioethanol is primarily used as a substitute for petrol in vehicles. Bioethanol is obtained by fermenting sugar from sources such as waste wheat starch and molasses, which is a by-product of sugar production. Up to about 10% anhydrous ethanol (E10) can be used as an additive to petrol without engine modification.

There are advantages and disadvantages to using ethanol-blended fuel. One advantage is that it reduces some pollutant emissions and contributes fewer greenhouse gases because production involves the use of a waste product. Environmentally, the presence of oxygen in the ethanol assists the complete combustion of the petrol, and emissions of carbon monoxide and aromatic hydrocarbons are reduced. However, the cost of processing ethanol compared with petrol will need to be improved, and ethanol produces less energy per gram. Ethanol can also contribute to the breakdown of some plastic and rubber parts in vehicles. In some countries there may be a dilemma concerning using land for food or fuel crops. Although burning ethanol puts back into the atmosphere carbon dioxide that was originally absorbed by photosynthesis, some carbon dioxide is released in the production of the ethanol.

FIGURE 1.11 Raw materials used in the production of bioethanol.



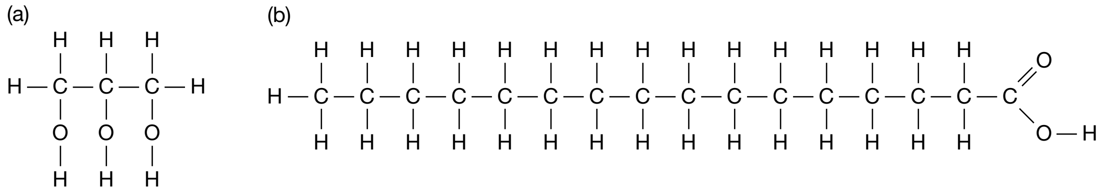
Biodiesel

Biodiesel is a diesel alternative that can be made from plant oils and animal fats. Typical sources include canola, palm oil and animal tallow. It can also be made from used cooking oil, such as that used in restaurant fryers. The CSIRO has estimated that Australia could reduce its petrodiesel demand by 4 to 8% if all current sources of plant oil, tallow and waste cooking oil were used.

Oils and fats are naturally occurring esters formed between long-chain carboxylic acids (known as fatty acids) and glycerol. Common fatty acids are summarised in table 1.1. Figure 1.13 shows the structure of glycerol and a typical fatty acid.

FIGURE 1.12 Using sugarcane instead of soy bean to make the oil which is processed into biodiesel improves the yield by around 12% per acre.

FIGURE 1.13 Structures of (a) glycerol and (b) a typical fatty acid



Biodiesel is produced by reacting oils or fats (also called triglycerides) with an alcohol. Although a number of small alcohols can be used, the most common is methanol. Heat and either concentrated sodium or potassium hydroxide, which acts as a catalyst, are used in this process. It can be made on a small scale, using homemade equipment or with specially purchased kits, or on a much larger scale for commercial distribution. The chemical reaction involved converts one type of ester into another and is called **transesterification**. A typical transesterification is shown in figure 1.14. The glycerol formed can be sold as a by-product for use in cosmetics and foods, and as a precursor for certain explosives.

TABLE 1.1 Formulas of some fatty acids

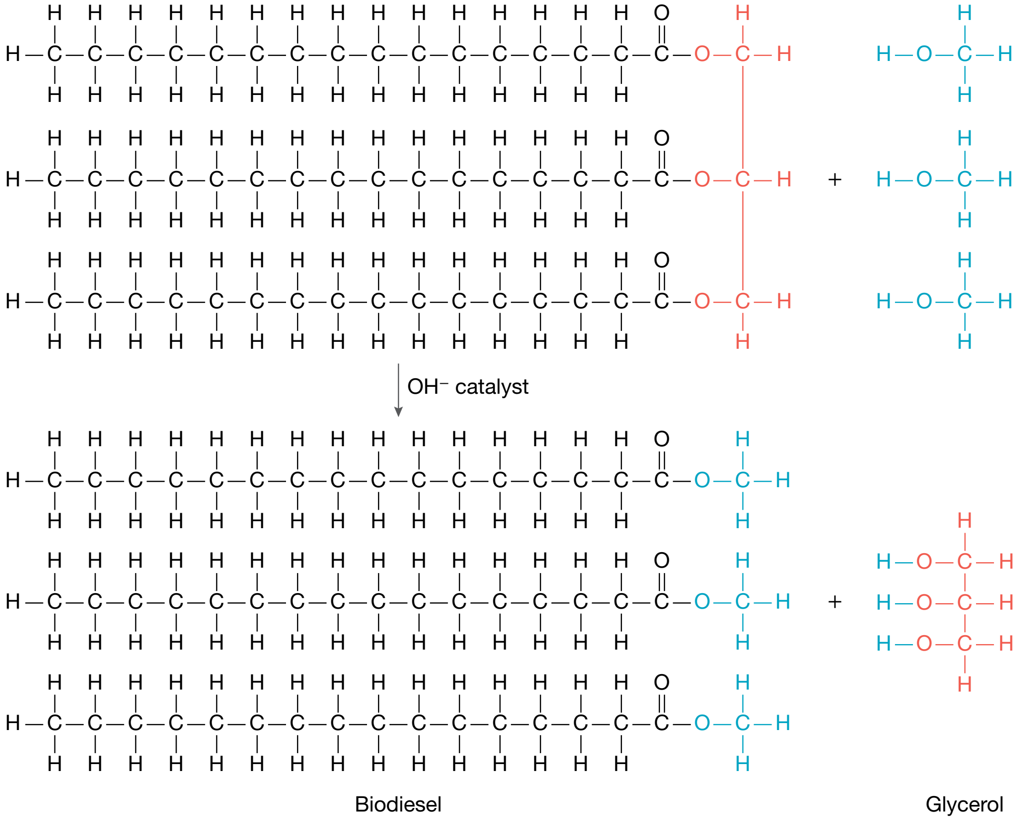
Name	Formula
Palmitic	$C_{15}H_{31}COOH$
Palmitoleic	$C_{15}H_{29}COOH$
Stearic	$C_{17}H_{35}COOH$
Oleic	$C_{17}H_{33}COOH$
Linoleic	$C_{17}H_{31}COOH$
Linolenic	$C_{17}H_{29}COOH$

While biodiesel is regarded as a more environmentally friendly choice than diesel, the most economical method of biodiesel production requires the use of non-renewable fossil fuels to make the methanol required for the transesterifcation process. In this process, steam reforming is used to produce ‘synthesis gas’, which then undergoes further reactions to make methanol. When natural gas (methane) is used as the feedstock, the overall equation for this process is:

$$CH_4(g) + H_2O(g) \rightarrow CH_3OH(g) + H_2(g)$$

To overcome this problem, a number of methods of producing methanol economically from renewable resources are being investigated. The most exciting of these involves using the glycerol produced in the transesterification reaction as the initial feedstock for producing synthesis gas to feed into the methanol production process. Another method involves using a catalyst to facilitate the direct conversion of glycerol to methanol. A number of new methods are also being developed to convert the cellulose in waste or low-quality plant material into biodiesel.

FIGURE 1.14 A typical transesterification reaction



1.2 EXERCISE

To answer questions online and to receive **immediate feedback** and **sample responses** for every question, go to your learnON title at www.jacplus.com.au.

1. Why do you think brown coal is used on such an extensive scale to generate electricity in Victoria, even though it has a relatively low energy content?
2. (a) What is a fuel?
   (b) Give four examples of fuels that you have used in the last week.
   (c) What is the difference between a fossil fuel and a biofuel?
3. Fuels, and energy sources in general, may be classified as either renewable or non-renewable.
   (a) Define the terms 'renewable' and 'non-renewable' as they apply to this context.
   (b) Are all biofuels renewable? Explain.
   (c) Are renewable energy sources always biofuels? Explain.
4. Write the formula for biodiesel if it is produced from palmitic acid and methanol.

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1.3 Combustion of fuels

KEY CONCEPT

- 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 and measurement of enthalpy change including symbol (ΔH) and common units (kJ mol^{-1}, kJ g^{-1}, MJ/tonne)

1.3.1 What is energy?

In scientific terms, 'energy' is defined as the capacity to do 'work'. Energy can be neither created nor destroyed but only changed from one form to another. It exists in various forms and, in chemistry, is focused on the potential energy stored and released from bonds. The SI unit for energy is the joule; it has the symbol J. One J is a relatively small amount of energy. It takes about 70 000 J to boil water for a cup of tea. Given that when a fuel combusts it produces large amounts of energy, chemists often convert joules into kilojoules (kJ) or megajoules (MJ).

FIGURE 1.15 Crude oil fires produce around 38 000 kJ L^{-1} of energy upon combustion.

1.3.2 Different forms of energy

Energy may take a number of different forms. These include:

- mechanical energy
- thermal (heat) energy
- chemical energy
- light energy
- sound energy
- electrical energy
- gravitational energy
- nuclear energy.

All of these forms of energy may be classified as either **potential energy** (energy that is stored, ready to do work) or **kinetic energy** (energy associated with movement, in doing work).

FIGURE 1.16 Types of potential energy

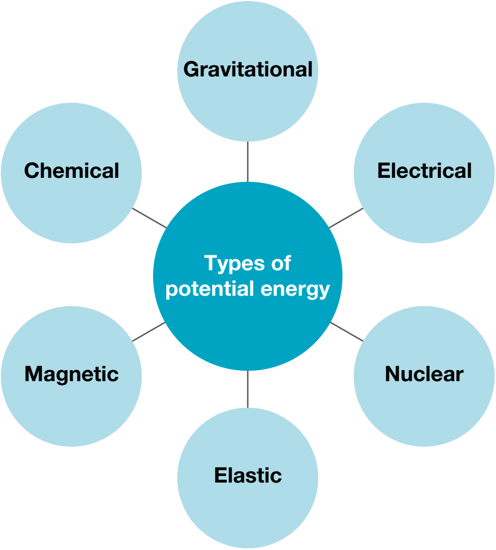
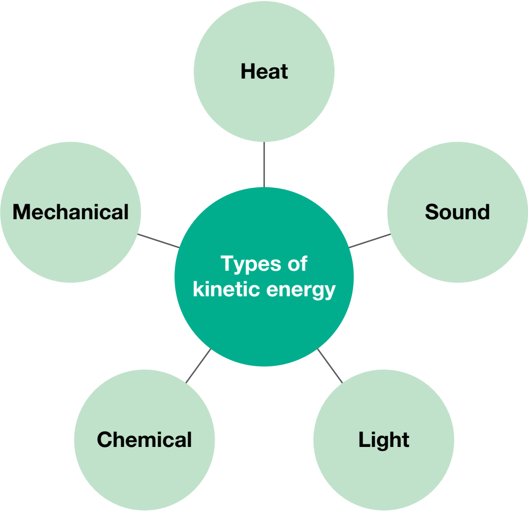


FIGURE 1.17 Types of kinetic energy



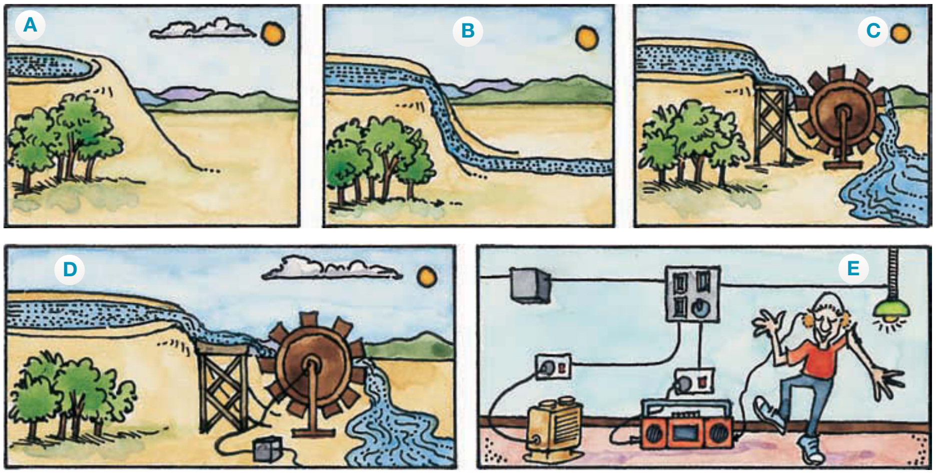
The total energy of an object is the sum of its potential and kinetic energy. All objects, from the smallest atom to the largest space rocket, have potential and kinetic energy.

1.3.3 Energy conversions

Whatever form energy takes, it is governed by two general laws of thermodynamics.

The first law states that energy is neither created nor destroyed, but simply changes from one form into another. Whenever energy is converted from one form to another, the total quantity of energy remains the same. This is sometimes called the **Law of Conservation of Energy**.

FIGURE 1.18 An illustration of the Law of Conservation of Energy.



- **A** Water stored in a dam has potential energy.
- **B** Water flows downhill and is converted to kinetic energy.
- **C** The falling water turns the blades of a waterwheel so that kinetic energy is converted to mechanical energy.
- **D** The waterwheel turns a generator to convert mechanical energy into electrical energy.
- **E** Electrical energy may be converted into light energy, sound energy and heat energy in the home.

The second law states that, although the quantity of energy in the universe may stay the same, the quality or usability gets worse. This is because whenever energy is converted from one form to another, heat is also produced. This is low-temperature heat, which is difficult to use. It simply warms up the Earth's atmosphere by a small amount. So, after each energy change, less usable energy remains.

Photosynthesis

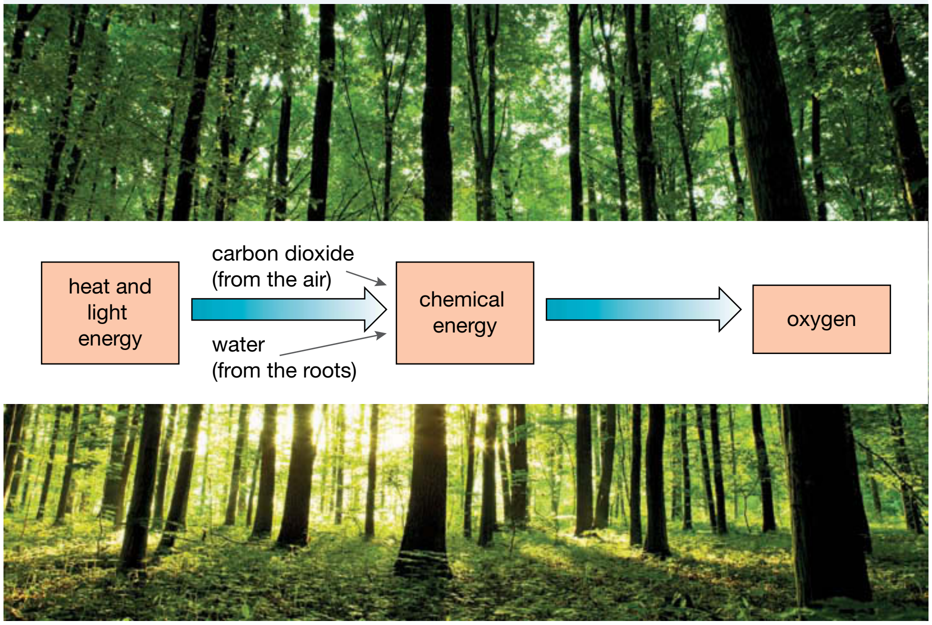
Plants take carbon dioxide from the air and water from the roots to effect the energy change in a process called photosynthesis. In addition to providing food for animals as a result of this process, they provide oxygen as a by-product of the reaction.

The following reaction outlines how plants produce simple sugars (in this case glucose) through photosynthesis and remove carbon dioxide from the atmosphere:

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

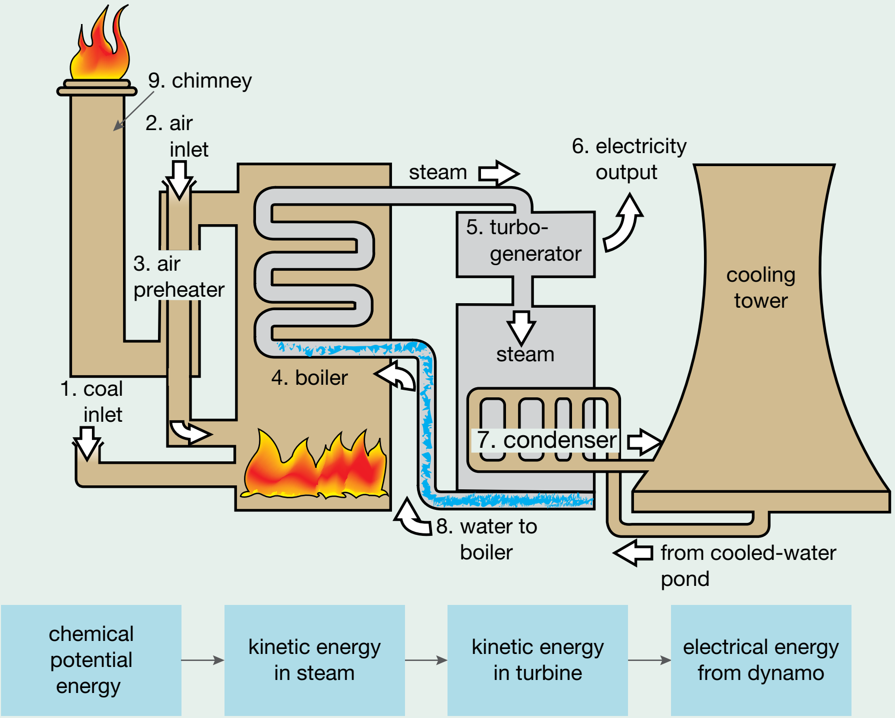
Using sunlight, plants create compounds that store energy in their bonds. Reversing the above reaction releases this stored bond energy and the carbon dioxide back into the atmosphere (a combustion reaction).

FIGURE 1.19 Plants act as energy converters. They change the heat and light energy from the Sun into chemical energy that is stored in the plant.



CONVERSION OF ENERGY IN POWER STATIONS

When coal is burned, its stored chemical potential energy is converted into heat energy. This heat energy is used to convert water into steam, so heat energy is converted into kinetic energy. The steam flows past a turbine so the kinetic energy of the steam is converted into mechanical energy in the spinning turbine. The turbine is connected to a generator, which converts mechanical energy into electrical energy. Electrical energy may then be used to power a wide range of appliances in the home and in industry.



1. Coal inlet
2. Air intake
3. Air is preheated by exhaust gases from boiler.
4. Water is converted to steam.
5. Heat energy is converted to mechanical energy.
6. Mechanical energy is converted to electrical energy.
7. Hot water from condenser
8. Steam from turbo-generator is cooled in condenser, then recycled to boiler.
9. Waste products of combustion

on Resources

Video eLesson Coal-fired power station (med-0433)

1.3.4 Energy efficiency

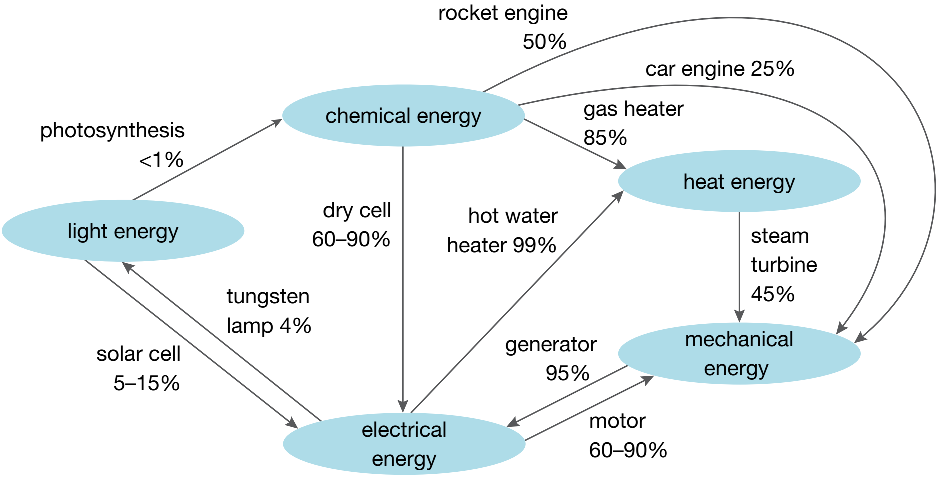
The **efficiency** of energy conversion is a concept that follows from the second law of thermodynamics. It takes the amount of usable energy obtained into account and is defined as a percentage.

Energy efficiency (%):

$$\%\text{efficiency} = \frac{\textbf{energy obtained in desired form}}{\textbf{energy available before conversion}} \times \frac{100}{1}$$

Energy transformations are not 100% efficient. This is because heat is also produced when energy conversions take place. The second law of thermodynamics states that a high quality of energy is transformed to a lower quality of energy and some heat.

FIGURE 1.20 The efficiency of changing one energy form into another varies.



When electricity generation is considered, the calculations must take into account the efficiency of the generation process. For example, to produce 1 MJ of electrical energy, assuming the generation process is

30% efficient, enough fuel would need to be burned to produce 3.33 MJ of heat energy. The mass of carbon dioxide produced in supplying 3.33 MJ would then need to be calculated.

Both transport and the generation of electricity consume large amounts of fossil fuels and, in the process, add large amounts of carbon dioxide to the atmosphere. As nations work to reduce their greenhouse gas emissions, alternative fuels need to be considered. When considering fuels, the amount of carbon dioxide emitted per unit of energy produced is a useful comparison.

FIGURE 1.21 The consumption of fossil fuels to produce energy releases large amounts of carbon dioxide and water vapour into the environment.

SAMPLE PROBLEM 1

A compact fluorescent light bulb converts electrical energy into light energy. As part of a quality control test, it was found to convert 9.0 kJ of electrical energy into 1.8 kJ of light energy. Calculate its efficiency.

Teacher-led video: SP1 (tlvd-0658)

THINK	WRITE
1. Recall the energy efficiency formula, %efficiency = $\frac{\text{energy obtained in desired form}}{\text{energy available before conversion}} \times \frac{100}{1}$ and identify the variables.	Energy obtained in desired form = 1.8 kJ Energy available before conversion = 9.0 kJ
2. Substitute in the appropriate values. If your answer is greater than 100 you have the energy values the wrong way around. Give your answer to 2 significant figures. **TIP:** A similar formula can be found in Table 3 of the VCE Chemistry Data Book: %yield and %atom economy.	$\%\text{efficiency} = \frac{\text{energy obtained in desired form}}{\text{energy available before conversion}} \times \frac{100}{1}$ $= \frac{1.8}{9.0} \times \frac{100}{1}$ $= 20\%$

PRACTICE PROBLEM 1

The electricity from a coal-fired power station is used to power an electric motor. If the overall efficiency of the power station is 28%, and the efficiency of the motor in producing mechanical energy is 75%, calculate the overall efficiency for the conversion of chemical energy in coal to mechanical energy.

1.3.5 Energy changes in reactions

The energy changes that accompany chemical reactions are vital to us. To survive, we depend on the energy content of the food we eat. Our bodies can convert the energy of the chemical bonds in food into other kinds of energy. The quality of lifestyle we lead depends on harnessing energy from different chemical sources, including coal, oil, natural gas and renewable fuels.

The study of the energy changes that accompany chemical reactions is called **thermochemistry** or **chemical energetics**. In general, all chemical reactions involve energy changes. The chemical energy stored in a substance has the potential to be converted to heat or electricity (for more on chemical energy converted to electricity see topic 3).

A certain amount of chemical energy is stored within every atom, molecule or ion. This energy is the sum of the potential energy and kinetic energy of the substance and results from:

- the attractions and repulsions present between protons and electrons within the atom
- the attractions and, to some degree, repulsions present between atoms within a molecule
- the motion of the electrons
- the movement of the atoms.

The total energy stored in a substance is called the **enthalpy** of the substance and is given the symbol H. Unfortunately, we cannot directly measure the heat content of a substance, but we can measure the **change in enthalpy** when the substance undergoes a chemical reaction. In virtually all chemical reactions, the energy of the reactants and products differ, so such reactions usually involve some change in enthalpy, which is indicated by a temperature rise or fall. The change in enthalpy during a reaction is denoted by ΔH and is usually known as the **heat of reaction**, but there are some reactions for which specific names have been given.

FIGURE 1.22 A change in enthalpy occurs when magnesium burns.

- *Heat of solution* is the change in enthalpy when 1 mole of any substance dissolves in water.
- *Heat of neutralisation* is the change in enthalpy when an acid reacts with a base to form 1 mole of water.
- *Heat of vapourisation* is the change in enthalpy when 1 mole of liquid is converted to a gas.
- *Heat of combustion* is the enthalpy change when a substance burns in air, and is always exothermic.

The change in enthalpy, ΔH, is determined by:

$$\text{Change in enthalpy } (\Delta H) = (\text{enthalpy of products}) - (\text{enthalpy of reactants})$$

$$\Delta H = H_P - H_R$$

The enthalpy change, or heat change, of a reaction depends on the amount and temperature of reactants used, compared with that of the final products. To remove these variables in enthalpy studies, the following conditions are assumed:

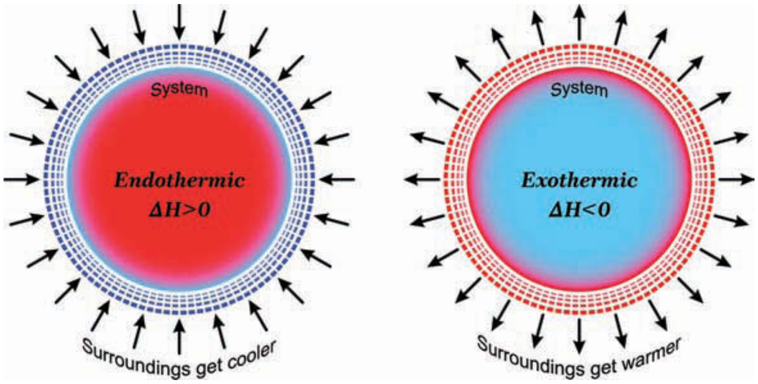
- the initial temperature of the reactants and final temperature of the products is the same and is 25 °C
- 1 mole of the substance is involved
- solutions have a concentration of 1 M
- the heat absorbed or released is measured in kilojoules
- the pressure is kept at 100.0 kPa.

These conditions are referred to as **standard laboratory conditions (SLC)**.

1.3.6 Exothermic and endothermic reactions

Chemical reactions accompanied by heat energy changes can be divided into two groups: **exothermic** reactions and **endothermic** reactions.

FIGURE 1.23 In endothermic reactions, the surroundings lose energy and get cooler. In exothermic reactions the surroundings gain energy and get warmer.



Enthalpy change, ΔH, is equal to heat energy produced or absorbed. When bonds are broken in reactants, energy is consumed and is therefore endothermic. When bonds are formed in the products, energy is given out and is therefore exothermic. If the energy given out when product bonds are formed is greater than the energy taken in when reactant bonds are broken, the reaction is exothermic. This would result in a *negative value*.

Exothermic reactions

Chemical reactions that release heat to the environment are called exothermic reactions. Consider the reaction between magnesium and hydrochloric acid shown in figure 1.24.

The following data was taken from an enthalpy databook for the reaction between magnesium and hydrochloric acid.

$$\begin{aligned}\text{change in enthalpy} &= (\text{enthalpy of products}) - (\text{enthalpy of reactants})\\ \text{change in enthalpy} &= (-797\,\text{kJ}) - (+334\,\text{kJ})\\ \Delta H &= -463\,\text{kJ mol}^{-1}\end{aligned}$$

The energy change in a reaction can be drawn as an energy diagram or energy profile. Chemicals with more energy are drawn higher up and those with less energy, lower down. The reactants are drawn on the left and the products are drawn on the right. Figure 1.25 is an energy diagram for an exothermic reaction.

In exothermic reactions, the ΔH is always negative because the heat content of the reactants is greater than that of the products. The bonds in the products are more stable than the bonds in the reactants.

FIGURE 1.24 An exothermic reaction — magnesium ribbon dissolving in hydrochloric acid.

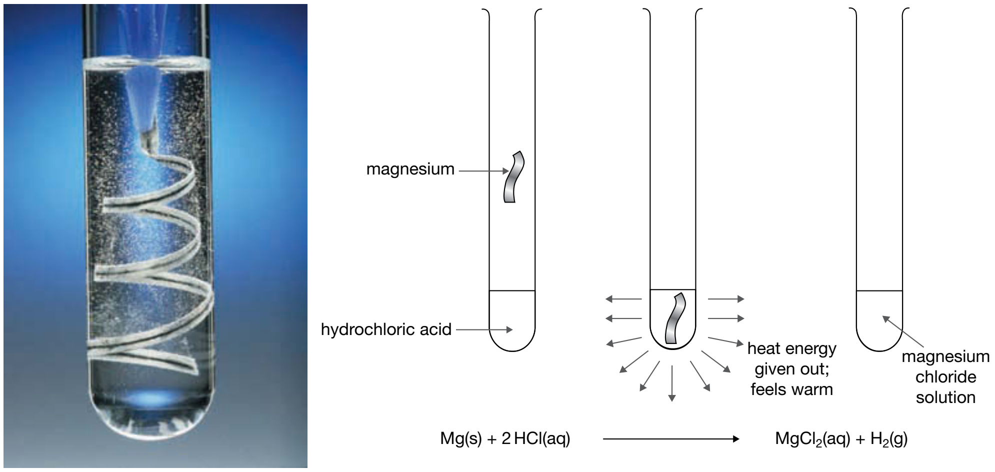
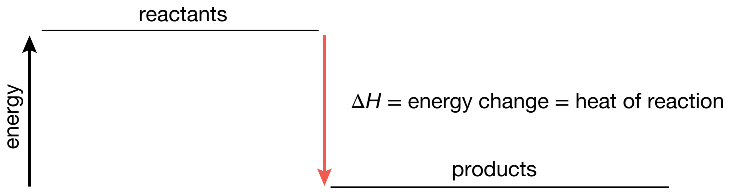


FIGURE 1.25 Exothermic reaction energy diagram demonstrating the negative ΔH



Endothermic reactions

Chemical reactions that absorb heat from the environment are called endothermic reactions.

When ammonium nitrate is dissolved in water, heat is absorbed from the environment. If you were holding the test tube in figure 1.26 it would feel cold because the reaction takes in energy from the water and your hand. This means that the enthalpy of the products is greater than the enthalpy of the reactants. Therefore, the enthalpy change is positive. The difference in energy between the reactants and the products is absorbed from the environment.

FIGURE 1.26 An endothermic reaction — ammonium nitrate dissolving in water.

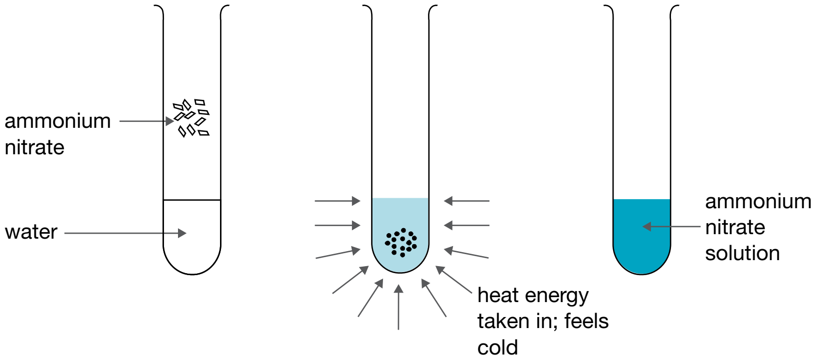


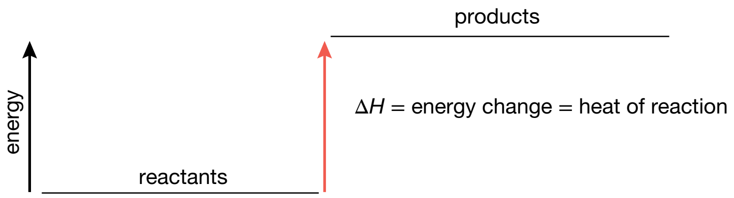
FIGURE 1.27 Instant cold packs contain solid ammonium nitrate and water.

The following data was taken from an enthalpy databook for the reaction between ammonium nitrate and water.

$$\text{change in enthalpy} = (\text{enthalpy of products}) - (\text{enthalpy of reactants})$$
$$\text{change in enthalpy} = (-231\ \text{kJ mol}^{-1}) - (+256\ \text{kJ mol}^{-1})$$
$$\Delta H = +25\ \text{kJ mol}^{-1}$$

Figure 1.28 is an energy diagram for an endothermic reaction. In endothermic reactions, ΔH is always positive because the heat content of the reactants is less than that of the products. The bonds in the products are less stable than the bonds in the reactants.

FIGURE 1.28 Endothermic reaction energy diagram demonstrating the positive ΔH



1.3.7 Units of energy

The SI unit of energy is the joule. Depending upon the energy of the system, the kilojoule, kJ, and megajoule, MJ, can also be used. How to convert between these units is shown in figure 1.29.

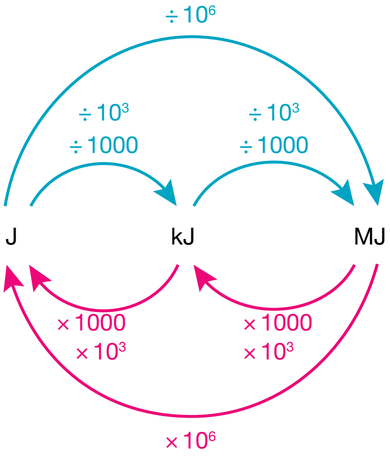
To convert between different units of energy:

$$\mathbf{1\,000\,000\ J = 1000\ kJ = 1\ MJ}$$
$$\mathbf{1 \times 10^{6}\ J = 1 \times 10^{3}\ kJ = 1\ MJ}$$

OR

$$\mathbf{1\ J = 0.001\ kJ = 0.000001\ MJ}$$
$$\mathbf{1\ J = 1 \times 10^{-3}\ kJ = 1 \times 10^{-6}\ MJ}$$

FIGURE 1.29 How to convert between different units of energy



1.3 EXERCISE

To answer questions online and to receive **immediate feedback** and **sample responses** for every question, go to your learnON title at www.jacplus.com.au.

1. State whether the following are exothermic or endothermic processes.
   (a) Water changing from liquid to gaseous state
   (b) A reaction in which the total enthalpy of the products is greater than that of the reactants
   (c) Burning kerosene in a blow torch
   (d) Burning fuel in a jet aircraft engine
   (e) A chemical reaction that has a negative ΔH value
   (f) A reaction in which the reactants are at a lower level on an energy profile diagram than the products

For questions 2 to 4, use efficiency figures from figure 1.20.

2. A device converts 350 J of mechanical energy into 120 J of output energy. Calculate the efficiency of this device.
3. Calculate the energy input required for a gas heater to produce 72 MJ if the gas heater runs at 85% efficiency. Give your answer in MJ, kJ and J.
4. Heat energy in steam is used to drive a steam turbine that, in turn, drives an electrical generator. Calculate the electrical energy produced from steam containing 400 000 kJ. Give your answer in MJ.
5. Calculate the carbon dioxide emissions, in kg MJ^{-1}, from a power station that has an overall efficiency of 33.0% and burns black coal with a carbon content of 81.5%. (Heat evolved from black coal is 34.0 kJ g^{-1}.)

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1.4 Thermochemical equations

KEY CONCEPT

- 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

1.4.1 Writing balanced thermochemical equations

A **thermochemical equation** is an equation that includes the amount of heat produced or absorbed by a reaction. As with other chemical equations, charge and mass must balance, but thermochemical equations must also include the enthalpy change.

In writing a thermochemical equation, the following points should be remembered:

- A positive or negative sign must be included with the ΔH value to indicate whether the reaction is either endothermic or exothermic. If an enthalpy change is given as $\Delta H = 345$ kJ mol^{-1}, the lack of sign does not mean that it is an endothermic reaction.
- Enthalpy is measured in kJ mol^{-1}. This means the coefficients in the equation represent the amount of moles of each reacting substance that the ΔH value refers to.

  The following equation can be read as: when 2 moles of hydrogen react with 1 mole of oxygen, 2 moles of water form and 572 kJ of energy is produced.

$$2\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{H}_2\text{O}(\text{l}) \quad \Delta H = -572\,\text{kJ mol}^{-1}$$

  ΔH refers to the equation as it is written, even though the unit is expressed as kJ mol^{-1}.
- The physical state of matter must be shown because changes of state require energy changes.
- Thermochemical equations can be written from direct experimental data (primary data) or utilising published tabulated data (secondary data).

  Study the following equations. In the first case, the product is a liquid; in the second case, the product is a gas. So, the condensation of 2 moles of water vapour to 2 moles of liquid water at 25 °C produces 88 kJ of energy, which is the difference between the two enthalpies.

$$2\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{H}_2\text{O}(\text{l}) \qquad \Delta H = -572\,\text{kJ mol}^{-1}$$
$$2\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{H}_2\text{O}(\text{g}) \qquad \Delta H = -484\,\text{kJ mol}^{-1}$$

- If the coefficients are doubled, the ΔH value must be doubled. The amount of energy produced by a chemical reaction is directly proportional to the amount of substance initially present. If twice as much reactant is used, then twice as much energy can be produced.

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(l) \qquad \Delta H = -572\,\text{kJ mol}^{-1}$$
$$4H_2(g) + 2O_2(g) \rightarrow 4H_2O(l) \qquad \Delta H = -1144\,\text{kJ mol}^{-1}$$

- If a reaction is reversed, ΔH is equal to, but opposite in sign, to that of the forward reaction.

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

You will notice that the key point is that the enthalpy change in a reaction is proportional to the amount of substance that reacts. If these two quantities are measured in an experiment, it is possible to write the accompanying thermochemical equation.

To correctly write thermochemical equations, Table 11 of the VCE Chemistry Data Book (Heats of combustion of common fuels) should be used. When assigning ΔH values it is important to take note of the number of moles of fuel that are combusted. If the number of moles in the equation is changed, the ΔH value will also change.

For example:

$$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(g) \quad \Delta H = -282\,\text{kJ mol}^{-1}(\text{from } 2\text{ g of } H_2)$$

If twice as much hydrogen was to react, then twice the energy would be released.

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(g) \quad \Delta H = -564\,\text{kJ mol}^{-1}(\text{from } 4\text{ g of } H_2)$$

Regardless of the number of moles reacting the units for ΔH is kJ mol^{-1}.

SAMPLE PROBLEM 2

The molar heat of combustion of ethanol is tabulated as –1360 kJ mol^{-1}.

a. Write the thermochemical equation for the combustion of ethanol.

b. If the density of ethanol is 0.790 g mL^{-1}, calculate the energy evolved in MJ when 1.00 L of ethanol is burned.

Teacher-led video: SP2 (tlvd-0659)

THINK	WRITE
a. 1. The formula and state symbol for ethanol can be found in Table 11 of the VCE Chemistry Data Book. Both ethanol and methanol complete combustion equations should be learned or correctly generated.	$CH_3CH_2OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(g)$

TIP: The state symbol of water would expect to be a gas (as combustion reactions produce enough heat to vaporise water) but liquid is also acceptable.	
2. The given heat value refers to 1 mole. Therefore the value of –1360 kJ is equivalent to the 1 mole of ethanol shown in the balanced equation.	$CH_3CH_2OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(g)$ $\Delta H = -1360 \text{ kJ mol}^{-1}$
b. 1. Identify the given and unknown quantities.	density of ethanol = 0.790 g mL^{-1} volume = 1.00 L mass of ethanol = ?
2. Recall the equation for density: $\text{density} = \frac{\text{mass}}{\text{volume}}$ Compare the units given to those required. **TIP:** The actual formula for density is not in the VCE Chemistry Data Book. However, in Table 4, the density of water is given with units of mass per volume, hence the formula can be determined.	1.00 L ethanol = 1.00 × 1000 = 1000 mL ethanol $\text{density} = \frac{\text{mass}}{\text{volume}}$ $m(\text{ethanol}) = d(\text{ethanol}) \times V(\text{ethanol})$ $= 0.790 \times 1000$ $= 790 \text{ g}$
3. Calculate the number of moles using the mass determined in **b.2.** and M of ethanol by applying the formula $n = \frac{m}{M}$.	$(n)\text{ethanol} = \frac{m}{M}$ $= \frac{790}{46.0}$ $= 17.17 \text{ mol}$
4. From the equation, 1 mole of ethanol evolves 1360 kJ. By direct proportion, 17.17 mol produces x kJ	$x = 17.17 \times \frac{1360}{1}$ $= 23\,356 \text{ kJ}$
5. Convert kJ to MJ and give the answer to 3 significant figures.	$\frac{23\,356}{1000} = 23.4 \text{ MJ}$

PRACTICE PROBLEM 2

In an experiment, it was found that the combustion of 0.240 g of methanol in excess oxygen yielded 5.42 kJ.

a. Write the thermochemical equation for this reaction.

b. If the density of methanol is 0.792 g mL^{-1}, calculate the energy evolved in MJ when 10.00 L of methanol is burned.

SAMPLE PROBLEM 3

The combustion of ethene can be represented by the following thermochemical equation.

$$C_2H_4(g) + 3O_2(g) \rightarrow 2CO_2(g) + 2H_2O(l) \quad \Delta H = -1409 \text{ kJ mol}^{-1}$$

Calculate the mass of ethene required to produce 500 kJ of heat energy.

Teacher-led video: SP3 (tlvd-0660)

THINK	WRITE
1. From the equation, 1 mole of C_2H_4 evolves 1409 kJ. By ratio, x moles are required to evolve 500 kJ.	$x = 500 \times \frac{1}{1409}$ $= 0.3548$
2. Use the formula $m = n \times M$, where the molar mass of ethene = 28.0 g mol^{-1}.	$m(C_2H_4) = n \times M$ $= 0.3548 \times 28.0$
3. Give the answer to 3 significant figures.	$m(C_2H_4) = 9.94$ g

PRACTICE PROBLEM 3

The air pollutant sulfur trioxide reacts with water in the atmosphere to produce sulfuric acid according to the equation: $SO_3(g) + H_2O(l) \rightarrow H_2SO_4(aq) \quad \Delta H = -129.6 \text{ kJ mol}^{-1}$
Calculate the energy released, in kJ, when 0.500 kg $SO_3(g)$ reacts with water.

TIP: Don't forget to indicate whether the enthalpy of the reaction is exothermic (−) or endothermic (+).

1.4.2 Combustion of hydrocarbons, methanol and ethanol

Water is always formed in any type of combustion reaction. When oxygen is in excess, complete combustion can occur where all the fuel is fully oxidised to carbon dioxide and water. When the supply of oxygen is limited, incomplete combustion will occur where not all the fuel is fully oxidised. The products of incomplete combustion vary and may contain a combination of carbon, carbon monoxide and even amounts of carbon dioxide with very large hydrocarbons.

TABLE 1.2 Complete combustion of hydrocarbons methane and butane

Equation type	Reactants			→	Products		
Word equation	methane gas	+	oxygen gas	→	carbon dioxide gas	+	water vapour
Symbol equation	$CH_4(g)$	+	$O_2(g)$	→	$CO_2(g)$	+	$H_2O(l)$
Balanced equation	$CH_4(g)$	+	$2O_2(g)$	→	$CO_2(g)$	+	$2H_2O(l)$
Thermochemical equation	$CH_4(g)$	+	$2O_2(g)$	→	$CO_2(g)$	+	$2H_2O(l)$ $\Delta H = -890 \text{ kJ mol}^{-1}$
Word equation	butane gas	+	oxygen gas	→	carbon dioxide gas	+	water vapour
Symbol equation	$C_4H_{10}(g)$	+	$O_2(g)$	→	$CO_2(g)$	+	$H_2O(l)$
Balanced equation	$2C_4H_{10}(g)$	+	$13O_2(g)$	→	$8CO_2(g)$	+	$10H_2O(l)$
Thermochemical equation	$2C_4H_{10}(g)$	+	$13O_2(g)$	→	$8CO_2(g)$	+	$10H_2O(l)$ $\Delta H = -5760 \text{ kJ mol}^{-1}$

TABLE 1.3 Incomplete combustion of hydrocarbons methane and butane

Equation type	Reactants			→	Products		
Word equation	methane gas	+	oxygen gas	→	carbon monoxide gas	+	water vapour
Symbol equation	$CH_4(g)$	+	$O_2(g)$	→	$CO(g)$	+	$H_2O(l)$
Balanced equation	$2CH_4(g)$	+	$3O_2(g)$	→	$2CO(g)$	+	$4H_2O(l)$
Thermochemical equation	$2CH_4(g)$	+	$3O_2(g)$	→	$2CO(g)$	+	$4H_2O(l)$ $\Delta H = -1780\ \text{kJ mol}^{-1}$
Word equation	butane gas	+	oxygen gas	→	carbon monoxide gas	+	water vapour
Symbol equation	*$C_4H_{10}(g)$	+	$O_2(g)$	→	$CO(g)$	+	$H_2O(l)$
Balanced equation	$2C_4H_{10}(g)$	+	$9O_2(g)$	→	$8CO(g)$	+	$10H_2O(l)$
Thermochemical equation	$2C_4H_{10}(g)$	+	$9O_2(g)$	→	$8CO(g)$	+	$10H_2O(g)$ $\Delta H = -5760\ \text{kJ mol}^{-1}$
Word equation	butane gas	+	oxygen gas	→	carbon dioxide gas	+	water vapour + carbon solid
Symbol equation	*$C_4H_{10}(g)$	+	$O_2(g)$	→	$CO_2(g)$	+	$H_2O(l)$ + $C(s)$
Balanced equation	$C_4H_{10}(g)$	+	$5O_2(g)$	→	$2CO_2(g)$	+	$5H_2O(l)$ + $C(s)$
Thermochemical equation	$C_4H_{10}(g)$	+	$5O_2(g)$	→	$2CO_2(g)$	+	$5H_2O(l)$ + $C(s)$

*many different combinations of products can occur.

TABLE 1.4 Complete combustion of methanol and ethanol

Equation type	Reactants			→	Products		
Word equation	methanol liquid	+	oxygen gas	→	carbon dioxide gas	+	water vapour
Symbol equation	$CH_3OH(l)$	+	$O_2(g)$	→	$CO_2(g)$	+	$H_2O(l)$
Balanced equation	$2CH_3OH(l)$	+	$3O_2(g)$	→	$2CO_2(g)$	+	$4H_2O(l)$
Thermochemical equation	$2CH_3OH(l)$	+	$3O_2(g)$	→	$2CO_2(g)$	+	$4H_2O(l)$ $\Delta H = -1452\ \text{kJ mol}^{-1}$
Word equation	ethanol liquid	+	oxygen gas	→	carbon dioxide gas	+	water vapour
Symbol equation	$C_2H_5OH(l)$	+	$O_2(g)$	→	$CO_2(g)$	+	$H_2O(l)$
Balanced equation	$C_2H_5OH(l)$	+	$3O_2(g)$	→	$2CO_2(g)$	+	$3H_2O(l)$
Thermochemical equation	$C_2H_5OH(l)$	+	$3O_2(g)$	→	$2CO_2(g)$	+	$3H_2O(l)$ $\Delta H = -1360\ \text{kJ mol}^{-1}$

TABLE 1.5 Incomplete combustion of methanol and ethanol

Equation type	Reactants			→	Products		
Word equation	methanol liquid	+	oxygen gas	→	carbon monoxide gas	+	water vapour
Symbol equation	$CH_3OH(l)$	+	$O_2(g)$	→	$CO(g)$	+	$H_2O(l)$
Balanced equation	$CH_3OH(l)$	+	$O_2(g)$	→	$CO(g)$	+	$2H_2O(l)$
Thermochemical equation	$CH_3OH(l)$	+	$O_2(g)$	→	$CO(g)$	+	$2H_2O(l)$ $\Delta H = -726 \text{ kJ mol}^{-1}$
Word equation	ethanol liquid	+	oxygen gas	→	carbon monoxide gas	+	water vapour
Symbol equation	$C_2H_5OH(l)$	+	$O_2(g)$	→	CO	+	$H_2O(l)$
Balanced equation	$C_2H_5OH(l)$	+	$2O_2(g)$	→	2CO	+	$3H_2O(l)$
Thermochemical equation	$C_2H_5OH(l)$	+	$2O_2(g)$	→	2CO	+	$3H_2O(l)$ $\Delta H = -1360 \text{ kJ mol}^{-1}$
Word equation	ethanol liquid	+	oxygen gas	→	carbon solid	+	water vapour
Symbol equation	$C_2H_5OH(l)$	+	$O_2(g)$	→	C(S)	+	$H_2O(l)$
Balanced equation	$C_2H_5OH(l)$	+	$O_2(g)$	→	2C(S)	+	$3H_2O(l)$
Thermochemical equation	$C_2H_5OH(l)$	+	$O_2(g)$	→	2C(S)	+	$3H_2O(l)$ $\Delta H = -1360 \text{ kJ mol}^{-1}$

TIPS:

- **Remember to use the correct state symbol when referring to alcohols, they are often incorrectly assumed to be aqueous (aq) instead of pure liquid (l).**
- **When balancing equations with alcohols do not forget to count the oxygen in the alcohol. This is a common mistake that leads to an unbalanced equation.**

SAMPLE PROBLEM 4

Write the thermochemical equation showing the complete combustion of ethane gas.

Teacher-led video: SP4 (tlvd-0661)

THINK	WRITE
1. Find the formula and molar heat of combustion of ethane using the VCE Chemistry Data Book (Table 11).	C_2H_6 1560 kJ mol^{-1}
2. Write out the formula and balance the equation.	$2C_2H_6(g) + 7O_2(g) \rightarrow 4CO_2(g) + 6H_2O(g)$
3. Add the value, taking care with multiples of molar heat of combustion and the corresponding units.	$\Delta H = 2 \times -1560$ $= -3120 \text{ kJ mol}^{-1}$
Alternatively: the equation can be written for the combustion of one mole of ethane gas.	$C_2H_6(g) + \frac{7}{2}CO_2 \rightarrow 2C_2 + 3H_2O$ $\Delta H = -1560 \text{ kJ mol}^{-1}$

PRACTICE PROBLEM 4

Write the balanced equation showing the incomplete combustion of ethane gas.

on Resources

Interactivity Combustion equations (int-1370)

1.4.3 Calculating *ΔH* values from two or more related reactions

If the enthalpy change of a desired reaction is not known, it is possible to calculate it from a series of related reactions. The calculated value may then be used to make thermochemical predictions.

The following sample problem demonstrates how to find the enthalpy change.

SAMPLE PROBLEM 5

Calculate the enthalpy change for the incomplete combustion of methane in a limited oxygen supply, given the following two equations.

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

$$2CO(g) + O_2(g) \rightarrow 2CO_2(g) \qquad \Delta H = -556\ \text{kJ mol}^{-1}\ [2]$$

THINK	**WRITE**
1. The required equation for the incomplete combustion of methane needs to be written and labelled.	$2CH_4(g) + 3O_2(g) \rightarrow 2CO(g) + 4H_2O(g) \quad [3]$
2. Equations [1] and [2] need to be manipulated so that, when added together, equation [3] is produced. This can be achieved by multiplying equation [1] by 2 and reversing equation [2].	$2CH_4(g) + 4O_2(g) \rightarrow 2CO_2(g) + 4H_2O(g) \quad [4]$ $\Delta H = -1780\ \text{kJ mol}^{-1}$ $2CO_2(g) \rightarrow 2CO(g) + O_2(g) \quad [5]$ $\Delta H = +556\ \text{kJ mol}^{-1}$
3. Adding the new equations [4] and [5] results in cancelling to produce the required equation [3]. The CO_2 cancel out and the O_2 changes to 3 moles. Similarly, the Δ*H* values of [4] and [5] are also added.	[4] + [5] $2CH_4(g) + {}^{3}\cancel{4}O_2(g) + \cancel{2CO_2(g)} \rightarrow$ $\cancel{2CO_2(g)} + 2CO(g) + 4H_2O(g) + \cancel{O_2(g)}$ $2CH_4(g) + 3O_2(g) \rightarrow 2CO(g) + 4H_2O(g) \quad [3]$ $\Delta H = -1780 + 556 = -1224\ \text{kJ mol}^{-1}$
Alternatively: The enthalpy for 1 mole can be calculated by using the equation given.	If the following equation was used: $CH_4(g) + \frac{3}{2}O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$ $\Delta H = -612\text{kJ mol}^{-1}$

PRACTICE PROBLEM 5

Fossil fuels such as coal and petroleum contain sulfur as an impurity. This produces sulfur oxides when they are burned. These are atmospheric pollutants.

Develop the thermochemical equation for the reaction

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

given the following equations.

$$2SO_2(g) + O_2(g) \rightarrow 2SO_3(g) \quad \Delta H = -196 \text{ kJ mol}^{-1} \quad [1]$$

$$2S(s) + 3O_2(g) \rightarrow 2SO_3(g) \quad \Delta H = -760 \text{ kJ mol}^{-1} \quad [2]$$

1.4 EXERCISE

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1. The combustion of 3.15 g of methanol was found to yield 71.5 kJ of heat. Calculate the ΔH value for this reaction and write the thermochemical equation.
2. Calculate the energy released, in kJ, when 3.56 g of carbon undergoes combustion according to the thermochemical equation:

$$2C(s) + O_2(g) \rightarrow 2CO(g) \quad \Delta H = -788 \text{ kJ mol}^{-1}$$

3. The use of hydrogen as a renewable and environmentally friendly fuel is currently the subject of much research. The main product of hydrogen combustion is water. The production of liquid water from the reaction between gaseous hydrogen and gaseous oxygen can be represented by the following thermochemical equation.

$$O_2(g) + 2H_2(g) \rightarrow 2H_2O(l) \quad \Delta H = -564 \text{ kJ mol}^{-1}$$

   Calculate how much energy, in kJ, would be released or absorbed by the following reactions.
   (a) $2O_2(g) + 4H_2(g) \rightarrow 4H_2O(l)$
   (b) $H_2O(l) \rightarrow \frac{1}{2}O_2(g) + H_2(g)$
4. During the production of sulfuric acid by the Contact process, sulfur dioxide is converted to sulfur trioxide according to the equation:

$$2SO_2(g) + O_2(g) \rightarrow 2SO_3(g) \quad \Delta H = -197 \text{ kJ mol}^{-1}$$

   Calculate the heat energy released in the production of 1.00 tonne (10^6 g) of sulfur trioxide gas.
5. Calculate the energy released when 18.5 g of carbon undergoes combustion in a plentiful supply of air according to the equation:

$$C(s) + O_2(g) \rightarrow CO_2(g) \quad \Delta H = -394 \text{ kJ mol}^{-1}$$

6. Methanol burns according to the equation:

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

   Calculate the mass of methanol required to produce 1.000 MJ of energy.
7. Butane and octane are two hydrocarbons commonly used as fuels. The thermochemical equations for these two fuels are:

$$2C_4H_{10}(g) + 13O_2(g) \rightarrow 8CO_2(g) + 10H_2O(l) \quad \Delta H = -5760 \text{ kJ mol}^{-1}$$

$$2C_8H_{18}(g) + 25O_2(g) \rightarrow 16CO_2(g) + 18H_2O(l) \quad \Delta H = -10\,920 \text{ kJ mol}^{-1}$$

   (a) Calculate the heat evolved by the combustion of 100 g of butane.
   (b) Use your answer to (a) to calculate the mass of octane required to produce the same amount of energy. Explain why it is critical to show symbols of state in thermochemical equations.

8. Calculate the ΔH value for the incomplete combustion of pentane, according to the equation:

$$2C_5H_{12}(l) + 11O_2(g) \rightarrow 10CO(g) + 12H_2O(l)$$

given the following equations.

$$2CO(g) + O_2(g) \rightarrow 2CO_2(g) \qquad \Delta H = -556\ \text{kJ mol}^{-1}$$
$$C_5H_{12}(l) + 8O_2(g) \rightarrow 5CO_2(g) + 6H_2O(l) \qquad \Delta H = -3509\ \text{kJ mol}^{-1}$$

9. Calculate ΔH for the reaction:

$$CH_3CH_2OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(g)$$

given the following equations.

$$CH_3CH_2OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l) \qquad \Delta H = -1360\ \text{kJ mol}^{-1}$$
$$H_2O(l) \rightarrow H_2O(g) \qquad \Delta H = +44.0\ \text{kJ mol}^{-1}$$

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1.5 Gaseous fuels and the universal gas equation

KEY CONCEPT

- The definition of gas pressure including units, the universal gas equation and standard laboratory conditions (SLC) at 25 °C and 100 kPa

1.5.1 Working with gases

When considering fuels as energy sources, it is often necessary to deal with gases. The products of combustion are nearly always gases, and some of the fuels themselves are gases. While it is possible to measure their masses, it is often more convenient and meaningful to measure their volumes.

Gases have properties and exhibit behaviours that are different from liquids and solids. Scientists use the **kinetic molecular theory of gases** to explain observed gas properties. The theory consists of five postulates (or points) that form a mental picture of how the particles in a gas would look and behave if we could observe them directly. These are applicable to gas samples under 'moderate conditions', which is usually taken to mean pressures that are not much greater than atmospheric pressure and temperatures considerably greater than those at which the gases liquefy.

FIGURE 1.30 The air in a hot air balloon is heated using a propane burner. The molecules move more rapidly, hitting each other in a random chaotic motion. As they move further apart, the density of the air decreases and the balloon rises.

Kinetic molecular theory of gases

The five postulates that make up the kinetic molecular theory of gases can be summarised as follows.

1. Gases are made up of particles moving constantly and at random.
2. Gas particles are very far apart, and the volume of the particles is very small compared with the volume that the gas occupies.
3. The forces of attraction and repulsion between gas particles are practically zero.
4. Gas particles collide with each other and the walls of their container, exerting pressure. The collisions are perfectly elastic. This means that no kinetic energy is lost when they collide.
5. The higher the temperature, the faster the gas particles move, because they have increased kinetic energy.

1.5.2 Gas behaviour

In any consideration of gas behaviour, the **pressure** each gas exerts, the volume that it occupies, its temperature and the number of gas molecules present in the sample must be determined.

Gas pressure

Gas pressure is the force exerted by particles colliding with the walls of a container. Each tiny collision adds to all the others to make up the continuous force that we call pressure.

The surface of an inflatable airbed, such as the one in figure 1.31, exerts a force and tries to collapse. For the airbed to stay inflated, the particles inside the airbed must be able to exert a large enough force to balance the forces exerted by the surface of the airbed and the external air pressure.

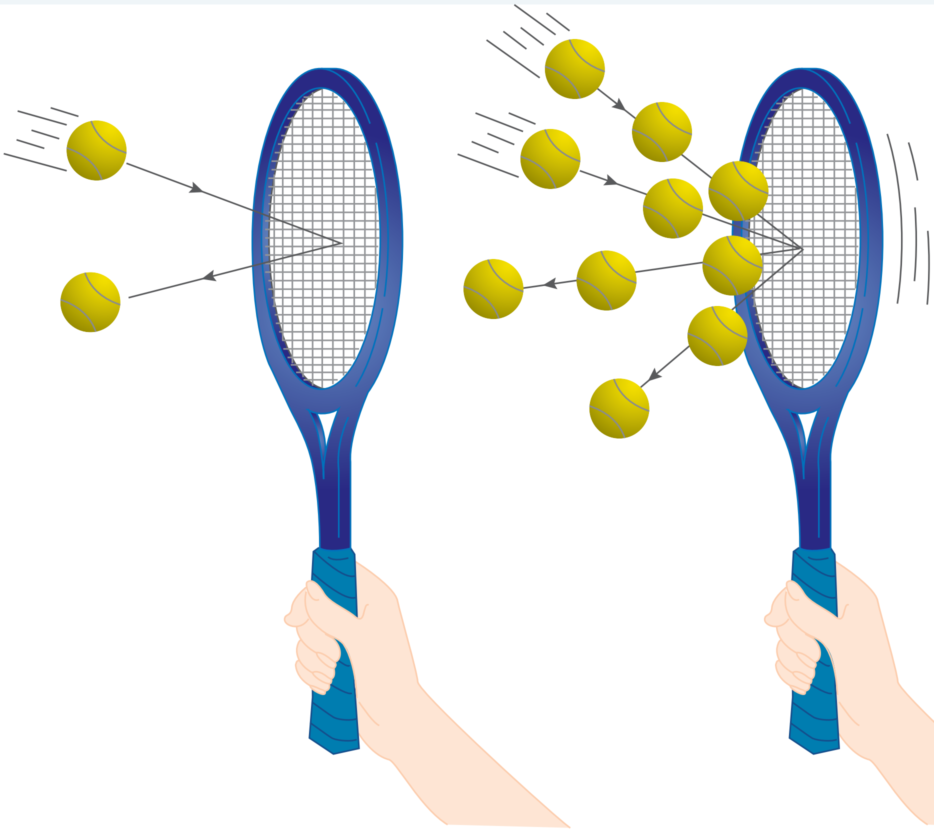
FIGURE 1.31 The particles inside the airbed create pressure.

Pressure (p) is defined as *the force exerted per unit area.*

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

The SI unit of pressure is the pascal (Pa), where 1 pascal is equivalent to a force of 1 newton exerted over an area of 1 square metre (Nm^{-2}).

FIGURE 1.32 If a tennis racquet is struck by a tennis ball, a small force is felt. If a stream of balls is fired at the racquet, it is felt as a continuous pressure.



Atmospheric pressure

Atmospheric pressure is the pressure exerted by the weight of the atmosphere. This is measured by a barometer. Atmospheric pressure at sea level is 101 325 Pa, which is usually simplified to read 101.3 kPa (kilopascal).

Two older units of pressure are millimetres of mercury and atmospheres. One millimetre of mercury (1 mmHg) is defined as the pressure needed to support a column of mercury 1 mm high. This unit developed from the early use of mercury barometers. 0.987 atmospheres (0.987 atm) is the pressure required to support 750 mm of mercury (750 mmHg) in a mercury barometer at 25 °C.

Therefore:

$$750\,\text{mmHg} = 0.987\,\text{atm} = 1.013 \times 105\,\text{Pa} = 101.3\,\text{kPa}$$

Bars and hectopascals (hPa) are used to measure gas pressure in the weather.

$$1\,\text{bar} = 100\,000\,\text{Pa} = 100\,\text{kPa}$$

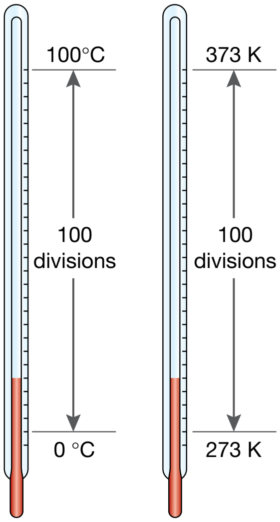
$$1\,\text{millibar (mb)} = \frac{1}{1000}\text{bar} = 100\,\text{Pa} = 1\,\text{hPa}$$

Temperature

Temperature is the amount of heat present in a substance. The Celsius scale takes the freezing point of water as 0 °C and the boiling point of water as 100 °C. The space between these two fixed points is divided into 100 equal intervals, known as degrees. Temperatures below the freezing point of water are assigned negative values, such as −10 °C.

Another temperature scale is the **kelvin**, or absolute, scale. On the Kelvin scale, the freezing point of water is 273 K and its boiling point is 373 K. Notice that a change of 1 ° on the Celsius scale is the same as that on the Kelvin scale. The zero point on the Kelvin scale, 0 K or **absolute zero**, is −273 °C. The relationship between the temperature on the Celsius scale and that on the Kelvin scale is given by the following equations.

FIGURE 1.33 These thermometers show a comparison of the Celsius and Kelvin temperature scales.



Conversion between Celsius and Kelvin

$$\mathrm{K} = {}^\circ\mathrm{C} + 273$$
$${}^\circ\mathrm{C} = \mathrm{K} - 273$$

For example, to convert 25 °C to the absolute scale:

$$\begin{aligned}\mathrm{K} &= 25 + 273 \\ &= 298\end{aligned}$$

Note that temperatures given in K do not have a ° sign.

Volume

Volume is the amount of space a substance occupies. The volume of a gas is commonly measured in cubic metres (m^3), litres (L) or millilitres (mL). The conversion between these is shown below.

$$1\,\mathrm{m}^3 = 1000\,\mathrm{L} = 1\,000\,000\,\mathrm{mL}$$
$$1\,\mathrm{m}^3 = 10^3\,\mathrm{L} = 10^6\,\mathrm{mL}$$

1.5.3 Laws to describe the behaviour of gases

The behaviour of gases has been studied for centuries. As a result, a number of laws have evolved to describe their behaviour mathematically. These laws are independent of the type of gas — it does not matter what the gas is or if the gas is a mixture such as air, these laws apply in exactly the same way to all gases. Two very useful such laws are **Boyle’s law** and **Charles’ law.**

Boyle’s law for pressure–volume changes

Boyle’s law is named after the English physicist and chemist who discovered the relationship between pressure and volume for a sample of gas. It states that, for a fixed amount of gas at constant temperature, pressure is inversely proportional to volume. Mathematically, this can be represented as:

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

where $\propto$ means ‘is proportional to’. From this relationship it can be stated that pV = a constant value. If p_1V_1 = a constant value and p_2V_2 = a constant value, then:

$$p_1V_1 = p_2V_2$$

Charles' law for temperature–volume changes

The relationship between temperature and volume was first identified by the French scientist Jacques Charles, after whom the law is named. While the expansion of all materials with increasing temperature is well known, Charles subjected constant amounts of various gases (at constant pressure) to changes in temperature, each time making accurate measurements of the resulting volume.

To understand this law better, consider a typical set of results as shown in table 1.6.

If these results are graphed a pattern emerges, as shown in figure 1.34.

If the Celsius scale is used to measure temperature, a linear relationship is observed. However, this is not a directly proportional relationship as the graph does not pass through the origin. If the kelvin scale is used, it does. We can therefore state Charles' law as follows.

For a given amount of gas at constant pressure, volume is directly proportional to the absolute temperature.

Mathematically, this can be represented as, $V \propto T$, (where T is the absolute temperature), from which it can be stated that $\frac{V}{T}$ = a constant value.

If $\frac{V_1}{T_1}$ = a constant value and $\frac{V_2}{T_2}$ = a constant value, then:

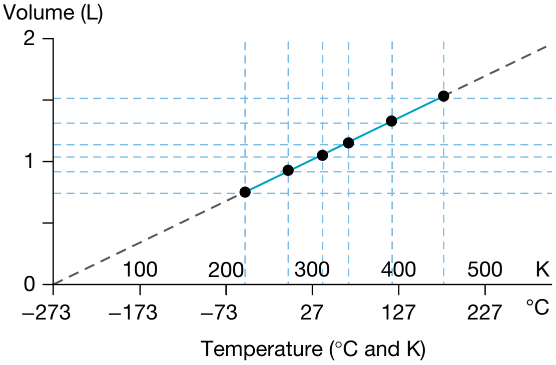
$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

You will notice that figure 1.34 implies a 'lowest possible temperature' — the temperature at which it intersects the x-axis. This temperature is −273.15 °C or 0 K and is known as absolute zero.

TABLE 1.6 Sample results showing the relationship between the temperature and volume of a gas.

Temperature (°C)	Volume (L)
−50	0.75
0	0.92
40	1.05
70	1.15
120	1.32
180	1.52

FIGURE 1.34 Representation of Charles' law showing the two temperature scales, kelvin and degrees Celsius.



Resources

Digital document Experiment 1.1 The relationship between pressure and volume (doc-31252)

1.5.4 Standard laboratory conditions (SLC)

Boyle's law and Charles' law tell us that the volume of a gas sample is sensitive to both temperature and pressure. This makes the comparison of gas volumes tricky. In order to make these comparisons easier, scientists have established sets of standard conditions. These are accepted worldwide and enable gas volumes to be compared meaningfully without temperature or pressure having unwanted effects.

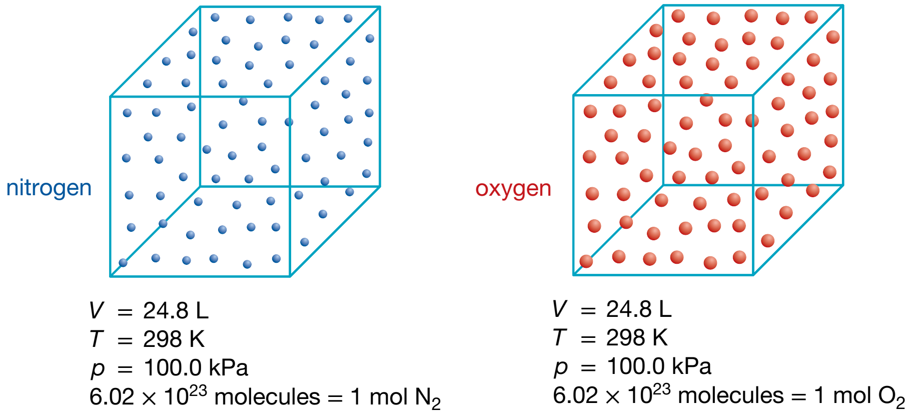
Most experiments are carried out in the laboratory, so the standard laboratory conditions are a temperature of 25 °C (298 K) and a pressure of 100 kPa.

1.5.5 Molar gas volume and Avogadro's hypothesis

Amedeo Avogadro was an Italian scientist who put forward the hypothesis that 'equal volumes of all gases measured at the same temperature and pressure contain the same number of particles'. This means that, if two gases have the same temperature, pressure and volume, they must contain the same number of moles.

It has been found that 1 mole of any gas at SLC occupies a volume of 24.8 L. This volume is called the **molar gas volume** and means that 1 mole of any gas occupies 24.8 L at 25 °C and 100.0 kPa.

FIGURE 1.35 Under the same conditions of temperature and pressure, the volume of a gas depends only on the number of molecules it contains, and not on what the particles are.



The molar volume of a gas varies with temperature and pressure but, at any given temperature and pressure, it is the same for all gases. There is a direct relationship between the number of moles of a gas (n), its molar volume (V_m) and in the actual volume (V); where V is measured in litres.

At a given temperature and pressure, the relationship between the number of moles of a gas (n) and its molar volume (V_m):

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

At SLC, $V_m = 24.8\ \text{L mol}^{-1}$.
The number of moles of gas at SLC:

$$n_{SLC} = \frac{V}{24.8}$$

FIGURE 1.36 A mole of hydrogen gas would occupy the same volume as a mole of oxygen molecules, but because hydrogen weighs less than oxygen, it floats upwards in the air.

SAMPLE PROBLEM 6

Find the mass of 1556.5 mL of H_2 gas that was collected at SLC.

Teacher-led video: SP6 (tlvd-0663)

THINK	WRITE
1. Identify the given and unknown quantities and compare the units given to those required. Convert the volume to litres.	$V = \frac{1556.5\text{ mL}}{1000} = 1.5565\text{ L}$ $m = ?$
2. Determine the number of moles of H_2 gas using the formula, $n = \frac{V}{V_m}$.	$n = \frac{V}{24.8}$ $= \frac{1.5565}{24.8}$ $= 0.06276\text{ mol}$
3. Determine the mass (m) of 0.06276 moles of H_2 gas using the formula, $n = \frac{m}{M}$. **TIP:** The formulas $n = \frac{V}{V_m}$ and $n = \frac{m}{M}$ can be found in table 3 of the VCE Chemistry Data Book.	$n(H_2) = \frac{m}{M}$ $0.0627 = \frac{m}{2.0}$ $m = 2.0 \times 0.0627$ $m = 0.126\text{ g}$
4. Give your answer to 2 significant figures.	The mass of H_2 gas collected was 0.13 g.

PRACTICE PROBLEM 6

a. **5345 mL of a gas was collected at SLC and weighed. Its mass was 9.50 g. Find the molar mass of the gas.**

b. **Given that the gas is one of the main constituents of air, identify the gas.**

1.5.6 The universal gas equation

The **universal gas equation** is used to describe the behaviour of a hypothetical, ideal gas, to help predict the behaviour of a real gas. It is obtained by combining Boyle's law and Charles' law with Avogadro's hypothesis.

Universal gas equation

$$pV = nRT$$

where R is the molar gas constant.

The **molar gas constant**, R, has a value of 8.31 J K^{-1} mol^{-1} when:

- *pressure* (p) is measured in kilopascals (kPa)
- *volume* (V) is measured in litres (L)
- *temperature* (T) is measured in degrees kelvin (K)
- the *quantity* of gas is measured in moles (n).

SAMPLE PROBLEM 7

Find the volume of 6.30 mol of carbon dioxide gas at 23.0 °C and 550 kPa pressure.

Teacher-led video: SP7 (tlvd-0664)

THINK	WRITE
1. Use the molar gas constant (*R*) taken from Table 4 in the VCE Chemistry Data Book.	$R = 8.31\ \text{J K}^{-1}\ \text{mol}^{-1}$
2. Identify the given and unknown quantities and compare the units given to those required. No unit conversion is required. **TIP:** The majority of incorrect calculations when using the universal gas equation arise from not converting other units (e.g. Pa, mL, mass or °C) in the question into the correct units of kPa, L, *n* and K.	$p = 550\ \text{kPa}$ $n = 6.30\ \text{mol}$ $T = 23.0 + 273 = 296\ \text{K}$ $R = 8.31\ \text{J K}^{-1}\text{mol}^{-1}$ $V = ?\ \text{L}$
3. Rearrange the universal gas equation to find volume, *V*. The universal gas equation can be found in Table 3 of the VCE Chemistry Data Book.	$pV = nRT$ $V = \dfrac{nRT}{p}$ $= \dfrac{6.30 \times 8.31 \times 296}{550}$
4. Give your answer to 3 significant figures.	$V = 28.2\ \text{L}$

PRACTICE PROBLEM 7

Calculate the volume of gas, in litres, occupied by 12.8 mol of CH_4 at 9.87 atm and 60 °C.

1.5 EXERCISE

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1. Make the following conversions.
   (a) 780 mmHg to atm
   (b) 4.0 atm to Pa
   (c) 1000 mmHg to Pa
   (d) 1250 mmHg to kPa
   (e) 200 °C to K
   (f) 500 K to °C
   (g) 3.0 m^3 to L
   (h) 250 L to mL
   (i) 1600 mL to L
   (j) 3×10^6 mL to L
   (k) 5×10^3 mL to m^3
   (l) 600 mL to m^3
2. Consider table 1.7.
   (a) Convert each pressure measurement (*p*) into its reciprocal $\left(\dfrac{1}{p}\right)$.
   (b) Plot a graph of pressure versus volume. Put pressure on the horizontal (*x*) axis and volume on the vertical (*y*) axis.
   (c) Plot a second graph with the volume on the vertical axis and $\dfrac{1}{p}$ on the horizontal axis, and extrapolate the graph to the origin.
   (d) Compare and account for the two graphs.

TABLE 1.7 Sample results showing the relationship between the pressure and volume of a gas

Pressure (kPa)	Volume (L)
120	0.261
145	0.218
162	0.193
180	0.171
200	0.159
216	0.145
240	0.130
258	0.120

3. Calculate the numbers of moles of the following gases at SLC.
   (a) 15 L of oxygen, O_2
   (b) 25 L of chlorine, Cl_2
4. Calculate the volumes of the following gases at SLC.
   (a) 1.3 mol hydrogen, H_2
   (b) 3.6 g of methane, CH_4
   (c) 0.35 g of argon, Ar
5. Calculate the masses of the following gas samples at SLC.
   (a) 16.5 L of neon, Ne
   (b) 1050 mL of sulfur dioxide, SO_2
6. What is the mass (in kg) of 850 L of carbon monoxide gas measured at SLC?
7. A 0.953 L quantity of a gas measured at SLC has a mass of 3.20 g. What is the molar mass of the gas? What is the gas?
8. Calculate the volume of gas, in litres, occupied by the following.
   (a) 3.5 mol of O_2 at 100 kPa and 50 °C
   (b) 6.5 g of Ar at 50 kPa and 100 °C
   (c) 0.56 g of CO_2 at 50 atm and 20 °C
   (d) $1.3\ 10^{-3}$ g He at 60 kPa and −50 °C
   (e) 1.5×10^{21} molecules of Ne at 40 kPa and 200 °C
9. (a) Calculate the volume occupied by 42.0 g of nitrogen gas at a pressure of 200 kPa and a temperature of 77 °C.
   (b) A 5.00 L balloon contains 0.200 mol of air at 120 kPa pressure. What is the temperature of air in the balloon?
10. (a) If 55 mol of H_2 gas is placed in a 10 L flask at 7 °C, what would be the pressure in the flask?
    (b) Calculate the energy released when 200 mL of diborane, B_2H_6, is burned at 150 °C and 1.50 atm according to the following equation.

$$B_2H_6(g) + 3O_2(g) \rightarrow B_2O_3(s) + 3H_2O(g) \qquad \Delta H = -2035\ \text{kJ mol}^{-1}$$

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1.6 Calculations related to the combustion of fuels

KEY CONCEPT

- 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

1.6.1 Mass–volume calculations

Many chemical reactions involve gases. For example, 48ptbarbecues, furnaces and engines burn fuel and produce carbon dioxide and water vapour. In order to ensure that the reactions are efficient and as complete as possible, it is essential to calculate the volumes or masses of the gases or fuels required.

SAMPLE PROBLEM 8

In a gas barbecue, propane is burned in oxygen to form carbon dioxide and water vapour. If 22.0 g of CO_2 is collected and weighed, find the volume of propane at 200 °C and 1.00×10^5 Pa. The balanced equation for this reaction is $C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(g)$.

Teacher-led video: SP8 (tlvd-0665)

THINK	WRITE
1. Identify the given and unknown quantities and compare the units given to those required. Convert the temperature units to Kelvin.	$p = 1.00 \times 10^5$ Pa $m(CO_2) = 22.0$ g $T = 200\ °C + 273 = 473$ K $V = ?$ L
2. Calculate the number of moles of the known quantity of substance using the following formula, found in Table 3 of the VCE Chemistry Data Book. $n = \frac{m}{M}$	$n = \frac{m}{M}$ M of $CO_2 = 12.0 + (2 \times 16.0)$ $= 44.0\ g\ mol^{-1}$. $n(CO_2) = \frac{22.0}{44.0}$ $= 0.500$ mol
3. Use the combustion equation given to find the molar ratio of unknown to known quantities, and calculate the number of moles of the required substance. From the given reaction, we know that 3 moles of CO_2 are produced from 1 mole of C_3H_8.	$n(C_3H_8) = \frac{n(CO_2)}{3}$ $= \frac{0.500}{3}$ $= 0.1666$
4. Rearrange the universal gas equation, $pV = nRT$, to determine the volume of the propane.	$V(C_3H_8) = \frac{nRT}{p}$ $= \frac{0.1666 \times 8.31 \times 473}{100} \times 100$
5. Give your answer to 3 significant figures.	$V = 6.55$ L

PRACTICE PROBLEM 8

Using the following equation, calculate the mass of hexane that is required to produce 100 L of carbon dioxide gas at SLC.

$$2C_6H_{14}(l) + 19O_2(g) \rightarrow 12CO_2(g) + 14H_2O(g)$$

1.6.2 Volume–volume calculations

Consider the reaction between nitrogen and hydrogen gas.

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

This equation says that when 1 mole of N_2 reacts with 3 moles of H_2 it will produce 2 moles of ammonia.

According to Avogadro's hypothesis, if the gases are at the same pressure and temperature, their *molar* ratios are equal to their *volume* ratios. Therefore, we use volumes instead of moles and can say that 10 mL of N_2 reacts with 30 mL of H_2 to form 20 mL of ammonia.

$$\begin{array}{ccc} N_2(g) + & 3H_2(g) \rightarrow & 2NH_3(g) \\ 1\text{ mol} & 3\text{ mol} \rightarrow & 2\text{ mol} \\ 1\text{ vol} & 3\text{ vol} \rightarrow & 2\text{ vol} \\ 10\text{ mL} & 30\text{ mL} \rightarrow & 20\text{ mL} \end{array}$$

$$\frac{V(\text{unknown})}{V(\text{known})} = \frac{\text{coefficient of unknown}}{\text{coefficient of known}}$$

SAMPLE PROBLEM 9

If 100 m^3 of ethene is burned according to

$$C_2H_4(g) + 3O_2(g) \rightarrow 2CO_2(g) + 2H_2O(g)$$

calculate the volume of:

a. **carbon dioxide produced**

b. **oxygen consumed.**

(Assume all gas volumes are measured at the same temperature and pressure.)

THINK	WRITE
1. Because all gas volumes are measured at the same temperature and pressure, the equation may be interpreted in terms of volume ratios.	**a.** $V(CO_2) = 2\,V(C_2H_4)$ Therefore, $V(CO_2) = 2 \times 100 = 200$ m^3. **b.** $V(O_2) = 3V(C_2H_4)$ Therefore, $V(O_2) = 3 \times 100 = 300$ m^3.

PRACTICE PROBLEM 9

Methane gas burns in air at room temperature and pressure, according to the equation:

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

If 25 mL of methane is burned at room temperature and pressure, find the volumes of the following reactants and products:

a. **oxygen**
b. **carbon dioxide**
c. **water**

1.6.3 Applying volume stoichiometry to thermochemistry

Just as the principles of mass–mass **stoichiometry** can be extended to include gas volumes, the thermochemical calculations introduced earlier in this topic can also be extended to include gas volumes. This is very useful because it is often more convenient to measure a gas's volume than its mass. If pressure and temperature are also measured, the universal gas equation provides a formula to change between volumes and moles.

SAMPLE PROBLEM 10

Calculate the heat energy released when 375 mL of methane at 21.0 °C and 767 mmHg pressure is burned according to:

$$\mathbf{CH_4(g + 2O_2(g) \; \rightarrow \; CO_2(g) + 2H_2O(l) \quad \Delta \mathit{H} = -890\,kJ\,mol^{-1}}$$

Teacher-led video: SP10 (tlvd-0667)

THINK	WRITE
1. Use the universal gas equation to calculate the number of moles of methane used. Identify the given and unknown quantities and compare the units given to those required. Convert the temperature units to Kelvin, volume to litres and pressure to kPa. Convert pressure to kPa by dividing the given mmHg in the question by 750 and then multiplying by 100. Remember 750 mmHg = 100 kPa.	$T = 21.0\,°\mathrm{C} + 273$ $= 294\,\mathrm{K}$ $V = 375\,\mathrm{mL}$ $= 0.375\,\mathrm{L}$ $p = 767\,\mathrm{mmHg}$ $= \frac{767}{750} \times 100$ $= 102.2\,\mathrm{kPa}$
2. To determine the number of mole of methane, rearrange the universal gas equation and apply the value of R from Table 4 in the VCE Chemistry Data Book.	$p\mathrm{V} = nRT$ $n(\mathrm{CH_4}) = \frac{pV}{RT}$ $= \frac{102.2 \times 0.375}{8.31 \times 294} \times 100$ $= 1.569 \times 10^{-2}\,\mathrm{mol}$
3. Calculate the heat evolved from 1.569×10^{-2} moles of CH_4.	Heat evolved $= 889 \times 1.569 \times 10^{-2}$ $= 13.9484\,\mathrm{kJ}$
4. Give the answer to 3 significant figures.	14.0 kJ

PRACTICE PROBLEM 10

Calculate the energy required to convert 2.50 L of carbon dioxide, at SLC, to glucose according to the equation:

$$6CO_2(g) + 6H_2O(l) \rightarrow C_6H_{12}O_6(aq) + 6O_2(g) \quad \Delta H = +2816\text{ kJ}$$

1.6.4 Mass–mass calculations

Mass–mass calculations were introduced in unit 2. The unknown mass of a substance can be calculated using a known mass of another substance and their balanced chemical equation.

SAMPLE PROBLEM 11

If it is assumed that petrol is entirely octane, and that it burns according to:

$$2C_8H_{18}(g) + 25O_2(g) \rightarrow 16CO_2(g) + 18H_2O(l) \qquad \Delta H = -10\,928\text{ kJ mol}^{-1}$$

calculate the:

a. **mass of carbon dioxide produced per MJ of energy evolved**

b. **volume of carbon dioxide produced at 100 kPa and 20.0 °C per MJ of energy evolved.**

Teacher-led video: SP11 (tlvd-0668)

THINK	WRITE
a. 1. From the equation given, 10 928 kJ accompanies the formation of 16 moles of CO_2. Calculate the number of moles of CO_2 for 1 MJ generated.	$\frac{10928\text{ kJ}}{1000} = 10.928\text{ MJ}$ $n(CO_2) = \frac{16}{10.928}$ $= 1.4641\text{ mol}$
2. To determine the mass of CO_2 generated apply the formula $n = \frac{m}{M}$.	$n = \frac{m}{M}$ $m(CO_2) = n \times m$ $= 1.4641 \times 44.0$ $= 64.4\text{ g}$
b. 1. Rearrange the universal gas equation to find equal volume. Identify the given and unknown quantities and compare the units given to those required.	$V = \frac{nRT}{p}$ $n = 1.4641$ $T = 273 + 20.0 = 293\text{ K}$ $p = 100\text{ kPa}$
2. Calculate the volume.	$V(CO_2) = \frac{1.4641 \times 8.31 \times 293}{100}$ $= 35.6483\text{ L}$
3. Give your answer to 3 significant figures.	35.6 L of CO_2 is produced per megajoule of energy released, (35.6 L MJ^{-1}), at the stated conditions of temperature and pressure.

PRACTICE PROBLEM 11

According to the following reaction, what mass of ethyne is required to produce 50.0 g of water vapour?

$$2C_2H_2(g) + 5O_2(g) \rightarrow 4CO_2(g) + 2H_2O(g)$$

on Resources

Interactivity Mole relationships (int-1214)

1.6.5 Fuels and greenhouse gases

The principles of stoichiometry and thermochemistry can be combined to quantify the effect that energy production, especially through the combustion of fossil fuels, has on the environment. Gases such as carbon dioxide, methane, nitrous oxide and ozone contribute to the **enhanced greenhouse effect**. Of these, carbon dioxide is produced in the greatest amounts due to the use of fossil fuels as energy sources. The increasing level of these gases has led to international treaties such as the Kyoto Protocol of 1997 and the Paris Agreement of 2016. These treaties obligate signatory countries to reduce their **greenhouse gas** emissions in an attempt to combat climate change and move towards a sustainable, low-carbon future.

In order to meet targets for reduction, countries need to estimate their energy requirements, both current and future, and compare the energy sources available for the required energy production. A useful unit in such comparisons is the amount of greenhouse gas produced (usually carbon dioxide) per megajoule of energy released. Typical units are g MJ^{-1} and L MJ^{-1}.

FIGURE 1.37 Carbon dioxide is the most significant greenhouse gas due to the massive amounts produced by human activity. However, it is not the strongest greenhouse gas.

Greenhouse effects of methane gas and water vapour

Methane is produced by a number of natural processes and, in many of these situations, it can easily enter the atmosphere. Methane is a more potent greenhouse gas than carbon dioxide because it is better at absorbing heat. However, it can also be used as a fuel. The equation for burning methane is:

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

Assuming that all volumes are measured at the same temperature and pressure, if methane is captured and used as a fuel, the calculated net change in greenhouse gas volume that would occur is:

$$V(CH_4)\text{ consumed} = V(CO_2)\text{ produced.}$$

Therefore, there is no net change because 1 mole of methane produces 1 mole of carbon dioxide.

It would be incorrect to assume that capturing and burning methane would produce no net environmental benefit. Because methane is a more potent greenhouse gas than carbon dioxide, there is an environmental benefit gained from burning it, rather than just letting it escape into the atmosphere. However, if carbon dioxide could also be captured and prevented from entering the atmosphere, the environmental benefit would be even greater.

Carbon dioxide is the most significant greenhouse gas due to the large volumes in which it is produced. For this reason, other greenhouse gas emissions are often measured in 'carbon dioxide equivalent'. That is, all these other gases are converted to the volume of carbon dioxide that would produce the same effect.

1.6 EXERCISE

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1. Oxygen gas can be prepared in the laboratory by the decomposition of potassium nitrate according to the equation:

$$2KNO_3(s) \rightarrow 2KNO_2(s) + O_2(g)$$

When 14.5 L of O_2 is formed at 1.00 atm and 25.0 °C, what mass of KNO_2 is also formed?

2. Magnesium reacts with hydrochloric acid according to the equation:

$$Mg(s) + 2HCl(aq) \rightarrow MgCl_2(aq) + H_2(g)$$

What mass of magnesium, when reacted with excess hydrochloric acid, would produce 5.0 L of hydrogen gas, measured at 26.0 °C and 1.2 kPa?

3. At high temperatures, such as those in a car engine during operation, atmospheric nitrogen burns to produce the pollutant nitrogen dioxide, according to the equation:

$$N_2(g) + 2O_2(g) \rightarrow 2NO_2(g)$$

(a) If 20 mL of nitrogen is oxidised, calculate the volume of oxygen needed to produce the pollutant. Assume that temperature and pressure remain constant.
(b) What is the initial volume of reactants in this combustion reaction?
(c) What is the final volume of products in the reaction?
(d) Is there an overall increase or decrease in the volume of gases on completion of the reaction?

4. (a) Calculate the net change in mass of greenhouse gas produced by the combustion of 128 g of methane.
(b) Express your answer as a percentage increase or decrease.
(c) Comment on how the units used (mass or volume) may influence the conclusions drawn from calculations such as in this question and in sample problem 11.

5. The molar heat of combustion for ethanol is –1364 kJ mol^{-1}. Calculate the mass of carbon dioxide emitted when ethanol is used to produce 1.00 MJ of heat.

6. (a) Methanol is also a fuel. Its molar heat of combustion is –725 kJ mol^{-1}. What mass of carbon dioxide would be produced using methanol to generate 1.00 MJ of heat?
(b) What volume of carbon dioxide would be produced at SLC?
(c) Comment on your answers to questions 5 and 6(a) in relation to the masses of CO_2 produced.

7. A coal-fired power station using brown coal as its fuel operates at 37.0% overall energy efficiency. The brown coal has a heat value of 16.0 kJ g^{-1} and a carbon content of 29.0%. Assuming that all the carbon present forms carbon dioxide, calculate the carbon dioxide produced per MJ of electrical energy produced in units of:
(a) g MJ^{-1}
(b) L MJ^{-1} (at SLC).

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1.7 Calculating heat energy using the specific heat capacity of water

KEY CONCEPT

- The use of specific heat capacity of water to determine the approximate amount of heat energy released in the combustion of a fuel

1.7.1 Specific heat capacity

Specific heat capacity is the amount of heat required to increase the temperature of one gram by 1 °C or 1 K.

Theory and formula

So far, we have made predictions relating to fuel quantities and heat outputs using thermochemical equations. However, there are two issues that have not yet been addressed.

- How are ΔH values obtained in the first place?
- Thermochemical equations can be used for fuels that are pure substances, but how are heat outputs and predictions made for fuels that are mixtures, such as petrol, diesel, wood and coal?

FIGURE 1.38 Making pyrex test tubes requires a very hot flame because glass has a low specific heat capacity of around 0.7 J $g^{-1}K^{-1}$.

The answer to both these questions is to burn a small amount of fuel and capture the heat evolved in some way so that it can be measured. The results obtained are then scaled up to a reference amount so that comparisons can be made. The values obtained are quoted in units that take into account the units used to measure the energy output and the particular reference amount being used. Common units are kJ mol^{-1}, kJ g^{-1} and MJ $tonne^{-1}$.

For this process to be done accurately, a device called a calorimeter must be used. There are two main types of calorimeters: solution calorimeters and bomb calorimeters. The features of these and their uses are discussed in topic 12.

An alternative method is to use the fuel to heat a known mass of water and measure the resultant temperature increase. This method produces only approximate results, with the degree of accuracy depending on the steps taken to minimise heat loss to the surroundings.

Specific heat capacity:

$$q = mc\Delta T$$

where:
q is the amount of energy required
m is mass of the substance
c is the specific heat capacity
T is temperature.

The specific heat capacity formula can be used to calculate the heat required to raise a given mass (m) of a substance of known specific heat (c) by a certain temperature (ΔT). The specific heat capacity, c, of a substance is the amount of energy needed to raise the temperature of 1 g of the substance by 1 °C or 1 K. This formula is used to calculate the heat added to the water.

1.7.2 Using specific heat capacity in calculations

SAMPLE PROBLEM 12

The heat content of kerosene was determined by using a kerosene burner to heat 250 mL of water. It was found that burning 0.323 g of kerosene raised the temperature of the water by 11.2 °C.

Given that the specific heat capacity of water is 4.18 J g^{-1} K^{-1}, calculate the heat energy released from kerosene in kJ g^{-1} and MJ $tonne^{-1}$.

THINK	WRITE
1. Identify the given and unknown quantities and compare the units given to those required.	$q = ?$ $m = 250$ mL of water $= 250 \times 0.997$ g $= 249.25$ g $c = 4.18\text{J g}^{-1}\text{ K}^{-1}$ $\Delta T = 11.2\ °\text{C}$
2. Calculate the heat energy (q) transferred to the water using the formula, $q = mc\Delta T$, which can be found in Table 3 in the VCE Chemistry Data Book. Convert J to kJ for easier manipulation. The specific heat capacity is given in J g^{-1} K^{-1}. **TIP**: 1 mL of water has a mass 0.997 g (see Table 4 in the VCE Chemistry Data Book).	$q = mc\Delta T$ $= 249.25\text{ g} \times 4.18\text{ J g K}^{-1} \times 11.2\ °\text{C}$ $= 11\,669$ J $= 11.67$ kJ
3. Scale this value up to the chosen reference amount (in this case, from 0.323 g to 1 g).	Heat evolved $= 11.67 \times \dfrac{1}{0.323\text{ g}} = 36.13\text{ kJ g}^{-1}$
4. Convert this to MJ $tonne^{-1}$. Recall: 1 tonne = 10^6 g = 1 000 000 g 1000 kJ = 1 MJ	$36.13\text{ kJ g}^{-1} = \dfrac{36.13\text{ kJ}}{1\cancel{000}} \times 1\,000\,\cancel{000}$ $= 36\,130\text{ MJ tonne}^{-1}$
5. Give your answer to 3 significant figures.	$36\,130\text{ MJ tonne}^{-1} = 36.1 \times 10^3\text{ MJ tonne}^{-1}$

Note: This represents a minimum value. Not all of the heat from the kerosene would have gone into the water. Some of it would have been wasted in heating the surrounding air and the equipment used to hold the water.

PRACTICE PROBLEM 12

It takes 78.2 J of energy to raise the temperature of 45.6 g of lead from 19.2 °C to 32.5 °C. Calculate the specific heat capacity of lead.

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Interactivity Simulating a heat of combustion experiment (int-1254)

1.7 EXERCISE

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An experiment to compare the energy output of candle wax, ethanol and butane was performed by setting up the apparatus shown in figure 1.39. The ethanol was poured into a crucible. A small wax candle stuck onto a watch glass and a gas cigarette lighter were each used as a 'burner' after being lit. Each burner was weighed before and after it was used to heat 200 g of water. The results are shown in table 1.8. (Assume the formula for candle wax is $C_{20}H_{42}$.)

FIGURE 1.39 Apparatus for testing the energy output of candle wax

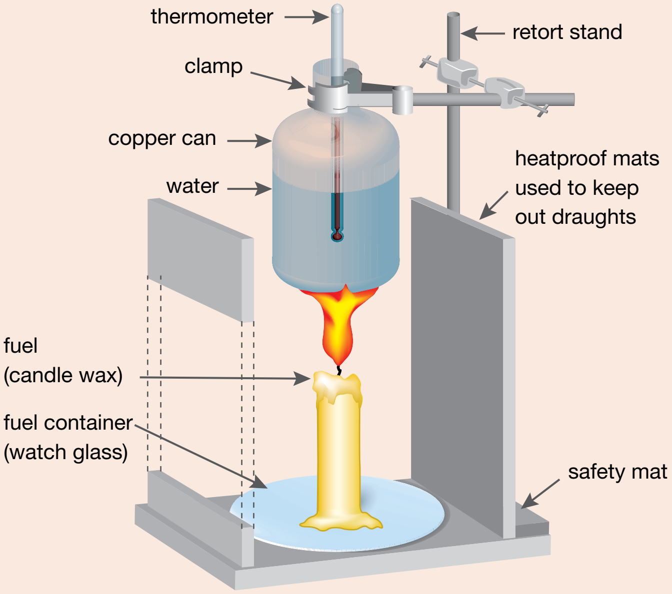

TABLE 1.8 Results of combustion of different fuels

Property	Ethanol	Candle wax	Butane
Mass of 'burner' before heating (g)	23.77	32.72	43.94
Mass of 'burner' after heating (g)	22.54	32.50	43.71
Mass of fuel used (g)			
Mass of water (g)	200	200	200
Initial temperature of water (°C)	20.0	20.0	20.0

Highest temperature of water (°C)	35.0	30.0	29.0
Temperature rise (°C)			
Molar mass (g mol^{-1})			

1. (a) Complete table 1.8.
   (b) Taking the specific heat capacity of water as 4.18 J g^{-1} $°C^{-1}$, calculate the energy produced from 1.00 g of each substance. How do the results compare?
   (c) Calculate the heat of combustion (enthalpy per mole of substance used) for each substance. How do the results compare?
   (d) The molar heat of combustion of ethanol has been found to be –1364 kJ mol^{-1}.
      i. Is the combustion exothermic or endothermic?
      ii. What was the percentage accuracy of the experiment in figure 1.39?
      iii. List the sources of error in the experiment and describe how some of these errors can be minimised.

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1.8 Review

1.8.1 Summary

Fossil fuels and biofuels

- Fossil fuels include coal, petroleum and natural gas, and are formed from the decaying remains of plants and small marine creatures.
- Biofuels are carbon-based energy sources primarily formed from plant matter.
- Renewable fuels can be replaced by natural processes at a faster rate than they are consumed. For example, biofuels, solar, hydro-electric, tidal, geothermal and wave energy.
- Non-renewable fuels cannot be replaced by natural processes at a faster rate than they are consumed. For example, fossil fuels and nuclear fuels.
- Petroleum (crude oil) is a fossil fuel that is refined by fractional distillation to produce different fuels based on their different boiling points.
- Biogas is largely methane and is produced when organic matters rots in the absence of oxygen.
- Bioethanol is produced from fermenting sugar from waste materials such as wheat starch or molasses. It is used as an additive to petrol.
- Biodiesel is made from the reaction of plant oils and animal fats with alcohol through transesterification.

Combustion of fuels

- Energy is the ability to do work.
- The SI unit of energy is the joule (J).
- 1000 J = 1 kJ; 1 000 000 J = 1000 kJ = 1 MJ
- The study of energy changes that accompany chemical reactions is called thermochemistry or chemical thermodynamics.
- The total energy stored in a substance is called the enthalpy, or heat content, of the substance and is represented by the symbol *H*.

- The change in enthalpy as a reaction is known as the heat of a reaction and can be determined according to the relationship: $\Delta H = H_{\text{products}}$- $H_{\text{reactants}}$.
- The environmental effect of a fuel can be measured in terms of its greenhouse gas emissions per megajoule of energy produced.
- Energy exists in a number of different forms that are interconvertible, including mechanical, thermal, chemical, sound, light, electrical, gravitational and nuclear.
- According to the Law of Conservation of Energy, whenever energy is converted from one form to another, the total quantity of energy remains the same.
- The efficiency of changing one form of energy into another form of energy varies.
- Efficiency is defined as a percentage according to the formula:

$$\%\text{ efficiency} = \frac{\text{energy obtained in desired form}}{\text{energy available before conversion}} \times \frac{100}{1}$$

- Exothermic reactions release energy to their surroundings and have a negative ΔH value.
- Endothermic reactions absorb energy from their surroundings and have a positive ΔH value.
- Energy diagrams or profiles may be used to visually represent changes in enthalpy.

Thermochemical equations

- Thermochemical equations are chemical equations that, besides being balanced with respect to charge and mass, also include a ΔH value.
- Thermochemical equations are chemical equations that, in addition to balancing charge and mass, include the enthalpy change and may be used in stoichiometric calculations to determine the energy changes associated with chemical reactions.
- ΔH values in thermochemical equations can be evaluated from experimental data and from the ΔH values of related equations.
- Water is formed in any combustion reaction.
- Complete combustion occurs in excess oxygen when the fuel is completely oxidised to carbon dioxide and water
- Incomplete combustion occurs when oxygen is not in excess and products will be variable and contain a combination of carbon, carbon monoxide or carbon dioxide.

Gaseous fuels and the universal gas equation

- The kinetic molecular theory of gases helps explain gas properties and begins with five assumptions about gas particles. These particles:
  - are moving constantly and at random
  - experience an increase in kinetic energy and move more quickly when temperature is increased
  - have insignificant attractive or repulsive forces between them
  - are very far apart and their volume is small compared to the volume they occupy
  - collide with one another and the walls of their container, exerting pressure.
- When considering gas behaviour, we are concerned with the pressure a gas exerts, the volume it occupies, its temperature and the number of molecules it has. We express these in SI units.
  - Pressure is measured in pascal (Pa). 1000 Pa = 1 kPa.

$$750\,\text{mmHg} = 0.987\,\text{atm} = 100\,\text{kPa}$$

  - Temperature is converted from degrees Celsius (°C) to the absolute or Kelvin scale, where absolute zero is –273 °C.

$$\text{K} = {}^\circ\text{C} + 273$$

  - Volume is measured in cubic metres (m^3), litres (L) or millilitres (mL).

$$1\ \text{m}^3 = 10^3\ \text{L} = 10^6\ \text{mL}$$

  - Quantity is measured in moles (mol).
- Boyle's law states that the volume of a fixed mass of gas at constant temperature is inversely proportional to the pressure exerted on it.

$$p_1V_1 = p_2V_2$$

- Charles' law states that the volume of a fixed mass of gas at constant pressure is directly proportional to its absolute (Kelvin) temperature.

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

- Gas volumes are measured using a standard set of fixed conditions, called standard laboratory conditions (SLC), where temperature is 25 °C (298 K) and pressure is 100.0 kPa.
- The molar gas volume is the volume that 1 mole of gas occupies. At SLC, this equals 24.8 L. To calculate amounts of gases at SLC, we use the equation:

$$n_{\text{SLC}} = \frac{V}{24.8} \text{ where } V \text{ is measured in litres.}$$

- The universal gas equation combines several of the gas laws and contains the universal gas constant (R).

$$pV = nRT$$

The constant R is equal to 8.31 J K^{-1} mol^{-1} and V is measured in litres, T in Kelvin and p in kPa.
- The universal gas equation enables stoichiometric calculations that link masses and volumes together (mass–volume calculations).

Calculations related to the combustion of fuels

- Volume–volume stoichiometry can be performed using volumes rather than moles because, for gases at the same pressure and temperature, mole ratios are equal to volume ratios.

$$\frac{V(\text{unknown})}{V(\text{known})} = \frac{\text{coefficient of unknown}}{\text{coefficient of known}}$$

Calculating heat energy using the specific heat capacity of water

- The specific heat capacity (c) of a substance is defined as the amount of energy needed to raise the temperature of 1 g of the substance by 1 °C or 1 K.
- The heat energy in a fuel can be estimated by using a known amount of the fuel to heat a known amount of water. The formula $q = mc\Delta T$ is used to calculate the heat energy added to the water; where q is the amount of energy required, m is the mass of the substance, c is the specific heat capacity and T is temperature.

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1.8.2 Key terms

absolute zero the lowest temperature that is theoretically possible; 0 K

absorbed taken into another substance

aquifer underground rock layers that contain water; this groundwater can be extracted using a well

biodiesel a fuel produced from vegetable oil or animal fats and combined with an alcohol, usually methanol

bioethanol ethanol produced from plants, such as sugarcane, and used as an alternative to petrol

biofuel renewable, carbon-based energy source formed in short period of time from from living matter

biogas fuel produced from the fermentation of organic matter

Boyle's law describes the relationship between pressure and volume of a gas, such that for a fixed amount of gas at constant temperature, pressure is inversely proportional to volume. $p_1V_1 = p_2V_2$

change in enthalpy the amount of energy released or absorbed in a chemical reaction

Charles' law describes the relationship between temperature and volume of a gas, such that for a given amount of gas at constant pressure, volume is directly proportional to the absolute temperature. $\frac{V_1}{T_1} = \frac{V_2}{T_2}$

chemical energetics a branch of science that deals with the properties of energy and the way it is transformed in chemical reactions

coal the world's most plentiful fossil fuel; formed from the combined effects of pressure, temperature, moisture and bacterial decay on vegetable matter over several hundred million years

efficiency (of energy conversion) the ratio between useful energy output and the energy input

endothermic describes a chemical reaction in which energy is absorbed from the surroundings

enhanced greenhouse effect the increasing concentrations of greenhouse gases

enthalpy a thermodynamic quantity equivalent to the total heat content of a system

exothermic describes a chemical reaction in which energy is released to the surroundings

fossil fuels fuels formed from once-living organisms

fracking the process of pumping a large amount of mainly water under high pressure into a drilled hole, in order to break rock so that it will release gas or oil

fractional distillation the process of separating component fuels based on their different boiling points

fuel a substance that burns in air or oxygen to release useful energy

global warming a gradual increase in the overall temperature of the Earth's atmosphere

greenhouse gases gases that contribute to the greenhouse effect by absorbing infrared radiation

heat of reaction the heat evolved or absorbed during a chemical reaction taking place under conditions of constant temperature and of either constant volume or, more often, constant pressure

Kelvin the SI base unit of thermodynamic temperature, equal in magnitude to the degree Celsius

kinetic energy energy associated with movement, in doing work

kinetic molecular theory of gases Gas particles are in continuous, random motion. Collisions between gas particles are completely elastic.

Law of Conservation of Energy Energy cannot be created or destroyed but only changed from one form into another or transferred from one object to another.

liquefied petroleum gas (LPG) a hydrocarbon fuel that consists mainly of air propane and butane; non-toxic, non-corrosive, lead-free and denser than air

molar gas constant R, the constant of the universal gas equation; $R = 8.31 \text{ J mol}^{-1} \text{ K}^{-1}$ when pressure is measured in kPa, volume is measured in L, temperature is measured in K and the quantity of the gas is measured in moles (n).

molar gas volume the volume occupied by a mole of a substance at a given temperature and pressure. At SLC, 1 mole of gas occupies 24.8 litres.

natural gas a source of alkanes (mainly methane) of low molecular mass

non-renewable (with reference to energy sources) energy sources are consumed faster than they are being formed

pascal (Pa) unit of pressure

petroleum viscous, oily liquid composed of crude oil and natural gas that was formed by geological processes acting on marine organisms over millions of years; a mixture of hydrocarbons used to manufacture other fuels and many other chemicals

potential energy energy that is stored, ready to do work

pressure the force per unit area that one region of a gas, liquid or solid exerts on another

renewable (with reference to energy sources) energy sources that can be produced faster than they are used

standard laboratory conditions (SLC) 100 kPa and 25°C

stoichiometry calculating amounts of reactants and products using a balanced chemical equation

thermochemical equations balanced stoichiometric chemical equations that include the enthalpy change

thermochemistry the branch of chemistry concerned with the quantities of heat evolved or absorbed during chemical reactions

transesterification the reaction between an ester of one alcohol and a second alcohol to form an ester of the second alcohol and an alcohol from the original ester

universal gas equation $PV = nRT$, where pressure is in kilopascals, volume is in litres and temperature is in Kelvin

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Digital document Key terms glossary – Topic 1 (doc-31392)

1.8.3 Practical work and investigations

Experiment 1.1

Fractional distillation of an ethanol/water mixture

Aim: To separate a mixture of ethanol and water by fractional distillation

Digital document: doc-31250

Teacher-led video: eles-3225

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Digital documents Practical investigation logbook (doc-31393)
Experiment 1.2 The relationship between pressure and volume (doc-31252)

1.8 Exercises

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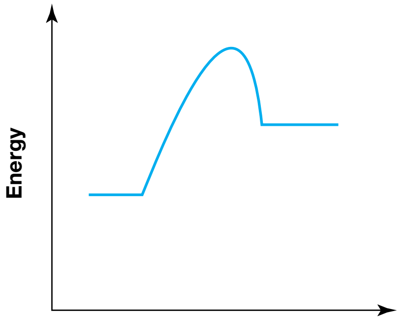
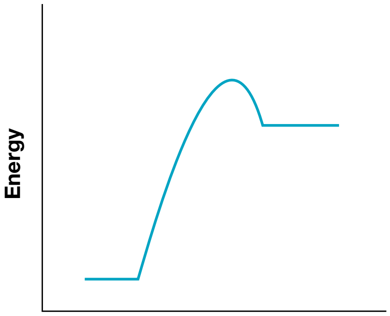
1.8 Exercise 1: Multiple choice questions

1. Which of the energy profiles below represents the *most exothermic* reaction?

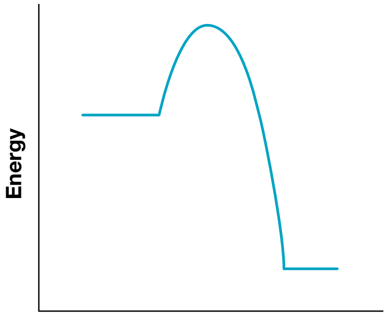
A.



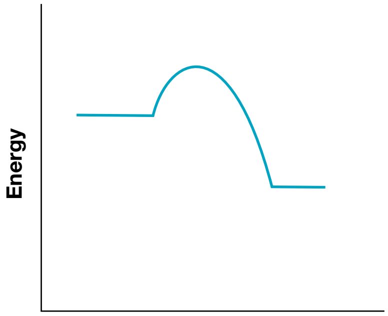
B.



C.



D.



2. Consider the following equation for the formation of hydrogen chloride gas.

$$H_2(g) + Cl_2(g) \rightarrow 2HCl(g) \qquad \Delta H = -184\,\text{kJ mol}^{-1}$$

When 2 moles of hydrogen gas react completely with 2 moles of chlorine gas:

A. 184 kJ of energy is released
B. 184 kJ of energy is absorbed
C. 368 kJ of energy is released
D. 368 kJ of energy is absorbed.

3. Dry ice is solid carbon dioxide. It is stable at very low temperatures but sublimes at room temperature according to the reaction:

$$CO_2(s) + \text{heat} \rightarrow CO_2(g)$$

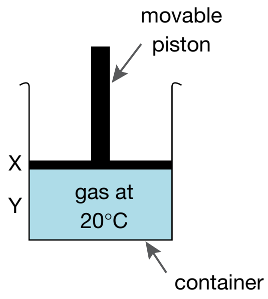
Handling dry ice with bare hands can cause severe skin damage because solid carbon dioxide:

A. is a strong oxidising agent
B. releases considerable heat to the skin while subliming
C. absorbs considerable heat from the skin while subliming
D. forms a strong acid when dissolved in the moisture of the skin.

4. The diagram shows a container filled with gas and sealed by a movable piston. There is sufficient gas to support the piston at point X when the temperature is 20 °C.

Assume that the piston is locked at X. If the gas is heated, the pressure it exerts will:

A. increase
B. decrease
C. remain the same
D. change in an unpredictable manner.



5. The apparatus in question 4 remains at a constant temperature of 20 °C, but the piston is pushed down to point Y and locked, so that the volume of the container is halved. The average number of molecules striking a unit area of the wall of the container per unit time will:

A. double
B. halve
C. remain the same
D. change in an unpredictable manner.

6. A rigid container holds a fixed volume of gas at a certain temperature and pressure. In order to double the pressure of the gas inside the container, a person could:

A. halve the amount of gas in the container
B. halve the amount of gas, but double the absolute temperature
C. double the amount of gas and double the absolute temperature
D. double the absolute temperature.

7. 10 L of hydrogen gas is collected at 110 kPa and 20 °C. It is then compressed into a 2 L container at a pressure of 1100 kPa. The new temperature will be:
   - **A.** 40 °C
   - **B.** 200 °C
   - **C.** 273 °C
   - **D.** 313 °C.
8. Tired of working in laboratories that are either freezing or too hot, Jenny has proposed a third set of standard conditions. She has defined these as a temperature of 15 °C and a pressure of 100 kPa. Under these conditions, the molar volume of a gas would be:
   - **A.** less than 22.7 L
   - **B.** 22.7 L
   - **C.** between 22.7 L and 24.8 L
   - **D.** greater than 24.8 L.

Questions 9 and 10 refer to the following thermochemical equation for the combustion of ethyne, commonly known as acetylene.

$$2C_2H_2(g) + 5O_2(g) \rightarrow 4CO_2(g) + 2H_2O(l) \;\; \Delta H = -2600\,\text{kJ mol}^{-1}$$

9. The combustion of 0.26 g of ethyne will:
   - **A.** absorb 13 J of energy
   - **B.** evolve 13 J of energy
   - **C.** absorb 13 kJ of energy
   - **D.** evolve 13 kJ of energy.
10. The carbon dioxide contribution from the use of ethyne is:
    - **A.** 17 kg MJ^{-1}
    - **B.** 34 kg MJ^{-1}
    - **C.** 68 kg MJ^{-1}
    - **D.** 134 kg MJ^{-1}.
11. If burning 4.5 g of a fuel raises the temperature of 75 g of water by 30 °C, the heat of combustion of this fuel is:
    - **A.** 0.0075 kJ g^{-1}
    - **B.** 0.057 kJ g^{-1}
    - **C.** 2.1 kJ g^{-1}
    - **D.** 2.4 kJ g^{-1}.
12. Which of the following best describes a renewable energy source?
    - **A.** A renewable energy source can be produced at a slower rate than the rate at which it is used by society.
    - **B.** A renewable energy source can be produced at a faster rate than the rate at which it is used by society.
    - **C.** A renewable energy source can be produced at the same rate as the rate at which it is used by society.
    - **D.** The rate at which a renewable energy source can be produced is unrelated to the rate at which it is used by society.
13. Which of the following is a renewable source of energy?
    - **A.** Coal
    - **B.** Bioethanol
    - **C.** Natural gas
    - **D.** Oil

14. Methanol can be burned as a fuel and its heat output can be described by the following thermochemical equation.

$$2CH_3OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 4H_2O(g) \quad \Delta H = -1.45 \times 10^3 \text{ kJ mol}^{-1}$$

The predicted heat output from the combustion of 3.20 g of methanol would be:

- A. 72.5 J
- B. 7.25 kJ
- C. 72.5 kJ
- D. 7250 kJ.

15. A device converts 85 MJ of input energy into 50 MJ of usable output energy. The efficiency of this device is closest to:

- A. 50%
- B. 60%
- C. 64%
- D. 85%.

1.8 Exercise 2: Short answer questions

1. State whether each of the following reactions is exothermic or endothermic.
   - a. $H_2(g) + Cl_2(g) \rightarrow 2HCl(g)$ $\Delta H = -185 \text{ kJ mol}^{-1}$
   - b. $H_2(g) + CO_2(g) \rightarrow CO(g) + H_2O(g)$ $\Delta H = +41 \text{ kJ mol}^{-1}$
   - c. $SnO_2(s) + 2C(s) \rightarrow Sn(s) + 2CO(g)$ $\Delta H = +360 \text{ kJ mol}^{-1}$
   - d. $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$ $\Delta H = -92.2 \text{ kJ mol}^{-1}$
2. Draw an energy profile diagram for each of the reactions in question 1. In each diagram, label the reactants and the products as given by the equation, and show the ΔH value and its magnitude.
3. Ethanol burns in oxygen to produce water and either carbon dioxide or carbon monoxide. The particular oxide produced depends on whether the oxygen supply is plentiful or limited. The molar heats of combustion for these two reactions are –1364 kJ mol^{-1} and –1192 kJ mol^{-1} respectively.
   - a. Write the thermochemical equation for the combustion of ethanol to produce carbon dioxide.
   - b. Write the thermochemical equation for the combustion of ethanol to produce carbon monoxide.
   - c. Use the equations from (a) and (b) to explain how the amount of oxygen consumed influences the oxide produced.
   - d. Calculate ΔH for the following reaction.

$$2CO(g) + O_2(g) \rightarrow 2CO_2(g)$$

4. Data tables give the heat output from the complete combustion of ethane and ethene as 51.9 kJ g^{-1} and 50.3 kJ g^{-1} respectively. Write thermochemical equations for the complete combustion of these fuels, showing ΔH values in units of kJ mol^{-1}.
5. Use the kinetic molecular theory to explain:
   - a. why gases exert pressure
   - b. why, for a fixed amount of gas at constant volume, pressure increases with temperature.
6. a. Convert 1.34 atm to mmHg and kPa.
   - b. Convert 365 mmHg to Pa and atm.
   - c. Convert 102 576 Pa to atm and mmHg.
7. Convert the following Kelvin temperatures to Celsius.
   - a. 300 K
   - b. 427 K
   - c. 173 K
   - d. 392 K
   - e. 73 K

8. Calculate the number of moles of the following gases at SLC.
   a. 1.5 L oxygen, O_2
   b. 2.56 L of hydrogen, H_2
   c. 250 mL of nitrogen, N_2
9. Calculate the volume of the following gases at SLC.
   a. 1.53 mol hydrogen, H_2
   b. 13.6 g of methane, CH_4
   c. 2.5×10^{30} molecules of nitrogen, N_2
10. Calculate the mass of the following gas samples at SLC.
    a. 150 mL of oxygen, O_2
    b. 4.5 L of carbon dioxide, CO_2
11. The pressure on a gas remains constant. Its volume is 700 mL. The temperature is 27 °C. Calculate the temperature needed to change the volume to:
    a. 14.0 mL
    b. 420.0 mL.
12. Calculate the number of moles of gas present in each of the following gas samples.
    a. 32.3 L of argon at 102.0 kPa and 15 °C
    b. 24.3 L of nitrogen at 13.2 atm and 35 °C
13. Calculate the volumes occupied by the following gas samples.
    a. 0.560 mol of carbon dioxide gas at 101.5 kPa and 17 °C
    b. 15.5 mol of ethyne gas at 10.35 atm and 20 °C
14. An aerosol can of deodorant has a volume of 120 mL. The contents exert a pressure of 9.0×10^5 Pa at 27 °C.
    a. Calculate the number of moles of gas present in the can.
    b. How many particles are present in the can of deodorant?
    c. If the contents of the can are transferred to a 200 mL container, what would be the temperature if the pressure drops to 6.0×10^5 Pa?
15. An empty 200 mL flask has a mass of 84.845 g. It is filled with a gas at 17.0 °C and 770 mmHg pressure and then weighs 85.084 g. Calculate the molar mass of the gas. What is the gas?
16. Each time Nick breathes, he inhales about 400 mL of air. Oxygen makes up about 20% by volume of air. How many oxygen molecules does he inhale in one breath at 25 °C and 1.0×10^4 Pa?
17. Butan-1-ol (density = 0.81 g mL^{-1}) burns according to the following equation.

    $$CH_3CH_2CH_2CH_2OH(l) + 6O_2(g) \rightarrow 4CO_2(g) + 5H_2O(l)$$

    When 10.0 mL of butan-1-ol is burned, calculate:
    a. the mass of water produced
    b. the volume of carbon dioxide produced at SLC
    c. the volume of carbon dioxide produced at 200 °C and 1.2 atm pressure.
    d. If the butan-1-ol is used to produce 100 mL of carbon dioxide at SLC, calculate the volume of butan-1-ol needed.
18. A number of technologies either exist or are being developed to remove carbon dioxide from flue gases. Some of these are also being investigated for the removal of carbon dioxide directly from the air. One such process uses calcium oxide and steam (at 400 °C). The overall equation for this reaction is:

    $$CaO(s) + CO_2(g) \xrightarrow[\text{Steam}]{400^\circ C} CaCO_3(s)$$

    a. Calculate the maximum volume of carbon dioxide at SLC that can be removed per 1.00 tonne of calcium oxide.
    b. Calculate the maximum mass of calcium carbonate that would be formed per tonne of calcium oxide.

19. In the Haber process, nitrogen and hydrogen are combined under specific conditions of temperature and pressure to industrially manufacture ammonia.
    a. Write the balanced equation.
    b. What volume of nitrogen combines with 45 m^3 of hydrogen?
    c. What volume of ammonia would be produced if the reaction went to completion?
20. Iron can react with carbon dioxide according to the following equation.

$$2Fe(s) + 3CO_2(g) \rightarrow Fe_2O_3(s) + 3CO(g) \quad \Delta H = +26.3\,kJ\,mol^{-1}$$

    a. Explain why this equation may be described as a thermochemical equation.
    b. Calculate the heat change, in kJ, when 2 g of iron reacts completely with excess carbon dioxide.
    c. Calculate the heat change, in kJ, when 200 mL of carbon dioxide is used at SLC.
    d. What mass of iron would be needed to absorb 1000 kJ of heat energy?
    e. What volume of carbon dioxide would be needed at SLC to absorb 1000 kJ of energy?
21. Hydrazine, N_2H_4, is a liquid fuel that has been used for many years in the engines of space probes. It was famously used in the terminal-descent engines that successfully landed the *Curiosity* rover on the surface of Mars in 2012. When passed over a suitable catalyst, it decomposes quickly in a multi-step exothermic chemical reaction. The overall equation for this process is:

$$N_2H_4(l) \rightarrow N_2(g) + 2H_2(g) \quad \Delta H = -50.3\,kJ\,mol^{-1}$$

    a. Calculate the energy released per kilogram of hydrazine in the equation.
    b. Given that the average temperature and pressure of the Martian atmosphere are –60 °C and 600 Pa respectively, calculate the total volume of gas added to the Martian atmosphere if 50 kg of hydrazine is used.
22. Petrol and LPG are two fuels commonly used in Australia. It is claimed that LPG is better for the environment because it releases less carbon dioxide. It is also attractive to motorists because, even though more litres are used, it is cheaper than petrol. As an approximation, petrol may be assumed to be octane, whereas LPG is a mixture of propane and butane. Some relevant data is shown in the following table.

Fuel	Molar enthalpy of combustion (kJ mol^{-1})	Density (g mL^{-1})
Propane	–2217	0.51 (as LPG)
Butane	–2874	0.51 (as LPG)
Octane	–5464	0.70 (as petrol)

    a. Calculate the mass of LPG (assuming it to be propane) required to produce 1.00 MJ of heat energy.
    b. Calculate the mass of carbon dioxide produced from **a** and express your answer as g MJ^{-1}.
    c. Calculate the mass of petrol (assuming it to be octane) required to produce 1.00 MJ of heat energy.
    d. Calculate the mass of carbon dioxide produced from **c** and express your answer as g MJ^{-1}.
    e. State the net reduction (in g MJ^{-1}) of carbon dioxide emission when LPG is used in preference to petrol.
    f. Repeat **a**, **b** and **e** for LPG if it is assumed to be butane.
    g. Calculate the volume of LPG (assuming it to be propane) required to produce the same energy as 1.00 L of petrol (assuming it to be octane).
    h. Is it true that LPG is better than petrol? Use your answers to **a**–**g** to explain your response.

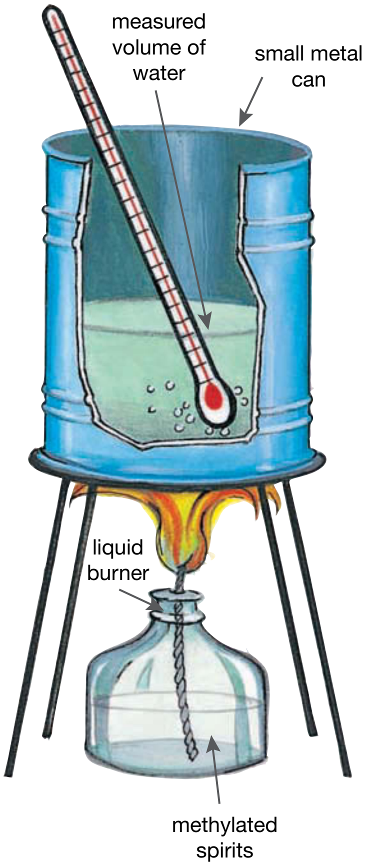
23. It is useful to know how much energy can be obtained from different fuels in order to determine which would be the best fuel for a particular purpose. The apparatus in the following figure can be constructed in the laboratory to measure the heat given out when a fuel such as ethanol is burned.

The heat produced when the fuel burns is absorbed by the water in the metal can. The temperature can be measured so, given that the specific heat of water is 4.18 J and the density of water is 1.00 g mL^{-1}, the heat of combustion may be determined.

The results of one experiment are shown in the following table.

Volume of water in metal can =	200 mL
Thus, mass of water in can =	200 g
Rise in temperature of water =	11.0 °C
Mass of ethanol burned =	0.500 g

a. From these results, calculate the heat produced when 1 g of ethanol is burned.
b. Calculate the heat of combustion for ethanol using the above results.
c. An accurate value for the heat produced when 1 mole of ethanol burns is 1364 kJ mol^{-1}. Calculate the percentage accuracy of this experiment.
d. Outline the sources of error in the experiment and then suggest how the design of the experiment could be improved so that more accurate heats of combustion for different fuels may be determined.



24. Explain why the overall energy efficiency of a coal-fired power station that generates electricity is said to be only 30% efficient.

25. A waste management/energy project near Ballarat uses organic waste from local piggeries to produce biogas (methane and carbon dioxide). The biogas is then converted to heat and electricity.
a. Outline the energy changes in the conversion of organic waste to heat and electricity.
b. Initial proposals for construction of the project were rejected by the local council. On what grounds could the council object to such a scheme?
c. How could the success of such a scheme be gauged?

1.8 Exercise 3: Exam practice questions

Question 1 (3 marks)

Nitroglycerine, $C_3N_3H_5O_9$, is a dangerous explosive that releases all gaseous products according to the equation:

$$4C_3N_3H_5O_9(l) \rightarrow 6N_2(g) + 12CO_2(g) + 10H_2O(g) + O_2(g)$$

Calculate the total volume of gaseous products that results when 1.00 kg of liquid nitroglycerine explodes at a temperature of 250 °C and a pressure of 300 kPa.

Question 2 (3 marks)

Kerosene is a hydrocarbon fuel that may be used in lamps, jet engines and camp stoves. It has a heat of combustion of 44 100 kJ kg^{-1}.

a. Explain why the heat evolved from the combustion of kerosene is measured in kJ kg^{-1} rather than kJ mol^{-1}. **1 mark**

b. A cup of billy tea contains 250 g of water. How many cups of tea can be made if 12.5 mL of kerosene is used to heat the water? Assume that the temperature of the water increases from 20.0 °C to 100.0 °C, the specific heat capacity of water is 4.18 J g^{-1} $°\text{C}^{-1}$ and the heat of combustion of kerosene is 37 000 kJ L^{-1}. **2 marks**

Question 3 (10 marks)

Consider the following two equations.

$$2CH_3OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 4H_2O(l)\ \Delta H = -1450\,\text{kJ mol}^{-1}$$

$$2CH_3CH_2CH_2OH(l) + 9O_2(g) \rightarrow 6CO_2(g) + 8H_2O(l)\ \Delta H = -4032\,\text{kJ mol}^{-1}$$

a. Calculate the mass of methanol required to produce 1.00 MJ of heat energy. **2 marks**

b. Calculate the mass of 1-propanol required to produce 1.00 MJ of heat energy. **2 marks**

c. Assuming that methanol and 1-propanol are made from non-renewable resources, calculate the net mass reduction (in g MJ^{-1}) of carbon dioxide when methanol is used as a fuel in preference to 1-propanol. **3 marks**

d. Calculate the net volume reduction (in L MJ^{-1}) from (c), assuming the carbon dioxide is at 101.3 kPa and 15 °C. **3 marks**

Question 4 (6 marks)

Methane gas is used as a fuel in many industrial and domestic situations. Sources of methane include biogas, natural gas and coal seam gas.

a. Write an equation for the combustion of methane in excess oxygen. **1 mark**

b. Methane may be classified as both a renewable and a non-renewable resource. Explain this using the information provided above. **2 marks**

c. In certain situations, the burning of methane may produce carbon monoxide gas. Under what conditions might this occur? **1 mark**

d. Write an equation for the combustion of methane to produce carbon monoxide. **1 mark**

e. Why is the production of carbon monoxide undesirable? **1 mark**

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2 Fuel choices

2.1 Overview

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2.1.1 Introduction

About 80% of the world's energy requirements is provided by coal, oil and gas, which are all fossil fuels. Scientists overwhelmingly agree that the burning of fossil fuels continues to be a major cause of climate change. The Paris Agreement was ratified in 2016 by fifty-five Parties, who account for 55% of the world's total greenhouse gas emissions and became signatories to the agreement. The Paris Agreement's central aim is to strengthen the global response to the threat of climate change by keeping the global temperature rise of the 21^{st} century to less than two degrees above pre-industrial levels. Chemistry plays a major role in combating climate change as scientists worldwide work towards more efficient, sustainable fuel sources.

FIGURE 2.1 Time is running out on humans' reliance on fossil fuels.

2.1.2 What you will learn

KEY KNOWLEDGE

In this topic, you will investigate:

- the comparision 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 comparision 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.

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2.2 Comparing energy sources

KEY CONCEPT

- 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

2.2.1 Generating energy in Australia

Australia has a diverse range of energy resources, but the availability, **abundance** and relatively low cost of fossil fuels mean that they are in high demand — about 95% of Australia's energy requirements are provided by coal, oil and gas. Most of Australia's electricity (75%) is generated by black and brown coal, and 16% is supplied by natural gas. Access to these low-priced fuels is important for our manufacturing industry.

Although energy can be obtained from the direct combustion of fossil fuels, electricity is a more convenient form of energy. Electricity can be carried from one place to another, switched on and off, and used as an energy source for many different devices.

FIGURE 2.2 Projected depletion of world reserves of fossil fuels based on current usage

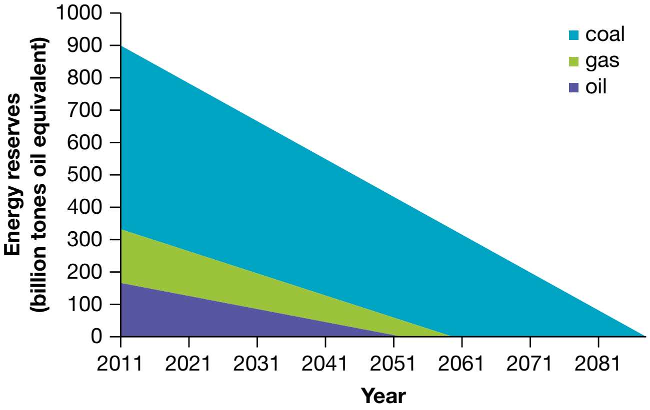
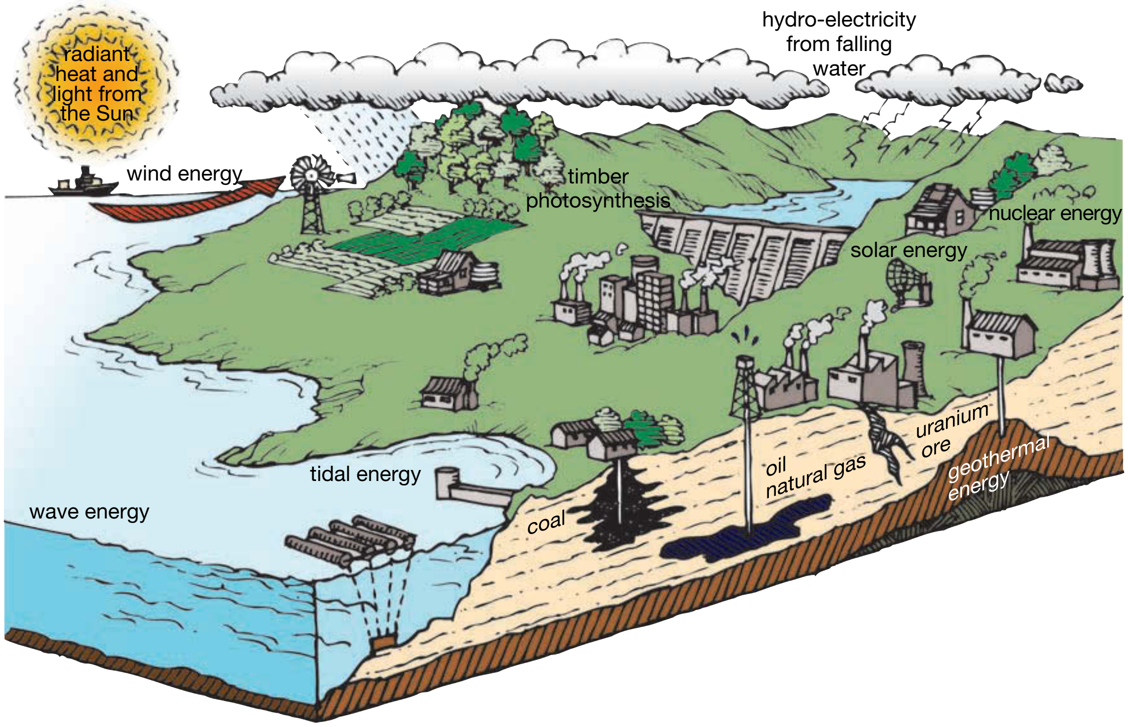


FIGURE 2.3 Sources of energy for society



Electricity is sometimes described as a **secondary fuel**, because it is not a natural source of power — it is produced from other fuels or energy sources.

At present, most of Australia's electricity is generated by burning fuel at power stations. Fossil fuels could be made to last longer, and the environmental impacts of fossil fuel combustion could be reduced, if electricity was generated using other means. Replacement options include nuclear energy — although this poses significant risks should an incident occur — or renewable energy options such as wind, moving water, wave motion, falling water, tides and biomass reactions. Electricity can also be generated directly from chemical reactions, as in fuel cells, which are thought to be a possible energy source for the future. Photovoltaic (PV) cells, which convert solar energy into electrical energy, are another method, and are already becoming more popular as people install them on the roofs of their houses. PV cells have the added benefit of feeding any excess electricity produced back into the grid.

Table 2.1 details the energy production in Australia for 2016–17 and the ten-year average annual growth rate. While fossil fuels still comprise approximately 85% of all energy produced in Australia, over the last ten years there have been significant annual increases in the growth of **renewable** energy.

TABLE 2.1 Electricity production in Australia by energy source, 2016–17

	2016–17		Average annual growth	
	GWh	Share (%)	2016–17 (%)	10 years (%)
Fossil fuels	**217 562**	**84.3**	**–0.8**	**–0.3**
Black coal	118 272	45.8	3.5	–1.0
Brown coal	43 558	16.9	–10.7	–2.5
Gas	50 460	19.6	–0.2	4.2
Oil	5273	2.0	–6.8	3.0
Renewables	**40 455**	**15.7**	**6.1**	**8.2**
Hydro	16 285	6.3	6.3	3.4
Wind	12 597	4.9	3.3	16.9
Bioenergy	3501	1.4	–7.6	–3.0
Solar PV	8072	3.1	18.0	59.2
- Small scale	7399	2.9	16.0	57.7
- Large scale	672	0.3	47.1	N/A
Geothermal	1	0.0	133.3	N/A
Total	**258 017**	**100**	**0.2**	**0.7**

Source: www.energy.gov.au/sites/default/files/australian_energy_update_2018.pdf

2.2.2 The effect of fossil fuels on the environment

Fossil fuels make up the vast majority of the energy resources consumed in Australia today. There is great concern that their use has led to a number of environmental problems, particularly the **enhanced greenhouse effect** and acid rain.

The greenhouse effect

The **greenhouse effect** helps to keep the Earth at the appropriate temperature to support life. It begins when radiation from the Sun strikes the Earth and warms its surface, which then radiates heat energy back into space. Gases in the atmosphere known as **greenhouse gases**, including carbon dioxide (CO_2), methane (CH_4), nitrous oxide (N_2O), and ozone (O_3), absorb some of this heat radiation, so the air warms up. The air may also radiate this energy back into space or down to Earth (see figure 2.5). Unfortunately, human activities have led to an increase in the amount of greenhouse gases, so that more heat is absorbed, which continues to adversely affect weather and climate. This results in an enhanced greenhouse effect, causing **global warming** and **climate change** (see figure 2.6). Global warming specifically refers to the Earth's rising temperature, due mainly to the increasing concentrations of greenhouse gases in the atmosphere (see figure 2.7). Climate change is a broader and more accurate term that encompasses the side effects of global warming and refers to changes in various measures of climate over a long period of time.

FIGURE 2.4 Cattle and other livestock release significant amounts of methane into the atmosphere as a result of their digestive processes.

FIGURE 2.5 The greenhouse effect allows some heat to be trapped in the atmosphere, maintaining a constant temperature.

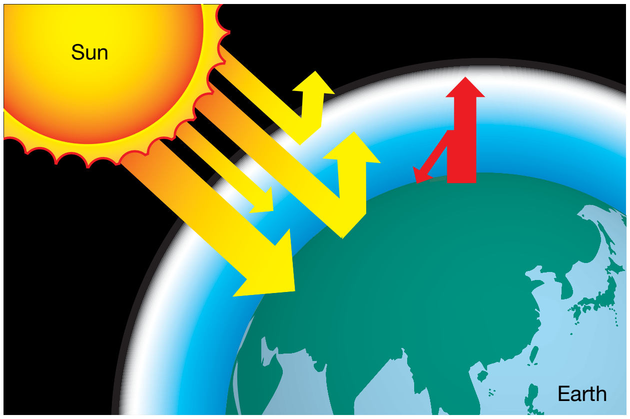
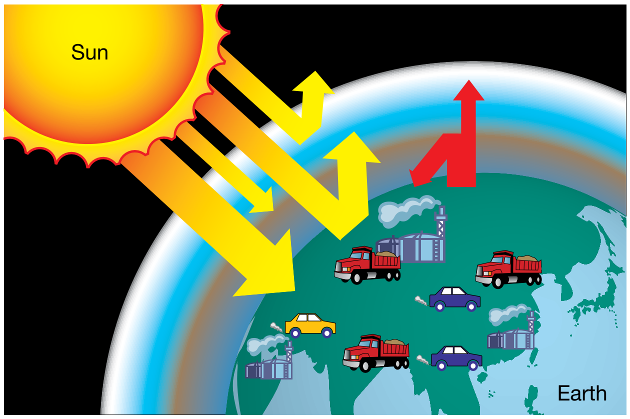

Greenhouse effect

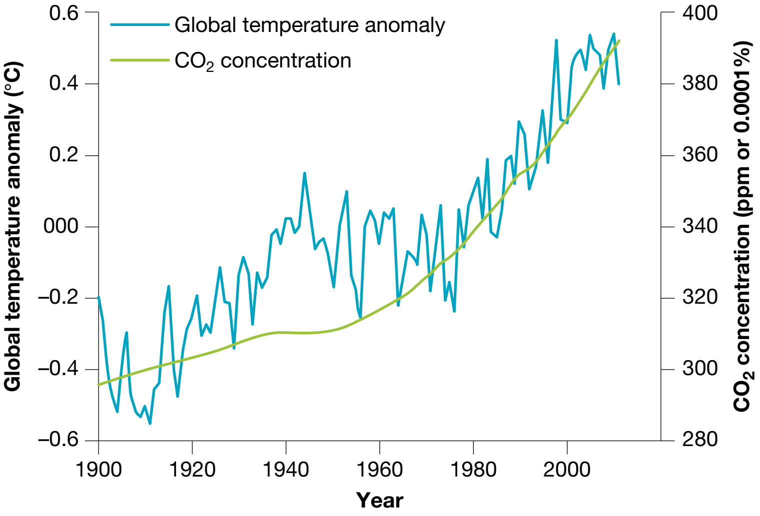
FIGURE 2.6 Excess production of greenhouse gases means the atmosphere retains more heat energy, increasing the average temperature of the Earth.


Enhanced greenhouse effect

Greenhouse gases absorb more energy than others and contribute to global warming in the atmosphere. Carbon dioxide is the major greenhouse gas emitted by human activities and is generated during transportation, industrial processes, land use change and energy production.

Carbon dioxide is essential to life because plants absorb it, enabling them to manufacture their own sugars and produce oxygen through photosynthesis. The quantity of carbon dioxide on Earth remained almost constant for thousands of years, but

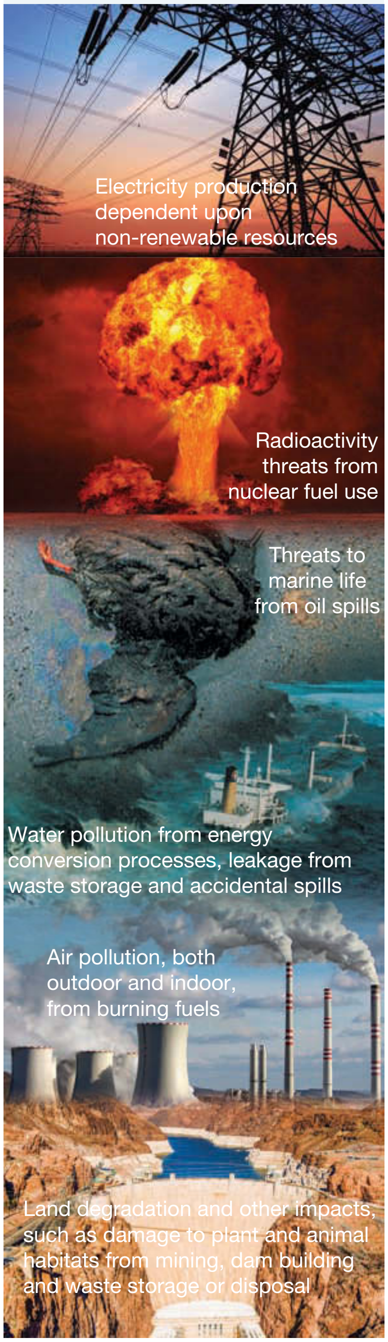
FIGURE 2.7 Global temperature variation and atmospheric CO_2 concentration against time



now we are producing more carbon dioxide than can be converted into oxygen. As the quantity of carbon dioxide increases, the amount of heat that is retained by the atmosphere increases, thereby contributing to the greenhouse effect, creating the enhanced greenhouse effect.

Biofuels are renewable energy sources made from plant and animal matter. When comparing the burning of fossil fuels with biofuels, at first glance it might appear that both contribute to the greenhouse effect because both produce carbon dioxide upon combustion. However, burning fossil fuels puts carbon into the atmosphere that has been locked underground for millions of years, while the carbon in biofuels has been obtained from the atmosphere much more recently via photosynthesis. Theoretically, this carbon dioxide will once again be removed when the next source crops for the biofuel are grown. This is described as being **carbon neutral**.

FIGURE 2.8 Major energy-related environmental issues



Acid rain

Many industrial processes burn fossil fuels and many of these fuels contain sulfur in varying amounts. When sulfur is burned in the air, it forms sulfur dioxide, SO_2. This gas is often released into the air in vast quantities. **Acid rain** results from the reaction between rainwater and SO_2 that is released into the atmosphere.

Sulfur dioxide is also released during many natural processes. In particular, active volcanoes release a large amount of sulfur dioxide into the air. The atmosphere can cope with large quantities of sulfur dioxide if the gas is given time to disperse. When a large number of industries are all producing the gas over a small area, it cannot disperse in the air fast enough and becomes too concentrated to be safe.

When sulfur dioxide reacts with water it becomes sulfuric acid. So, when rain comes into contact with SO_2, it becomes dangerous to plant and animal life.

$$SO_2(g) + H_2O(g) \rightarrow H_2SO_3(g)$$
$$SO_3(g) + H_2O(g) \rightarrow H_2SO_4(g)$$

In heavily industrialised countries, entire forests have been denuded by the effects of acid rain. Our energy use is responsible for more than half of the greenhouse emissions and widespread pollution of land, sea and air. These environmental impacts threaten our quality of life and, perhaps, existence.

FIGURE 2.9 Acid rain is damaging forests worldwide.

2.2.3 Sustainable energy

A **sustainable energy** future means providing for the needs of today's society without compromising the ability of future generations to meet their own needs. Various responses have been proposed to meet society's increasing energy demands. These include:

- promoting energy conservation in the domestic, commercial and industrial sectors
- funding research into producing viable alternative energy sources
- decreasing our dependence on coal by using more renewable energy sources
- increasing the efficiency with which energy is produced from each resource
- developing technologies to reduce emissions when using fossil fuels.

The availability of low-cost, clean and reliable energy will improve land, air and water quality, increase employment and promote health.

TIP: It is important to know the exact definitions of 'renewable', 'non-renewable', 'abundance', 'sustainable', 'reuseable' and 'recyclable' — these terms are often confused.

2.2.4 Properties of fossil fuels and biofuels

The origin of fossil fuels and biofuels were discussed in topic 1 and a summary of their advantages and disadvantages are shown in table 2.2.

TABLE 2.2 Properties of fossil fuels and biofuels

Fuel	Energy content (kJ g^{-1})	Carbon dioxide emissions in kg of CO_2 per gigajoule	Advantages	Disadvantages
Black coal	34	114	• Large Australian reserves • Source of revenue via exports • Easily mined • Most efficient type of coal	• Non-renewability • Contributes to air pollution, acid rain and global warming • Open cast mining
Brown coal	16	94	• Large Australian reserves • Source of revenue via exports • Easily mined	• Less efficient (high moisture content) • Lower dry carbon content • Open cast mining
Diesel Petrol LPG	48 46 46	70 67 60	• Ease of transportation • Wide range of uses • Some Australian sources	• Non-renewability • Limited world supplies • Pollution
E10*	44	60	• Ease of transportation • Wide range of uses • Some Australian sources • Uses 10% renewable bioethanol	• 10% renewability • Limited world supplies • Pollution
Methane**	56	51	• High efficiency • Some Australian sources • Moderate cost (drilling)	• Non-renewability • Pollution

(continued)

TABLE 2.2 Properties of fossil fuels and biofuels *(continued)*

Fuel	Energy content (kJ g^{-1})	Carbon dioxide emissions in kg of CO_2 per gigajoule	Advantages	Disadvantages
Biogas	26	0	• Renewability • Productive use of wastes	• Energy inefficiency • Low supplies
Bioethanol	30	0	• Renewability	• Possible conflict in land use
Biodiesel	42	0	• Less harmful emissions	• Low temperatures can be problematic for biodiesel

Source: Australian National Greenhouse and Energy Reporting (Measurement) Determination 2008 (Schedule 1).
**a blend of normal petrol with 10% ethanol*
***methane is the main constituent of both natural gas and coal seam gas*

2.2 EXERCISE

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1. List the following fuels in order of increasing energy output, as measured in kJ g^{-1}: Brown coal, black coal, biogas, diesel, natural gas, bioethanol, petrol, biodiesel.
2. What is the enhanced greenhouse effect? Explain how energy choices can be used to reduce its effect.
3. Fossil fuels and biofuels can undergo complete combustion to release carbon dioxide and water. Explain why the complete combustion of fossil fuels contributes to the enhanced greenhouse effect, whereas the complete combustion of biofuels does not.

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2.3 Suitability of fuels for transport

KEY CONCEPT

- 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

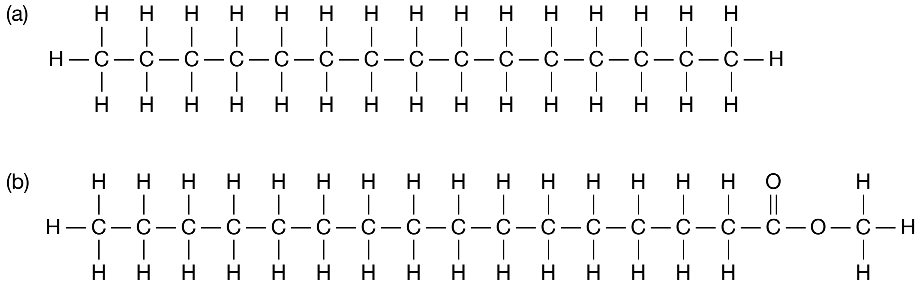
2.3.1 Comparing petrodiesel and biodiesel

After petrol, diesel is the most widely used transport fuel in the world. Traditionally used in larger scale engines such as those in boats, trucks, trains and buses, it is now becoming more popular as an alternative fuel for the smaller engines found in cars. Diesel engines, although heavier and initially more expensive, are more efficient than their petrol counterparts, have better fuel economy and tend to last longer. They produce less power than petrol engines of the same size but more torque, which is the amount of turning power. This makes diesel-powered vehicles slower to accelerate but ideal for hauling heavier loads. Biodiesel can easily be substituted, either straight or blended with petrodiesel, as a fuel for diesel engines and requires little or no modification to the engine.

Source and chemical structure

As discussed in topic 1, diesel is sourced from fractional distillation of petroleum and is a mixture of (largely unsaturated) hydrocarbons. Often referred to as petrodiesel to distinguish it from biodiesel, it is predominantly alkane molecules, both straight-chain and branched, of 12–24 carbon atoms per molecule. Biodiesel is formed from the transesterification of esters from long-chain fatty acids and alcohol (typically methanol). The long-chain is preserved with 15–20 carbon atoms per molecule. These differences in formation and structure can be seen in figure 2.10.

FIGURE 2.10 Examples of structural formulas of (a) petrodiesel and (b) biodiesel



Combustion

As crude oil is mostly a mixture of alkanes, so too is the petrodiesel component obtained from it. Therefore, its combustion follows the typical pattern of an alkane and, in the presence of sufficient oxygen, carbon dioxide and water are produced. For example, hexadecane, $C_{16}H_{34}$, burns according to:

$$2C_{16}H_{34}(l) + 49O_2(g) \rightarrow 32CO_2(g) + 34H_2O(g)$$

Other products of combustion may include sulfur dioxide (from sulfur impurities), nitrogen oxides, carbon monoxide and particulate carbon (soot). The latter two are produced in situations where insufficient oxygen is present. Soot is often seen as black smoke under conditions of heavy acceleration or when engines are poorly tuned. The following equation illustrates how less oxygen is required to make particulate carbon.

$$2C_{16}H_{34}(l) + 17O_2(g) \rightarrow 32C(s) + 34H_2O(g)$$

In the past decade, considerable advances in both engine technology and fuel quality have led to a significant reduction in all of these emissions. Two such examples are the introduction of ultra-low-sulfur diesel (ULSD), which not only lowers emissions of SO_2 but also allows for more sophisticated pollution control measures in the engine itself, and the introduction of computer-controlled, self-cleansing exhaust filters designed to remove soot.

FIGURE 2.11 Black soot exhaust is less common because modern engines and fuels reduce undesired emissions.

Environmental issues

Biodiesel appears to be an excellent substitute for petrodiesel. It can be used in diesel engines with little or no modification, and aids in engine lubrication and can clean engines of built-up deposits that result from the long-term use of petrodiesel. Emissions from a biodiesel-fuelled engine are similar to those from a petrodiesel engine but are generally lower in quantity, the exception being nitrogen oxides, which may be slightly higher. As manufacturers strive to meet more stringent emission standards, it is anticipated that more petro- and biodiesel blends will be recommended.

FIGURE 2.12 Deforestation for palm oil plantations is endangering the habitat of the Sumatran orangutan.

Two additional environmental positives of biodiesel are that it is biodegradable and that it can be produced from a waste product, notably used cooking oil. In Australia, the main feedstocks are oil seeds such as canola, used cooking oil and tallow. Elsewhere in the world, soybeans and sunflower seeds, as well as palm oil, are the main sources being used to meet this demand. However, as demand increases, new economical sources will need to be found and there are some environmental concerns, including the debate about land use: should crops be grown for food production or fuel production? In south-east Asia, massive deforestation is occurring to make way for palm oil plantations for fuel and this is endangering the habitats of many species, the best known of which is the Sumatran orangutan.

Two possible ways of overcoming these issues are the use of algae and the seeds from jatropha trees. Research is being undertaken into the development of algae as an oil source. It is envisaged that such algae could grow in low-quality water bodies and possibly the ocean. Seeds from the jatropha tree are being investigated due to their high oil content. Jatropha trees can be grown in marginal agricultural land and require minimal cultivation and irrigation. Additionally, they do not have to be replanted from season to season. Both of these possibilities would overcome the conflicting issues of whether to use land for food or fuel.

TABLE 2.3 Approximate yields of some biodiesel oil sources

Oil source	Yield (L/ha)
Algae*	47 000–140 000
Palm oil	5900
Jatropha	1900
Canola	1200
Sunflower	950
Safflower	800
Soy	450

*estimate; depends on species

Besides the effects on the environment of exhaust emissions, other environmental considerations are associated with the use of petrodiesel. The extraction of crude oil can cause significant degradation to the immediate environment, and its subsequent transportation, especially by sea, has resulted in a number of significant, environmentally damaging spills. The refining process of petrodiesel and vehicle exhaust emissions can release unburned hydrocarbons into the air. Under the right conditions, which are often found in large cities, these can react to form photochemical smog. To this must also be added the emissions involved in the transport of both the crude oil and its petrodiesel product.

Technical issues

Two major technical issues facing the introduction of biodiesel are that it is **hygroscopic** and it can gel at low temperatures. If a substance is hygroscopic, it absorbs water vapour from the air, and this property is enhanced if a biodiesel is poorly processed as the transesterification process will not be completed and will result in partially converted mono- and diglycerides. This can affect engine life as the mono- and diglicerides act as an emulsifier, allowing water to mix with the biodiesel. This can result in several problems including allowing microbes to grow in the fuel. It also accelerates gelling and reduces the energy liberated upon combustion. Gelling at low temperatures is a major problem but is somewhat dependent on the type of oil used in the original manufacture. Gelling increases viscosity of the fuel, reducing or even preventing its flow along fuel lines and through diesel injectors. A number of potential solutions to this problem are being investigated, including blending it with petrodiesel, additives to lower the gel point, special fuel tanks that are heated as the car warms up and special reserve tanks containing petrodiesel for starting and warming up the engine.

Comparision of petrodiesel and biodiesel

TABLE 2.4 Comparison of petrodiesel and biodiesel

Property	Petrodiesel	Biodiesel
Sources	Petroleum	• Used cooking oil, tallow, oil seed crops, such as canola and palm oil • Oil from algae is possible • Methanol production requires fossil fuels but production of methanol from glycerol (a by-product) is currently under investigation
Chemical structure	Alkanes, both straight-chain and branched (typically containing 12–24 carbon atoms per molecule)	• Esters from long-chain fatty acids (typically 15–20 carbon atoms per molecule) and methanol • Other simple alcohols
Combustion products	• Carbon dioxide • Water • Carbon monoxide • Particulate carbon (soot) • Sulfur dioxide • Nitrogen oxides	• Same as petrodiesel but generally lower in quantity • May be increased emission of nitrogen oxides
Viscosity	Hygroscopic, but not generally an issue as seasonal blending allows for changes in outside temperature	Hygroscopic and low outside temperatures; can lead to increased viscosity due to fuel gelling
Environmental impact	• Non-renewable • Non-biodegradable • Spills in transportation of both crude oil and refined products • Combustion emissions in transportation chain	• Renewable • Biodegradable • Issues with growing crops for food versus fuel • Deforestation issues, especially in south-east Asia

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Weblink Biofuels for transportation

2.3 EXERCISE

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1. It is difficult to determine the total world reserves of fossil fuels. Estimates are constantly revised to take into account new discoveries, new information about known deposits and new techniques for extracting them. Conservation strategies will enable us to extend the life of fossil fuels.
   Discuss how each of the following factors affect the rate at which fossil fuels are used.
   (a) Population growth rate
   (b) Community awareness of the need for energy conservation

- (c) Alternative technologies and fuel sources
- (d) Fuel pricing policies, nationally and internationally
- (e) Trade relations between nations.

2. Fossil fuels took millions of years to form, yet they are likely to be used up within a few hundred years. Draw up a table with two columns.
   - (a) In the first column of the table, list the activities you do during the week that require energy from fossil fuels.
   - (b) Assume that our supply of fossil fuels stops tomorrow. In the second column of the table, write down alternative ways in which your energy could be supplied for each of the activities you have listed.
   - (c) How important are fossil fuels to your life?
3. You have been invited to debate the statement ‘The world should stop using fossil fuels and replace their use with biofuels’.
   - (a) Outline three environmental or societal issues you would argue if you were in favour of this statement.
   - (b) Outline three environmental or societal issues you would argue if you were against this statement.
4. (a) Define the terms ‘biodiesel’ and ‘petrodiesel’.
   - (b) State one disadvantage of using biodiesel in cold climates.
   - (c) Give one environmental advantage of increasing the usage of biodiesel.
   - (d) Give one environmental disadvantage that an increased usage of biodiesel may lead to.

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2.4 Review

2.4.1 Summary

Comparing energy sources

- Fuels produce energy through combustion reactions.
- Good fuels have the properties of being easily ignited, releasing significant energy on combustion, having minimal negative environmental impact and being relatively inexpensive, readily available and safe.
- In future, greater reliance on renewable fuels will be necessary as non-renewable fuels (particularly petroleum and coal) become depleted.
- Our use of energy, whether from renewable or non-renewable sources, affects the environment. Issues such as air pollution, the enhanced greenhouse effect, spillages, land degradation, water pollution and habitat damage need to be carefully monitored and improved.
- A significant issue with the increasing use of biofuels is land use. Should land be used for growing fuel crops at the expense of food crops?
- The process of global warming, also known as the enhanced greenhouse effect, arises when the amount of heat striking the Earth’s surface is greater than the amount that is radiated, causing the Earth to warm up.
- The major greenhouse gas emitted by human activities in Australia is carbon dioxide.
- Acid rain results from the reaction between rainwater and sulfur dioxide that is released into the atmosphere.

Suitability of fuels for transport

- Biodiesel is gradually finding more use as a replacement transport fuel for petrodiesel, both as a straight fuel and in blends with petrodiesel.
- The fuels on which modern society relies are mainly non-renewable fossil fuels.

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2.4.2 Key terms

abundance	the relative amount of a substance
acid rain	rain that has a pH lower than 5
climate change	changes in various measures of climate over a long period of time
carbon neutral	no net release of carbon dioxide into the atmosphere
enhanced greenhouse effect	the effect of increasing concentrations of greenhouse gases in the atmosphere as the result of human activity
global warming	a gradual increase in the overall temperature of the Earth's atmosphere
greenhouse effect	a natural process that warms the Earth's surface. When the Sun's energy reaches the Earth's atmosphere, some of it is reflected back to space and the rest is absorbed and re-radiated by greenhouse gases.
greenhouse gases	gases that contribute to the greenhouse effect by absorbing infrared radiation
hygroscopic	a tendency to absorb water vapour from the atmosphere
renewable	(with reference to energy sources) energy sources that can be produced faster than they are used
secondary fuel	a fuel that is produced from another energy source
sustainable energy	energy that meets present needs without compromising the ability of future generations to meet their own needs

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Digital document Key terms glossary – Topic 2 (doc-31395)

2.4 Exercises

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2.4 Exercise 1: Multiple choice questions

1. One of the criteria for the choice of fuels is the amount of heat released on combustion per gram of fuel. On this basis, which of the following would be the best fuel?

	Heat of combustion (kJ mol^{-1} of reactant)
A. H_2	238
B. CO	284
C. CH_3CH_2OH (ethanol)	1371
D. C_8H_{18} (n-octane)	5447

2. Coal and ethanol are both produced from plants. Which of the following statements about the classification of these two fuels is correct?
   - **A.** Coal and ethanol are both fossil fuels.
   - **B.** Coal is a fossil fuel but ethanol is a biofuel.
   - **C.** Coal and ethanol are both biofuels.
   - **D.** Coal is a biofuel but ethanol is a fossil fuel.

3. A hygroscopic substance is a substance that:
   - A. absorbs heat
   - B. evolves heat
   - C. evolves water
   - D. absorbs water.
4. When petrodiesel is compared with biodiesel in terms of their chemical components, it can be said that:
   - A. both consist of alkanes
   - B. petrodiesel consists of alkanes whereas biodiesel consists of esters
   - C. petrodiesel consists of esters whereas biodiesel consists of alkanes
   - D. both consist of esters.
5. When biofuels are burned, the carbon dioxide produced:
   - A. puts carbon atoms back into the atmosphere that were only recently removed
   - B. puts carbon atoms back into the atmosphere that were removed millions of years ago
   - C. puts oxygen atoms back into the atmosphere that were removed millions of years ago
   - D. puts carbon atoms back into the atmosphere at a slower rate than when an equivalent amount of fossil fuel is burned.

2.4 Exercise 2: Short answer questions

1. a. What is a fossil fuel?
   b. Give at least three examples of fossil fuels.
2. 'Coal, gas and oil should be made more expensive to deter people from wasting them.' Discuss this statement, offering at least two arguments for and against the proposal.
3. a. What is a biofuel?
   b. Give three examples of biofuels.
4. Consider the advantages and disadvantages of ethanol and petrol as transport fuels. Present your findings as a table.
5. Consider the advantages and disadvantages of biodiesel and petrodiesel as transport fuels. Present your findings as a table.
6. Coal seam gas has become a significant energy source in Australia since the year 2000.
   a. Is coal seam gas a renewable or non-renewable energy source?
   b. Describe how coal seam gas is obtained.
   c. Which gas is the main component of coal seam gas?
   d. List two environmental concerns associated with the production of coal seam gas.
7. Fossil fuels may be used to produce electricity.
   a. Explain how energy waste may occur in the conversion of fossil fuels to electricity.
   b. Explain how energy waste may occur in the use of electricity in the home.
8. a. Assuming that each kilowatt hour of electricity produces about 1.44 kilograms of carbon dioxide, examine your family's electricity bills and determine how much carbon dioxide your family produces annually.
   b. Explain why the production of carbon dioxide might lead to environmental problems.
   c. Suggest three ways in which your family could decrease electricity use to contribute to the minimisation of carbon dioxide release into the atmosphere.
9. In a fuel efficiency test, the percentage of petrol wasted due to incorrect handling techniques and altered car conditions was calculated for a particular car.

Altered variable	Percentage use
Speeding	14
Overloaded car	15
Roof rack	10
Soft tyres	5
Poor tuning	28

The car has a fuel consumption of 15.0 km per litre of fuel.

- a. If fuel costs 130 cents per litre, calculate the money wasted on a 100 km trip if the car had roof racks on.
- b. After completing the first trip, the driver realises they left their bag behind. Calculate the cost of the trip back if they speed the whole way home.

10. A power station using brown coal as its fuel consumes 40 000 tonnes of coal per day. If it generates an average of 27.8 GWh of electricity per day, calculate its overall efficiency. (Heat energy evolved by 1.000 tonne brown coal 6.7 GJ; 1 kWh = 3600 kJ.)

2.4 Exercise 3: Exam practice questions

Question 1 (14 marks)

Biodiesel is a fuel that is steadily gaining popularity as an alternative to petrodiesel. It is produced by a process called transesterification. Another chemical is also produced.

- a. Define the term 'transesterification'. **1 mark**
- b. A sample of biodiesel is analysed and found to consist only of methyl stearate. With the aid of suitable structural diagrams, show how this would have been made. You should make mention of any special reaction conditions required. **6 marks**
- c. Write the equation for the combustion of methyl stearate in excess oxygen. **3 marks**
- d. Name the other chemical produced by transesterification. **1 mark**
- e. To what class of organic compounds do the majority of molecules in biodiesel belong? **1 mark**
- f. Give one advantage and one disadvantage associated with the use of biodiesel as a fuel. **2 marks**

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3 Galvanic cells as a source of energy

3.1 Overview

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3.1.1 Introduction

FIGURE 3.1 The remains of an early telegraph station at Eucla, near the South Australia–Western Australia border.

In today's world of mobile phones and satellite communication, it is difficult to imagine what life would have been like before the invention of the telegraph and a suitable battery or cell to power it. The almost immediate communication we now take for granted would have taken weeks or even months just within Australia. Overseas communications may have taken up to a year. In the late nineteenth century, redox reactions were responsible for bringing the world together via the telegraph. Today, redox reactions still perform this vital role. They are at the heart of the battery technology that powers our mobile phones and other electronic devices.

Critical to the functioning of early telegraph stations was the Daniell cell — an electrochemical cell that harnessed the redox reaction between zinc and copper ions to produce electricity.

3.1.2 What you will learn

KEY KNOWLEDGE

In this topic, you will investigate:

- 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
- 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 comparision of 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.

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PRACTICAL WORK AND INVESTIGATIONS

Practical work is a central component of learning and assessment. Experiments and investigations, supported by a **Practical investigation logbook** and **Teacher-led videos**, are included in this topic to provide opportunities to undertake investigations and communicate findings.

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Digital documents Key science skills (doc-30903)
Key terms glossary – Topic 3 (doc-31403)
Practical investigation logbook (doc-31404)

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3.2 Redox reactions and half-equations

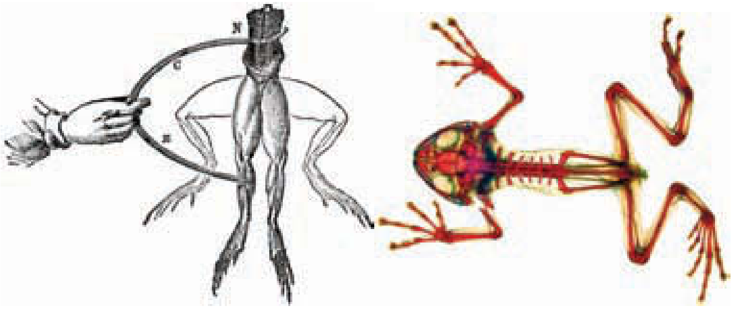
KEY CONCEPTS

- 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

3.2.1 What is a redox reaction?

The production of electricity from chemical reactions began in 1780 when Luigi Galvani (1739–1798), an Italian anatomist, conducted a series of experiments investigating the responses obtained from the hind legs of frogs when static electricity was applied to them. He found that the frogs' legs could be made to twitch by connecting the nerve and muscle tissues to different metals such as copper and iron. The dead frog was literally galvanised into action. Galvani thought that the muscles of the frog must contain electricity and advocated the idea of 'animal electricity'.

FIGURE 3.2 During the eighteenth century, many people believed that the nerves and muscles of animals contained a fluid that acted like an electric current. How do Galvani's results support this idea?



Redox reactions involve the transfer of electrons to and from substances. The term 'redox' is derived from two separate words: **reduction** and **oxidation**. A substance is said to be reduced when it accepts (or gains) electrons, and said to be oxidised when it donates (or loses) electrons. In a redox reaction, reduction and oxidation always occur simultaneously. Note that oxidation and reduction are *processes*.

- **Reduction is the *process* in which electrons are added to a substance.**
- **Oxidation is the *process* in which electrons are removed from a substance.**
- **Use the acronym OIL RIG:**
  Oxidation Is Loss Reduction Is Gain

Oxidising agents (**oxidants**) and **reducing agents** (**reductants**) are *substances* in a redox reaction. Because oxidation and reduction always occur together, an oxidising agent can be thought of as a substance that allows (or causes) another substance to undergo oxidation. It does this by accepting the electrons that are produced. In the same way, a reducing agent is a substance that permits another substance to undergo reduction, by supplying the electrons that are required. As a result, oxidising agents undergo the *process* of reduction, while reducing agents undergo the *process* of oxidation.

- **Oxidising agents are substances that cause or permit another substance to be oxidised.**
- **Reducing agents are substances that cause or permit another substance to be reduced.**

All of these definitions can be clarified by remembering that oxidation and reduction are *processes*, whereas oxidising agents and reducing agents are *substances* involved in these processes.

Redox reactions may be represented by **balanced half-equations** and by overall equations. For example, the burning of magnesium may be represented by the overall equation:

$$2\text{Mg(s)} + \text{O}_2\text{(g)} \rightarrow 2\text{MgO(s)}$$

This equation may be deconstructed into two half-equations that illustrate the transfer of electrons.

$$\text{Mg(s)} \rightarrow \text{Mg}^{2+}\text{(s)} + 2\text{e}^-\text{(oxidation)}$$

$$\text{O}_2\text{(g)} + 4\text{e}^- \rightarrow 2\text{O}^{2-}\text{(s)}\ \text{(reduction)}$$

In this reaction, magnesium is acting as a reducing agent because it is losing electrons. Magnesium is a group 2 metal, and losing 2 electrons allows it to attain a full outer shell configuration. Oxygen is acting as an oxidising agent because it is gaining electrons. As a member of group 16, the gain of 2 electrons allows it to to attain a full outer shell configuration. If the oxidation half-equation is multiplied by two and the two half-equations are then added, the electrons cancel out and the *overall* balanced (in terms of both charge and species) equation is produced.

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Video eLesson Redox-electron transfer (eles-2495)

3.2.2 Oxidation numbers

The deconstruction of an equation into oxidation and reduction half-equations prove that a reaction is a redox reaction. While this is a relatively simple process for some reactions, there are many redox reactions that are more complex. For example, the reaction between the acidified dichromate (VI) ion and hydrogen disulfide:

$$\text{Cr}_2\text{O}_7^{2-}\text{(aq)} + 3\text{H}_2\text{S(aq)} + 8\text{H}^+\text{(aq)} \rightarrow 2\text{Cr}^{3+}\text{(aq)} + 3\text{S(s)} + 7\text{H}_2\text{O(l)}$$

is also a redox reaction but it is much harder to produce the half-equations for this reaction. To assist in situations such as this, chemists use **oxidation numbers**. These are a set of rules that assist in the identification of redox reactions.

When using oxidation numbers remember that:

- oxidation is an increase in the oxidation number of an atom (e.g. the number becomes more positive: –3 to –1 or –1 to +1)
- reduction is a decrease in the oxidation number of an atom (e.g. the number becomes more negative: +3 to +1 or +1 to –1).

Alternatively, we can determine what is oxidised and what is reduced. Oxidisation occurs if a substance is gaining oxygen, and reduction occurs if a substance is losing oxygen. Oxidation can also be determined if a substance is losing hydrogen and reduction can be determined if a substance is gaining hydrogen.

FIGURE 3.3 Determining oxidation and reduction through gain and loss of oxygen

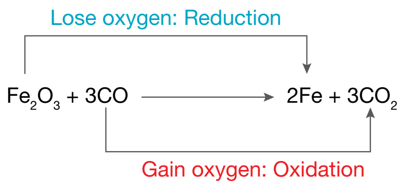
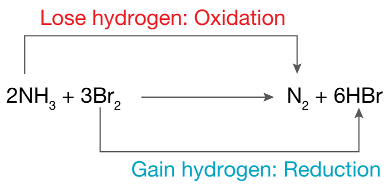


FIGURE 3.4 Determining oxidation and reduction through loss and gain of hydrogen



The following rules can be used to determine oxidation numbers. Remember that oxidation numbers are theoretical numbers and should not be confused with ionic charges.

TABLE 3.1 Oxidation number rules

Oxidation number rule	Oxidation number example
1. The oxidation number of an atom in its elemental form is 0.	Oxidation number: Copper metal, Cu(s) = 0 Nitrogen gas, N_2(g) = 0.
2. The oxidation number of a simple ion is the charge on the ion.	Al^{3+} = +3 S^{2-} = –2
3. The oxidation number of hydrogen in non-metal compounds is +1. The oxidation number of hydrogen in metal hydrides is –1.	In HCl, H_2O and NH^{4+} H = +1 In NaH or CaH_2, H = –1
4. The oxidation number of oxygen in a compound is usually –2. Except in • peroxide compounds where the oxidation number is –1 • compounds with oxygen bonded to fluorine where the oxidation number is +2.	Magnesium oxide, O = –2 Peroxide compounds: H_2O_2 and BaO_2, O = –1 Oxygen difluoride: OF_2, O = –2
5. Fluorine always has an oxidation number of –1 because it is the most electronegative element.	F = –1
6. In a neutral compound the sum of all the oxidation numbers must equal 0.	In $MgCl_2$, oxidation numbers are added as follows: +2 + (2 × –1) = 0.
7. In a polyatomic ion, the sum of the oxidation numbers must equal the charge on the ion.	In NO_3^-, they are added as follows: +5 + (3 × –2) = –1.

(continued)

TABLE 3.1 Oxidation number rules *(continued)*

Oxidation number rule	Oxidation number example
8. In covalent compounds that do not involve oxygen or hydrogen, the more electronegative element has the negative oxidation number. This is equal to the charge that it would have if it was a negative ion.	In ICl_3, the chlorine is the more electronegative atom. It is therefore assigned an oxidation number of –1, because this is the charge on a chloride ion. (*Note:* This is just the way the oxidation number is worked out. This molecule is a covalent, neutral molecule; it *does not* contain chloride ions.) Using rule 6, we can now calculate that the oxidation number of the iodine in ICl_3 is +3.

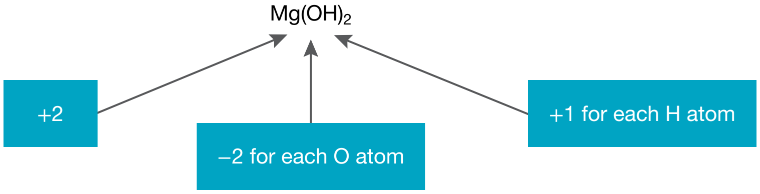
Using oxidation numbers

The rules for determining oxidation numbers can be used to assign an oxidation number to each atom in a compound. Magnesium hydroxide, $Mg(OH)_2$, has been used in figure 3.5 to demonstrate this.

The oxidation numbers of oxygen and hydrogen must be multiplied by two because each formula unit contains two of each of these atoms. Remember that the sum of the oxidation numbers must equal 0 (for a balanced formula).

$$\begin{aligned} \mathrm{Mg} + (2 \times \mathrm{O}) + (2 \times \mathrm{H}) &= +2 + (2 \times -2) + (2 \times +1) \\ &= 2 - 4 + 2 \\ &= 0 \end{aligned}$$

FIGURE 3.5 How to determine the oxidation numbers in magnesium hydroxide.



SAMPLE PROBLEM 1

The main compound in limestone statues or common chalk is calcium carbonate. What is the oxidation number of carbon in the carbonate ion, CO_3^{2-}?

THINK	WRITE
1. Assign as many oxidation numbers as possible, and then find the oxidation number of the unknown atom. Oxygen's oxidation number is only ever –1 if it is hydrogen peroxide (H_2O_2) or +2 if bonded to fluorine.	The oxidation number of oxygen is –2.
2. Obtain the oxidation number for carbon by recognising the sum of the oxidation numbers for O and C are equal to the charge on the ion (–2).	(oxidation number for C) + 3 × (oxidation number for O) = –2 (oxidation number for C) + 3 × (–2) = –2 (oxidation number for C) – 6 = –2 oxidation number for C = +4

PRACTICE PROBLEM 1

The photographs obtained by the *Voyager 1* space probe showed that Io, one of the moons of Jupiter, has active volcanoes and a surface composed of sulfur and sulfur dioxide, SO_2. Assign oxidation numbers to each atom in the molecule sulfur dioxide.

FIGURE 3.6 Io has a thin atmosphere of sulfur dioxide, and sulfur compounds in liquid and solid states cover its surface.

on Resources

Interactivity Assigning oxidation numbers (int-1220)

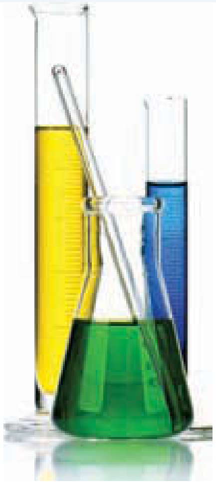
Identifying redox reactions

Oxidation was originally defined as the process in which a substance gained oxygen. Therefore, the burning of magnesium was described as an oxidation process. However, oxidation and reduction occur simultaneously. In figure 3.7, magnesium is oxidised as oxygen is reduced. Oxygen gains electrons and its oxidation number decreases from 0 to –2.

Oxidation numbers can be used to determine whether or not a reaction is a redox reaction. If the oxidation number of an element changes between the reactant species and the product species, then that element has undergone either oxidation or reduction. Given that oxidation cannot happen without reduction, it is easy to determine if the reaction can be classified as redox.

FIGURE 3.7 Magnesium powder burning in a Bunsen burner flame. Here, magnesium is oxidised while oxygen is reduced. Burning magnesium powder gives out a great deal of light. It is commonly used in flash bulbs and fireworks.

FIGURE 3.8 Different oxidation states of chromium compounds. Left to right: K_2CrO_4, $CrCl_3$, $CrCl_2$



SAMPLE PROBLEM 2

Determine whether the following reaction is a redox reaction: $H_2(g) + I_2(g) \rightarrow 2HI(g)$

Teacher-led video: SP2 (tlvd-0671)

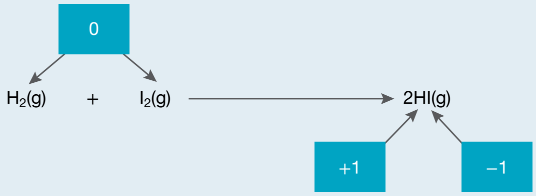
THINK

1. Assign oxidation numbers to each element. The oxidation number of an atom in its elemental form is 0.

   The oxidation number of H in non-metal compounds is +1.

2. Determine whether a change in oxidation number has taken place.

WRITE



The oxidation number of hydrogen has changed from 0 to +1, so the hydrogen has been oxidised (because its oxidation number has increased).
The oxidation number of iodine has changed from 0 to –1, so the iodine has been reduced (because its oxidation number has decreased).
Therefore, this is a redox reaction.

PRACTICE PROBLEM 2

Although tungsten, W, is a rare element, it has been used extensively in the past in light globes. Tungsten is still used to make filaments for specialist incandescent globes because it has the highest melting point (3410 °C) and boiling point (5900 °C) of any metal.

The metal is obtained from tungsten(VI) oxide by heating it with hydrogen, according to the equation:

$$WO_3(s) + 3H_2(g) \rightarrow W(s) + 3H_2O(g)$$

Using oxidation numbers, determine whether this equation represents a redox reaction and, if so, identify the oxidising agent and reducing agent.

FIGURE 3.9 Tungsten metal filaments used in specialist light bulbs. If hot tungsten is exposed to air, it oxidises to form tungsten oxide. To prevent this, inert argon gas is used to fill the inside of light globes.

Conjugate oxidising agents and reducing agents

Every time oxidising agents and reducing agents gain and lose electrons, they form a pair. This means that they have conjugated. A conjugate redox pair consists of:

- an electron donor and its corresponding electron acceptor

  or
- an electron acceptor and its corresponding electron donor.

For example, when the half-equation $Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$ occurs, the Cu(s) donates two electrons and is oxidised, which means it is acting as a reducing agent. Now that a $Cu^{2+}(aq)$ ion has been formed, it can do the opposite of the Cu(s) and accept two electrons back. This reduces it and allows it to behave as a conjugate oxidising agent. Therefore, species that are reduced (act as an electron acceptor, which is an oxidising agent) form conjugate reducing agents, and species that are oxidised (act as an electron donor, which is a reducing agent) form conjugate oxidising agents.

SAMPLE PROBLEM 3

In the following redox reaction, identify the oxidising agent, the reducing agent and their conjugates.

$$Fe(s) + CuSO_4(aq) \rightarrow FeSO_4(aq) + Cu(s)$$

Teacher-led video: SP3 (tlvd-0672)

THINK	WRITE
1. Recall the definitions of oxidation and reduction. Recall that all elements have an oxidation number of 0. **TIP**: Use these acronyms: Oxidation is Loss (OIL) of electrons. Reduction is Gain (RIG) of electrons.	$Cu^{2+}(aq)$ forms Cu(s) . Cu^{2+} has an initial oxidation number of 2+ and has become less positive (gained negatives) to have a final oxidation number for Cu(s) of 0. This means it has been reduced. Fe(s) has an initial oxidation number of 0 and has become more positive (lost negatives), forming $Fe^{2+}(aq)$ (because the charge on the sulfate group is –2). This means it has been oxidised.
2. Oxidising agents are reduced and reducing agents are oxidised. **TIP**: When a question asks for the reducing agent, you must always specify whether the agent is in the ion or elemental form. In this example the answer should be the copper ions or $Cu^{2+}(aq)$. Note that Cu(s) is actually the conjugate oxidising agent.	$Cu^{2+}(aq)$ acts as an oxidising agent. Fe(s) acts as a reducing agent.
3. Species that are reduced (oxidising agents) form conjugate reducing agents and species that are oxidised (reducing agents) form conjugate oxidising agents.	Cu(s) is the conjugate reducing agent. $FeSO_4(aq)$ is the conjugate oxidising agent.

In Sample problem 3, Fe(s) is reduced and $CuSO_4(aq)$ is oxidised. The relationship between oxidising and reducing agents and their conjugates are shown in table 3.2.

TABLE 3.2 The relationship between oxidising and reducing agents and their conjugates

Fe(s)	+	$CuSO_4(aq)$	→	$FeSO_4(aq)$	+	Cu(s)
Fe(s) gets oxidised Acts as a reducing agent Forms a conjugate oxidising agent		$Cu^{2+}(aq)$ gets reduced Acts as an oxidising agent Forms a conjugate reducing agent		Fe^{2+} can act as a conjugate oxidising agent		Cu(s) can act as a conjugate reducing agent

PRACTICE PROBLEM 3

In the following redox reaction, identify the oxidising agent, the reducing agent and their conjugates.

$$2Na(s) + 2H_2O(l) \rightarrow 2NaOH(aq) + H_2(g)$$

Rules for balancing half-equations and redox reactions

There is a set of rules for balancing half-equations (KOHES method) and full redox equations, which are useful for the more complicated types of redox reactions mentioned earlier.

We can illustrate these steps by considering the following equation.

$$Cr_2O_7^{2-}(aq) + 3H_2S(aq) + 8H^+(aq) \rightarrow 2Cr^{3+}(aq) + 3S(s) + 7H_2O(l)$$

TABLE 3.3 Balancing half-equations and redox reactions

Rule	Example:
1. Identify the conjugate pairs that are involved in the reaction. Oxidation numbers may be useful in doing this. Write these pairs down with the reactant on the left and the product on the right.	Reduction: $Cr_2O7^{2-} \rightarrow Cr^{3+}$ Oxidation: $H_2S \rightarrow S$
2. Balance **K**ey elements (undergoing reduction or oxidation).	Reduction: $Cr_2O_7^{2-} \rightarrow 2Cr^{3+}$ Oxidation: $H_2S \rightarrow S$
3. Balance **O**xygen atoms, where needed, by adding water molecules.	Reduction: $Cr_2O_7^{2-} \rightarrow 2Cr^{3+} + 7H_2O$ Oxidation: $H_2S \rightarrow S$
4. Balance **H**ydrogen atoms, where needed, by adding H^+ ions.	Reduction: $Cr_2O_2^- + 14H^+ \rightarrow 2Cr^{3+} + 7H_2O$ Oxidation: $H_2S \rightarrow S + 2H^+$
5. **E**qualise the overall charge by adding electrons.	Reduction: $Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$ Oxidation: $H_2S \rightarrow S + 2H^+ + 2e^-$
Once this process is done for each conjugate pair, the following steps then produce the overall equation.	At this stage, the two half-equations have been produced, and reduction and oxidation can be confirmed from the position of the symbols of state would now be added. However, if the overall equation is required, the following two steps are used.
6. Multiply each half-equation from step 5 by factors that produce the same number of electrons in each half-equation.	Reduction: $Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$ (not necessary to adjust) Oxidation: $3H_2S \rightarrow 3S + 6H^+ + 6e^-$ (multiplied by 3 so that there are $6e^-$ on both sides)
7. Add the two half-equations together, cancelling the electrons. There may be other substances that also partially cancel out at this stage.	$Cr_2O_7^{2-} + \cancel{14}\,{}_8H^+ + \cancel{6e^-} + 3H_2S \rightarrow 2Cr^{3+} + 7H_2O + 3S + \cancel{6H^+} + \cancel{6e^-}$ After cancelling the electrons and hydrogen ions, this becomes: $Cr_2O_7^{2-} + 3H_2S + 8H^+ \rightarrow 2Cr^{3+} + 3S + 7H_2O$
8. Identify the **S**tates for all species.	Adding symbols of state now gives the original equation. $Cr_2O_7^{2-}(aq) + 3H_2S(aq) + 8H^+(aq) \rightarrow 2Cr^{3+}(aq) + 3S(s) + 7H_2O(l)$

TIP: Ensure that you balance the charge on both sides of the overall equation. The charge on each side of the equation should be the same. They do not cancel each other out or have to equal zero.

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Video eLesson Balancing redox reactions (eles-2489)

3.2 EXERCISE

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1. Assign oxidation numbers to the atoms in the following substances.
   (a) HBr
   (b) Na_2O
   (c) CH_4
   (d) $NaClO_3$
   (e) Al_2O_3
   (f) H_3PO_4
2. Determine the oxidation number of S in each of the following compounds.
   (a) H_2SO_4
   (b) SO_2
   (c) SO_3
   (d) H_2S
3. Determine the oxidation number of chromium in each of the following solutions.
   (a) K_2CrO_4
   (b) $CrCl_3$
   (c) $CrCl_2$
4. Assign oxidation numbers to the atoms in the following ions.
   (a) NH_2^-
   (b) MnO_4^-
   (c) HS^-
   (d) VO^{2+}
   (e) IO_3^-
   (f) PO_4^{3-}
5. Identify if the following equations are redox equations. If the reaction is a redox reaction, identify the substances that have been oxidised and reduced.
   (a) $2Fe(s) + 3Cl_2(g) \rightarrow 2FeCl_3(s)$
   (b) $NH_3(g) + HCl(g) \rightarrow NH_4Cl(s)$
   (c) $2NO(g) + O_2(g) \rightarrow 2NO_2(g)$
   (d) $NaOH(aq) + HCl(aq) \rightarrow NaCl(aq) + H_2O(l)$
   (e) $K_2O(s) + H_2O(l) \rightarrow 2KOH(aq)$
   (f) $P_4O_{10}(s) + 6H_2O(l) \rightarrow 4H_3PO_4(aq)$
   (g) $2CO(g) + O_2(g) \rightarrow 2CO_2(g)$
   (h) $C_2H_4(g) + H_2(g) \rightarrow C_2H_6(g)$
6. (a) Permanganate ions, $MnO_4^-(aq)$, are strong oxidising agents. They can be used to oxidise ethanol, $CH_3CH_2OH(l)$, to ethanal, $CH_3CHO(l)$. In the process, they are converted to $Mn^{2+}(aq)$ ions.
      i. Write the equation for the above oxidation.
      ii. Write the equation for the reduction reaction that also occurs.
      iii. From your answers to (i) and (ii), write the overall redox equation for this reaction.
      iv. Identify the oxidising agent and the reducing agent in this reaction.
   (b) The oxidising strength of permanganate ions permits the ethanal produced in part (a) to be further oxidised to ethanoic acid, CH_3COOH. ($Mn^{2+}(aq)$ is produced in this stage as well.)
      i. Write the equation for the oxidation that takes place in this situation.
      ii. Write the equation for the reduction reaction.
      iii. Write the overall redox equation for this reaction.
7. Nitric acid may act as an oxidising agent, especially when hot and concentrated. Many otherwise unreactive metals may be oxidised in this way. Write the overall redox equation for the oxidation of copper metal by $NO_3^-(aq)$ ions to produce $Cu^{2+}(aq)$ ions and $NO_2(g)$ gas using this method.

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3.3 Galvanic cells

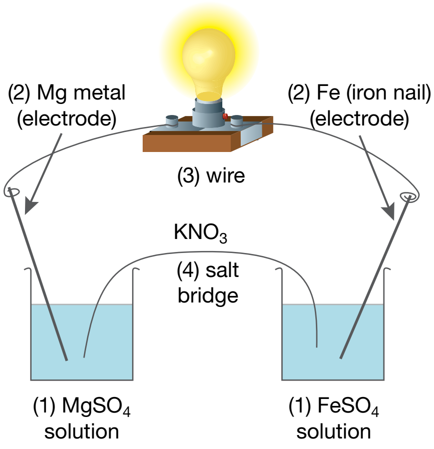
KEY CONCEPTS

- 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)

3.3.1 Common laboratory galvanic cells

A galvanic cell is an electrochemical cell that takes electrical energy from spontaneous redox reactions occurring within the cell. Galvanic cells constructed in a laboratory have the following features in common. An example is shown in figure 3.10.

FIGURE 3.10 A simple galvanic cell



1. Two separate **half-cells** that contain electrolytes: Oxidation occurs in one half-cell and reduction in the other. Each half-cell contains a different conjugate redox pair, and has spectator ions that balance the reacting ions, making the cell electrically neutral. So, in the **Daniell cell,** Cu^{2+} (present as $CuSO_4(aq)$) is reacting and Zn^{2+} (present as $Zn(NO_3)_2(aq)$) is produced; the $SO_4^{2-}(aq)$ and the $NO_3^-(aq)$ are spectator ions.
2. One electrode in each half-cell: Each electrode may be one of the reactant pairs or may be inert, such as graphite or platinum. Redox half-cell reactions occur at the electrode surface. The polarity refers to the charge on the electrode; the anode is negative (due to the electrons being attracted to the surface) and the cathode is positive.
3. A connecting wire between the electrodes that forms an external circuit: This allows electrons to flow from the reducing agent to the oxidising agent — that is, from the site of oxidation (anode) to the site of reduction (cathode).
4. A **salt bridge** connecting the two solutions allows charge (ions) to flow without allowing the solutions to mix. This contains a strong electrolyte (often potassium nitrate or potassium chloride) that allows a slow migration of ions (such as K^+ and NO_3^-) to maintain the cell's electrical neutrality. The negative ions (anions) flow into the cell containing the anode; they are needed to balance the positive ions (cations) that are produced at the anode surface. The positive ions flow into the cell containing the cathode. Because electrons are accepted by the ions in this cell, positive ions are consumed. The original negative ions remaining must be balanced by additional positive charges from the salt bridge.

The ions from the salt bridge must not react with the electrolytes in the cells. This would interfere with the cell's operation.

TIP: For all cells (galvanic, fuel, and electrolytic)

- **RedCat: Reduction always occurs at the Cathode**
- **AnOx: Oxidation always occurs at the Anode**

Types of half-cell

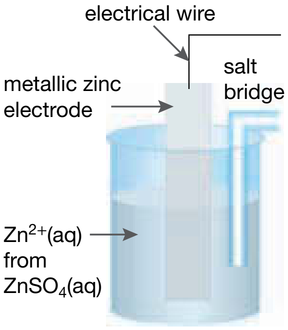
Each half-cell in a laboratory galvanic cell contains a conjugate oxidising agent–reducing agent pair. Oxidation occurs in one of the half-cells and reduction occurs in the other. Half-cells are constructed by dipping an electrode into an electrolyte. The electrode may or may not take part in the reaction.

It is convenient to group half-cells into three types based on design.

The three types are:

- the metal ion–metal half-cell
- the solution half-cell
- the gas–non-metal half-cell.

FIGURE 3.11a Metal ion–metal half-cells



Metal ion–metal half-cells (figure 3.11a) consist of a metal rod in a solution of its ions, usually from the sulfate salt. The sulfate ion is unreactive. Ions that are more reactive, such as bromide ions or nitrate ions, may set up a competing reaction.

Solution half-cells (figure 3.11b) use an inert electrode in the reacting solution. The reacting solution may contain an oxidising agent, for example MnO_4^-(aq) in solution (with Mn^{2+}(aq)), or a reducing agent, for example Fe^{2+}(aq) in solution (with Fe^{3+}(aq)).

FIGURE 3.11b Solution half-cell

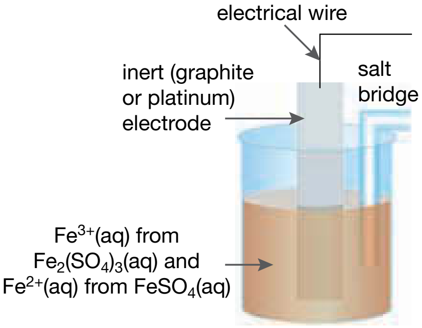
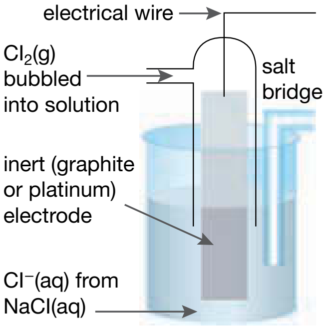


FIGURE 3.11c Gas–non-metal ion half-cell



Although gases are reactive, they are usually more difficult to manage in the laboratory. As a result, gaseous half-cells are not very common (figure 3.11c). In a gaseous half-cell, the gas bubbles over an inert electrode that is connected to the external wire. Its conjugate redox non-metal ion is in solution.

on Resources

Video eLesson Galvanic cells 1 (eles-2594)

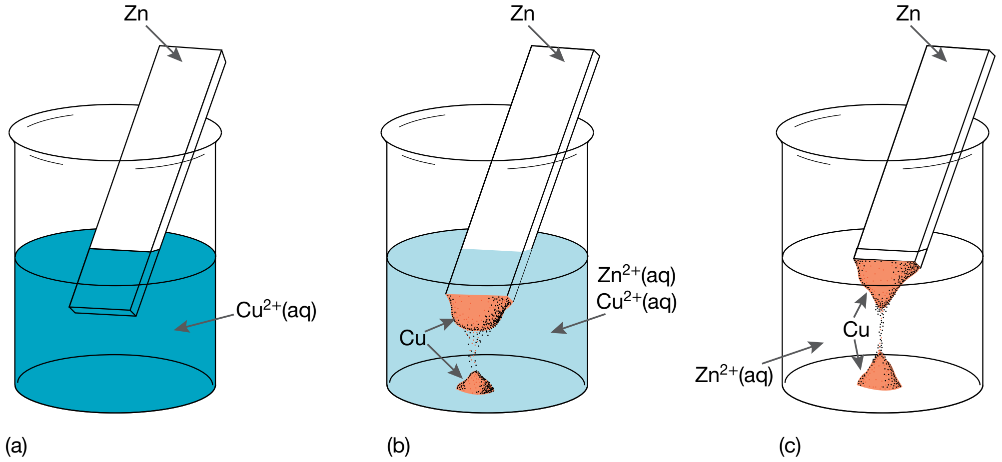
3.3.2 Comparison of energy transformations in redox reactions

Energy may be released in a number of forms such as heat, light, electricity or sound. The set-up of the reaction determines the form of energy that is released.

Converting chemical energy to thermal energy

When a zinc strip is placed in copper(II) sulfate solution (Cu ions), the zinc is oxidised and electrons flow from the zinc metal to the copper ions. This is a spontaneous reaction and requires no energy; in fact, it releases energy (figure 3.12a). As the zinc dissolves, copper ions are reduced to copper metal and the original blue colour of the solution begins to fade (figure 3.12b). If the zinc strip remains in the solution for an extended period of time, the solution in the beaker becomes colourless. All the copper ions in the solution are reduced to form copper metal, and the zinc goes into the solution as zinc ions (figure 3.12c).

FIGURE 3.12 A zinc strip in copper(II) sulfate solution creates a spontaneous redox reaction.



All the chemical energy of the reaction is released as thermal energy (heat) and the transfer of electrons from zinc to copper ions occurs on the surface of the zinc metal. This can be seen in figures 3.13 and 3.14.

FIGURE 3.13 Chemical energy is released as thermal energy.

FIGURE 3.14 As Zn reacts with Cu^{2+} ions, it goes into solution as Zn^{2+} ions. Cu(s) is deposited on the surface of the zinc.

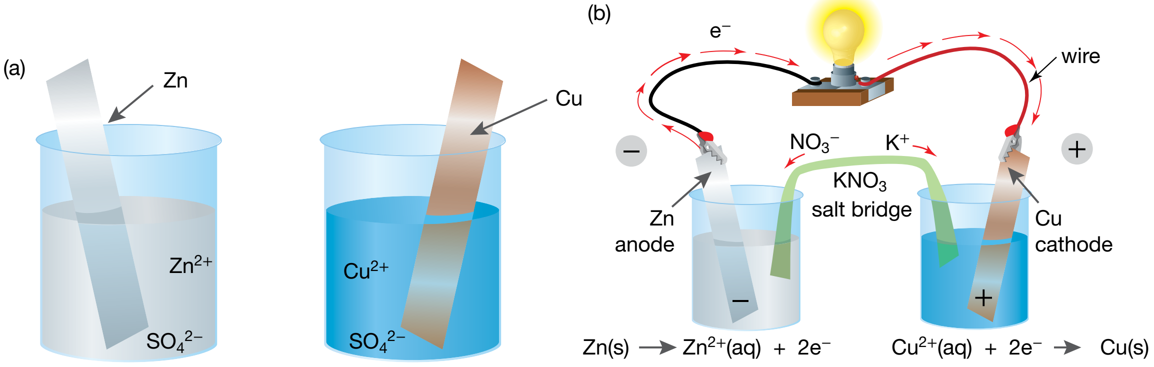
Converting chemical energy to electrical energy

If the site of oxidation is physically separated from the site of reduction (for example, if each of the solutions is in a separate beaker), and a connecting wire is placed between them, the electrons are forced to travel through this wire to complete the redox reaction. Such movement of electrons constitutes an electric current. This arrangement converts chemical energy directly into electrical energy.

To do this for the $Zn(s)/Cu^{2+}(aq)$ reaction that we have been discussing, a strip of zinc metal is placed in a beaker containing zinc sulfate solution (see figure 3.15a). This is connected by a wire to a strip of copper placed in a beaker containing a copper sulfate solution. The wire provides a pathway for the electrons to pass from the zinc atoms to the copper cations, but no reaction is observed because the circuit is not complete.

As the zinc atoms donate electrons and become zinc cations in the first beaker, the electrical neutrality must be maintained, so anions are required. These anions are supplied by the salt bridge, which can be a simple filter paper or a U-tube with cotton wool in it. It is soaked in a salt solution, such as potassium nitrate solution, $KNO_3(aq)$, and used to connect the two beakers (figure 3.15b). Potassium nitrate solution provides NO_3^- anions for the first beaker to balance the positive charges created by zinc cations. In the second beaker, copper cations accept electrons and become copper atoms, leaving behind negative sulfate ions in solution that must be balanced. So the salt bridge supplies cations (in this case, $K^+(aq)$). Electrons carry the current in the wire from zinc to copper, and ions carry the current in solution. The flow of ions completes the circuit. It is important that the ions in the salt bridge do not react with chemicals in the beakers. The movement of ions in the solutions is called the **internal circuit**.

FIGURE 3.15 (a) Two strips of different metals and solutions of each of their ions. (b) With the addition of a wire and a salt bridge, a simple electrochemical cell — a device that converts chemical energy into electrical energy — is constructed.



Each beaker in figure 3.15 is a half-cell. The metal conducting strips are called **electrodes** and, combined with the wire, they are referred to as the **external circuit**. Electrons in the external circuit can be made to do useful work such as lighting a light bulb.

Solutions that can conduct a current are known as **electrolytes**. The electrode at which oxidation occurs is called the **anode**, and it has a negative charge; the electrode at which reduction occurs is called the **cathode**, and it has a positive charge. All of these components together are known as a galvanic cell or an **electrochemical cell**.

The example above of an electrochemical cell containing the half-cells $Zn(s)/Zn^{2+}(aq)$ and $Cu(s)/Cu^{2+}(aq)$ is known as the Daniell cell.

TIP: When constructing answers remember:
- **Internal circuit always involves Ions**
- **External circuit always involves Electrons.**

A simple galvanic cell consists of:

- **two half-cells, containing two electrodes (anode and cathode) and two electrolytes**
- **a conducting wire**
- **a salt bridge, containing another electrolyte.**

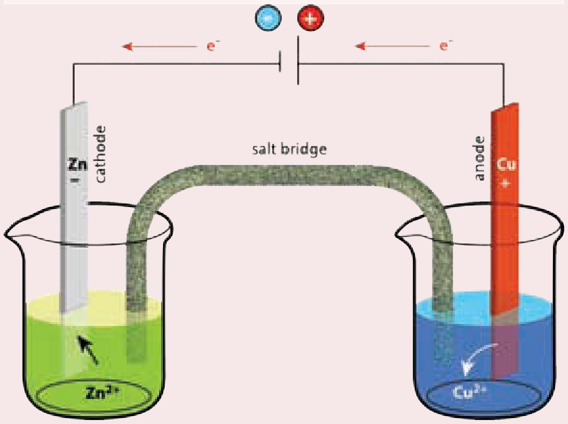
An electrolyte is a solution containing ions that can conduct electricity.

An electrode is a conductor through which electrons enter or leave a galvanic cell.

The anode is the electrode where oxidation occurs.

The cathode is the electrode where reduction occurs.

FIGURE 3.16 A simple galvanic cell (Daniell cell)



TIP: **When describing your observations of a functioning galvanic cell ensure you include colour or state changes.**

SAMPLE PROBLEM 4

A galvanic cell was set up in the following way. A strip of clean magnesium was dipped into a beaker containing a solution of $MgSO_4$ and, in a separate beaker, an iron nail was dipped into a solution of $FeSO_4$. The iron nail and magnesium strip were connected with a wire, and the circuit was completed with a salt bridge consisting of filter paper dipped into a solution of KNO_3. The magnesium electrode was known to have a negative charge. Predict the following.

a. **The substance that is oxidised and the one that is reduced**
b. **The anode and cathode**
c. **The direction of electron flow**
d. **The half-cell reactions**
e. **The overall redox reaction.**

Teacher-led video: SP4 (tlvd-0673)

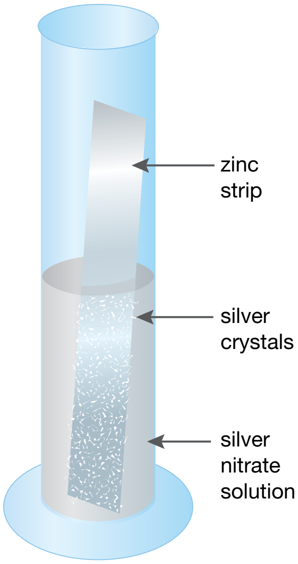
THINK	WRITE
a. Electrons always flow from the site of oxidation to the site of reduction.	Electrons are produced at the magnesium electrode and consumed at the zinc electrode. Therefore, magnesium is being oxidised and iron(II) ions are being reduced.
b. Oxidation always occurs at the anode.	Magnesium is the anode and iron is the cathode.
c. Electrons flow from the anode to the cathode.	Electrons flow from the magnesium electrode through the wire to the iron electrode.
d. Write out the two half equations that represent oxidation and reduction.	$Mg(s) \rightarrow Mg^{2+}(aq) + 2e^-$ (oxidation) $Fe^{2+}(aq) + 2e^- \rightarrow Fe(s)$ (reduction)
e. Adding these half-equations and cancelling the electrons results in the following overall redox reaction.	$Mg(s) + Fe^{2+}(aq) \rightarrow Mg^{2+}(aq) + Fe(s)$

PRACTICE PROBLEM 4

When zinc metal is dipped into a solution of silver nitrate, it forms a coating of silver, as shown in the diagram.

Use this reaction to draw a diagram of a galvanic cell, using KNO_3 in the salt bridge and zinc sulfate as one of the electrolytes. Complete the following steps to construct your diagram.

- **a.** **Draw the two half-cells.**
- **b.** **Write half-equations for the oxidation and reduction reactions.**
- **c.** **Write the overall cell reaction.**
- **d.** **Label the flow of:**
  - **electrons in the wire**
  - **anions in the salt bridge**
  - **cations in the salt bridge.**
- **e.** **Label the anode and the cathode.**



TIP: **In the internal circuit anions always travel towards the anode and cations travel towards the cathode.**

on Resources

Digital document Experiment 3.1 Investigating the Daniell cell (doc-31253)
Video eLesson Galvanic cells 2 (eles-2595)

3.3 EXERCISE

To answer questions online and to receive **immediate feedback** and **sample responses** for every question, go to your learnON title at www.jacplus.com.au.

1. Why is a salt bridge or porous barrier used to connect two half-cells in a galvanic cell?
2. A student was doing an experiment in the school laboratory. She placed a fresh piece of zinc metal into a beaker of silver nitrate solution and left it to stand for a short period of time. She then noted the following observations:
   - The temperature of the solution increased.
   - The zinc metal became coated with silver.
     - (a) Write the ionic equation for the reaction occurring in the beaker.
     - (b) Draw a galvanic cell that allows the energy released during the reaction to be readily used. On your diagram, identify the anode, the cathode and the polarity of these electrodes. Indicate the direction of electron flow.
     - (c) Write half-equations for the reactions occurring at each electrode.
     - (d) Explain the significance of the increase in temperature of the solution.
3. A galvanic cell was set up by combining half-cells containing zinc and magnesium electrodes dipped into the appropriate sulfate solutions. A conducting wire and a salt bridge completed the circuit. After three hours, the two electrodes were removed and weighed. The mass of the Zn electrode had increased, while the mass of the Mg electrode had decreased. Draw this galvanic cell, clearly indicating the following.
   - (a) The anode and the cathode
   - (b) The ions present in the half-cells
   - (c) The electrolyte in the salt bridge
   - (d) Anion and cation flow within the salt bridge

(e) The direction of the flow of electrons
(f) The anode reaction and the cathode reaction
(g) The oxidation reaction and the reduction reaction
(h) The overall cell reaction
(i) The oxidising agent and the reducing agent

4. A half-cell containing $Cr_2O_7^{2-}(aq)/Cr^{3+}$ is connected to a half-cell containing $Fe^{2+}(aq)/Fe(s)$. A voltmeter indicates that electrons flow from the beaker containing $Fe^{2+}(aq)/Fe(s)$ to the half-cell containing $Cr_2O_7^{2-}(aq)/Cr^{3+}$.
   (a) Draw a labelled diagram of this set-up, indicating the contents of each beaker, the salt bridge and the materials that each electrode is made from. Also mark the direction of electron flow.
   (b) Write the equation for each half-reaction under the appropriate half-cell.
   (c) On your diagram, label the anode, cathode and the polarity of each electrode.
   (d) Why is it necessary to acidify the $Cr_2O_7^{2-}(aq)/Cr^{3+}$ half-cell?

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3.4 The electrochemical series

KEY CONCEPT

- 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.

3.4.1 Standard electrode potentials

The **electrical potential** of a galvanic cell is the ability of the cell to produce an electric current. Electrical potential is usually measured in volts (V). Although we cannot measure the electrode potential for an isolated half-cell, we can measure the difference in potential between two connected half-cells.

The electrical potential of a cell results from competition between the two half-cells for electrons. The half-cell with the greater tendency to attract electrons undergoes reduction, while the other half-cell loses electrons and is oxidised. The half-cell in which reduction occurs has a greater **reduction potential** than the half-cell in which oxidation occurs.

The reduction potential of a half-cell is a measure of the tendency of the oxidising agent to accept electrons and undergo reduction. The difference between the reduction potentials of the two half-cells is called the **cell potential difference**. The **standard cell potential difference** (E cell) is the measured cell potential difference, under standard conditions, when the concentration of each species in solution is 1 M, the pressure of a gas, where applicable, is 100 kPa and the temperature is 25 °C (298 K).

$$E^0_{\text{cell}} = E^0_{\text{oxidising agent}} - E^0_{\text{reducing agent}}$$

Half-cell E^0 values are measured against the standard hydrogen half-cell, which is arbitrarily assigned 0.00 volts.

To obtain a comparative measure of the reduction potentials of different half-cells, the **standard hydrogen half-cell** is used as a standard reference electrode. This allows the determination of a redox half-cell's ability to accept electrons. It consists of hydrogen gas bubbling around an inert platinum electrode in a solution of hydrogen ions (see figure 3.17). The standard hydrogen half-cell is arbitrarily assigned a standard reduction potential of 0.00 V at 25 °C. The reaction that occurs at the electrode surface is:

$$2H^+(aq) + 2e^- \rightleftharpoons H_2(g) \quad E^0 = 0.00\ \text{V}$$

FIGURE 3.17 A diagram of a hydrogen half-cell

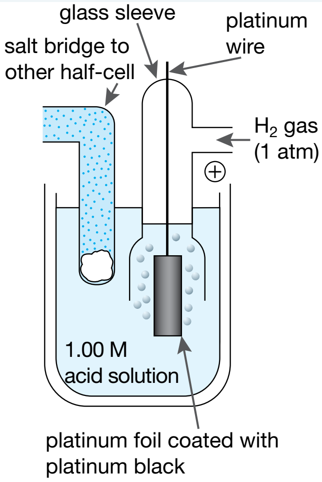


FIGURE 3.18 A hydrogen half-cell

The standard hydrogen electrode is used with other half-cells so that the reduction potentials of those cells can be measured. If a species accepts electrons more easily than hydrogen, its electrode potential is *positive*. If it accepts electrons less easily than hydrogen, its electrode potential is *negative*.

TIP: If a half-equation has electrons on the reactant (left-hand) side, it is a reduction half-equation.

When a standard hydrogen half-cell is connected to a standard $Cu^{2+}(aq)/Cu(s)$ half-cell, the voltmeter measures a potential difference of 0.34 volts (see figure 3.19). Because electrons flow towards the $Cu^{2+}(aq)/Cu(s)$ half-cell, $Cu^{2+}(aq)$ has a greater tendency to accept electrons, which means it is a stronger oxidising agent, than $H^+(aq)$. Therefore, the measured E^0 value for the half-cell reaction:

$$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$$

is positive in sign and equal to +0.34 volts.

When a standard hydrogen half-cell is connected to a standard $Zn^{2+}(aq)/Zn(s)$ half-cell, the voltmeter measures a potential difference of 0.76 volts (see figure 3.20). Because electrons flow to the $H^+(aq)/H_2(g)$ half-cell, $H^+(aq)$ has a greater tendency to accept electrons than $Zn^{2+}(aq)$. Therefore, the measured E^0 value for the half-cell reaction:

$$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s)$$

is negative in sign and equal to –0.76 volts.

FIGURE 3.19 Measuring the standard half-cell potential of a Cu^{2+}/Cu half-cell

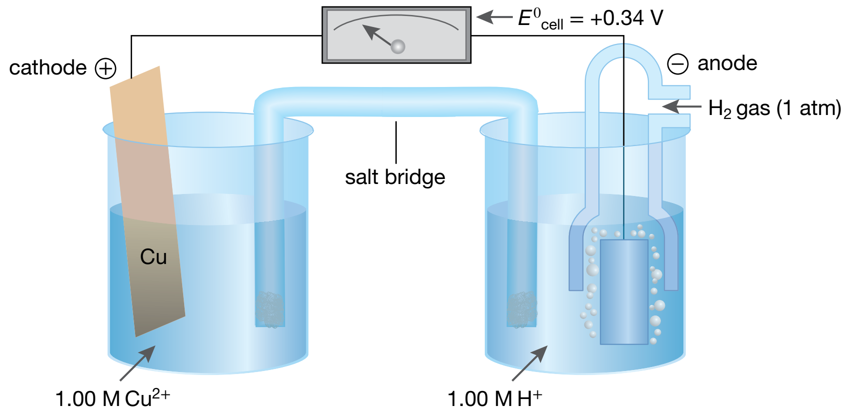
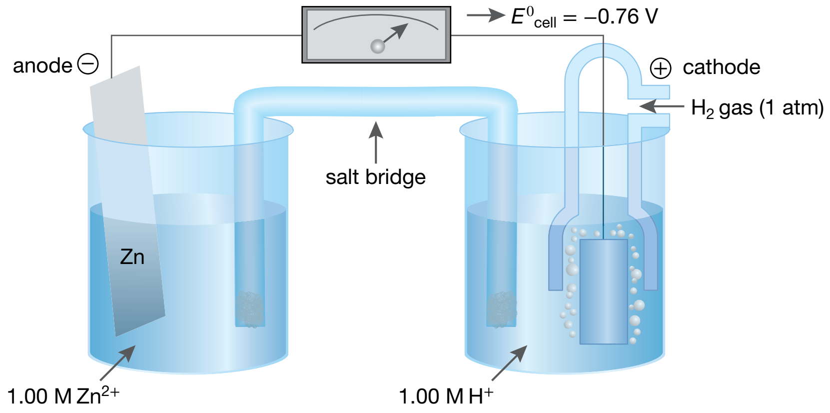


FIGURE 3.20 Measuring the standard half-cell potential of a Zn^{2+}/Zn half-cell



Half-cell potentials are often listed in a table such as table 3.4. These tables may be referred to as tables of standard electrode potentials or standard reduction potentials, and may also be called an **electrochemical series**. The half-cell potentials are usually arranged from the largest E^0 value to the smallest.

TIP: An electrochemical series table can be found in Table 2 of the VCE Chemistry Data Book.

on Resources

Video eLessons	Galvanic cells 3 (eles-2596)
	Galvanic cells and measuring cell potential (eles-0436)
Interactivity	Electrochemical series (int-1256)

TABLE 3.4 The electrochemical series

	Half-reaction		E^0 (volts)
strongest oxidising agent	$F_2(g) + 2e^- \rightleftharpoons 2F^-(aq)$	weakest reducing agent	+ 2.87
	$H_2O_2(aq) + 2H^+(aq) + 2e^- \rightleftharpoons 2H_2O(l)$		+ 1.77
	$MnO_4{}^-(aq) + 8H^+(aq) + 5e^- \rightleftharpoons Mn^{2+}(aq) + 4H_2O(l)$		+ 1.52
	$PbO_2(s) + 4H^+(aq) + 2e^- \rightleftharpoons Pb^{2+}(aq) + 2H_2O(l)$		+ 1.46
	$Cl_2(g) + 2e^- \rightleftharpoons 2Cl^-(aq)$		+ 1.36
	$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightleftharpoons 2Cr^{3+}(aq) + 7H_2O(l)$		+ 1.33
	$O_2(g) + 4H^+(aq) + 4e^- \rightleftharpoons 2H_2O(l)$		+ 1.23
	$Br_2(l) + 2e^- \rightleftharpoons 2Br^-(aq)$		+ 1.09
	$NO_3^-(aq) + 4H^+(aq) + 3e^- \rightleftharpoons NO(g) + 2H_2O(l)$		+ 0.95
	$NO_3^-(aq) + 2H^+(aq) + e^- \rightleftharpoons NO_2(g) + H_2O(l)$		+ 0.81
	$Ag^+(aq) + e^- \rightleftharpoons Ag(s)$		+ 0.80
	$Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+}(aq)$		+ 0.77
	$O_2(g) + 2H^+(aq) + 2e^- \rightleftharpoons H_2O_2(l)$		+ 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
increasing oxidising strength	$SO_4{}^{2-}(aq) + 4H^+(aq) + 2e^- \rightleftharpoons SO_2(g) + 2H_2O(l)$	increasing reducing strength	+ 0.20
	$Sn^{4+}(aq) + 2e^- \rightleftharpoons Sn^{2+}(aq)$		+ 0.15
	$S(s) + 2H^+(aq) + 2e^- \rightleftharpoons H_2S(g)$		+ 0.14
	$2H^+(aq) + 2e^- \rightleftharpoons H_2(g)$ (defined)		0.00
	$Pb^{2+}(aq) + 2e^- \rightleftharpoons Pb(s)$		– 0.13
	$Sn^{2+}(aq) + 2e^- \rightleftharpoons Sn(s)$		– 0.14
	$Ni^{2+}(aq) + 2e^- \rightleftharpoons Ni(s)$		– 0.25
	$PbSO_4(s) + 2e^- \rightleftharpoons Pb(s) + SO_4{}^{2-}(aq)$		– 0.36
	$Fe^{2+}(aq) + 2e^- \rightleftharpoons Fe(s)$		– 0.44
	$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s)$		– 0.76
	$2H_2O(l) + 2e^- \rightleftharpoons H_2(g) + 2OH^-(aq)$		– 0.83
	$Al^{3+}(aq) + 3e^- \rightleftharpoons Al(s)$		– 1.66
	$Mg^{2+}(aq) + 2e^- \rightleftharpoons Mg(s)$		– 2.37
	$Na^+(aq) + e^- \rightleftharpoons Na(s)$		– 2.71
	$Ca^{2+}(aq) + 2e^- \rightleftharpoons Ca(s)$		– 2.87
weakest oxidising agent	$K^+(aq) + e^- \rightleftharpoons K(s)$	strongest reducing agent	– 2.93
	$Li^+(aq) + e^- \rightleftharpoons Li(s)$		– 3.04

Note: Standard electrode reduction potentials at a temperature of 25 °C, a pressure of 1 atm and a concentration of 1 M for all aqueous species.

3.4.2 Use of standard half-cell reduction potentials

A table such as the electrochemical series in table 3.4 provides a great deal of information about a redox reaction. This includes:

- determination of the relative strengths of oxidising agents and reducing agents
- prediction of whether a redox reaction will occur whether by direct contact or in a suitably designed galvanic cell
- prediction of the overall reaction occurring in a cell and the potential difference of that cell.

However, the table does not tell us the rate of a reaction or if intermediates form. E^0 values and their order are temperature dependent, and the E^0 table predicts reactions only at standard conditions of 25 °C, 1 atm and 1 M concentration for solutions.

In the electrochemical series, the best oxidising agents are at the top left and have the most positive voltage.

Predicting and calculating the potential difference of spontaneous reactions in galvanic cells

In galvanic cells, at least two oxidising agents and two reducing agents are present. The following procedure can be useful in predicting which spontaneous reaction occurs in a galvanic cell. The Daniell cell is used as an example.

1. Write the half-equations occurring in the galvanic cell in descending order of E^0 For example:

$$\begin{aligned} &Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s) \qquad E^0 = +0.34\ \text{V} \\ &Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s) \qquad E^0 = -0.76\ \text{V} \end{aligned}$$

2. Circle the species present in the galvanic cell that could participate.

$$\begin{aligned} &\enclose{circle}{Cu^{2+}(aq)} + 2e^- \rightleftharpoons Cu(s) \qquad E^0 = +0.34\,\text{V} \\ &Zn^{2+}(aq) + 2e^- \rightleftharpoons \enclose{circle}{Zn(s)} \qquad E^0 = -0.76\,\text{V} \end{aligned}$$

3. Select the oxidising agent with the highest E^0. This is reduced at the cathode, which accepts electrons more easily than an oxidising agent with a lower E^0.

$$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s) \quad E^0 = +0.34\,\text{V}$$

4. Select the reducing agent with the lowest E^0. This is oxidised at the anode, which donates electrons more easily than a reducing agent with a higher E^0. Write this equation as an oxidation equation — that is, reverse it.

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

5. Balance electrons if necessary from the half-equations.
6. Write the full equation.

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

7. Determine the cell potential difference by using the formula:

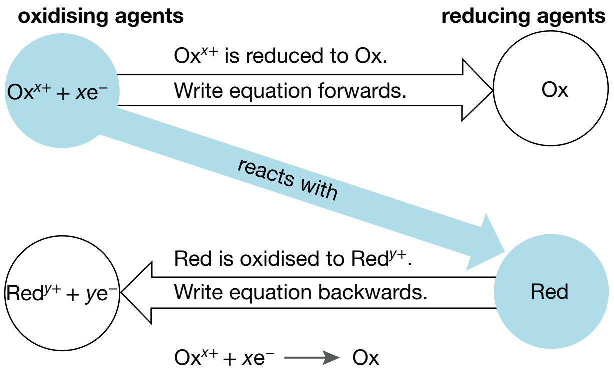
$$\begin{aligned}\text{cell potential difference} &= E^0_{\text{oxidising agent}} - E^0_{\text{reducing agent}}\\ &= +0.34 - (-0.76)\\ &= +1.10\text{ V}\end{aligned}$$

In summary, when the electrode reactions are written in descending order of E^0 values, the strongest oxidising agent (highest E^0) on the left-hand side of the equation reacts with the strongest reducing agent (lowest E^0) on the right.

In the E^0 table, the strongest oxidising agent, top left, reacts with the strongest reducing agent, bottom right.

TIP: When working out the potential difference (V) of a cell, always subtract the least positive number from the most positive number. Always add + or − to the value calculated.

FIGURE 3.21 Whatever the cell, reduction always occurs at the cathode (REDCAT) and oxidation always occurs at the anode (ANOX).



$$Ox^{x+} + xe^- \longrightarrow Ox$$
$$Red \longrightarrow Red^{y+} + ye^-$$

Ox = oxidising agent; Red = reducing agent

SAMPLE PROBLEM 5

The standard half-cell potentials of some metal–metal ion half-cells are:

Half-cell	**E^0 (volts)**
$Ag^+(aq)/Ag(s)$	+0.80
$Co^{2+}(aq)/Co(s)$	–0.28
$Ba^{2+}(aq)/Ba(s)$	–2.90

Determine which species is the best oxidising agent and which is the best reducing agent.

Teacher-led video: SP5 (tlvd-0674)

THINK	**WRITE**
1. Cations are formed when atoms donate electrons. Therefore, cations can readily accept electrons back, reducing them and acting as an oxidising agent.	Ag^+(aq), Co^{2+}(aq) and Ba^{2+}(aq) are all oxidising agents.
2. Atoms are formed when cations accept electrons. Therefore, atoms can readily donate electrons back, oxidising them and acting as a reducing agent.	Ag(s), Co(s) and Ba(s) are all reducing agents.
3. In a conventional table of standard half-cell reduction potentials, the strongest oxidising agent has the most positive E^0 value, while the strongest reducing agent has the most negative E^0 value. **TIP:** Students must clearly identify whether the atom or the ion is the strongest when describing the reaction occurring.	Ag^+(aq) is the strongest oxidising agent, while Ba(s) is the strongest reducing agent.

PRACTICE PROBLEM 5

Consider the following conjugate redox pairs and their E^0 values.

$Cl_2(g)/Cl^-(aq)$	+1.36 V
$I_2(s)/I^-(aq)$	+0.54 V
$Al^{3+}(aq)/Al(s)$	−1.67 V
$MnO_4^-(aq)/Mn^{2+}(aq)$	+1.52 V
$Pb^{2+}(aq)/Pb(s)$	−0.13 V

a. **Which species is:**
  - i. **the strongest oxidising agent**
  - ii. **the strongest reducing agent**
  - iii. **the weakest oxidising agent**
  - iv. **the weakest reducing agent?**

b. **Write fully balanced half-equations for each conjugate redox pair.**

SAMPLE PROBLEM 6

Given the two half-equations:

$$Br_2(l) + 2e^- \rightleftharpoons 2Br^-(aq) \quad E^0 = +1.09\text{ V}$$

$$Mg^{2+}(aq) + e^- \rightleftharpoons Mg(s) \quad E^0 = -2.34\text{ V}$$

predict the likely spontaneous redox reaction.

THINK	WRITE
1. For a redox reaction to occur, a reducing agent must react with an oxidising agent.	Br_2(l) does not react with Mg^{2+}(aq) (because they can act only as oxidising agents) and Br^-(aq) does not react with Mg(s) (because they can act only as reducing agents).
2. For a spontaneous redox reaction to occur, the E^0 of the oxidising agent must be more positive than the E^0 of the reducing agent. **TIP**: In galvanic cells the most positive half-equation gets reduced (forward reaction in the table).	Br_2(l) reacts spontaneously with Mg.

PRACTICE PROBLEM 6

Given the two half-equations:

$$\mathbf{Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+}(aq) \quad E^0 = +0.77\ V}$$

$$\mathbf{Ni^{2+}(aq) + 2e^- \rightleftharpoons Ni(s) \quad E^0 = -0.23\ V}$$

Identify the anode and cathode, write the overall equation and calculate the standard cell potential that would be produced in a galvanic cell made from these half-cells.

TIP: **When writing balanced chemical equations from redox half-equations, make sure to cancel out electrons/species.**

on Resources

Video eLesson	Predicting products of redox reactions (med-0437)
Digital documents	Experiment 3.2 Predicting redox reactions (doc-31254)
	Experiment 3.3 Galvanic cells and redox potentials (doc-31255)
Teacher-led video	Experiment 3.3 Galvanic cells and redox potentials (tlvd-0739)

3.4.3 Limitations of using the electrochemical series

Although E^0 values can be added to decide whether a spontaneous reaction will occur between an oxidising agent and a reducing agent, they do not provide any information about the rate of the reaction. It may be predicted that a redox reaction is possible between two reactants, but no reaction may be observed if the reaction proceeds very slowly. Redox predictions may be checked by experiment.

Non-standard conditions may change redox reaction E^0 values. If the redox reaction conditions deviate significantly from those at which standard electrode potentials are measured, the relative order of redox conjugate pairs in the table of standard electrode potentials could be altered. This could mean that previously favourable reactions become unfavourable under the new conditions.

3.4.4 Common commercial cells and batteries

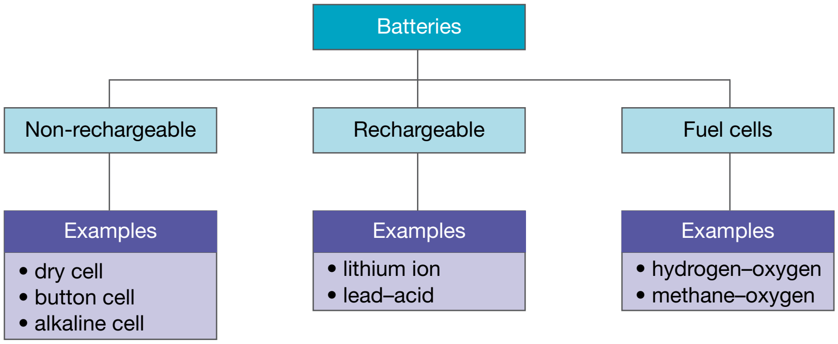
Batteries are practical applications of electrochemical cells. They are used as small, portable and efficient sources of electrical energy. A battery is a combination of cells in series or parallel, but common cells such as the **dry cell** are also often referred to as batteries.

One of the first electrochemical cells used widely was invented by Daniell in 1836. At the time, it was used extensively in telegraph and telephone work as a reliable source of electricity. However, Daniell cells are examples of wet cells, where the electrolyte is in a liquid state, and they could not be stored easily and were easily spilled. This meant their application was limited. The demand for portable, leakproof electrochemical cells led to the development of the **Leclanché cell**, or dry cell.

Cells come in **rechargeable** and non-rechargeable varieties. Common dry cells are used until the supply of electrical energy is exhausted and are then discarded. Once the chemical reaction is over, they are useless. These cells are sometimes called **primary cells** and are not rechargeable. Other cells, such as the lead–acid accumulator battery or nickel–cadmium cells, are rechargeable. Rechargeable batteries are sometimes referred to as **secondary cells**, which are discussed in topic 7.

Another type of cell is the fuel cell, which uses a supply of fuel in order to create a flow of electrons and is discussed in topic 4.

FIGURE 3.22 Cells can be primary (non-rechargeable) cells, secondary (rechargeable) cells or fuel cells.



Factors affecting selection of cells

Many factors must be considered when selecting a cell for a particular use. These include:

- *initial and operating cost:* This depends on the materials used and the technology involved in development and production.
- *size and shape:* The main shapes are cylindrical, coin, button, pouch and prismatic.
- *mass:* In portable devices, lightness is a priority, whereas transport vehicles can accommodate heavier or bulkier cells.
- *single-use* or *rechargeable*
- *memory effect:* Some cells have decreased capacity to be fully charged. This occurs when rechargeable batteries are not fully discharged before recharging.
- *voltage provided:* Different cells output different levels of voltage. For example, cells with aqueous electrolytes cannot provide more than 2 volts.
- *discharge curve:* This is how the voltage changes over time. For some batteries, the voltage decreases steadily; other batteries supply relatively constant voltage until most of the charge is consumed.
- *current:* The greater the surface area of the electrodes, the greater the current, although this limits the amount of electrolyte present.
- *shelf life:* Some cells discharge over time even when not being used.
- *ease of disposal and other environmental factors:* The mercury button cell has been phased out due to environmental concerns, and there is also concern about the toxicity of cadmium in nickel–cadmium (NiCd) cells. All rechargeable batteries should be recycled.

3.4.5 Primary cells

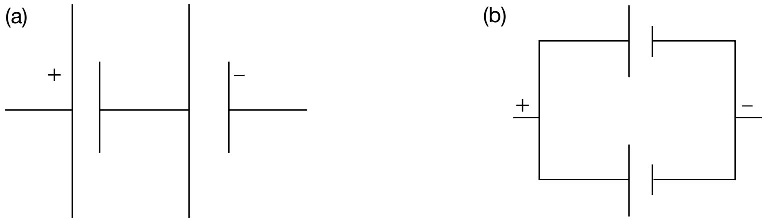
There are different types of primary cells. The most common are the dry cell, the alkaline zinc/manganese dioxide cell and the **button cell**.

The dry cell

An electrochemical cell in which the electrolyte is a paste, rather than a liquid, is known as a dry cell, or Leclanché cell. The most commonly used dry cell is a C battery, which has a voltage of 1.5 V. Dry cells are commonly used in torches, toys and transistor radios because they are cheap, small, reliable and easy to use. The oxidising agents and reducing agents used in such cells should:

- be far enough apart in the electrochemical series to produce a useful voltage from the cell
- not react with water in the electrolyte too quickly, or they will discharge early (therefore, highly reactive metals such as sodium, potassium and calcium are not found in such batteries)
- be inexpensive.

FIGURE 3.23 Arrangement of cells in circuits: (a) Two 1.5 V cells connected in series make a 3.0 V battery and (b) tTwo 1.5 V cells connected in parallel allow a higher current at 1.5 V.



A dry cell consists of a zinc container filled with an electrolyte paste. This paste contains manganese(IV) oxide, MnO_2, zinc chloride, $ZnCl_2$, ammonium chloride, NH_4Cl, and water. A carbon rod is embedded in the paste and forms the cathode. The zinc container is the anode. The thick paste prevents the contents of the cell from mixing, so a salt bridge is not needed. Intermittent use or slight warming of the cell prevents the build-up of these products around the electrodes, increasing the life of the cell. Once the materials around the electrodes have been used up, the cell stops operating.

The electrode half-equations are:
Anode (oxidation):

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

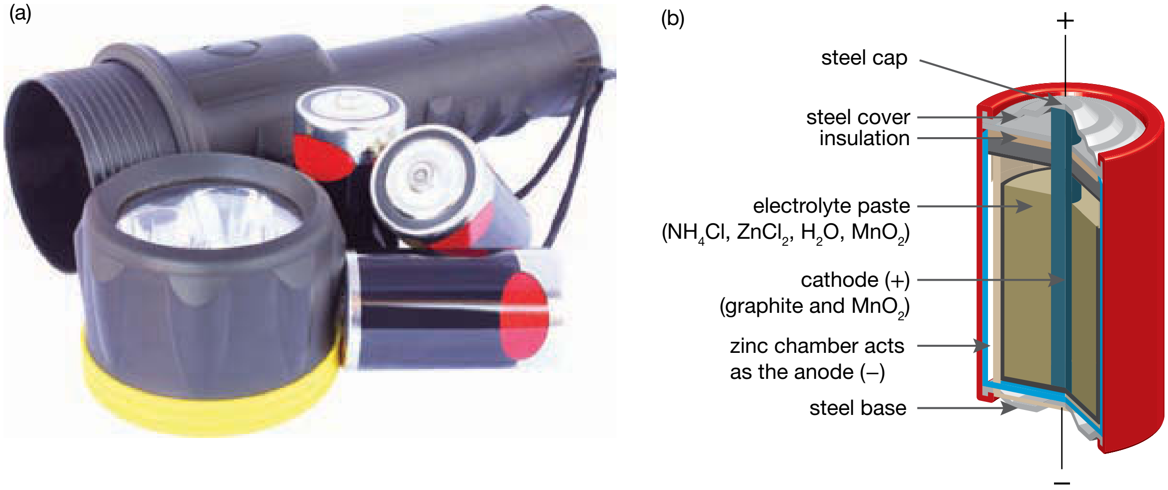
Cathode (reduction):

$$2MnO_2(s) + 2NH_4^+(aq) + 2e^- \rightarrow Mn_2O_3(s) + 2NH_3(aq) + H_2O(l)$$

The overall cell reaction can be written as:

$$2MnO_2(s) + 2NH_4^+(aq) + Zn(s) \rightarrow Mn_2O_3(s) + 2NH_3(aq) + H_2O(l) + Zn^{2+}(aq)$$

FIGURE 3.24 (a) Dry cells in a torch and (b) a simplified cross-section of a dry cell



on Resources

Digital document Experiment 3.4 Looking at a dry cell (doc-31256)

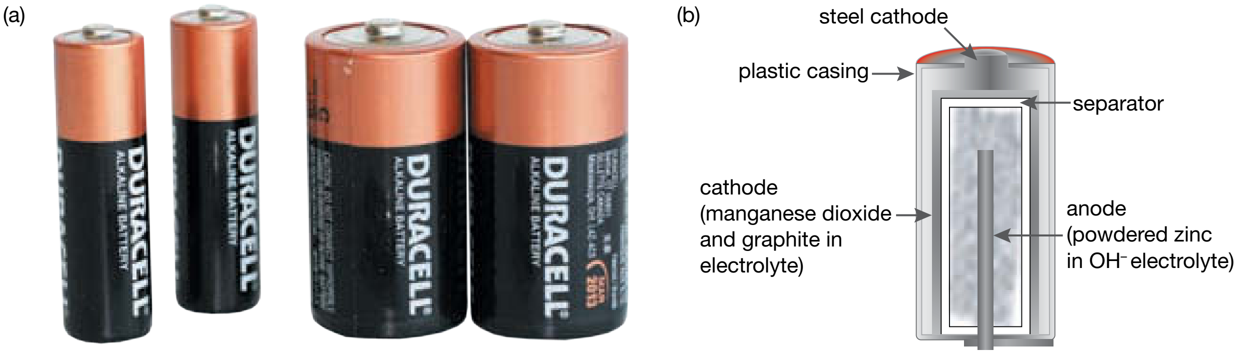
The alkaline zinc/manganese dioxide cell

Alkaline cells were developed as a consequence of the greater demand for a higher capacity portable energy source than the dry cell could provide. An alkaline cell is designed to give a greater current output than the standard dry cell and the voltage output falls off more slowly. Alkaline batteries also have longer shelf lives than dry cells. Less electrolyte needs to be used in an alkaline cell than in a dry cell, which means that more electrode reactants can be packed into the cell. Alkaline cells are commonly used in a variety of hand-held devices including remote controls, high-drain toys and head torches.

The alkaline cell is a primary cell that is more expensive than a dry cell but lasts much longer.

The alkaline cell has a powdered zinc anode in an electrolyte paste of potassium hydroxide. The cathode is a compressed mixture of manganese dioxide and graphite. A separator, consisting of a porous fibre soaked in electrolyte, prevents mixing of the anode and cathode components. The cell is contained within a steel shell.

FIGURE 3.25 (a) Alkaline zinc/manganese dioxide cells and (b) a simplified cross-section of an alkaline zinc/manganese dioxide cell



The electrode half-equations are:
Anode (oxidation):

$$Zn(s) + 2OH^-(aq) \rightarrow Zn(OH)_2(s) + 2e^-$$

Cathode (reduction):

$$2MnO_2(s) + 2H_2O(l) + 2e^- \rightarrow 2MnO(OH)(s) + 2OH^-(aq)$$

The overall cell reaction is:

$$2MnO_2(s) + 2H_2O(l) + Zn(s) \rightarrow 2MnO(OH)(s) + Zn(OH)_2(s)$$

The alkaline cell has a voltage of 1.55 V, but this drops slowly with time. Although it may last up to five times longer than a dry cell, it is more difficult to make and more expensive. The alkaline is also bulky, making it unsuitable for smaller devices such as watches and calculators.

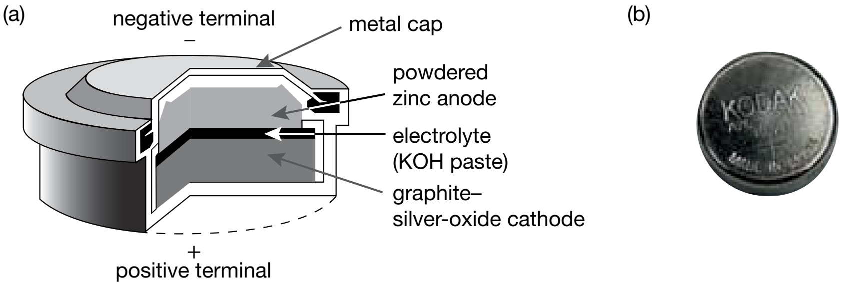
The button cell

Button cells are primary cells that were developed because some appliances require the use of very small electrochemical cells, although they are expensive to produce. However, they give a very steady voltage during operation. Button cells are small, long-life cells used in devices such as calculators, hearing aids, pacemakers, cameras and watches. They also last longer than dry cells and alkaline cells. There are a number of different types of button cells, including the silver oxide cell and the zinc–air cell.

Silver-oxide cell

Silver-oxide cells are ideal for very small devices, such as watches, calculators and hearing aids. This cell has a flat discharge curve and the voltage is 1.5 V.

FIGURE 3.26 The silver-oxide cell has a good shelf life and a long operating life.



The reactions at each electrode may be written as:
Anode (oxidation):

$$Zn(s) + 2OH^-(aq) \rightarrow Zn(OH)_2(s) + 2e^-$$

At the cathode in the zinc/silver cell, silver(I) oxide is reduced.

$$Ag_2O(s) + H_2O(l) + 2e^- \rightarrow 2Ag(s) + 2OH^-(aq)$$

This means the overall equation for this reaction is:

$$Zn(s) + Ag_2O(s) + H_2O(l) \rightarrow Zn\ (OH)_2(s) + 2Ag(s)$$

Zinc–air cell

A **zinc–air cell** uses oxygen from the air as a reactant (see figure 3.27). It is less expensive to produce than the silver-oxide cell and is mainly used for hearing aids. The electrolyte is potassium hydroxide and the half-equations for each electrode may be written as follows.

Anode (oxidation):

$$2Zn(s) + 4OH^-(aq) \rightarrow 2ZnO(s) + 2H_2O(l) + 4e^-$$

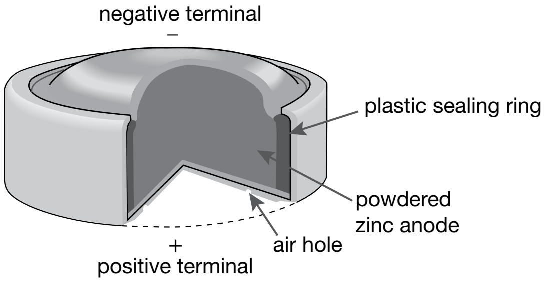
Cathode (reduction):

$$O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq)$$

The overall cell reaction is:

$$2Zn(s) + O_2(g) \rightarrow 2ZnO(s)$$

FIGURE 3.27 The zinc–air cell has a small vent and material to absorb the carbon dioxide from the air to prevent it from reacting with the hydroxide electrolyte.



A zinc–air cell produces a voltage of about 1.4 V and can be considered a fuel cell because the oxygen is continually drawn from the air. Fuel cells use a continuous supply of fuel to produce a flow of electrons, and are discussed in detail in topic 4.

3.4.6 Lithium cells

Lithium cells are cells based on lithium anodes. Lithium is a very reactive metal, and also very light, so these batteries can produce a high cell voltage. They require a more robust construction and are far more expensive than common batteries, but have a shelf life of ten years. Owing to their relatively long shelf life, lithium cells are mainly used as power sources for electronic memory, but may also be used in electronic switchboards, navigation systems, industrial clocks and even poker machines. In many applications lithium cells outlast the probable useful lifetime of the equipment they power.

Primary lithium cells include lithium manganese dioxide and lithium thionyl chloride cells. The most common is the lithium–manganese cell. This has a lithium anode, a manganese dioxide cathode, and a non-aqueous electrolyte, such as propylene carbonate. The half-equations are written as follows.

Anode (oxidation):

$$Li(s) \rightarrow Li^+(l) + e^-$$

Cathode (reduction):

$$MnO_2(s) + Li^+(l) + e^- \rightarrow LiMnO_2(s)$$

FIGURE 3.28 A pacemaker can be powered by a lithium battery. A magnetic switch operates the device, and the lithium battery usually lasts for three to five years.

These cells can be used in watches, calculators, games and cameras. Lithium cells come in button, flat, cylindrical, solid core or spiral wound form.

Spiral wound cells (figure 3.29) consist of two coiled sheets, one of lithium foil and one of manganese dioxide, separated by a sheet containing electrolytic salts. They have a good shelf life and produce about 3 V.

Another type of lithium battery, the lithium thionyl chloride cell (figure 3.30), consists of a lithium anode, a carbon cathode and an electrolyte solution of lithium aluminium chloride, $LiAlCl_4$, in thionyl chloride, $SOCl_2$. The cathode is a highly porous Teflon-coated carbon cylinder that is saturated with the electrolyte material. The SO_2 produced at the cathode dissolves in the thionyl chloride. The anode and cathode are kept apart by a separator.

The half-equations at each electrode may be written as follows.

Anode (oxidation):

$$Li(s) \rightarrow Li^+(aq) + e^-$$

Cathode (reduction):

$$2SOCl_2(l) + 4e^- \rightarrow SO_2(g) + S(s) + 4Cl^-(aq)$$

The overall equation for the reaction is:

$$2SOCl_2(l) + 4Li(s) \rightarrow SO_2(g) + S(s) + 4LiCl(aq)$$

FIGURE 3.29 A simplified diagram of a spiral-wound lithium cell

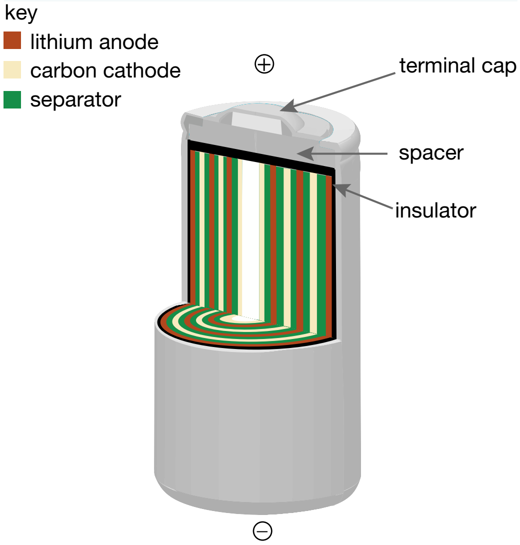
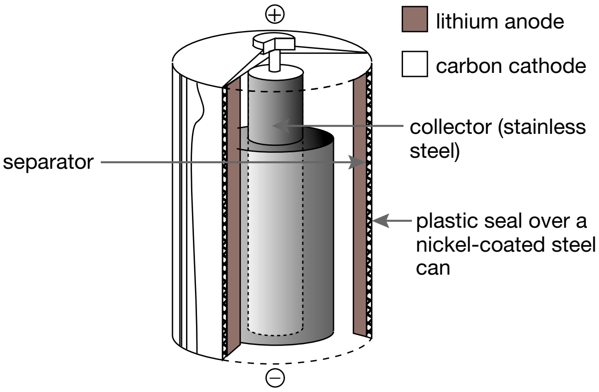


FIGURE 3.30 A simplified cross-section of a lithium/thionyl chloride battery



3.4 EXERCISE

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1. Use a table of standard electrode potentials to determine whether the following reaction is a spontaneous redox reaction. Justify your decision.

$$2Ag^+(aq) + 2Br^-(aq) \rightarrow 2Ag(s) + Br_2(l)$$

2. Write the likely spontaneous redox reactions that would occur given the following half-equations.
   (a) $Cl_2(g) + 2e^- \rightleftharpoons 2Cl^-(aq) \quad E^0 = +1.36\,V$
   $Ni^{2+}(aq) + 2e^- \rightleftharpoons Ni(s) \quad E^0 = -0.23\,V$
   (b) $Al^{3+}(aq) + 3e^- \rightleftharpoons Al(s) \quad E^0 = -1.67\,V$
   $Mg^{2+}(aq) + 2e^- \rightleftharpoons Mg(s) \quad E^0 = -2.34\,V$
   (c) $MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightleftharpoons Mn^{2+}(aq) + 4H_2O(l) \quad E^0 = +1.52\,V$
   $ClO_4^- + 2H^+(aq) + 2e^- \rightleftharpoons ClO_3 + H_2O(l) \quad E^0 = +1.19\,V$
   (d) $Fe^{2+}(aq) + 2e^- \rightleftharpoons Fe(s) \quad E^0 = -0.44\,V$
   $MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightleftharpoons Mn^{2+}(aq) + 4H_2O(l) \quad E^0 = +1.52\,V$
3. Suggest two reasons why predicted spontaneous redox reactions may not be observed.
4. Identify the anode and cathode, write the overall equation, label the direction of electron flow and calculate the standard cell potential that would be produced in a galvanic cell constructed from half-cells using the following redox half-equations.
   (a) $Pb^{2+}(aq) + 2e^- \rightleftharpoons Pb(s) \quad E^0 = -0.13\,V$
   $Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s) \quad E^0 = -0.76\,V$
   (b) $Ag^+(aq) + e^- \rightleftharpoons Ag(s) \quad E^0 = +0.80\,V$
   $Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+}(aq) \quad E^0 = +0.77\,V$
   (c) $O_2(g) + 4H^+(aq) + 4e^- \rightleftharpoons 2H_2O(l) \quad E^0 = 1.23\,V$
   $Fe^{2+}(aq) + 2e^- \rightleftharpoons Fe(s) \quad E^0 = -0.44\,V$
5. Sketch the galvanic cells based on the following overall equations, labelling the direction of electron flow, cathode, anode, polarity and direction of cation movement in the salt bridge.
   (a) $Cu^{2+}(aq) + Mg(s) \rightarrow Cu(s) + Mg^{2+}(aq)$
   (b) $2Co^{3+}(aq) + Pb(s) \rightarrow Pb^{2+} + 2Co^{2+}(aq)$
6. A galvanic cell constructed by a VCE student in a school laboratory recorded zero cell voltage after it had been operating previously at +0.38 V. Suggest three possible reasons for this observation.
7. Describe the difference between primary cells and secondary cells.
8. What is the reducing agent in a Leclanché cell? Justify your answer.
9. Calculate the change in oxidation number of manganese during discharge in a Leclanché cell.
10. Draw a diagram of a galvanic cell, consisting of two half-cells that could be constructed in the laboratory, to investigate the half-reactions in a silver-oxide button cell. Label the electrodes and the direction of the electron flow.
11. At the cathode of a zinc–air cell, has the oxidation number of the substance reacting increased or decreased?
12. What property of lithium batteries makes them so useful for electronic devices?

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3.5 Review

3.5.1 Summary

Redox reactions and half-equations

- Redox reactions involve the transfer of electrons between an oxidising agent and a reducing agent.
- Redox reactions can be divided into a reduction process and an oxidation process.
- Reduction is the process of gaining electrons whereas oxidation is the process of losing electrons.
- Redox reactants can be divided into oxidising agents and reducing agents. Reducing agents allow (or cause) another substance to undergo reduction because they supply electrons (as they undergo the process of oxidation). Oxidising agents allow another substance to undergo oxidation because they consume electrons (as they undergo the process of reduction).

- Spontaneous redox reactions can transform chemical energy into either heat or electrical energy, depending on the physical arrangements under which the reactions are carried out.
- A set of rules can be used for balancing the half-equations that represent the oxidation and reduction processes.
- Oxidation numbers can be used to determine the species in a redox reaction that may act as an oxidising agent or a reducing agent, because reduction corresponds to a decrease in oxidation number, whereas oxidation corresponds to an increase in oxidation number.

Galvanic cells

- Galvanic cells consist of two separate half-cells, with each half-cell containing a different conjugate redox pair. A connecting wire between the electrodes forms the external circuit through which electrons travel from the reducing agent to the oxidising agent, and a salt bridge forms an internal circuit through which ions can travel to maintain cell neutrality.
- In a galvanic cell, oxidation occurs at the negatively charged anode whereas reduction occurs at the positively charged cathode.
- The electrical potential of a galvanic cell is the ability of the cell to produce an electric current and is measured in volts (V).
- The reduction potential of a half-cell is a measure of the tendency of the oxidising agent to accept electrons and thus undergo reduction.
- The difference between the reduction potentials of two electrically connected half-cells is called the cell potential difference.

The electrochemical series

- An electrolyte is a solution containing ions that can conduct electricity.
- The standard cell potential difference $\left(E^0_{\text{cell}}\right)$ is the measured cell potential when the concentration of each species in solution is 1 M, the pressure of a gas is 1 atm and the temperature is 25 °C. It may be calculated according to:

$$E^0_{\text{cell}} = E^0_{\text{oxidising agent}} - E^0_{\text{reducing agent}}$$

- The standard hydrogen half-cell is used as a standard reference electrode and has been assigned an arbitrary value of 0.00 volts.
- The standard electrode potential (SEP) table, also known as the electrochemical series, can be used to predict whether a particular redox reaction can proceed to an appreciable extent.
- The SEP table gives no indication of the rate of a reaction or whether the reaction is spontaneous. It can only be used to predict if the reaction is feasible.
- Strong oxidising agents have high E^0 values and are found at the top left of the SEP table, whereas strong reducing agents have low E^0 values and are found at the bottom right of the SEP table.
- 'Wet' cells are electrochemical cells where the electrolyte is in a liquid state.
- An electrochemical cell in which the electrolyte is a paste, rather than a liquid, is known as a dry cell.
- A battery is a small, portable, efficient source of electrical energy that is constructed from a combination of electrochemical cells connected in series or in parallel.
- Electrochemical cells that are used until the supply of electrical energy is exhausted are called primary cells. Primary cells cannot be recharged.
- Different types of primary cells currently in use include Leclanché cells (dry cells), alkaline Zn(s)/MnO_2(s) cells, button cells, Zn(s)/air cells and lithium cells. Each of these contains an anode, cathode and an electrolyte, and is a practical application of a galvanic cell.

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3.5.2 Key terms

anode the electrode at which oxidation occurs. In a galvanic cell, it is the negative electrode, since it is the source of negative electrons for the circuit. If the reducing agent is a metal, it is used as the electrode material.
button cell a small, long-life cell used in devices such as calculators, hearing aids, pacemakers, cameras and watches
cathode the electrode at which reduction occurs. In a galvanic cell, it is the positive electrode, since the negative electrons are drawn towards it and then consumed by the oxidising agent, which is present in the electrolyte.
cell potential difference the difference between the reduction potentials of two half-cells
Daniell cell one of the first electrochemical cells to produce a reliable source of electricity; it uses the redox reactions between zinc metal and copper ions to produce electricity
dry cell an electrochemical cell in which the electrolyte is a paste, rather than a liquid; also called a Leclanché cell
electrical potential the ability of a galvanic cell to produce an electric current
electrochemical cell cell that generates electrical energy from chemical reactions
electrochemical series a series of chemical elements arranged in order of their standard electrode potentials
electrodes a solid used to conduct electricity in a galvanic half-cell
electrolytes liquids that can conduct electricity
external circuit circuit composed of all the connected components within an electrolytic or a galvanic cell to achieve desired conditions
half-cell one half of a galvanic cell containing an electrode immersed in an electrolyte that may be the oxidising agent or the reducing agent depending on the oxidising strength of the other cell to which it is connected
internal circuit a circuit within a conductor. Anions flow to the anode and cations flow to the cathode.
Leclanché cell see **dry cell**
lithium cells cells that use lithium anodes and can produce a high voltage
oxidants see **oxidising agents**
oxidation an increase in the oxidation number; a loss of electrons
oxidation numbers a set of rules that assist in the identification of redox reactions
oxidising agents electron acceptors
primary cells an electrolytic cell in which the cell reaction is not reversible
rechargeable describes a battery that is an energy storage device; it can be charged again after being discharged by applying DC current to its terminals
redox reactions reactions that involve the transfer of one or more electrons between chemical species
reducing agents electron donors
reductants see **reducing agents**
reduction a decrease in the oxidation number; a gain of electrons
reduction potential a measure of the tendency of an oxidising agent to accept electrons and so undergo reduction
salt bridge a component that provides a supply of mobile ions that balance the charges built up in the half-cells of a galvanic cell during reaction
secondary cells electrolytic cells in which the cell reaction is reversible
standard cell potential difference the measured cell potential difference, under standard conditions, when the concentration of each species in solution is 1 M, the pressure of a gas, where applicable, is 100 kPa and the temperature is 25 °C (298 K)
standard hydrogen half-cell a standard reference electrode; assigned 0.00 volts
zinc–air cell cell that uses oxygen from the air as a reactant

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Digital document Key terms glossary-Topic 3 (doc-31403)

3.5.3 Practical work and experiments

Experiment 3.3

Galvanic cells and redox potentials
Aim: To set up galvanic cells, measure the cell voltages and predict the relative oxidising–reducing strength of four redox pairs.

Digital document: doc-31255
Teacher-led video: eles-3460

Resources

Digital documents	Practical investigation logbook (doc-30404)
	Experiment 3.1 Investigating the Daniell cell (doc-31253)
	Experiment 3.2 Predicting redox reactions (doc-31254)
	Experiment 3.4 Looking at a dry cell (doc-31256)

3.5 Exercises

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3.5 Exercise 1: Multiple choice questions

1. In a particular reaction, it is observed that electrons are transferred from substance A to substance B. Which of the following statements is correct?
   A. A undergoes oxidation and is an oxidising agent.
   B. A undergoes oxidation and is a reducing agent.
   C. B undergoes oxidation and is a reducing agent.
   D. A undergoes reduction and is an oxidising agent.
2. The oxidation number of each sulfur atom in $S_2O_3{}^{2-}$ is:
   A. –2
   B. +2
   C. +6
   D. +4.
3. For the reaction

$$NO_2(aq) + H_2O(l) \rightarrow e^- + NO_3^-(aq) + 2H^+(aq)$$

   the oxidation number of nitrogen changes from:
   A. 0 to +1
   B. 0 to –1
   C. +2 to –3
   D. +4 to +5.
4. In a reaction, the oxidation numbers of two elements were found to change as follows.
   X changes from +2 to +5.
   Y changes from +7 to +5.
   Which of the following describes the changes correctly?

A. X and Y are both oxidised.
B. X is oxidised and Y is reduced.
C. X is reduced and Y is oxidised.
D. X and Y are both reduced.

5. The half-equation for the reduction of NO_3^- to N_2O can be represented as:

$$\mathrm{aNO_3^-(aq)} + b\mathrm{H^+(aq)} + 8\mathrm{e^-} \rightarrow c\mathrm{N_2O(g)} + d\mathrm{H_2O(l)}$$

where the values of a and b respectively are:
A. 2 and 5
B. 2 and 10
C. 1 and 4
D. 1 and 5.

6. The tarnish on silverware, Ag_2S, can be removed by placing the articles in an aluminium pan and covering them with a warm solution of dilute sodium hydroxide. The following half-reactions show why this method is effective.

$$\mathrm{Ag_2S(s)} + 2\mathrm{e^-} \rightarrow 2\mathrm{Ag(s)} + \mathrm{S^{2-}(aq)}$$
$$\mathrm{Al(s)} + 3\mathrm{OH^-(aq)} \rightarrow \mathrm{Al(OH)_3(s)} + 3\mathrm{e^-}$$

Which of the following equations represents a balanced ionic equation for the reaction that occurs?
A. $3Ag_2S(s) + 2Al(s) + 6OH^-(aq) \rightarrow 6Ag(s) + 3S^{2-}(aq) + 2Al(OH)_3(s)$
B. $Ag_2S(s) + Al(s) + 3OH^-(aq) \rightarrow 2Ag^+(aq) + S^{2-}(aq) + Al(OH)_3(s) + e^-$
C. $Ag_2S(s) + Al(OH)_3(s) \rightarrow 2Ag^+(aq) + S^{2-}(aq) + Al(s) + 3OH^-(aq)$
D. $Al(s) + 3OH^-(aq) + 2Ag(s) + S^{2-}(aq) \rightarrow Ag_2S(s) + Al(OH)_3(s) + 3e^-$

7. An electrochemical cell functions only when there is a complete circuit for electrical flow. For reactions to occur that produce an electric current, it is necessary to have an:
A. external and internal circuit for the flow of ions
B. external circuit for electron flow and an internal circuit for ion flow
C. external circuit for ion flow and an internal circuit for electron flow
D. internal and external circuit for the flow of electrons.

8. In any electrochemical cell, the cathode is the electrode:
A. that is closest to the outside of the cell
B. at which electrons are liberated by some species
C. at which reduction occurs
D. at which hydrogen is liberated.

9. In a lithium–manganese dioxide button battery, the anode is made from lithium foil on a stainless steel backing and the cathode is manganese dioxide mixed with carbon black to act as an organic electrolyte. The equations occurring at the electrodes are:
Anode: $Li(s) \rightarrow Li^+(l) + e^-$
Cathode: $MnO_2(s) + e^- \rightarrow MnO_2^-(l)$
The lithium manganese dioxide button battery is a primary cell. Which of the following is the strongest oxidising agent?
A. $Li(s)$
B. $Li^+(aq)$
C. $MnO_2(s)$
D. $MnO_2^-(aq)$

10. A small piece of silver was placed in a solution containing both magnesium nitrate and copper(II) nitrate. Which one of the following will occur?
- **A.** No reaction occurs.
- **B.** The silver dissolves and only copper is precipitated.
- **C.** The silver dissolves and only magnesium is precipitated.
- **D.** A mixture of copper and magnesium forms on the silver.

11. In which of the following pairs of elements does neither metal release hydrogen gas when dilute hydrochloric acid is added?
- **A.** Zn and Ag
- **B.** Cu and Ag
- **C.** Fe and Al
- **D.** Mg and Ni

12. Which of the following reactions does *not* occur spontaneously?
- **A.** $Cu^{2+}(aq) + Pb(s) \rightarrow Pb^{2+}(aq) + Cu(s)$
- **B.** $Fe(s) + Pb^{2+}(aq) \rightarrow Pb(s) + Fe^{2+}(aq)$
- **C.** $2Ag(s) + 2H^{+}(aq) \rightarrow 2Ag^{+}(aq) + H_2(g)$
- **D.** $Li(s) + H^{+}(aq) \rightarrow \frac{1}{2}H_2(g) + Li^{+}(aq)$

13. A piece of nickel is placed in a solution of copper(II) sulfate.

Given:

$Ni^{2+}(aq) + 2e^{-} \rightleftharpoons Ni(s)\ E^0 = -0.23\ V$

$Cu^{2+}(aq) + 2e^{-} \rightleftharpoons Cu(s)\ E^0 = +0.34\ V$

which one of the following statements is incorrect?
- **A.** Copper is precipitated from solution.
- **B.** Copper ions are oxidised.
- **C.** Nickel dissolves into solution.
- **D.** There is no increase in electrical charge in the solution.

14. A student is given five metals and 1 M solutions of nitrates of the metals. The metals are labelled *M, N, O, P* and *Q*, and the solutions are labelled M^{2+}, N^{2+}, O^{2+}, P^{2+} and Q^{2+}.

The student carries out a number of experiments and the results obtained are listed below.
- **i.** Metal *M* remains unchanged in all solutions.
- **ii.** Metal *O* becomes coated with another metal when placed in each of solutions M^{2+}, N^{2+}, P^{2+} and Q^{2+}.
- **iii.** Metal *P* becomes coated with another metal when placed in each of solutions M^{2+} and N^{2+}, but not when placed in solution Q^{2+}.

Considering the experimental data above, which of the following reactions takes place spontaneously with the greatest observed cell voltage?
- **A.** $M(s) + O^{2+}(aq) \rightarrow M^{2+}(aq) + O(s)$
- **B.** $O(s) + M^{2+}(aq) \rightarrow O^{2+}(aq) + M(s)$
- **C.** $N(s) + P^{2+}(aq) \rightarrow N^{2+}(aq) + P(s)$hesher
- **D.** $Q(s) + O^{2+}(aq) \rightarrow Q^{2+}(aq) + O(s)$

15. Which of the following reactions occurs spontaneously in the direction indicated?
- **A.** $2I^{-}(aq) + Cl_2(g) \rightarrow 2Cl^{-}(aq) + I_2(s)$
- **B.** $Br_2(aq) + 2Cl^{-}(aq) \rightarrow 2Br^{-}(aq) + Cl_2(g)$
- **C.** $I_2(s) + 2Br^{-}(aq) \rightarrow 2I^{-}(aq) + Br_2(aq)$
- **D.** $2F^{-}(aq) + Cl_2(g) \rightarrow F_2(g) + 2Cl^{-}(aq)$

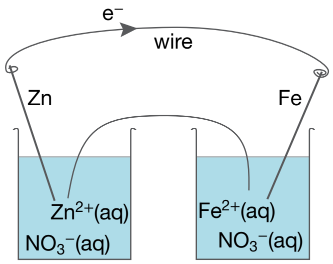
3.5 Exercise 2: Short answer questions

1. Early definitions of oxidation were:
- the addition of oxygen
- the loss of hydrogen

whereas early definitions of reduction were:
- the removal of oxygen
- the addition of hydrogen.

a. Choose an example of a reaction that illustrates the *adequacy* of each of these definitions.
b. Choose an example of a reaction that illustrates the *inadequacy* of each of these definitions.
c. Use the examples chosen in (b) to show the redox nature of the reaction by considering the modern definitions of oxidation as the loss of electrons and reduction as the gain of electrons.
d. Provide a definition of oxidation and reduction with respect to oxidation numbers and illustrate your definition with an example.

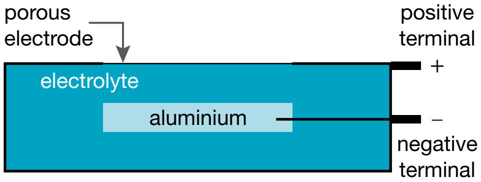
2. In each of the following reactions, use oxidation numbers to find which species has been reduced and which has been oxidised.
   a. $Zn(s) + 2HCl(aq) \rightarrow ZnCl_2(s) + H_2(g)$
   b. $2NO(g) + O_2(g) \rightarrow 2NO_2(g)$
   c. $Mg(s) + H_2SO_4(aq) \rightarrow MgSO_4(aq) + H_2(g)$
   d. $2Al(s) + 3Cl_2(g) \rightarrow 2AlCl_3(s)$
3. Identify the oxidising agent and reducing agent in each of the following redox equations.
   a. $2I^-(aq) + Cl_2(g) \rightarrow 2Cl^-(aq) + I_2(s)$
   b. $Br_2(aq) + 2Cl^-(aq) \rightarrow 2Br^-(aq) + Cl_2(g)$
   c. $I_2(s) + 2Br^-(aq) \rightarrow 2I^-(aq) + Br_2(aq)$
   d. $2Co^{3+}(aq) + Pb(s) \rightarrow Pb^{2+}(aq) + 2Co^{2+}(aq)$
   e. $Fe(s) + Pb^{2+}(aq) \rightarrow Pb(s) + Fe^{2+}(aq)$
   f. $Hg(l) + 2H^+(aq) \rightarrow H_2(g) + Hg^{2+}(aq)$
   g. $2F^-(aq) + Cl_2(g) \rightarrow F_2(g) + 2Cl^-(aq)$
4. Balance the following equations using half-equations.
   a. $Br^-(aq) + SO_4{}^{2-}(aq) \rightarrow SO_2(g) + Br_2(l)$
   b. $Al(s) + Cl_2(g) \rightarrow AlCl_3(s)$
   c. $I_2(s) + H_2S(g) \rightarrow I^-(aq) + S(s)$
   d. $Cu(s) + HNO_3(aq) \rightarrow Cu^{2+}(aq) + NO(g)$
   e. $Cu(s) + HNO_3(aq) \rightarrow Cu^{2+}(aq) + NO_2(g)$
   f. $CuO(s) + NH_3(g) \rightarrow N_2(g) + Cu(s)$
   g. $PbS(s) + H_2O_2(l) \rightarrow PbSO_4(s) + H_2O(l)$
   h. $Cr_2O_7{}^{2-}(aq) + CH_3CH_2OH(aq) \rightarrow CH_3COOH(aq) + Cr^{3+}(aq)$
5. Consider the reaction occurring in the diagram shown, and complete the following.
   a. State the anode reaction.
   b. State the cathode reaction.
   c. Find the overall cell reaction.



6. Define the following terms.
   a. Galvanic cell
   b. Internal circuit
   c. External circuit
   d. Cathode
   e. Anode
   f. Salt bridge
   g. Inert electrode
7. By referring to a table of standard electrode potentials, state whether you would expect:
   a. bromine gas to form if chlorine gas was bubbled into a solution of bromide ions
   b. chlorine gas to form if bromine gas was bubbled into a solution of chloride ions
   c. iron to be oxidised by acidified hydrogen peroxide solution
   d. iron(II) ions to be reduced when reacted with hydrogen peroxide solution.

8. Design a galvanic cell that produces electricity from each of the reactions below. For each cell, show how it is constructed. Identify the anode and cathode, showing the equations occurring at each. Indicate the direction of electron flow and the migration of each kind of ion in the cell and the salt bridge.
   a. $2Ag^+(aq) + Mg(s) \rightarrow 2Ag(s) + Mg^{2+}(aq)$
   b. $2Al(s) + 3I_2(s) \rightarrow 2Al^{3+}(aq) + 6I^-(aq)$
   c. $Cl_2(g) + Zn(s) \rightarrow Zn^{2+}(aq) + 2Cl^-(aq)$
   d. $2Fe^{3+}(aq) + Fe(s) \rightarrow 3Fe^{2+}(aq)$
9. Draw a galvanic cell that uses the reaction between solid aluminium metal and an aqueous solution of blue copper sulfate. Potassium nitrate can be used in the salt bridge.
   a. Clearly label the following:
   - the anode, the cathode and the appropriate electrolytes
   - equations for the reactions at the anode and cathode, marked as either oxidation or reduction
   - the overall cell reaction
   - the direction of electron flow
   - the direction of flow of anions and cations in the salt bridge.
   b. What would happen if the salt bridge was removed? Explain.
   c. What happens to the colour of the copper sulfate solution? Explain.
10. Considering the positions of iron, magnesium and zinc in the electrochemical series, explain why iron is protected from rusting when blocks of magnesium or zinc are attached to it.
11. Explain the difference between a cell and a battery.
12. Electrochemical cells constructed in the laboratory often consist of two separate half-cells connected by electrical wire and a salt bridge.

    Explain the features of commercial cells that enable electrical power to be generated from chemicals in only one cell.
13. The structure of an aluminium–air battery is shown in the figure.



In the aluminium–air battery, a piece of aluminium is immersed in an electrolyte near a porous electrode. This porous electrode has air on one side and the electrolyte on the other. The electrolyte can be a common salt, NaCl, solution, an alkali solution, such as potassium hydroxide, KOH, or sea water. Although the choice of electrolyte is quite flexible, only special alloys of aluminium can be used. With ordinary alloys, the aluminium immediately becomes coated with a protective oxide layer or simply dissolves as aluminium oxide, giving off hydrogen gas.

In this battery, the aluminium anode reacts with hydroxide ions to form aluminium hydroxide, with the release of three electrons.

$$\text{Anode:}\quad Al(s) + 3OH^-(aq) \rightarrow Al(OH)_3(s) + 3e^-$$

The OH^- ions are present either because the electrolyte is an alkali solution or because they are produced at the cathode.

At the porous cathode, the water in the electrolyte reacts with oxygen from the air and the electrons from the anode to produce hydroxide ions.

$$\text{Cathode:}\quad O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq)$$

If the cathode is covered (for example, with water) so that oxygen cannot enter the cell, a slightly different reaction occurs in the cell in which hydrogen gas is produced.

$$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$$

a. Write the overall equation for the aluminium–air battery operating under optimal conditions.
b. Write the overall equation if the cathode is covered with water.

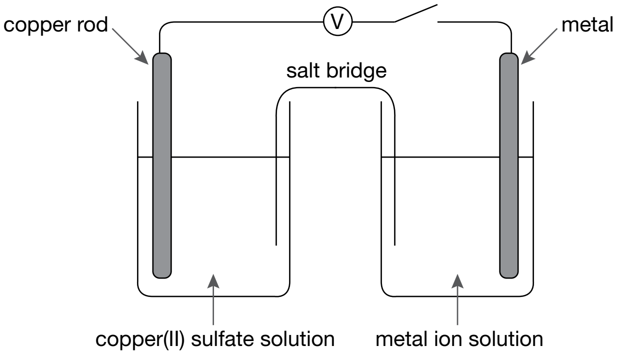
3.5 Exercise 3: Exam practice questions

Question 1 (5 marks)

A student set up an electrochemical experiment as shown in the figure.

He kept the copper half-cell constant, but changed the other half-cell. For each cell, he recorded the metal that was used as the anode and the overall cell voltage.

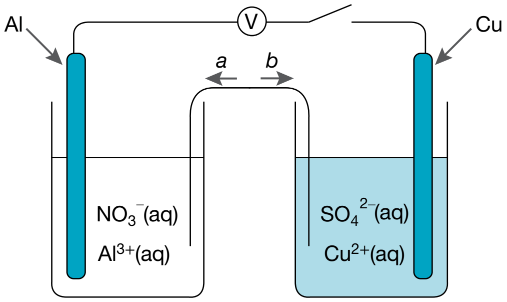
Cell	Anode	Voltage (V)
copper–lead	lead	0.49
copper–silver	copper	0.31
copper–magnesium	magnesium	1.45
copper–iron	iron	0.57
copper–aluminium	aluminium	0.94
copper–copper	copper	0.00
copper–nickel	nickel	0.31



a. How did the student determine which of the metals in the cell acted as the anode? **2 marks**
b. Why did the copper–copper cell produce no voltage? **1 mark**
c. Determine the likely order of reactivity of the metals. Justify your placements. **2 marks**

Question 2 (6 marks)

A half-cell is constructed with a copper electrode in a 1.0 M copper(II) sulfate solution. It is connected by a salt bridge to another half-cell containing an aluminium electrode in a 1.0 M aluminium nitrate solution.



a. A voltmeter is connected into the external circuit. What would be the expected E^0 value for this cell? **1 mark**
b. Give two changes that might be observed in the copper half-cell if a large current flowed for many hours. **2 marks**
c. What is the polarity of the copper electrode? **1 mark**
d. Which arrow, *a* or *b*, shows the direction of negative ions in the salt bridge? **1 mark**
e. Write a balanced half-equation for the reaction occurring at the anode. **1 mark**

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4 Fuel cells as a source of energy

4.1 Overview

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4.1.1 Introduction

Fuel cells are similar to batteries but they do not run out of stored energy or need recharging — they continue to convert chemical energy to electrical energy as long as the fuel is supplied. The US Space program has used hydrogen fuel cells for all of their missions to space. The Space Shuttle would consume nearly 3 million litres of liquefied hydrogen gas on each mission. On the International Space Station, hydrogen is generated by splitting water into oxygen for breathing and hydrogen for fuel. In the future, hydrogen will be further recycled by recombining it with exhaled carbon dioxide to create water. Hydrogen generation and recycling in space will reduce the need for supplies to be delivered from Earth and may bring us closer to a trip to Mars.

FIGURE 4.1 The US Space program has used hydrogen fuel since their first missions.

4.1.2 What you will learn

KEY KNOWLEDGE

In this topic, you will investigate:

- the common design features of fuel cells including 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.

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PRACTICAL WORK AND INVESTIGATIONS

Practical work is a central component of learning and assessment. Experiments and investigations, supported by a **Practical investigation logbook** and **Teacher-led videos**, are included in this topic to provide opportunities to undertake investigations and communicate findings.

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Digital documents Key science skills (doc-30903)
Key terms glossary — Topic 4 (doc-31406)
Practical investigation logbook (doc-31407)

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4.2 Fuel cells

KEY CONCEPTS

- The common design features of fuel cells including 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

4.2.1 What is a fuel cell?

A **fuel cell** is a type of galvanic cell that converts chemical energy into usable DC electricity and heat through redox reactions. It does not rely upon combustion as an intermediate step. Unlike batteries, fuel cells do not store energy but rather rely on a constant external source of reactants. By combining fuels such as hydrogen and oxygen in the presence of an electrolyte, the products of a fuel cell are electricity, heat and water. The process was first demonstrated in 1839, but fuel cell technology grew significantly in the 1960s, as part of the US space program.

Fuel cell technology has advanced with the search for energy alternatives that have greater operating efficiencies and lower costs. Power generation from fuel cells averages between 40 and 60% efficiency compared with 30 to 35% efficiency from fossil fuel combustion. Fuel cells produce no air pollutants, and have the added advantage of portability.

FIGURE 4.2 Will today's batteries be replaced by refillable fuel cells in the near future?

4.2.2 Where are fuel cells used?

Fuel cells are used, or are being investigated for use, in the following situations.

- As a portable power source for charging small appliances, such as batteries in laptops or smartphones
- For larger scale, stationary applications, including backup power in hospitals and industry
- For transport applications such as forklifts, boats and buses. The silent operation of fuel cells is advantageous for submarines, and considerable research is being undertaken to improve the efficiency and reduce costs of fuel cell cars.

4.2.3 Fuel cell design

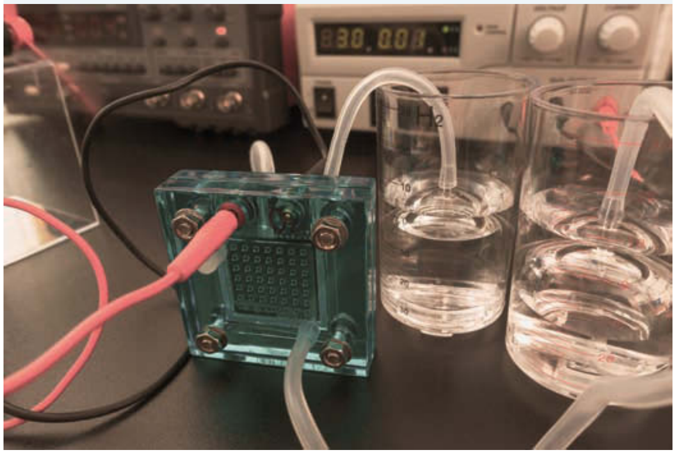
Similarities between fuel cells and other galvanic cells

Fuel cells have many design features in common with galvanic cells.

- Both convert chemical energy to electrical energy through redox reactions
- Site of oxidation physically separated from site of reduction
- Oxidation occurs at the negative electrode (anode) and reduction at the positive electrode (cathode)
- Electrolytes occur between electrodes to allow the flow of ions that make up the internal circuit
- Fuel cells and batteries occur in groups called stacks to obtain a usable voltage and power output.

Differences between fuel cells and other galvanic cells

FIGURE 4.2 A typical fuel cell that can be used in a laboratory



Although fuel cells are galvanic cells, there are a few significant differences in fuel cell design compared to other galvanic cells.

- Fuel cells do not store reactants, they must be continuously supplied from an external source
- Primary galvanic cells produce electricity until the chemical reaction is finished, at which point the electrical energy is exhausted. Secondary galvanic cells are rechargeable and are discussed in topic 7.
- Fuel cell electrodes are porous. This provides a high surface area and the opportunity to introduce catalysts (which makes the reactions on their surfaces more efficient). Porous electrodes also allow more effective contact between fuels (which are often gases) and the electrolyte.
- Fuel cells do not lose charge. They convert the energy in fuels directly into electricity and operate as long as they are supplied with fuel and an oxidising agent. This means that fuel cells do not have to be recharged. The input fuel passes over the anode (and oxygen over the cathode) where it is split into ions and electrons. The electrons go through an external circuit while the ions move through the electrolyte towards the oppositely charged electrode. At this electrode, ions combine to create by-products. Depending on the input fuel and electrolyte, different chemical reactions occur.

Economic and environmental impacts

Although fuel cells are often expensive to manufacture, the low operating and maintenance costs over their lifetime make them a more efficient method for generating electricity than many single-use primary cells in current use. At present, energy efficiency of fuel cells is 35–70% while single use galvanic cells have an energy efficiency of 45–90%.

Fuel cells emit almost none of the sulfur and nitrogen compounds released by the burning of fossil fuels, and can operate using a wide variety of fuels including methane, coal-derived gas, landfill gas, biogas, alcohols, hydrogen and other hydrocarbons. They are quieter and can operate more cheaply than a conventional electric generator. A detailed comparison of fuels cells and the fuel combustion is presented in section 4.2.5, and comparison with other galvanic cells is presented in section 4.2.8.

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Weblink New methane fuel cell runs on cheap fuel

4.2.4 Types of fuel cell

There are six main types of fuel cell, which are categorised according to the type of electrolyte and/or the fuel they used. These types are:

- **alkaline fuel cell (AFC)**, also known as the hydrogen–oxygen fuel cell
- **proton exchange membrane fuel cell (PEMFC)**
- phosphoric acid fuel cell (PAFC)
- molten carbonate fuel cell (MCFC)
- solid oxide fuel cell (SOFC)
- **direct methanol fuel cell (DMFC)**.

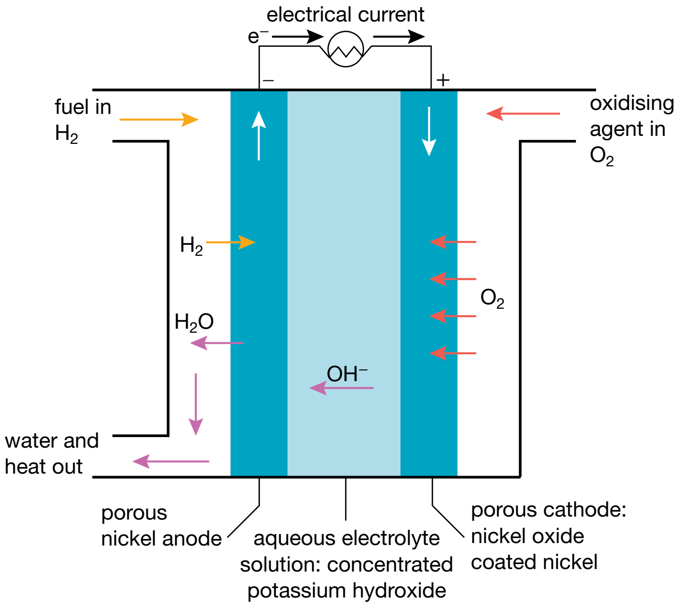
There is ongoing research into new designs for fuel cells, not only for new fuels, but also new electrolytes. For example, there is a current line of research investigating the use of biological materials as electrolytes.

Alkaline fuel cell

The alkaline fuel cell (AFC), also known as the hydrogen–oxygen fuel cell, is one of the oldest and furthest travelled fuel cells. It uses potassium hydroxide as the electrolyte and was used in the Gemini and Apollo space programs during the 1960s and 70s to produce electrical energy and water. The AFC is clean and very efficient but requires pure hydrogen and oxygen.

The AFC has three compartments: the cathode compartment, the anode compartment and the central compartment, which are separated from each other by two electrodes. Oxygen (the oxidising agent) is fed into the cathode compartment and hydrogen (the fuel) is fed into the anode compartment. The gases diffuse slowly through the electrodes. The electrolyte in the central compartment is a hot, concentrated solution of potassium hydroxide. Electrons from the oxidation reaction at the anode pass through an external circuit to enter the reduction reaction at the cathode.

FIGURE 4.3 A cross-section of an alkaline fuel cell



The equation for the anode reaction (oxidation) may be written as:

$$2H_2\,(g) + 4OH^-\,(aq) \rightarrow 4H_2O\,(l) + 4e^-$$

The equation for the cathode reaction (reduction) may be written as:

$$O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq)$$

The equation for the overall reaction may be written as:

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

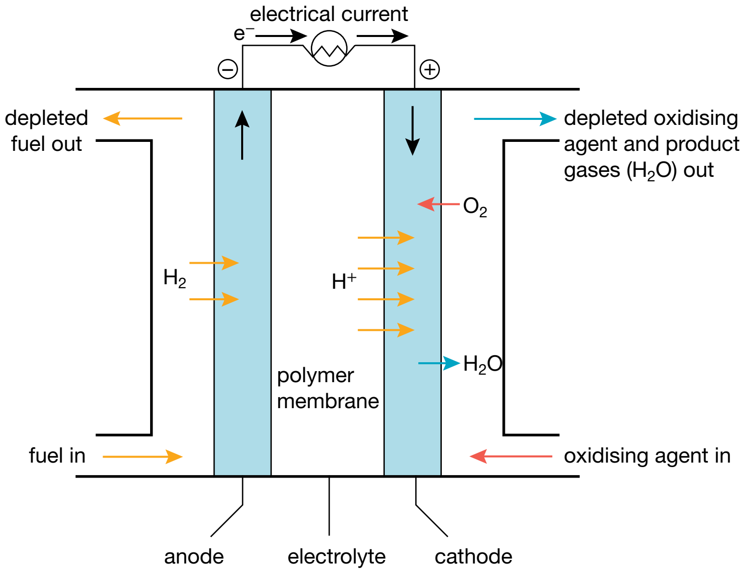
Proton exchange membrane fuel cell

The proton exchange membrane fuel cell (PEMFC) offers high power density and operates at relatively low temperatures. They are used in cars, forklifts and buses, as well as some large-scale systems. Suitable fuels for the PEMFC include hydrogen gas, methanol and reformed fuels.

A typical PEMFC uses a polymer membrane as its electrolyte, which eliminates the corrosion and safety concerns associated with liquid electrolyte fuel cells. Although it is an excellent conductor of hydrogen ions, the membrane is an electrical insulator. The electrolyte is sandwiched between the anode and cathode, forming a unit less than one millimetre thick. Its low operating temperature provides instant start-up and requires no thermal shielding to protect personnel.

Hydrogen from the fuel gas stream is consumed at the anode, producing electrons that flow to the cathode via the electric load and hydrogen ions that enter the electrolyte. At the cathode, oxygen combines with electrons from the anode and hydrogen ions from the electrolyte to produce water. The PEMFC operates at about 80 °C, so the water does not dissolve in the electrolyte. Instead, it is collected from the cathode as it is carried out of the fuel cell by excess oxidising agent flow.

FIGURE 4.4 A cross-section of a PEMFC



The equation for the anode reaction (oxidation) may be written as:

$$H_2(g) \rightarrow 2H^+(aq) + 2e^-$$

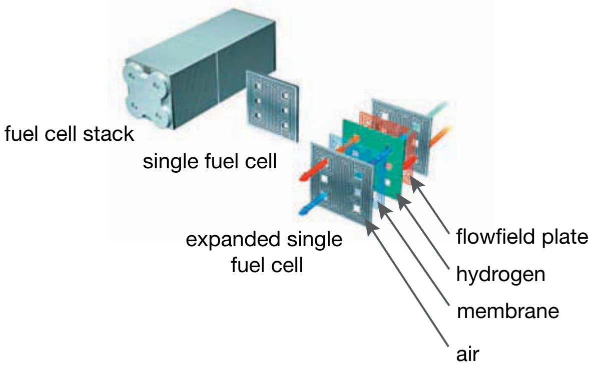
The equation for the cathode reaction (reduction) may be written as:

$$O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$$

The equation for the overall reaction may be written as:

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

FIGURE 4.5 The design of a PEMFC allows the depleted gases and excess oxidising agent gas to flow through the cell stack.



The fuel cell equation:
All fuel cells that use $H_2(g)/O_2(g)$ as reactants have the same overall equation:

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

However, they have different half-equations depending on whether they are in acidic or alkaline conditions. It is important to consider whether the cell involves the acid or alkali half equations.

Direct methanol fuel cell (acidic)

The direct methanol fuel cell (DMFC) is relatively new technology and is powered by pure methanol, which has a higher energy density than hydrogen and is easier to transport. The anode catalyst withdraws hydrogen from the liquid methanol. DMFCs are suitable for mobile phones, portable music devices and laptops, due to the small size of their cells and low operating temperature, and because there is no requirement for a fuel reformer, which allows devices to operate for longer periods of time.

The equation for the anode reaction (oxidation) may be written as:

$$2CH_3OH(aq) + 2H_2O(l) \rightarrow 2CO_2(g) + 12H^+(aq) + 12e^-$$

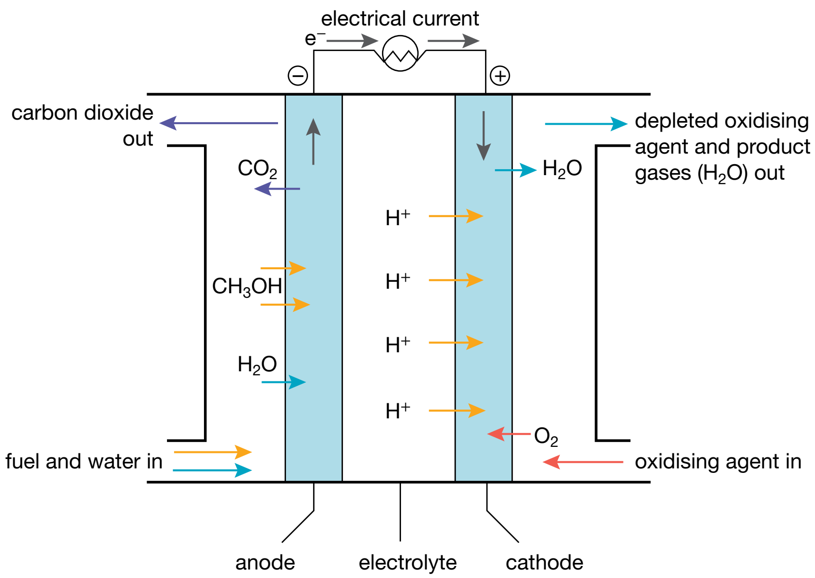
The equation for the cathode reaction (reduction) may be written as:

$$12H^+(aq) + 12e^- + 3O_2(g) \rightarrow 6H_2O(l)$$

The equation for the overall reaction may be written as:

$$2CH_3OH(aq) + 3O_2(g) \rightarrow 2CO_2(g) + 4H_2O(l)$$

FIGURE 4.6 A cross-section of a direct methanol fuel cell.



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Video eLesson	Direct methanol fuel cell (med-0438)
Digital document	Experiment 4.1 Investigating the hydrogen–oxygen fuel cell (doc-31257)
Teacher-led video	Experiment 4.1 Investigating the hydrogen–oxygen fuel cell (tlvd-0741)
Weblink	Fuel cells

4.2.5 Advantages and disadvantages of fuel cells

Table 4.1 summarises the advantages and disadvantages of fuel cells.

TABLE 4.1 Advantages and disadvantages of fuel cells

Advantages	Disadvantages
• High energy conversion efficiency • Modular design, different sizes available • Low chemical pollution • Fuel flexibility • Co-generation capability by using heat produced • Quiet operation • Unlimited run time while fuel is supplied • No need to be recharged • Low maintenance due to lack of moving parts • Low running costs • Lower weight and volume than conventional batteries for electric-powered vehicles • Potential to power portable devices for longer times than conventional batteries	• Manufacturing process and materials are expensive; infrastructure required for pumping gases • The need for reliable and continual supply of fuel • Distribution, storage and transportation of hydrogen is difficult • Technology of producing hydrogen from other fuels is still being developed • Few refuelling stations are available for fuel-cell vehicles • Some technological issues with water regulation and temperature control in some fuel cells • Electrodes are expensive because they must also function as catalysts

4.2.6 Comparing fuels cells

Fuel cells offer great potential for the future. The reactions in fuel cells are the same as when burning the fuels in a combustion reaction. A check of the overall reactions in the AFC, PEMFC and DMFC illustrates this. As infrastructure is developed for the distribution and storage of their fuels (particularly hydrogen), and electrode manufacturing techniques are improved and become cheaper, fuel cell use should become more widespread. They are generally no more dangerous than generating electricity by currently used methods.

TABLE 4.2 Comparison of fuel cells

Fuel cell type	Electrolyte	Anode gas	Cathode gas	Temperature	Efficiency	Applications
Alkaline (AFC)	Potassium hydroxide	Hydrogen	Pure oxygen	below 80 °C	50–70%	Transportation Water, heat and electricity
Phosphoric acid (PAFC)	Phosphoric acid	Hydrogen, reformed hydrocarbon fuels	Oxygen and air	210 °C	35–50%	Stationary power generation including backup power Larger scale electricity production
Molten carbonate (MCFC)	Alkali, carbonates	Hydrogen, carbon monoxide, methane, reformed hydrocarbon fuels	Oxygen and air, carbon dioxide	650 °C	45–60%	Stationary power generation including backup power Larger scale electricity production
Proton exchange membrane (PEMFC)	Solid polymer membrane	Hydrogen	Pure oxygen or oxygen mixed with air	75 °C	35–55%	Powering small devices Other portable applications Stationary power generation including backup power Larger scale electricity production
Solid oxide (SOFC)	Ceramic oxide	Hydrogen, methane, reformed hydrocarbon fuels	Oxygen and air	800–1000 °C	45–60%	Stationary power generation including backup power Larger scale electricity production
Direct methanol (DMFC)	Solid polymer membrane	Methanol solution in water	Oxygen and air	75 °C	35–45%	Powering small devices Other portable applications

FIGURE 4.7 Countries such as the US are already using fuel cells to provide the energy requirements for mass transport.

4.2.7 Comparison of fuel cells and the combustion of fuels

TABLE 4.3 Comparison of fuels for energy efficiency, safety, supply, greenhouse gas emissions and applications

Fuel	Energy efficiency	Safety	Supply	Greenhouse gases (during operation)	Applications
Petrol (octane)	20–35% (in a combustion engine)	Very flammable Special storage considerations	Crude oil	On average, produces 8 molecules of carbon dioxide and 9 molecules of water per mole of octane	Transportation vehicles — mainly cars
Diesel	25–40% (in a combustion engine)	Less flammable than petrol Special storage considerations	Crude oil	On average, produces 12 molecules of carbon dioxide and 12 molecules of water per mole of dodecane ($C_{12}H_{24}$).	Transportation vehicles — cars, tractors, trucks and trains.
AFC	60%	Contains KOH(aq), which is corrosive and uses hydrogen gas Special storage considerations	Mainly methane gas (from crude oil) and steam	On average, produces 1 mole of water per mole of hydrogen	The military and space programs
PEMFC	35–60%	Uses hydrogen gas Special storage considerations	Mainly methane gas (from crude oil) and steam	On average, produces 1 mole of water per mole of hydrogen	Backup power, portable power and specialty vehicles

Fuel cell efficiency:
Although fuel cells can more efficiently convert chemical energy to electrical energy than fossil fuel power stations, it is important to remember that fuel cells are not 100% efficient in that conversion.

FIGURE 4.8 The Hyundai Nexo is powered by a fuel cell stack that uses oxygen from the air and hydrogen stored in specially-constructed tanks. Water is the only significant emission.

4.2.8 Precautions for using hydrogen gas in fuel cells

Hydrogen is a fuel and an awareness of its properties is essential for producing, storing and using it safely.

Hydrogen storage

Hydrogen has a high energy content by weight but not by volume. This means that storing hydrogen can be difficult, because it is the lightest element and must undergo considerable compression to be contained in a suitably sized tank, which must withstand the extreme pressures required. Hydrogen can be stored as a liquid, but this requires keeping its temperature at −252.8 °C in very well-insulated containers. Hydrogen can also be stored by combining it with certain metal or complex hydrides that can absorb the hydrogen — from there it can be released by heating it or adding water. Carbon nanomaterials or glass microspheres and other chemical methods are also being investigated as a means of storage (see figure 4.9).

FIGURE 4.9 Research into improving high pressure hydrogen storage systems for use in cars continues. This is a recently released polymer gas tank.

Hydrogen safety

Hydrogen has a lower ignition point than hydrocarbons, is highly flammable and has a much lower radiant heat when ignited than burning hydrocarbons. The flame of burning hydrogen is almost invisible, and this would pose a problem to firefighters. It is a colourless, tasteless and odourless gas, so leaks are difficult to detect. However, hydrogen is not toxic and, due to its lightness, leaks would rise and rapidly dissipate into the air. By contrast, vapour from petrol leaks is denser than air, and can collect below a vehicle and potentially ignite. Hydrogen can be explosive at relatively higher concentrations than petrol, but, because of its tendency to rise rapidly, it is less likely to explode than heavier hydrocarbon gases.

FIGURE 4.10 The Hindenburg airship disaster was caused by leaking hydrogen gas that was ignited by electrostatic discharge.

4.2.9 Environmental impact of using fuels cells

Molten carbonate and solid oxide cells use methanol or a hydrocarbon, such as natural gas, because the high operating temperatures allow the reforming hydrogen to occur within the fuel cell structure. Direct methanol fuel cells use the anode catalyst to remove the hydrogen from the liquid methanol without a fuel reformer. This process is a more efficient way of producing energy than burning fuel to produce steam to drive a turbine, which means that less fuel is wasted and that fewer amounts of greenhouse gases are generated.

In general, fuel cells rely on hydrogen as a fuel, making them more environmentally friendly than combustion fuels. The hydrogen can be obtained from the electrolysis of water (for more about decomposition using electricity, see topic 7) or reformed from another fuel, such as methanol, natural gas, petrol and diesel. Enzymes in cyanobacteria can also generate hydrogen biologically. Solar power, wind power or bioethanol can be used to power the electrolysis of water into hydrogen and oxygen, and the reformation process produces fewer greenhouse gases than combustion of these fuels. If hydrogen can be produced by renewable means, the use of hydrogen results in water being the main by-product of fuel cells. Additionally, fuel cells do not have the same problems of disposal as lead–acid batteries or the fumes associated with the use of diesel generators.

4.2 EXERCISE

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1. Explain the difference between electrochemical cells and fuel cells.
2. For the following fuel cells, write half-equations to show the reactions taking place at each of the electrodes and then write the overall equation.
   (a) An alkaline hydrogen fuel cell.
   (b) An acid methane fuel cell.
   (c) An ethanol fuel cell.
3. State two advantages of fuel cell vehicles over conventional vehicles.
4. State the three ways in which hydrogen can be stored in a fuel cell vehicle.
5. Discuss two advantages and two disadvantages of using fuels cells rather than fossil fuels for energy.

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4.3 Review

4.3.1 Summary

Fuel cells

- A fuel cell is an electrochemical device that converts chemical energy into usable DC electricity and heat using a continuous supply of fuel, without combustion as an intermediary step.
- The simplest fuel cell is the alkaline fuel cell. Its function can be represented by the equation:

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

- There are six basic types of fuel cells, which are based on the electrolyte used:
  - alkaline fuel cell
  - phosphoric acid fuel cell
  - molten carbonate fuel cell
  - solid oxide fuel cell
  - proton exchange membrane fuel cell
  - direct methanol fuel cell.
- Fuel cells are more efficient at generating electricity than combustion of the fuel.
- Fuel cells and galvanic cells both have an anode and a cathode, and an electrolyte to carry ions between these electrodes. However, in a fuel cell the reactants (fuel and oxidising agent) are supplied continuously, which means it can generate electricity as long as this supply is maintained.
- The structure and nature of the electrodes in a fuel cell are critical to the effective operation of the cell. They are often porous and may also contain catalysts.
- The most common fuel for fuel cells is hydrogen, which can be obtained by a reforming process using hydrocarbon fuels or by using renewable sources to provide electricity to break down water into hydrogen and oxygen.
- Hydrogen can be stored using compression, liquefying or chemical means.
- Hydrogen is a low molecular mass, a colourless, odourless, non-toxic and flammable gas that requires particular safety precautions.

TABLE 4.4 Comparison of fuel cells and galvanic cells

Cell	Definition	Function	Design features	Energy transformations	Energy efficiency	Applications
Fuel	Electrochemical cell that produces electrical energy directly from a fuel	To provide an electrical current (DC)	Site of oxidation (negative anode) is separated from site of reduction (positive cathode) Electrolyte between electrodes to allow flow of ions (internal circuit) Electrodes are porous (higher surface area as fuels are often gases) Uses catalysts If fuel and oxidising agent are continuously supplied, then they do not go flat. Can be stacked in parallel to increase voltage.	Convert the reactant's chemical energy into electrical energy	35–70%	Portable power source for appliances Backup power (e.g. in hospitals) Transport vehicles (forklifts, buses and boats) Submarines (very quiet operation)
Galvanic	Electrochemical cell that produces electrical energy from chemical reactions	To provide an electrical current (DC)	Site of oxidation (negative anode) is separated from site of reduction (positive cathode) Electrolyte between electrodes to allow flow of ions (internal circuit) Uses catalysts Single use — primary cells cannot be recharged. Can be stacked in parallel to increase voltage.	Converts the stored chemical energy into electrical energy	45–90%	Portable power source for small devices (e.g. mobile phones, laptops, etc)

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4.3.2 Key terms

alkaline fuel cell (AFC)	fuel cell that converts oxygen (from the air) and hydrogen (from a supply) into electrical energy and heat
direct methanol fuel cell (DMFC)	a new technology that is powered by pure methanol
fuel cell	an eletrochemical cell that produces electrical energy directly from a fuel
proton exchange membrane fuel cell (PEMFC)	a fuel cell being developed for transport applications as well as for stationary fuel cell applications and portable fuel cell applications

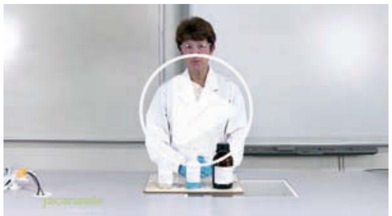
on Resources

Digital document Key terms glossary – Topic 4 (doc-31406)

4.3.3 Practical work and investigations

Experiment 4.1

Investigating the hydrogen–oxygen fuel cell
Aim: To investigate the chemistry of the hydrogen–oxygen fuel cell
Digital document doc-31257
Teacher-led video tlvd-0741



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Digital document Practical investigation logbook (doc-30407)

4.3 Exercises

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4.3 Exercise 1: Multiple choice questions

1. In a hydrogen–oxygen fuel cell that uses an acidic electrolyte:
   - A. hydrogen gas is oxidised at the anode to form hydrogen ions
   - B. hydrogen gas is reduced at the anode to form hydrogen ions
   - C. hydrogen ions are oxidised at the cathode to form hydrogen gas
   - D. hydrogen ions are reduced at the cathode to form hydrogen gas.
2. A fuel cell designed to produce electricity from the reaction between grain alcohol and oxygen has the following overall equation.

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

   Which of the following statements is true?
   - A. Carbon dioxide is evolved at the negatively charged anode.
   - B. The grain alcohol and oxygen are mixed together in a 1 : 3 ratio within the electrolyte.
   - C. The grain alcohol undergoes reduction at the negatively charged electrode.
   - D. Oxide ions travel through the external circuit to the cathode.
3. A major hurdle to the widespread use of fuel cells that use hydrogen and oxygen is:
   - A. the difficulty in obtaining the oxygen required
   - B. that they cannot function without the use of an alkaline electrolyte
   - C. the current difficulty of transporting and storing the hydrogen fuel required
   - D. that the voltage produced is too small.
4. Which of the following is a feature of a fuel cell but not a galvanic cell?
   - A. Small size
   - B. An anode and a cathode
   - C. A suitable electrolyte
   - D. Input connections for chemicals
5. The process of fuel reforming involves:
   - A. adding oxygen to a fuel to assist combustion
   - B. converting a fossil fuel into carbon monoxide
   - C. removing carbon monoxide from a fossil fuel
   - D. converting a fossil fuel into hydrogen.

6. When hydrogen burns in air, it reacts to form:
   - A. H_2O
   - B. N_2
   - C. CO_2
   - D. CH_4
7. Hydrogen can be stored as a:
   - A. compressed gas
   - B. liquid
   - C. metal hydride
   - D. all of the above.

4.3 Exercise 2: Short answer questions

1. a. What is a fuel cell?
   b. List the advantages of a fuel cell over a primary galvanic cell.
2. Fuel cells have been used in spacecraft for a number of years as a source of electrical energy. To obtain sufficient current, two gases, hydrogen and oxygen, are kept in cylinders under high pressure. The gases are passed over nickel electrodes. The product of these fuel cells is water, which is drunk by the astronauts. Each hydrogen–oxygen fuel cell used in the Apollo spacecraft weighed approximately 100 kg.
   a. What advantages do fuel cells have over internal combustion engines for use in spacecraft?
   b. What are the limitations of fuel cells, compared with the internal combustion engine?
3. Fuel cells have been developed to run on methane. Assuming that the electrolyte is acidic:
   a. write the half-equation for the oxidation reaction
   b. write the half-equation for the reduction reaction.
   Draw a diagram of this cell and label the following.
   c. The methane and oxygen inlets
   d. The anode and cathode and their polarities
   e. The direction of electron flow
   f. The ion flow in the electrolyte.
4. Obtaining hydrogen for use in fuel cells is not yet economically viable, but researchers have come up with a fuel cell that runs on octane, the main component of petrol. Previously, the reforming process caused a build-up of carbon on the electrodes in the fuel cell, reducing efficiency. A new system combines the reformer and the fuel cell and uses a more advanced catalyst.
   a. Write the equation for the combustion of octane, C_8H_{18}.
   b. This reaction is the same as the one that occurs in the fuel cell and produces the same amount of carbon dioxide. Explain what benefit there is in using a fuel cell to supply energy to power a vehicle.
   c. Write the half-equations for the anode and cathode reactions in this fuel cell assuming an acidic electrolyte.
   d. Add the two half-equations from question 4c to get the overall reaction. Compare your answer with question 4a. What do you notice?
5. Discuss the statement ‘Electrochemical cells may help decrease our use of fossil fuels as an energy source’.
6. Describe how the method of producing electricity from an electrochemical cell differs from the method of producing electricity from:
   a. a hydro-electricity scheme
   b. a coal-fired power station.

4.3 Exercise 3: Exam practice questions

Question 1 (5 marks)

Fuel cells have been developed to use different alkanes for fuels. An example is the propane–oxygen fuel cell. The overall reaction (assuming an acidic electrolyte) is identical to the combustion of propane in oxygen.

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

a. Write an equation showing the reaction occurring at the anode. **1 mark**
b. Write an equation showing the reaction occurring at the cathode. **1 mark**
c. Describe two advantages in using propane in a fuel cell instead of burning propane in a power station. **2 marks**
d. How do the electrodes in a fuel cell differ from those in a primary cell? **1 mark**

Question 2 (4 marks)

The chairperson of a leading car manufacturer says, 'Cars powered by hydrogen will be pollution-free and are therefore carbon-neutral'.

a. Give two reasons why this state is not true. **2 marks**

Hydrogen has been proposed by many car manufacturers as a future alternative to fossil fuels. One possibility is to store hydrogen as a solid hydride, which generates hydrogen gas when heated.

b. What is one advantage of using hydrogen instead of petrol as a fuel for vehicles? **1 mark**
c. What is one advantage of storing the hydrogen as a solid hydride rather than as a gas? **1 mark**

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AREA OF STUDY 1 What are the options for energy production?

OUTCOME 1

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.

PRACTICE EXAMINATION

STRUCTURE OF PRACTICE EXAMINATION		
Section	**Number of questions**	**Number of marks**
A	20	20
B	6	31
	Total	**51**

Duration: 50 minutes

Information:

- This practice examination consists of two parts. You must answer all question sections.
- Pens, pencils, highlighters, erasers, rulers and a scientific calculator are permitted.
- You may use the VCE Chemistry Data Book for this task.

on Resources

Weblink VCE Chemistry Data Book

SECTION A – Multiple choice questions

All correct answers are work 1 mark each; an incorrect answer is worth 0.

1. Which of the following statements concerning renewability is correct?

A. Biodiesel is a renewable fuel source because carbon dioxide is taken in as the plant grows.

B. Petrodiesel is a non-renewable fuel because it releases pollutants such as sulfur-containing compounds.

C. Biogas is a renewable fuel source because it can be produced at the same rate as it is being used.

D. Crude oil is a non-renewable fuel because its extraction is damaging to the environment.

2. Which is the correct thermochemical equation for the complete combustion of butane?

A. $2C_4H_{10}(g) + 13O_2(g) \rightarrow 8CO_2(g) + 10H_2O(l) \quad \Delta H = -2880 \text{ kJ mol}^{-1}$

B. $2C_4H_{10}(g) + 9O_2(g) \rightarrow 8CO(g) + 10H_2O(l) \quad \Delta H = +2880 \text{ kJ mol}^{-1}$

C. $2C_4H_{10}(g) + 13O_2(g) \rightarrow 8CO_2(g) + 10H_2O(l) \quad \Delta H = -5760 \text{ kJ mol}^{-1}$

D. $2C_4H_{10}(g) + 9O_2(g) \rightarrow 8CO(g) + 10H_2O(l) \quad \Delta H = +5760 \text{ kJ mol}^{-1}$

3. A petrol engine has been found to be 35% efficient. If the heat content of petrol is 48.0 kJ g^{-1}, what mass of petrol is required to produce 1.00 MJ of energy using the petrol engine?

A. 32.1 g
B. 20.8 g
C. 59.5 g
D. 7.29 g

4. Petrodiesel is obtained through fractional distillation of crude oil. Biodiesel can be produced from plant crops such as canola oil in a process called transesterification. Which of the following statements is *correct?*

A. Petrodiesel has a higher viscosity than biodiesel and gels at lower temperatures.
B. Petrodiesel has a lower viscosity than biodiesel and gels at lower temperatures.
C. Petrodiesel has a higher viscosity than biodiesel and gels at higher temperatures.
D. Petrodiesel has a lower viscosity than biodiesel and gels at higher temperatures.

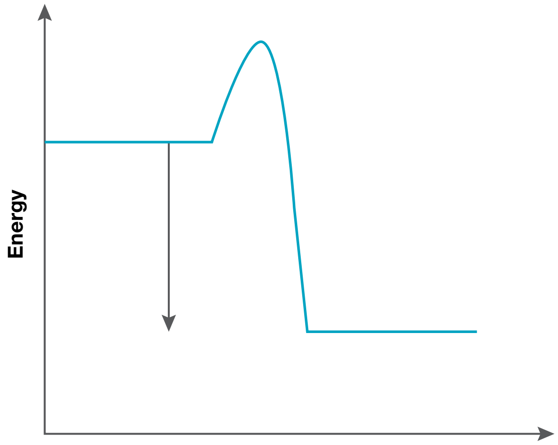
5. The amount of energy in MJ produced by combustion of 2.0 kg of ethane is closest to:

A. 1.0×10^2 MJ
B. 2.1×10^2 MJ
C. 1.0×10^3 MJ
D. 2.1×10^3 MJ

6. 46.0 L of CO_2 are released from the complete combustion of propane at SLC. The amount of energy released, in kJ, is closest to:

A. 1.4×10^3 kJ
B. 7.6×10^6 kJ
C. 8.4×10^5 kJ
D. 1.2×10^3 kJ

7. What do the arrow and the shape of the diagram represent, respectively, in the following diagram?



A. Net energy released, exothermic
B. Net energy absorbed, exothermic
C. Net energy released, endothermic
D. Net energy absorbed, endothermic

8. Consider the following equations:

$$2NH_3(g) \rightarrow N_2(g) + 3H_2(g) \qquad \Delta H = +92 \text{ kJ mol}^{-1}$$
$$N_2(g) + O_2(g) \rightarrow 2NO(g) \qquad \Delta H = +181 \text{ kJ mol}^{-1}$$

Using the two equations above what is the enthalpy for the following reaction?
$4NO(g) + 3H_2(g) \rightarrow N_2(g) + 2O_2(g) + 2NH_3(g)$

A. -454 kJ mol^{-1}
B. $+270$ kJ mol^{-1}
C. -270 kJ mol^{-1}
D. -456 kJ mol^{-1}

9. Consider the following equation for incomplete combustion of carbon.

$$2C(s) + O_2(g) \rightarrow 2CO\ (g) \qquad \Delta H = -221\ \text{kJ mol}^{-1}$$

500 mL of CO is produced at SLC. How much energy is released?

A. 4.4 kJ
B. 1.4 MJ
C. 2.2 kJ
D. 2.2 MJ

10. The equation for photosynthesis is:

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

What volume of carbon dioxide, at SLC, is required to produce 200 mL of oxygen?

A. 200 mL
B. 1200 mL
C. 33.3 mL
D. 60.0 mL

11. The oxidation number of Mn, in $KMnO_{4,}$ is:

A. +1
B. +3
C. +5
D. +7

12. When metallic lead is placed in a solution of Fe^{2+} and Fe^{3+} ions, a redox reaction occurs. The correct reduction equation is:

A. $Fe^{2+}(aq) \rightarrow Fe^{3+}(aq) + e^-$
B. $Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq)$
C. $Fe^{2+}(aq) + 2e^- \rightarrow Fe(s)$
D. $Pb^{2+}(aq) + 2e^- \rightarrow Pb(s)$

13. The reaction given is a reduction half-equation. The correct values for the coefficients *a, b, c, d* and *e,* respectively, are:

$$aCr_2O_7^{\,2-}(aq) + bH^+(aq) + ce^- \rightarrow dCr^{3+}(aq) + eH_2O(l)$$

A. 1, 14, 9, 1, 7
B. 1, 14, 9, 2, 7
C. 1, 14, 6, 2, 7
D. 2, 28, 12, 4, 14

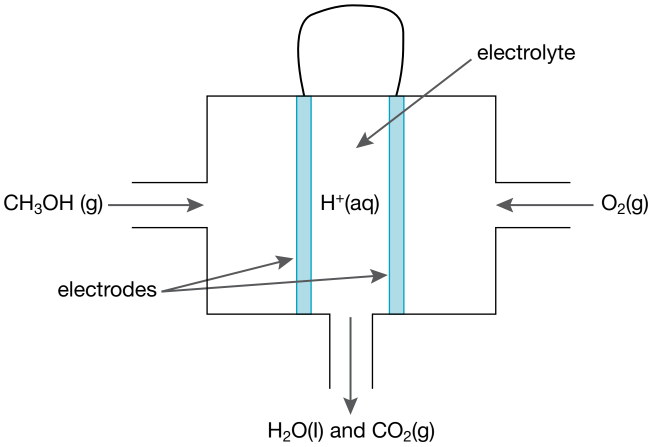
14. In a simple galvanic cell:

A. Electrons flow through the external circuit from anode to cathode
B. Electrons flow through the internal circuit from anode to cathode
C. Anions flow through the external circuit to the anode
D. Anions flow through the internal circuit to the cathode.

15. Nickel can displace silver ions from solution. This reaction can therefore be used to construct a galvanic cell. Use the electrochemical series to predict the voltage and the material of the cathode when the two half-cells are combined.

A. 0.55 V, silver
B. 1.05 V, silver
C. 0.55 V, nickel
D. 1.05 V, nickel

16. The following diagram shows a simplified fuel cell that uses the reaction between methanol and oxygen.



The equation for the reaction occurring at the cathode of this fuel cell is:

A. O_2(g) + $2H_2O$(l) + $4e^-$ → $4OH^-$(aq)
B. O_2(g) + $2H^+$(aq) + $2e^-$ → H_2O_2(l)
C. O_2(g) + $4H^+$(aq) + $4e^-$ → $2H_2O$(l)
D. CH_3OH(l) → CO_2(g) + $4H^+$(aq) + $4e^-$

17. A key difference between fuel cells and galvanic cells is that:

A. In fuel cells, the cathode is negative and the anode is positive
B. In fuel cells the oxidising and reducing agents are always gaseous
C. In fuel cells there is a continuous supply of reactants
D. Fuel cells produce noise pollution when operating.

18. The zinc–air cell makes use of oxygen from the air as a reactant.
The overall equation for the cell is:

$$2Zn(s) + O_2(g) \rightarrow 2ZnO(s)$$

The oxidation half-equation is:

$$2Zn(s) + 4OH^-(aq) \rightarrow 2ZnO(s) + 2H_2O(l) + 4e^-$$

The correct reduction half-equation is:

A. O_2(g) + $4H^+$(aq) + $4e^-$ → $2H_2O$(l)
B. O_2(g) + $2H^+$(aq) + $2e^-$ → H_2O_2(aq)
C. O_2(g) + $2H_2O$(l) + $4e^-$ → $4OH^-$(aq)
D. O_2 + $2e^-$ → $2O^-$(aq)

19. The electrodes in fuel cells:

A. Are porous to allow electrons to flow through them
B. Are always made of graphite
C. Are porous so that they maximise contact with gaseous reactants
D. Act as the salt bridge.

20. The following half-equation is for the reduction of lead(IV) oxide to lead(II) ions.

$$PbO_2(s) + 4H^+(aq) + 2e^- \rightarrow Pb^{2+}(aq) + 2H_2O(l)$$

When this half-cell is combined with the Fe^{3+}/Fe^{2+} half-cell, the voltage recorded under standard conditions is 0.69 V. What is the standard electrode potential for the PbO_2/Pb^{2+} half-cell?

A. +0.08 V
B. +0.25 V
C. +1.46 V
D. +1.13 V

SECTION B – Short answer questions

Question 1 (4 marks)

A sample of ethanol undergoes complete combustion to produce 80.0 L of carbon dioxide, collected at 35.0 °C and 105 kPa. The density of ethanol is 0.789 g L^{-1} and $M(C_2H_5OH)$ = 46.0 g mol^{-1}.
Calculate the volume of ethanol that reacted.

Question 2 (10 marks)

It is hoped that biofuels can eventually replace fuels sourced from crude oil and other non-renewable sources. One benefit of this would be reducing carbon dioxide emissions. Biodiesel can be made from a variety of different fats and oils, predominantly from plants.

a. By what process is biodiesel produced from plant oils? **1 mark**

b. Write balanced chemical equations for the combustion of a biodiesel molecule produced from:

  i. palmitic acid **1 mark**

  ii. a petrodiesel with chains that are 10 carbons long. **1 mark**

c. Calculate the volume, in litres, of carbon dioxide produced by 5.0 kg of biodiesel produced from palmitic acid at SLC. **3 marks**

d. Why does biodiesel contribute less to greenhouse gases than petrodiesel? **1 mark**

e. At the same temperatures, the viscosity of petrodiesel and biodiesel differ. State which of these fuels is more viscous and explain why. **3 marks**

Question 3 (3 marks)

The overall equation for a zinc–air button cell with a KOH electrolyte is:

$$2Zn(s) + O_2(g) + 2H_2O(l) \rightarrow 2Zn(OH)_2(s)$$

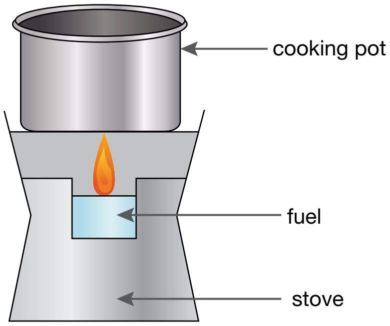
a. Write the oxidation half-equation for this cell. **1 mark**

b. Suggest a suitable material for the cathode. **1 mark**

c. Given that the cell produces a voltage of 1.4 V, determine the electrode potential for the oxidation half-equation. **1 mark**

Question 4 (6 marks)

An experiment was carried out in which ethanol was burnt to heat 150.0 mL of water at 15.0 °C to 70.0 °C. The experimental set up is shown in the following diagram.

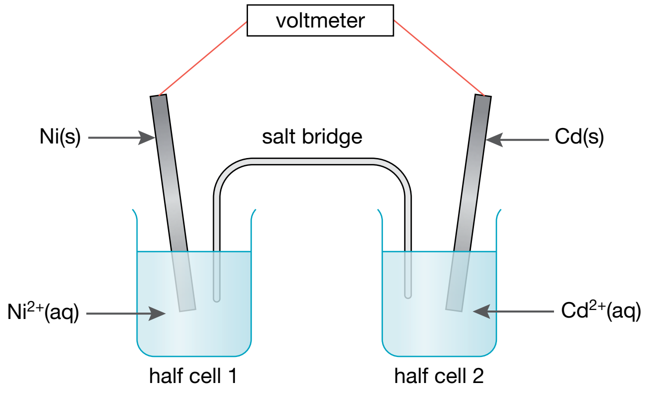


a. Calculate the mass of ethanol burnt to produce this temperature rise. **3 marks**

b. Is the actual value likely to be higher or lower than the calculated value? Explain your answer. **2 marks**

c. Comment on the reliability of the value calculated in question **4a**. **1 mark**

Question 5 (3 marks)



a. For the galvanic cell above, which half-cell will the cations of the salt bridge travel to? **1 mark**

b. What is the polarity of the nickel electrode? **1 mark**

c. What will happen to the mass of the Cd electrode? **1 mark**

Question 6 (5 marks)

44 kJ of energy is required to convert 1 mol of liquid water to steam.

a. Write this as a balanced thermochemical equation. **2 marks**

b. Sketch an energy profile diagram for the reaction, with labels. **3 marks**

PRACTICE SCHOOL-ASSESSED COURSEWORK

ASSESSMENT task – Reflective journal

In this task you will be required to write a reflective journal outlining different energy sources, with an analysis of energy efficiency, renewability and environmental impact.

- Students are permitted to use pens, pencils, highlighters, erasers, rulers and a scientific calculator.
- Students may use the VCE Chemistry Data Book for this task.

Total time: Two 50-minute lessons (50 minutes for literature search, 50 minutes for writing time)

Total marks: 50 marks

Why do we need current research into the advancement of energy sources?

Recent events in Australia, such as mounting power outages in Victoria, especially over the summer months, and the ‘Stop Adani’ campaign and rallies have forced our society to question the role of fossil fuels in everyday life. As the world population continues to increase, there is a desperate need to find an energy source that is efficient, renewable and effective.

Write a reflective journal outlining different energy sources. For each energy source, include an analysis of energy efficiency, renewability and environmental impact. Your response should provide a personal and justified opinion about the viability of the energy sources explored.

The title of the reflective journal is:

Why do we need current research into the advancement of energy sources?

Your response must include:

1. An evidence-based introduction as to why there is a need for alternative energy sources
2. Discussion of the environmental and financial impact of new sources of energy
3. Research on at least three new energy sources. Each energy source analysis must include:
   (a) Advantages and disadvantages of each new energy source
   (b) Detailed chemistry of each new energy source.
4. At least five scientific references.

Resources

Digital document U3AOS1 School-assessed coursework (doc-32005)

AREA OF STUDY 2
HOW CAN THE YIELD OF A CHEMICAL PRODUCT BE OPTIMISED?

5 Rate of chemical reactions

5.1 Overview

Numerous **videos** and **interactivities** are available just where you need them, at the point of learning, in your digital formats, learnON and eBookPLUS at www.jacplus.com.au.

5.1.1 Introduction

The speed, or rate, of a chemical reaction can make all the difference between it being useful or not. For example, the reactions of blasting chemicals would be useless if they did not occur at an extremely fast rate. If a potentially useful reaction is either too fast or too slow, being able to change the rate of a chemical reaction can be very useful. To achieve this, you need to understand how a reaction occurs and the different factors that affect its rate.

In this topic, you will learn about collision theory and activation energy, and use these to develop a simple picture of how a reaction takes place. Factors that can affect the rate of reaction include as temperature, concentration, pressure, surface area and catalysts. These factors are applied with the Law of Conservation of Mass across a range of industries where the rate of chemical reactions are fundamental. These industries include mining, vehicle manufacture and performance, petrochemical extraction and the subsequent removal of impurities. Knowledge of rates of reaction and how these can be manipulated allows chemists to create more energy efficient, less wasteful chemical processes.

FIGURE 5.1 The explosions used in mining are chemical reactions designed to happen almost instantaneously. They release huge volumes of gases and vast amounts of energy.

5.1.2 What you will learn

KEY KNOWLEDGE

In this topic, you will investigate:
- chemical reactions with reference to collision theory, including qualitative interpretation of Maxwell–Boltzman distribution curves
- the comparison of exothermic and endothermic reactions including their enthalpy changes and representations in energy profile diagrams
- 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.

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PRACTICAL WORK AND INVESTIGATIONS

Practical work is a central component of learning and assessment. Experiments and investigations, supported by a **Practical investigation logbook** and **Teacher-led videos**, are included in this topic to provide opportunities to undertake investigations and communicate findings.

on Resources

Digital documents Key science skills (doc-30903)
Key terms glossary – Topic 5 (doc-31397)
Practical investigation logbook (doc-31398)

studyon

To access key concept summaries and past VCAA exam questions download and print the **studyON: Revision and practice exam question booklet** (doc-31399).

5.2 How does a chemical reaction occur?

KEY CONCEPT

- Chemical reactions with reference to collision theory, including qualitative interpretation of Maxwell–Boltzman distribution curves

5.2.1 Collision theory

The Law of Conservation of Mass states that matter cannot be created or destroyed in a chemical reaction. This means that all chemical reactions involve the rearrangement of atoms that are already present. For such a rearrangement to occur existing, or ‘old’, bonds need to be broken and ‘new’ bonds allowed to form.

A chemical reaction may be pictured as particles that are moving around in constant random motion and sometimes colliding with each other. Some of these collisions will have enough energy to break the old bonds — these may be regarded as ‘successful’ collisions. This is then followed by the resulting pieces rearranging and forming new bonds to make the products. The greater the number of successful collisions, the faster the rate. Not all collisions result in a reaction; the particles may simply bounce off each other if they do not have enough energy, resulting in nothing more than changes in velocity. In other cases, the particles might not hit each other in the right orientation for bonds to break.

For a reaction to take place the reactants must:

- **collide**
- **have the correct orientation for bond breaking to occur**
- **have sufficient energy for the reaction to occur.**

Activation energy

The minimum amount of energy required to break the old bonds in a chemical reaction is called the **activation energy**, E_a. Collisions that do not have this minimum energy requirement will not result in a reaction. The activation energy acts as a barrier that must be overcome in order for a reaction to occur. The activation energy is shown as the peak of an energy profile diagram, which are discussed in detail in section 5.3.2.

For a reaction to occur, reactants must have energy equal to or greater than the level of activation energy, E_a.

Measuring reaction rates

The progress of a reaction may be conveniently monitored by following either the decrease in the amount of a reactant or the formation of a product. Methods used to observe reaction rates include measuring the change over a period of time of:

- the volume of a gas evolved
- the mass of a solid formed
- the decrease in mass due to a gas evolved
- the intensity of colour of a solution
- the formation of a precipitate
- pH
- temperature.

A typical example of apparatus used to measure rates is illustrated in figure 5.2 with the reaction between calcium carbonate and hydrochloric acid.

$$CaCO_3(s) + 2HCl(aq) \rightarrow CaCl_2(aq) + H_2O(l) + CO_2(g)$$

The rate of the reaction can be observed by measuring the change in mass over fixed intervals of time, such as grams per 10 seconds. As the reaction proceeds, the mass of the flask and contents decrease due to formation (and escape from the flask) of $CO_2(g)$. The variables that might be tested are temperature, concentration of the hydrochloric acid or the size of the particles of calcium carbonate (surface area).

Figure 5.3 displays the mass of $CO_2(g)$ lost, which is found by subtracting the mass at each time interval from the initial mass of the apparatus. The gradient (steepness) of the green line is greater, indicating a faster rate than the blue line. Factors that increase the rate of reaction include higher temperature, higher concentrations of reactants and smaller pieces of solid reactants, which have a larger surface area. These factors are discussed in subtopic 5.4. The graph flattens when the limiting reactant is consumed.

FIGURE 5.2 Apparatus used to measure rate

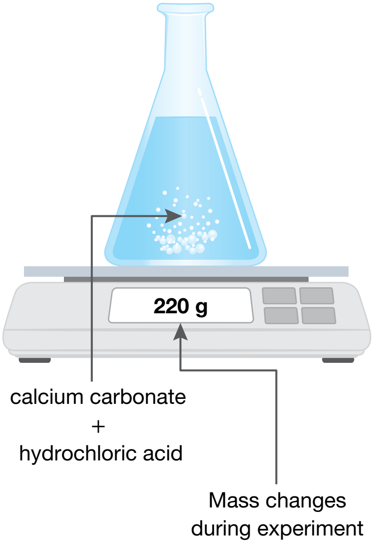
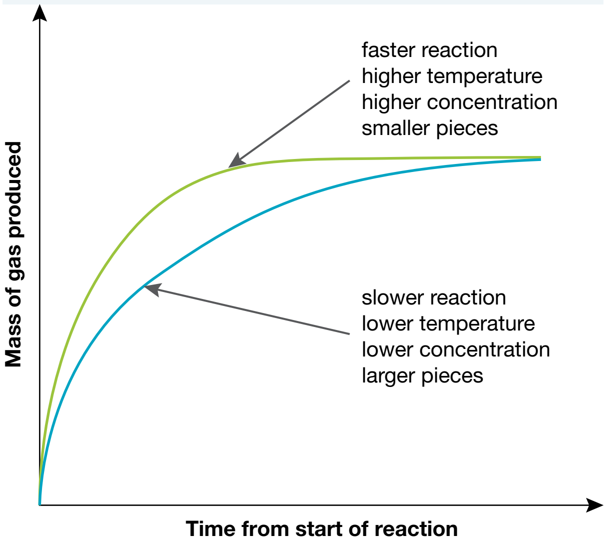


FIGURE 5.3 Graph displaying mass of gas lost from apparatus



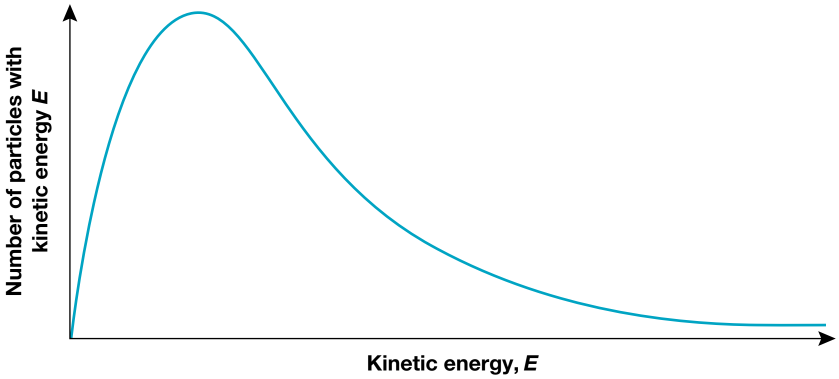
HOW BONDS FORM

Visualising a reaction as breaking old bonds first and *then* forming new ones is a simplification of how reactants are turned into products for many reactions. Often, old bonds weaken at the same time that new ones begin to form. Once quantitative measurements of rate are made, such as changes in concentration, a mathematical relationship, called *the rate law of the reaction* concerned may be produced. Investigate how these rate laws are calculated.

5.2.2 Maxwell–Boltzmann distribution curves

During the second half of the seventeenth century, work by scientists James Clerk Maxwell and Ludwig Boltzmann led to what is now known as the Maxwell–Boltzmann distribution. This is a statistical analysis of the range of energies present in the particles of a gas sample, although many of its ideas can also be applied to liquids and reactions in solution. Shown on a **Maxwell–Boltzmann distribution curve**, it is useful in explaining some of the factors that influence chemical reactions and their rates.

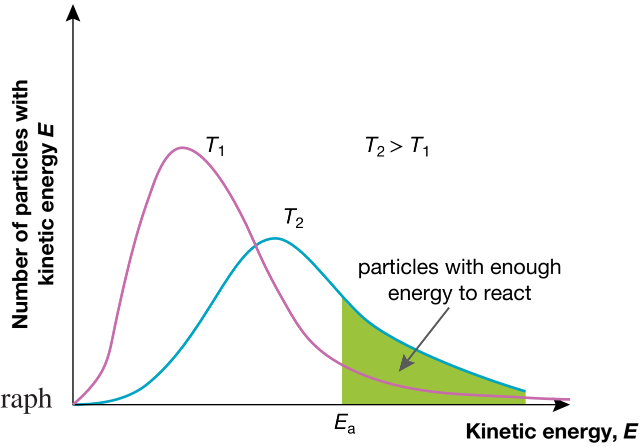
FIGURE 5.4 The Maxwell–Boltzmann curve shows the number of particles with a particular energy graphed against the value of that particular energy.



There are some points to note about a Maxwell–Boltzmann curve.

- The particles in a sample have a wide range of kinetic energies. As kinetic energy is given by the formula $KE = \frac{1}{2}mv^2$ (where m is mass and v is the velocity of the particles), there is also a range of velocities. This is due to the collisions that the particles are constantly undergoing.
- Only a small proportion of particles in the sample have kinetic energy that is equal to or greater than the activation energy, E_a.
- It is not symmetrical.
- The highest point represents the most probable velocity; this is not the same as the average velocity.
- The area under the graph represents the total number of particles in the sample.
- If the temperature of a sample is increased, the graph changes in a predictable manner (see figure 5.5).

FIGURE 5.5 Increasing the temperature of a gas sample stretches the Maxwell–Boltzmann curve to the right.



Increasing the temperature of the gas sample stretches the graph to the right. As a result, there are more particles with higher kinetic energies. Although the area under the graph is the same (the total number of particles has not been altered), on average they all move faster and the average kinetic energy is higher. Therefore, more particles have energy levels at or above activation energy (E_a) and can therefore react.

Note that, at the higher temperature, the graph is *stretched* to the right, rather than *moved* to the right. The graph is always anchored to the origin, because there are always a few particles with very low or zero velocity.

SAMPLE PROBLEM 1

State two scenarios that will decrease the number of collisions in a given time period. Use collision theory to explain the effect that these will have on the rate of a reaction.

THINK	WRITE
1. Identify required scenarios.	Decreasing temperature will mean particles have less energy, which will result in fewer successful collisions per unit time. Decreasing concentration, or pressure in a gas, will result in fewer successful collisions.
2. Recall the effect of collision theory on rates of reaction.	A decreased number of successful collisions per unit time will result in a slower rate of reaction. Lower temperatures, lower concentrations, and lower pressures for gases mean a slower rate of reaction as less particles will have the required activation energy, E_a.

PRACTICE PROBLEM 1

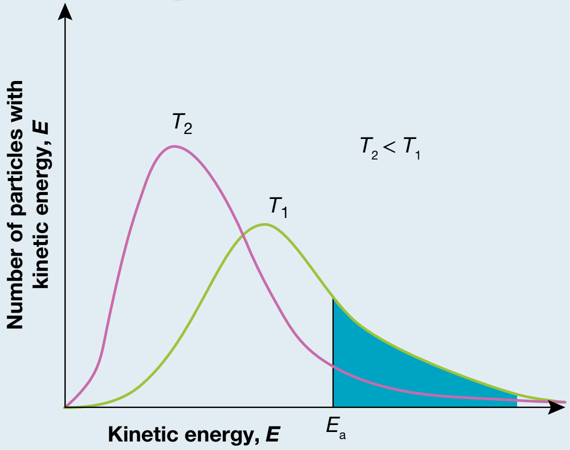
State two scenarios that will increase the number of collisions in a given time period. Use collision theory to explain the effect that these will have on the rate of a reaction.

SAMPLE PROBLEM 2

The figure shows the distribution of energies for a fixed amount of gas, before and after a particular change is made to its conditions.

a. Is the area under each graph the same?

b. What change has been made to the sample?



Teacher-led video: SP2 (tlvd-0677)

THINK	WRITE
a. Recall that the area under the curve represents the number of particles (amount) that is present.	a. Yes the area under each curve is the same, because it represents the same amount of gas.
b. Recall that as temperature is lowered, the particles will move more slowly and have less energy.	b. The temperature has been lowered. This is indicated by the graph for T_2 has particles that, on average, have lesser energy.

PRACTICE PROBLEM 2

Refer to the figure in sample problem 2.

If the same sample is returned to T_1 and is then heated to produce T_3 how will this effect:

a. the area under the graph?

b. the shape of the graph?

5.2 EXERCISE

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1. State the three requirements of the collision theory of chemical reactions.
2. Describe the effect on the shape of the Maxwell–Boltzmann distribution curve of increasing temperature and the concentration.
3. Explain why the shape of the Maxwell–Boltzmann distribution changes the way it does when temperature is increased.
4. Describe how the graph of the Maxwell–Boltzmann distribution for a sample of gas is altered if additional gas is added at the same temperature.
5. Use collision theory to explain:
   (a) why there is always a range of particle velocities at any temperature.
   (b) why there will always be an amount of reaction, however small, at any given temperature. Make reference to the Maxwell–Boltzmann distribution in your answer.
6. If the distribution curve for a sample of gas uses velocity on the horizontal axis instead of energy, how will each pair of graphs in the following scenarios compare
   (a) Oxygen gas at 298 K and oxygen gas at 350 K.
   (b) Hydrogen gas at 313 K and methane gas at 313 K.
   (c) Propane gas at 283 K and carbon dioxide gas at 283 K.

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5.3 Exothermic and endothermic reactions

KEY CONCEPT

- The comparison of exothermic and endothermic reactions including their enthalpy changes and representations in energy profile diagrams

5.3.1 Enthalpy

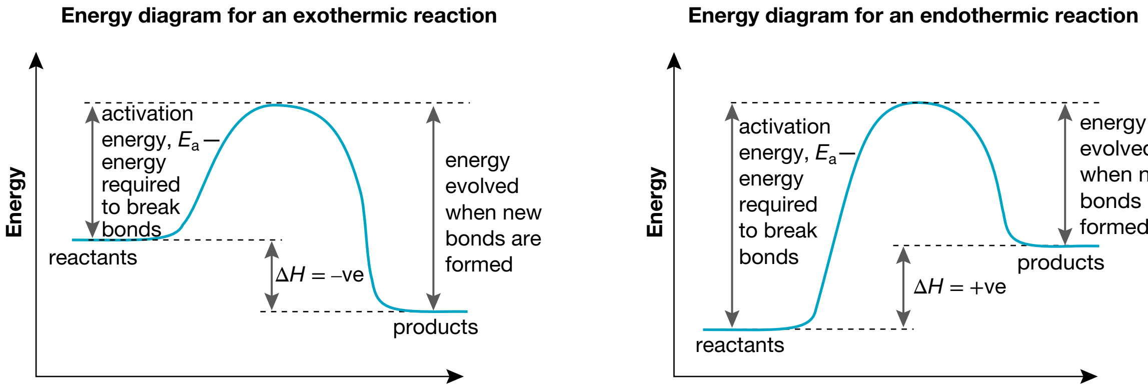
Energy is critical to all chemical reactions. As we have already seen, a minimum amount of energy is required before a reaction can proceed. Often a reaction may occur in a number of steps, with unstable intermediate products being temporarily formed. These are called activated complexes or transition states. Due to their instability (and corresponding high energy content), these quickly decompose and, in the process, give out energy as the new bonds in the final products form. Therefore, it is useful to consider chemical reactions from the viewpoint of energy and energy changes.

The total energy stored in a substance is called the **enthalpy**, or **heat content**, of the substance and is given the symbol H. It is not possible to measure H directly but the **change in enthalpy** (ΔH) can be measured when a substance undergoes a chemical reaction. Change in enthalpy was discussed in topic 1.

5.3.2 Energy profile diagrams

Energy changes can be summarised using the **energy profile diagrams** shown in figure 5.6.

FIGURE 5.6 A chemical reaction can be recognised as either exothermic or endothermic by its ΔH value. If the ΔH value is negative, the reaction is exothermic. If the ΔH value is positive, the reaction is endothermic.



From these diagrams we can note a number of points:

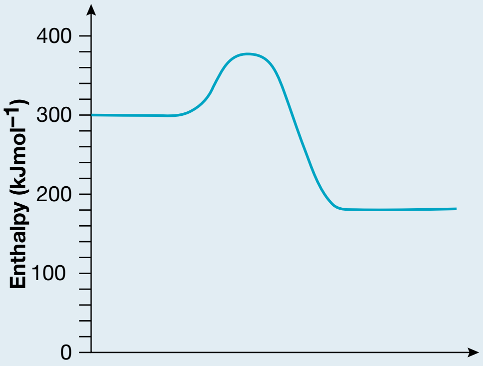
- The energy required to break the old bonds is called the activation energy, E_a.
- For an **exothermic** reaction, the activation energy is less than the energy released when new bonds form. Consequently, there is a net release of energy (usually as heat released to the surroundings).
- In an **endothermic** reaction, the activation energy is greater than the energy released when new bonds form. Consequently, there is a net input of energy (in most cases, heat is absorbed from the surroundings).
- In exothermic and endothermic reactions, the activation energy represents a requirement for the progress of the chemical reaction. This must be overcome before a reaction proceeds.

$$\text{Energy needed for bond breaking} > \text{Energy released for bond forming} \quad +\Delta H$$
$$\text{Energy needed for bond breaking} < \text{Energy released for bond forming} \quad -\Delta H$$

For exothermic reactions $+\Delta H$
For endothermic reactions $-\Delta H$

SAMPLE PROBLEM 3

The following diagram shows the energy profile for a particular reaction. Some values for enthalpy have been inserted on the vertical axis.



a. **Is this reaction exothermic or endothermic?**
b. **What is the value of the activation energy?**

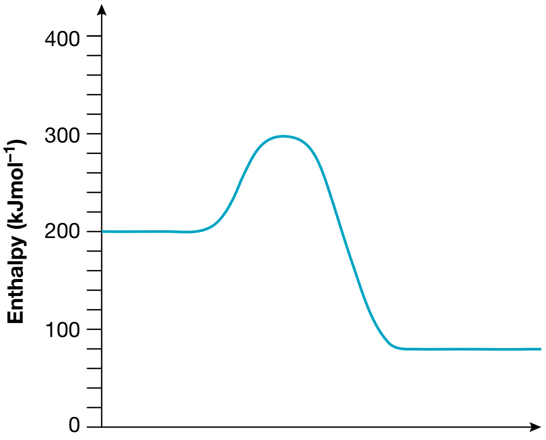
Teacher-led video: SP3 (tlvd-0678)

THINK	**WRITE**
a. Recall that an exothermic or endothermic reaction is indicated by comparing enthalpies of the reactants and the products. Here the products are lower in enthalpy than the reactants so it is exothermic.	**a.** Exothermic.
b. Recall that the activation energy is the difference in enthalpy between the reactants and the highest point of the energy profile diagram. **TIP:** Remember that the value of the activation energy is always positive, because all reactions need energy to start them.	**b.** $380 - 300 = 80$ kJ mol^{-1}

PRACTICE PROBLEM 3

The reaction profile shown refers to a particular reaction and has some enthalpy values indicate as shown.

a. **Is this reaction exothermic or endothermic?**
b. **What is the activation energy for this reaction?**



on Resources

Digital document Experiment 5.1 Investigating heat changes in reactions (doc-31251)

Teacher-led video Experiment 5.1 Investigating heat changes in reactions (tlvd-0742)

Video eLesson Exothermic and endothermic reactions (med-0424)

Interactivities Identifying exothermic and endothermic reactions (int-1242)

Constructing energy profile diagrams (int-1243)

5.3 EXERCISE

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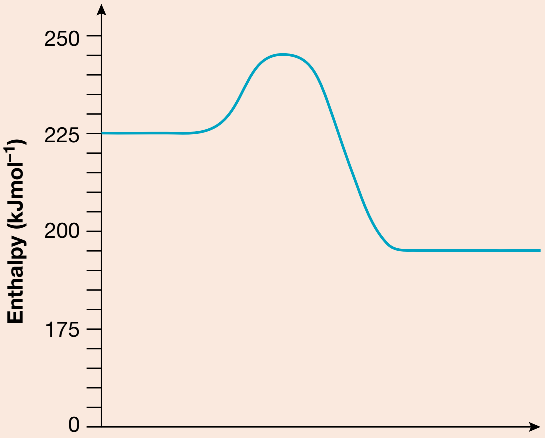
Question 1 refers to the following energy profile diagram.



1. (a) Is this reaction exothermic or endothermic?
   (b) For this reaction, what is the value of:
      i. ΔH
      ii. the minimum energy required to break the reactant bonds
      iii. the activation energy
      iv. the energy evolved when the new bonds form.
2. The gas silane, SiH_4, reacts spontaneously with oxygen at normal temperatures to produce silicon dioxide, SiO_2. What does this indicate about the activation energy for this reaction?
3. Why is it not possible to have a reaction with an activation energy of 200 kJ mol^{-1} and a ΔH of +350 kJ mol^{-1}?
4. Many chemical reactions are reversible, meaning that they can react in a backward direction. These are discussed in more detail in topic 6.
   How does the activation energy of the forward reaction compare to the activation energy of the backward reaction for:
   (a) an exothermic reaction?
   (b) an endothermic reaction?

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5.4 Factors affecting the rate of a chemical reaction

KEY CONCEPT

- Factors affecting the rate of a chemical reaction including temperature, surface area concentration of solutions, gas pressures and presence of a catalyst

There are four main factors that affect the rate of a chemical reaction: concentration, gas pressure, temperature and surface area.

5.4.1 Concentration

Concentration is the amount of a substance in a space. Table 5.1 shows some results from an experiment involving the reaction:

$$2H_2(g) + 2NO(g) \rightarrow 2H_2O(g) + N_2(g)$$

TABLE 5.1 Rate of reaction between NO and H_2 at 800 °C

Experiment	Initial concentrations (M) [NO]	[H_2]	Initial rate of H_2O production (M s^{-1})
1	6.0×10^{-3}	1.0×10^{-3}	0.64×10^{-2}
2	6.0×10^{-3}	2.0×10^{-3}	1.28×10^{-2}
3	1.0×10^{-3}	6.0×10^{-3}	1.00×10^{-3}
4	2.0×10^{-3}	6.0×10^{-3}	3.90×10^{-3}

Note that square brackets denote concentration in mol L^{-1} (M).

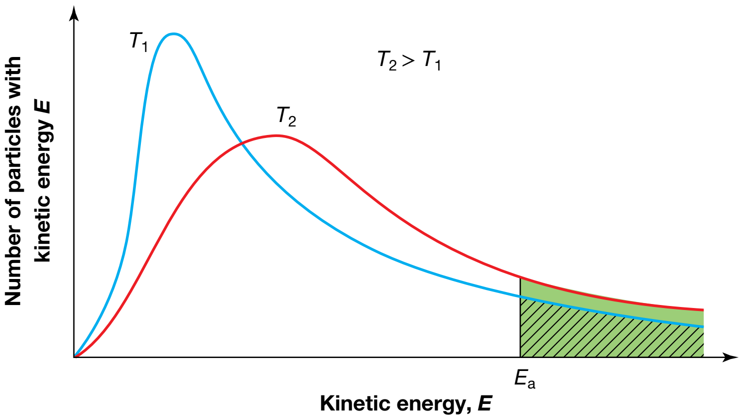
In experiments 1 and 2, [NO] is the same but [H_2] is different. In experiments 3 and 4, [H_2] is the same but [NO] is different. Therefore, each pair of experiments allows us to analyse the effect of changing the concentration of one of the two substances. Compare experiment 1 with experiment 2, and then compare experiment 3 with experiment 4. Increasing the concentration of either reactant causes an increase in the rate of the reaction. In terms of our model of a chemical reaction, we can explain this by the crowding together of the reacting particles as the concentration is increased. This results in an increased number of overall collisions during a given period of time. With more collisions, there will be an increase in the number of successful collisions, resulting in a higher rate of reaction. The relative proportion of successful collisions does not increase.

5.4.2 Gas pressure

For reactions involving gases, the effect of increasing pressure is the same as increasing concentration. Both effects result in more crowding together of the particles and therefore more collisions. This ensures more successful collisions within a certain time. This can be verified using the **universal gas equation**, $pV = nRT$. For a given temperature, it can easily be shown that pressure is proportional to concentration by manipulating the equation to produce $p = \frac{nRT}{V}$, where n is the number of moles.

5.4.3 Temperature

FIGURE 5.7 Increasing the temperature means that there are more particles with enough energy to overcome the activation energy barrier.



Most chemical reactions are observed to proceed more quickly as the temperature is increased. Examples from everyday life that demonstrate this are the cooking of food and setting of some glues. An examination of the Maxwell–Boltzmann curves at different temperatures in figure 5.7 reveals why this is so.

For the given activation energy (E_a), the shape of the graph shows that there is more area under the graph (and hence more particles) to the right of E_a at the higher temperature than at the lower one. A greater proportion of collisions will therefore be successful in overcoming the activation energy barrier.

Another effect of increasing the temperature is that there is an increased frequency of collisions due to the particles moving faster. However, a more sophisticated analysis of the situation reveals that this is secondary to the effect of the energy distributions.

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Video eLesson Temperature and reaction rate (eles-1670)

5.4.4 Surface area

FIGURE 5.8 The higher surface area of the powder (left) results in a higher reaction rate than the solid on the right.

Surface area is an important factor in heterogeneous reactions — reactions where the reactants are in different phases, such as a solid and a liquid. Its effect is due to the fact that, by increasing the surface area, more of a substance is brought into contact with other substances with which it might react. For example, the same mass of wood on a fire burns much faster if it is cut into small pieces than if it is left as a log, and powdered calcium carbonate reacts faster in acid solution than a block of calcium carbonate of the same mass.

In terms of collision theory, an increase in surface area means that more reactant particles can collide with one another which logically produces more collisions. More collisions produces more successful collisions between them in a given period of time, leading to an increased rate of reaction. This is demonstrated in figure 5.8, in which both beakers contain 25 mL of hydrochloric acid and 1 g of calcium carbonate (marble). The marble in the beaker on the left has been ground into a powder; in the beaker on the right, it is in large chunks. The powder has a much higher surface area than the large chunks, resulting in a much higher reaction rate, which is shown by the faster release of carbon dioxide bubbles.

The effect of increasing surface area on the rate of combustion reactions can lead to unexpected, and sometimes catastrophic, results. Solids such as coal and wheat do not normally burn very fast, but as a dust they present a huge surface area to the oxygen in air. All that is needed is an errant spark, from a machine or from static electricity, and the resulting reaction is so fast that it causes an explosion. This effect has destroyed wheat silos and caused tragedies in underground mines.

SAMPLE PROBLEM 4

A gas phase reaction is carried out at four different sets of conditions of temperature and pressure as shown below.
Which set of conditions will produce the fastest rate and why?
Set A. 25 °C and 100 kPa
Set B. 50 °C and 100 kPa
Set C. 50 °C and 150 kPa
Set D. 25 °C and 150 kPa

THINK	WRITE
Recall that higher temperatures and higher pressures will increase the rate of a reaction. Condition Set C meets both these criteria.	Set C will produce the fastest reaction rate because it occurs at both the highest temperature and at the highest pressure. Both these factors increase the rate of a reaction.

PRACTICE PROBLEM 4

With reference to the conditions shown in sample problem 4, which set of conditions will produce the slowest rate of reaction?

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Digital document Experiment 5.2 Rate of hydrogen production – a problem solving exercise (doc-32160)

5.4 EXERCISE

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1. State four methods that can be used to increase the rate of a reaction.
2. Explain why the chemicals used in fireworks are present in powdered form.
3. The reaction between two gases occurs at a measurable rate at 700 °C. If the temperature is held constant at 700 °C and the reacting mixture is compressed, predict and explain what will happen to the rate of this reaction.
4. The evolution of bubbles when a soft drink is opened is due to dissolved carbonic acid decomposing to carbon dioxide and water. The equation for this process is:

$$H_2CO_3(aq) \rightleftharpoons CO_2(g) + H_2O(l)$$

   - (a) This evolution is initially fast, but gradually slows down with time. Why does the rate of carbon dioxide evolution decrease?
   - (b) How would the rate of reaction be affected if the soft drink was warm?

5. The use of powdered coal is being investigated in experimental railway locomotives as an alternative to oil. Powdered coal can be introduced in smaller doses that burn much faster than the traditional lump coal once used in steam locomotives.
   Why does the powdered coal have a much faster rate of combustion?
6. In an investigation of the rate of reaction of gas produced from magnesium and hydrochloric acid, HCl, a student has available three forms of magnesium: powder, small turnings and a strip. Also available are reagent bottles of 0.5 M HCl, 1 M HCl and 2 M HCl. The student could also use a hot water bath and a cool water bath.
   (a) Which combination of reactants and conditions would produce the fastest rate of reaction?
   (b) Which combination would produce the slowest rate of reaction?
7. (a) Gas leaks in confined spaces can be very dangerous — a single spark can lead to an explosion. Explain, in terms of reaction rates, why this is so.
   (b) This reaction is exothermic. Why is this important in producing the explosion?

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5.5 Catalysts and reaction rates

KEY CONCEPT

- The role of catalysts in changing the rate of chemical reactions with reference to alternative reaction pathways and their representation in energy profile diagrams

5.5.1 Catalysts

A **catalyst** is a substance that alters the rate of a chemical reaction without being consumed. It provides an alternative reaction pathway with a lower activation energy. This increases the proportion of collisions with energy greater than the activation energy.

Catalysts are usually used to speed up a reaction. Sometimes they are added to slow a reaction down, in which case they are called negative catalysts or inhibitors. Adding a catalyst does not alter the value of ΔH.

Appropriate catalysts lie at the heart of many industrial processes, especially in green chemistry industries, which attempt to reduce the use of hazardous substances. Companies spend large amounts of money on research into new and improved catalysts, and the results of such research are often among a company's most closely guarded secrets. Biological catalysts, or enzymes, are also responsible for the management of thousands of biological reactions important in maintaining life.

The presence of a catalyst in a chemical reaction provides an alternative pathway for particles to collide with sufficient energy to break bonds. This pathway has a lower activation energy, as shown in figure 5.10.

FIGURE 5.9 A catalyst acts by providing an alternative pathway with a lower activation energy for reactants to form products.

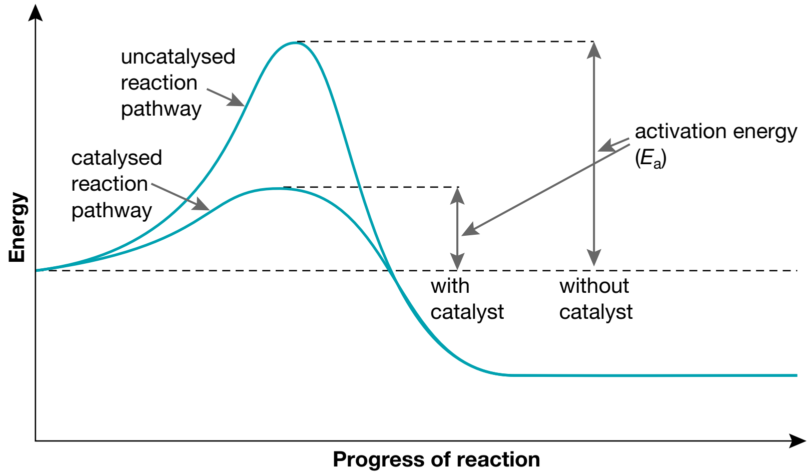
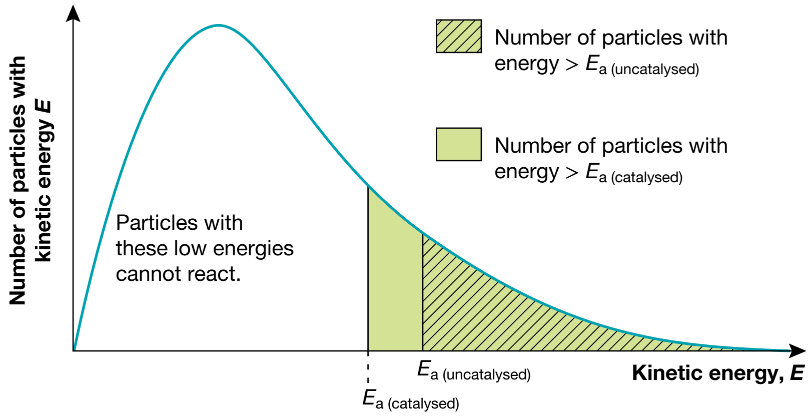
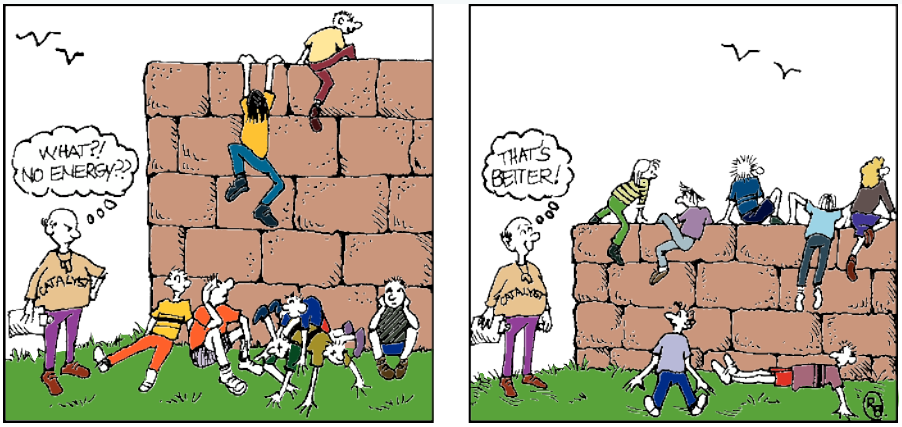


FIGURE 5.10 A catalyst provides an alternative pathway with a lower activation energy, which allows more particles to overcome the new activation energy requirement.



This means that the value of E_a on the Maxwell–Boltzmann curve is shifted to the left and that there are a greater proportion of particles under the curve to the right of this new E_a value. These are the particles that have enough energy to overcome the activation energy requirement, allowing the reaction to occur at a faster rate due to the increase in successful collisions.

FIGURE 5.11 Catalysts reduce the energy required for a reaction to occur.



TIP: Lowering the activation energy characteristic of a catalyst is not the same as increasing the energy of reactant molecules.

on Resources

Digital documents	Experiment 5.3 Reaction rates 1 (doc-31258) Experiment 5.4 Reaction rates 2 (doc-31259)
Video eLesson	Role of catalysts (med-0425)

CATALYTIC CONVERTERS — CATALYSTS IN CAR EXHAUSTS

Catalytic converters are used in the exhaust systems of cars to reduce the amount of gaseous pollutants emitted into the atmosphere. The essential feature of these converters is a rare metal catalyst made from platinum and rhodium. This is finely dispersed over an internal structure that provides a very large surface area, over which the exhaust gases are forced to pass. Table 5.2 shows the effect that these catalysts have on the exhaust gases that pass over them. Catalytic converters not only convert poisonous carbon monoxide and nitrogen oxides to carbon dioxide, nitrogen and oxygen, they also convert hydrocarbons that have not combusted to water and carbon dioxide. They are a very effective way to reduce air pollution and all vehicle manufacturers must include catalytic converters for cars sold in Australia.

FIGURE 5.12 A typical catalytic converter from the exhaust system of a modern car.

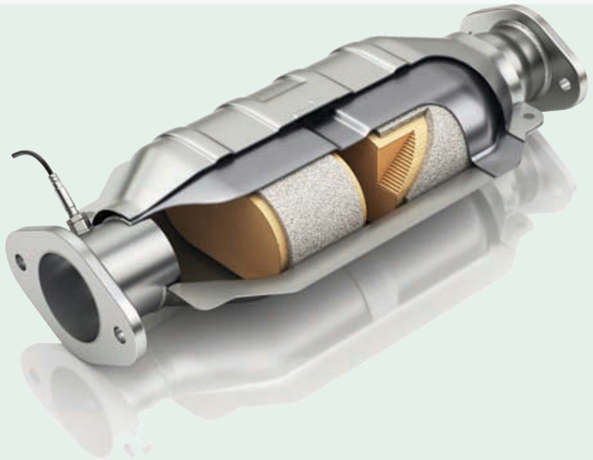


TABLE 5.2 The changes in exhaust gas composition caused by catalytic converters

Before reaction	After reaction
$CO + O_2$	CO_2
hydrocarbons + O_2	$H_2O + CO_2$
nitrogen oxides	$N_2 + O_2$

5.5 EXERCISE

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1. Can a catalyst turn an exothermic reaction into an endothermic one? Explain.
2. Draw an energy profile for an exothermic reaction that occurs with a catalyst. On the same diagram, add an energy profile for the reaction without a catalyst.
3. By referring to a Maxwell–Boltzmann graph, explain how a catalyst increases the rate of a reaction.
4. Catalysts X and Y both catalyse an endothermic reaction that occurs slowly under typical laboratory conditions. It is noted that X produces a faster rate of reaction than Y.
   Summarise this information in the form of an energy profile diagram.

5. Consider a reaction that is represented by the equation below, and is catalysed by a finely divided metal powder, X.

$$\text{A—B(g)} + \text{C(g)} \rightarrow \text{C—A(g)} + \text{B(g)}$$

An important part of the catalytic mechanism is that the catalyst forms temporary bonds with AB on its surface.

(a) Explain why this catalyst is more effective in powdered form than in a metallic lump.
(b) Given that a catalyst lowers the activation energy, what effect do you think the temporary bonds that form between X and AB have on the bonds that need to be broken for this reaction to occur?
(c) Given that the catalyst temporarily holds AB on its surface in a certain way, what else is happening here to increase the rate of the reaction?
(d) Given that product CA does not bind to the surface of the catalyst, explain why X can keep performing its function and is not used up.

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5.6 Review

5.6.1 Summary

How does a chemical reaction occur?

- Chemical reactions show a wide range of reaction rates.
- The Law of Conservation of mass states that matter cannot be created or destroyed in a chemical reaction. A chemical reaction involves breaking old bonds and allowing new bonds to form between atoms that are already present.
- Chemical reaction rates may be explained in terms of collisions between the particles involved. Such collisions must possess the correct orientation and a certain minimum amount of energy — the activation energy.
- A Maxwell–Boltzmann distribution curve is a graph that shows the number of particles with a particular energy graphed against kinetic energy.
- Maxwell–Boltzmann curves are useful in explaining how factors such as temperature increase and catalysts affect the rate of a chemical reaction.

Exothermic and endothermic reactions

- The activation energy is the energy required to break the original bonds, before new bonds can form.
- Enthalpy is a term that may be interpreted as the heat content of a substance. Because all substances have different enthalpies, a chemical reaction will always involve a change in enthalpy, denoted by the symbol ΔH.
- A chemical reaction is exothermic (and has a negative ΔH value) if the energy released as new bonds form is greater than the energy required to break the old bonds.
- A chemical reaction is endothermic (and has a positive ΔH value) if the energy released as new bonds form is less than the energy required to break the old bonds.
- The energy or enthalpy changes that take place during a chemical reaction may be represented by an energy profile diagram.

Factors affecting the rate of a chemical reaction

- The rate of a chemical reaction is affected by factors such as the concentration of the particles, the pressure, the temperature, the surface area and the presence of a catalyst. Each of these can be explained using collision theory.

Catalysts and reaction rates

- A catalyst is a substance that provides an alternative pathway for a reaction. This pathway has a lower activation energy.
- Although a catalyst plays an important role in a reaction, it is not used up and does not affect the nature of the actual products formed.

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5.6.2 Key terms

activation energy the minimum energy required by reactants in order to react
catalyst a substance that alters the rate of a reaction without a change in its own concentration
change in enthalpy the amount of energy released or absorbed in a chemical reaction
endothermic describes a chemical reaction in which energy is absorbed from the surroundings
energy profile diagram a graph or diagram that shows the energy changes involved in a reaction from the reactants through the intermediate stages to the products.
enthalpy a thermodynamic quantity equivalent to the total heat content of a system
exothermic describes a chemical reaction in which energy is released to the surroundings
heat content a thermodynamic quantity equivalent to the total heat content of a system
Maxwell–Boltzmann distribution curve a graph that plots the number of particles with a particular energy (vertical axis) against energy (horizontal axis)
universal gas equation $PV = nRT$, where pressure is in kilopascals, volume is in litres and temperature is in kelvin

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Digital document Key terms glossary – Topic 5 (doc-31397)

5.6.3 Practical investigations

Experiment 5.1

Investigating heat changes in reactions
Aim: To investigate and draw energy diagrams for some exothermic and endothermic reactions.

Digital document doc-31251
Teacher-led video tlvd-0742

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Digital document Practical investigation logbook (doc-31398)
Experiment 5.2 Rate of hydrogen production – a problem solving exercise (doc-32160)
Experiment 5.3 Reaction rates 1 (doc-31258)
Experiment 5.4 Reaction rates 2 (doc-31259)

5.6 Exercises

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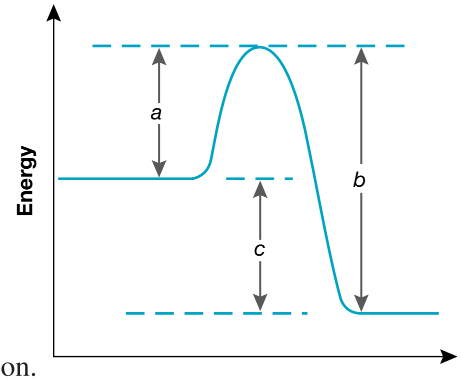
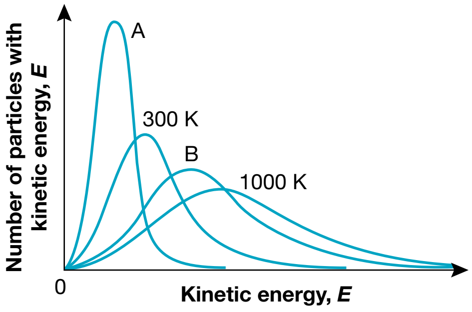
5.6 Exercise 1: Multiple choice questions

1. Most chemical reactions display a rate increase with increasing temperature. This can be explained by:
   - A. the temperature lowering the activation energy
   - B. the particles having more collisions involving higher energies
   - C. the temperature making the reactant's bonds weaker
   - D. the temperature making the collisions between the particles more elastic.
2. An energy profile diagram for a chemical reaction is shown on this graph. On this graph:
   - A. *a* represents the activation energy for the forward reaction and *c* represents the activation energy for the backward reaction
   - B. *a* represents the activation energy for both the forward and the reverse reactions
   - C. *b* represents the activation energy for both the forward and the reverse reactions
   - D. *a* represents the activation energy for the forward reaction and *b* represents the activation energy for the backward reaction.



3. Which of the following statements about activation energies is correct?
   - A. Activation energies are always positive.
   - B. Activation energies are always negative.
   - C. Activation energies are positive only for endothermic reactions.
   - D. Activation energies are negative only for exothermic reactions.
4. These Maxwell–Boltzmann distribution graphs show a sample of gas at four different temperatures.
   Which of the following statements is true?
   - A. Graph A represents the highest temperature.
   - B. The area under graph A is greater than the area under graph B.
   - C. A possible temperature for graph B could be 600 K.
   - D. Graph A contains more fast-moving molecules than graph B.



5. A sample of gas is heated. Which of the following statements is incorrect?
   - **A.** The most common speed for its molecules increases.
   - **B.** The average speed of its molecules increases.
   - **C.** The number of collisions between molecules, per unit time, increases.
   - **D.** The area under the Maxwell–Boltzmann distribution curve increases.
6. When zinc is added to hydrochloric acid, the rate at which hydrogen gas is evolved can be used as a measure of reaction rate. Which of the following combinations produces the fastest rate of hydrogen gas evolution?
   - **A.** Powdered zinc added to 2 M HCl at 20 °C
   - **B.** Powdered zinc added to 2 M HCl at 40 °C
   - **C.** Granular zinc added to 2 M HCl at 20 °C
   - **D.** Granular zinc added to 2 M HCl at 40 °C
7. When a reaction occurs at a higher temperature, two important things happen.
   Effect 1: More collisions between particles occur each second.
   Effect 2: More energy is involved in these collisions.
   Which of the following statements is true?
   - **A.** Effect 1 is more important than effect 2 for increasing the rate of a reaction.
   - **B.** Effect 2 is more important than effect 1 for increasing the rate of a reaction.
   - **C.** Effects 1 and 2 are both equally significant for any increase in reaction rate.
   - **D.** Neither 1 nor 2 affects the rate of the reaction.
8. An industrial process involving an exothermic reaction requires that the reaction be slowed down so that the heat evolved can be collected safely. In order to achieve this:
   - **A.** the ΔH value of the reaction needs to be decreased
   - **B.** the ΔH value of the reaction needs to be increased
   - **C.** the activation energy of the reaction needs to be increased
   - **D.** the activation energy of the reaction needs to be decreased.
9. To lower the activation energy of a reaction,
   - **A.** an increase in temperature is required.
   - **B.** a catalyst is required.
   - **C.** an increase in concentration is required.
   - **D.** an increase in the surface area of reactants is required.
10. The following reaction has an activation energy of 183 kJ mol^{-1}.

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

The reverse reaction: $$H_2(g) + I_2(g) \rightarrow 2HI(g)$$

has an activation energy of 157 kJ mol^{-1}.
The ΔH value for the first equation above is:

A. -340 kJ mol^{-1} **B.** $+340$ kJ mol^{-1} **C.** -26 kJ mol^{-1} **D.** $+26$ kJ mol^{-1}.

5.6 Exercise 2: Short answer questions

1. Based on your everyday experience, classify the following chemical reactions as either slow, moderate of fast.
   - **a.** The rusting of iron.
   - **b.** The burning of petrol in a car engine.
   - **c.** The reacting of chemicals in a glow stick to produce light.
   - **d.** The reacting of chemicals in the battery of a mobile phone to produce electricity.
   - **e.** The dissolving of old nail polish by nail polish remover.
   - **f.** The drying of plaster in a cast around a broken bone.

2. Using the concepts of activation energy and reaction pathways, explain how a catalyst can speed up the rate of a chemical reaction.
3. The dehydration properties of concentrated sulfuric acid are often demonstrated using sucrose, $C_{12}H_{22}O_{11}$. Black carbon and steam, along with sulfur dioxide and considerable heat, are produced. The equation for this reaction is:

$$2C_{12}H_{22}O_{11}(s) + 2H_2SO_4(aq) + O_2(g) \rightarrow 22C(s) + 2CO_2(g) + 24H_2O(g) + 2SO_2(g)$$

   Explain why this reaction occurs much faster when castor sugar, rather than granulated sugar, is used as a source of sucrose.
4. Maxwell–Boltzmann curves show that particles have a wide range of velocities and energies. Using collision theory, explain why this is so.
5. Use a Maxwell–Boltzmann curve to clearly explain why:
   a. a catalyst can alter the rate of a reaction
   b. increasing temperature usually increases the rate of a reaction.
6. Comment on the rates observed for each of the following situations. For each one, use the collision theory for chemical reactions to explain the rate behaviour observed.
   a. Nail polish dries quicker on a hot day than on a cold day.
   b. A piece of steel wool burns in a Bunsen flame, but the same mass of solid steel does not.
   c. A pinch of manganese dioxide added to hydrogen peroxide continues to produce oxygen for as long as fresh hydrogen peroxide is added.
   d. The chemicals mixed by a panelbeater to make body filler harden faster on a hot day than on a cold day.
   e. The addition of vinegar to bicarbonate of soda causes an evolution of gas that is quick at first but then slows down.
   f. Photographers using infrared-sensitive film store it in a refrigerator before use.
7. The reaction between hydrogen gas and nitrogen(IV) oxide is represented by the equation:

$$2H_2(g) + 2NO_2(g) \rightarrow 2H_2O(g) + N_2(g)$$

   a. Explain why the rate of this reaction decreases with time.
   b. Explain why the progress of this reaction can be monitored by measuring the drop in pressure.
8. The decomposition of ammonia to produce nitrogen and hydrogen according to:

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

   has an activation energy of 330 kJ mol^{-1} and a ΔH value of +92 kJ mol^{-1}. If tungsten is used as a catalyst, the activation energy is 163 kJ mol^{-1}.
   a. Give a definition for the term 'catalyst'.
   b. Show all of the information above on an energy profile diagram for this reaction.
   The reverse reaction to this as shown by the equation:

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

   is a very important reaction in industry.
   c. Calculate the activation energy for the uncatalysed version of this reaction.
   d. Calculate the activation energy when tungsten is used as a catalyst.

9. Enzymes are a very important class of biochemical molecules that are often described as biological catalysts. For example, the enzyme lipase is an important digestive enzyme that assists in the breakdown of fats according to the following generalised equation.

$$\text{fat} + \text{water} \overset{\text{lipase}}{\rightleftharpoons} \text{fatty acids} + \text{glycerol}$$

   a. Using the concept of activation energy, explain why the rates of reactions such as this are much greater in the presence of lipase.
   b. How does the amount of lipase present at the start of a reaction such as this compare with the amount present at its completion?

10. The rate of a chemical reaction is a very important consideration in industrial chemistry where chemicals are made on a large scale. Reactions need an acceptable rate to be economical. A number of important industrial reactions have rates that are too slow at even moderate temperatures and, therefore, need to be sped up. Further increasing the temperature is a common means of achieving this; however, sometimes this is an inappropriate strategy.

    Suggest two other methods by which an increase in reaction rate may be produced in these situations.

5.6 Exercise 3: Exam practice questions

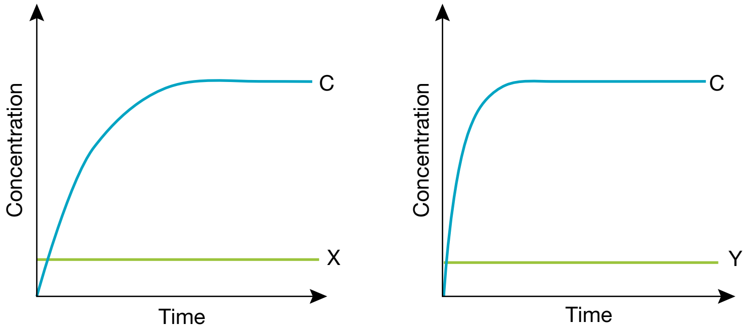
Question 1 (8 marks)

The gas phase reaction between two gases, A and B, to form C, may be represented by the following equation.

$$A(g) + B(g) \rightarrow C(g)$$

The progress of this reaction can be monitored by measuring the production of product (C).

This reaction was investigated in the presence of a fourth substance, X, and then again in the presence of substance Y. Equal amounts of A and B were used in both experiments. The concentrations of C and either X or Y are shown in the following graphs.



a. At which stage in each reaction is the production of C occurring at the fastest rate? Explain. **2 marks**
b. Explain why the concentration of C reaches the same maximum in both experiments. **1 mark**
c. What role can be attributed to substance Y in the second experiment? Give two pieces of evidence to support your answer. **3 marks**
d. Substance X may or may not be performing the same role as substance Y. Suggest an experiment that would help you decide. **2 marks**

Question 2 (7 marks)

An important chemical (C) is made on a large scale in industry from two immiscible liquids (A and B). Both B and C are less dense than A. The equation for the reaction involved is:

$$\mathrm{A\,(l)} + \mathrm{B\,(l)} \rightarrow \mathrm{C\,(s)}\ \Delta H = +\text{ve}.$$

The traditional process involves pumping liquid B across the surface of a vat containing liquid A. The rate of pumping is carefully adjusted so that by the time liquid B has reached the opposite side of the vat, the reaction is complete. This process is shown in diagram 1.

A modification to this method has been proposed for making substance C. In this method, substance B is introduced into the base of the vat in the form of a fine spray, but at a rate to match the pumping rate from before. A fan blowing air across the surface assists in the collection of C as it rises to the surface. It is planned that this new process will operate at the same temperature as the original one. This process is shown in diagram 2.

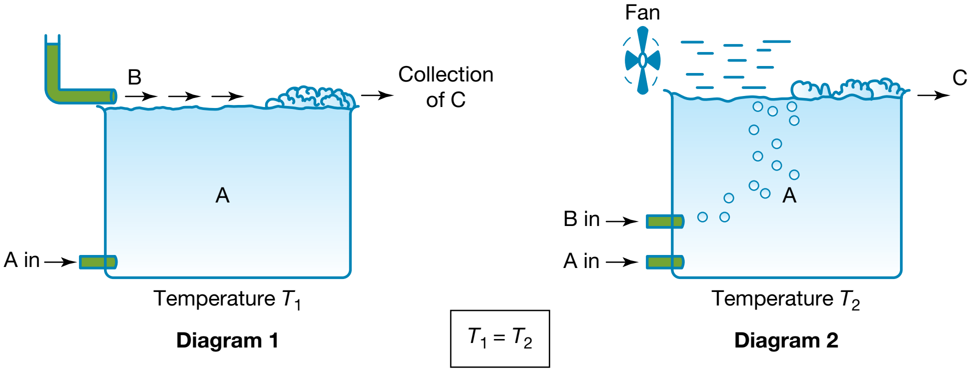


Diagram 1

$T_1 = T_2$

Diagram 2

a. Is the above reaction exothermic or endothermic? **1 mark**

b. Which of the above methods would produce substance C the quickest? **1 mark**

c. Use the collision theory for reacting particles to explain your answer for (b). In your answer, consider which methods would change the reaction rate, and which methods would be expected to have little influence. **2 marks**

d. In terms of substance C, explain one disadvantage of the second method and how this can be minimised. **2 marks**

e. As an alternative modification to the original method, it has been proposed that the temperature of the two reacting liquids (A and B) be increased, even though this will require more energy.

Explain why this will enable liquid B to be pumped across the surface of liquid A at a faster rate. **1 mark**

Question 3 (8 marks)

In chemistry, a number of reactions are collectively referred to as 'clock reactions'. These reactions produce a sudden colour change after a period of time. One of the better known examples of such reactions is that between iodide ions and persulfate ions ($S_2O_8^{2-}$) in the presence of thiosulfate ions ($S_2O_3^{2-}$) and starch.

Two reactions are involved:

$$\text{Reaction 1: } 2I^-(aq) + S_2O_8^{2-}(aq) \rightarrow I_2(aq) + 2SO_4^{2-}(aq)$$

$$\text{Reaction 2: } I_2(aq) + 2S_2O_3^{2-}(aq) \rightarrow 2I^-(aq) + S_4O_6^{2-}(aq)$$

The iodine produced by reaction 1 is immediately removed by reaction 2. However, $S_2O_3^{2-}$ ions are also consumed and are eventually all used up. After this time, iodine builds up and is detected by the starch present, which forms an intensely coloured dark blue complex. This occurs at iodine concentrations as low as 10^{-5} M, making starch an excellent indicator for this reaction.

If the amount of $S_2O_3^{2-}(aq)$ is kept constant, the appearance of the dark blue colour may be used to measure the rate of reaction 1.

In one such experiment using 0.2 M $KI(aq)$ solution, 0.2 M $Na_2S_2O_8(aq)$ and 0.1 M $Na_2S_2O_3(aq)$ solutions, the following results were obtained.

Trial number	*V*(I– (aq)) solution (mL)	$S_2O_8^{2-}(aq)$ volume solution (mL)	$S_2O_3^{2-}(aq)$ volume solution (mL)	*V*(water) (mL)	*V*(starch) solution (mL)	Time for blue colour to appear (s)
1	20	20	20	40	10	220
2	20	40	20	20	10	150
3	40	20	20	20	10	142

a. Explain how these results show that increasing $S_2O_8^{2-}(aq)$ concentration produces a faster rate in reaction 1. Compare two appropriate trials from the data above as part of your explanation. **2 marks**

b. Use the results above to explain how the rate of reaction is affected by the concentration of iodide ions. Select two appropriate trials to support your explanation. **2 marks**

c. The experiment is repeated using solutions that were stored in a refrigerator for 24 hours. These solutions were used immediately after being removed. How would the reaction times in the table be affected? **1 mark**

d. What is the purpose of the two different amounts of water used in the trials? **2 marks**

e. Explain why the amount of $S_2O_3^{2-}(aq)$ solution is kept constant in each trial. **1 mark**

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AREA OF STUDY 2
HOW CAN THE YIELD OF A CHEMICAL PRODUCT BE OPTIMISED?

6 Extent of chemical reactions

6.1 Overview

Numerous **videos** and **interactivities** are available just where you need them, at the point of learning, in your digital formats, learnON and eBookPLUS at www.jacplus.com.au.

6.1.1 Introduction

Equilibrium reactions, or reversible reactions, are chemical reactions that appear not to use up all their reactants. While this might seem strange at first, such reactions are very common. Chemical reactions involving equilibria are all around us. Weak acids are examples of substances that produce equilibrium reactions when dissolved in water. The sour taste of lemons is due to a weak acid — citric acid. Many other equilibrium reactions occur inside our bodies and play a vital role in keeping us alive and healthy.

Equilibrium reactions respond to changes, which is an important feature in how they function to keep us healthy. Knowledge of the equilibrium law and the ability to predict the response to change is vital to the understanding of these reactions. Additionally, equilibrium reactions are at the heart of processes that manufacture some of our most widely used chemicals. A thorough knowledge of equilibrium reactions is therefore essential to their efficient manufacture.

Understanding of equilibrium principles presented in this topic, is built upon knowledge of reaction rates and their explanations using collision theory, thermochemical equations and the broad division of reactions into exothermic and endothermic classifications. These principles are then combined with moles ratios and stoichiometry to calculate moles, concentrations of substances and how to manipulate chemistry to maximise products.

FIGURE 6.1 The sour taste of lemons is due to an equilibrium reaction involving citric acid and water.

6.1.2 What you will learn

KEY KNOWLEDGE

In this topic, you will investigate:
- 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 (*Kc* 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.

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PRACTICAL WORK AND INVESTIGATIONS

Practical work is a central component of learning and assessment. Experiments and investigations, supported by a **Practical investigation logbook** and **Teacher-led videos**, are included in this topic to provide opportunities to undertake investigations and communicate findings.

on Resources

Digital documents	Key science skills (doc-30903)
	Key terms glossary – Topic 6 (doc-31400)
	Practical investigation logbook (doc-31401)

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To access key concept summaries and past VCAA exam questions download and print the **studyON: Revision and practice exam question booklet** (doc-31402).

6.2 Reversible and irreversible reactions

KEY CONCEPT

- The distinction between reversible and irreversible reactions, and between rate and extent of a reaction

6.2.1 Reversible reactions

In all the stoichiometric calculations you have done so far, an important assumption has been that the reaction proceeds to completion. In other words, you have assumed, subject to mole ratios and amounts present, that all reactants are converted into products. This allowed the amount of expected product to be calculated. While many reactions follow this pattern, many do not go to completion. The following two examples illustrate this point.

Reaction 1: The decomposition of hydrogen bromide

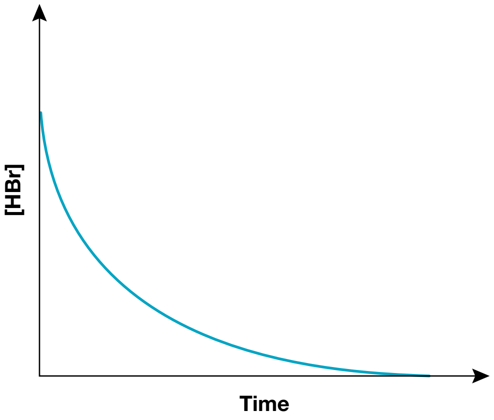
If hydrogen bromide is placed in a suitable container and heated, it decomposes according to the following equation:

$$2HBr(g) \rightarrow H_2(g) + Br_2(g)$$

If the products are analysed after some time, it is found that the amounts of hydrogen and bromine are as predicted from a normal stoichiometric calculation. If the concentration of the hydrogen bromide is monitored against time, a graph similar to that shown in figure 6.2 is obtained.

Another way to describe this reaction is that it 'goes completely to the right'. The 'right', of course, means the product side of the chemical equation.

FIGURE 6.2 A typical concentration versus time graph for the decomposition of hydrogen bromide



Reaction 2: The decomposition of hydrogen iodide

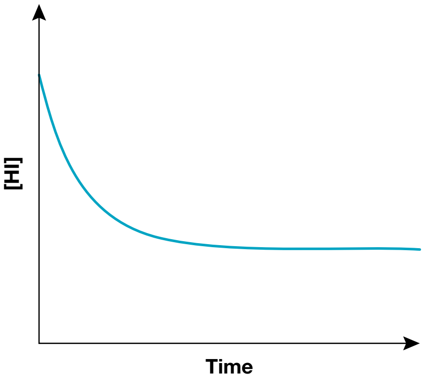
The equation for the decomposition of hydrogen iodide is:

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

At first glance, you might expect this decomposition to be very similar to that shown for hydrogen bromide. However, when this decomposition is attempted under similar conditions to the hydrogen bromide reaction, *the yield of hydrogen and iodine is always less than the stoichiometric prediction*. This occurs no matter how long you wait. Furthermore, it appears that the concentrations of all species reach certain values and thereafter remain constant. The graph in figure 6.3 shows this effect.

This second example illustrates what we call an **equilibrium reaction**, which occur when reactions do not completely convert all the reactants into products — some reactants always remain, mixed with the products of the reaction. Because such reactions are quite common, a method using them to make predictions would be an advantage. The profitability of an important industrial process costing millions of dollars to research and develop could depend on such calculations.

FIGURE 6.3 A typical concentration versus time graph for the decomposition of hydrogen iodide



Strictly speaking, all chemical reactions are equilibrium reactions. However, in many cases the degree of backward reaction (that is, products re-forming reactants) is so small that it can effectively be ignored.

Equilibrium reactions are also called **reversible reactions**, as opposed to **irreversible reactions**. Their equations show a double arrow ($\rightleftharpoons$) rather than a single arrow ($\rightarrow$). An example of an irreversible reaction is the combustion of fuel. When a fuel burns to produce carbon dioxide and water, these products do not react with each other to re-form the fuel.

Equilibrium reactions can be classified as homogeneous or heterogeneous, depending on the physical states of the substances involved. If these states are all the same, it is called a homogeneous equilibrium. If they are different, it is heterogeneous, and are discussed in greater detail in section 6.3.1.

- **Reversible reactions are equilibrium reactions where reactants re-form into products to a significant extent. The yield of the products is always less than the stoichiometric prediction.**
- **Irreversible reactions occur only in the forward direction; reactants do not re-form from products.**

6.2.2 The distinction between rate and extent of a reaction

It is important that the terms ‘rate’ and ‘extent of a reaction’ are not confused. The rate of a reaction is simply an indication of how fast it occurs. This shows how long it takes to establish the position of equilibrium. The extent of a reaction describes the degree to which reactants are converted into products. This can also be thought of as the ‘position’ of equilibrium or ‘how far to the right’ (with respect to the equation) it is situated. This degree of conversion may be quantified by reference to the equilibrium constant, K_c, for the reaction concerned (see section 6.4.1 for more on the determination and use of K_c values). A high value for K_c indicates a significant conversion of reactants into products, and such a reaction would be described as having occurred to a significant extent. A low value indicates the opposite — that the reaction has occurred only to a small extent and there has been only a small amount of conversion of reactants into products.

It is possible to have slow reactions occur to a great extent as well as other combinations between rate and extent. An explosion, for example, can be described as a fast reaction that occurs to a large extent, whereas it is possible to have equilibrium reactions that occur at moderate rates and to moderate extents.

A catalyst has no effect on the degree of conversion of reactants into products (the position of equilibrium). A catalyst affects the rate of the forward reaction and the rate of the backward reaction equally. It merely alters the time taken to get to equilibrium, not the position of it.

- **The rate of reaction is an indication of how fast a reaction proceeds.**
- **The extent of a reaction is the degree to which reactants are converted into products and describes the equilibrium position.**
- **Catalysts alter the rate of reactions but not their extent. They do not alter the equilibrium position.**

6.2 EXERCISE

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1. What is the difference between a reversible reaction and an irreversible reaction?
2. What is the difference between the rate of a reaction and the extent of a reaction?
3. Hydrogen peroxide decomposes to water and oxygen. The extent of this reaction is large. Explain why bottles of hydrogen peroxide may be kept for long periods of time but eventually need to be replaced.

Questions 4 and 5 refer to the following information.

A student decides to investigate three different reversible reactions as a prelude to her practical investigation. Each of these is set up during the same lesson and then observed again during her next lesson the next day.

Her initial purpose is to attempt a classification of each reaction according to the following table.

		Extent	
		Small	**Large**
Rate	**Slow**	Type 1	Type 2
	Fast	Type 3	Type 4

Upon her return the following day, she observes the following:

- Reaction I: Large amount of product. No detectable reactants.
- Reaction II: No apparent change. No detectable products.
- Reaction III: A mixture of reactants and products is observed.

4. Attempt to classify each of the reactions according to the table. Note that there may be more than one classification for each reaction.
5. For those reactions with multiple classifications, suggest a possible follow up experiment that might be able to distinguish them.

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6.3 Homogenous equilibria

KEY CONCEPT

- 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

6.3.1 Homogeneous and heterogeneous reactions

Chemical reactions may be classified in a number of ways, and the chosen classification often depends on the context in which the reaction is being studied. One simple classification is based on the physical states (or phases) of the reagents involved. In a **homogenous reaction**, the reaction occurs entirely within the same physical state. The most common examples of such reactions occur either in the gaseous phase or in solution. A homogeneous equilibrium is one in which all the species in the equilibrium mixture are all in the same physical state. A **heterogeneous reaction** is one that occurs at a boundary or interface between two different physical states. An obvious example of a heterogeneous reaction is a solid reacting with either a liquid or gas. Heterogeneous reactions can also occur between liquids that are **immiscible**, thus forming a boundary when they are mixed together.

6.3.2 The dynamic nature of equilibrium

Although it is tempting to think that the reaction has stopped when it reaches equilibrium, further investigation reveals that this is not so. Instead, *the forward and reverse reactions are still occurring, but at the same rate*. The reagents in the reaction are thus being formed and used at the same rate, with their concentrations showing no overall change. Equalibrium is dynamic, not static.

Experiments involving the use of radioactive tracers may be used to verify the dynamic nature of the equilibrium state. For example, if the hydrogen iodide system in section 6.2.1 is heated and allowed to come to equilibrium, it is possible to remove some of the iodine and replace it with the same amount of radioactive iodine — iodine containing the ^{131}I isotope. As isotopes are chemically identical, such a change would have no effect on the chemical nature of the equilibrium. If the system is examined again some time later, the radioactive iodine is found to be distributed between the hydrogen iodide and the iodine molecules. This can be explained only if the forward and reverse reactions are still proceeding.

During dynamic equilibrium the forward and reverse reactions are still occurring, but at the same rate. The reaction does not stop.

There are many different ways that a reaction can work itself towards equilibrium. The scenario that most people would think of first is when the reactants are mixed together. In this situation, concentration effects dictate that the initial rate of the forward reaction would be considerably greater than the initial rate of the backward reaction. However, as the reaction proceeds, concentrations change — reactant concentrations drop, while product concentrations rise. This means that the rate of the forward reaction decreases, while the rate of the backward reaction increases. These changes will occur until the two reaction rates are equal. The reaction will now be at equilibrium. However, another scenario might be when products are mixed together, of the two reactions that occur, the backward reaction will initially be faster than the forward reaction. However, concentration changes will once again affect these rates until they are both equal and the reaction attains equilibrium.

In between these two extremes there are an infinite number of possible starting conditions for an equilibrium reaction. In each case it will be how the initial rate of the forward reaction compares with the initial rate of the backward reaction that determines how the reaction ultimately reaches its equilibrium state.

on Resources

Video eLesson Dynamic equilibrium and concentrations of products and reactants (med-0426)

6.3.3 Dynamic equilibrium and collision theory

As a reaction proceeds towards equilibrium, there are collisions between reactant particles and collisions between product particles. Some of these collisions have enough energy to overcome their respective activation energies and so form either more products or re-form more reactants. As the concentrations of the reactants and products rise and fall because of this, there will come a point where the number of successful collisions going in one direction is balanced by the number of successful collisions in the opposite direction. In other words, the rates of these opposing reactions will be equal and the reaction will be at equilibrium.

6.3.4 Representing chemical equilibria

Chemical equilibria can be represented using balanced chemical and thermochemical equations, and using graphs.

Using balanced chemical and thermochemical equations

Balanced chemical and thermochemical equations can be used to summarise equilibrium reactions in the same way as for the reactions you have met previously in this course. The main difference is that double arrows ($\rightleftharpoons$) are used to emphasise that the reaction is reversible. As the position of an equilibrium is affected by temperature differently for exothermic and endothermic reactions, thermochemical equations convey slightly more information about a reversible or equilibrium reaction than do equations without a ΔH value.

Because a reversible reaction involves both forward and reverse reactions, it is just as valid to write the equation the opposite way around. For example, the equations

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

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

both refer to the same equilibrium reaction.

This has the potential to produce confusion when discussing forward and reverse reactions. To overcome this, the accepted procedure is to write the equation either way. It is then understood that any subsequent discussion of reactants, products, forward, reverse reactions, K_c, etc refers to the equation as it has been written.

Graphical representations

Using graphs of equilibrium situations can be a very informative way to summarise and understand an equilibrium reaction, as well as produce a deeper understanding of what is happening in such situations.

Two types of graphs are frequently used:

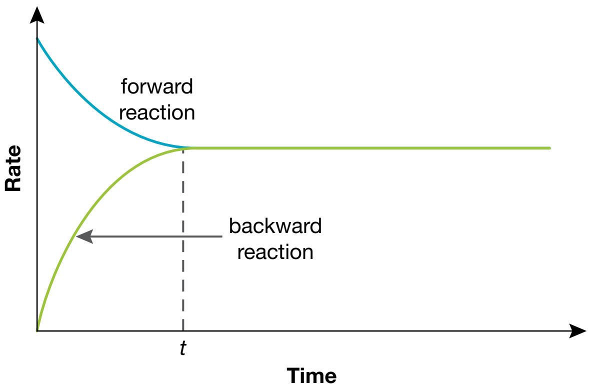
- rate versus time graphs
- concentration versus time graphs.

To illustrate these, consider a situation where substance A is added to a container and allowed to come to equilibrium with products B and C at constant temperature, according to the equation:

$$A(g) \rightleftharpoons B(g) + 2C(g)$$

As discussed in topic 5, the rate of a reaction depends on concentration. As substance A is used up, its concentration drops and so does the rate of the forward reaction. Conversely, as the concentrations of substances B and C increase, so too does the rate of the backward reaction. A general rate versus time graph, as shown in figure 6.4, illustrates this. There will be a net forward reaction until time t, when the two rates become equal and equilibrium is established. Thereafter, there will be no change in these rates as the net concentrations of reactants and products remain constant.

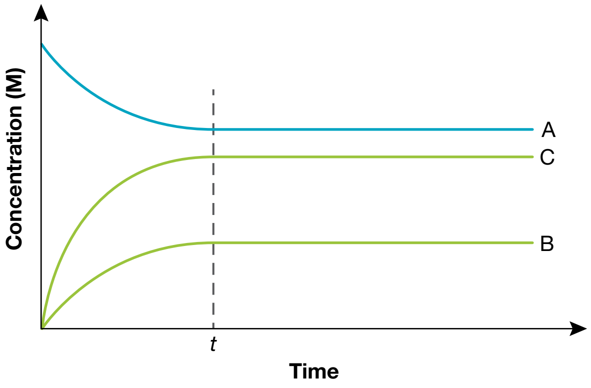
FIGURE 6.4 An example of a rate versus time graph



This equilibrium could just as easily be produced by mixing substances B and C together and allowing a net backward reaction to produce equilibrium. In this case, the graph would show a decreasing rate for the backward reaction and an increasing rate for the forward reaction until equilibrium is once again established.

It is also possible to represent this scenario using concentration versus time graphs. In the first scenario above (forward reaction), such a graph might appear as shown in figure 6.5. Here, the final concentrations of substances A, B and C depend on their initial concentrations, the stoichiometry in the equation and the value of the equilibrium constant (i.e. the degree of conversion).

FIGURE 6.5 An example of a concentration versus time graph



The concentrations of the substances involved in figure 6.5 increase or decrease depending on whether they are produced or consumed. They also change by amounts that reflect the stoichiometry of the reaction. In this example, substance A decreases by the same amount that substance B increases, which can be seen by the 1:1 ratio between them in the equation. Substance C increases by twice the amount that substance B does, shown by the 2:1 ratio involved.

If this reaction had a catalyst added to it, the only change to this graph would be that time, *t*, would be lower. In other words, equilibrium would be attained faster. However, the final concentrations of substances A, B and C would not be altered.

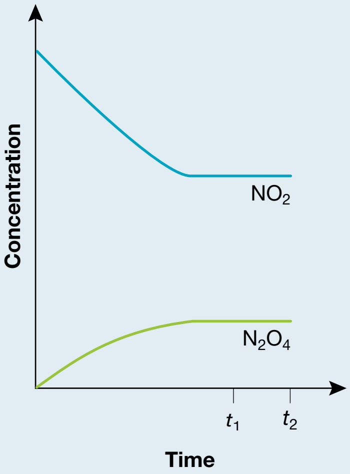
Concentration–time graphs are very useful when considering changes made to a reaction once it has reached equilibrium. This is discussed further in section 6.6.2.

SAMPLE PROBLEM 1

The following graph shows the reversible reaction for

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

Use this graph to answer the following questions.



a. **How does the concentration of NO_2 at t_1 compare to t_2?**
b. **Describe what is happening to the NO_2 using the information in the graph.**
c. **What is the significance of the flattening out of the NO_2 graph at the same time as the flattening out of the N_2O_4 graph?**

Teacher-led video: SP1 (tlvd-0680)

THINK	WRITE
a. This is a concentration–time graph. Horizontal sections mean that the species is at its equilibrium concentration and will not alter further unless a change is made. Here NO_2 is at equilibrium.	**a.** The concentration of NO_2 at t_1 will be equal to its concentration at t_2.
b. The graph indicates that NO_2 is decreasing (but at an ever slower rate) while N_2O_4 is increasing (indicating an ever faster rate). This is due to the dynamic nature of equilibrium. The changes will occur until the two rates equalise at equilibrium.	**b.** NO_2 is decreasing but at an ever slower rate until the reaction reaches equilibrium. After this its value stays constant. This happens because a competing backward reaction that reforms NO_2 gradually gets faster, which reduces the rate at which NO_2 drops. Eventually the rates of the two reactions equalise and the reaction is at equilibrium. After this there will be no further concentration changes.
c. Equilibrium always occurs at a point in time when the two rates first become equal. This cannot happen at different times otherwise concentration changes would still occur.	**c.** Equilibrium has been attained. This occurs when the two rates first become equal, resulting in no net change to concentrations thereafter.

PRACTICE PROBLEM 1

Answer the following questions with reference to the same reaction and graph for sample problem 1

a. How does the concentration of N_2O_4 at t_1 compare to t_2?

b. Explain what is happening to the N_2O_4 in the light of the information in the graph.

on Resources

Digital document Experiment 6.1 Modelling an equilibrium (doc-31261)

6.3 EXERCISE

To answer questions online and to receive **immediate feedback** and **sample responses** for every question, go to your learnON title at www.jacplus.com.au.

1. Explain what is meant by the phrase ‘the dynamic nature of equilibrium’.
2. Using radioactive tracers (small amounts of radioactive isotopes), it is possible to demonstrate the dynamic nature of equilibrium. Describe how such an experiment may be performed, choosing a specific example to illustrate your answer.
3. When molecular iodine is mixed with iodide ions, an equilibrium is set up as triiodide ions are produced. The equation for this process is:

$$I_2(aq) + I^-(aq) \rightleftharpoons I_3^-(aq)$$

Suppose that, once this equilibrium is established, some iodine is removed and replaced by exactly the same amount of radioactive iodine.

If this reaction is examined sometime later, describe the expected observations if

(a) equilibrium is static.
(b) equilibrium is dynamic.

4. When hydrogen iodide is placed in a sealed container and heated, it begins to decompose into its constituent elements according to the equation

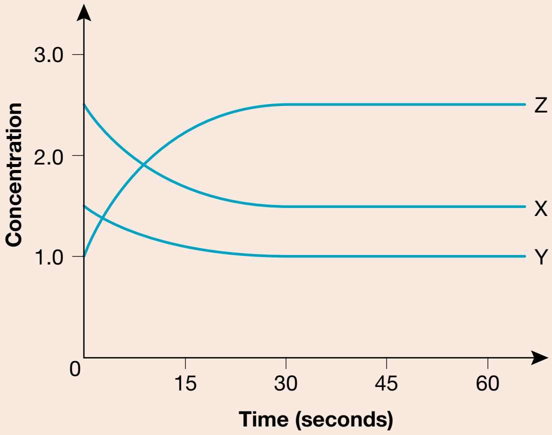
$$2HI(g) \rightleftharpoons H_2(g) + I_2(g)$$

Comment on the comparative rates of the forward and reverse reactions at the following stages.

(a) Just after the reaction has started
(b) As the reaction is approaching equilibrium
(c) When the reaction reaches equilibrium
(d) After the reaction has reached equilibrium

Question 5 refers to the following concentration–time graph for the equilibrium reaction represented by the equation

$$2X(g) + Y(g) \rightleftharpoons 3Z(g)$$



5. (a) Describe the appearance of this graph if it was extended to the 120 second mark.
   (b) Explain the changes in the concentration of Z in comparison to the changes in concentrations of X and Y.
   (c) At time zero, describe the initial constitution of the reaction mixture and what subsequently happens in terms of reaction rates.
6. In terms of collision theory, explain why one reaction always slows down while the other always speeds up when a reaction is progressing towards equilibrium.

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6.4 Calculations involving equilibrium systems

KEY CONCEPT

- 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

6.4.1 The equilibrium law and K_c values

Every reaction, given enough time, reaches a point at which the composition of the reaction mixture no longer changes and the system is said to be at equilibrium. If the concentrations of the substances present are measured at this stage, a large amount of seemingly unrelated data may be obtained. However, on closer analysis, a surprising result emerges.

Recall the hydrogen iodide reaction from section 6.2.1.

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

Table 6.1 shows the results of experiments where different initial amounts of the three substances involved were mixed and heated, and enough time allowed for equilibrium to be reached. The resulting equilibrium concentrations were then measured. Table 6.2 shows a similar set of results for the synthesis of ammonia from nitrogen and hydrogen.

The right-hand column in both tables shows that it is possible to write a concentration fraction involving the equilibrium concentrations that has a constant value. A closer inspection of this fraction reveals that its form is closely related to the equation for the reaction. The numerator of the fraction contains the products and the denominator contains the reactants. The coefficients from the chemical equation become indices to their respective concentrations in this fraction. This is the **equilibrium law**. The value of this fraction at equilibrium is called the **equilibrium constant**, which is often assigned the symbol K_c.

Note that square brackets are used to denote concentration measured in M (or mol L^1).

TABLE 6.1 Data for the reaction $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ (at 458 °C)

Equilibrium amounts			$K_c = \frac{[HI]^2}{[H_2][I_2]}$	
$[H_2]$ (M)	$[I_2]$ (M)	[HI] (M)		
0.002 484	0.002 514	0.016 95	46.0	(i)
0.002 636	0.002 305	0.016 64	45.7	
0.004 173	0.001 185	0.014 94	45.1	
0.003 716	0.001 478	0.015 76	45.2	
0.002 594	0.002 597	0.017 63	46.3	(ii)
0.001 894	0.001 896	0.012 83	45.9	
0.001 971	0.001 981	0.013 42	46.1	
0.002 413	0.002 424	0.016 41	46.0	

(i) Equilibrium established by combination of hydrogen and iodine

(ii) Equilibrium established by decomposition of hydrogen iodide

TABLE 6.2 Data for the reaction $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

	Equilibrium amounts			$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3}$
Run	**$[N_2]$ (M)**	**$[H_2]$ (M)**	**$[NH_3]$ (M)**	
1	0.0011	0.0011	2.73×10^{-7}	0.051
2	0.0025	0.0055	4.58×10^{-6}	0.050
3	0.55	0.65	0.0886	0.052
4	0.25	0.75	0.074	0.052

For the general reaction:

$$aA + bB + cC + dD + \ldots \rightleftharpoons zZ + yY + xX + \ldots$$

the equilibrium constant is:

$$K_c = \frac{[Z]^z[Y]^y[X]^x \ldots}{[A]^a[B]^b[C]^c[D]^d \ldots}$$

The value of the equilibrium constant can be used to indicate the extent of the reaction.

- If the value is large ($K_c > 10^4$), we can predict that there has been a significant conversion of reactants into products by the time that equilibrium was reached.
- If the value is between $K_c = 10^4$ and $K_c = 10^{-4}$ we can predict the extent of the reaction is moderate with concentrations of both products and reactants present at equilibrium.
- If the value is small ($K_c < 10^{-4}$) we can predict that not much conversion has occurred, and the position of equilibrium favours the back reaction.

When describing an equilibrium qualitatively, the phrase ‘position of equilibrium’ is often used. If the value of the equilibrium constant is small, the equilibrium is said to lie to the left. If the value of the equilibrium constant is large, the equilibrium is said to lie to the right. Left and right refer to the equation as it has been written and used to evaluate K_c.

SAMPLE PROBLEM 2

Write the K_c expression for the following reaction.

$$2CH_3OH(g) + O_2(g) \rightleftharpoons 2CH_2O(g) + 2H_2O(g)$$

THINK	WRITE
The K_c expression is a fraction related to the equation. The products form the numerator and the reactants form the denominator. The co-efficients become indices to their respective concentrations. Use square brackets to denote concentrations.	$K_c = \frac{[CH_2O]^2\,[H_2O]^2}{[CH_3OH]^2\,[O_2]}$

PRACTICE PROBLEM 2

Write the K_c expression for the following reaction.

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

SAMPLE PROBLEM 3

At 250 °C, phosphorus(V) chloride decomposes to phosphorus(III) chloride plus chlorine, according to the following equation:

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$

In a particular investigation, a quantity of PCl_5 was heated in a 12.0 L reaction vessel to 250 °C and allowed to reach equilibrium. Subsequent analysis revealed that 0.210 mol of PCl_5, 0.320 mol of PCl_3 and 0.320 mol of Cl_2 were present. Calculate the value of the equilibrium constant.

Teacher-led video: SP3 (tlvd-0682)

THINK	WRITE
1. Write the equilibrium expression.	$K_c = \dfrac{[PCl_3][Cl_2]}{[PCl_5]}$
2. Calculate the equilibrium concentrations for each substance recalling that $c = \dfrac{n}{V}$ **TIP:** A variation of this formula can be found in table 3 of the VCE Chemistry Data Book.	$[PCl_3] = \dfrac{0.320}{12.0} = 0.0267\text{ M}$ $[Cl_2] = \dfrac{0.320}{12.0} = 0.0267\text{ M}$ $[PCl_5] = \dfrac{0.210}{12.0} = 0.0175\text{ M}$
3. Substitute these values to obtain K_c.	$K_c = \dfrac{(0.0267)(0.0267)}{(0.0175)} = 0.0407$
4. Work out the units.	Units: $\dfrac{\text{M} \times \text{M}}{\text{M}} = \text{M}$
5. Give the answer to 3 significant figures.	$K_c = 0.0407\text{ M}$

PRACTICE PROBLEM 3

Consider an equilibrium reaction that is represented by the equation:

$$3A(aq) + B(aq) \rightleftharpoons 2Y(aq) + Z(aq)$$

In a particular experiment, random amounts of the above substances were mixed and allowed to come to equilibrium in 500 mL of solution. The amounts present at equilibrium were:

A: 0.351 mol **Y: 0.632 mol**
B: 0.18 mol **Z: 1.21 mol**

Use this information to calculate the value of the equilibrium constant.

on Resources

Interactivity Matching equations and equilibrium constant expressions (int-1244)

6.4.2 A closer look at equilibrium constants

The equilibrium constant is affected by temperature, and its value may depend on how the reaction equation is written, which also determines the units of the equilibrium constant. This means that the equilibrium constant is not always constant. Putting it another way, a particular chemical reaction may have an equilibrium constant with different values and different units, depending on how its equation is written and the temperature at which the reaction occurs. To illustrate these points, consider the data in table 6.3 for the dissociation of dinitrogen tetroxide gas, N_2O_4, into nitrogen dioxide gas, NO_2, at a constant temperature.

TABLE 6.3 Equilibrium data for the reaction $N_2O_4 \rightleftharpoons 2NO_2$

Experiment number	$[N_2O_4]$ (M)	$[NO_2]$ (M)
1	0.127	0.150
2	0.253	0.216
3	0.364	0.255
4	0.492	0.293
5	0.645	0.338

Case 1:

The equation is written as $N_2O_4(g) \rightleftharpoons 2NO_2(g)$, using data from experiment 1:

$$\begin{aligned} K_c &= \frac{[NO_2]^2}{[N_2O_4]} \\ &= \frac{(0.150)^2}{0.127} \\ &= 0.177 \end{aligned}$$

Units for K_c: $\frac{M^2}{M} = M$

Case 2:

The equation is written as $\frac{1}{2}N_2O_4(g) \rightleftharpoons NO_2(g)$, using data from experiment 1:

$$\begin{aligned} K_c &= \frac{[NO_2]}{[N_2O_4]^{\frac{1}{2}}} \\ &= \frac{0.150}{(0.127)^{\frac{1}{2}}} \\ &= 0.421 \end{aligned}$$

Units for K_c: $\frac{M}{M^{\frac{1}{2}}} = M^{\frac{1}{2}}$

Case 3:

Using the reverse reaction, $2NO_2(g) \rightleftharpoons N_2O_4(g)$, as there are two reactions involved in every equilibrium reaction and using data from experiment 1.

$$K_c = \frac{[N_2O_4]}{[NO_2]^2} = \frac{0.127}{(0.150)^2} = 5.64$$

Units for K_c: $\frac{M}{M^2} = M^{-1}$

These three cases show that the same reaction can have different equilibrium constants and different units. Therefore, when discussing equilibrium constants, it is important to be clear about the equation being used to represent the reaction.

A special situation is when an equation has the same number of total moles on each side, such as in the hydrogen iodide reaction mentioned earlier:

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

If we analyse the equilibrium expression for this reaction, all concentrations cancel out. The equilibrium constant (K_c) is therefore *without* units.

Temperature and the equilibrium constant

Equilibrium constants are also affected by temperature. However, in many situations, such as the $N_2O_4(g)/NO_2(g)$ equilibrium discussed previously, we deal with a situation at a particular temperature. Therefore, when the equation is clearly written or understood, K_c is always constant. The effect of temperature on the value of K_c is discussed further in section 6.6.2.

In summary, when dealing with equilibrium reactions and equilibrium constants, it is important that the equation being used to represent the reaction is clearly understood. It is also assumed that, in the absence of information to the contrary, temperature is constant.

SAMPLE PROBLEM 4

The reaction

$$2X(aq) \rightleftharpoons Y(aq) + 2Z(aq) \quad (1)$$

has an equilibrium constant of 250 M at a particular temperature.

Calculate the equilibrium constant for the reaction

$$X(aq) \rightleftharpoons \frac{1}{2}Y(aq) + Z(aq) \quad (2)$$

Teacher-led video: SP4 (tlvd-0683)

THINK	WRITE
1. Write and examine the K_c expression for each equation.	$K_c(1) = \frac{[Y][Z]^2}{[X]^2}$
2. Recognise that the desired value is the square root of the given value.	$K_c(2) = \frac{[Y]^{\frac{1}{2}}[Z]}{[X]} = (K_c(1))^{\frac{1}{2}}$

3. Evaluate including units.

$$K_c(2) = (250)^{\frac{1}{2}} \frac{M^{\frac{1}{2}}M}{M}$$
$$= 15.8\,M^{\frac{1}{2}}$$

PRACTICE PROBLEM 4

The reaction

$$\mathbf{2X(aq) \rightleftharpoons Y(aq) + 2Z(aq) \qquad (1)}$$

has an equilibrium constant of 250 M at a particular temperature.

Calculate the equilibrium constant for the reaction

$$\mathbf{Y(aq) + 2Z(aq) \rightleftharpoons 2X(aq) \qquad (2)}$$

6.4.3 Using stoichiometry in equilibrium law calculations

Equilibrium calculations can involve situations with more steps than the simple examples introduced in section 6.4.2. Typical examples of these more complicated types of calculations include:

- situations where initial concentrations are given and only one of the equilibrium concentrations
- situations where an equilibrium constant is known and you are asked to calculate something about one of the substances in the reaction. This may be a concentration, a mass or a variable relating to a gas.

The ICEBOX method uses stoichiometry in equilibrium calculations when one or more equilibrium concentrations is not known. This involves setting up a table with row headings ‘I’ (initial), ‘C’ (change) and ‘E’ (equilibrium). This table can be used when working with moles (which are then converted to concentrations) or directly with concentrations as demonstrated in sample problem 5.

SAMPLE PROBLEM 5

In studying the reaction represented by the equation:

$$\mathbf{A(g) \rightleftharpoons 2Y(g) + Z(g)}$$

a small amount of substance A was added to a reaction vessel, such that its initial concentration was 1.0 M. When equilibrium was subsequently attained, the concentration of product Z was measured and found to be 0.3 M.

Use this information to determine the value of the equilibrium constant for this reaction.

Teacher-led video: SP5 (tlvd-0684)

THINK

1. Using stoichiometry, work out changes to concentration to determine equilibrium values. Use the ICEBOX method with row headings ‘I’ (initial), ‘C’ (change) and ‘E’ (equilibrium). Take care to distinguish between initial and equilibrium concentrations.

WRITE

	$[A] \rightleftharpoons$	$[2Y] +$	$[Z]$
Initial amount	1	0	0
Change in amount	−0.3	+0.6	+0.3
Equilibrium amount	0.7	0.6	0.3

2. Write the expression and substitute values to determine K_c. Don't forget units and significant figures.	$K_c = \frac{[Y]^2[Z]}{[A]}$ Units: $\frac{M^2 \times M}{M} = M^2$ $= \frac{(0.6)^2(0.3)}{(0.7)}$ $= 0.2\ M^2$

PRACTICE PROBLEM 5

For the reaction represented by:

$$B(aq) \rightleftharpoons W(aq) + X(aq)$$

initial concentrations of 2.0 M and 3.0 M were recorded for substances B and X respectively. After allowing sufficient time for the reaction to reach equilibrium, the concentration of X had increased to 3.5 M.

Calculate the value of the equilibrium constant.

SAMPLE PROBLEM 6

The equilibrium constant for the reaction represented by the equation:

$$2A(g) + 3B(g) \rightleftharpoons X(g) + 2Y(g)$$

is 300 M^{-2}. In a vessel of volume 4.00 L, equilibrium is established and the following concentrations are determined:

[A] = 0.326 M [B] = 1.537 M [X] = 2.541 M

Calculate the number of moles of substance Y that were present at equilibrium.

Teacher-led video: SP6 (tlvd-0685)

THINK	WRITE
1. Substitute all known information into the K_c expression. **TIP:** Remember to check that equilibrium concentrations (not initial concentrations) are substituted into the equation.	$K_c = \frac{[X][Y]^2}{[A]^2[B]^3}$
2. Transpose and evaluate to determine [Y]. Don't forget the square root.	$300 = \frac{(2.541)[Y]^2}{(0.326)^2(1.537)^3}$ $[Y]^2 = \frac{300 \times (0.326)^2 \times (1.537)^3}{(2.541)}$ $= 45.6$ $[Y] = 6.75\ M$
3. Determine the number of moles of Y by using $n = c \times V$.	$n = c \times V$ $n(Y) = 6.75 \times 4.00$ $= 27.0$ mol.

PRACTICE PROBLEM 6

The formation of ammonia gas is represented by the following equation:

$$\mathrm{N_2(g) + 3H_2(g) \rightleftharpoons NH_3(g)}$$

At a particular temperature, the equilibrium constant for this reaction is 0.052 $\mathrm{M^{-2}}$.

In one particular investigation, it was established that the concentrations of N_2 and H_2 at equilibrium were 0.55 M and 0.65 M respectively. Calculate the concentration of ammonia at equilibrium.

on Resources

Video eLesson Calculations involving initial and equilibrium concentrations (med-0428)

6.4.4 How can we tell if a reaction is at equilibrium?

In some cases, it can be unclear when a reaction is at equilibrium. If a reaction reaches equilibrium quickly because its rate is fast, then it will soon become apparent that no further concentration changes are occurring and that chemical equilibrium has been attained. However, if concentrations are changing slowly in reactions that are slower, it may appear that the concentrations have become constant. To overcome this problem, we use the idea of the **reaction quotient**, Q (also known as the **concentration fraction**).

Reaction quotient, Q, and the equilibrium constant, K_c

The equilibrium law generates an expression that can be called a ‘concentration fraction’. This is just a fraction that involves concentrations, so it is possible to write a similar fraction *at any other stage* during a reaction. When we do this, we often give it the symbol Q (for reaction quotient). It therefore follows that:

- if $Q = K_c$ the reaction is at equilibrium.
- If the value of Q is *different* to the value of K_c, *the reaction has yet to reach equilibrium.*
- If $Q > K_c$ a net backward reaction is occurring. The rate of the backward reaction is greater than the rate of the forward reaction as this mixture moves towards equilibrium.
- If $Q < K_c$, a net forward reaction is occurring. The rate of the forward reaction is greater than the rate of the backward reaction as this reaction seeks equilibrium.

SAMPLE PROBLEM 7

At 25 °C, the reaction

$$\mathrm{W(aq) + 2X(aq) \rightleftharpoons Y(aq)}$$

has an equilibrium constant of 109 $\mathrm{M^2}$. In an experimental trial of this reaction, the concentrations of all species are measured and the following results obtained.

[W] = 0.13 M **[X] = 0.092 M** **[Y] = 0.090 M**

Is this reaction at equilibrium? If not, how does the rate of the forward reaction compare to the rate of the backward reaction?

THINK	WRITE
1. Write the formula for Q.	$Q = \dfrac{[\mathrm{Y}]}{[\mathrm{W}][\mathrm{X}]^2}$

▶

2. Calculate Q by substituting the given concentrations.	$Q = \dfrac{(0.090)}{(0.13)(0.092)^2}$ $= 82\ \text{M}^{-2}$
3. The value of K_c is given, $K_c = 109\ \text{M}^2$. If $Q < K_c$ a net forward reaction is occurring. If $Q > K_c$ a net backward reaction is occurring. If $Q = K_c$ the reaction is at equilibrium.	As $Q < K_c$ there is a net forward reaction. The rate of the forward reaction is faster than the rate of the backward reaction.

PRACTICE PROBLEM 7

In another trial of the same reaction as in sample problem 7, the following concentrations were obtained.

$[W] = 0.14$ M $\quad$ $[X] = 0.085$ M $\quad$ $[Y] = 1.0$ M.

Is this reaction at equilibrium? If not, how does the rate of the forward reaction compare to the rate of the backward reaction?

6.4 EXERCISE

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1. It has been estimated that the reaction between methane and oxygen represented by the equation:

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

has an equilibrium constant of 10^{140} at room temperature.

(a) What does this value suggest about the extent of this reaction?

(b) Do you think the use of the $\rightleftharpoons$ arrow is justified?

2. (a) Write an expression for the equilibrium constant for each of the following equations.

   i. $Cl_2(g) + 3F_2(g) \rightleftharpoons 2ClF_3(g)$

   ii. $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$

   iii. $4HCl(g) + O_2(g) \rightleftharpoons 2H_2O(g) + 2Cl_2(g)$

   iv. $2COF_2(g) \rightleftharpoons CF_4(g) + CO_2(g)$

   v. $P_4(g) + 10F_2(g) \rightleftharpoons 4PF_5(g)$

   (b) For each of the reactions shown in part (a), state the units for K_c.

3. A reaction has an equilibrium expression of:

$$K_c = \frac{[C][D]^2}{[A]^2[B]}$$

What is the equation for this reaction?

4. When COF_2 is held at 1000 °C, the following equilibrium occurs.

$$2COF_2(g) \rightleftharpoons CO_2(g) + CF_4(g)$$

Calculate the value of the equilibrium constant, given the following equilibrium data.

$[COF_2] = 0.024$ M

$[CO_2] = [CF_4] = 0.048$ M

5. Consider the following information for the reaction

$$W(aq) + 2X(aq) \rightleftharpoons 3Y(aq) + Z(aq)$$

This reaction is carried out in a 250 mL beaker.

At equilibrium, the respective concentrations of W, X and Y are 1.24 M, 0.56 M and 0.85 M.
The molar mass of Z is 56.5 g mol^{-1}.
The equilibrium constant for this reaction at the temperature of the investigation is 1.89 M^2.
(a) Calculate the mass of Z that is present.
(b) If the equation is rewritten as follows, calculate the equilibrium constant.

$$2W(aq) + 4X(aq) \rightleftharpoons 6Y(aq) + 2Z(aq)$$

6. The equilibrium represented by the equation

$$H_2(g) + CO_2(g) \rightleftharpoons H_2O(g) + CO(g)$$

has a K_c value of 1.62 at 985 °C.
(a) What is the value of K_c for the reaction

$$H_2O(g) + CO(g) \rightleftharpoons H_2(g) + CO_2(g)$$

(b) What is the value of K_c for the reaction

$$2H_2(g) + 2CO_2(g) \rightleftharpoons 2H_2O(g) + 2CO(g)$$

7. In a reaction specified by the equation:

$$A(g) \rightleftharpoons 2B(g) + C(g)$$

3.5 mol of substance A is initially introduced into a 500 mL reaction vessel and allowed to reach equilibrium. At this stage, its concentration was found to be 2.0 M. Calculate the value of the equilibrium constant for this reaction.

8. An equilibrium reaction is represented by the following equation:

$$W(aq) + 2X(aq) \rightleftharpoons 2Y(aq) + Z(aq)$$

The magnitude of the equilibrium constant at a particular temperature is 6.3.
(a) What are the units of the equilibrium constant?
(b) Calculate the value of the equilibrium constant for the reaction:

$$2Y(aq) + Z(aq) \rightleftharpoons W(aq) + 2X(aq)$$

9. The reaction represented by the equation:

$$A + 2B \rightleftharpoons C + D$$

was investigated by mixing various amounts of these four substances. After a period of time, the concentration of each species was measured. This procedure was repeated a number of times to give the results shown in the following table.

Experiment	[A]	[B]	[C]	[D]
1	1.7	1.2	2.5	2.8
2	1.4	0.9	2.3	2.7
3	1.6	1.1	2.3	2.4
4	1.5	0.9	2.6	2.8
5	1.4	1.0	2.5	2.7

At the temperature of this experiment, it is known that the value of the equilibrium constant is 6.0.
In which of the above experiments was the reaction mixture at equilibrium when it was analysed?

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6.5 Measuring the efficiency of a reaction or process

Background knowledge

- The yield of a chemical reaction

6.5.1 Percentage yield

There are many situations in chemistry where we want to know how much reactant has been converted into product. Chemists use the concept of reaction **yield** to express this idea in quantitative terms. The yield of a reaction is often quoted as a percentage and is defined as follows.

$$\textbf{\% yield} = \frac{\textbf{actual yield}}{\textbf{theoretical yield}} \times \frac{\textbf{100}}{\textbf{1}}$$

The equilibrium reactions we have been studying in this topic are examples of reactions that display yields of less than 100%, that is, the actual mass obtained is less than the theoretical or predicted maximum mass. However, there are often additional reasons why a given reaction does not achieve a 100% yield. Some of these may be practical (to do with the method by which the chemical is made), or may involve a very slow reaction that has not been given enough time to either reach equilibrium or go to completion. This is an important consideration in equilibrium work and in the design of large-scale manufacturing techniques for chemicals produced from equilibrium reactions.

SAMPLE PROBLEM 8

A student is collecting silver chloride produced from a reaction between sodium chloride and silver nitrate. Using the starting amounts of each chemical, he uses stoichiometry to calculate that 2.197 g should be produced. Upon collection and weighing, the silver chloride produced is found to have a mass of 1.112 g. Calculate the percentage yield obtained.

THINK	WRITE
1. Recall the formula for calculation of percentage yield. **TIP:** The % yield formula can be found in table 3 of the VCE Chemistry Data Book.	$\% \text{ yield} = \frac{\text{actual yield}}{\text{theoretical yield}} \times \frac{100}{1}$

2. Substitute given values into the formula and calculate.
Don't forget significant figures.

$$\% \text{ yield} = \frac{1.112}{2.197} \times 100$$
$$= 50.61\%$$

PRACTICE PROBLEM 8

A student is collecting silver chloride produced from a reaction between sodium chloride and silver nitrate. Using the starting amounts of each chemical, she uses stoichiometry to calculate that 2.356 g should be produced. Upon collection and weighing, the silver chloride produced is found to have a mass of 1.476 g. Calculate the percentage yield obtained.

6.5.2 Green chemistry and atom economy

The chemical industry has traditionally focused on getting the best yields from the chemical synthesis of products — that is, getting the most products. A lesser focus has been on the impact of chemical processes on the environment and their long-term viability. Although getting high yields is important, there are other issues that need to be addressed in the production of chemicals for a sustainable future, including:

- high atom efficiency
- minimising the number of steps in the production
- ensuring safer, simpler and energy efficient processes
- reducing the amount of wastes produced
- using renewable and recyclable resources.

Green chemists think that it is necessary to change from secondary prevention (costly cleaning up of wastes after they have been generated) to primary prevention (the development of manufacturing processes that are essentially non-polluting). This process of clean production not only targets the elimination of pollution, it also aims to encourage profitable manufacturing with more efficient use of raw materials and energy.

Because **green chemistry** not only aims to maximize the yield but also to reduce waste, the concept of atom economy is a used. This is a very useful concept when planning or reviewing a process. Atom economy is expressed as a percentage, according to the following formula:

$$\textbf{\% atom economy} = \frac{\textbf{molar mass of desired product}}{\textbf{molar mass of all reactants}} \times \frac{\textbf{100}}{\textbf{1}}$$

SAMPLE PROBLEM 9

A postgraduate student is examining whether it would be possible to remove carbon dioxide from the air by a process of reverse fermentation to produce glucose. The equation for such a process would be:

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

Calculate the % atom economy of this potential process.

Teacher-led video: SP9 (tlvd-0688)

THINK	**WRITE**
1. Recall the formula for the calculation of % atom economy. **TIP:** The % atom economy formula can be found in table 3 of the VCE Chemistry Data Book.	$\% \text{ atom economy} = \frac{\text{molar mass of desired product}}{\text{molar mass of all reactants}} \times \frac{100}{1}$
2. Calculate molar masses for the desired product and for all reactants.	$M(C_6H_{12}O_6) = 180.0 \text{ g mol}^{-1}$ $M(CH_3CH_2OH) = 46.0 \text{ g mol}^{-1}$ $M(CO_2) = 44.0 \text{ g mol}^{-1}$
3. Substitute into the formula and calculate the answer. Make sure that the stoichiometry of the equation is taken into account.	$\% \text{ atom economy} = \frac{180.0}{(2 \times 46.0) + (2 \times 44.0)} \times \frac{100}{1}$ $= 100\%$

Note: A consequence of this formula is that if the *desired* product is the *only* product, the figure will always be 100%, because all the reactant atoms are used to make the product and none end up in a waste or by-product.

PRACTICE PROBLEM 9

Calculate the % atom economy of the fermentation of glucose to ethanol. The equation for this process is:

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

6.5 EXERCISE

To answer questions online and to receive **immediate feedback** and **sample responses** for every question, go to your learnON title at www.jacplus.com.au.

1. Calculate the percentage yield of a reaction that produces 34.5 tonne of product out of a theoretical maximum of 40.0 tonne.
2. Hydrogen can be made by reacting methane with steam.

$$CH_4(g) + H_2O(g) \rightarrow 3H_2(g) + CO(g)$$

   (a) Calculate the % atom economy for making hydrogen using this process.
   (b) If a use for all of the carbon monoxide produced is found, what would the % atom economy now be? Explain.

3. The production of quicklime (CaO) takes place when calcium carbonate is heated to a high temperature. Carbon dioxide is also produced. If this occurs in an open system so that the carbon dioxide can escape, the reaction essentially goes to completion.

   If 100.1 g of calcium carbonate produces 50.3 g of quicklime, calculate the percentage yield. The equation for this reaction is:

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

Fully worked solutions and sample responses are available in your digital formats.

6.6 Le Châtelier's principle

KEY CONCEPT

- 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

6.6.1 Making changes to equilibrium mixtures

An important consequence of the equilibrium law is that it is possible for every equilibrium mixture belonging to a particular reaction to be different. This is because the whole equilibrium expression is constant, while individual concentrations within this expression may vary quite considerably from one equilibrium situation to another. However, so long as the value of the whole expression is equal to the value of the equilibrium constant, a mixture will be at equilibrium.

This property can be put to use in the manufacture of some important chemicals. It is often possible to make these economically, despite the fact that the reactions from which they are formed have low equilibrium constants. By altering the concentrations of the other species involved in the equilibrium expression, it is often possible to maximise the production of the desired product, thereby increasing its yield.

To see how changes made to an equilibrium mixture affect its components, we often make use of an important predictive tool — **Le Châtelier's principle**.

6.6.2 Introduction to Le Châtelier's principle

> **Le Châtelier's principle**
>
> ***Any change that affects the position of an equilibrium causes that equilibrium to shift, if possible, in such a way as to partially oppose the effect of that change.***

Using this, we can make predictions about what will happen if we disturb a system that is at equilibrium. There are three common ways in which a system at equilibrium might be disturbed:

- by adding or removing a substance that is involved in the equilibrium
- by changing the volume (at constant temperature)
- by changing the temperature.

We will now consider the effect of each of these in turn.

6.6.3 Adding or removing a substance that is involved in the reaction

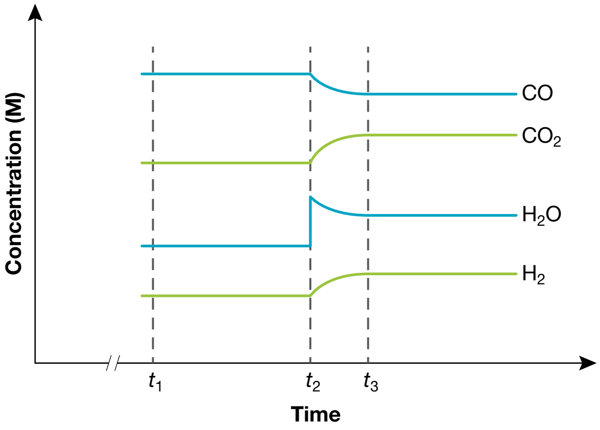
Consider the reaction between carbon monoxide and water vapour to produce carbon dioxide and hydrogen.

$$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$$

If extra water vapour is added to this system once it has attained equilibrium, the equilibrium will be disturbed. According to Le Châtelier's principle, the system will then react by trying to use up some of this extra water vapour in its efforts to get back to a new equilibrium position. The only way that this can be done is by causing some of the reactants to be transformed into products. Thus, more CO_2 and H_2 will be made as a result of consuming CO and H_2O. Although all the amounts, and hence all the concentrations, involved will now be different from their original values, the value of the equilibrium constant will remain unchanged (the same value as before the water vapour was added).

Changes like this, where a substance has been added or removed, can be identified from concentration–time graphs by a sudden spike or dip in only one of the substances involved. A concentration–time graph for this situation is shown in figure 6.6.

FIGURE 6.6 An example of a concentration–time graph where a substance has been added to the equilibrium mixture



- Time t_1 represents the time when equilibrium was first reached.
- Time t_2 is when the extra water vapour was added.
- Time t_3 is when equilibrium is re-established. The equilibrium may be described as having been shifted to the right (the forward reaction is favoured).

A more informative way to describe these changes is in terms of reaction rates. At the first equilibrium, the rates of the forward and reverse reactions are equal. On addition of the water vapour, the forward reaction becomes faster than the backward one for some time. However, as more products are made, the two rates eventually become equal again and equilibrium is re-established.

When considering these reactions, the method of addition (continuous supply) or removal (ducting gas away) may be physical, or it may be achieved by chemical means. Regardless of the method, the system always tries to oppose us in its efforts to re-attain equilibrium. However, it should be noted that equilibrium is only disturbed if products and/or reactants are added or removed. If an inert gas is added to the system, it will have no effect on the reaction.

USING LE CHÂTELIER'S PRINCIPLE TO DISSOLVE AN INSOLUBLE SALT

Le Châtelier's principle may be used to dissolve an otherwise insoluble salt. Silver chloride is only sparingly soluble in water. In other words, the equilibrium constant for the reaction:

$$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$$

is very low ($K_s = 1.8 \times 10^{-10}$). This is an example of a heterogeneous equilibrium. In these cases, the equilibrium constant is usually denoted by K_s, a special type of K_c value.

However, if a chemical is added to remove the Ag^+ ions, this reaction responds by trying to replace them. To do this, more AgCl(s) has to dissolve. If enough of the Ag^+ ions are removed, it is possible that all the silver chloride would dissolve. A suitable chemical for the removal of Ag^+ ions is ammonia, NH_3. Ammonia achieves this by forming a complex ion according to the reaction:

$$Ag^+(aq) + 2NH_3(aq) \rightleftharpoons Ag(NH_3)_2^+(aq)$$

SAMPLE PROBLEM 10

Predict the effect of adding carbon dioxide on the position of the equilibrium for the reaction:

$$\mathrm{CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)}$$

Teacher-led video: SP10 (tlvd-0689)

THINK	WRITE
Recall that Le Châtelier's principle predicts that adding a substance involved in the equilibrium will lead to its partial removal. In this case, the reaction will respond by removing some of the added CO_2. The equilibrium will therefore shift to the left, i.e. there will be a net backward reaction until the reaction is once again at equilibrium	Product has been added so there will be a net backward reaction until the reaction is once again at equilibrium. *Note:* Other answers are possible.

PRACTICE PROBLEM 10

Predict the effect of removing hydrogen on the position of the equilibrium for the reaction:

$$\mathrm{CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)}$$

on Resources

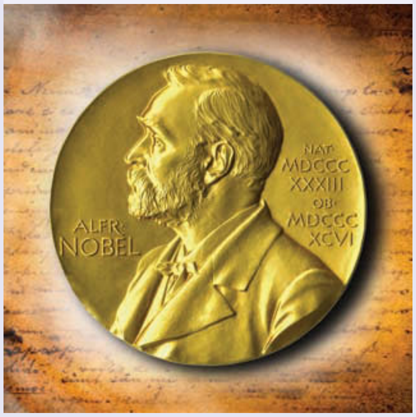
Interactivity	Le Châtelier's principle (int-1246)
Digital document	Experiment 6.2 Investigating changes to the position of an equilibrium (doc-31262)
Teacher-lead video	Experiment 6.2 Investigating changes to the position of an equilibrium (tlvd-0747)

USING CHEMISTRY: HOW TO HIDE A COUPLE OF NOBEL MEDALLIONS

A Nobel Prize is one of the highest awards that a scientist can achieve. The award consists of a pure gold medallion engraved with the winner's name, a diploma and a considerable sum of money. While a medallion would normally be a prize possession, there was a time in the past when it could have been a threat to one's life. Such a situation occurred in Europe during World War II as Nazi Germany invaded much of Europe.

As the Nazis rose to power in the 1930s, two German Nobel laureates and opponents of the regime, Max von Laue and James Franck, sent their medals to the famous physicist Niels Bohr in Copenhagen, Denmark, for safe keeping. The exporting of gold from Germany at this time was strictly forbidden and the two would have faced harsh penalties if they were discovered. When the Germans invaded Denmark in 1940, the discovery of the two medallions might have proven a death sentence for those involved. An associate of Niels Bohr, the chemist George de Hevesy, came to the rescue with a clever application of Le Châtelier's principle.

FIGURE 6.7 The prestigious Nobel medallion



Gold is a famously unreactive metal. One of the few things that it will react with is a mixture called aqua regia, which is a mixture of concentrated hydrochloric and nitric acids. By themselves, neither of these two acids reacts with gold but together they are able to slowly dissolve it. De Hevesy famously dissolved the medallions belonging to von Laue and Franck in this way, producing a beaker containing a bright orange solution, which he placed on a high shelf in his laboratory among bottles of other chemicals. De Hevesy escaped to Sweden in 1943 when the Nazis moved to ransack the laboratory and looking for evidence of wrongdoing. When he returned after the war, he found the beaker untouched, exactly as he had left it. He was then able to precipitate out the gold using some simple chemistry. This was then returned to Sweden where it was cast into new medallions and re-presented to the two original recipients.

The mechanism by which aqua regia dissolves gold is another example involving Le Châtelier's principle.

The first step is a redox reaction between nitrate ions and the gold. This reaction is very slight (the value of its equilibrium constant is very low) and would not normally be noticed.

$$Au(s) + 3NO_3^-(aq) + 6H^+(aq) \rightleftharpoons Au^{3+}(aq) + 3NO_2(g) + 3H_2O(l)$$

The small number of Au^{3+} ions formed then react almost completely with Cl^- ions according to the equation

$$Au^{3+}(aq) + 4Cl^-(aq) \rightarrow AuCl_4^-(aq)$$

This means that Au^{3+} ions are removed from the first equilibrium reaction. According to Le Châtelier's principle, there will now be a net forward reaction to replace them resulting in more gold atoms being dissolved. If an excess of aqua regia is present, this process will continue until all the gold is dissolved.

FIGURE 6.8 A stamp of George de Hevesy (1885-1966), who co-discovered Hafnium and invented the technique of using radioactive tracers, for which he was awarded a Nobel Prize

FIGURE 6.9 Gold dissolved in aqua regia produces a bright orange solution.

Explaining Le Châtelier's principle mathematically

Consider the reaction that is represented by the equation:

$$3A(aq) + 2B(aq) \rightleftharpoons C(aq) + 2D(aq)$$

Suppose that some extra substance A is added to the equilibrium mixture, and that we wish to predict the effect on substance D.

For this reaction we can write two expressions:

$$Q = \frac{[C][D]^2}{[A]^3[B]^2} \quad \text{and} \quad K_c = \frac{[C][D]^2}{[A]^3[B]^2}$$

where the concentrations for the equilibrium constant, K_c, are equilibrium concentrations but the concentrations for the reaction quotient, Q, can be at any stage during the reaction. If $Q = K_c$, equilibrium has been established.

Immediately after the addition of substance A, the value of Q is decreased, making Q less than K_c. Therefore, the reaction is no longer at equilibrium, and the value of Q must increase for equilibrium to be re-established. There needs to be a higher concentration of products and a lower concentration of reactants. This can be achieved by a net forward reaction — the rate of the forward reaction becomes greater than the rate of the backward reaction, and the equilibrium therefore shifts to the right. Essentially, $K_c = \frac{[\text{products}]}{[\text{reactants}]}$. Thus, if $Q < K_c$, [reactants] > [products] and [products] must increase to re-establish equilibrium. This means a net forward reaction.

This is exactly what is predicted by Le Châtelier's principle. After the sudden increase in substance A, some of it is used by the net forward reaction predicted. The effect of changing volume can be predicted in the same way.

6.6.4 The effect of changing volume

When considering changes in volume (at constant temperature), it is important to think of the effect on the total concentration of all the species present. Le Châtelier's principle can then be interpreted in terms of how the system changes the total number of particles present to produce an opposing trend in total concentration.

Three situations present themselves:

1. The change in volume causes an increase in the total concentration of particles. To decrease this, the system reacts in the direction that produces fewer particles. (Fewer particles means a lower overall concentration, in line with the opposition predicted by Le Châtelier's principle.)
2. The change in volume causes a decrease in the total concentration of particles. To increase this concentration, the system must react in the direction that produces more particles if it is to re-establish equilibrium.
3. Although the change in volume affects the total concentration, the system cannot change the number of particles present. This situation occurs when the total number of moles on the left-hand side of the equation equals the number of moles on the right-hand side. Mathematically, it can be shown that a volume change for such a reaction does not disturb the equilibrium.

As an example of situation 1, consider the reaction represented by:

$$A(g) \rightleftharpoons B(g) + C(g)$$

It might be predicted that an increase in volume, such as by dilution, would lead to an increase in the total number of particles as the reaction attempts to re-build the total concentration. In this case, this can be achieved if the equilibrium shifts to the right (forward reaction).

A change in volume of an equilibrium mixture is identified on concentration–time graphs as a sudden spike or dip involving all substances. This is shown in figure 6.10.

on Resources

Video eLesson Changing the position of an equilibrium — gas pressure (eles-1672)

A special note about gases

For a change in volume at constant temperature, the universal gas equation allows a concentration interpretation to be replaced by a pressure interpretation. Therefore:

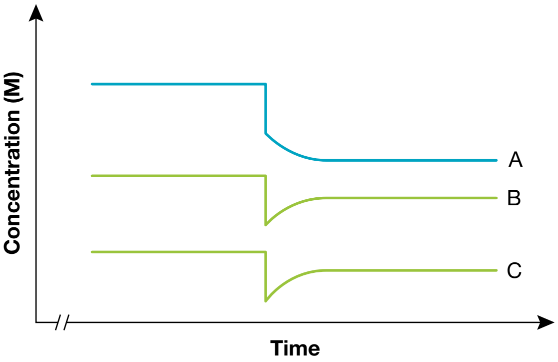
$$PV = nRT$$

$$P = \left(\frac{n}{V}\right)RT$$

$$P \propto c$$

As $\frac{n}{V}$ is concentration (c), and $R \times T$ is constant, we can see that pressure is proportional to concentration.

FIGURE 6.10 A concentration–time graph illustrating the effect of increasing the volume of the reaction $A(g) \rightleftharpoons B(g) + C(g)$



For gaseous reactions, volume changes may also be interpreted in terms of partial pressures, rather than concentrations.

SAMPLE PROBLEM 11

a. The following gaseous system is set up and allowed to reach equilibrium.

$$2NOBr(g) \rightleftharpoons 2NO(g) + Br_2(g)$$

What would be the effect on the amount of bromine present if the volume is then increased?

b. Would a volume change affect the following reaction?

$$H_2(g) + Cl_2(g) \rightleftharpoons 2HCl(g)$$

THINK	WRITE
a. A volume change requires thinking in terms of the total number of particles. Increasing volume decreases the total concentration. The reaction will respond in the direction that makes a net gain in particles. This will partially increase the total concentration in response to the initial increase in volume. In this case, there is a net gain in the number of particles (from 2 moles to 3 moles) if the reaction moves to the right.	**a.** The reaction will respond by making more products (NO and Br_2). At the same time, it will use up more of the NOBr. i.e. there will be a net forward reaction.
b. This reaction has equal numbers of particles (and hence moles) on each side of the equation (2 and 2). Hence, the equilibrium will not be affected by a change in volume.	**b.** A volume change will not affect this reaction because there are the same number of moles on each side.

PRACTICE PROBLEM 11

a. Consider the reaction represented by the equation:

$$I_2(aq) + I^-(aq) \rightleftharpoons I_3^-(aq)$$

What would be the effect on the amount of I_3^- caused by increasing the volume by adding more water?

b. Would a volume change effect the following reaction?

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

6.6.5 The effect of changing temperature

Of all the possible ways to change an equilibrium mixture, changing the temperature is the *only method that actually alters the value of the equilibrium constant,* K_c, because changing the temperature also changes the energy available to the system.

At a particular temperature, the system has a certain amount of energy, which is distributed between all the species present. The equilibrium expression describes the concentrations of all species once they have settled on a way to share that energy, and the value of K_c is interpreted as sharing in favour of reactants or products.

Varying the concentration of a species (n or V) causes a redistribution of the available energy and a different equilibrium position is reached. However, because the available energy remains the same, the value of K_c is the same.

- **The equilibrium constant, K_c, of a reaction can only be changed by changing the temperature.**
- **Changing the temperature changes the energy available to the system.**

Changing the temperature changes the total amount of energy in the system. Hence, K_c has a different value. How this value responds to temperature change depends on whether the reaction is exothermic or endothermic. Classifying an equilibrium reaction as exothermic or endothermic relates, by convention, to the forward reaction as written in the equation. An endothermic reaction absorbs heat and has a positive ΔH value. An exothermic reaction evolves heat and has a negative ΔH value.

If we consider an exothermic reaction, typified by the thermochemical equation:

$$A(g) + B(g) \rightleftharpoons C(g) \qquad \Delta H \text{ is negative}$$

an increase in temperature requires the application of heat. Le Châtelier's principle would predict that the system tries to absorb some of this added heat. Hence, the backward reaction is favoured as it is endothermic. A and B are produced at the expense of C, lowering the value of the equilibrium constant. Thinking mathematically, when the value of the denominator in K_c increases, the value of K_c decreases.

This equation can also be written as:

$$A(g) + B(g) \rightleftharpoons C(g) + \text{heat}$$

where heat can be treated as a product.

A change in temperature can be identified on concentration–time graphs by its effect on the concentrations without an obvious sudden change to any of the substances involved. For the reaction above, the concentration–time graph might look like figure 6.11.

In an endothermic reaction under the same conditions, the forward reaction would oppose the addition of heat. Upon re-establishing equilibrium, the value of the equilibrium constant would, therefore, be higher.

In summary:

- if a reaction is exothermic, an increase in temperature decreases the equilibrium constant because more reactants are favoured.
- if a reaction is endothermic, an increase in temperature increases the equilibrium constant because more products are favoured.

FIGURE 6.11 A concentration–time graph showing the effect of increasing temperature on the equilibrium $A(g) + B(g) \rightleftharpoons C(g)$, where ΔH is negative

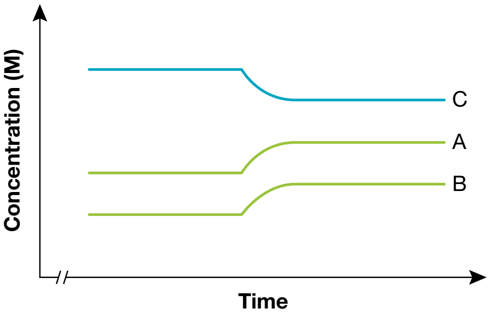


FIGURE 6.12 The equilibrium reaction between brown NO_2 and colourless N_2O_4 is affected by temperature. These tubes initially contained equal amounts of gas; the tube on the left is being cooled.

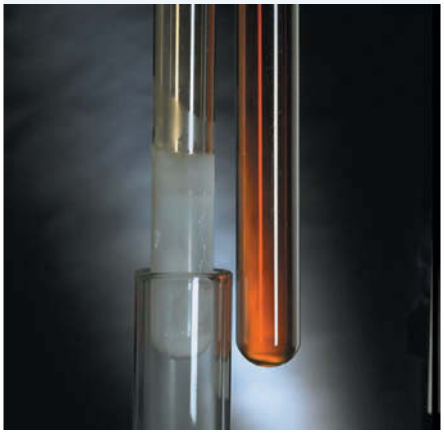
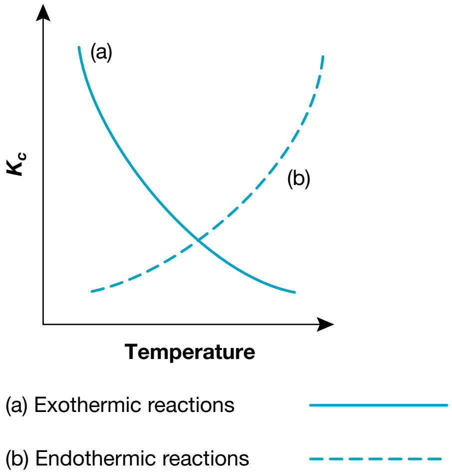


FIGURE 6.13 The general relationship between K_c and temperature for (a) exothermic reactions and (b) endothermic reactions



SAMPLE PROBLEM 12

Suppose that, in the reaction:

$$A(aq) + 2B(aq) \rightleftharpoons C(aq)$$

substance C has an easily detected red colour.

It is observed that heating the equilibrium mixture causes the red colour to fade.

a. What is the resulting effect on the K_c value?

b. Is this reaction an exothermic or an endothermic reaction?

Teacher-led video: SP12 (tlvd-0691)

THINK	WRITE
a. The fading of the red colour implies that there has been a net backward reaction. The value of K_c will, therefore, be lower.	The K_c value will be lower.

b. K_c has dropped as a result of an increase in temperature, which means that the reaction (as written above) must be an exothermic reaction.	It is an exothermic reaction.

PRACTICE PROBLEM 12

NO_2 reacts with itself to produce N_2O_4 according to the following equation.

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

The progress of this reaction may be monitored by noting the change in the brown colour of NO_2 because N_2O_4 is colourless (see figure 6.12). It is noted that as a sample of this mixture is heated, its colour darkens. Is this reaction exothermic or endothermic?

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Video eLesson Le Châtelier's principle – change in temperature (med-0430)

Identifying a change graphically

As already established, concentration–time graphs are an informative way of summarising changes made to an equilibrium system. The important features of such graphs are:

- changes in concentration that reflect the stoichiometric ratios of the equation
- the attainment of equilibrium as reflected by each concentration becoming a horizontal line and the fact that each such concentration reaches a certain constant value. This occurs at the same time for each substance.
- a sudden dip or spike in only one of the concentrations, which occurs when one substance has been added or removed
- a sudden dip or spike in all the concentrations, which is reflective of a volume change. For a reaction in the aqueous phase, this would represent a dilution. For a gas phase reaction, it could represent either the compression or expansion of the sample.
- a change in the equilibrium values without an obvious spike or dip, which indicates that there has been a temperature change
- all the reactants either increasing or decreasing together. All the products will change together in the opposite way, i.e. one side of the equation will go up or down and the other side will go down or up.

Open versus closed systems

All reactions can be considered either **closed systems** or **open systems**. All the examples used so far have been assumed to be closed systems, in which none of the substances involved is lost. In an open system this is not the case. Because of this, equilibrium reactions that occur in open systems will need to have Le Châtelier's principle applied to them. For example, the decomposition of calcium carbonate upon heating in a closed system reaches an equilibrium where the gaseous CO_2 is in equilibrium with the solid $CaCO_3$ and CaO, according to the equation

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

However, if this reaction is carried out in an open container, the CO_2 can escape. This is effectively removing a product from the equilibrium mixture. Therefore, Le Châtelier's principle predicts that more

$CaCO_3$ will decompose in an effort to replace it. As this is a continuous process, the end result will be that all the $CaCO_3$ present will eventually decompose.

on Resources

Digital document Experiment 6.3 Temperature and the equilibrium constant (doc-31263)

6.6.6 Le Châtelier's principle in industry

The manufacture of some important chemicals involves allowing for the fact that, at certain desired temperatures, the values of their equilibrium constants are low. Examples of such chemicals are ammonia (NH_3), nitric acid (HNO_3), and sulfuric acid (H_2SO_4). To make these chemicals on a large scale, the chemical engineer must have a sound knowledge of equilibrium principles and also of rate principles. In designing a plant, the engineer will ultimately be trying to:

- maximise the yield of the desired product by applying Le Châtelier's principle to make as much of the chemical as possible
- produce the desired chemical at an acceptable rate — it has to be made quickly enough to satisfy market demand if the plant is to be economical
- balance the above two requirements against other variables, such as plant operating costs, to ensure that the whole process is as economical and safe as possible.

The final design of such a plant is often a compromise between these factors.

THE HABER PROCESS

The Haber process is a single-step process in which nitrogen and hydrogen are reacted to produce ammonia according to the equation:

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \qquad \Delta H \text{ is negative}$$

This reaction is a good example of a dilemma often faced by a chemical engineer. At normal temperatures, the value of the equilibrium constant is quite high, but the rate of reaction is very slow. In other words, the mixture of nitrogen and hydrogen is metastable. However, if the temperature is increased to bring about a better rate, the yield of ammonia quickly begins to suffer. This is because the above reaction is exothermic and, as temperature is increased, the value of its equilibrium constant decreases. This puts the yield and rate, two of the most important industrial factors, in conflict. The ultimate design of the plant and its operating conditions must reflect a compromise between these factors.

A closer look at these factors reveals that we can lessen the effect of this compromise in a number of ways. These are:

- use a suitable catalyst to help obtain the rate required. This means that the temperature needed is lower than that needed without a catalyst. The use of a lower temperature increases the yield by increasing the value of the equilibrium constant. A lower temperature reduces the rate, but this can be compensated for by using a catalyst, which increases the rate.
- compress the gases so that the reaction is carried out at high pressure. Le Châtelier's principle predicts that, if a system is pressurised, it tries to reduce that pressure. Consequently, there should be a tendency to reduce the number of particles present. In this case, this means that the reaction proceeds to the right, as the forward reaction converts four molecules into two molecules, thus favouring the production of ammonia.

FIGURE 6.14 Production plant for ammonia and nitrogen fertilizer. Note the large cooling towers.

- separate the ammonia from the unreacted nitrogen and hydrogen in the exit gases from the converter. This nitrogen and hydrogen can then be recycled and may be converted into more ammonia.

In the operation of a typical plant, nitrogen and hydrogen are mixed in the 1 : 3 ratio required by the equation. The gases are then compressed to about 250 atm and heated to about 500 °C. (These precise conditions may vary slightly from one plant to another.) The gases then pass into the converter, which is a huge reinforced steel cylinder containing 7 to 8 tonnes of pea-sized catalyst beads. The catalyst most often used is an iron catalyst made from iron oxide, Fe_3O_4, with traces of aluminium oxide and potassium oxide.

When the gases leave this chamber they contain about 20% ammonia. By cooling the mixture, the ammonia can be liquefied and separated. The unreacted nitrogen and hydrogen can then be recycled so that they pass through the converter again. This is an example of green chemistry.

The energy costs in the operation of such a plant are one of its most important overheads. With careful planning, energy costs can be minimised. In this case, the actual formation of the ammonia from its elements is an exothermic process. The heat generated from this reaction can be made use of elsewhere in the plant, rather than just being allowed to go to waste so heat exchangers are used. For example, the incoming cold nitrogen/hydrogen mixture can be passed over pipes containing the hot gases that exit from the converter. The resultant transfer of heat helps to heat the incoming gases and cool the exit gases.

There are further compromises in operation. Better yields of ammonia might be obtained by using higher pressures, but this necessitates the use of more powerful pumping equipment and stronger reaction vessels to withstand the extra pressure. Economically, it is not worthwhile to do this, because the extra ammonia produced does not offset the extra costs involved in building such a plant.

6.6.7 An important biological application of Le Châtelier's principle

An important concept in biology is that of homeostasis. This is the ability of an organism to maintain a fairly constant internal environment, despite changes to the external environment. Such systems in the human body are extremely important to our wellbeing and continued survival. We have many different ways of maintaining homeostasis, most of which include chemical processes at equilibrium. Oxygen transport is one such example.

Transport of oxygen by the blood

Although oxygen is soluble in water, this solubility is not high enough to enable the blood to supply adequate amounts of oxygen to our cells. Therefore, the blood transports oxygen by a different mechanism — the red blood cells. These cells contain a special protein called **haemoglobin**, which can combine with oxygen to form oxyhaemoglobin. This is a reversible reaction that can be represented by the equation:

$$Hb_4 + 4O_2 \rightleftharpoons Hb_4(O_2)_4$$

where the symbol Hb_4 represents the very complex haemoglobin molecule.

The position of this equilibrium is such that normal bodily variations in oxygen concentration can push it in either direction. When blood enters the lungs, it is exposed to a high concentration of oxygen. As oxygen is a reactant in this equation, Le Châtelier's principle predicts that more oxyhaemoglobin is produced. The red blood cells thus become loaded with oxygen. This mechanism allows much more oxygen to be transported around the body than by dissolving it in the plasma alone.

FIGURE 6.15 Red blood cells carry oxygen around our bodies.

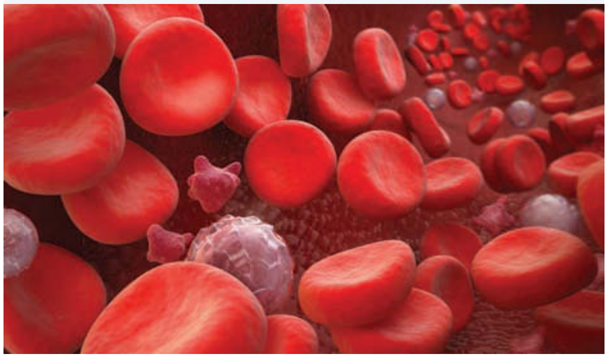
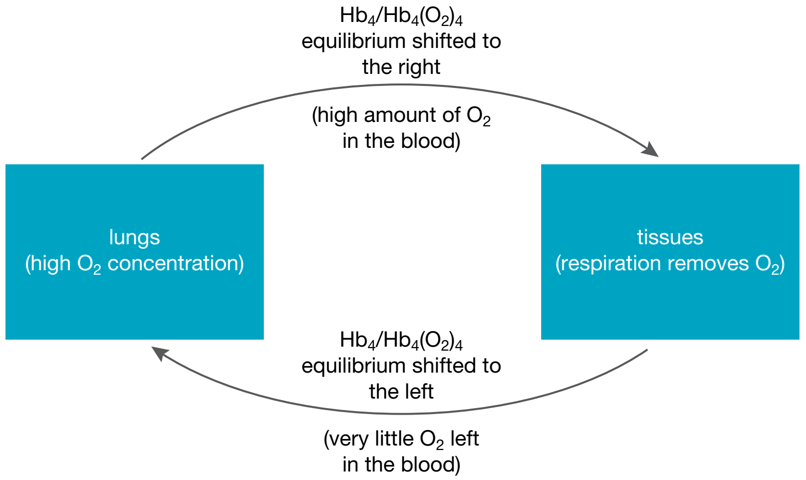
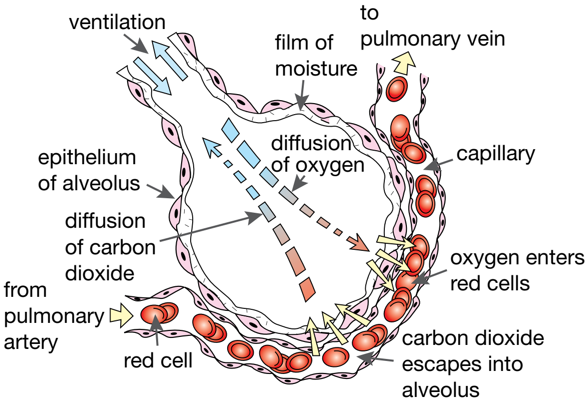


FIGURE 6.16 The transport of oxygen around the body relies on how the differing conditions in the lungs and in the tissues affect the haemoglobin–oxyhaemoglobin equilibrium.



When the blood reaches the cells, there is a much lower oxygen concentration because it is used in cellular respiration. In response to this removal of oxygen by respiration, the reaction responds by moving to the left in an effort to replace this oxygen. The oxyhaemoglobin decomposes back to haemoglobin, its oxygen being unloaded for use by the cells, and the haemoglobin molecules return to the lungs to start the cycle again.

FIGURE 6.17 The exchange of gases in an alveolus, part of the lungs. The alveoli are the structures in the lungs that transfer gases into and out of the blood supply.



Carbon monoxide poisoning

Carbon monoxide (CO), is an odourless and very poisonous gas. It is produced from the incomplete combustion of fossil fuels, typically in situations where the supply of oxygen to the combustion process is limited. This lack of odour makes it particularly dangerous because it can be inhaled without a person realising it. This can quickly lead to unconsciousness. Typical situations in which this may occur include leaking car exhausts, improperly maintained central heating units and the use of outdoor appliances such as camping heaters and barbeques in enclosed spaces.

Carbon monoxide is so poisonous because the reaction between carbon monoxide and haemoglobin:

$$Hb_4 + 4CO \rightleftharpoons Hb_4(CO)_4$$

is similar to that between oxygen and haemoglobin. This sets up a competing equilibrium with the oxygen–haemoglobin system. An important difference is that *the position of this equilibrium lies much further to the right*. The equilibrium constant for this reaction is about 20 000 times greater than that for the oxygen–haemoglobin system. If there is carbon monoxide in the lungs, carboxyhaemoglobin will readily form. When these blood cells reach the respiring cells, the reaction cannot be reversed. These blood cells are thus effectively removed from the pool available to carry oxygen. If this happens to enough of them, consequences can be fatal. A person would die of oxygen starvation, even though there might still be a plentiful supply of oxygen in their lungs.

SAMPLE PROBLEM 13

Explain why carbon monoxide is such a dangerous gas to inhale.

THINK	WRITE
Recall that oxygen transport around the body relies on free haemoglobin molecules being able to bind with oxygen in the lungs, and then being able to reverse this reaction in the vicinity of respiring cells. Recall that haemoglobin can bind with both oxygen (normal) and carbon monoxide (abnormal). Of these possibilities, the second occurs to a far greater extent (it is essentially irreversible under normal conditions).	Carbon monoxide reacts to a much greater extent with haemoglobin than does oxygen. Once carboxyhaemoglobin is formed it is very difficult to reverse. The haemoglobin molecules are thus removed from the pool of molecules available for oxygen transport. If too many are removed, oxygen starvation of cells will occur and death may result.

PRACTICE PROBLEM 13

Explain how oxygen is transported around the body.

Treating victims of carbon monoxide poisoning

The level of carbon monoxide in the blood that can cause death is surprisingly low. The reason for this is its ability to compete much more effectively than oxygen for the available haemoglobin.

If a victim of carbon monoxide poisoning is discovered soon enough, giving them oxygen-rich air to breathe may reverse the dangerous changes that have taken place in their red blood cells. This treatment relies on competing equilibria and Le Châtelier's principle.

The two equations involved are:

$$\mathrm{Hb_4 + 4O_2 \rightleftharpoons Hb_4(O_2)_4}$$

$$\mathrm{Hb_4 + 4CO \rightleftharpoons Hb_4(CO)_4}$$

The extra oxygen has two effects. First, it pushes the first equilibrium further to the right, thus making more efficient use of the few uncombined haemoglobin molecules that remain. The second effect follows from the first: as haemoglobin is used up by this extra oxygen, a reactant is effectively being removed from the second equilibrium. Despite its higher equilibrium constant, this reaction is forced in the backward direction to replace this haemoglobin. Thus, the carboxyhaemoglobin complex is encouraged to decompose and frees up the haemoglobin for normal oxygen transport.

FIGURE 6.18 Carbon monoxide fumes are a serious problem in traffic-congested cities.

6.6 EXERCISE

To answer questions online and to receive **immediate feedback** and **sample responses** for every question, go to your learnON title at www.jacplus.com.au.

1. Explain why a thermochemical equation is necessary to predict the effect of temperature on the extent of a reversible reaction.
2. Describe the effect of each of the following changes on a reaction at equilibrium.
   (a) Removing a product
   (b) Adding a reactant
   (c) Compressing a mixture being used to make ammonia according to

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

   (d) Increasing the temperature of an exothermic reaction
   (e) Adding water to double the volume in which the following reaction is occurring.

$$A(aq) + 2B(aq) \rightleftharpoons 3C(aq)$$

3. Predict the effect of the stated change on each of the systems represented by the equations below.
   (a) $CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$
   (adding methanol)
   (b) $CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$
   (increasing the pressure)
   (c) $4HCl(g) + O_2(g) \rightleftharpoons 2H_2O(g) + 2Cl_2(g)$
   (increasing temperature, given that the reaction is exothermic)
   (d) $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$
   (removing chlorine)
4. A student was asked to explain why the use of increased pressure should favour the formation of sulfur trioxide, SO_3, according to the equation:

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

   As part of her answer, she stated that '. . . the increased pressure will cause the system to move to the right. The resulting increase in the equilibrium constant means that there will be more SO_3 present'. Criticise the chemical accuracy of her answer.
5. Making methanol on a commercial scale involves pumping a mixture of carbon monoxide and hydrogen through a reaction chamber containing a mixture of ZnO and Cr_2O_3. This reaction is best carried out at a particular temperature and at a particular pressure. The equation for this reaction is:

$$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g) \quad \Delta H = -91\ \text{kJ mol}^{-1}$$

   (a) To maximise the rate of this reaction, should it be carried out at high or low temperatures?
   (b) To maximise the yield of this reaction, should it be carried out at high or low temperatures?
   (c) Describe the function of the ZnO/Cr_2O_3 mixture and how it partially solves the problem posed by your answers to (a) and (b).
   (d) How could the methanol be easily separated from the exit gases? What should be done with the unreacted CO and H_2?
   (e) Calculate the percentage atom efficiency for this reaction.
6. Haemoglobin is involved in the following two reactions:

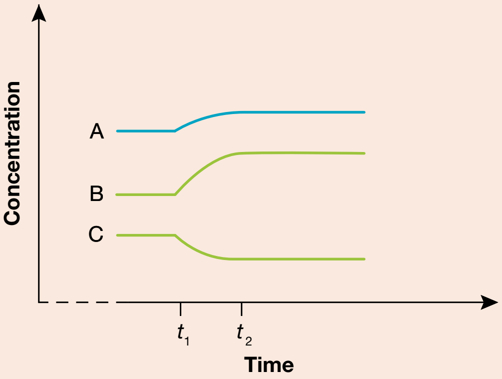
$$Hb + 4O_2 \rightleftharpoons Hb(O_2)_4 \text{ (reaction I)}$$
$$Hb + 4CO \rightleftharpoons Hb(CO)_4 \text{ (reaction II)}$$

   (a) How does the value of the equilibrium constant for reaction II compare to that for reaction I?
   (b) Respiring cells require oxygen. Explain how this triggers the reverse reaction in reaction I.
   (c) Give two reasons why the reverse reaction for reaction II is not triggered by respiring cells.
   (d) Patients suffering mildly from the effects of carbon monoxide may be given pure oxygen to breathe. In terms of Le Châtelier's principle, explain why this is done.

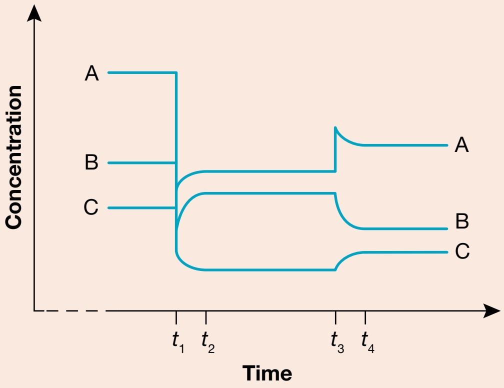
Questions 7 and 8 refer to the following reaction.

$$A(aq) + 2B(aq) \rightleftharpoons C(aq) \quad \Delta > 0$$

7. (a) What change was made to the equilibrium mixture at time t_1? Explain.
(b) How does the rate of the forward reaction compare to the rate of the backward reaction in the time period between t_1 and t_2?
(c) What will be the effect on this graph if some substance D is added at time t_3? Explain.



8. In another experiment using the same reaction, the following graph was obtained.
(a) What is the significance of the lines to the left of t_1?
(b) What change was made at time t_1? Explain.
(c) What change was made at time t_3? Explain.
(d) If a catalyst is also added at t_3, what effect will this have on the graph? Explain.
(e) Between them, a group of students use concentration values immediately before t_1, immediately before t_3 and immediately after t_4 to calculate K_c. How will their values compare? Explain.



9. Pure hydrogen iodide is a gas that partially decomposes when heated according to the equation:

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

At 500 K, the equilibrium constant for this reaction is 6.25×10^{-3}. At 600 K_c, the equilibrium constant is 2.04×10^{-2}.
(a) Is this reaction exothermic or endothermic?
(b) Calculate the value of the equilibrium constant at 500 K for the reaction:

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

10. Methanol may be prepared commercially from carbon monoxide and hydrogen using a suitable catalyst, according to the equation:

$$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g) \qquad \Delta H = -92\,\text{kJ mol}^{-1}$$

(a) How could the pressure under which the reaction is performed be adjusted to maximise the yield of methanol?
(b) How could the temperature at which the process is performed be adjusted to make more methanol?
(c) If extra carbon monoxide is added, how would this affect the amount of methanol produced?
(d) Which of the above proposals would actually change the value of the equilibrium constant?

11. The symbols of chemistry form an international language that can be read by anyone who understands it, regardless of the language they speak. Following is one item from a Hungarian book of chemistry questions.

Az ammónia oxidációs folyamatát az alábbi egyenlet fejezi ki:

$$4NH_3 + 5O_2 \rightleftharpoons 4NO + 6H_2O$$
$$Q = -226.5\ \text{kJ/mól}$$

Az egyenletekben szereplö vegyületek közül a NO képzödéshöje pozitív, az NH_3 és a víz kép′ódéshöje negatív. Ennek ismeretében magyarázzuk meg, miért kell a reakciót nagy reakciósebességgel lejátszatni, majd a reakciótermékeket gyorsan lehüteni?
(a) Describe the reaction referred to in the question.
(b) Is this reaction an exothermic or an endothermic reaction?

(c) Would this reaction be best performed at a high or low temperature to obtain a high value for the equilibrium constant?
(d) Would the formation of products in this reaction be favoured by high or low pressure?

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6.7 Review

6.7.1 Summary

Reversible and irreversible reactions

- Many chemical reactions have lower yields than might otherwise be expected. They do not go to completion. Such reactions are called equilibrium reactions. They can also be called reversible reactions.
- The rate of a chemical reaction is different from its extent. Rate measures how quickly the reaction takes place. Extent is a measure of the degree to which reactants are converted into products.

Homogenous equilibria

- Homogeneous reactions are reactions that occur in a single phase. Two common examples are aqueous reactions and gas phase reactions.
- Equilibrium reactions always reach a point at which no further change seems to be occurring. Such reactions have not stopped, the rate of the forward reaction has just become equal to the rate of the backward reaction. This is referred to as the dynamic nature of the equilibrium state.
- The process of attaining equilibrium, and the equilibrium state itself, can be explained in terms of reaction rates and collision theory.
- Equilibrium reactions may be represented by rate–time graphs and concentration–time graphs.
- Equilibrium reactions are also represented by balanced chemical and thermochemical equations. In such equations, the single arrow is replaced by a double arrow ($\rightleftharpoons$) to highlight the reversible nature of these reactions.

Calculations involving equilibrium systems

- At equilibrium, it is possible to write a fraction involving the equilibrium concentrations of all species present, which is related to the stoichiometry of the reaction. This fraction always has a constant value (at a particular temperature) and is given the symbol K_c. This is called the equilibrium law.
- It is also possible to write and evaluate this fraction at any stage of a reaction, in which case, it is usually given the symbol Q. If the value obtained for Q is not equal to K_c, the reaction is not at equilibrium. The changes taking place as the reaction seeks to attain equilibrium can be predicted by comparing the values of K_c and Q.
- The magnitude of the equilibrium constant, K_c, gives us an indication of the extent of an equilibrium reaction.
- The equilibrium constant has units that depend on the equation that it refers to. For some reactions, it is also possible that it has no units.
- Quantitative predictions may be made by performing calculations based on the equilibrium law.

Measuring the efficiency of a reaction or process

- The yield of a chemical reaction is usually expressed as a percentage and is given by the formula

$$\%\ \text{yield} = \frac{\text{actual yield}}{\text{theoretical yield}} \times \frac{100}{1}$$

- The atom efficiency of a reaction or process is usually expressed as a percentage and is given by the formula

$$\%\ \text{atom economy} = \frac{\text{molar mass of desired product}}{\text{molar mass of all reactants}} \times \frac{100}{1}$$

Le Châtelier's principle

- There are a number of ways that changes may be made to a reaction that is at equilibrium. These include the addition or removal of a participating substance, dilution, pressure changes (through compression or expansion) and temperature changes.
- Le Châtelier's principle may be used to predict the effect of a change to a mixture that is at equilibrium.
- Concentration–time graphs are a particularly useful way of summarising changes made to equilibrium mixtures and the subsequent response of the system to these changes.
- Equilibrium reactions are important in many situations. Many useful chemicals are manufactured industrially using such reactions. They are also important biologically, as illustrated by the way that oxygen is transported around the body using haemoglobin.
- Carbon monoxide poisoning involves competing equilibrium reactions. Carbon monoxide competes very effectively with oxygen, resulting in a drastic reduction in the amount of haemoglobin available for oxygen transport.

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6.7.2 Key terms

closed system a system in which all the reactants and products are contained in some manner with no escape to the surrounding environment.

concentration fraction essentially, the concentrations of the products divided by the concentrations of the reactants, including the coefficients of each component in the reaction

dynamic nature of equilibrium refers to the fact that at equilibrium forward and backward reactions are occurring at the same rate.

equilibrium constant the value of the concentration fraction at equilibrium; also called the equilibrium constant, Kc

equilibrium law the relationship between the concentrations of the products and the reactants, taking into account their stoichiometric values

equilibrium reaction a reaction in which both forward and reverse reactions are significant.

green chemistry a relatively new branch of chemistry that emphasises reducing the amounts of wastes produced, the more efficient use of energy and the use of renewable and recyclable resources.

haemoglobin the oxygen-carrying pigment and predominant protein in red blood cells

heterogeneous reaction a reaction in which some of the substances involved are in different phases.

homogeneous reaction a reaction in which all of the substances involved are in the same phase.

immiscible does not form a homogeneous mixture when mixed with another liquid

irreversible reaction a reaction which, to all practical purposes, occurs only on the forward direction.

Le Châtelier's principle When a change is made to an equilibrium system, the system moves to counteract the imposed change and restore the system to equilibrium.

open system a system in which some or all the reactants or products can escape to the surrounding environment.

percentage atom economy given by the formula

$$\%\,\text{atom economy} = \frac{\text{molar mass of desired product}}{\text{molar mass of all reactants}} \times \frac{100}{1}$$

percentage yield given by the formula

$$\%\,\text{yield} = \frac{\text{actual yield}}{\text{theoretical yield}} \times \frac{100}{1}$$

reaction quotient essentially, the concentrations of the products divided by the concentrations of the reactants, including the coefficients of each component in the reaction

reversible reaction a reaction in which the reformation of products into reactants occurs to a significant extent.

yield amount of product

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Digital document Key terms glossary — Topic 6 (doc-31400)

6.7.3 Practical work and experiments

Experiment 6.2

Investigating changes to the position of an equilibrium

Aim: To observe the effect of a number of changes on the position of the equilibrium represented by the equation:

$Fe^{3+}(aq) + SCN(aq) \rightleftharpoons Fe(SCN)^{2+}(aq)$

Digital document: doc-31262

Teacher-led video: tlvd-0747

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Digital documents Practical investigation logbook (doc-31401)

Experiment 6.1 Modelling an equilibrium (doc-31261)

Experiment 6.3 Temperature and the equilibrium constant (doc-31263)

6.7 Exercises

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6.7 Exercise 1: Multiple choice questions

1. A reaction has an equilibrium constant, K_c, of magnitude 2.56×10^{-7}. From this we can say that:
   - **A.** there will be minimal conversion of reactants into products
   - **B.** equilibrium will be established very quickly
   - **C.** equilibrium will be established very slowly
   - **D.** the backward reaction will have a faster rate than the forward reaction.

Use the following information to answer questions 2–4.
An equilibrium reaction is represented by the thermochemical equation:

$$2\mathrm{A(g)} + 2\mathrm{B(g)} \rightleftharpoons 3\mathrm{C(g)} \quad \Delta H = -10\,\mathrm{kJmol^{-1}}$$

2. The correct expression from which to calculate the equilibrium constant for this reaction is:
   - **A.** $\frac{[\mathrm{A}][\mathrm{B}]}{[\mathrm{C}]}$
   - **B.** $\frac{[\mathrm{A}]^2[\mathrm{B}]^2}{[\mathrm{C}]^3}$
   - **C.** $\frac{[\mathrm{C}]^3}{[\mathrm{A}]^2[\mathrm{B}]^2}$
   - **D.** $\frac{[\mathrm{C}]}{[\mathrm{A}][\mathrm{B}]}$
3. The units for the equilibrium constant for this reaction are:
   - **A.** M
   - **B.** $\mathrm{M}^{-\frac{1}{2}}$
   - **C.** M^{-1}
   - **D.** $\mathrm{M}^{\frac{1}{2}}$
4. If the temperature at which this reaction is carried out is lowered, the value of K_c will:
   - **A.** increase
   - **B.** decrease
   - **C.** remain the same
   - **D.** change in a manner related to the total number of particles on each side of the equation.
5. If some product is removed from a system that is at equilibrium:
   - **A.** the value of the equilibrium constant would decrease
   - **B.** a net backward reaction would result
   - **C.** the rate of the backward reaction would increase
   - **D.** extra product would be produced to re-establish the equilibrium.

Use the following information to answer questions 6–8.
The reaction represented by the equation:

$$\mathrm{CO_2(g)} + \mathrm{H_2(g)} \rightleftharpoons \mathrm{CO(g)} + \mathrm{H_2O(g)}$$

has an equilibrium constant, K_c, of 1.58 at 990 °C.

In an experiment, the concentrations of these four substances were measured at a particular time. The values obtained were:

$[CO_2] = 0.00208$ M
$[H_2] = 0.00221$ M
$[CO] = 0.00270$ M
$[H_2O] = 0.00250$ M

6. Which of the following statements is true of this reaction at this time?
- **A.** There is a net forward reaction.
- **B.** There is a net backward reaction.
- **C.** The rate of the backward reaction is faster than the rate of the forward reaction.
- **D.** The reaction is at equilibrium.

7. After equilibrium was established, the volume of the container was increased. Which of the following statements about the effect of this change is true?
- **A.** There will be no effect on the concentrations of any of the substances.
- **B.** There will be no effect on the amounts of any of the substances.
- **C.** The concentration of carbon monoxide will increase.
- **D.** The amount of carbon monoxide will increase.

8. In another experiment involving the same reaction (and at the same temperature), a mixture was allowed to reach equilibrium. At this point, the concentrations of CO_2, H_2 and CO were 0.0046 M, 0.00067 M and 0.0022 M respectively. The concentration of H_2O would therefore have been:
- **A.** 0.0009 M
- **B.** 0.0016 M
- **C.** 0.0022 M
- **D.** 0.0044 M

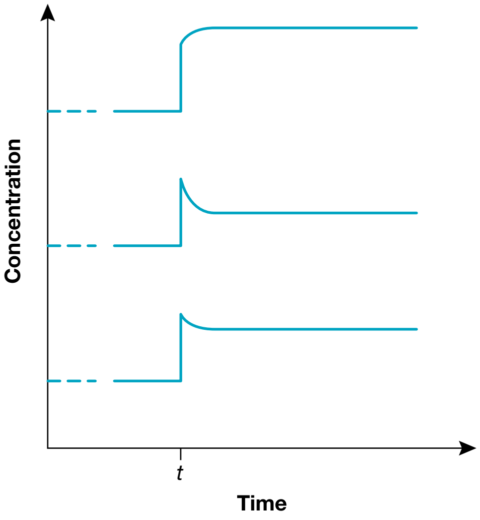
Use the following information to answer questions 9 and 10.

A reaction between the chemicals A, B and C is allowed to reach equilibrium. The equation for this reaction is:

$$A(g) + 2B(g) \rightleftharpoons C(g)$$

At a certain time, *t*, a change is made.

The following graph shows the concentration of each of these substances before and after this change.



9. What type of change was made at time *t*?
- **A.** The addition of one of the substances
- **B.** The removal of one of the substances
- **C.** An increase in volume
- **D.** A decrease in volume

10. From top to bottom, the graphs refer to the substances:
- **A.** C, B, A
- **B.** A, B, C
- **C.** B, A, C
- **D.** C, A, B.

6.7 Exercise 2: Short answer questions

1. Two students, Isla and Colin, were discussing the use of M as a unit. Colin stated that K_c can't have these units because M is a unit of concentration. However, Isla maintained that, although it is a unit of concentration, K_c could also sometimes have this unit. Who is correct? Explain.

2. In a 10 L vessel, 0.20 mol of SO_2, 0.40 mol of O_2 and 0.70 mol of SO_3 were mixed and allowed to come to equilibrium. Upon establishment of equilibrium, it was found that 0.30 mol of SO_3 remained. Calculate the value of the equilibrium constant for this reaction, given that the equation is:

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

3. An equilibrium mixture consisting of hydrogen, iodine and hydrogen iodide was analysed. It was found that 1.1 mol of hydrogen and 3.3 mol of hydrogen iodide were present in a 3.0 L container at a temperature of 600 K.
   a. If the value of the equilibrium constant, K_c, is 49 for the reaction:

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

   calculate the concentration of iodine.
   b. Why is the temperature specified in this question?
4. Both oxygen, O_2, and carbon monoxide, CO, can attach to the haemoglobin molecule. Under the normal biological conditions within the body, O_2 attaches itself to haemoglobin in the lungs and detaches itself when the haemoglobin is in the vicinity of respiring tissues. Carbon monoxide can also attach itself to haemoglobin while in the lungs, but is unable to detach when near respiring tissues.
   a. Using the symbol Hb_4 as an abbreviation for the haemoglobin molecule, write an equation for the reaction between haemoglobin and oxygen.
   b. Write an equation for the reaction between haemoglobin and carbon monoxide.
   c. Write the expression for the equilibrium constant for each of the reactions.
   d. From the information above, comment on the relative values of the equilibrium constants for the reactions.
   e. From your answer to (d), explain why carbon monoxide is such a poisonous gas.
5. The formation of ethyl acetate, $CH_3COOCH_2CH_3$, is represented by the equation:

$$CH_3COOH(l) + CH_3CH_2OH(l) \rightleftharpoons CH_3COOCH_2CH_3(l) + H_2O(l)$$

The value of K_c for this reaction is 4.

A number of experiments were conducted in which various amounts of these chemicals were mixed and allowed to react for varying periods of time. The results are tabulated below.

Experiment	$[CH_3COOH]$	$[CH_3CH_2OH]$	$[CH_3COOCH_2CH_3]$	$[H_2O]$
1	1	1	1	1
2	4	0.5	2	4
3	1.5	1	3	1.5
4	0.5	1	1.5	2
5	1	1.5	2	3
6	3	2	1.5	1

   a. In which experiments had equilibrium been achieved by the time of the analysis?
   b. For those not at equilibrium, in which direction would the reaction proceed to establish equilibrium?
6. The table shows the percentage formation of a product in equilibrium mixtures at different temperatures and pressures.

Pressure ($\times 10^5$ Pa)	Temperature (°C)			
	200	**300**	**400**	**500**
1	10	3.5	1.3	0.5
200	64	30	23	19
300	98	62	43	21

- **a.** Is the reaction under study exothermic or endothermic?
- **b.** If the equation for this reaction was written, how would the number of particles on the right-hand side compare with the number on the left?

7. Ammonia may be prepared according to the equation:

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \quad \Delta H = -92\,\text{kJ mol}^{-1}$$

In a particular experiment using typical industrial equipment, at a particular temperature, T, equilibrium was obtained with 4.32 mol of N_2, 2.00 mol of H_2 and 4.00 mol of NH_3 present in a 2.00 L pressure vessel.

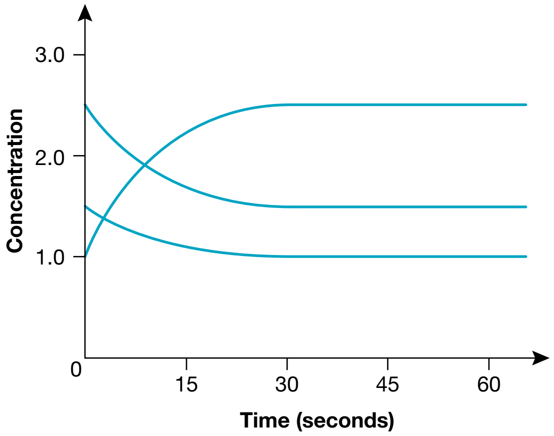
- **a.** Calculate the value of the equilibrium constant at the temperature of this experiment.
- **b.** Calculate the pressure exerted by the mixture of gases at equilibrium in terms of T.
- **c.** If the volume of the pressure vessel is reduced (at constant temperature), what effect would this have on the amount of NH_3 present?

8. In an experiment, the equilibrium established between substances A, B and C was investigated. Certain initial concentrations of each substance were mixed and then allowed to come to equilibrium.

The reaction between these three substances may be represented by the equation:

$$A + yB \rightleftharpoons zC$$

The changes in concentration are shown in the graph.

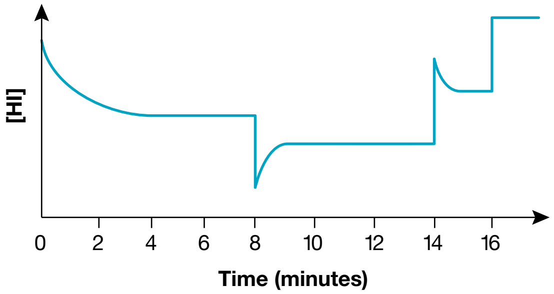


- **a.** Identify which line belongs to which substance.
- **b.** During the first 30 seconds of the experiment, how does the rate of the forward reaction compare with the rate of the backward reaction?
- **c.** After 30 seconds, how does the rate of the forward reaction compare with the rate of the backward reaction?
- **d.** From the graph, identify the values of y and z in the equation.
- **e.** Calculate the equilibrium constant for this reaction.

9. In an investigation of the decomposition of hydrogen iodide, represented by the equation:

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

the following concentration–time graph was obtained.



- **a.** Describe what happened during the first two minutes of the experiment.
- **b.** Describe what was happening from the four- to eight-minute marks.
- **c.** Give an explanation for the cause of the dip in the graph at the eight-minute mark.
- **d.** What do you think might have happened at the 14-minute mark?

e. What do you think might have happened at the 16-minute mark?

f. Did the change occurring at the 16-minute mark affect the equilibrium or not? Explain.

10. Upon dissolving in water, the sugar α-d-glucose undergoes conversion into an isomer called β-d-glucose. This process is called mutarotation and reaches equilibrium when 63.6% of the original α- d-glucose has been converted. Calculate the value of the equilibrium constant for this process.

6.7 Exercise 3: Exam practice questions

Question 1 (10 marks)

A simple form of colorimetric analysis may be used to study the equilibrium represented by the following equation.

$$Br_2(aq) + 2OH^-(aq) \rightleftharpoons OBr^-(aq) + Br^-(aq) + H_2O(l) \qquad \Delta H = +15\ kJ\ mol^{-1}$$

As molecular bromine, Br_2, is the only coloured species in this reaction, its red-brown colour may be used to monitor various changes made to this equilibrium.

A student performed an experiment where 10 mL samples of reaction mixture were poured into identical test tubes. The three changes listed below were then made to different samples of the equilibrium mixture. The colours before and after the changes were compared.

Change 1: A small amount of solid potassium bromide was added and the mixture stirred to dissolve it.

Change 2: A small amount of solid sodium chloride was added and the mixture stirred to dissolve it.

Change 3: The solution was warmed from room temperature to 50 °C.

For each of these three changes:

a. state whether you would expect the solution to darken, lighten or stay the same **3 marks**

b. use Le Châtelier's principle to explain your answer in (a). **7 marks**

Question 2 (9 marks)

Consider an equilibrium at room temperature that is represented by the following equation.

$$2A(g) + B(g) \rightleftharpoons 2C(g) \qquad \Delta H = -100\ \ kJ\ mol^{-1}; K_c = 10.0\ \ M^{-1}$$

For this reaction, it is possible to calculate the value of Q at any stage of the reaction using the following formula.

$$Q = \frac{[C]^2}{[A]^2[B]}$$

In one particular experiment, 1.5 mol of A, 0.50 mol of B and 2.5 mol of C are mixed in a 2.0 L container at room temperature.

a. Calculate the value of Q at the start of this experiment. **2 marks**

b. Use your answer to (a) to explain how the rate of the forward reaction compares with the rate of the backward reaction at the start of this experiment. **1 mark**

c. Some time later, the rates of the forward and backward reactions are measured and found to be equal. What is the value of Q at this time? Explain. **2 marks**

The experiment is now repeated under identical conditions, except that a catalyst is added to the initial mixture. The rates of the forward and backward reactions are again monitored over a period of time.

d. How would the initial rate of the forward reaction in the second experiment compare with the initial rate of the forward reaction in the first experiment? **1 mark**

e. How would the initial rate of the backward reaction in the second experiment compare with the initial rate of the backward reaction in the first experiment? **1 mark**

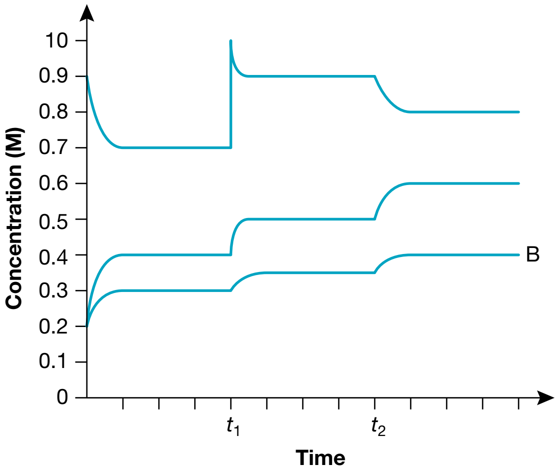
f. After waiting the same amount of time as for (c), what would be the value of Q in the second experiment? Explain. **2 marks**

Question 3 (11 marks)

The reaction represented by the equation:

$$xC(g) \rightleftharpoons yA(g) + B(g)$$

is studied by monitoring the concentration of its three species over time. The following graph shows the results that were obtained. Note that one of the substances is already labelled.



a. Label the other two lines on the graph with their correct substances. **2 marks**

b. What are the values of x and y in the equation above? **2 marks**

c. Calculate the value of the equilibrium constant immediately before time t_1. **2 marks**

d. What change was made to this system at time t_1? Explain. **2 marks**

e. At time t_2, the temperature was increased. Is this reaction exothermic or endothermic? Explain your reasoning, clearly showing any necessary calculations. **3 marks**

Question 4 (12 marks)

The highly toxic gas hydrogen cyanide (HCN) may be produced by the reaction of carbon monoxide with ammonia, according to the following equation.

$$2CO(g) + NH_3(g) \rightleftharpoons HCN(g) + CO_2(g) + H_2(g) \quad \Delta H > 0$$

This reaction is being investigated in a well-equipped laboratory using a 500 mL gas syringe.

In one particular experiment a mixture of CO and NH_3, along with a suitable catalyst, was injected into the syringe and the mixture allowed to come to equilibrium at a particular temperature. The mixture was then analysed and the following results were obtained.

Mass of CO present = 0.035 g
Mass of NH_3 present = 0.011 g
Mass of HCN present = 0.057 g

a. List two safety concerns for this experiment. Suggest how one of these could be minimised. **3 marks**

b. Write the expression for the equilibrium constant for this reaction. **1 mark**

c. Calculate the equilibrium concentrations of each of the substances involved. **4 marks**

d. Calculate the value and units for the equilibrium constant for this reaction at the temperature of the experiment. **2 marks**

e. If the volume of the syringes is reduced from 500 mL to 400 mL

- **i.** what will be the effect on the mass of hydrogen cyanide present? **1 mark**
- **ii.** what will be the effect on the concentration of hydrogen cyanide present? **1 mark**

Question 5 (5 marks)
Nitrogen oxides are serious air pollutants and are commonly found in areas where there is a high concentration of cars.

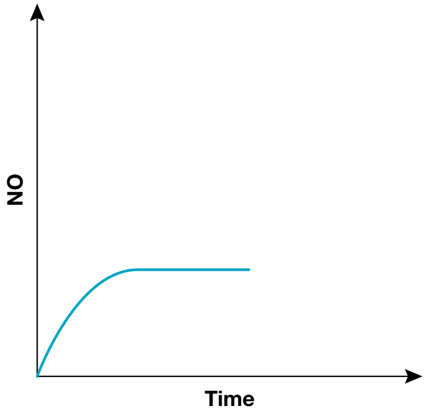
Nitrogen monoxide, NO, is produced from the reaction between nitrogen and oxygen at high temperatures, typically 1500 °C. The equation for this reaction is

$$N_2(g) + O_2(g) \rightleftharpoons 2NO(g) \qquad \Delta H = +181 \text{ kJ mol}^{-1}$$

a. This temperature is often reached during the combustion of petrol in a car engine. Explain how these conditions favour NO production. **2 marks**

This reaction was investigated by placing a mixture of nitrogen and oxygen gas in a sealed container, the volume of which can be increased or decreased. The temperature was held steady at 1500 °C.Using a data logging device, the concentration of NO is monitored to produce a concentration time graph.

b. The volume is now halved. Continue the graph to show how this change would affect the reaction system and how the system would respond to this change until equilibrium is restored. **2 marks**



c. The volume is now returned to its original value and the temperature increased to 2000 °C. How does the equilibrium mixture at this temperature compare to that at 1500 °C? Explain your reasoning. **1 mark**

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7 Production of chemicals by electrolysis and rechargeable batteries

7.1 Overview

Numerous **videos** and **interactivities** are available just where you need them, at the point of learning, in your digital formats, learnON and eBookPLUS at www.jacplus.com.au.

7.1.1 Introduction

Chlorine is one of the most widely used chemicals in the world. It is perhaps best known for its use as disinfectant in large public swimming pools. Upon addition to the pool water, chlorine reacts to form hypochlorite ions which serve as a powerful disinfectant. But chlorine has many more uses — it is used in the manufacture of organic compounds, plastics, bleach and chlorinated lime.

Chlorine is made on a large scale by the process of electrolysis. Electrolysis is also used to make sodium hydroxide and aluminium, and is central to electroplating and the production of extremely pure copper.

FIGURE 7.1 Chlorine is used extensively as a disinfecting agent in swimming pools.

This topic introduces the process of electrolysis and how the variables involved can alter the nature of the products produced. Faraday's Laws can be then applied to make quantitative predictions concerning electrolytic cells.

You will use your prior knowledge of basic redox concepts. Features of galvanic cells that you learnt about in topic 3 will be critical to your understanding of electrolytic cells. Furthermore, you will make extensive use of the electrochemical series as a tool for predicting electrode reactions and of your skills in stoichiometry.

7.1.2 What you will learn

KEY KNOWLEDGE

In this topic, you will investigate:

Production of chemicals by electrolysis

- 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.

Rechargeable batteries

- 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).

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PRACTICAL WORK AND INVESTIGATIONS

Practical work is a central component of learning and assessment. Experiments and investigations, supported by a **Practical investigation logbook** and **Teacher-led videos**, are included in this topic to provide opportunities to undertake investigations and communicate findings.

on Resources

Digital documents Key science skills (doc-30903)
Key terms glossary — Topic 7 (doc-31409)
Practical investigation logbook (doc-31410)

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To access key concept summaries and past VCAA exam questions download and print the **studyON: Revision and practice exam question booklet** (doc-31411).

7.2 What is electrolysis?

KEY CONCEPT

- Electrolysis of molten liquids and aqueous solutions using different electrodes

7.2.1 The process of electrolysis

In an electrochemical cell or galvanic cell, a spontaneous chemical reaction produces an electric current. In an electrolytic cell, the reverse process takes place. The passage of an electric current through an electrolytic solution causes a chemical reaction. This process is known as **electrolysis**.

In galvanic cells, chemical reactions can be used to generate a flow of electrons (an electric current). If a zinc rod is placed in copper(II) sulfate solution, a coating of copper appears on the zinc rod. This may be explained by considering the standard electrode potentials of each half-equation:

$$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)\ E^0 = +0.34\,V$$

$$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s)\ E^0 = -0.76\,V$$

Because the E^0 value for the Cu^{2+}/Cu redox pair is greater than the E^0 value for the Zn^{2+}/Zn redox pair, Cu^{2+} ions react spontaneously with zinc metal. A galvanic cell constructed from these two half-cells would produce electrical energy. The overall equation for such a galvanic cell would be:

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

However, if a copper rod is placed in a zinc sulfate solution, no reaction occurs. This reaction is the reverse of the one that produces energy, so energy must be supplied for the reaction to occur.

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

Electrolytic cells

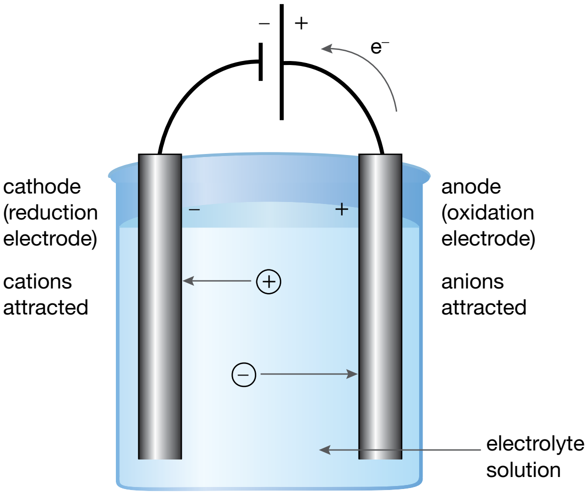
The chemical reaction that occurs when electricity passes through a molten ionic compound or through an electrolyte solution is called electrolysis. Solutes that form solutions that can conduct electricity are called **electrolytes**. An electrolyte solution conducts electricity. Positive ions gain electrons at the **cathode** and negative ions lose electrons at the **anode**. This transfer of electrons has the same effect as a flow of electrons, and the solution conducts electricity. The apparatus in which electrolysis occurs is called an **electrolytic cell**.

An electrolytic cell has three essential features.

1. An electrolyte solution that contains free-moving ions — these ions can donate or accept electrons, allowing electrons to flow through the external circuit.
2. Two electrodes at which the electrolysis reactions occur
3. An external source of electrons, such as a battery or power pack. This electron flow is in one direction only and is referred to as DC (direct current).

The external power source supplies the electrons. Electrons flow from the external power source to the negative electrode (the cathode), which is the site of reduction. Electrons are withdrawn by the power source from the positive electrode (the anode), which is the site of oxidation. Cations are attracted to the cathode and anions are attracted to the anode. The cations gain electrons from the cathode and the anions give up electrons to the anode.

FIGURE 7.2 An electrolytic cell



on Resources

Video eLesson Features of electrolytic cells (med-0439)

7.2.2 Electrolysis of molten ionic compounds

The simplest cases of electrolysis involve the electrolysis of molten ionic substances that are pure, using inert electrodes. As an example, let us consider the electrolysis of molten sodium chloride.

Solid sodium chloride does not conduct electricity. However, when an electric current is passed through molten sodium chloride, a chemical reaction can be clearly observed — a shiny bead of sodium is produced at the cathode and chlorine gas is evolved at the anode.

In solid sodium chloride, the oppositely charged sodium ions, Na^+, and chloride ions, Cl^-, are held tightly together. Heating the solid causes the ions in the crystal to separate and they are then free to move. The molten liquid is called a melt. In an electrolytic cell, the sodium ions are attracted to the negative cathode where they are reduced.

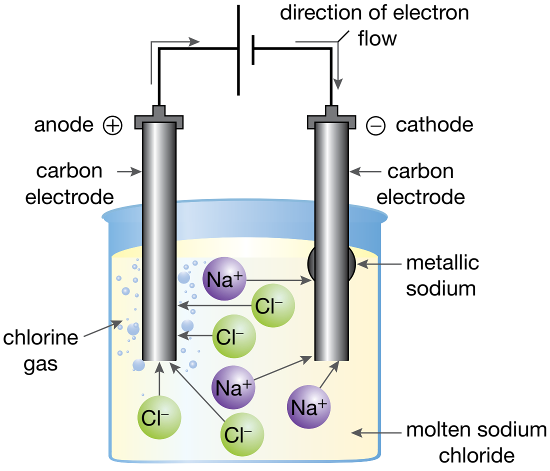
$$Na^+(l) + e^- \rightarrow Na(l)$$

The chloride ions are attracted to the positive anode where they undergo oxidation.

$$2Cl^-(l) \rightarrow Cl_2(g) + 2e^-$$

In a redox reaction the same number of electrons are consumed as are produced, so the overall equation is:

FIGURE 7.3 Electrolysis of molten sodium chloride



$$2Na^+(l) + 2Cl^-(l) \rightarrow 2Na(l) + Cl_2(g)$$

SAMPLE PROBLEM 1

a. **Write the equations for the reactions at each inert electrode when pure molten magnesium chloride undergoes electrolysis.**

b. **Write the overall equation for this reaction.**

Teacher-led video: SP1 (tlvd-0693)

THINK	WRITE
a. In molten magnesium chloride there are mobile Mg^{2+} and Cl^- ions. These are the only possible reactants for electrolysis.	
The Mg^{2+} ions will move to the negative electrode (the cathode) where they will accept electrons and be reduced.	Cathode: $Mg^{2+}(l) + 2e^- \rightarrow Mg(l)$
The Cl^- ions will move to the positive electrode (the anode) where they will give up electrons and be oxidised.	Anode: $2Cl^-(l) \rightarrow Cl_2(g) + 2e^-$
b. Obtain the overall equation by adding the half equations together, making sure that the electrons cancel out. **TIP:** Make sure that you use the correct symbols of state for magnesium. It is liquid (not aqueous) under these conditions.	$Mg^{2+}(l) + 2Cl^-(l) \rightarrow Mg(l) + Cl_2(g)$

PRACTICE PROBLEM 1

a. **Write the equations for the reactions at each electrode when pure molten potassium iodide undergoes electrolysis.**

b. **Write the overall equation for this reaction.**

7.2.3 Electrolysis of water

When a current is applied via two electrodes in pure water, nothing happens. There is no current flow and no electrolysis. But, if an electrolyte such as H_2SO_4 or KNO_3 is added in *low* concentration, the resulting solution conducts electricity and electrolysis occurs. The products of the electrolysis of water, in this case, are hydrogen and oxygen.

At the cathode, water is reduced to form hydrogen.

$$\text{Cathode: } 2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$$

At the anode, water is oxidised to form oxygen.

$$\text{Anode: } 2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$$

The region around the cathode becomes basic, owing to an increase in OH^- ions, whereas the region around the anode becomes acidic, owing to an increase in H^+ ions. The overall cell reaction may be obtained by adding the half-equations.

$$6H_2O(l) \rightarrow 2H_2(g) + O_2(g) + 4H^+(aq) + 4OH^-(aq)$$

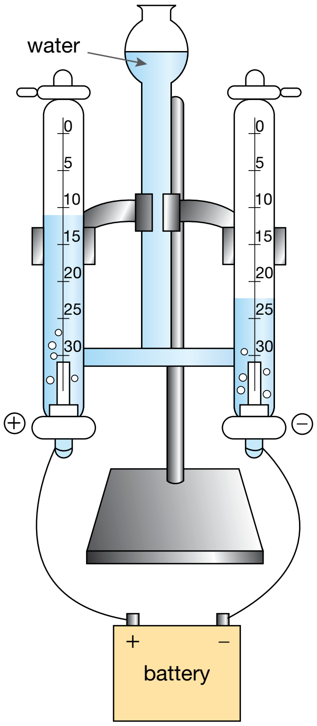
However, some of the ions produced re-form into reactants.

$$4H^+(aq) + 4OH^-(aq) \rightarrow 4H_2O(l)$$

These do not need to be included in the final overall equation.

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

FIGURE 7.4 Electrolysis of water using a Hofmann voltameter — when an electric current is passed through water, it decomposes into oxygen and hydrogen.

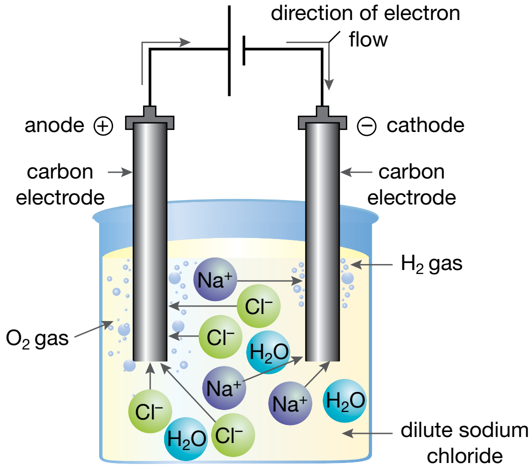


7.2.4 Electrolysis of aqueous solutions

In the electrolysis of water, it is necessary to add a small amount of electrolyte before electrical conduction can take place. This is done at a very low concentration and, as a result, water is effectively the only substance that can react to the passing of the electrical current. In the electrolysis of molten sodium chloride in section 7.2.3, there was also only one reaction possible at each electrode.

More complicated electrolysis systems involve situations where more than one reaction is possible at each electrode. The next two examples illustrate this. Note that in the second example, the choice of the electrode itself may also be a significant factor in the reactions that take place.

FIGURE 7.5 The electrolysis of dilute sodium chloride solution using inert electrodes



Electrolysis of dilute sodium chloride solution with inert electrodes

In many electrolysis reactions, inert electrodes are used. These are electrodes that do not affect the reactions taking place on their surfaces, and which conduct a current but do not tend to go into solutions as ions. They are usually carbon, in the form of graphite, or platinum, which is much more expensive. As shown in figure 7.5, there is a choice of reactants at each electrode when dilute sodium chloride is electrolysed.

At the cathode, sodium ions are present and the cathode is in contact with water molecules from the solvent. It is observed that a gas is produced, which proves to be hydrogen. If a few drops of phenolphthalein indicator are added to the region around the cathode it turns pink. From these observations we can infer that OH^- ions are also produced.

The production of H_2 and OH^- is consistent with the water being reduced in preference to the Na^+ ions, according to:

$$\text{Cathode: } 2H_2O(l)2e^- \rightarrow H_2(g) + 2OH^-(aq)$$

At the anode, a choice between water and chloride ions is possible. The observed evolution of oxygen gas, together with a few drops of phenolphthalein remaining clear, support the conclusion that water is once again reacting at this electrode, but this time it is being oxidised. This is due to the relative reducing strength of water and chlorine and is discussed in section 7.3.

$$\text{Anode: } 2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 2e^-$$

Electrolysis of dilute sodium chloride solution with copper electrodes

If the previous experiment is repeated using copper electrodes instead of inert electrodes, the results change. This illustrates that the choice of electrodes has an effect on the nature of the products of an electrolysis.

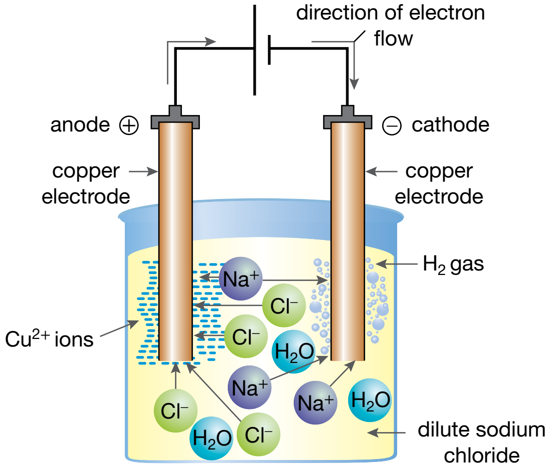
This time the equations occurring at each electrode are:

$$\text{Cathode: } 2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$$

$$\text{Anode: } Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$$

It can be seen that Cu^{2+} ions are produced instead of O_2 gas at the anode. This is due to the relative reducing strength and is discussed in section 7.3.

FIGURE 7.6 The electrolysis of dilute sodium chloride solution using copper electrodes



SAMPLE PROBLEM 2

What are the possible reactants around each electrode when a dilute copper sulfate solution is electrolysed?

Note that under conditions of dilute electrolysis in aqueous solutions, ions such as sulfate and nitrate are typically inert.

THINK	WRITE
1. Identify the constituents of the electrolyte.	Cu^{2+}, SO_4^{2-} and H_2O
2. Around the cathode reduction occurs and Cu^{2+} ions and H_2O molecules can potentially be reduced.	Possible reactants cathode: Cu^{2+} ions and H_2O molecules
3. Around the anode oxidation occurs and SO_4^{2-} ions and H_2O molecules can potentially be oxidised. The SO_4^{2-} ions can be ignored.	Possible reactants anode: H_2O

PRACTICE PROBLEM 2

What are the possible reactants around each electrode when a dilute potassium nitrate solution is electrolysed?

7.2 EXERCISE

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1. Predict the products that are formed when molten potassium chloride (KCl) undergoes electrolysis.
2. Give two observations that would be noted during the electrolysis of dilute sodium chloride with copper electrodes.
3. Explain how the addition of a small amount of KNO_3 allows water to conduct electricity and hence undergo electrolysis.
4. With reference to figure 7.4, and also to the equation for the decomposition of water, predict which side of the apparatus collects hydrogen gas and which collects oxygen gas.
5. Glass is an inert substance under virtually all conditions. Explain why glass cannot be used as an electrode material.
6. (a) Explain why the cathode has a negative charge in an electrolysis cell.
   (b) Explain why the anode has a positive charge in an electrolytic cell.
7. Explain why the reactants in a galvanic cell must be kept separated whereas the reactants in an electrolytic cell are usually contained within a single compartment.
8. Give an example of an electrolysis reaction where the nature of the electrodes influences the products produced.
9. During the electrolysis of molten lithium iodide, what product will form around the cathode and what will form around the anode? Explain.
10. Answer the following questions for electrolysis of molten potassium bromide.
    (a) Write the equation for the reaction occurring at the cathode.
    (b) State the sign of the cathode.
    (c) Write the equation for the reaction occurring at the anode.
    (d) State the sign of the anode.
    (e) Write the overall ionic equation for this electrolysis.

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7.3 Predicting reactions that occur during electrolysis

KEY CONCEPT

- 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

7.3.1 Using the electrochemical series

When a molten salt is electrolysed, the products are predictable. However, as shown in subtopic 7.2, when an aqueous solution of an ionic compound is electrolysed, water may react at one or both of the electrodes in preference to the ions from the salt. Hydrogen sometimes appears at the cathode, rather than a metal, and oxygen sometimes appears at the anode, rather than a metal cation or a halogen. For this reason, *we need to be able to predict the products of electrolysis when there is more than one possible reaction around an electrode*. From the examples seen so far, when there is a choice of two possible oxidising agents or reducing agents, one of these is preferentially reacted. As explained in topic 4, oxidising agents and reducing agents have different strengths, which can be used to produce an **electrochemical series**. As we shall now see, the electrochemical series also plays an important part in the redox reactions that occur during electrolysis. It can be used to help predict the products of electrolysis when multiple reactions are possible.

Predicting the products of electrolysis

In aqueous solutions, there is a mixture of at least two oxidising agents and two reducing agents. If non-inert electrodes are used, then even more possibilities may exist. Which oxidising agent and which reducing agent react?

Although electrolytic products depend on a number of factors, the following procedure is useful.

1. List the species present, including all metals that are used as electrodes.
2. Write half-equations involving these species in descending order of E^0.
3. Circle the species present in the electrolytic cell that could participate.
4. Select the oxidising agent with the highest E^0 (the strongest oxidising agent). This will be reduced at the cathode, because it requires less energy for reduction than an oxidising agent with a lower E^0.
5. Select the reducing agent with the lowest E^0 (the strongest reducing agent). This will be oxidised at the anode, because it requires less energy for oxidation than a reducing agent with a higher E^0.
6. Write the overall equation by combining the relevant half-equations.
7. Determine the minimum voltage required to achieve the reaction by subtracting the E^0 of the reducing agent from the E^0 of the oxidising agent.

FIGURE 7.7 Competing reactions are like wrestlers: the strongest challengers (strongest oxidising agent and strongest reducing agent) make it to the final round.

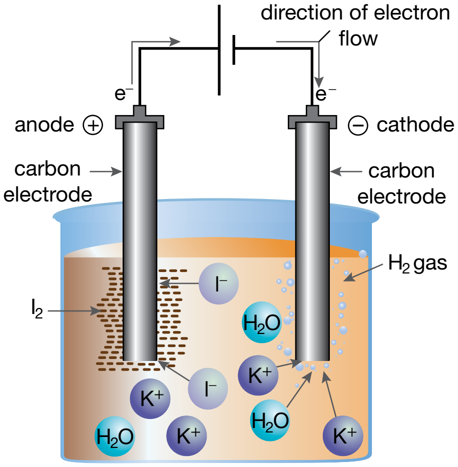
$$\textbf{minimum voltage required} = \boldsymbol{E^0_{\text{oxidising agent}} - E^0_{\text{reducing agent}}}$$

Consider the electrolysis of dilute potassium iodide (as shown in figure 7.8).

1. The species present in the cell are K^+, I^- and H_2O.
2. The possible half-equations for these species, in descending order of E^0 are listed using table 2 of the VCE Chemistry Data Book.
3. The species present in the electrolytic cell that could participate are then circled.

$$\begin{aligned}
&O_2(g) + 4H^+(aq) + 4e^- \rightleftharpoons \boxed{2H_2O(l)} && E^0 = +1.23\text{ V}\\
&I_2(s) + 2e^- \rightleftharpoons \boxed{2I^-}(aq) && E^0 = +0.54\text{ V}\\
&\boxed{2H_2O(l) +} 2e^- \rightleftharpoons H_2(g) + 2OH^-(aq) && E^0 = -0.83\text{ V}\\
&\boxed{K^+}(aq) + e^- \rightleftharpoons K(s) && E^0 = -2.93\text{ V}
\end{aligned}$$

FIGURE 7.8 Electrolysis of dilute potassium iodide



4. Recall the acronym OILRIG (oxidation is loss, reduction is gain) and that reduction occurs at the cathode, so there are two possible reactions in this cell. The oxidising agent with the highest E^0 value (the strongest oxidising agent) requires the least energy for reduction and is reduced at the cathode. So, water reacts in preference to potassium ions at the cathode.

$$\text{Cathode: } 2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq) \;\; E^0 = -0.83\text{ V}$$

   Hydrogen gas is evolved at this electrode and the solution around the cathode becomes alkaline, owing to an increase in hydroxide ion concentration.
5. Oxidation occurs at the anode, so there are two possible reactions. The reducing agent with the lowest E^0 value (the strongest reducing agent) requires the least energy for oxidation and is oxidised at the anode. Thus, iodide ions react in preference to water molecules at the anode.

$$\text{Anode: } 2I^-(aq) \rightarrow I_2(s) + 2e^- \;\; E^0 = +0.54\text{ V}$$

   The solution around the anode appears yellow-brown, owing to the formation of iodine.
6. The overall electrolytic cell reaction would be:

$$2H_2O(l) + 2I^-(aq) \rightarrow H_2(g) + 2OH^-(aq) + I_2(s)$$

7. Determine the minimum voltage required to achieve this reaction. A potential difference greater than the spontaneous reverse reaction would need to be applied, so more than $+0.54 - (-0.83) = 1.37$ volts should be delivered to this electrolytic cell.

   The products formed from the electrolysis of some electrolytes are shown in table 7.1.

TABLE 7.1 Products of electrolysis

(a) Using inert electrodes (platinum or graphite)

Electrolyte	Product formed at cathode	Product formed at anode
$PbBr_2$(l) — a melt	Pb(s)	Br_2(g)
NaCl(l) — a melt	Na(s)	Cl_2(g)
$CuCl_2$(aq)	Cu(s)	Cl_2(g), O_2*
NaCl(aq)	H_2(g)	Cl_2(g), O_2*
KNO_3(aq)	H_2(g)	O_2(g)
$CuSO_4$(aq)	Cu(s)	O_2(g)
H_2SO_4(aq)	H_2(g)	O_2(g)
NaOH(aq)	H_2(g)	O_2(g)

*depending on concentration

(b) When the electrodes take part in the reaction

Electrolyte	Copper cathode	Copper anode
$CuSO_4$(aq)	Cu(s) deposited	Cu(s) dissolves to form Cu^{2+} ions

SAMPLE PROBLEM 3

A dilute solution containing tin(II) chloride and copper sulfate is electrolysed using inert electrodes. Predict the products that will form at each electrode and write the relevant half-equations. Use these to write the overall equation and determine the minimum voltage required to achieve the reaction.

Teacher-led video: SP3 (tlvd-0695)

THINK	WRITE
1. Identify the constituents of the solution.	Sn^{2+}, Cl^-, Cu^{2+}, $SO_4{}^{2-}$ and H_2O molecules
2. From table 2 (Electrochemical series) of the VCE Chemistry Data Book, copy the half-equations for the species in descending order of standard electrode potentials. $SO_4{}^{2-}$ ions will not react. **TIP:** When using the electrochemical series, be careful with Sn^{2+} because it occurs in more than one place. (The same applies to Fe^{2+}.)	$Cl_2(g) + 2e^- \rightleftharpoons 2Cl^-(aq) \quad E^0 = +1.36\text{ V}$ $O_2(g) + 4H^+(aq) + 4e^- \rightleftharpoons 2H_2O(l) \quad E^0 = +1.23\text{ V}$ $Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s) \quad E^0 = +0.34\text{ V}$ $Sn^{4+}(aq) + 2e^- \rightleftharpoons Sn^{2+}(aq) \quad E^0 = +0.15\text{ V}$ $Sn^{2+}(aq) + 2e^- \rightleftharpoons Sn(s) \quad E^0 = -0.14\text{ V}$ $2H_2O(l) + 2e^- \rightleftharpoons H_2(g) + 2OH^-(aq) \quad E^0 = -0.83\text{ V}$
3. Circle the species present in the electrolytic cell that could participate.	$Cl_2(g) + 2e^- \rightleftharpoons \boxed{2Cl^-}(aq) \quad E^0 = +1.36\text{ V}$ $O_2(g) + 4H^+(aq) + 4e^- \rightleftharpoons \boxed{2H_2O}(l) \quad E^0 = +1.23\text{ V}$ $\boxed{Cu^{2+}}(aq) + 2e^- \rightleftharpoons Cu(s) \quad E^0 = +0.34\text{ V}$ $Sn^{4+}(aq) + 2e^- \rightleftharpoons \boxed{Sn^{2+}}(aq) \quad E^0 = +0.15\text{ V}$ $\boxed{Sn^{2+}}(aq) + 2e^- \rightleftharpoons Sn(s) \quad E^0 = -0.14\text{ V}$ $\boxed{2H_2O}(l) + 2e^- \rightleftharpoons H_2(g) + 2OH^-(aq) \quad E^0 = -0.83\text{ V}$
4. At the cathode, the strongest oxidising agent (highest E^0) undergoes reduction. Copper metal will form.	Cathode: $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s) \quad E^0 = +0.34\text{ V}$
5. At the anode, the strongest reducing agent (lowest E^0) undergoes oxidation. Sn^{4+} ions will form.	Anode: $Sn^{2+}(aq) \rightarrow Sn^{4+}(aq) + 2e^- \quad E^0 = +0.15\text{ V}$
6. Write the overall equation by combining the relevant half-equations.	$Cu^{2+}(aq) + Sn^{2+}(aq) \rightarrow Cu(s) + Sn^{4+}$
7. Determine the minimum voltage required by subtracting the E^0 of the reducing agent from the E^0 of the oxidising agent.	Minimum voltage required $= +0.34 - 0.15$ $= +0.19\text{ V}$

PRACTICE PROBLEM 3

A dilute solution containing silver nitrate and cobalt(II) chloride is electrolysed using inert electrodes. Predict the products that will form at each electrode and write the relevant half-equations. Use these to write the overall equation and determine the minimum voltage required to achieve the reaction.

TIP: The electrochemical series is written as a series of reversible reduction reactions. Don't forget to reverse these equations when writing an oxidation reaction. When you have decided whether an oxidation or reduction equation is required remember to use only a single arrow in your equation.

7.3.2 Factors affecting electrolysis of solutions

What happens during electrolysis depends on a number of factors, including:

- the concentration of the electrolyte
- the nature of the electrolyte
- the nature of the electrodes.

In any electrolysis reaction, alteration of any of these factors can change the nature of the products. The identity of products of an electrolysis reaction under fixed conditions is found by experiment. When the products are known, the reactions occurring at the electrodes can be written.

The effect of concentration

The electrochemical series (see table 3.2 in section 3.4.1 or Table 2 of the VCE Chemistry Data Book) is a useful tool for predicting the products of an electrolysis reaction. However, it must be remembered that it is based on standard conditions, in particular, where the concentrations of dissolved species are 1 M. If the concentrations of potential reactants are different from this, the observed results might be different from those predicted. For example, in the electrolysis of dilute sodium chloride reduction occurs at the cathode. The possible reactions are:

$$\begin{aligned}\text{Cathode: } & 2H_2O(l) + 2e^- \rightleftharpoons H_2(g) + 2OH^-(aq) \quad E^0 = -0.83\text{ V}\\ & Na^+(aq) + e^- \rightleftharpoons Na(l) \quad E^0 = -2.71\text{ V}\end{aligned}$$

As predicted from a table of standard redox potentials, water, rather than sodium ions, is reduced at the cathode. At the anode, chloride ions or water molecules may be oxidised:

$$\begin{aligned}\text{Anode: } & Cl_2(g) + 2e^- \rightleftharpoons 2Cl^-(aq) \quad E^0 = +1.36\text{V}\\ & O_2(g) + 4H^+(aq) + 4e^- \rightleftharpoons 2H_2O(l) \quad E^0 = +1.23\text{ V}\end{aligned}$$

As predicted from the table of standard redox potentials, oxygen gas is evolved in preference to chlorine gas at the anode.

The overall equation is:

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

However, at higher concentrations of chloride ions (6 M), the discharge of chlorine becomes more favourable. The reduction of water, rather than of sodium ions, still occurs at the cathode at higher concentrations of sodium ions. Therefore, the electrolysis of dilute sodium chloride produces hydrogen gas at the cathode and oxygen gas at the anode, but electrolysis of 6 M sodium chloride produces hydrogen gas at the cathode and chlorine gas at the anode.

This can be understood when the E^0 values for the following reactions are examined.

$$\begin{gathered}Cl^2(g) + 2e^- \rightleftharpoons 2Cl^-(aq) \quad E^0 = 1.36\text{V}\\ O_2(g) + 4H^+(aq) + 4e^- \quad \rightleftharpoons \quad 2H_2O(l) \quad E^0 = 1.23\text{ V}\end{gathered}$$

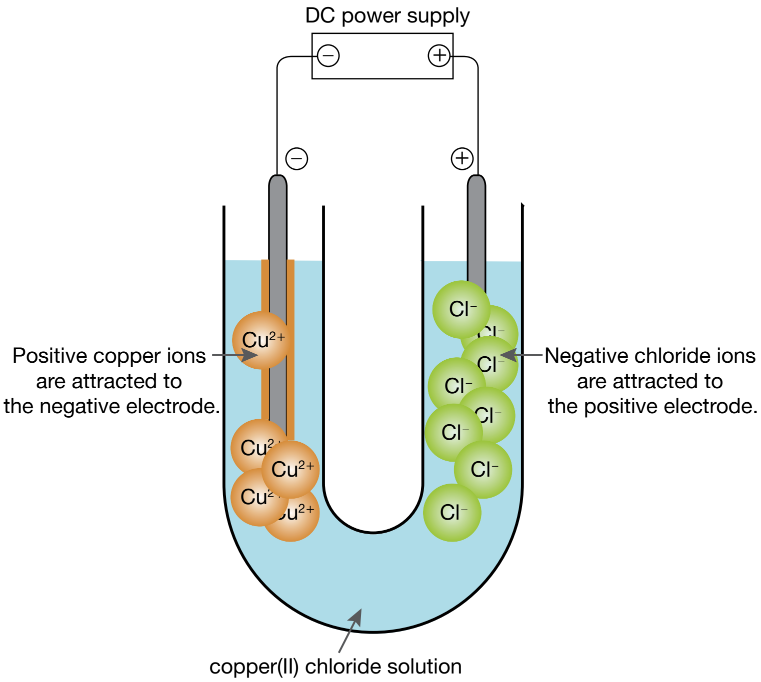
Values change when conditions are non-standard. In fact, they change enough to swap the order around, thus making the oxidation of chloride ions to chlorine gas the preferred reaction at the anode. Such a reversal at the cathode does not occur because the difference between H_2O and Na^+ ions is too large. Thus, when concentrated sodium chloride (>6 M) is electrolysed, the overall reaction becomes:

$$2H_2O(l) + 2Cl^-(aq) \rightarrow H_2(g) + Cl_2(g) + 2OH^-(aq)$$

The nature of the electrolyte

If concentrated copper(II) chloride solution is electrolysed instead of concentrated sodium chloride solution, the results are different. At the anode, chlorine gas is evolved in both cells, because the solution is concentrated and the only species present initially are chloride ions and water molecules. At the cathode, hydrogen gas is evolved in the sodium chloride cell, as discussed previously. In the copper chloride cell, two reactions are possible at the cathode.

FIGURE 7.9 Electrolysis of a concentrated copper(II) chloride solution produces copper (in solid form) and chlorine gas.



$$\begin{aligned} \text{Cathode: } & Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s) \quad E^0 = +0.34\text{ V} \\ & 2H_2O(l) + 2e^- \rightleftharpoons H_2(g) + 2OH^-(aq) \quad E^0 = -0.83\text{ V} \end{aligned}$$

As may be predicted from a consideration of the standard electrode potentials, copper is deposited in preference to the evolution of hydrogen gas. So, the products in an electrolytic reaction depend on the nature of the electrolyte.

The nature of the electrodes

If the anode is made of a metal such as silver, copper or iron, electrons may be removed preferentially from the metal atoms in the electrode rather than from the ionic species in solution or the water molecules themselves. There is no corresponding effect at the cathode because metals have no tendency to gain electrons.

The electrolysis of copper(II) chloride solution using inert electrodes results in the production of oxygen gas or chlorine gas (depending on the concentration of the solution; see table 7.1) at the anode. However, if copper electrodes are used, copper(II) ions are produced at the anode because the electrode itself acts as a stronger reducing agent than either water molecules or chloride ions. The copper anode dissolves to form Cu^{2+} ions.

$$\begin{aligned} Cl_2(g) + 2e^- \rightleftharpoons 2Cl^-(aq) \quad & E^0 = +1.36 \\ O_2(g) + 4H^+(aq) + 4e^- \rightleftharpoons 2H_2O(l) \quad & E^0 = +1.23\text{ V} \\ Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s) \quad & E^0 = +0.34\text{ V} \end{aligned}$$

SAMPLE PROBLEM 4

A solution of copper(II) sulfate is electrolysed using nickel electrodes. Write the half-equations for the reaction occurring at each electrode. Use these to write the overall equation and determine the minimum voltage required to achieve the reaction.

Teacher-led video: SP4 (tlvd-0696)

THINK	WRITE
1. Identify the constituents of the solution.	Cu^{2+}, SO_4^{2-} and H_2O molecules. Ni from the electrode might react as well.
2. From table 2 (Electrochemical series) of the VCE Chemistry Data Book, copy the half-equations for the species in descending E^0 order.	$O_2(g) + 4H^+(aq) + 4e^- \rightleftharpoons 2H_2O(l) \quad E^0 = +1.23\ V$ $Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s) \quad E^0 = +0.34\ V$ $Ni^{2+}(aq) + 2e^- \rightleftharpoons Ni(s) \quad E^0 = -0.25\ V$ $2H_2O(l) + 2e^- \rightleftharpoons H_2(g) + 2OH^-(aq) \quad E^0 = -0.83\ V$
3. Circle the species present in the electrolytic cell that could participate.	$O_2(g) + 4H^+(aq) + 4e^- \rightleftharpoons \boxed{2H_2O}(l) \quad E^0 = +1.23\ V$ $\boxed{Cu^{2+}}(aq) + 2e^- \rightleftharpoons Cu(s) \quad E^0 = +0.34\ V$ $\boxed{Ni^{2+}}(aq) + 2e^- \rightleftharpoons \boxed{Ni}(s) \quad E^0 = -0.25\ V$ $\boxed{2H_2O}(l) + 2e^- \rightleftharpoons H_2(g) + 2OH^-(aq) \quad E^0 = -0.25\ V$
4. At the cathode, the strongest oxidising agent (highest E^0) undergoes reduction.	Cathode: $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s) \quad E^0 = +0.34\ V$
5. Identify the strongest reducing agent and write the equation for the anode.	Anode: $Ni(s) \rightarrow Ni^{2+}(aq) + 2e^- \quad E^0 = -0.25\ V$
6. Write overall equation by combining the relevant half-equations.	$Cu^{2+}(aq) + Ni(s) \rightarrow Cu(s) + Ni^{2+}$
7. Determine the minimum voltage required by subtracting the E^0 of the reducing agent from the E^0 of the oxidising agent.	Minimum voltage required $= +0.34 - (-0.25)$ $= +0.59\ V$

PRACTICE PROBLEM 4

A solution of lead(II) nitrate is electrolysed using iron electrodes. Write the half-equations for the reaction occurring at each electrode. Use these to write the overall equation and determine the minimum voltage required to achieve the reaction.

on Resources

Video eLesson	Predicting the products of electrolysis (med-0440)
Digital documents	Experiment 7.1 Electrolysis of aqueous solutions (doc-31264) Experiment 7.2 Factors affecting electrolysis (student design) (doc-31265)
Teacher-led video	Experiment 7.1 Electrolysis of aqueous solutions (tlvd-0749)

7.3 EXERCISE

To answer questions online and to receive **immediate feedback** and **sample responses** for every question go to your learnON title at www.jacplus.com.au.

1. Write the equations for the reaction at each electrode when a 1 M solution of $ZnBr_2$ undergoes electrolysis. Use these equations to write the overall equation for this reaction.
2. (a) Write the equations for the reaction at each electrode when a 1 M solution of hydrochloric acid is electrolysed using silver electrodes. Use these equations to write the overall equation for this reaction.
   (b) Why is it not possible to electrolyse this solution with nickel electrodes?
   Remember from Unit 2 that hydrochloric acid is a strong acid and a 1 M solution will therefore consist almost entirely of H^+ ions and Cl^- ions.)
3. Write the half-equation that occurs at the cathode and the anode when a dilute solution of Na_2SO_4 is electrolysed using inert electrodes.
4. Predict the products and the minimum cell voltage required for the electrolysis of a 1 M solution of aluminium chloride.
5. Using inert electrodes, predict the products formed from the electrolysis of:
   (a) molten lead (II) chloride
   (b) 1 M solution of lead (II) chloride.
6. A solution containing lead, magnesium and copper ions is electrolysed for a long time.
   (a) What will be the first product formed at the cathode?
   (b) If the electrolysis is continued until all the ions responsible for the product in question 6a are used up, what will be the next product observed at the cathode?
   (c) If the electrolysis is continued further until the product from question 6b is observed to stop forming, what will be the third product formed at the cathode?
7. Write the half-equations and overall ionic equations for the electrolysis of:
   (a) molten nickel iodide (NiI_2)
   (b) 1 M nickel iodide solution.
8. Magnesium can be obtained commercially from sea water. During the last stage of this process, molten magnesium chloride undergoes electrolysis in a cell that contains an iron cathode and a graphite anode.
   (a) Why can iron be used to form the cathode but not the anode?
   (b) Draw a fully labelled diagram of an electrolytic cell that could be used to produce magnesium. Include equations.
9. A solution containing both $Zn(NO_3)_2$ and $AgNO_3$, with both at 1 M concentration, undergoes electrolysis using platinum electrodes. If this electrolysis is allowed to proceed for a long time, in what order will the products at the cathode appear?
10. A dilute solution of copper sulfate is electrolysed using platinum electrodes.
    (a) Write the half-equations for the reactions at each electrode.
    (b) How will the concentration of Cu^{2+} ions change during this process?
    If the platinum electrodes are replaced by copper electrodes:
    (c) Write the half-equations for the reactions that now occur at each electrode.
    (d) How will the concentration of Cu^{2+} ions change during this time?
11. Sometimes reaction products from an electrolysis reaction may be different to those predicted. How might this happen?
12. Why is it not possible to electrolyse a solution containing tin(II) chloride and iron(III) chloride?

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7.4 Commercial applications of electrolysis

KEY CONCEPT

- 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)

TIP: Some examples of commercial electrolytic cells are provided in this subtopic. Although you are not required to know the details of any specific cell, you should examine these examples and make sure that you understand the principles behind their operation. It is expected that you should be able to apply these principles in an examination, rather than just restating facts that you have learnt.

7.4.1 Producing aluminium

Although aluminium is the most abundant metallic element in the Earth's crust, it was difficult to extract before 1886. The most common process involved its extraction from the ore and conversion into $AlCl_3$. This was then chemically reduced using either sodium or potassium, metals that were also difficult to produce. Compared with today's methods, this process was on a small scale and very expensive. One hundred and thirty years ago, only the wealthy could afford aluminium. Napoleon III of France was famous for serving food to special guests at banquets on aluminium plates, while ordinary guests were served food on plates made from gold! The aluminium extraction breakthrough came in 1886 with the development of what we now call the Hall–Héroult cell.

FIGURE 7.10 Today, aluminium products, such as this aluminium scooter, are common.

The Hall–Héroult cell

Paul Héroult, a French scientist, and Charles Hall, an American inventor and chemist, almost simultaneously filed patent applications for the industrial electrolytic production of aluminium, despite working completely independently of each other. Today, the **Hall–Héroult** method of aluminium production is used in primary aluminium smelters throughout the world. It has resulted in an enormous growth in aluminium production, from 13 tonnes per year in 1885 to more than 64 million tonnes per year today.

The industrial production of aluminium occurs in a Hall–Héroult cell (see figure 7.11) and involves electrolysis of alumina that is dissolved in molten cryolite (Na_3AlF_6). The electrolysis takes place in a steel vessel called a cell. The cell is lined with carbon, and contains the molten cryolite and dissolved alumina mixture maintained at a temperature of about 980 °C. Carbon blocks suspended above the cell and partially immersed in the electrolyte act as anodes, while the carbon lining of the cell acts as the cathode.

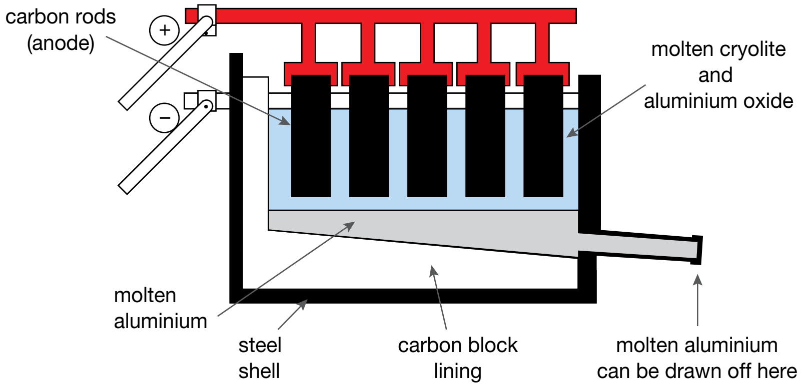
Aluminium cannot be reduced by electrolysis of an aqueous solution of a soluble aluminium salt because water, a stronger oxidising agent than aluminium ions, is preferentially reduced.

$$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq) \quad E^0 = -0.83\text{ V}$$

$$Al^{3+}(aq) + 3e^- \rightarrow Al(s) \quad E^0 = -1.67\text{ V}$$

Cryolite, Na_3AlF_6, acts as a solvent and an electrolyte due to its unique combination of properties. It has a melting point less than half that of alumina (960 °C compared with aluminas 2020 °C), a low vapour pressure and a density lower than molten aluminiums (2.05 g cm^{-3} compared with aluminiums 2.30 g cm^{-3}). Cryolite can dissolve sufficient alumina to allow deposition of aluminium at about 980 °C. Less energy is used, saving the industry fuel costs.

FIGURE 7.11 Schematic diagram of a cross-section of a Hall–Héroult cell for the electrolytic production of aluminium



The carbon anode and cathode are both made from petroleum coke with pitch as a binder. The anode takes part in the chemical reactions in the cell.

Alumina, Al_2O_3, is fed into the electrolyte at regular intervals where it dissolves, forming aluminium ions, Al^{3+}, and oxide ions, O^{2-}. The direct current applied across each cell moves the ions in opposite directions.

At the anode, the oxide ions are oxidised to form oxygen gas. The oxygen then immediately reacts with the carbon anode to form carbon dioxide.

$$\begin{aligned}\text{Anode: } & 2O^{2-}(l) \rightarrow O_2(g) + 4e^- \\ & O_2(g) + C(s) \rightarrow CO_2(g)\end{aligned}$$

The overall reaction at the anode can therefore be written as:

$$\text{Anode: } C(s) + 2O^{2-}(l) \rightarrow CO_2(g) + 4e^-$$

As the carbon anodes are gradually consumed during the process, they are lowered to maintain the optimum distance between the anode and cathode surfaces, until they are burned away and replaced. The anodes are generally replaced every three weeks so that the process is continuous.

The positively charged aluminium ions that are dissolved in the cryolite are drawn to the negatively charged cathode where they form aluminium.

$$\text{Cathode: } Al^{3+}(l) + 3e^- \rightarrow Al(l)$$

The density difference between cryolite and the newly formed molten aluminium allows the aluminium to settle at the bottom of the cell where it is regularly drained out. After draining, the molten aluminium can be cast.

The overall reaction for the electrolytic production of aluminium by electrolysis can be represented as:

$$2Al_2O_3(l) + 3C(s) \rightarrow 4Al(l) + 3CO_2(g)$$

Carbon dioxide is the main gas produced in this process. Other gases produced include fluorides that are initially confined by gas hoods, then continuously removed and treated.

The amount of alumina added to a cell must be strictly controlled. If too little alumina is added, maximum yields and productivity rates of aluminium production become economically unfavourable. If too much alumina is added, it falls to the bottom of the cell instead of dissolving (because it is denser than molten aluminium). There, it settles below the aluminium and interferes with the flow of current.

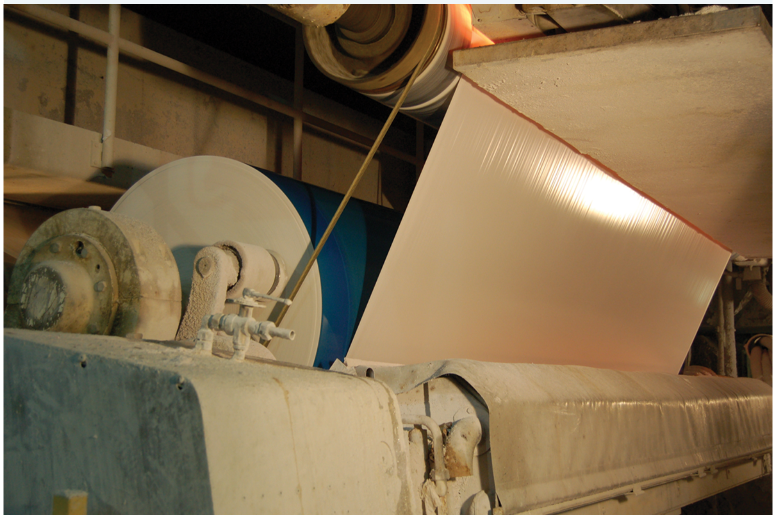
Hall–Héroult cells operate continuously at low voltage of about 4–5 V but require a high current of 50 000–280 000 A. The electrical resistance to the flow of this current generates enough heat to keep the electrolyte in a liquid state.

7.4.2 The industrial electrolysis of brine

Chlorine gas, hydrogen gas and sodium hydroxide are three important industrial chemicals. They can be produced simultaneously by electrolysis of a concentrated aqueous sodium chloride solution (brine). Recently, a new type of electrolytic cell, the **membrane cell**, was developed for this reaction.

Although chloride ions are weaker reducing agents than water molecules, chlorine may be produced electrolytically from aqueous solutions of sodium chloride. This is done by altering the operating conditions of electrolytic cells to favour the reduction of chloride ions rather than water molecules.

FIGURE 7.12 In the manufacture of paper, wood pulp is broken down by soaking it in concentrated sodium hydroxide solution. Sodium hydroxide has many other industrial applications and may be produced in large quantities by electrolysis.



Membrane cells

Early cells for the electrolysis of brine used either mercury or asbestos in their design. Membrane cells were developed in response to the potential health hazards involved with such cells. Industrial membrane cells can be very large.

A membrane cell is characterised by its plastic, semipermeable membrane that separates the anode half-cell from the cathode half-cell of the electrolytic cell. This semipermeable membrane allows sodium ions and hydroxide ions to pass from one electrode half-cell to the other but does not allow chloride ions or water to pass through. As a result, sodium ions and hydroxide ions are trapped in the cathode compartment, thus producing pure sodium hydroxide and hydrogen gas, which is evolved at the cathode. Chlorine gas is produced at the anode. The relevant equations are:

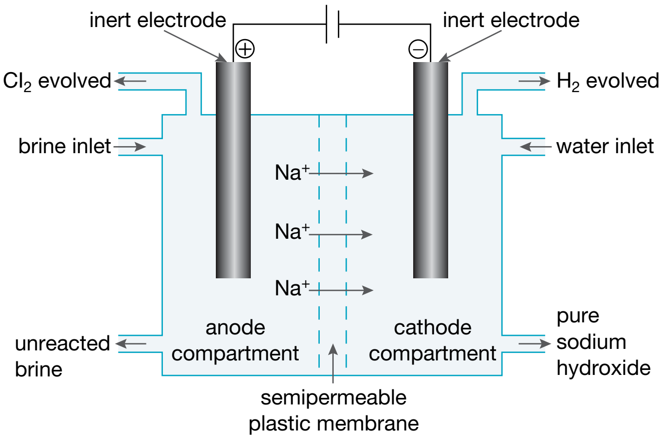
$$\text{Cathode: } 2Na^+(aq) + 2H_2O(l) + 2e^- \rightarrow 2Na^+(aq) + 2OH^-(aq) + H_2(g)$$

$$\text{Anode: } 2Cl^-(aq) \rightarrow Cl_2(g) + 2e^-$$

As with all electrolytic cells, the products are prevented from coming into contact with each other. The overall reaction for the production of chlorine via the membrane cell process is:

$$2NaCl(aq) + 2H_2O(l) \rightarrow 2NaOH(aq) + H_2(g) + Cl_2(g)$$

FIGURE 7.13 A membrane cell



on Resources

Video eLesson Using the membrane cell to manufacture sodium hydroxide (med-0569)

7.4.3 Electroplating

Electroplating is the process of coating an object in a metal. Inexpensive silver-plated jewellery can be produced through electroplating. 'Gold' rings that turn fingers green are actually copper rings that have been electroplated with gold.

In the electroplating process, the article to be plated is used as the cathode and the metal being plated onto the article is used as the anode. The electrolytic solution or 'bath' contains a salt of the metal being plated. A low-voltage electric current causes metal ions from the bath to gain electrons at the cathode and to deposit as a metal coating on the cathode (the object). It also causes metal atoms in the anode to lose electrons and go into the bath as ions. As the plating proceeds, the anode gradually disappears and maintains the metal ion's concentration in the bath.

Electroplating operations involve the use of many toxic solutions. Objects to be plated are thoroughly cleaned of all grease and dirt using concentrated acidic or basic solutions. The cleaning solutions eventually become ineffective, owing to contamination, and must be disposed of.

A number of factors contribute to the quality of the metal coating formed in electroplating. These include:

- the carefully controlled concentration of the cations to be reduced in the plating solution. Unwanted side reactions must be avoided.
- the careful consideration of the type and concentration of electrolyte
- the solution, which must contain compounds to control the acidity and increase the conductivity
- the compounds, some of which make the metal coating brighter or smoother
- the shape of the anode, which must often be shaped like the object at the cathode to achieve an even metal coating.

Silver-plating

In silver-plating, objects such as cutlery are coated at the cathode. The plating solution contains silver ions, $Ag^+(aq)$. The anode is pure silver. When current flows, silver is deposited on the metal object.

$$\text{Cathode: } Ag^+(aq) + e^- \rightarrow Ag(s)$$

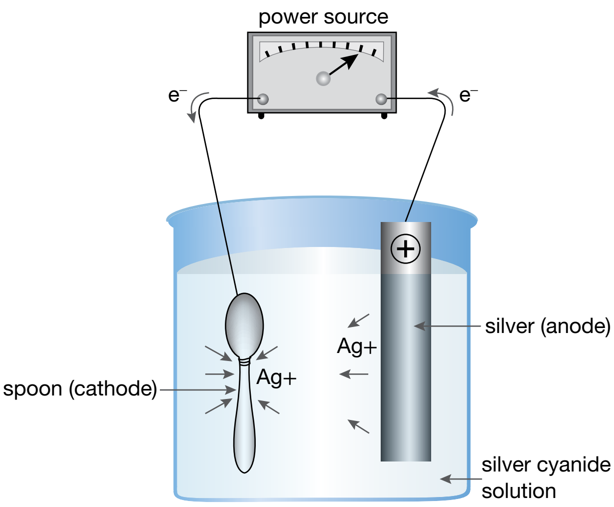
At the same time, silver atoms at the anode form silver ions.

Anode: $Ag(s) \rightarrow Ag^+(aq) + e^-$

The above reactions are possible due to their positions on the electrochemical series relative to water. At the cathode, silver ions are a stronger oxidising agent than water and so they are preferentially reduced. At the anode, silver metal is a stronger reducing agent than water. Therefore, the silver metal reacts in preference to water and is oxidised to silver ions.

The plating is only a few hundredths of a centimetre thick. If the experimental conditions are right, the metal coating adheres strongly and may be polished. However, if conditions are not satisfactory, the metal becomes powder-like and drops off.

FIGURE 7.14 Silver-plating mechanism for cutlery



Resources

Interactivity Electroplating simulation (int-1258)
Digital documents Experiment 7.3 Electroplating (doc-31266)
Teacher-led video Experiment 7.3 Electroplating (tlvd-0751)

7.4 EXERCISE

To answer questions online and to receive **immediate feedback** and **sample responses** for every question go to your learnON title at www.jacplus.com.au.

1. List all the products produced from the commercial electrolysis of a brine solution using a membrane cell.
2. Why is it important that the membrane used in a membrane cell be impervious to OH^- ions?
3. Aluminium metal cannot be produced by the electrolysis of an aqueous solution of its ions. List two other metals that also cannot be produced this way.
4. (a) What is the main advantage of the electrolytic production of aluminium from alumina, Al_2O_3, dissolved in cryolite rather than from straight molten alumina?
   (b) Why can't a solution of alumina dissolved in water at normal temperatures be used instead?
5. Membrane cells operate using a concentrated solution of sodium chloride. Explain what would happen if this solution was allowed to become diluted.
6. The addition of cryolite, Na_3AlF_6, in the Hall–Héroult process introduces $Na^+(l)$ and $F^-(l)$ into the mixture. Why is there no issue with contamination?
7. In the production of aluminium in a Hall–Héroult cell, the cathode and anode are made of carbon. The anode needs to be replaced every three weeks whereas the cathode can last up to five years. Explain this difference using an appropriate equation.
8. Using a fully labelled diagram, explain how you would plate a piece of lead with nickel by electroplating.
9. In electroplating, why is the object being electroplated made the cathode?
10. In nickel-plating, what substance would you choose for:
    (a) the anode?
    (b) the electrolyte?

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7.5 Comparing galvanic and electrolytic cells

KEY CONCEPT

- The comparison of an electrolytic cell with a galvanic cell with reference to the energy transformations involved and basic structural features and processes

7.5.1 Similarities and differences between galvanic and electrolytic cells

Consider the following redox half-equations:

$$\begin{aligned} &Cu^{2+}(aq) + 2e^- \rightarrow Cu(s) \quad E^0 = +0.34\text{ V} \\ &Zn^{2+}(aq) + 2e^- \rightarrow Zn(s) \quad E^0 = -0.76\text{ V} \end{aligned}$$

Electrical energy can be obtained from the spontaneous reaction between copper(II) ions and zinc metal in a galvanic cell.

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

When standard half-cells are used, 1.1 volts may be generated by the cell. However, if an external DC power source is placed in the external circuit and connected so that the applied voltage is opposite to that generated by the galvanic cell, the reverse reaction proceeds.

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

When standard half-cells are used, more than 1.1 volts are needed to force this non-spontaneous reaction to occur.

In both galvanic and electrolytic cells, oxidation occurs at the anode and reduction occurs at the cathode. However, in an electrolytic cell, the cathode is negative because the external DC source forces electrons onto it. Therefore, zinc ions, Zn^{2+}, are attracted to the cathode where they pick up electrons to form zinc atoms.

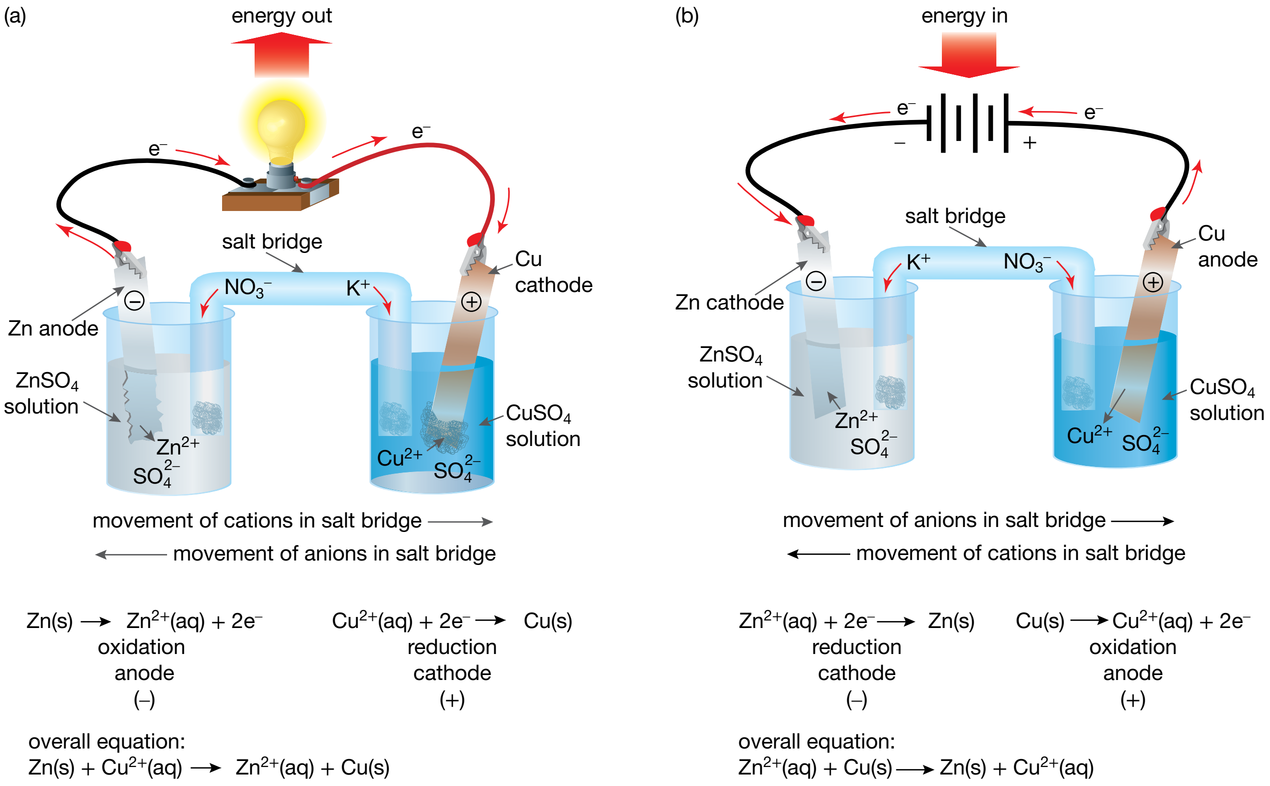
The anode in an electrolytic cell is positive because the DC source withdraws electrons from it. Electrons are supplied to the positive anode by the oxidation of the copper electrode itself.

In an electrolytic cell, the polarity of the electrodes is determined by the external DC source. In contrast, the polarity of the electrodes in a galvanic cell develops due to the spontaneous redox reaction occurring within the cell itself. Table 7.2 summarises the major similarities and differences between galvanic and electrolytic cells.

TABLE 7.2 Comparison of galvanic and electrolytic cells

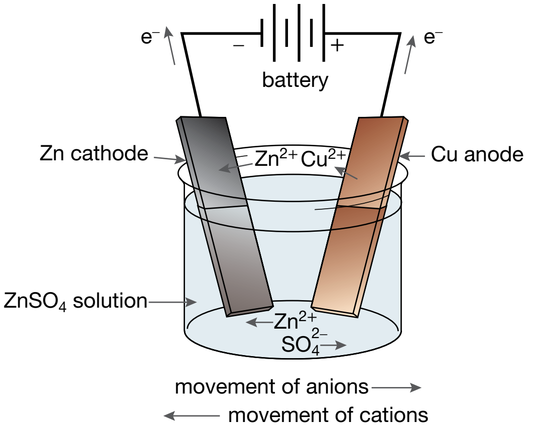
Feature	Galvanic cell	Electrolytic cell
Type of redox reaction	Spontaneous	Non-spontaneous
Energy produced or required	Produced	Required
Where oxidation occurs	Anode	Anode
Where reduction occurs	Cathode	Cathode
Anode polarity	Negative	Positive
Cathode polarity	Positive	Negative
How cell polarity is determined	Depends on reactions occurring within cell	External power source

FIGURE 7.15 Comparison of zinc–copper half-cells in electrochemical and electrolytic reactions
(a) Galvanic cell showing fully labelled components, half-equations and overall equation (b) Electrolytic cell showing fully labelled components, half-equations and overall equation.



Electrolysis is most often carried out in a single container (see figure 7.16) and almost never in double containers connected with a salt bridge (see figure 7.15). This is possible because the reactants in an electrolytic cell do not react spontaneously and can be mixed. Reaction only occurs once electrical energy is supplied to bring about the non-spontaneous reactions of the electrolysis process.

FIGURE 7.16 In an electrolytic cell, the two electrodes are usually immersed in a common electrolyte. In this example, the same reactions would occur if the electrolysis was carried out with copper and zinc electrodes immersed in a zinc sulfate solution.



$Zn^{2+}(aq) + 2e^- \longrightarrow Zn(s)$	$Cu(s) \longrightarrow Cu^{2+}(aq) + 2e^-$
reduction	oxidation
cathode	anode
(–)	(+)

Resources

Interactivity Comparing galvanic and electrolytic cells (int-1257)

Weblink Introduction to electrolysis

7.5 EXERCISE

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1. What are the main energy transformations occurring in:
   (a) a galvanic cell?
   (b) an electrolytic cell?
2. Explain why the cathode is positive in a galvanic cell but negative in an electrolytic cell.
3. Explain why the anode is negative in a galvanic cell but positive in an electrolytic cell.

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7.6 Calculations in electrolysis using Faraday's Laws

KEY CONCEPT

- The application of stoichiometry and Faraday's Laws to determine amounts of product, current or time for a particular electrolytic process

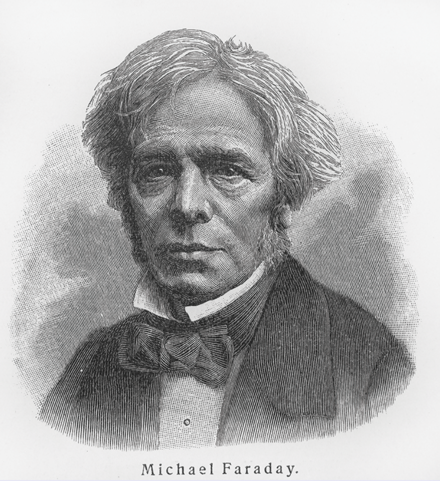
MICHAEL FARADAY

Michael Faraday (1791–1867) was a bookbinder who became an assistant to the English chemist Sir Humphrey Davy. Although the job was menial, he advanced quickly, gaining a reputation for dedication and thoroughness.

Faraday first learned about the phenomenon of electricity from an article in an encyclopedia that was brought to his employer for rebinding. His interest in science was kindled and he became an avid reader of scientific papers, in addition to attending lectures on science. Furthermore, he wrote complete notes on every book he read and every lecture he attended.

Faraday began working as an assistant at the Royal Institution in London, which is dedicated to scientific education and research. After 10 years of hard work, Faraday began his own research in analytical chemistry. He discovered benzene in 1825 and was the first person to produce compounds of carbon and chlorine in the laboratory, but he is most famous for his work on electricity. In 1833, he published the results of his studies of electrolysis. Faraday had made careful measurements of the amount of electricity involved during electrolysis and related it to the amount of substances produced. His work established two 'laws' of electrochemistry. The amount of charge carried by 1 mole of electrons is called a faraday in honour of Michael Faradays contribution to science.

FIGURE 7.17 Michael Faraday



7.6.1 Faraday's first law of electrolysis

Faraday's first law of electrolysis describes the relationship between the mass of a substance deposited or liberated during electrolysis and the quantity of electric charge passed through the cell. That is, mass is proportional to charge.

Faraday's first law of electrolysis:
The amount of any substance deposited, evolved or dissolved at an electrode during electrolysis is directly proportional to the quantity of electric charge passed through the cell.

The quantity of electric charge transferred by an electric current depends on the magnitude of the current used and the time for which it flows.

The electric charge can be calculated using the formula:

$$Q = It$$

where:
***Q* is the electrical charge in coulombs (C)**
***I* is the current in amperes (A)**
***t* is the time in seconds (s).**

In an experimental circuit, there is no meter that measures the charge in coulombs. However, an ammeter could be used to measure the rate at which charge flows in a circuit. A current of 1 ampere (1 A) indicates that 1 coulomb (6.24×10^{18} electrons) of charge flows every second. For example, if a current of 3.00 amperes flows for 10.0 minutes, the quantity of electricity is $(3.00 \times 10.0 \times 60) = 1.80 \times 10^3$ coulombs. The charge flowing through an electrolytic cell can be increased by either increasing the magnitude of the current or by increasing the time.

In an experiment to investigate the relationship between the quantity of electricity and the mass of electrolytic products, copper(II) sulfate was electrolysed using copper electrodes. The copper cathode was weighed before the electrolysis. After 10.0 minutes of electrolysis with a current of 3.00 amperes, the experiment was stopped and the cathode reweighed. The mass of copper deposited was calculated, the cathode was replaced, and the experiment continued for another 10.0 minutes. The mass of copper deposited in 20.0 minutes was then found. This procedure was repeated several times and the results obtained are shown in table 7.3.

TABLE 7.3 Experimental results between quantity of electricity in electrolysis and mass of copper deposited

Current (A)	Time (s)	Quantity of electricity (C)	Mass of copper (g)
3.00	600	1800	0.59
3.00	1200	3600	1.19
3.00	1800	5400	1.78
3.00	2400	7200	2.38

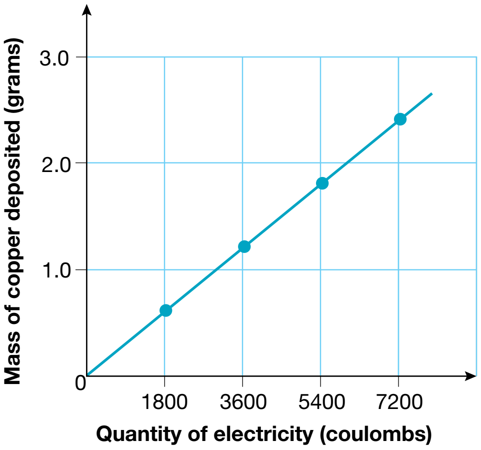
The graph of these results (see figure 7.18) yields a straight line passing through the origin. This shows that the mass of the product is directly proportional to the quantity of electricity. The mass of copper deposited on the cathode during electrolysis is directly proportional to the quantity of electricity used.

The charge on one electron is 1.602×10^{-19} C.

Therefore, one mole of electrons has a charge of $(6.023 \times 10^{23} \times 1.602 \times 10^{-19}) = 9.649 \times 10^{4}$ C. This quantity of charge carried by a mole of electrons is referred to as the faraday (F), or **Faraday constant**, and is usually given the value of 96 500 C mol^{-1}.

TIP: The Faraday constant, 96 500 C mol^{-1} can be found in table 4 of the VCE Chemistry Data Book.

FIGURE 7.18 Graph of copper deposited versus quantity of electricity in electrolysis



SAMPLE PROBLEM 5

When a current of 3.2 A is passed through a solution for 10.0 minutes, 0.010 mol of gas B is evolved.

What amount of B will be evolved if a current of 2.0 A is used for 15 minutes?

THINK	WRITE
1. Charge used is calculated from the formula $Q = It$. The formula can be found in Table 3 of the VCE Chemistry Data Book. **TIP:** When using $Q = It$, remember that units must be considered. While t should be in seconds because we are using a ratio to determine the amount of B evolved, as long as the same units for time are used, they do not need to be converted to seconds.	$Q = It$ $Q = 3.2 \times 10.0 \times 60$ $= 1920$ C (original) $Q = 2.0 \times 15 \times 60$ $= 1800$ C (new)

2. Recall that amount evolved is proportional to charge flowing through the cell (Faraday's first law). Give answer to two significant figures.

$$\text{Amount B} = 0.010 \times \frac{1800}{1920} = 0.0094\text{ mol (2 sig.figs)}$$

PRACTICE PROBLEM 5

When a current of 3.4 A is passed through a solution for 7.0 minutes, 0.015 mol of metal X is deposited.

What amount of X will be deposited if a current of 2.5 A is used for 20 minutes?

7.6.2 Faraday's second law of electrolysis

Faraday's second law of electrolysis describes the stoichiometric relationship between the moles of substance produced by electrolysis and the moles of electrons required.

> **Faraday's second law of electrolysis:**
> **To produce 1 mole of a substance by electrolysis, 1, 2, 3 or another whole number of moles of electrons (faradays) must be consumed, according to the relevant half-cell equation.**

In the half-cell equation:

$Ag^+(aq)$	+	e^-	→	$Ag(s)$
1 mole of silver ions		1 mole of electrons		1 mole of silver atoms

1 mole of electrons is needed to discharge 1 mole of $Ag^+(aq)$ ions. This liberates 1 mole of silver atoms. Thus, 1 faraday, or 96 500 coulombs, is needed to discharge 1 mole of silver atoms.

The number of faradays needed to liberate 1 mole of an element during electrolysis is found from the equation for the electrode reaction. Some examples are given below.

Sodium: $Na^+ + e^- \rightarrow Na$	1 faraday must be passed to liberate 1 mole of sodium atoms (23.0 g).
Copper: $Cu^{2+} + 2e^- \rightarrow Cu$	2 faradays must be passed to liberate 1 mole of copper atoms (63.5 g).
Magnesium: $Mg^{2+} + 2e^- \rightarrow Mg$	2 faradays must be passed to liberate 1 mole of magnesium atoms (24.3 g).
Aluminium: $Al^{3+} + 3e^- \rightarrow Al$	3 faradays must be passed to liberate 1 mole of aluminium atoms (27.0 g).
Chlorine: $2Cl^- \rightarrow Cl_2 + 2e^-$	2 faradays must be passed to liberate 1 mole of chlorine molecules (71.0 g).

The number of moles of electrons, $n(e^-)$ (the number of faradays), corresponding to a given charge (in coloumbs) can be determined by the equation:

$$n(e^-) = \frac{Q}{F}$$

where:

***n* is the number of moles of electrons**

***Q* is the electrical charge in coulombs (C)**

***F* is the Faraday constant, 96 500 C mol^{-1}.**

SAMPLE PROBLEM 6

When 7720 C is passed through a copper(II) sulfate solution, 0.040 mol of copper is produced. If the same amount of charge is passed through a solution containing Ag^+ ions, how many moles of Ag will be produced?

Teacher-led video: SP6 (tlvd-0698)

THINK	WRITE
1. Write the equation for the electrode reaction for both Cu and Ag deposition.	$Cu^{2+} + 2e^- \rightarrow Cu(s)$ $Ag^+(aq) + e^- \rightarrow Ag(s)$
2. The reaction in step 1 shows that 2 F of charge is required to deposit 1 mol of Cu. The same 2 F will deposit 2 mol of Ag because it only has a single charge on its ion. Hence, there is a 2:1 ratio when equal amounts of charge are used. Give your answer to two significant figures.	$n(Ag) = 2 \times n(Cu)$ $= 2 \times 0.040$ $= 0.080\ \text{mol}$

PRACTICE PROBLEM 6

When 7720 C is passed through a copper(II) sulfate solution, 0.040 mol of copper is produced. If the same amount of charge is passed through a solution containing W^{3+} ions, how many moles of W will be produced?

7.6.3 Applying Faraday's Laws of electrolysis

Most calculations in electrolysis involve finding the mass of a metal deposited on an electrode, the mass or volume of a gas produced, or the charge of an ion in the electrolytic reaction. Such problems can be solved by using the formulas:

$$Q = It$$

$$n(e^-) = \frac{Q}{F}$$

where:
Q = the electrical charge (C)
I = the current (A)
t = the time (s)
$F = 96\,500\ \text{C mol}^{-1}$.
Together these relationships summarise Faraday's two laws of electrolysis.

SAMPLE PROBLEM 7

A solution of copper(II) sulfate is electrolysed for 30.0 minutes using a current of 0.500 A. Calculate:

a. **the mass of copper deposited on the cathode**
b. **the volume (at SLC) of oxygen gas evolved at the anode.**

Teacher-led video: SP7 (tlvd-0699)

THINK	**WRITE**
a. 1. To determine the mass of copper deposited, first calculate the amount of charge and convert it to faradays (same as moles of charge). Remember to convert time to seconds.	$Q = It$ $= 0.500 \times (30.0 \times 60)$ $= 900\text{ C}$
2. Determine the equation at the cathode and the number of moles of electrons.	$Cu^{2+} + 2e^- \rightarrow Cu(s)$ $n(e^-) = \frac{Q}{F}$ $= \frac{900}{96500}$ $= 9.33 \times 10^{-3}\text{ mol}$
3. Use stoichiometry involving electrons to calculate moles of copper produced. One mole of copper requires two moles of electrons.	$n(Cu) = \frac{n(e^-)}{2}$ $= \frac{(9.33 \times 10^{-3})}{2}$ $= 4.67 \times 10^{-3}\text{ mol}$
4. Determine the mass of the copper produced using the molar mass formula. **TIP:** Formulas and the value of the Faraday constant can be found in Tables 3 and 4 of the VCE Chemistry Data Book.	$n = \frac{m}{M}$ $\therefore m(Cu) = n \times M$ $= (4.67 \times 10^{-3}) \times 63.5$ $= 0.296\text{ g}$
b. 1. Determine the equation at the anode.	$2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$
2. Using the number of electrons determined in step **a. 1.**, use stoichiometry involving electrons to calculate moles of oxygen produced. There is one mole of oxygen to four moles of electrons.	$n(O_2) = \frac{n(e^-)}{4}$ $= \frac{(9.33 \times 10^{-3})}{4}$ $= 2.33 \times 10^{-3}\text{ mol}$
3. Determine the volume of oxygen produced using the molar volume formula.	$n = \frac{V}{V_m}$ $V(O_2)_{SLC} = n \times V_m$ $= (2.33 \times 10^{-3}) \times 24.8$ $= 0.0578\text{ L or } 57.8\text{ mL}$

PRACTICE PROBLEM 7

A solution of copper(II) sulfate is electrolysed for 17.5 minutes using a current of 0.500 A. Calculate:

a. the mass of copper deposited on the cathode

b. the volume (at SLC) of oxygen gas evolved at the anode.

SAMPLE PROBLEM 8

When molten calcium chloride is electrolysed by a current of 0.200 A flowing for 965 seconds, 0.0401 g of calcium is formed. What is the charge on a calcium ion?

Teacher-led video: SP8 (tlvd-0700)

THINK	WRITE
1. To determine the charge on the calcium ion, first determine the number of moles of calcium.	$n(\text{Ca}) = \frac{m}{M}$ $= \frac{0.0401}{40.1}$ $= 0.00100\ \text{mol}$
2. Determine the amount of electricity used and the number of moles of electrons. Compare the units given to those required. Time must be in seconds.	$Q = It$ $= 0.200 \times 965$ $= 193\ \text{C}$ $n(e^-) = \frac{Q}{F}$ $= \frac{193}{96500}$ $= 0.00200\ \text{mol}$
3. According to step **2**, 0.00200 moles of electrons are needed to produce 0.00100 moles of calcium. Let the charge on ions will be $x+$. Use stoichiometry to calculate x.	$\text{Ca}^{x+}(\text{l}) + xe^- \rightarrow \text{Ca(s)}$ $\frac{n(e^-)}{x} = n(\text{Ca})$ $x = \frac{n(e^-)}{n(Ca)}$ $= \frac{0.00200}{0.00100}$ $= 2$
	The charge on the calcium ion is 2+ (Ca^{2+}).

PRACTICE PROBLEM 8

When a molten aluminium chloride solution is electrolysed by a current of 0.300 A flowing for 965 seconds, 0.0270 g of aluminium is formed. What is the charge on the aluminium ion?

Faraday's Laws in industry

Calculations based on Faraday's Laws are critical to industrial electrolytic processes. Due to the large scale of these processes, small variations and inefficiencies can result in the loss of many thousands of dollars. In order to determine the efficiency of a particular process, knowledge of the theoretical maximum amount is required.

SAMPLE PROBLEM 9

A typical Hall–Héroult cell in an aluminium plant operates at an average current of 1.70×10^4 A. Calculate the theoretical mass of aluminium produced in a Hall–Héroult cell over 24 hours.

Teacher-led video: SP9 (tlvd-0701)

THINK	WRITE
1. Determine the equation at the cathode.	$\text{Al}^{3+}(\text{l}) + 3\text{e}^- \rightarrow \text{Al(l)}$

2. Calculate the amount of charge used by applying the formula $Q = It$. Compare the units given to those required. Time must be in seconds. Calculate the number of moles of electrons.	$Q = It$ $= 1.70 \times 10^4 \times (24 \times 60 \times 60)$ $= 1.47 \times 10^9$ C $n(\text{electrons}) = \frac{Q}{F}$ $= \frac{1.47 \times 10^9}{96\,500}$ $= 1.52 \times 10^4$ mol
3. Using the number of moles of electrons determined in step **2**, use stoichiometry involving electrons to calculate the moles of aluminium produced. There is one mole of aluminium to three moles of electrons.	$n(\text{Al}) = \frac{1.52 \times 10^4}{3}$ $= 5.07 \times 10^3$ moles of Al
4. Convert moles to mass of aluminium using the molar mass formula, $n = \frac{m}{M}$	$m(\text{Al}) = n(\text{Al}) \times M(\text{Al})$ $= 5.07 \times 10^3 \times 27.0$ $= 1.37 \times 10^5$ g $= 1.37 \times 10^2$ kg

PRACTICE PROBLEM 9

Calculate the mass of magnesium produced over 24 hours when a current of 10000 A is used.

7.6 EXERCISE

To answer questions online and to receive **immediate feedback** and **sample responses** for every question go to your learnON title at www.jacplus.com.au.

1. When 2200 C is passed through a copper(II) sulfate solution, 0.011 mol of copper is produced. If the same amount of charge is passed through a solution containing Cr^{3+} ions, how many moles of Cr will be produced?
2. A solution of silver nitrate is electrolysed for 20.0 minutes using a current of 0.600 A. Calculate:
   (a) the mass of silver deposited at the cathode
   (b) the volume (at SLC) of oxygen gas evolved at the anode.
3. When a solution containing gold ions is electrolysed by a current of 0.100 A flowing for 965 seconds, 0.197 g of gold is formed. What is the charge on the gold ion?
4. How long will it take to deposit 1.00 g of cobalt in an electrolytic cell that uses a current of 3.50 A? The equation for the reduction is $Co^{2+}(aq) + 2e^- \rightarrow Co(s)$.
5. A current of 4.25 A is passed through molten Al_2O_3 for 13.5 hours.
   (a) How many grams of aluminium would be produced?
   (b) What volume of oxygen, at 152 kPa (1.50 atm) and 29.0 °C, would be evolved?
6. When a current of 10.0 A was passed through a concentrated solution of sodium chloride using carbon electrodes, 2.80 L of chlorine (at SLC) was collected. How long (in minutes) did the electrolysis take?
7. A given quantity of electricity is passed through two aqueous cells connected in series. The first contains silver chloride and the second contains calcium chloride. What mass of calcium is deposited in one cell if 2.00 g of silver is deposited in the other cell?

8. Calculate the amount of time (in days) required to produce 2.00 kg of magnesium metal by the electrolysis of molten magnesium chloride, $MgCl_2$, using a current of 45.0 A.
9. For the following scenarios:
   (i) a current of 1.2 A flows for 8.0 minutes
   (ii) a current of 0.75 A flows for 3.0 hours
   (iii) a current of 3.5 A flows for 2.0 hours and 25 minutes
   (iv) a current of 2.4 A flows for 1.0 day.
   Calculate:
   (a) the mass of copper deposited during the electrolysis of aqueous copper(II) sulfate using carbon electrodes
   (b) the volume of oxygen formed at SLC during the electrolysis of aqueous copper(II) sulfate using carbon electrodes.
10. Calculate the time taken to deposit gold from a solution of gold(I) cyanide to a thickness of 0.0100 mm onto a copper disc that has a diameter of 10.0 mm and a thickness of 5.00 mm if a current of 0.750 A is used. (The density of gold is 19.3 g cm^{-3}.)

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7.7 Rechargeable batteries (secondary cells)

KEY CONCEPT

- 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).

TIP: Some examples of secondary cells are provided in this subtopic. Although you are not required to know the details of any specific cell, you should examine these examples and make sure that you understand the principles behind their operation. It is expected that you should be able to apply these principles in an examination, rather than just restating facts that you have learnt.

7.7.1 What is a secondary cell?

A secondary cell is essentially a galvanic cell combined with an electrolytic cell.

Secondary cells, often referred to as **rechargeable** batteries, are devices that can be recharged when they become ‘flat’. They are galvanic cells using spontaneous redox reactions to produce electricity during discharge, but they become electrolytic cells converting electrical energy back into chemical energy when they are recharged. To enable this to happen, they are designed so that the discharge products remain in contact with the electrodes at which they are produced. The process of recharging involves connecting the negative terminal of the charger to the negative terminal of the battery or cell, and the positive to the positive. This forces the electrons to travel in the reverse direction and, because the discharge products are still in contact with the electrodes, the original reactions are reversed. The cell or battery is, therefore, recharged.

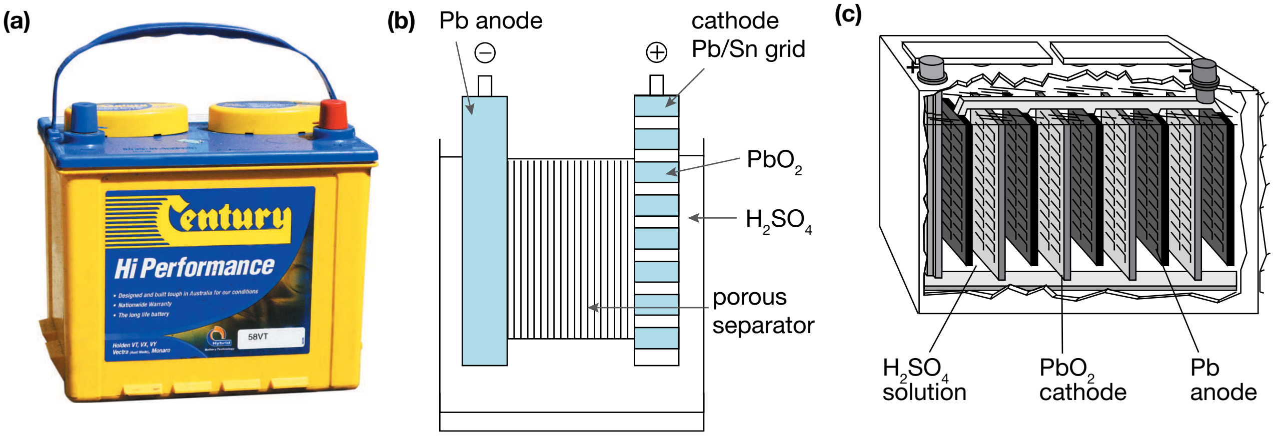
The lead–acid accumulator is a common example of a secondary cell that has been widely used for many years. Other smaller more portable designs are now familiar to us. Although initially more expensive, their ability to be recharged many hundreds of times makes them a cheaper alternative in the long-term.

7.7.2 Lead–acid accumulator

Developed in the late-nineteenth century, the **lead–acid accumulator** has remained the most common and durable of battery technologies. Lead–acid accumulators are secondary cells. They have a relatively long life and high current, and they are cheap to produce. Largely used in transport applications, they rely on a direct current generator or alternator in the vehicle to apply enough voltage to reverse the spontaneous electrochemical reaction that provides electricity for the car.

A 12-volt lead–acid storage battery consists of six 2-volt cells connected in series. The cells do not need to be in separate compartments, although this improves performance (see figure 7.19).

FIGURE 7.19 (a) A motor vehicle battery (b) A lead–acid storage cell (c) A simplified cross-section of a lead–acid battery



Each cell consists of two lead electrodes or grids. The grid structure provides a larger surface area for electrode reactions. The grid that forms the anode (the negative terminal) of the cell is packed with spongy lead. The grid that form the cathode (the positive terminal), is packed with lead(IV) oxide, PbO_2. The electrodes are both immersed in approximately 4 M sulfuric acid and are separated by a porous plate.

The discharging process in a lead–acid accumulator

When a lead–acid accumulator discharges, it produces electric power to start the car. Discharge results from a spontaneous redox reaction.

The half-equations at each electrode may be written as follows.

$$\text{Anode (oxidation): } Pb(s) + SO_4^{2-}(aq) \rightarrow PbSO_4(s) + 2e^-$$

$$\text{Cathode (reduction): } PbO_2(s) + 4H^+(aq) + SO_4^{2-}(aq) + 2e^- \rightarrow PbSO_4(s) + 2H_2O(l)$$

At the anode, lead is oxidised to Pb^{2+} ions. These react immediately with the sulfuric acid solution to produce insoluble lead(II) sulfate, which deposits on the grid.

At the cathode, lead(IV) oxide is reduced to Pb^{2+} ions, which again react with the sulfuric acid to form a lead(II) sulfate deposit on the grid. The overall equation for the discharging reaction is:

$$PbO_2(s) + 4H^+(aq) + Pb(s) + 2SO_4^{2-}(aq) \rightarrow 2PbSO_4(s) + 2H_2O(l)$$

Note that the pH of the cell increases during the discharge cycle.

The recharging process in a lead–acid accumulator

The products of the discharge process remain as a deposit on the electrodes. This means that the reactions at these electrodes can be reversed by passing a current through the cell in the opposite direction. The battery is then said to be **recharging**. When the battery is recharged, the electrode reactions are reversed by connecting the terminals to another electrical source of higher voltage and reversing the direction of the electric current through the circuit. Recharging occurs while the car is in motion.

While recharging, the flow of e^- is reversed and the electrode forming the negatively-charged anode in the discharging process becomes the negatively-charged cathode, where reduction occurs.

$$\text{Cathode (reduction):}\quad PbSO_4(s) + 2e^- \rightarrow Pb(s) + SO_4^{2-}(aq)$$

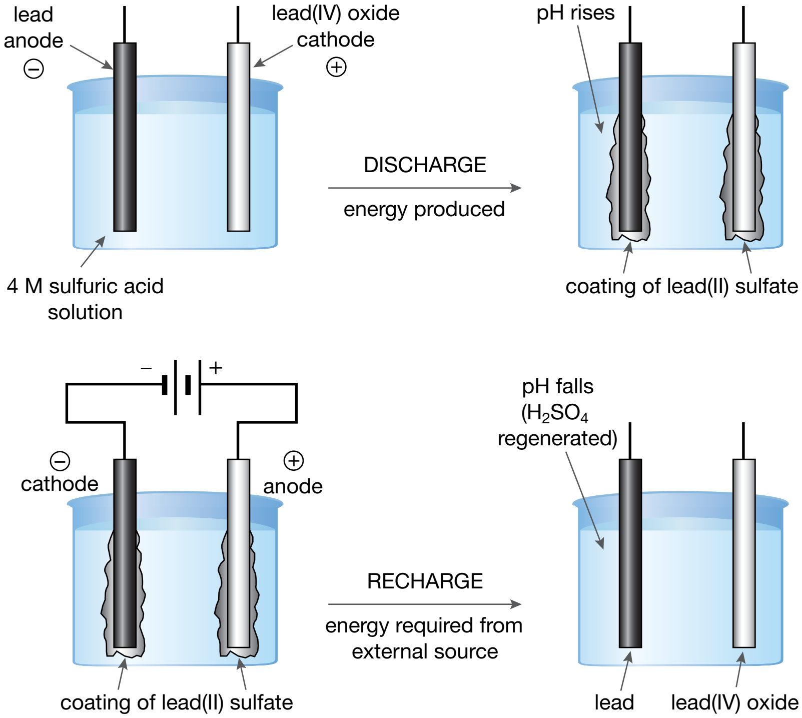
The electrode previously forming the positively-charged cathode in the discharging process now becomes the positively-charged anode, where oxidation occurs, in the recharging process.

$$\text{Anode (oxidation):}\quad PbSO_4(s) + 2H_2O(l) \rightarrow PbO_2(s) + SO_4^{2-}(aq) + 4H^+(aq) + 2e^-$$

The overall reaction for the recharging process is therefore the reverse of the discharging process.

$$2PbSO_4(s) + 2H_2O(l) \rightarrow PbO_2(s) + 4H^+(aq) + Pb(s) + 2SO_4^{2-}(aq)$$

FIGURE 7.20 Discharge/recharge effect on electrodes



Note that the pH of the cell decreases during the recharge cycle.

This reaction is not spontaneous so a direct current must be applied in order for it to proceed. This is achieved by the alternator (a motor-driven electrical source of higher voltage than the battery), which has a potential difference of 14 V. The recharging process converts electrical energy into chemical energy and is an example of an electrolytic reaction.

In theory, a lead storage battery can be recharged indefinitely, but in practice it may only last for about four years. This is because small amounts of lead(II) sulfate continually fall from the electrodes and drop to the bottom of the cell. Eventually, the electrodes lose so much lead(II) sulfate that the recharging process is ineffective.

7.7.3 Nickel–metal hydride (NiMH) rechargeable cell

Although the nickel–cadmium (NiCd) cell was the first rechargeable cell to find widespread use in many common household devices, it has largely been replaced today by the nickel–metal hydride (NiMH) cell. This shares a number of features with the NiCd cell but is environmentally safer due to the absence of cadmium. An additional problem with NiCd cells was the so-called memory effect. If the cell was only partially discharged before recharging occurred, it would not receive a full charge. NiMH cells show much less of this effect. They also have nearly 50% more charge per gram, can recharge faster and can run longer on each charge.

The reactions involved during discharge to produce an electric current are:

Oxidation takes place at the (anode):

Anode: $M\text{H(s)} + \text{OH}^-\text{(aq)} \rightarrow M\text{(s)} + \text{H}_2\text{O(l)} + \text{e}^-$ (note the M here refers to a metal)

Reduction takes place at the positive electrode (cathode):

Cathode: $\text{NiO(OH)(s)} + \text{H}_2\text{O(l)} + \text{e}^- \rightarrow \text{Ni(OH)}_2\text{(s)} + \text{OH}^-\text{(aq)}$

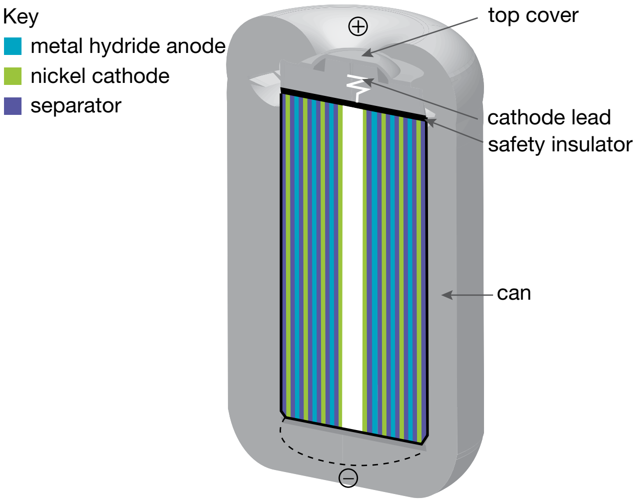
Overall equation for the discharging reaction is:

$$\text{NiO(OH)(s)} + M\text{H(s)} \rightarrow \text{Ni(OH)}_2\text{(s)} + M\text{(s)}$$

Nickel–metal hydride batteries are similar to nickel–cadmium batteries except that a hydrogen-absorbing metal is used as the anode. These metals (M) can be alloys of lanthanum and rare earths. The electrolyte is potassium hydroxide and the voltage produced is 1.2 volts.

Nickel–metal hydride batteries have many advantages but also some disadvantages. They suffer from self–discharge — a problem that is worse at higher temperatures — and require more complicated charging devices to prevent over–charging. They are used in laptops, electric shavers and toothbrushes, cameras, camcorders, mobile phones and medical instruments, and are being developed for car batteries.

FIGURE 7.21 A nickel–metal hydride cell for a digital camera



LITHIUM–ION BATTERIES

A new type of cell rapidly gaining popularity in portable devices such as digital cameras, phones and computers is the lithium–ion battery. These cells have a good shelf life and a very high energy density; they supply a voltage of about 3.7 volts, which is more than double that of most other cells. However, their state of charge needs to be monitored carefully. If they are over–discharged, they cannot be recharged. On the other hand, if they are over–charged, serious safety concerns may arise. To prevent both of these extremes, they are nearly always produced with a protection circuit that prevents both of these situations from arising, but this adds to their cost.

FIGURE 7.22 The Mars Exploration Rovers *Spirit* and *Opportunity* were powered by lithium–ion batteries, which are light and reliable.

Find out more about this type of cell, specifically:
- The voltage they produce
- The reactions that produce the electricity
- The operating conditions that they are designed for
- Safety concerns, especially 'thermal runaway'.

7.7.4 Factors affecting battery life

While there are specialist batteries designed to operate at extreme temperatures, the majority of batteries used today are designed to operate over an optimum range of temperatures that encompass normal room temperature. If they are used outside this range, breakdowns in both the electrochemistry and their physical components may occur, rendering the battery inoperative and even dangerous.

Each battery type also has its own specific problems related to temperature and componentry. In a lead–acid accumulator over-discharge thickens the layers of lead sulfate that build up on the electrodes. Particles can break off and fall to the base of the cell, thereby lowering the amount remaining for recharge. In extreme cases, due to the closeness of the electrodes, internal short circuits may also occur if the insulation is damaged and the electrodes touch. At low temperatures, especially if the sulfuric acid content is low (because of a low state of charge), the electrolyte may even freeze and cause damage to the battery on expansion. If temperatures are too high, due to over-charging or the operating environment, the plates (electrodes) may buckle, damaging the insulation between them and possibly leading to internal short circuits. Unwanted side reactions are more likely to occur.

7.7 EXERCISE

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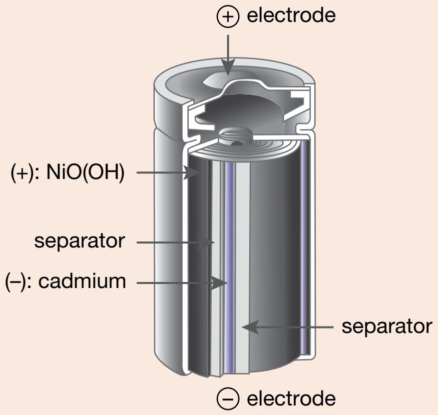
1. During the recharging process for the lead–acid accumulator, will the pH of the contents rise or fall? Explain.
2. Explain why the positive terminal of the charging device must be connected to the positive terminal of the battery, and the negative to the negative, when a rechargeable battery is to be recharged.
3. The nickel-cadmium rechargeable cell was a widely-used predecessor to today's nickel–metal hydride cells and lithium–ion cells. The figure shows some of the components of this type of cell.



The cell contains cadmium and NiO(OH) as its reactants. These are kept apart by a porous separator that has been soaked in KOH. During *discharge*, the reaction at the anode is:

$$Cd(s) + 2OH^-(aq) \rightarrow Cd(OH)_2(s) + 2e^-$$

The overall cell reaction is:

$$Cd(s) + 2NiO(OH)(s) + 2H_2O(l) \rightarrow Cd(OH)_2(s) + 2Ni(OH)_2(s)$$

(a) Write the equation that occurs at the cathode during recharging.
(b) During recharging, what terminal of the recharging device should the anode be connected to?
(c) Write the equation for the overall cell reaction during the recharging process.
(d) Write the equation for the reaction that occurs at the anode during recharging.

4. Batteries based on vanadium chemistry are increasingly being used to store energy from solar panels. During the day, solar cells store energy in the battery as it is charged. At night, the battery functions as a galvanic cell, producing electricity to power the household.

The two relevant half-equations for the functioning of this battery are:

$$\begin{aligned} VO_2^+(aq) + 2H^+(aq) + e^- &\rightarrow VO^{2+}(aq) + H_2O(l) \quad && E^0 = +1.00\,V \\ V^{3+}(aq) + e^- &\rightarrow V^{2+}(aq) && E^0 = -0.26\,V \end{aligned}$$

(a) Write the overall equation for this battery as it is discharging.
(b) Write the overall equation for this battery as it is recharging.
(c) Write the half-equations for the reactions occurring at each electrode as the cell recharges.

5. The Edison cell is a 1.3-volt storage battery that can be recharged, even after long periods of being left uncharged. Its electrolyte is 21% potassium hydroxide solution and the reaction on discharge is:

$$Fe(s) + 2NiO(OH)(s) + 2H_2O(l) \rightarrow Fe(OH)_2(s) + 2Ni(OH)_2(s)$$

(a) Give electrode reactions during:
  i. discharging
  ii. recharging.
(b) What materials would be used for the electrodes?
(c) In the discharge process, which electrode is the anode and which is the cathode?
(d) In the recharge process, which electrode is the anode and which is the cathode?

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7.8 Review

7.8.1 Summary

What is electrolysis?

- Electrolysis is the process by which electricity passes through a molten ionic compound or through an electrolyte solution to produce new substances.
- The apparatus in which electrolysis occurs is called an electrolytic cell.
- Solutes that form solutions that can conduct electricity are called electrolytes.
- The electrolysis of a single molten salt forms products that are easily predicted.
- The electrolysis of water to which a tiny amount of electrolyte has been added forms hydrogen gas and oxygen gas.

Predicting reactions that occur during electrolysis

- The products of the electrolysis of molten ionic compounds are predictable whereas the products of the electrolysis of an aqueous solution may be affected by factors including concentration, the nature of the electrolyte and the nature of the electrodes.
- The electrochemical series can be used to predict reactions where more than one species is available for reaction at an electrode.
- Cations of reactive metals, including aluminium, cannot be reduced from aqueous solutions because water is a stronger oxidising agent and is preferentially reduced.

Commercial applications of electrolysis

- Electrolysis can be used to produce highly reactive elements such as the strong reducing agent metals in groups 1 and 2 in the periodic table, as well as chlorine and fluorine, because production by chemical reduction is not practical.
- Chlorine, sodium hydroxide and hydrogen gas can be produced industrially in the membrane cell according to the overall reaction:

$$2NaCl(aq) + 2H_2O(l) \rightarrow 2NaOH(aq) + H_2(g) + Cl_2(g)$$

- Aluminium can be produced industrially by the Hall–Héroult process according to the overall equation:

$$2Al_2O_3(l) + 3C(s) \rightarrow 4Al(l) + 3CO_2(g)$$

- Electroplating is the process of coating an object with a thin film of metal deposited from an electrolytic solution by electrolysis.
- In electroplating, the object to be plated is always connected to the cathode.

Comparing galvanic and electrolytic cells

- Electrolytic cells differ from galvanic cells in a number of ways, which are summarised in the following table.

Factor	Galvanic cell	Electrolytic cell
Type of reaction	Spontaneous redox reaction	Non-spontaneous redox reaction
Energy	Produce electricity	Require energy
Structure	Two half-cells connected by a wire (external circuit) and a salt bridge (internal circuit)	One cell, connecting wires and an external power supply (e.g. battery, DC power supply)
Anode	Negatively charged, oxidation	Positively charged, oxidation
Cathode	Positively charged, reduction	Negatively charged, reduction
Source of electrons	Reducing agent	External power supply

Calculations in electrolysis using Faraday's Laws

- Faraday's Laws can be applied to a range of problems involving quantitative calculations in electrolysis.
- Faraday's first law of electrolysis can be summarised as:

$$Q = It,$$

where:
Q is the electric charge in coulombs
I is the current in amperes
t is the time in seconds.

- Faraday's second law of electrolysis can be summarised as:

$$\text{number of moles of electrons, } n(e^-) = \frac{Q}{\mathrm{F}}$$

where F is the Faraday constant representing the quantity of charge carried by 1 mole of electrons (96 500 coulombs).

Rechargeable batteries (secondary cells)

- Secondary cells are electrochemical cells that can be recharged by reversing the spontaneous forward reaction through the application of a DC power source.
- The lead–acid accumulator is a secondary cell that is rechargeable; its largest use is to power transport vehicles. The discharging reaction for the operation of a lead–acid accumulator produces 12 volts and is represented by the overall equation:

$$\mathrm{PbO_2(s) + 4H^+(aq) + Pb(s) + 2SO_4^{2-}(aq) \rightarrow 2PbSO_4(s) + 2H_2O(l)}$$

The recharging process is the reverse of the discharging process and requires approximately 14 volts of DC power to occur according to the reaction:

$$\mathrm{2PbSO_4(s) + 2H_2O(l) \rightarrow PbO_2(s) + 4H^+(aq) + Pb(s) + 2SO_4^{2-}(aq)}$$

- The nickel–metal hydride cell takes advantage of the property that some metal alloys have of storing hydrogen atoms. The overall equation representing discharge is:

$$\mathrm{NiO(OH)(s) + MH(s) \rightarrow Ni(OH)_2(s) + M(s)}$$

- Battery life can be affected by temperature, depth of discharge and operating voltage. These can reduce its ability to be fully recharged and affect its safe operation.
- Physical factors that affect the integrity of a battery's construction will also affect its life.

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7.8.2 Key terms

anode the electrode at which oxidation occurs. In a galvanic cell, it is the negative electrode, because it is the source of negative electrons for the circuit. If the reducing agent is a metal, it is used as the electrode material.

cathode the electrode at which reduction occurs. In a galvanic cell, it is the positive electrode, because the negative electrons are drawn towards it and then consumed by the oxidising agent, which is present in the electrolyte.

electrochemical series a series of chemical elements arranged in order of their standard electrode potentials

electrolysis the decomposition of a chemical substance (in solution or the molten state) by the application of electrical energy

electrolytes liquids that can conduct electricity

electrolytic cell an electric cell in which a non-spontaneous redox reaction is made to occur by the application of an external potential difference across the electrodes

electroplating adding a thin metal coating by electrolysis

Faraday constant a constant that represents the amount of electric charge carried by 1 mole of electrons

Faradays first law of electrolysis The amount of current passed through an electrode is directly proportional to the amount of material released from it.

Faraday's second law of electrolysis When the same quantity of electricity is passed through several electrolytes, the mass of the substances deposited are proportional to their respective chemical equivalent or equivalent weight.

Hall–Héroult the method of aluminium production used in primary aluminium smelters throughout the world

lead–acid accumulator a battery with lead electrodes using dilute sulfuric acid as the electrolyte; each cell generates about 2 volts

membrane cell used for the electrolysis of brine

rechargeable describes a battery that is an energy storage device; it can be charged again after being discharged by applying DC current to its terminals

recharging forcing electrons to travel in the reverse direction and, because the discharge products are still in contact with the electrodes, the original reactions are reversed

secondary cell a cell that can be recharged once its production of electric current drops; often called a rechargeable battery

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Digital documents Key terms glossary - Topic 7 (doc-31409)

7.8.3 Practical work and experiments

Experiment 7.1

Electrolysis of aqueous solutions

Aim: To conduct electrolysis on aqueous solutions and test for the products at each electrode

Digital document: doc-31264

Teacher-led video: tlvd-0749

Experiment 7.3

Electroplating

Aim: To plate a piece of copper with nickel metal

Digital document: doc-31266

Teacher-led video: tlvd-0751

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Digital documents Practical investigation logbook (doc-31410)
Experiment 7.2 Factors affecting electrolysis (student design) (doc-31265)

7.8 Exercises

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7.8 Exercise 1: Multiple choice questions

1. In an electrolytic cell:
   - A. the cathode is positive and it is the site of reduction
   - B. the cathode is negative and it is the site of oxidation
   - C. the anode is positive and it is the site of reduction
   - D. the cathode receives electrons from the external power source.
2. During the operation of an electrolytic cell:
   - A. there is a flow of electrons through the solution between the cathode and anode
   - B. inert electrodes must always be used
   - C. a salt bridge is required to complete the circuit
   - D. electrical energy is converted into chemical energy.
3. Which of the following statements about reactions in electrochemical cells and electrolytic cells is correct?
   - A. Oxidation occurs at the anode of electrochemical cells and at the cathode of electrolytic cells.
   - B. Electrochemical cell reactions are spontaneous whereas electrolytic cell reactions are driven by external power supplies.
   - C. Electrochemical cell reactions are redox reactions whereas electrolytic cell reactions are deposition reactions.
   - D. Oxidation occurs at the positive electrode in both electrochemical and electrolytic cells.
4. Which of the following occurs in the electrolysis of molten potassium bromide?
   - A. Potassium is produced at the anode.
   - B. Potassium ions are oxidised at the cathode.
   - C. Bromine gas is produced at the cathode.
   - D. Bromide ions are oxidised at the anode.
5. In the electrolysis of molten sodium chloride using inert electrodes, which of the following occurs?
   - A. Chlorine gas is produced at the cathode and oxygen gas is produced at the anode.
   - B. Chlorine gas is produced at the anode and oxygen gas is produced at the cathode.
   - C. Chlorine gas is produced at the cathode and sodium metal is produced at the anode.
   - D. Chlorine gas is produced at the anode and sodium metal is produced at the cathode.
6. An electrolytic cell consists of two carbon electrodes and an electrolyte of aqueous sodium chloride to which phenolphthalein has been added. When an electric current is passed through the cell:
   - A. bubbles of chlorine appear at the cathode
   - B. bubbles of hydrogen appear at the anode
   - C. a pink colour surrounds the cathode
   - D. sodium metal collects at the cathode.
7. Consider the following standard reduction potentials.

$$\begin{array}{ll} Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s) & E^0 = -0.76\,V \\ 2H^+(aq) + 2e^- \rightleftharpoons H_2(g) & E^0 = 0.00\,V \\ Ag^+(aq) + e^- \rightleftharpoons Ag(s) & E^0 = +0.80\,V \\ 2H_2O(l) + 2e^- \rightleftharpoons H_2(g) + 2OH^-(aq) & E^0 = -0.83\,V \end{array}$$

   Which product would be liberated first at the cathode if a solution containing $Zn(NO_3)_2$ and $AgNO_3$ is electrolysed with platinum electrodes?

- **A.** $H_2(g)$
- **B.** $Ag(s)$
- **C.** $Zn(s)$
- **D.** $OH^-(aq)$

8. Which of the following groups of substances would normally be extracted by electrolysis in a non-aqueous environment?
   - **A.** Iron, nickel and chromium
   - **B.** Gold, copper, silver and platinum
   - **C.** Magnesium, aluminium, sodium and chlorine
   - **D.** Oxygen, neon, argon and nitrogen.
9. When concentrated brine solution is electrolysed in the membrane cell, the electrode products are:
   - **A.** $Na(l)$ and $Cl_2(g)$
   - **B.** $H_2(g)$ and $O_2(g)$
   - **C.** $Na(l)$ and $O_2(g)$
   - **D.** $H_2(g)$, $Cl_2(g)$ and $NaOH(aq)$.
10. A solution contains $CuCl_2$, $NiCl_2$ and $ZnCl_2$, with each solute being at 1 M concentration. The solution is electrolysed using graphite electrodes. Which of the following reactions takes place first at the cathode?
    - **A.** $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$
    - **B.** $Ni^{2+}(aq) + 2e^- \rightarrow Ni(s)$
    - **C.** $Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$
    - **D.** $2Cl^-(aq) \rightarrow Cl_2(g) + 2e^-$
11. In the electrolytic extraction of aluminium from its oxide, a substance called cryolite is used. Which of the following best describes the function of cryolite in this process?
    - **A.** It oxidises alumina.
    - **B.** It reduces alumina.
    - **C.** It acts to absorb ore impurities from the alumina.
    - **D.** It acts as a solvent for alumina.
12. In a rechargeable battery:
    - **A.** the negatively charged cathode in the discharging reaction becomes the positively charged anode in the recharging process
    - **B.** the negatively charged cathode in the discharging reaction becomes the negatively charged anode in the recharging process
    - **C.** the positively charged cathode in the discharging reaction becomes the positively charged anode in the recharging process
    - **D.** the positively charged cathode in the discharging reaction becomes the negatively charged anode in the recharging process.
13. During the discharging process in a lead–acid accumulator:
    - **A.** the concentration of hydrogen ions, H^+, increases, resulting in an increase in pH
    - **B.** the concentration of hydrogen ions, H^+, decreases, resulting in a decrease in pH
    - **C.** the concentration of hydrogen ions, H^+, increases, resulting in a decrease in pH
    - **D.** the concentration of hydrogen ions, H^+, decreases, resulting in an increase in pH.
14. The cathode reaction during discharge in a nickel–metal hydride cell is:

$$NiO(OH)(s) + H_2O(l) + e^- \rightarrow Ni(OH)_2(s) + OH^-(aq)$$

During recharging, which of the following statements is correct?
- **A.** Nickel is reduced from the +3 to +2 oxidation state.
- **B.** Oxidation of nickel occurs from the +2 to the +3 oxidation state.
- **C.** The reverse of the reaction occurs at the negative electrode.
- **D.** Oxidation occurs at the surface of the negative electrode.

15. Consider two electrolytic cells connected in series. Cell 1 contained copper(II) sulfate solution with copper electrodes and cell 2 contained copper(II) chloride solution with platinum electrodes. Current was passed for a fixed time, after which the electrodes and electrolytes in each cell were examined. The mass of the cathode in cell 2 was found to have increased by 1.6 g.

The anode of cell 1 would have:

- A. increased by 1.6 g
- B. remained unchanged in mass
- C. given off oxygen gas
- D. decreased in mass by 1.6 g.

7.8 Exercise 2: Short answer questions

1. Complete the following table to summarise what happens at each electrode during electrolysis of NaCl in different forms.

		Reaction at	
Electrolyte type	**Electrodes**	**Anode(+)**	**Cathode(−)**
Molten salt	Inert		
1 M aqueous salt solution	Inert		
6 M aqueous salt solution	Inert		

2. In the electrolysis of molten sodium chloride, explain:
   - a. why electricity is conducted in the molten state but not in the solid state
   - b. why the products are formed only around the electrodes and not throughout the liquid
   - c. what causes the electric current to flow in the liquid and in the connecting wires.
3. For each of the following molten components, predict the products at the anode and cathode, determine the minimum cell voltage required for the electrolysis (using carbon electrodes) and write an overall equation.
   - a. sodium bromide
   - b. aluminium hydroxide
   - c. lead(II) chloride
   - d. magnesium chloride
4. For each of the following, predict the products at the anode and cathode, determine the minimum cell voltage required for the electrolysis (using carbon electrodes) of 1.0 M aqueous solutions and write an overall equation.
   - a. potassium hydroxide
   - b. potassium sulfate
   - c. magnesium chloride
   - d. zinc bromide
   - e. sodium iodide
   - f. hydrochloric acid
   - g. sulfuric acid
5. For each of the following, predict the products at the anode and cathode, determine the minimum cell voltage required for the electrolysis of 1.0 M aqueous solutions and write an overall equation
   - a. copper(II) chloride
   - b. copper(II) sulfate

     using:
     - i. carbon electrodes
     - ii. copper electrodes.

6. In what ways are galvanic and electrolytic cells:
   - a. similar?
   - b. different?
7. Why are lead–acid accumulators often referred to as storage batteries?
8. Which of the following temperature ranges would be expected to result in the greatest number of recharge cycles for most rechargeable batteries? Explain.
   - a. 30 °C to 45 °C
   - b. 25 °C to 35 °C
   - c. 5 °C to 25 °C
   - d. −10 °C to 10 °C
9. Sketch an electrolytic cell that could be used to plate copper onto a tin keyring. On your sketch, label the:
   - a. anode and cathode
   - b. direction of electron flow
   - c. nature of each electrode
   - d. electrode polarity
   - e. equations occurring at each electron.
10. How many faradays are needed to produce:
    - a. 1.0 mole of copper
    - b. 2.5 moles of hydrogen gas from water
    - c. 15 g of aluminium
    - d. 5.3 g of sodium
    - e. 87 mL of oxygen gas from water at SLC?
11. Chromium chloride is electrolysed using chromium electrodes. A current of 0.200 A flows for 1447 seconds. The increase in the mass of the cathode is 0.0520 g.
    - a. How many coulombs of electricity are used?
    - b. How many moles of electrons are transferred?
    - c. How many moles of chromium are liberated?
    - d. What is the charge on the chromium ion?
12. a. What volumes of hydrogen gas, H_2, and oxygen gas, O_2, are produced from the electrolysis of water by a current of 2.50 A in 15.0 minutes at SLC?
    - b. Identify the reactions occurring at the electrodes in the reaction in question 12a.
13. Sir Humphry Davy discovered sodium by electrolysing molten sodium hydroxide. How long must a current of 1.5 A flow to produce 1 g of sodium? Give your answer in minutes.
14. A given quantity of electricity is passed through three cells connected in series. These cells contain solutions of silver nitrate, tin (II) chloride and magnesium chloride respectively, all at 1 M concentration. All cells have inert electrodes. After a period of time it is observed that 2 g of silver has been deposited in the first cell.
    - a. What mass of tin would have been deposited in the second cell?
    - b. What mass of magnesium would have been deposited in the third cell?
15. A home renovator wants to chrome-plate her kitchen tap so that a layer of chromium 0.150 mm thick is evenly plated over the tap. The total surface area of the tap is 35.0 cm^2. Given that the density of chromium is 7.20 g cm^{-3}, calculate the time (in hours) that the tap should be left in the electrolytic bath of chromium(III) nitrate if the bath has a current of 4.55 A passing through it.

7.8 Exercise 3: Exam practice questions

Question 1 (9 marks)

An aqueous solution of $NiBr_2$ is electrolysed using inert electrodes.

- **a.** Sketch the cell showing:
  - **i.** the direction of current flow in the external circuit and through the electrolyte
  - **ii.** the cathode and anode, and their polarity. **2 marks**
- **b.** Write half-equations for the expected reactions at each electrode, and then write the overall equation. **3 marks**
- **c.** Calculate the minimum voltage needed to electrolyse the solution under standard conditions (SLC). **1 mark**
- **d.** Explain how the products of electrolysis would differ if nickel electrodes were used. **3 marks**

Question 2 (6 marks)

After Millikan showed that the charge on an electron was 1.6×10^{-19} coulomb, electrolytic reactions were used to obtain accurate estimates of the Avogadro constant. Consider a current of 0.10 A flowing through an electrolytic solution to produce a deposit of 0.10 g of copper.

- **a.** Find the charge passing through the cell if the time taken for the deposit was 50 minutes and 40 seconds. **1 mark**
- **b.** Calculate the amount of copper produced. **1 mark**
- **c.** Write the equation for the reaction and calculate the number of moles of electrons consumed. **2 marks**
- **d.** Calculate the charge on 1 mole of electrons. **1 mark**
- **e.** Calculate the Avogadro constant, given that the charge on an electron is 1.6×10^{-19} coulombs. **1 mark**

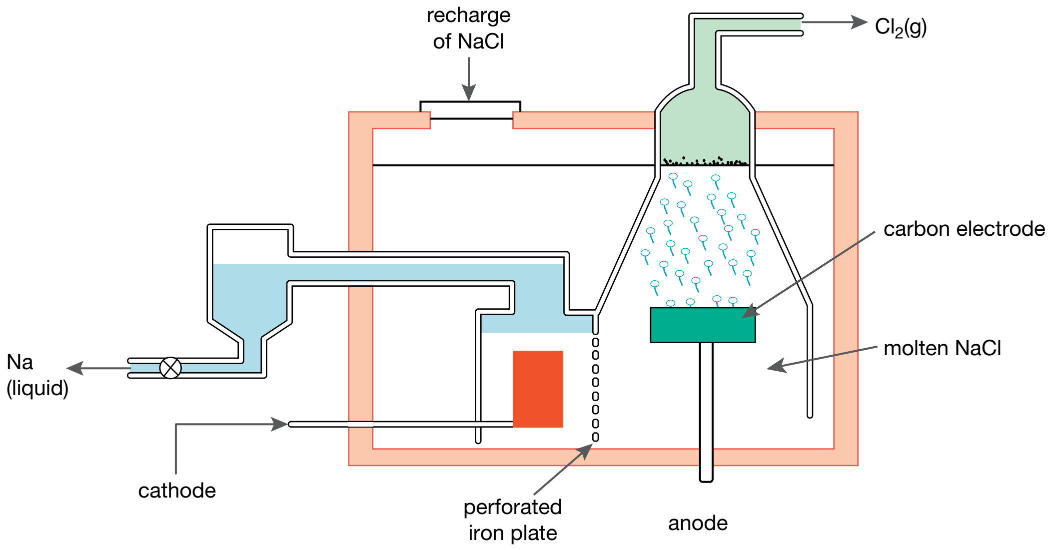
Question 3 (5 marks)

What mass (in kg) of chlorine gas is produced in 1 hour in an electrolytic cell using a concentrated NaCl electrolyte, given that the current is 1.40×10^3 A and the cell's efficiency is 90%? **5 marks**

Question 4 (12 marks)

Sodium is made commercially by the electrolysis of molten sodium chloride in a Downs cell. This cell contains an iron cathode and a carbon anode, and design features to collect and keep the products of electrolysis separate. A number of methods can be used to reduce the melting temperature of the sodium chloride and save on energy costs. A common method is to add an amount of calcium chloride to the melt.

The following diagram shows the essential features of this cell.



a. Which electrode forms the positive electrode and which electrode forms the negative electrode? **1 mark**

b. Write the equation for the half-reaction occurring at the anode. **1 mark**

c. Write the equation for the half reaction occurring at the cathode. **1 mark**

d. Suggest why the perforated iron plate, shown in the diagram, is important for the safe operation of this cell. **1 mark**

e. Explain why the carbon electrode cannot be replaced with an iron electrode. **3 marks**

f. Explain why the addition of calcium chloride does not interfere with the production of sodium. **2 marks**

g. Calculate the volume of Cl_2 gas, measured at SLC, that would be produced when this cell operates with a current of 2.50 A for 12.00 hours. **3 marks**

Question 5 (10 marks)

Both silver and gold may be electroplated onto an object to make it more attractive or resistant to corrosion. The electroplating of silver uses a silver anode and an aqueous solution that contains silver cyanide (AgCN). The electroplating of gold uses an inert anode and an aqueous solution containing potassium gold (I) cyanide ($KAu(CN_2)$).

a. To which electrode does the object to be electroplated need to be attached? **1 mark**

b. Write the equation for the reaction occurring at the cathode
  - **i.** during silver plating
  - **ii.** during gold plating **2 marks**

c. Write the equation for the reaction occurring at the anode
  - **i.** during silver plating
  - **ii.** during gold plating **2 marks**

d. Explain why a silver anode can be used for silver plating but a gold anode cannot be used for gold plating. **1 mark**

e. The concentration of the relevant ion in the electrolyte is one of the factors that determines the quality of the coating. Why does this have to be monitored more closely in gold plating than in silver plating? **1 mark**

f. Calculate the mass of gold deposited when a current of 3.00 A flows for 100 seconds. **3 marks**

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AREA OF STUDY 2 How can yield of processes be optimised?

OUTCOME 2

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.

PRACTICE EXAMINATION

STRUCTURE OF PRACTICE EXAMINATION		
Section	**Number of questions**	**Number of marks**
A	20	20
B	5	30
	Total	**50**

Duration: 50 minutes

Information:

- This practice examination consists of two parts. You must answer all question sections.
- Pens, pencils, highlighters, erasers, rulers and a scientific calculator are permitted.
- You may use the VCE Chemistry Data Book for this task.

on Resources

Weblink VCE Chemistry Data Book

SECTION A — Multiple choice questions

All correct answers are work 1 mark each; an incorrect answer is worth 0.

1. Select the *correct* statement about electrolysis.
  A. A spontaneous chemical reaction produces an electric current.
  B. Chemical energy is converted into electrical energy.
  C. Electrons flow in the internal circuit.
  D. The passage of an electric current through an electrolyte causes a chemical reaction.

2. Select the *incorrect* statement about electrolytic cells.
  A. Oxidation occurs at the anode.
  B. The cathode is positive.
  C. Anions travel to the anode.
  D. Electrons travel from anode to cathode.

3. In the electrolysis of molten sodium chloride:
  A. sodium is produced at the cathode
  B. sodium is produced at the anode
  C. chlorine is reduced
  D. sodium is the reducing agent.

4. Electrolysis of water can be carried out using an acidic or alkaline electrolyte in low concentration. As electrolysis occurs, the overall pH of the electrolyte will:

A. increase
B. decrease
C. remain the same because the electrolyte is not a reactant
D. remain the same due to the products formed.

5. Using inert electrodes, what will the product at the anode be when $CuSO_4(aq)$ is electrolysed?

A. Cu(s)
B. $SO_2(g)$
C. $Cu^{2+}(aq)$
D. $O_2(g)$

6. Using copper electrodes, what will the product at the anode be when $CuSO_4(aq)$ is electrolysed?

A. Cu(s)
B. $SO_2(g)$
C. $Cu^{2+}(aq)$
D. $O_2(g)$

7. When a spoon is electroplated with silver, the spoon:

A. is the cathode and accepts electrons
B. is the cathode and donates electrons
C. is the anode and accepts electrons
D. is the anode and donates electrons.

8. Consider the following equations for when a lead-acid accumulator is *discharging*.

$$Pb(s) + SO_4^{2-}(aq) \rightarrow PbSO_4(s) + 2e^-$$
$$PbO_2(s) + 4H^+(aq) + SO_4^{2-}(aq) + 2e^- \rightarrow PbSO_4(s) + 2H_2O(l)$$

The correct equation for the reaction at the anode when the cell is *recharging* is:

A. $PbO_2(s) + 4H^+(aq) + SO_4^{2-}(aq) + 2e^- \rightarrow PbSO_4(s) + 2H_2O(l)$
B. $Pb(s) + SO_4^{2-}(aq) \rightarrow PbSO_4(s) + 2e^-$
C. $PbSO_4(s) + 2e^- \rightarrow Pb(s) + SO_4^{2-}(aq)$
D. $PbSO_4(s) + 2H_2O(l) \rightarrow PbO_2(s) + SO_4^{2-}(aq) + 4H^+(aq) + 2e^-$

9. A solution of iron(II)sulfate is electrolysed by a current of 6.0 A for 5.0 minutes. What is the mass of iron deposited?

A. 1.04 g
B. 0.35 g
C. 0.52 g
D. 0.017 g

10. Which of the following is required for a battery to be rechargeable?

A. The products of discharge must be solid.
B. The products of discharge must remain in contact with the electrodes.
C. The electrolyte must be acidic.
D. Water must not be present in the battery.

11. At a particle level, reactions occur when:

A. particles collide at a certain angle
B. particles collide with high energy
C. particles collide with sufficient energy and at the correct orientation
D. a catalyst is used.

12. Which of the following is *not* a suitable method for determining changes in the rate of a reaction?

A. Measuring the volume of a gas evolved every 10 seconds for one minute

B. Measuring the change in intensity of the colour of a solution using colorimetry every 30 seconds for five minutes

C. Measuring the change in pH every second using a pH probe until a colour change is observed

D. Measuring the time it takes for a gas to stop forming in a reaction.

13. When a sample of gas is heated:

A. the area under the Maxwell–Boltzmann distribution curve increases

B. the average speed of the molecules increases

C. the molecules are more able to collide with the correct orientation

D. the activation energy for the reaction decreases.

14. What are the expression for the equilibrium constant and the units, respectively, for the reaction:

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

A. $\frac{[H_2][I_2]}{[HI]^2}$, M

B. $\frac{[H_2][I_2]}{[HI]^2}$, no units

C. $\frac{[HI]^2}{[H_2][I_2]}$, M

D. $\frac{[HI]^2}{[H_2][I_2]}$, no units

15. When a system is at equilibrium, it can be said that:

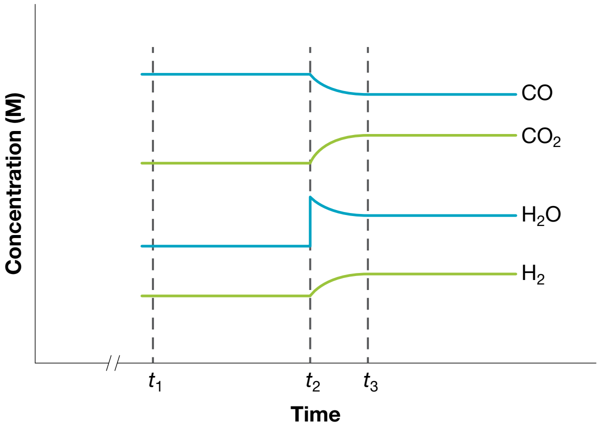
A. The forward and backward reaction are occurring at the same rate

B. The forward and backward reaction have stopped

C. The forward and backward reaction are both occurring to the same extent

D. The concentration of reactants and products is equal.

16.



What is the correct equation for the reaction illustrated?

A. $CO_2(g) + H_2(g) \rightleftharpoons CO(g) + H_2O(l)$

B. $CO_2(g) + 2H_2(g) \rightleftharpoons 2H_2O(l) + CO(g)$

C. $CO(g) + H_2O(l) \rightleftharpoons CO_2(g) + H_2(g)$

D. $CO(g) + H_2O(g) \rightarrow CO_2(g) + H_2(g)$

17. Consider the following reaction.

$$2NO(g) + Br_2(g) \rightleftharpoons 2NOBr(g)$$

If an inert gas is injected into the system when it is at equilibrium, what will happen?

A. The rate of the reaction will increase.
B. The position of equilibrium will shift to the right.
C. The position of equilibrium will shift to the left.
D. The position of equilibrium will remain the same.

18. Which of the following can change the value of the equilibrium constant, *Kc*?

A. Changing pressure
B. Changing temperature
C. Changing volume
D. Adding or removing a substance

19. The equilibrium constant, *Kc*, for the following reaction at 25 °C is $4.2\,M^{-1}$.

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

What is the numerical value of *Kc* for:

$$2SO_3(g) \rightleftharpoons 2SO_2(g) + O_2(g)$$

A. −4.2 M
B. 4.2 M
C. 2.1 M
D. 0.24 M

20. Making methanol on a commercial scale involves the following reaction.

$$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)\ \Delta H = -91\ kJ\ mol^{-1}$$

The ideal conditions for maximum yield of product for this reaction would be:

A. High temperature, high pressure
B. High temperature, low pressure
C. Low temperature, high pressure
D. Low temperature, low pressure

SECTION B — Short answer questions

Question 1 (3 marks)

Explain how using a catalyst affects:

a. The rate of a reaction **2 marks**

b. The extent of a reaction. **1 mark**

Question 2 (11 marks)

Consider the following reaction.

$$4NH_3(g) + 5O_2(g) \rightleftharpoons 4NO(g) + 6H_2O(g) \Delta H = -900 \text{ kJ mol}^{-1}$$

An initial mixture where all concentrations were 2.0 M was allowed to reach equilibrium. At equilibrium, the concentration of NO(g) was found to be 1.4 M.

a. Calculate the equilibrium constant, *Kc*, for the equation. **4 marks**

b. What can be said about the position of equilibrium? **1 mark**

c. Predict the effect of an increase in temperature, with reasoning, on:

- **i.** The rate of reaction **1 mark**
- **ii.** The position of equilibrium. **2 marks**

d. Predict the effect of a decrease in pressure, with reasoning, on:

- **i.** The rate of reaction **1 mark**
- **ii.** The position of equilibrium. **2 marks**

Question 3 (7 marks)

Using graphite electrodes, 1.0 M $MgCl_2(aq)$ undergoes electrolysis.

a. Write the oxidation and reduction half-equations when electrolysis is occurring. **2 marks**

b. Determine the overall equation for the reaction. **1 mark**

c. Determine minimum cell voltage required. **1 mark**

d. How would the products differ if concentrated $MgCl_2(aq)$ was electrolysed? **1 mark**

e. Write the half-equation for the negative electrode if the magnesium chloride was molten. **2 marks**

Question 4 (5 marks)

Chromium chloride undergoes electrolysis using chromium electrodes. A current of 0.400 A flows for 1.00 hour.
The increase in mass of the cathode is 0.259 g.
What is the charge on the chromium ion?

Question 5 (4 marks)

In a zinc–cerium secondary cell, the following reactions occur during discharge.

$$\text{Electrode 1: } Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$$
$$\text{Electrode 2: } Ce^{4+}(aq) \rightarrow Ce^{3+}(aq) + e^-$$

a. When recharging:

- **i.** Which electrode do electrons flow towards? **1 mark**
- **ii.** Which electrode is negative? **1 mark**
- **iii.** What will happen to the mass of electrode 1? **1 mark**

b. Write the overall reaction when the cell is recharging. **1 mark**

ASSESSMENT task — Media analysis

In this task you will analyse three articles related to aluminium production and industry.

- Students are permitted to use pens, pencils, highlighters, erasers, rulers and a scientific calculator.
- Students may use the VCE Chemistry Data Book for this task.

Total time: 55 minutes (5 minutes reading time, 50 minutes writing time)
Total marks: 78 marks

The aluminium industry

For this practice SAC, you will analyse the three articles related to aluminium production and industry in the Resources tab. Answer the following questions by referring to what you have learnt in class and interpreting the three articles in the Resources tab. Remember to answer each question fully and refer to relevant data to show evidence of understanding.

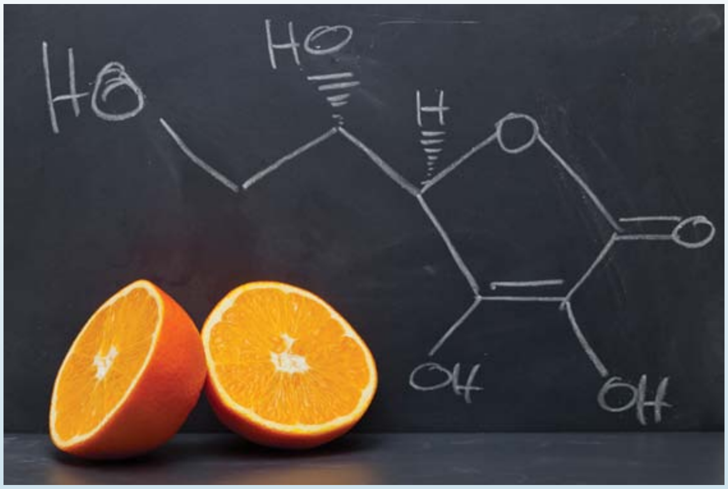
1. What are the three stages of producing aluminium? Explain each stage of production in detail.
2. What factors must be considered when setting up a refinery?
3. Based on the articles, summarise the impact of aluminium, alumina and bauxite commodities in Australia.
4. How does the aluminium industry contribute to environmental damage?
5. In October 2017, the Chinese government pledged a commitment to carry out further air pollution crackdowns at the 19th National Congress. State if and how you think this will impact the aluminium production industry in Australia by referring to relevant data.
6. Why does the general trend in bauxite exports continue to increase?
7. (a) What is the main region in Australia for bauxite production? How much does it produce per year and why is this so?
   (b) Based on the data, how many refineries, smelters and operating mines are in Australia?
8. The United States Administration has imposed a 10 per cent tariff on aluminium imports into the United States following the US Department of Commerce's release of investigations into the national security impact of aluminium and steel imports. How will this affect the United States, Australia and the rest of the world? Refer to Box 11.1 in the third article to answer this question.
9. Explain how electricity prices affect aluminium smelters. What other obstacles are currently facing the aluminium industry?
10. Using information from both articles, provide evidence to support your opinion on the future of the aluminium industry.

on Resources

Weblinks	Australia's major export commodities: aluminium, alumina and bauxite (2017)
	Boyne aluminium smelter poised to slash workforce, lower production
	Aluminium, alumina and bauxite: Resources and energy quarterly, March 2018 (for question 9 only)
Digital document	U3AOS2 School-assessed coursework (doc-32006)

UNIT 4

HOW ARE ORGANIC COMPOUNDS CATEGORISED, ANALYSED AND USED?



Although organic compounds make up a relatively small proportion of the Earth, their diversity is extraordinary, and life, in any form, could not exist without organic chemistry. There are more than 9 million known organic compounds. This diversity is due to the ability of carbon to form stable bonds with four other elements, and is enhanced by the creation of isomers. With the vast number of carbon compounds possible, a systematic, worldwide naming system has been developed to allow this variety of molecules to be identified.

The millions of organic compounds known to chemists are mainly covalent molecules. These could be simple molecules, such as methane and ethanol, or macromolecules, such as polyethene and proteins. The trends in physical properties of organic compounds, such as melting point, boiling point, viscosity, flashpoint and solubility, and their behaviours can be deduced from their structure, including size, shape, structure, degree of polarisation of their covalent bonds, and the presence of any functional groups. These factors depend on the strength of the intermolecular forces present.

Organic reactions are examined to understand the formation of other organic compound groups, which can be recognised through a variety of analytical techniques. This study of organic compounds is extended to the chemistry of food, which provides both the energy and raw materials that humans need. Hydrolysis reactions break down the food while condensation reactions create new biomolecules necessary for growth and repair.

AREA OF STUDY	OUTCOME	CHAPTERS
1. How can the diversity of carbon compounds be explained and categorised?	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.	8. Structure and nomenclature of organic compounds 9. Categories, properties and reactions of organic compounds 10. Analysis of organic compounds
2. What is the chemistry of food?	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.	11. Key food molecules 12. Metabolism of food in the human body 13. Energy content of food
3. Practical investigation	Design and undertake a practical investigation related to energy and/or food, and present methodologies, findings and conclusions in a scientific poster.	14. Practical investigation

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8 Structure and nomenclature of organic compounds

8.1 Overview

Numerous **videos** and **interactivities** are available just where you need them, at the point of learning, in your digital formats, learnON and eBookPLUS at www.jacplus.com.au.

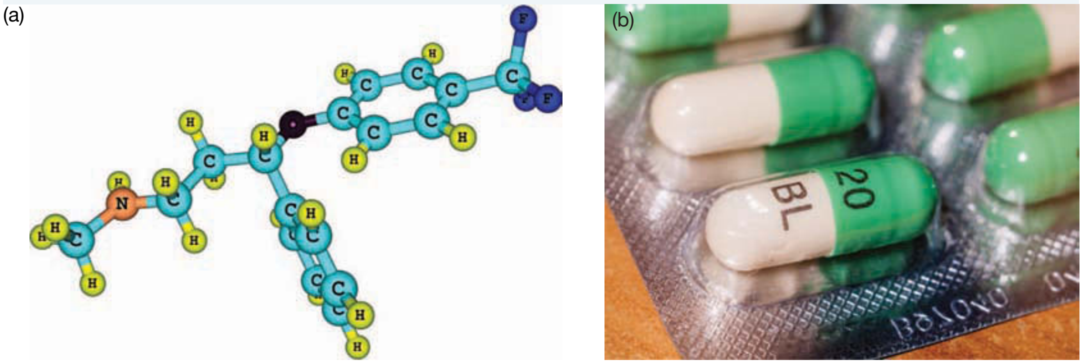
8.1.1 Introduction

Plastics, fuels, medicines, and simple and complex life forms are all part of the millions of natural or synthetic organic compounds that exist. To understand the basics of organic chemistry, we need to learn about carbon and why its unique chemical properties allow it to become a part of so many different organic compounds. We need to understand how these molecules are put together and how they exist physically and react chemically. Students of organic chemistry learn how to represent and name these molecules using a set of rules and symbols. It's a bit like learning a new language: the further you go the more complex it becomes.

Organic compounds are marketed and sold to us every day, but they might not be instantly recognisable. For example, Prozac is the brand name given to a medication that treats a variety of conditions including depression and anxiety. Calling it 'Prozac' is a lot easier than using its systematic name: N-methyl-3-phenyl-3-4-(trifluoromethyl)phenoxypropan-1-amine!

However, Prozac and other commercial names are variations used to market the same chemical. To avoid confusion, a naming system maintained by the International Union of Pure and Applied Chemistry (IUPAC) is used to classify organic compounds. This ensures consistency in the way the scientific community names and classifies organic compounds.

FIGURE 8.1 Prozac (a) as a chemical structure and (b) as capsules prescribed by doctors.



In this topic you will examine carbon and its tendency to bond with itself and other elements in many stable forms that result in compounds with diverse chemical and physical properties. These compounds are named systematically and can be drawn as full structures, semi-structures and skeletal structures of familiar functional groups including alkanes, alkenes, alkynes, alcohols, carboxylic acids and esters. Amines and the application of rules for naming compounds that contain two functional groups on the same molecule are introduced.

8.1.2 What you will learn

KEY KNOWLEDGE

In this topic, you will investigate:

- 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 semi-structural 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 C8 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.

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PRACTICAL WORK AND INVESTIGATIONS

Practical work is a central component of learning and assessment. Experiments and investigations, supported by a **Practical investigation logbook** and **Teacher-led videos**, are included in this topic to provide opportunities to undertake investigations and communicate findings.

Resources

Digital documents Key science skills (doc-30903)
Key terms glossary – Topic 8 (doc-31412)
Practical investigation logbook (doc-31413)

To access key concept summaries and past VCAA exam questions download and print the **studyON: Revision and practice exam question booklet** (doc-31414).

8.2 The carbon atom

KEY CONCEPT

- The carbon atom with reference to valence number, bond strength, stability of carbon bonds with other elements

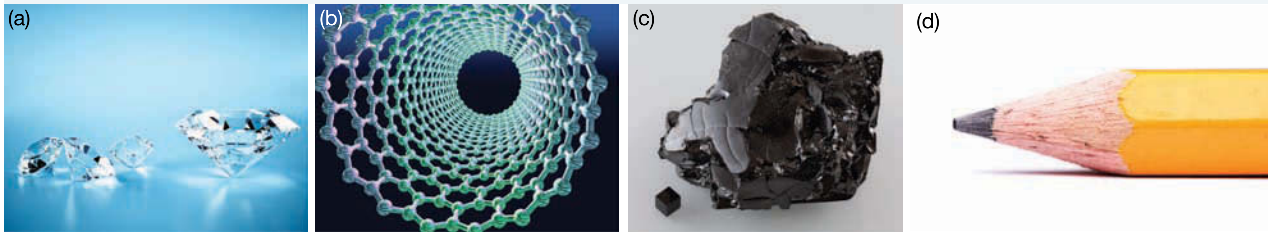
8.2.1 Carbon: a remarkable element

The carbon atom is the one constant in the millions of organic compounds either found in natural substances or made (synthesised) in the laboratory. This incredible variety can even be seen in samples of pure carbon, which exist in different chemical and physical forms. The different physical forms in which an element can exist are called **allotropes**.

Carbon is found in so many compounds due to its arrangement of electrons. You may recall from Unit 1 that electron shells contain three-dimensional regions of space, called orbitals, where electrons at any given time may be found around the nucleus of an atom. The number of electrons, shells, and potentially occupied orbitals are collectively known as an element's **electron configuration**.

Carbon is located at the top of group 14 of the periodic table of elements. This location is determined not only by the six protons in a carbon nucleus (atomic number) but also the electron configuration. A neutral carbon atom will have six electrons occupying its orbitals and these are situated in the first two electron shells of the atom.

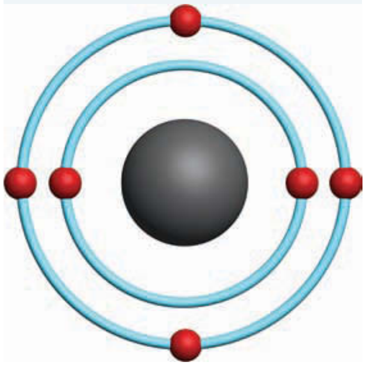
FIGURE 8.2 Allotropes — different physical forms of carbon (a) diamond, (b) carbon nanotube, (c) glassy carbon, (d) graphite pencil.



Valence number 4

The **valence number** of an element refers to the number of electrons occupying the orbitals in the outermost electron shell. Only two of carbon's six electrons occupy the first electron shell, therefore, the remaining four valence electrons are found in the second, outermost shell. These four electrons are available for bonding.

FIGURE 8.3 Carbon atom demonstrating four valence electrons.



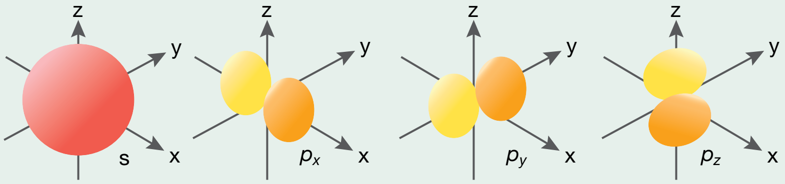
ELECTRON CONFIGURATION OF CARBON

The first two electron shells of carbon have a different number and type of orbitals. Each atomic orbital can hold a maximum number of two electrons. However, each orbital can contain one or two electrons, or none at all.

The first and second electron shells of a carbon atom have one *s* orbital each (called 1*s* and 2*s* respectively), and the valence shell has three *p* orbitals. An *s* orbital is a spherical shape around the nucleus; *p* orbitals are often described as having a dumbbell shape.

Figure 8.4 shows the orientation of the orbitals in three dimensions. If you are sitting at a table, reading this from your text book, the *x*- and *y*-planes cover the length and width of your page. The *z*-plane extends out of the page towards your eyes and behind the page towards your feet.

FIGURE 8.4 Electron shell orbitals of carbon

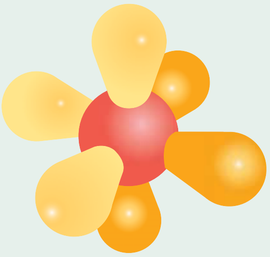


In its lowest energy state (ground state), the electron configuration of carbon is $1s^2 2s^2 2p^2$. This can also be written as $1s^2 2s^2 2p_x^{\,1} 2p_y^{\,1}$ to represent the different *p* orbitals potentially occupied.

The distance of the 2*p* orbitals from the nucleus is greater than the 2*s* orbital and this means electrons occupying *p* orbitals are higher in energy than those in *s* orbitals in the same shell. If energy is applied, the electrons move to higher energy orbitals. This is referred to as an **excited state**. For example, $1s^2 2s^1 2p^3$ ($1s^2 2s^1 2p_x^{\,1} 2p_y^{\,1} 2p_z^{\,1}$) is an excited state of carbon.

When *s* and *p* orbitals overlap they produce a blend of the two types called *sp* hybrids. These hybrid regions of space allow electron pairs to be more stable than if they were in *s* or *p* orbitals exclusively.

FIGURE 8.5 Visualisation of *s* and *p* orbitals



8.2.2 Bonding

Bond energy

Energy transfer is involved when chemical bonds are formed and broken. Recall from Unit 3 the energy profiles showing activation energy required to break bonds and then an amount of energy lost when new bonds are formed. Carbon forms stable, lower energy compounds when its valence shell resembles that of Neon (2, 8, 8). How and with what this happens is varied and complex.

Bond energy can have a variety of units. One such unit is kilojoule(s) per one mole (kJ mol^{-1}), which tells us the amount of energy required to break the bonds of the reactants or the amount of energy released per mole when the covalent bond forms between two atoms. Bond energy differs by the element(s) sharing a covalent bond and is affected by the distance between the two atoms. If atoms are too close they repel, and if they are too far away they are unable to share the electrons. The distance between the nuclei of the atoms sharing the electrons is known as **bond length**.

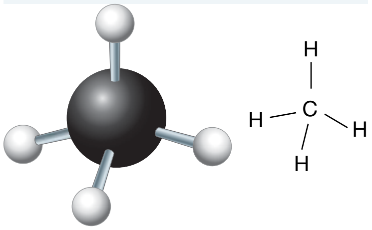
TABLE 8.1 Comparison of bond energies (kJ mol^{-1})

Hydrogen bonds		Carbon bonds		Nitrogen bonds		Oxygen bonds		Same elements	
H–H	436	C–H	414	N–H	391			C–C	346
H–C	414					O–C	358	C=C	614
		C–N	286	N–N	158	O–N	214	Cl–Cl	242
H–O	463	C–O	358	N–O	214	O–O	144	Br–Br	193
H–F	567	C–F	492	N–F	278	O–F	191	I–I	151
H–Cl	431	C–Cl	324	N–Cl	192	O–Cl	206		

Bond angle and stability

The ability of carbon to form millions of compounds is also dependent upon the geometry (spatial arrangement) of atoms attached to it. The orbitals of molecules can combine (hybridise) to produce bond angles and **covalent bonds** with greater stability. For example, when carbon forms four, single covalent bonds, the bonds separate so that the angle between the bonds is 109.5°, forming a tetrahedral molecule shape.

FIGURE 8.6 The tetrahedral geometry of CH_4



Multiple carbon to carbon bonds

The majority of carbon atoms bond with this approximate angle of 109.5°. However, carbon has the ability to overlap orbitals in such a way that C=C double covalent bonds form. In this scenario, other atoms bonded to the two carbon atoms have bonds that are spaced at an approximate 120°angle, resulting in a planar geometry.

The bonds in a C=C double bond are shorter and stronger that C–C single bonds. It takes almost twice the amount of energy to break a C=C bond than it does a C–C bond. This is not surprising given there are four electrons providing stability in a C=C bond compared to just two in a C–C bond.

All the bonds in C_2H_4 occur in the same plane. This is why it is often referred to as a flat molecule (see figure 8.7).

The same can be said of carbon to carbon triple bonds because they have a linear geometry and 180° between bonds (see figure 8.8). C≡C triple bonds are stronger than C=C bonds. They are the shortest of C to C bonds, with a length of approximately 120 picometres (1.2×10^{-10} m).

FIGURE 8.7 The planar, flat geometry of C_2H_4

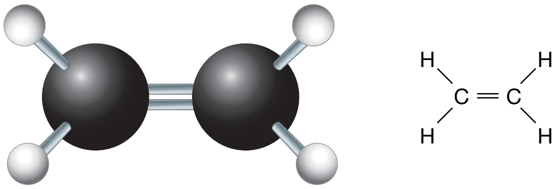
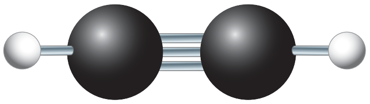


FIGURE 8.8 The planar, flat geometry of C_2H_2



$H-C\equiv C-H$

SAMPLE PROBLEM 1

Calculate the energy, in kJ, required to break all covalent bonds in 1.6 g of CH_4 gas.

Teacher-led video: SP1 (tlvd-0702)

THINK	WRITE
1. The standard unit for bond energy is kJ mol^{-1} but the question has given a mass of CH_4 and not an amount in mol. Therefore, we need to convert mass into moles using $n = \frac{m}{M}$.	$n = \frac{m}{M}$ $= \frac{1.6\text{ g}}{16.0\text{ g mol}^{-1}}$ $= 0.10\text{ mol}$
2. There are four C—H bonds in CH_4. Use table 8.1 to find the value stated for a C—H bond and multiply it by four.	Energy in C–H bonds $= 4 \times 414$ $= 1656\text{ kJ mol}^{-1}$
3. To find the total bond energy to break all the bonds in 1.6 g methane, multiply bond energy per mol calculated in step **2** by the number of moles in 1.6 g of methane. **TIP:** Remember to give your answer to the correct number of significant figures.	$0.10\text{ mol} \times 1656\text{ kJmol}^{-1} = 166\text{ kJ}$ $= 1.7 \times 10^2\text{ kJ}$

PRACTICE PROBLEM 1

Calculate the energy required, in kJ, to break all covalent bonds in 64 g of CH_4 gas.

8.2 EXERCISE

To answer questions online and to receive **immediate feedback** and **sample responses** for every question go to your learnON title at www.jacplus.com.au.

1. Which of the following molecules would have similar bond angles to CH_3Cl?
   A. C_2H_4
   B. C_2H_2
   C. CH_4
   D. CO_2
2. Why are C=C bonds stronger than C—C bonds?
3. If the bond energy of H—F is 565 kJ mol^{-1}, what is the overall bond energy of two moles of HF?
4. What is the difference in C—H bond angles between C_2H_2 and C_2H_4 molecules?
5. What amount of energy per mole would be released if all covalent bonds in CH_2F_2 were broken?

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8.3 Structure and naming of organic compounds

KEY CONCEPTS

- Structures including molecular, structural and semi-structural 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 C8 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.

8.3.1 Molecular modelling

We model the way atoms are bonded and arranged in a molecule in a number of ways. The simplest molecular models are electron dot (Lewis) diagrams and structural diagrams, which were covered in Unit 1. As molecules become larger and more complex, we look for easier ways to represent all of the bonded atoms.

Structural diagrams

Structural diagrams show all covalent bonds in the molecule. There are a number of different ways we draw structures. The simplest way is to show all atoms and all bonds in a molecule. These can then be modified to skeletal and semi-structural formulas.

Wedge–dash notation represents the spatial arrangement of atoms. Figure 8.9 shows the position of the hydrogen atoms in three-dimensional space relative to one another. The wedges shows the atom coming out of the page towards us, while dashes shows the atom going behind the page away from us. The unbroken lines represent bonds to atoms that are in the same plane as the page.

Wedge–dash diagrams can be simplified to structural formulas, as shown in figure 8.10. Structural formulas do not show the arrangement of atoms in three dimensions.

FIGURE 8.9 Three-dimensional space (wedge–dash) diagram of CH_4

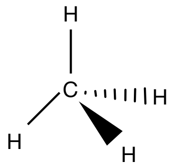
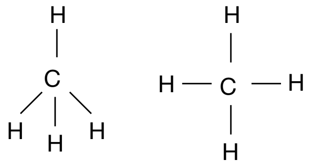


FIGURE 8.10 Structural formulas of CH_4

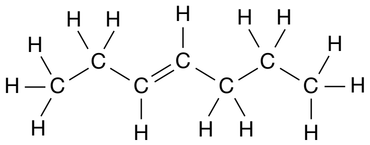


Semi-structural formulas

Semi-structural formulas are used to simplify the structure presented while preserving the order of groups of atoms. This is done by not including the covalent bonds shown in structural diagrams. Semi-structures are useful when showing larger molecules that require a lot of bonds to be drawn in full structures.

The structure of C_7H_{14} can be used to show the different ways of writing a semi-structure.

FIGURE 8.11 Structural formula of C_7H_{14}



First, condense the structure by removing the bonds while maintaining the order of groups of atoms.

$$CH_3CH_2CHCHCH_2CH_2CH_3$$

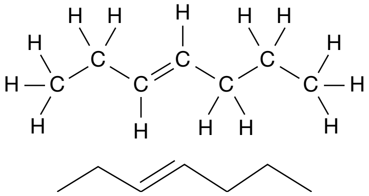
If there is a sequence of the same group, such as CH and CH_2 as in the semi-structure shown above, we can condense it further using brackets. This allows further simplification and is useful for large molecules.

Therefore, $CH_3CH_2CHCHCH_2CH_2CH_3$ becomes $CH_3CH_2(CH)_2(CH_2)_2CH_3$.

Skeletal structural formulas

Skeletal structural formulas are a further simplification of semi-structural formulas. Skeletal structures use lines and vertices to simplify a structural formula by omitting the carbon and the hydrogen atoms bonded to it. It is assumed that a carbon atom (and enough hydrogens to satisfy carbon's valency) is present at each vertex (and also at the ends). Double bonds and other different types of atoms are specifically shown. Skeletal structures preserve the bond angles in a carbon chain and are the preferred method for representing complex organic molecules that are large and often contain ring or cyclic structures.

FIGURE 8.12 Full structure and skeletal structure of C_7H_{14}



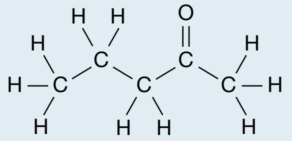
Returning to C_7H_{14}, the simplicity of skeleton structure compared to the full structure can be seen in figure 8.12. The C and associated H atoms have been omitted, but the C=C bond has been preserved.

SAMPLE PROBLEM 2

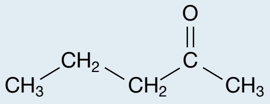
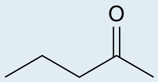
For the structure shown, draw:

a. a semi-structual formula

b. a skeletal structural formula.



Teacher-led video: SP2 (tlvd-0703)

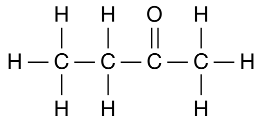
THINK	**WRITE**
1. Recall that semi-structures condense the carbon chain by removing the covalent bonds while preserving the order of the atoms and skeletal structures remove the C and their H atoms from the structural diagram. Draw the structure out but condense all hydrogen atoms connected to each carbon.	
a. For the semi-structure, remove all of the covalent bonds and write out the sequence of groups in the chain.	$CH_3CH_2CH_2COCH_3$
b. For the skeletal structure, remove all of the C and H atoms attached to the covalent bonds but retain the bonds.	

PRACTICE PROBLEM 2

For the structure shown, draw:

a. a semi-structural formula

b. a skeletal structural formula.

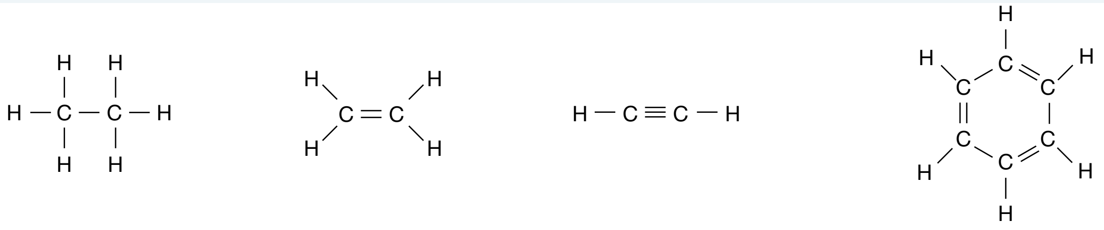


$$\begin{array}{ccccccccc} & & H & & H & & O & & H \\ & & | & & | & & \| & & | \\ H & - & C & - & C & - & C & - & C & - & H \\ & & | & & | & & & & | \\ & & H & & H & & & & H \end{array}$$

8.3.2 Hydrocarbons

Hydrocarbons are the simplest organic compounds and are composed solely of carbon and hydrogen. They are obtained mainly from crude oil and are used as fuels or solvents, or in the production of plastics, dyes, pharmaceuticals, explosives and other industrial chemicals. The organic families studied in this topic contain various percentages of carbon and hydrogen atoms. They include the alkanes, alkenes and alkynes, which are classified as **aliphatic** compounds, and benzene, which is an **aromatic** compound.

FIGURE 8.13 The structural arrangement of ethane (alkane), ethene (alkene), ethyne (alkyne) and the benzene ring (aromatic). Carbon can form ring structures as well as single or multiple bonds with itself.



ethane ethene ethyne benzene

A family of carbon compounds that are structurally related and where members of the family can be represented by a general formula is called a **homologous series**. Successive members of a homologous series have formulas that differ by CH_2. Each is named for the number of carbon atoms in the longest chain.

Alkanes

Alkanes with carbon atoms in long chains are known as straight-chain hydrocarbons. Alkanes have the structural formula C_nH_{2n+2}, where n is an integer. They are classified as saturated hydrocarbons because only single covalent bonds exist between atoms and there are no available multiple carbon bonds to break and add atoms into the molecule. The first four alkanes are gases at room temperature, and they are summarised in table 8.2.

FIGURE 8.14 Propane, the third member of the alkane homologous series, is used to fly hot air balloons

Alkanes are saturated hydrocarbons with single bonds between the carbon atoms, they have the general formula C_nH_{2n+2}

TABLE 8.2 The first four members of the alkane homologous series

Alkane	Semi-structural (condensed) formula	Source	Uses
Methane	CH_4	Natural gas or biogas	• Fuel • Synthesis of other chemicals
Ethane	CH_3CH_3	Natural gas	• Manufacture of ethene • Refrigerant in cryogenic systems

Alkane	Semi-structural (condensed) formula	Source	Uses
Propane	$CH_3CH_2CH_3$	Natural gas processing or petroleum refining	• Fuel (e.g. in gas cylinders for heating) • Propellant for aerosols
Butane	$CH_3CH_2CH_2CH_3$	Natural gas processing or petroleum refining	• Fuel (e.g. cigarette lighters and portable stoves) • Synthesis of other chemicals • Propellant for aerosols

The next four members of the alkane homologous series are:

- pentane, C_5H_{12}
- hexane, C_6H_{14}
- heptane, C_7H_{16}
- octane, C_8H_{18}.

The name of each alkane has two parts. The prefix (the start) of each name tells us how many carbon atoms are in the straight chain. The suffix (the end) *-ane* of each name tells us that the hydrocarbon is an alkane. The prefixes are used to name the number of carbon atoms in a chain in the majority of the homologous series studied in this topic.

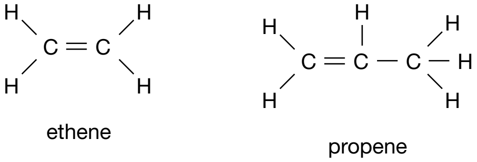
on Resources

Video eLesson Naming alkanes (eles-2484)

Alkenes

Double bonds between carbon atoms are formed when two hydrogen atoms are removed from alkanes. These hydrocarbons are said to be **unsaturated**. Hydrocarbons with one or more carbon–carbon double bonds per molecule are members of the homologous series called **alkenes**. The general formula for alkenes is C_nH_{2n}. The first two members of the alkene series are ethene, C_2H_4, and propene, C_3H_6. Their structural formulas are shown in figure 8.15.

FIGURE 8.15 Structural formulas of ethene and propene



Alkenes are unsaturated hydrocarbons with a double bond between two carbon atoms. They have the general formula C_nH_{2n}.

Ethene is also commonly known as ethylene. It is produced naturally by some plants and it aids in ripening fruit. It can also be produced artificially by heating petroleum in the absence of air in a process called cracking. Ethene is an important raw product for making many chemicals and plastics.

FIGURE 8.16 These tomatoes are the same age but the red one has been ripened using ethene gas.

TABLE 8.3 Members of the alkene homologous series

Systematic name	Formula	Semi-structural formula with double bonds
Ethene	C_2H_4	$H_2C{=}CH_2$
Prop-1-ene	C_3H_6	$H_2C{=}CHCH_3$
But-1-ene	C_4H_8	$H_2C{=}CHCH_2CH_3$
Pent-1-ene	C_5H_{10}	$H_2C{=}CH(CH_2)_2CH_3$
Hex-1-ene	C_6H_{12}	$H_2C{=}CH(CH_2)_3CH_3$
Hept-1-ene	C_7H_{14}	$H_2C{=}CH(CH_2)_4CH_3$
Oct-1-ene	C_8H_{16}	$H_2C{=}CH(CH_2)_5CH_3$

Table 8.3 shows the first seven members of the alkene series. Alkenes are named using the same general rules described for alkanes except that the suffix *-ene* is added instead of *-ane*, and the number of the carbon atoms after which the double bond is positioned is indicated. The longest unbranched chain must contain the double bond, so the molecule $CH_3CH_2CH{=}CHCH_3$ is named pent-2-ene. The '2' indicates the position of the double bond between carbon atoms 2 and 3 (the lower number is used in the formula, and numbering starts from the carbon atom closest to the double bond) and 'pent' indicates that five carbon atoms are present in the unbranched chain. Some people prefer to name it 2-pentene. Either way, the number of carbon atoms in the chain and the position of the carbon bond are indicated. For consistency, we will use the first naming method.

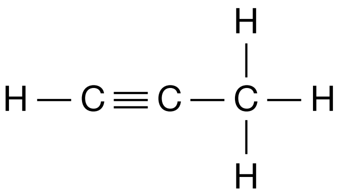
on Resources

Video eLesson: Homologous series of alkenes (eles-2477)

Alkynes

Alkynes contain a carbon–carbon triple bond and have the general formula C_nH_{2n-2}. Examples include ethyne, $HC{\equiv}CH$, and propyne, $HC{\equiv}CCH_3$. Ethyne is used to produce ethane and in oxyacetylene torches for welding to join metals. It can heat objects up to 3000 °C. Alkynes are named using the same general rules as for alkanes, but the *-ane* is dropped and replaced with *-yne*.

FIGURE 8.17 Prop-1-yne



Alkynes are unsaturated hydrocarbons with a triple bond between two carbon atoms. They have the general formula C_nH_{2n-2}.

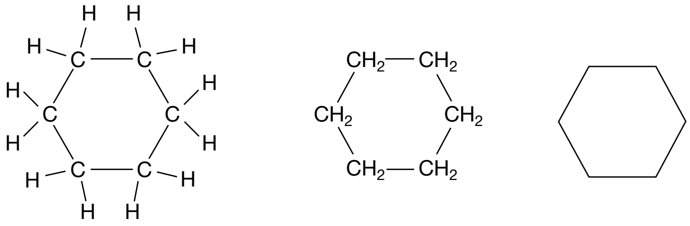
on Resources

Digital document Experiment 8.1 Constructing models of hydrocarbons (doc-31266)

Cyclic hydrocarbons

Cyclic hydrocarbons are also known as ring structures because the carbon chain is a closed structure without open ends. The single-ringed cycloalkanes have the same molecular formula as alkenes due to all carbon atoms being covalently bonded to two others either side to form the closed ring. As well as having a different molecular formula to straight chain alkanes, the prefix '*cyclo-*' is put at the start of the name to indicate the ring structure. The simplest cyclic hydrocarbon, cyclohexane, has the molecular formula C_6H_{12} and is a colourless, flammable liquid that is used as a reactant in the production of nylon.

FIGURE 8.18 Structural diagrams of cyclohexane

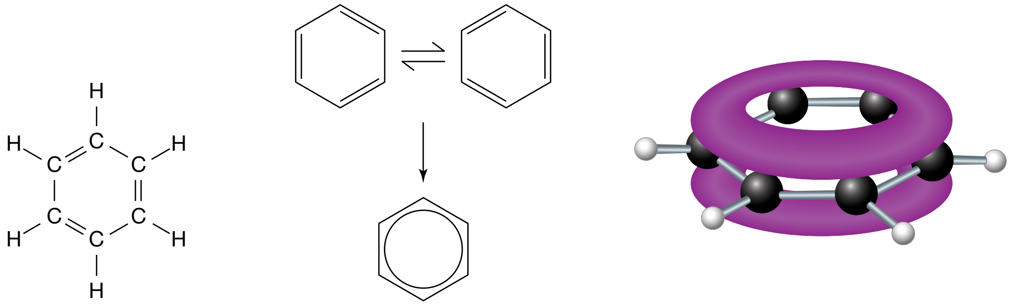


Another important group of cyclic hydrocarbons are the **arenes**. These compounds are derived from **benzene**. The benzene, C_6H_6, molecule consists of six carbon atoms arranged in a ring with one hydrogen atom bonded to each carbon. Originally, it was thought that there were alternating single and double carbon–carbon bonds in the ring. However, the lack of reactivity, high stability and same bond lengths between the carbon atoms did not support this theory. Currently, benzene is considered to be a molecule with six electrons from the three double bonds shared by all of the carbon atoms in the ring. The attraction of the electrons to all of the carbon atoms gives the molecule stability.

Benzene is a very important compound in organic chemistry. Even though benzene itself is carcinogenic, many of the chemicals produced from it are not. In fact, many foods and pharmaceuticals, such as paracetamol, contain benzene rings.

There are various ways of representing the benzene ring, as shown in figure 8.19.

FIGURE 8.19 Representations of benzene



Alkyl groups

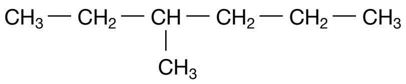
Alkyl groups are hydrocarbon branches coming off the longest carbon chain of an organic molecule. Alkyl branches use the same prefixes to represent the number of carbons in the branch as those used in straight chain molecules, but the suffix changes to '*-yl*'. To branch off the main chain, alkyl groups have one less hydrogen atom than the alkanes that share the same prefix in their name.

TABLE 8.4 The first three alkane and alkyl groups

Alkane	Semi-structural formula	Alkyl groups	Semi-structural formula
Methane	CH_4	Methyl	$-CH_3$
Ethane	CH_3CH_3	Ethyl	$-CH_2CH_3$
Propane	$CH_3CH_2CH_3$	Propyl	$-CH_2CH_2CH_3$

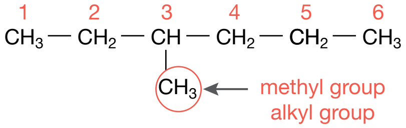
FIGURE 8.20 The polystyrene foam and the epoxy resin in surfboards make them light and strong. Both chemicals contain cyclic hydrocarbon groups.

Alkyl groups have to be named in both number and position on a carbon chain. As an example, let's follow the IUPAC rules for naming the following branched alkane.



$$CH_3-CH_2-\underset{\underset{\textstyle CH_3}{|}}{CH}-CH_2-CH_2-CH_3$$

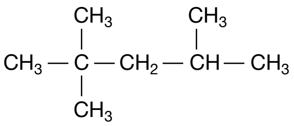
1. Count the longest carbon chain. This will determine the prefix used to name the main/parent chain.
2. Identify alkyl groups branching off the main chain.
3. Starting at the end, number the chain that gives the lowest number for an alkyl branch.



$$\overset{1}{CH_3}-\overset{2}{CH_2}-\overset{3}{\underset{\underset{\textstyle CH_3}{|}}{CH}}-\overset{4}{CH_2}-\overset{5}{CH_2}-\overset{6}{CH_3}$$

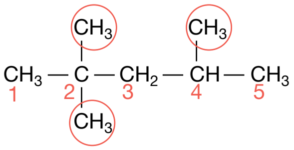
4. Write the number and the name of the alkyl group(s) attached in alphabetical order. 3-methyl
5. Write the name of the parent chain at the end. Six carbons separated by single bonds is a hex-ane: 3-methylhexane

When there are more than one of the same type of alkyl group branching off the parent chain, prefixes are used to indicate how many there are, and numbers are used to indicate which carbon atom they come off in the parent chain. For example, consider the following multi-branched alkane.



$$CH_3-\overset{\overset{\textstyle CH_3}{|}}{\underset{\underset{\textstyle CH_3}{|}}{C}}-CH_2-\overset{\overset{\textstyle CH_3}{|}}{CH}-CH_3$$

1. The longest chain is five carbons.
2. Three methyl (CH_3) groups are branching off the chain.
3. The chain is numbered from left to right because this gives two alkyl groups coming off C2 instead of C4 if named from the opposite end.



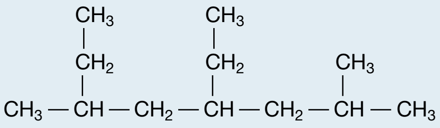
$$\underset{1}{CH_3}-\overset{\overset{\textstyle CH_3}{|}}{\underset{\underset{\textstyle CH_3}{|}}{\underset{2}{C}}}-\underset{3}{CH_2}-\overset{\overset{\textstyle CH_3}{|}}{\underset{4}{CH}}-\underset{5}{CH_3}$$

4. List the numbers of the C atoms the CH_3 groups are branching off separated by commas and then a hyphen before the prefix *'tri-'* to indicate there are three methyl groups.
5. Add the parent chain name to the end: 2,2,4-trimethylpentane.

TIP: **If there are molecules with two or more branches of the same type, the branch type is named and a prefix (di-, tri-, etc) is used to indicate the number of branches. Branches are listed in alphabetical order, ignoring the prefix (i.e. ethly is written before methyl or dimethyl).**

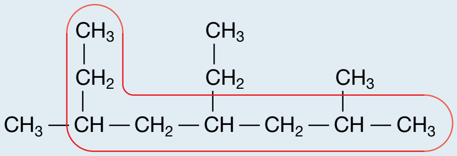
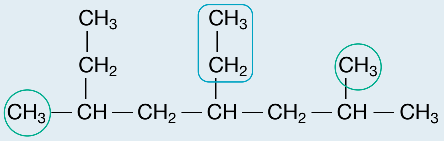
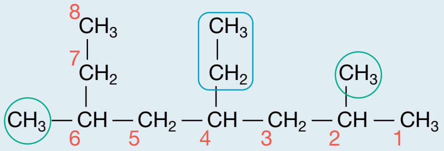
SAMPLE PROBLEM 3

Write the systematic (IUPAC) name of the following hydrocarbon.



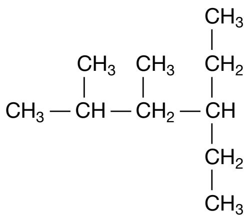
$CH_3-CH(CH_2CH_3)-CH_2-CH(CH_2CH_3)-CH_2-CH(CH_3)-CH_3$

Teacher-led video: SP3 (tlvd-0704)

THINK	WRITE
1. Examine the molecule to find the longest carbon chain.	
2. Locate the alkyl groups.	
3. Number the chain from an open end that gives one or more alkyl groups the lowest number.	
4. Write the number(s) of the alkyl groups separated by commas and then hyphenated to the prefix to indicate the number of the same type of alkyl group.	2,6-dimethyl 4-ethyl
5. List the different alkyl groups in alphabetical order, ignoring the prefix.	4-ethyl-2,6-dimethyl
6. Add the name of the parent chain to the end of the name.	4-ethyl-2,6-dimethyloctane

PRACTICE PROBLEM 3

Write the IUPAC name of the following hydrocarbon.



$CH_3-CH(CH_3)-CH_2(CH_3)-CH(CH_2CH_3)(CH_2CH_3)$

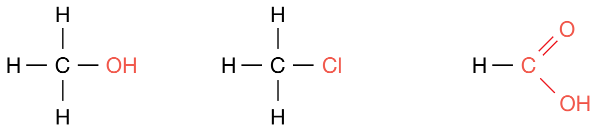
on Resources

Interactivity Systematic naming of alkanes, alkenes and alkynes (int-1231)

8.3.3 Functional groups

An atom or a group of atoms that determines the function (chemical nature) of a compound is called a **functional group**. As with the alkanes and alkenes, compounds containing the same functional group form a homologous series (a family with similar properties). A molecule with a functional group attached is usually less stable than the carbon backbone to which the functional group is attached and therefore more likely to participate in chemical reactions. Figure 8.21 shows three different functional groups attached to the basic carbon skeleton of methane.

FIGURE 8.21 Different functional groups (COOH) attached to the basic carbon skeleton of methane



CH_3OH methanol

CH_3Cl chloromethane

HCOOH methanoic acid

8.3.4 Haloalkanes

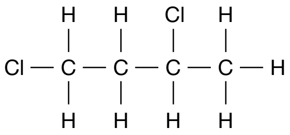
Haloalkanes are a class of molecules that have one or more **halogens** attached to the carbon chain. They are used in a variety of applications including solvents, refrigeration and medicine.

Haloalkanes are often represented as **R–X**. The **R** is used to represent the hydrocarbon chain of any length and the **X** is used to represent any of the halogens, such as fluorine (F), chlorine (Cl) and bromine (Br).

The naming system of haloalkanes follows the same rules as naming hydrocarbons. However, like all functional groups, halogen functional groups take priority over alkyl groups when numbering the longest carbon chain. We all use the same prefixes to name compounds with more than one of the same halogens.

Another difference in the naming is the replacement of the '-*ine*' with '-*o*'. Fluorine becomes fluoro, chlorine becomes chloro and bromine becomes bromo when they are part of a haloalkane.

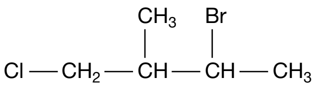
Consider the molecule:



The molecule has a four-carbon chain with two chlorine atoms attached on C1 and C3. The systematic name of this compound is 1,3-dichlorobutane.

When there are different halogens on the carbon chain, they are numbered as usual but written alphabetically, like alkyl groups.

For example:



$Cl-CH_2-CH(CH_3)-CH(Br)-CH_3$

3-bromo-1-chloro-2-methylbutane

Haloalkanes are hydrocarbons with one or more halogens attached to the carbon chain. They have the general formula R–X, where R is a hydrocarbon chain of any length and X is a halogen.

8.3.5 Alcohols

Organic hydroxyl compounds containing the —OH group belong to the homologous series called **alcohols**. A study of the properties of the —OH group is important to chemists because of the industrial importance of compounds containing this functional group, and because of its wide occurrence in biological molecules. Ethanol is the most common alcohol and it has many uses. It is present in beer, wine and spirits, and is used in the preparation of ethanoic acid (acetic acid) and for sterilising wounds. Methylated spirits (containing 95% ethanol) is a very useful solvent and is used in the manufacture of varnishes, polishes, inks, glues and paints. Other alcohols that are volatile at low temperatures are also good solvents and are used in deodorants, colognes and aftershave lotions. Glycerol, $C_3H_5(OH)_3$, is used for making fats and soaps. **Alkanols** are alcohols containing only carbon, hydrogen and oxygen.

For naming purposes, alcohols have the general formula **R—O—H**. The first three members of the alcohol homologous are shown in figure 8.22. Again, the standard prefixes are used to name the number of carbon atoms in the chain. In the first two members (methanol and ethanol), the hydroxyl group is not numbered because its position is always C1. However, with the third member, the —OH group could be on C1 or C2, and therefore needs to be stated in the name. The suffix '*-ol*' is used instead of hydroxy in the name, which tells us that the —OH is the functional group with priority. So the third member is named propan-1-ol rather than 1-hydroxypropane. When the hydroxyl group branches off C2 we simply change the ending of the name to **-2-ol** as shown in figure 8.23.

FIGURE 8.22 Members of the alcohols: ethanol, ethanol and propan-1-ol

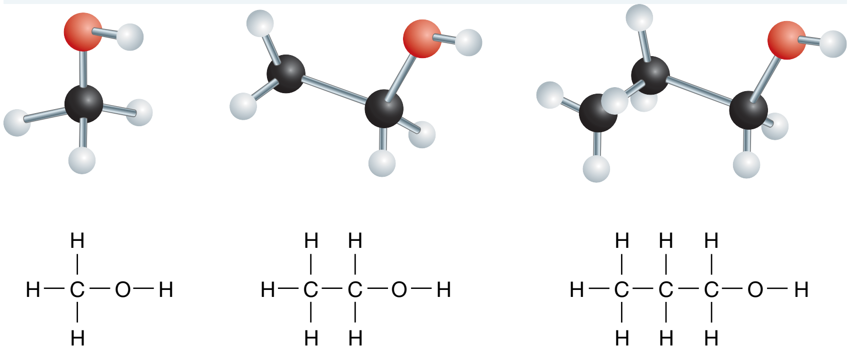


FIGURE 8.23 Butan- 2-ol

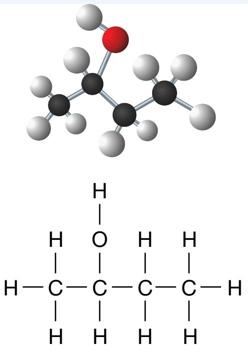


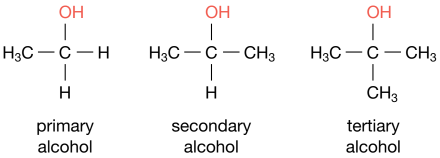
TABLE 8.5 The first eight alkanols. The —OH group is attached to the first carbon atom in each case.

Systematic name	Semi-structural formula
Methanol	CH_3OH
Ethanol	CH_3CH_2OH
Propan-1-ol	$CH_3(CH_2)_2OH$
Butan-1-ol	$CH_3(CH_2)_3OH$
Pentan-1-ol	$CH_3(CH_2)_4OH$
Hexan-1-ol	$CH_3(CH_2)_5OH$
Heptan-1-ol	$CH_3(CH_2)_6OH$
Octan-1-ol	$CH_3(CH_2)_7OH$

Alcohols are classified as primary, secondary or tertiary, based on the number of carbon atoms connected to the carbon atom attached to the hydroxyl functional group.

- Primary (1°) alcohol: The C—OH is attached to one other carbon atom.
- Secondary (2°) alcohol: The C—OH is attached to two other carbon atoms.
- Tertiary (3°) alcohol: The C—OH is attached to three other carbon atoms.

FIGURE 8.24 Primary, secondary and tertiary alcohols



Alcohols are hydrocarbons with the —OH functional group. They have the general formula R—OH.

- **Primary (1°) alcohols have the C—H group attached to one other C atom.**
- **Secondary (2°) alcohols have the C—H group attached to two other C atoms.**
- **Teritary (3°) alcohols have the C—H group attached to three other C atoms.**

on Resources

Video eLesson Molecular representations of butan-1-ol (eles-2485)

8.3.6 Aldehydes

The aldehyde functional group —CHO produces compounds that have characteristic odours. The familiar smells of vanilla and cinnamon are caused by aldehydes. Low-molecular-weight aldehydes, such as methanal (formaldehyde) and ethanal, have unpleasant odours; formaldehyde was previously used as a preservative but is now suspected to be carcinogenic. High-molecular-weight compounds have sweet, pleasant smells and are used in perfumes. Other uses of aldehydes include solvents and the manufacture of plastics, dyes and pharmaceuticals.

Aldehydes are generally written as **R—CHO** and are named by replacing the last *–e* on the name of the corresponding alkane with *–al*. For example, propane becomes propanal. Aldehydes have a C=O bond at the end of the carbon chain, at C1. Aldehydes are always named from C1, so they do not need a number in the name to reference where the functional group is.

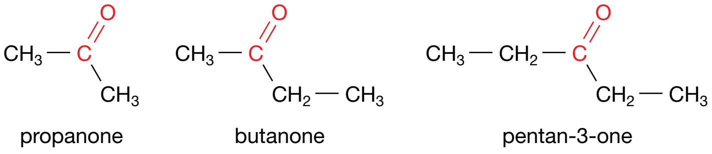
FIGURE 8.25 $C_7H_{15}CHO$ is added to fragrances to provide hints of citrus

Aldehydes are hydrocarbons with the —CHO functional group, with a C=O double bond at C1. They have the general formula R—CHO.

8.3.7 Ketones

Ketones contain the carbonyl (C=O) functional group and are used extensively to produce pharmaceuticals, perfumes, solvents and polymers. The '*–e*' is replaced by '*–one*' and the general formula of a ketone is **R—CO—R'**. Hence, the carbonyl functional group is never found at C1. They have important physiological properties and are found in medicinal compounds and steroid hormones, including cortisone. The most familiar ketone is propanone (acetone), which has unlimited solubility in water and is a solvent for many organic compounds. It evaporates readily because of its low boiling point, which contributes to its usefulness.

FIGURE 8.26 Propanone, butanone and pentan-3-one



Ketones are hydrocarbons with the carbonyl, C=O, functional group. They have the general formula R–CO–R'.

8.3.8 Carboxylic acids

The carboxyl functional group –COOH is part of the homologous series classed as carboxylic acids. They are generally written as **R–COOH** and the C in the carboxyl functional group is always assigned C1 for naming purposes. Because of this, the *1-* is left off the start of the names. The '*–e*' in the name is replaced by the suffix '*-oic acid*'.

Carboxylic acids are generally weak acids and occur widely in nature. Some common examples include citric acid, which is found in citrus fruits such as oranges and lemons, malic acid, found in apples, and ascorbic acid (vitamin C), found in a number of foods. Other carboxylic acids, such as stearic acid and oleic and palmitic acids, are used in the formation of animal and vegetable fats. Carboxylic acids are also used to make soaps and polyesters. The carboxylic acids with chains of four to eight carbons have a strong, unpleasant smell and are found in cheese, perspiration and rancid butter.

Carboxylic acids are hydrocarbons with the carboxyl, –COOH, functional group. They have the general formula R–COOH. The C in the carboxyl functional group is always assigned C1.

FIGURE 8.27 Different structural formulas of butanoic acid, $CH_3CH_2CH_2COOH$

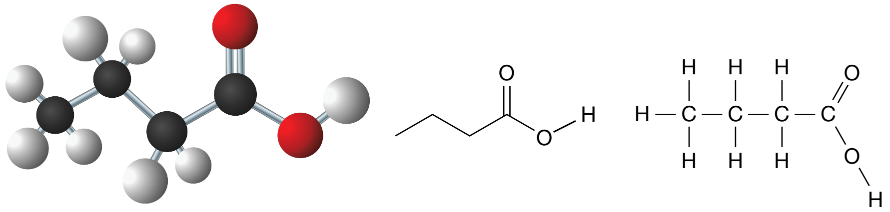


TABLE 8.6 Some carboxylic acids and their uses

Systematic name	Semi-structural formula	Non-systematic name	Occurrence and uses
Methanoic acid	HCOOH	Formic acid	Used by ants as a defence mechanism; also used in textile processing and as a grain preservative
Ethanoic acid	CH_3COOH	Acetic acid	Found in vinegar; used in making artificial textiles
Propanoic acid	CH_3CH_2COOH	Propionic acid	Calcium propanoate used as an additive in bread manufacture

(continued)

TABLE 8.6 Some carboxylic acids and their uses *(continued)*

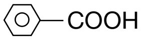
Systematic name	Semi-structural formula	Non-systematic name	Occurrence and uses
Butanoic acid	$CH_3CH_2CH_2COOH$	Butyric acid	Present in human sweat; responsible for the smell of rancid butter
Benzoic acid		Benzoic acid	Used as a preservative

FIGURE 8.28 Dogs can be trained to find fruit by sniffing out distinctive carboxylic acids, such as malic acid, which is found in apples. Sniffer dogs play an important part in quarantine procedures to prevent the illegal import and export of fruit.

on Resources

Interactivity Matching carboxylic acids and formula (int-1232)

8.3.9 Amines and amides

Primary amines (**R—NH$_2$**) and amides (**R—CONH$_2$**) contain the amino $-NH_2$ and amide $-CON$ functional groups. However, primary amides can be thought of as $-CONH_2$. With amines, the '*–e*' in the name is replaced by '*-amine*' and this suffix follows a number for C3 and up. Primary amides are named the same way as carboxylic acids except they have the suffix '*-amide*'.

FIGURE 8.29 (a) Butan-1-amine and (b) butanamide

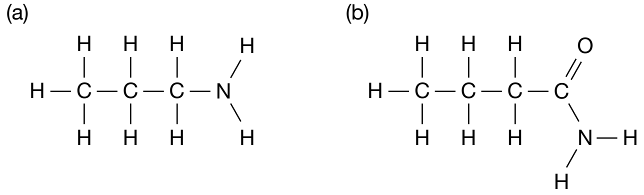


TABLE 8.7 The first eight compounds of the amine homologous series

Systematic name	Semi-structural formula
Methanamine	CH_3NH_2
Ethanamine	$CH_3CH_2NH_2$
Propan-1-amine	$CH_3(CH_2)_2NH_2$
Butan-1-amine	$CH_3(CH_2)_3NH_2$
Pentan-1-amine	$CH_3(CH_2)_4NH_2$
Hexan-1-amine	$CH_3(CH_2)_5NH_2$
Heptan-1-amine	$CH_3(CH_2)_6NH_2$
Octan-1-amine	$CH_3(CH_2)_7NH_2$

FIGURE 8.30 Wing suits are made from polymers containing amide links.

Amines are hydrocarbons with the amino, $-NH_2$, functional group. They have the general formula $R-NH_2$.
Amides are hydrocarbons with the amide, $-CON$ (or $-CONH_2$) functional group. They have the general formula $R-CONH_2$.

8.3.10 Esters

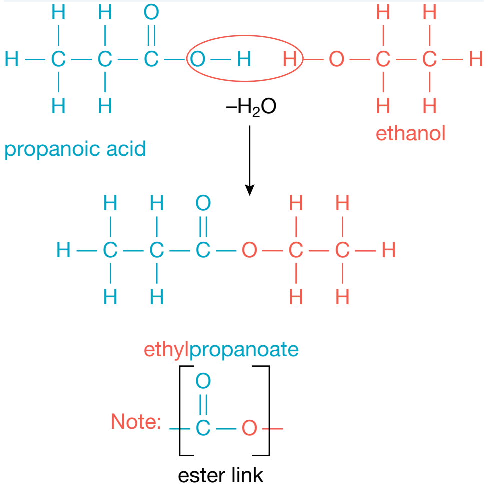
The ester functional group ($-COO$), also referred to as an ester link, forms via a condensation reaction between hydroxyl and carboxyl functional groups. Esters have the general formula **RCOOR'**.

The name of an unbranched ester is a product of the carboxylic acid and primary alcohol that produces it. The first part of the name comes from the hydrocarbon or alkyl part of the alcohol. For example, if methanol is used to make an ester the first part of the name will be methyl, and if ethanol is used, the first part of the name is ethyl.

The second part of the ester name comes from the carboxylic acid. The '*-oic acid*' suffix is removed and replaced with '*-oate*'. If methanoic acid was used to make an ester, the second part of the name would be methanoate.

Figure 8.31 shows propanoic acid and ethanol being used to make ethylpropanoate.

FIGURE 8.31 Formation of ethylpropanoate from propanoic acid and ethanol



This reaction can be summarised as:

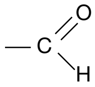
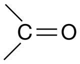
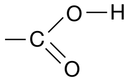
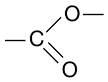
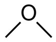
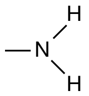
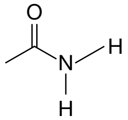
$$\begin{array}{ccccccc} CH_3CH_2COOH & + & CH_3CH_2OH & \rightleftharpoons & CH_3CH_2COOCH_2CH_3 & + & H_2O \\ \text{propanoic acid} & + & \text{ethanol} & \rightleftharpoons & \text{ethyl propanoate} & + & \text{water} \end{array}$$

Esters are used in a variety of applications. The small, volatile esters are used in artificial flavours and smells in food and fragrances. Larger esters occur naturally as fats and oils. They can also be used in the manufacture of materials as diverse as Perspex and artificial arteries used in open heart surgery.

Esters are hydrocarbons with the ester $-COO$, functional group. They have the general formula RCOOR’.
Esters form through condensation reactions between a primary alcohol and a carboxylic acid. The alcohol gives the first part of the name, the carboxylic acid gives the second half of the name, with the suffix ‘-oate’.

8.3.11 Functional group summary

TABLE 8.8 Functional group summary

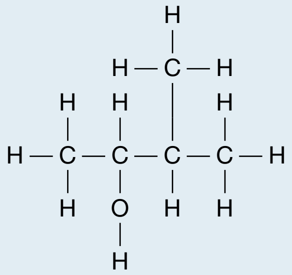
Group				
Formula	**Name**	**Homologous series**	**Method of naming**	**Example**
$-O-H$	hydroxyl	alcohol	suffix -*ol*	$CH_3CH_2CH_2OH$ propan-1-ol (1-propanol)
	aldehyde	aldehyde	suffix -*al*	CH_3CHO ethanal (acetaldehyde)
	carbonyl	ketone	suffix -*one*	$CH_3CH_2COCH_2CH_3$ pentan-3-one (3-pentanone)
	carboxyl	carboxylic acid	suffix -*oic acid*	CH_3COOH ethanoic acid (acetic acid)
	ester	ester	as alkyl alkanoate	$CH_3CH_2COOCH_3$ methyl propanoate
	ether	ether	as alkoxyalkane, or name the two groups attached to the ether linkage	CH_3OCH_3 methoxymethane or dimethyl ether
	amine	amine	suffix -*amine*	CH_3NH_2 methanamine $CH_3CH_2NH_2$ ethanamine
	primary amide	primary amide	suffix -*amide*	CH_3CONH_2 ethanamide $CH_3CH_2CONH_2$ propanamide
$-Cl$ $-Br$ $-I$	chloro bromo iodo	haloalkanes	prefix *chloro-* prefix *bromo-* prefix *iodo-*	CH_3Cl chloromethane CH_3CH_2Br bromoethane ICH_2CH_2I 1,2-diiodoethane

SAMPLE PROBLEM 4

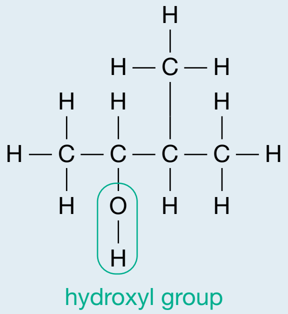
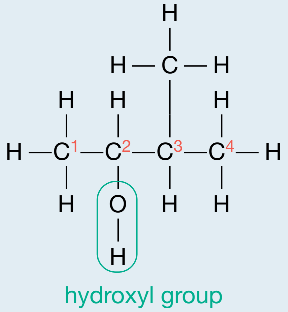
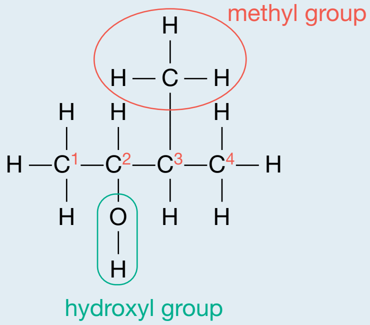
For the following molecule:

a. Name the functional group and the homologous series

b. Write its systematic (IUPAC) name.



Teacher-led video: SP4 (tlvd-0705)

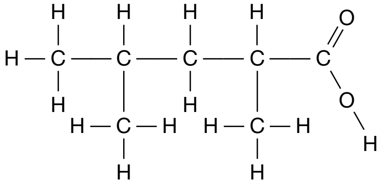
THINK	WRITE
a. Find groups of atoms that are not alkyl groups. Remember, alkyl groups are hydrocarbon branches coming off the longest carbon chain of an organic molecule. The functional group is the hydroxyl group in the alcohol homologous series. The name will end in '*-ol*'.	
b. 1. The longest chain is composed of 4 carbons, making the molecule butanol. Number the chain so that the functional group has the lowest number possible. The hydroxyl group is branching from C2.	
2. Identify any alkyl groups branching off the longest carbon chain. Methyl is branching from C3.	
3. Name the molecule.	3-methylbutan-2-ol

PRACTICE PROBLEM 4

For the following molecule:

a. Name the functional group and the homologous series

b. Write its systematic (IUPAC) name.



on Resources

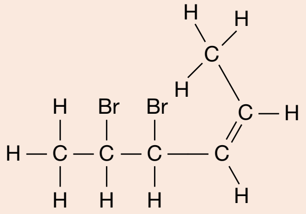
Interactivity Organic molecule structures (int-1234)

Digital document Experiment 8.2 Constructing models of organic compounds (doc-31267)

8.3 EXERCISE

To answer questions online and to receive **immediate feedback** and **sample responses** for every question go to your learnON title at www.jacplus.com.au.

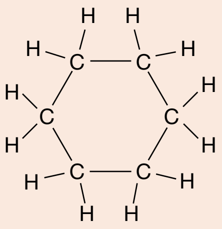
1. What is the molecular formula of the alkane containing 18 carbon atoms?
2. Show the molecular, empirical, semi-structural and skeletal formulas and structures of propane.
3. Study the following molecule.



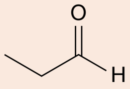
   (a) Write its systematic (IUPAC) name.
   (b) Write its semi-structural formula.
   (c) Write its molecular formula.
   (d) Write its empirical formula.
4. Draw structural, semi-structural and skeletal diagrams for 2-methylpropan-1-ol.
5. Draw the structures of butanoic acid and octanoic acid.
6. What are the systematic names of the following molecules?

   (a) $CH_3CH(NH_2)C(CH_3)_2CH_2CH_3$

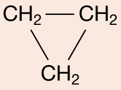
   (b)



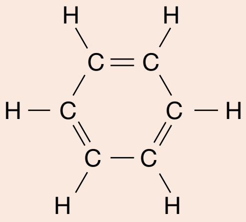
   (c)



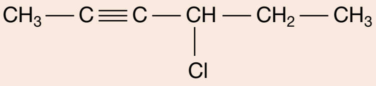
   (d)



   (e)

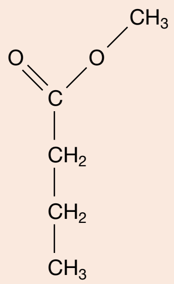


   (f)

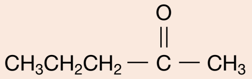


$CH_3-C\equiv C-\underset{\displaystyle Cl}{\underset{|}{CH}}-CH_2-CH_3$

(g)

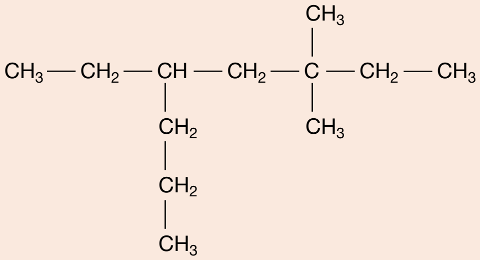


7. Which homologous series does this molecule belong to?



$CH_3CH_2CH_2-\overset{\overset{O}{\|}}{C}-CH_3$

8. Draw the structure of the primary amide with the molecular formula C_3H_7NO.
9. Draw structural, semi-structural and skeletal diagrams for:
   (a) ethylpropanoate
   (b) propylethanoate.
10. Consider the hydrocarbon shown.



$CH_3-CH_2-\underset{\substack{|\\CH_2\\|\\CH_2\\|\\CH_3}}{CH}-CH_2-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_2-CH_3$

   (a) Name the alkyl groups present.
   (b) Write the systematic name.

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8.4 Functional groups and naming priority

KEY CONCEPT

- IUPAC systematic naming of organic compounds up to C8 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.

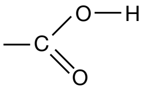
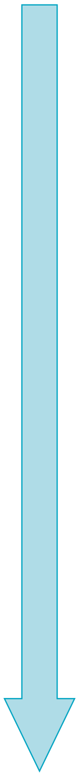
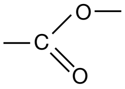
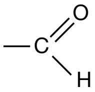
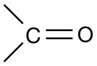
8.4.1 Naming compounds with two functional groups

When molecules have two or more functional groups, the naming becomes more complex. A lot of the molecules with many functional groups are referred to by their commercial or simplified names. Pharmaceuticals are typically branded or referred to using non-preferred IUPAC names.

IUPAC naming of compounds with two functional groups

Compounds with two or more functional groups are classified by the principal group (the main functional group) defining the series to which they belong. Table 8.9 shows the priority scale for the groups.

TABLE 8.9 Functional group priority scale

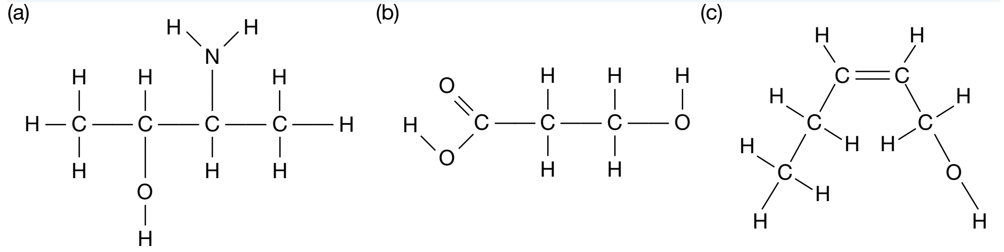
Group	Homologous series	Suffix	
carboxyl 	carboxylic acid	*-oic acid*	Highest priority name 
ester 	ester	*-oate*	
aldehyde 	aldehyde	*-al*	
carbonyl 	ketone	*-one*	
hydroxyl −O−H	alcohol	*-ol*	
amine $R{-}NH_2$	amine	*-amine*	
alkyne and alkene C≡C C=C	alkyne and alkene	*-yne -ene*	
alkane C−C	alkane	*-ane*	Lowest priority name

The parent name of the compound is derived from the principal group according to the following rules.

- The numbering system used is that of the principal group.
- An alcohol is regarded as a hydroxyl side group, an amine is regarded as an amino side group and a ketone is regarded as a carbonyl side group.
- A compound containing both alcohol and aldehyde functional groups is named as an aldehyde with a hydroxyl side group.
- A compound containing an alcohol, a ketone and an acid is named as an acid with hydroxyl and carbonyl side groups.

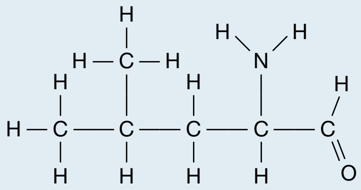
Some examples are listed below.

FIGURE 8.32 (a) 3-aminobutan-2-ol, (b) 3-hydroxypropanoic acid and (c) pent-2-en-1-ol

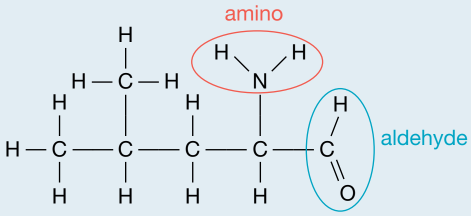
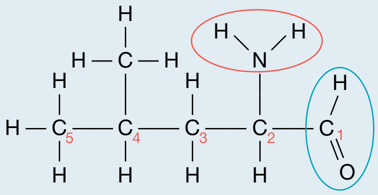
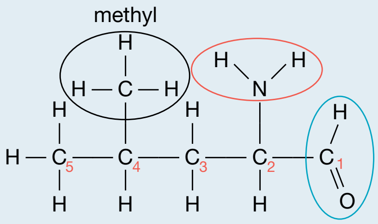


SAMPLE PROBLEM 5

Name the following organic compound.

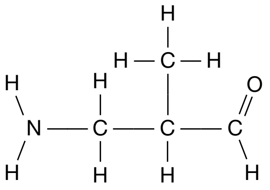


Teacher-led video: SP5 (tlvd-0706)

THINK	WRITE
1. Identify the functional groups on the molecule and assign priority. Aldehyde functional group takes priority over amino functional group. The name will end in '-*al*'.	
2. The longest chain is composed of five carbons, making the molecule pentanal. Number the carbon chain with the lowest number for the priority functional group, aldehyde. Determine the branch position of the second functional group, amino. Amino is branching at C2.	
3. Identify any alkyl groups branching off the longest carbon chain. Methyl is branching from C4.	
4. Write the name with substituents in alphabetical order.	2-amino-4-methylpentanal

PRACTICE PROBLEM 5

Name the following organic compound.



8.4 EXERCISE

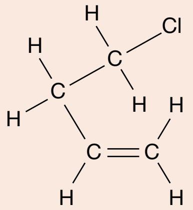
To answer questions online and to receive **immediate feedback** and **sample responses** for every question go to your learnON title at www.jacplus.com.au.

1. Complete the following table.

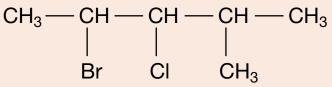
Functional group	Name	Priority	Homologous series
	Carboxyl	1	
			Ketones
NH_2		6	
	Hydroxyl		
COO			

2. Write the semi-structural formula for 4-aminopentan-1-ol.
3. (a) Name the following molecules.
   (b) Draw semi-structures for the molecules.
   (c) Draw skeletal structures for the molecules.

i.

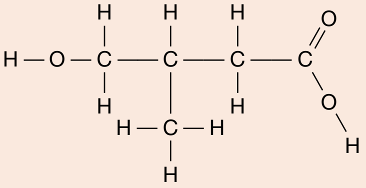


ii.

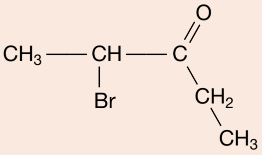


$$CH_3-\underset{\underset{Br}{|}}{CH}-\underset{\underset{Cl}{|}}{CH}-\underset{\underset{CH_3}{|}}{CH}-CH_3$$

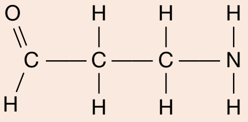
iii.



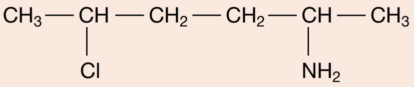
iv.



v.



4. A student named the molecule below 5-amino-2-chlorohexane. Is this name correct? Explain your answer.



$$CH_3-\underset{\underset{Cl}{|}}{CH}-CH_2-CH_2-\underset{\underset{NH_2}{|}}{CH}-CH_3$$

5. Draw the skeletal structure of but-3-en-1-ol.
6. Draw the structure and semi-structure of a four-carbon amide with 2,3-dihydroxy groups.

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8.5 Isomers

KEY CONCEPT

- 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

8.5.1 Introduction to isomers

Another reason for the enormous number of organic compounds is the existence of isomers. These are two or more compounds with the same molecular formula but different arrangements of atoms. The effect on the properties of the substances depends on the type of isomerism present. If the atoms are arranged in different orders, they are **structural isomers**. If the atoms are connected in the same order but are oriented differently in space, they are **stereoisomers**. In many cases, three-dimensional space diagrams (using wedges and dashes) are used to show the different positions.

on Resources

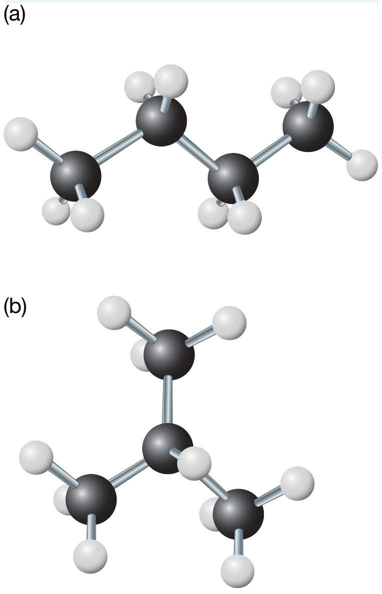
Video eLesson Isomers (eles-2478)

8.5.2 Structural (constitutional) isomers

Structural isomers are those where the connectivity (or arrangement) of atoms or groups of atoms are different. For the first three alkanes (methane, ethane and propane) there is only one way of arranging the atoms and that is the *straight-chain* arrangement. In butane, there ther are two ways of arranging the carbon and hydrogen atoms, therefore, there are two structures. One is the straight-chain structure and the other is the *branched-chain* structure.

Each of the two structures of butane satisfies the valence of carbon and hydrogen atoms, and each is a neutral and stable molecule (see figure 8.33). Their chemical and physical properties are similar but not identical. For instance, straight-chain butane has a boiling point of –1 °C, while the branched chain molecule, 2-methylpropane, has a boiling point of –12 °C. Butane and 2-methylpropane are called structural isomers because they have the same molecular formula but different arrangements of atoms.

FIGURE 8.33 Structural isomer models of (a) butane and (b) 2-methylpropane



Three types of structural isomers are chain, positional and functional isomers. An easy way of determining structural isomers is to go through the systematic naming process. A different name means a different structure.

Chain isomers

Chain isomers are structures that are different because of the size of the parent chain and the alkyl branches, if any, attached. Butane and 2-methylproane (methylpropane) are examples of chain isomers.

The number of possible ways of combining the atoms to form chain isomers increases with the number of carbon atoms in the molecule. Pentane, C_5H_{12}, has three isomers, and heptane, C_7H_{16}, has nine, while decane, $C_{10}H_{22}$, has 75 isomers. For $C_{15}H_{32}$, there are 4347 possible isomers and for $C_{40}H_{82}$, there are more than 6×10^{13} possible isomers. Isomerism is responsible for the enormous number of organic compounds that are known.

Positional isomers

Isomers where the functional group is located on different carbon atoms in the structure are called **positional isomers**. Propan-1-ol and propan-2-ol are examples.

SAMPLE PROBLEM 6

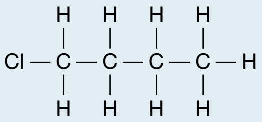
Draw and name all structural isomers of C_4H_9Cl.

Teacher-led video: SP6 (tlvd-0707)

THINK

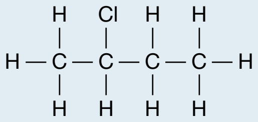
1. This is a haloalkane, so the easiest place to start is to draw the straight-chain and put the chlorine atom on C1 and name it.

WRITE



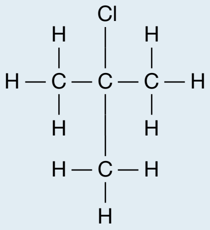
1-chlorobutane

2. Change the position of the Cl atom to make a different structure with a different name.
   TIP: There is no 3-chlorobutane or 4-chlorobutane because when they are flipped over they are actually just 1-chlorobutane and 2-chlorobutane.



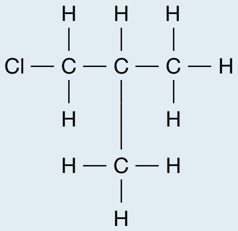
2-chlorobutane

3. Move the $-CH_3$ group to make it a methyl group and have the Cl branch off the same carbon. Make sure it has a different name in case you have drawn the same structure but a different way.



2-chloro-2-methylpropane

4. Make the last change possible by moving the chlorine back to C1 of the methylpropane.



1-chloro-2-methylpropane

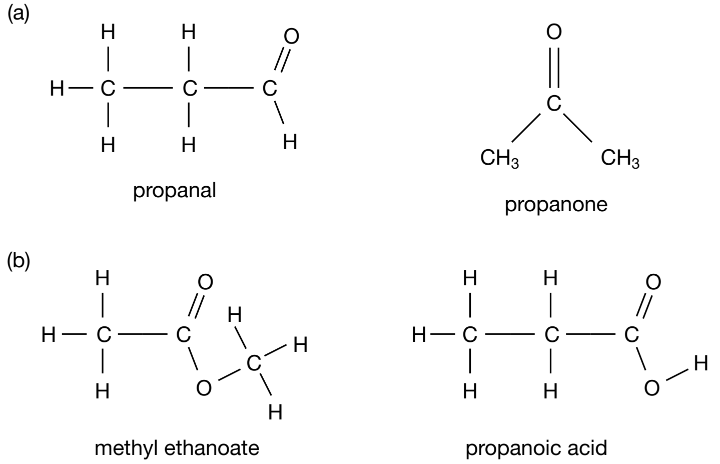
PRACTICE PROBLEM 6

Draw and name all structural isomers of C_4H_9OH with one hydroxyl functional group.

Functional isomers

If isomers have **functional isomerism** they have the same molecular formula but different functional groups in their structures. Figure 8.34 is an example.

FIGURE 8.34 Functional isomers of (a) C_3H_6O: propanone and propanal, and (b) $C_3H_6O_2$: methyl ethanoate and propanoic acid



propanal

propanone

methyl ethanoate

propanoic acid

Resources

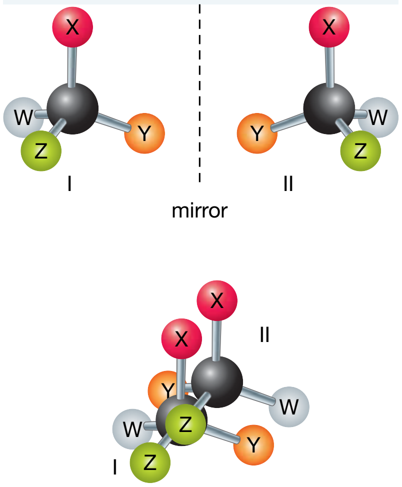
Interactivity Identifying structural isomers (int-1233)

8.5.3 Stereoisomers

Stereoisomers have the same type and order of connected atoms but a different three dimensional orientation or arrangement in space.

Enantiomers

FIGURE 8.35 Chiral objects are non-superimposable mirror images of each other.



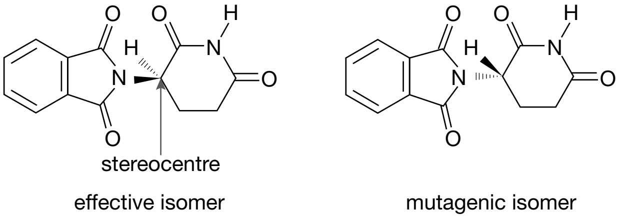
For a carbon atom to be able to form **enantiomers**, it must have four different atoms, or groups of atoms, bonded to it. Carbon atoms that meet this criteria are called **chiral** or have **chiral centres**.

Figure 8.35 shows a pair of enantiomers (I and II) with atoms bonded in a tetrahedral arrangement to the chiral carbon. They might look the same initially with the same atoms all connected to the same carbon atom, but W and Y have swapped places. They are reflections of each other. We can tell they are arranged differently in space because we cannot place or rotate them so that they sit exactly on top of one another. That is, the reflections cannot be superimposed. The only way we could make the two molecules exactly the same is if we pulled the ball and stick models apart and re-positioned the atoms.

Enantiomers are also called **optical isomers**. 'Optical' isomers cause (plane-polarised) light to be rotated in opposite directions once it has passed through a sample of each. When optically active substances are synthesised in the laboratory, they are often a 50:50 mixture of the two enantiomers. This is known as a **racemic mixture** or **racemate**.

A racemic mixture does not affect plane-polarised light and stereoisomers formed in biological systems consist of the one enantiomer. As a result of this, many of the natural and synthetic drugs used in medicine have different effects on the body. This is because the enantiomer in the body has a unique three-dimensional shape so the drug that interacts (binds) with it must have a matching three-dimensional shape. With 50:50 mixes of enantiomers produced when making medicines, synthetic chemists are looking to develop pathways that only produce the medicinal enantiomer. Different effects on the body can mean the medicines don't work as well, or at all. Worse, some medicines can produce beneficial and harmful enantiomers. For example, between 1957 and 1962, the drug thalidomide was used to treat morning sickness in pregnant women. More than 10 000 babies were born with birth defects as a result of using this drug. Eventually, investigations found that thalidomide was a racemic mix of two enantiomers due to the presence of one chiral carbon atom. While one enantiomer did indeed cure morning sickness, the other enantiomer caused deformities in organs and limbs.

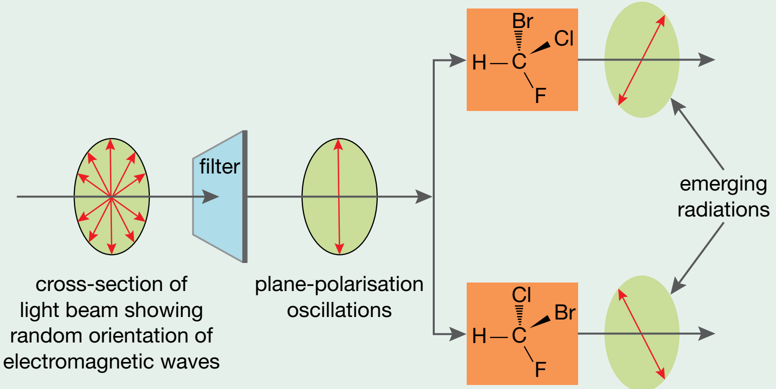
FIGURE 8.36 Enantomers of thalidomide



USING POLARISED LIGHT TO DISTINGUISH OPTICAL ISOMERS

Normally, a light wave is made up of a mixture of waves vibrating in every direction perpendicular to its direction of movement. Unpolarised light can be converted into a single polarised beam by passing it through a polarising filter. Sunglasses use a polarising filter to limit glare. Optically active molecules can rotate the plane of polarisation of plane-polarised light. An instrument called a polarimeter can be used to analyse this rotation. If it is rotated clockwise it is the (+) enantiomer; if it is rotated anticlockwise, it is the (–) enantiomer.

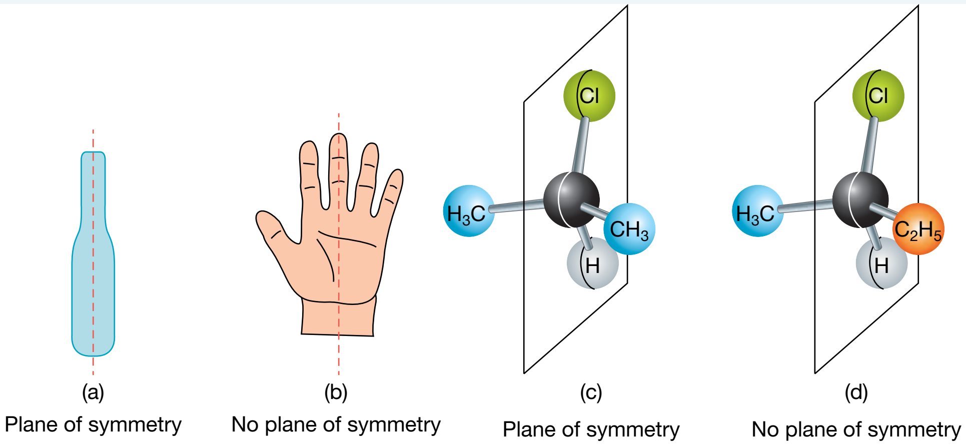
FIGURE 8.37 A polarimeter is used to distinguish between optical isomers.



Identifying chiral centres

We often use our hands, feet or household objects to demonstrate the difference between symmetrical and asymmetrical (not symmetrical) objects. Symmetry is observed when a line cuts through an object and one half is the mirror image of the other half, and this can be extended to organic molecules. Organic molecules with a plane of symmetry are achiral (not chiral), whereas asymmetrical molecules will have chiral carbons and form enantiomers.

FIGURE 8.38 Chirality is determined by the presence of a plane of symmetry: (a) A bottle has a plane of symmetry but (b) a hand does not have a plane of symmetry. (c) The 2-chloropropane molecule is achiral because it has a plane of symmetry but (d) the 2-chlorobutane molecule does not have a plane of symmetry and so is chiral.

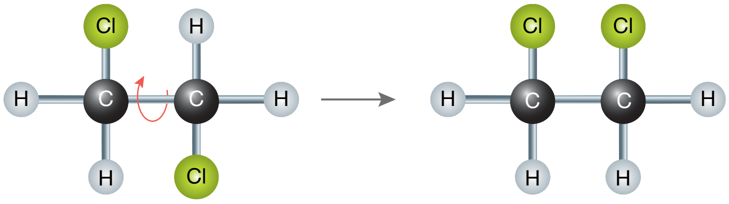


Geometric (*cis–trans*) isomers

Geometric isomers exist in compounds with C=C bonds. Unlike C—C single bonds, carbon to carbon double bonds do not rotate, so they can produce structures where the same type of atoms (substituents), or groups, are bonded to each carbon on either the same side of the double bond or on opposite sides of the double bond. As an example, let's compare $C_2H_4Cl_2$ and $C_2H_2Cl_2$. The first compound has one C—C bond, which is able to rotate.

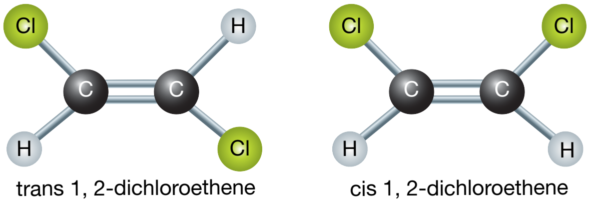
Although $C_2H_4Cl_2$ might look different initially, these molecules are the same due to the bond rotation. In other words, the C—C bond can be rotated to produce the same molecule.

FIGURE 8.39 The single bond between carbons is able to rotate, meaning these molecules are not isomers.



The second compound, $C_2H_2Cl_2$, with its restricted C=C bond will produce different geometric isomers. When the substituents (Cl atoms) are on the same side the molecule has a **cis** geometry but the molecule with the substituents on opposite sides has **trans** geometry.

FIGURE 8.40 The double bond between carbons is not able to rotate, meaning these molecules are isomers.



SAMPLE PROBLEM 7

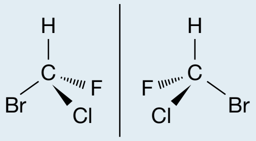
Which of the following organic molecules would produce two enantiomers?

a. CH_4 **b.** CH_2Cl_2 **c.** $CHBrF_2$ **d.** $CHBrClF$

Teacher-led video: SP7 (tlvd-0708)

THINK	WRITE
1. A carbon atom must have four different atoms or groups of atoms to be classified as chiral and produce enantiomers.	
a. CH_4 has four atoms of the same type attached to a carbon atom.	CH_4 does not have a chiral centre and will not produce enantiomers
b. CH_2Cl_2 has two sets of two atoms of the same type attached to a carbon atom. This will produce molecules that are symmetrical. Therefore, it is achiral.	CH_2Cl_2 does not have a chiral centre and will not produce enantiomers.
c. $CHBrF_2$ has one set of two atoms of the same type attached to a carbon atom. This will produce molecules that are symmetrical. Therefore, it is achiral.	$CHBrF_2$ does not have a chiral centre and will not produce enantiomers.

d. CHBrClF has four different atoms attached and therefore has a chiral centre. It will produce two enantiomers; that is, mirror images of each other that are not superimposable.



PRACTICE PROBLEM 7

Which of the following would produce two enantiomers?

A. CH_2ClF

B. CH_3CHBrF

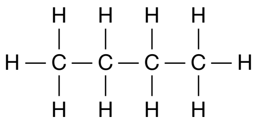
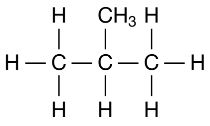
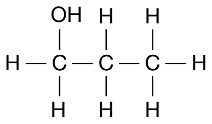
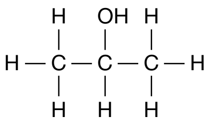
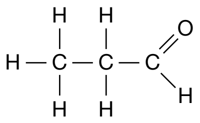
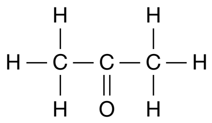
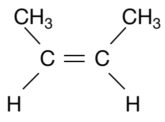
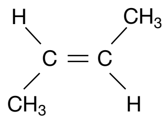
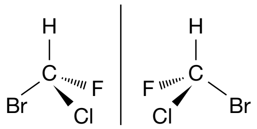
C. $(CH_3)_2CHF$

D. $CHBr_2F$

8.5.4 Isomer summary

Table 8.10 summaries the different types of isomers.

TABLE 8.10 Types of isomers

Isomer	Example
Structural isomers	
Chain isomers: different branching in carbon chain	 butane  methylpropane
Positional isomers: different positions of the functional group, which is usually indicated by a number in the name	 propan-1-ol  propan-2-ol
Functional isomers: same atoms but different functional groups	 propanal  propanone (acetone)
Stereoisomers	
Geometric *(cis* and *trans)* isomers: different arrangements of atoms around a double bond or in a ring, which restricts rotation. If the groups on each carbon atom are on the same side of the molecule, that molecule is the *cis* isomer. If they are on opposite sites, it is the *trans* isomer.	 *cis*-but-2-ene  *trans*-but-2-ene
Enantiomers or optical isomers: non-superimposable reflections containing an asymmetric carbon atom. These molecules are referred to as chiral.	

on Resources

Digital documents Experiment 8.3 Constructing models of structural isomers (doc-31268)

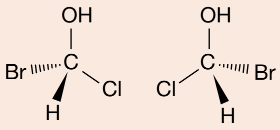
Experiment 8.4 Investigating optical isomers (doc-31269)

Teacher-led video Experiment 8.3 Constructing models of structural isomers (tlvd-0754)

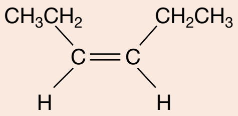
8.5 EXERCISE

To answer questions online and to receive **immediate feedback** and **sample responses** for every question go to your learnON title at www.jacplus.com.au.

1. What is the difference between chiral and achiral carbon atoms?
2. Why are enantiomers called optical isomers?
3. What is the difference between a stereoisomer and a structural isomer?
4. Draw the enantiomers of CH_3CHBrF.
5. Draw all isomers of C_4H_{10}.
6. Describe the type of isomerism that exists in the following two molecules.



7. Draw the structure of a functional group isomer of ethanol, C_2H_5OH.
8. Name this geometric stereoisomer.



9. Draw skeletal structures and give systematic names for the *cis* and *trans* isomers of C_5H_{10}.
10. Draw and give systematic names to all structural isomers with the molecular formula C_4H_8O that contain the carbonyl functional group.

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To answer past VCAA exam questions online and to receive immediate feedback and sample responses for every question go to your learnON title at www.jacplus.com.au.

studyON: Past VCAA exam questions online only

Fully worked solutions and sample responses are available in your digital formats.

8.6 Review

8.6.1 Summary

The carbon atom

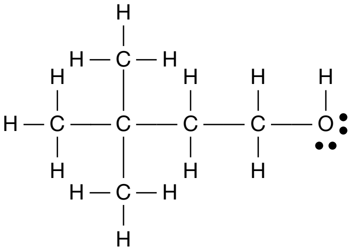
- Organic chemistry is the study of the compounds of carbon. This does not include the inorganic compounds of cyanides, carbonates and oxides of carbon.
- Historically, organic compounds were associated with living things, but these days chemists can manufacture organic compounds for a variety of uses.
- Carbon can form many different compounds due to its ability to create four covalent bonds with itself or other elements.
- The electron configuration of carbon is 2,4. Therefore, it has a valence number of four.

- In the methane molecule, a carbon atom can form covalent bonds with four other atoms. The resulting shape is tetrahedral, resulting in bond angles of 109.5°.
- Bond angle and bond length determine the strength of carbon covalent bonds. Bond strength in measured in kJ mol^{-1}.
- C≡C are stronger than C=C, which are stronger than C—C bonds.

Structure and naming of organic compounds

- Molecular modelling is used to show the structure of molecules.
- Molecular representations include:

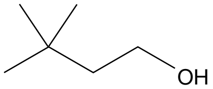
  Structures:



  Semi structures:

  $CH_3C(CH_3)_2(CH_2)_2OH$

  Skeletal structures:



- A homologous series is a group of organic chemical compounds that have a similar structure and whose structures differ only by the number of CH_2 units in the main carbon chain. They are compounds containing the same functional group and have similar properties.
- The alkanes, alkenes and alkynes are hydrocarbons and form homologous series with general formulas of C_nH_{2n+2}, C_nH_{2n} and C_nH_{2n-2}, respectively.
- Saturated hydrocarbons have only single C—C covalent bonds.
- Alkanes are saturated hydrocarbons. Alkenes and alkynes are unsaturated hydrocarbons with double and triple carbon bonds, respectively.
- Haloakanes (R—X) are formed when halogens such as F, Cl, Br and I are substituted into hydrocarbon chains.
- Functional groups change the family of molecules or the type of homologous series. These include:
  - Alcohols (primary, secondary and tertiary) contain the hydroxyl (—OH) functional group. The suffix for alcohols on systematic names is '*–ol*'.
  - Aldehydes (R—CHO) and ketones (RCOR') contain the carbonyl (C=O) functional group. The suffixes for naming are '*–al*' and '*–one*' respectively.
  - Carboxylic acids contain the carboxyl (—COOH) functional groups.
  - Primary amines ($R-NH_2$) contain the amino functional groups while primary amide links have the general formula $R-CONH_2$.
  - Straight chain esters are made from carboxylic acids and primary alcohols. The ester (—COO) link gives esters the general formula RCOOR' where R—CO comes from the carboxylic acid and R'—O comes from the alcohol. The first part of the ester name comes from the alkyl (R') part of the alcohol (e.g. methyl, ethyl, propyl, etc). The second part of the ester name comes from the number of carbons in the RCOOH. The suffix '*–oic acid*'' becomes '*–oate*' (e.g. methanoate, ethanoate, propanoate).
- Rules for naming organic compounds:
  - Identify and name the longest unbranched carbon chain containing the principal functional group. (It is helpful to highlight this chain.)

  - Number the carbon atoms in the longest unbranched chain, starting with the carbon atom nearest the functional group or branch (if an alkane).
  - Identify the branching group(s) of atoms and state the number of the carbon atom to which it is attached. Branches are named using *–yl*. For example, a branched group of $-$CH3 would be named methyl, CH_3CH_2- would be ethyl, and $CH_3CH_3CH_2-$ would be propyl. These go before the name of the longest chain.
  - For molecules with two or more branches of the same type, the branch type is named and a prefix (*di–*, *tri–*, *tetra–*, etc) is used to indicate the number of branches.
  - Branches are listed in alphabetical order, ignoring the prefix in the previous rule. Ethyl is written before methyl or dimethyl. Note that adjacent numbers in a name are separated by a comma and numbers are separated from words by a hyphen.
  - If two or more side chains are in equivalent positions, assign the lowest number to the one that will come first in the name.

Functional groups and naming priority

- If more than one functional group is present, the order of decreasing priority in determining the suffix is carboxylic acid > ester > aldehyde > ketone > alcohol > amine > alkyne = alkene > alkane.

Isomers

- Isomers are compounds with the same molecular formula but different arrangements of atoms.
- In structural isomers, the atoms are arranged in different ways, which means that the chemical bonding is different. Structural isomers have different physical properties and, if different functional groups, chemical reactivities.
  - Chain isomers have different branching in the carbon chain.
  - Positional isomers show different positions of the particular functional group, which is usually indicated by a number in the name.
  - Functional isomers have the same atoms but different functional groups.
- Stereoisomers have the same sequence of bonded of atoms, but the spatial arrangement of atoms differs.
  - Geometric isomers can be either *cis* or *trans*. They are non-mirror-image molecules that have the same chemical bonding but different spatial arrangements of atoms. In restricted bonded compounds, *cis* isomers involve atoms or groups that are next to each other and *trans* isomers involved atoms or groups on opposite sides of the molecule.
  - Enantiomers (optical isomers) are mirror-image molecules that cannot be superimposed on each other. These molecules are described as chiral. Enantiomers have identical physical properties and their chemical properties are also generally the same (except interactions with other molecules with optical properties). A chiral molecule rotates the plane of polarised light passing through the solution. Optical isomers can have radically different biological effects.

Resources

To access key concept summaries and practice exam questions download and print the **studyON: Revision and practice exam question booklet** (doc-31414).

8.6.2 Key terms

alcohols organic hydroxyl compounds containing the –OH group
aliphatic describes organic compounds in which carbon atoms form open chains
alkanols alcohols containing only carbon, hydrogen and oxygen
alkenes the family of hydrocarbons that contain one carbon–carbon double bond
alkyl groups hydrocarbon branches joined to the parent hydrocarbon chain (e.g. CH_3 (methyl) CH_2CH_3 (ethyl))
alkynes the family of hydrocarbons with one carbon–carbon triple bond

allotropes different physical forms in which an element can exist
arenes aromatic, benzene-based hydrocarbons
aromatic describes a compound that contains at least one benzene ring and is characterised by the presence of alternating double bonds within the ring
benzene an aromatic hydrocarbon with the formula C_6H_6
bond length the distance between two nuclei involved in covalent bonding
chain isomers a type of structural isomer that involves more branching
chiral describes compounds containing an asymmetric carbon atom or chiral centre. The molecule cannot be superimposed upon its mirror image.
chiral centres asymmetric carbon atoms
cis–trans isomers types of stereoisomers that are formed when the same two different groups are bonded to each of the carbon atoms in a carbon–carbon double bond. A cis isomer has identical groups on the same side of the double bond; a trans isomer has the groups on opposite sides.
covalent bonds bonds involving the sharing of electron pairs between atoms
electron configuration the number of electrons and shells they occupy (e.g. 2,4 or $1s^2 2s^2 2p^2$)
enantiomers chiral molecules that are non-superimposable mirror images of one another
excited state when electrons moved to higher energy orbitals when energy is applied
functional group a group of atoms attached to or part of a hydrocardon chain that influence the physical and chemical properties of the molecule
functional isomerism isomers containing different functional groups
halogens elements in Group 17 of the periodic table: F, Cl, Br, I and At
homologous series a series of organic compounds that have the same structure but in which the formula of each molecule differs from the next by a CH_2 group
optical isomers see **enantiomers**
positional isomers isomers where the position of the functional group differentiates the compounds
racemate a 50:50 mixture of two enantiomers; often occurs when optically active substances are synthesised in the laboratory
racemic mixture see **racemate**
stereoisomers two or more compounds differing only in the spatial arrangements of their atoms
structural isomers molecules that have the same molecular formula but different structural formulas
unsaturated describes hydrocarbons containing at least one double carbon–carbon bond
valence number the number of electrons occupying the orbitals in the outermost electron shell

on Resources

Digital document Key terms glossary - Topic 8 (doc-31412)

8.6.3 Practical work and experiments

Experiment 8.3

Constructing models of structural isomers
Aim: To construct models of structural isomers
Digital document: doc-31268
Teacher-led video: tlvd-0754

on Resources

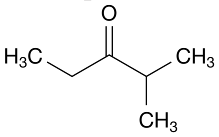
Digital documents Practical investigation logbook (doc-31413)
Experiment 8.1 Constructing models of hydrocarbons (doc-31266)
Experiment 8.2 Constructing models of organic compounds (doc-31267)
Experiment 8.4 Investigating optical isomers (doc-31269)

8.6 Exercises

To answer questions online and to receive **immediate feedback** and **sample responses** for every question go to your learnON title at www.jacplus.com.au.

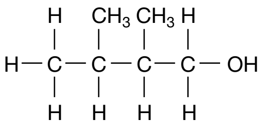
8.6 Exercise 1: Multiple choice questions

1. Which of the following does *not* apply to alkanes?
   - **A.** They have the general formula C_nH_{2n}.
   - **B.** They contain C and H.
   - **C.** Each has at least one C—C bond.
   - **D.** They are saturated hydrocarbons.
2. The functional groups and suffixes for naming alcohols and carboxylic acids respectively are:
   - **A.** —OH, —COOH, *-oate*, *-ol*
   - **B.** —COOH, —OH, *-ol*, *-oic*
   - **C.** —OH, —COOH, *-ol*, *-oic*
   - **D.** —OH, —COOH, *-ol*, *-oate*.
3. Cycloalkanes have the same molecular formula as:
   - **A.** alkanes
   - **B.** alkenes
   - **C.** alkynes
   - **D.** benzene.
4. In the IUPAC nomenclature system, the name of which of the following would end in *–al*?
   - **A.** An alcohol
   - **B.** An aldehyde
   - **C.** An alkane
   - **D.** A ketone.
5. This compound is:



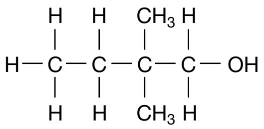
   - **A.** an ester
   - **B.** an aldehyde
   - **C.** a ketone
   - **D.** a carboxylic acid.
6. The structural arrangement of 2,2-dimethylbutan-1-ol is:

A.



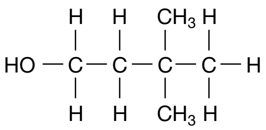
$$\begin{array}{ccccccccccc} & & H & & CH_3 & & CH_3 & & H & & \\ & & | & & | & & | & & | & & \\ H & - & C & - & C & - & C & - & C & - & OH \\ & & | & & | & & | & & | & & \\ & & H & & H & & H & & H & & \end{array}$$

B.



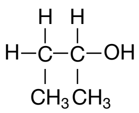
$$\begin{array}{ccccccccccc} & & H & & H & & CH_3 & & H & & \\ & & | & & | & & | & & | & & \\ H & - & C & - & C & - & C & - & C & - & OH \\ & & | & & | & & | & & | & & \\ & & H & & H & & CH_3 & & H & & \end{array}$$

C.



$$\begin{array}{ccccccccccc} & & H & & H & & CH_3 & & H & & \\ & & | & & | & & | & & | & & \\ HO & - & C & - & C & - & C & - & C & - & H \\ & & | & & | & & | & & | & & \\ & & H & & H & & CH_3 & & H & & \end{array}$$

D.

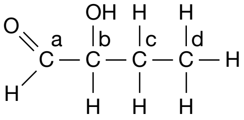


$$\begin{array}{ccccc} & & H & & H & & \\ & & | & & | & & \\ H & - & C & - & C & - & OH \\ & & | & & | & & \\ & & CH_3 & & CH_3 & & \end{array}$$

7. The IUPAC name for the compound $(CH_3)_2CHCH_2CH(NH_2)CH_3$ is:

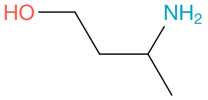
A. 2-methylpentanamine
B. 4-methylpentan-2-amine
C. 2-methyl-4-pentanamine
D. 4-methyl-2-pentanamine.

8. Identify the chiral carbon atom in the following molecule.



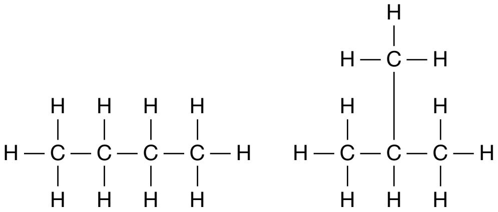
A. a
B. b
C. c
D. d

9. What is the IUPAC name of the following molecule?



A. 1-amino-2-methylbutan-4-ol
B. 2-aminobutan-4-ol
C. 4-amino-3-methylbutan-1-ol
D. 3-aminobutan-1-ol.

10. The following two molecules are best described as:



A. optical isomers
B. structural isomers
C. *cis–trans* isomers
D. stereoisomers.

8.6 Exercise 2: Short answer questions

1. Draw three-dimensional space (wedge–dash) diagrams for the following molecules.

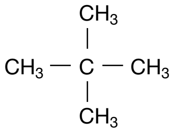
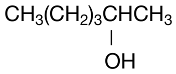
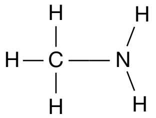
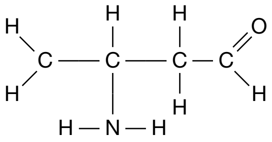
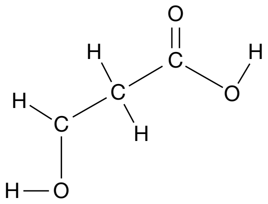
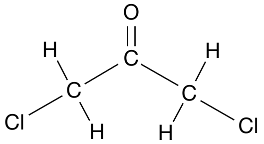
a. CH_4 **b.** C_2H_4 **c.** C_2H_2 **d.** C_2H_4ClF

2. Explain why carbon to carbon triple bonds are higher in energy than carbon to carbon double bonds.

3. Calculate the energy required to break all covalent bonds in 20.0 g of CCl_4. The C−Cl bond energy is 324 kJ mol^{-1}.

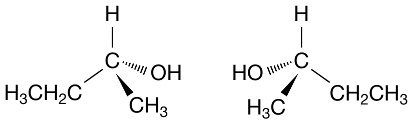
4. Define the following terms.

a. Hydrocarbon
b. Homologous series
c. Saturated hydrocarbon
d. Unsaturated hydrocarbon
e. Structural isomer

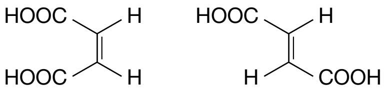
5. Define the terms ‘alkane’ and ‘alkene’ and describe their similarities and differences.
6. Name the following organic compounds.
   - a. $CH_3CH_2CH{=}CHCH_3$
   - b. $CH_2{=}CHCl$
   - c. CF_2Cl_2
   - d. CH_3CH_2OH
   - e. 
     $\mathrm{CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}-CH_3}$
   - f. 
     $\mathrm{CH_3(CH_2)_3\underset{\displaystyle OH}{CH}CH_3}$
   - g. $CHCl_2CHBr_2$
7. Draw the structural formulas for the following compounds.
   - a. 2-methylpentan-3-ol
   - b. butan-2-ol
   - c. 2,2-dimethylbutan-1-ol
   - d. 2,3-dimethylpentan-2-ol
   - e. pentanoic acid
   - f. 2-methylpropanoic acid
   - g. butanoic acid
   - h. pentanal
   - i. 2-chloropropan-1-amine
   - j. butyl methanoate
   - k. butanone
   - l. 2-pentyne
8. Give the systematic name of the following compounds.
   - a. 
   - b. 
   - c. 
   - d. 
9. Draw and label the *cis* and *trans* isomers with the molecular formula $C_2H_2F_2$.

10. Describe the type of isomerism present in each of the following pairs of compounds.

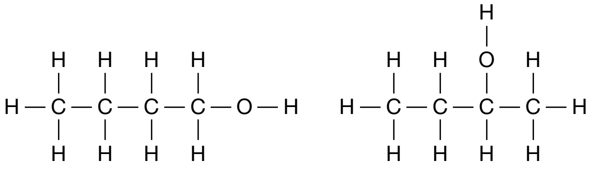
a.



b.



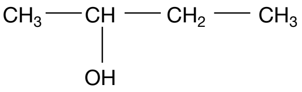
c.



8.6 Exercise 3: Exam practice questions

Question 1 (1 mark)

An organic molecule with the molecular formula $C_4H_{10}O$ is shown.



$CH_3-CH(OH)-CH_2-CH_3$

Which of the following statements about the molecule is true?

A. It is a primary alcohol and its systematic name is butan-2-ol.
B. It is a primary alcohol and its systematic name is butan-3-ol.
C. It is a secondary alcohol and its systematic name is butan-2-ol.
D. It is a secondary alcohol and its name is butan-3-ol.

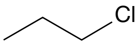
Question 2 (1 mark)

Which of the following contains a chiral carbon?

A. prop-1-ene CH_2CHCH_3
B. 1,2-dichloropropane $CH_2ClCHClCH_3$
C. 2-chloropropane $CH_3CHClCH_3$
D. 2-bromobutane $CH_3CHBrCH_2CH_3$

Question 3 (1 mark)

The semi-structure of the following compound is:

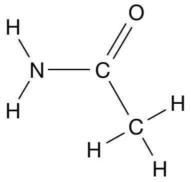


A. $CH_3(CH_2)_2CH_2Cl$
B. $CH_3CH_2CH_2Cl$
C. $(CH_3)_2CHCl$
D. $CH_3CHCHCH_2Cl$

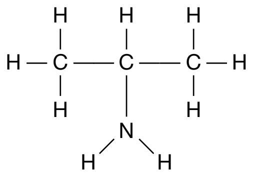
Question 4 (1 mark)

Which of the following structures is a primary amide?

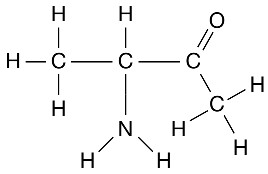
A.



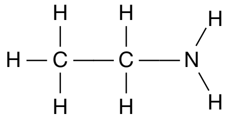
B.



C.



D.



Question 5 (10 marks)

The diverse nature of organic compounds can be attributed to carbon and its unique chemical properties. In fact, there are millions of organic compounds found in nature and synthesised in the laboratory. To be able to identify these molecules IUPAC has developed naming conventions and models.

a. Consider the alcohol 2-methylpropan-2-ol.
   - **i.** Draw the structural formula of the alcohol. **1 mark**
   - **ii.** What is the name of the functional group? **1 mark**
   - **iii.** Is this a primary, secondary or tertiary alcohol? Justify your answer. **1 mark**

b. Write the semi-structural formula of methyl butanoate. **1 mark**

c. Stereoisomers such as *cis*-but-2-ene and *trans*-but-2-ene are also known as geometric isomers.
   - **i.** Draw the structures of *cis* and *trans* but-2-ene. **2 marks**
   - **ii.** Write a balanced chemical equation for the combustion of but-2-ene gas. **2 marks**
   - **iii.** Calculate the volume of CO_2 gas collected from the complete combustion of 1.50 kg of but-2-ene at SLC. **2 marks**

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9 Categories, properties and reactions of organic compounds

9.1 Overview

Numerous **videos** and **interactivities** are available just where you need them, at the point of learning, in your digital formats, learnON and eBookPLUS at www.jacplus.com.au.

9.1.1 Introduction

Natural and synthetic organic reaction pathways can range from the fairly simple to quite complex. Chemists and engineers are constantly looking for ways to make new materials, improve products and reduce environmental impact. Finding the right pathway can be a challenging and time-consuming process. For example, engineers are looking to replace plastic bottles made from fossil fuels with furan-based polymers derived from sugars in biomass. Others have reduced the many steps involved in adding nitrogen to drugs, fertilisers and pesticides to a single step, making it possible to increase production and yield.

FIGURE 9.1 The variety of jelly bean flavours and colours is due to esters — changing even a small part of a molecule can provide a very different flavour.

This topic builds on the chemical interactions between the hydrocarbons and homologous series studied in topic 8. The relationships between intermolecular forces and physical properties and the types of functional groups that influence them are discussed in detail. You will learn about different reaction pathways to make a variety of organic compounds including alcohols, carboxylic acids and esters. You will learn about reaction yields and atom economy because chemists are increasingly looking for ways to improve the efficiency of reactions and reduce chemical waste. You look at the different types of chemical reactions including oxidation, addition, substitution, condensation and hydrolysis.

9.1.2 What you will learn

KEY KNOWLEDGE

In this topic, you will investigate:

- 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.

Source: VCE Chemistry Study Design (2017–2021) extracts © VCAA; reproduced by permission.

PRACTICAL WORK AND INVESTIGATIONS

Practical work is a central component of learning and assessment. Experiments and investigations, supported by a **Practical investigation logbook** and **Teacher-led videos**, are included in this topic to provide opportunities to undertake investigations and communicate findings.

on Resources

Digital documents Key science skills (doc-30903)
Key terms glossary – Topic 9 (doc-31415)
Practical investigation logbook (doc-31416)

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To access key concept summaries and past VCAA exam questions download and print the **studyON: Revision and practice exam question booklet** (doc-31417).

9.2 Explaining trends in physical properties

KEY CONCEPT

- An explanation of trends in physical properties (boiling point, viscosity) and flashpoint with reference to structure and bonding

The physical and chemical properties of organic compounds provide information that helps us understand and evaluate the interactions between organic chemicals. Depending on the types of atoms present in compounds, these interactions determine how organic molecules react to produce important chemicals for fuels, pharmaceuticals, manufacturing, industry and biological processes. The number of all the possible organic reactions that can occur is essentially infinite because there are so many combinations of organic compounds. However, certain general patterns involving addition, decomposition, combination, substitution or rearrangement of atoms or groups of atoms can be used to describe many common and useful reactions. It is not unusual to find that different pathways can produce the same organic substance.

9.2.1 Intermolecular forces

Intermolecular forces are those that act between molecules. They are influenced by the elements, bonds and shapes of molecules. These forces, along with the kinetic energies of the particles, determine properties such as melting and boiling points, density, etc.

In molecules (where atoms are connected by *intra*molecular covalent bonds), *inter*molecular forces may be of three types: dispersion forces, dipole–dipole attractions and hydrogen bonding.

Dispersion forces

In non-polar molecules such as methane (CH_4), wax and oils, electrons can momentarily be distributed unevenly within the molecules, inducing a temporary dipole. Neighbouring molecules with similar temporary dipoles are attracted weakly to each other. This results in weak dispersion forces between the molecules. The strength of the dispersion forces is affected by the size and shape of molecules. Dispersion forces are also called van der Waals forces.

Consider figure 9.2, which demonstrates a temporary dipole resulting in intermolecular attractions (dispersion forces). Molecule A has a temporary polarity due to uneven distribution of electrons. As the non-polar molecule B approaches A, its electrons are redistributed, because there is a tendency for them to be attracted to the end of A. This sets up an induced dipole in B. These intermolecular attractions are called dispersion forces. Dispersion forces are weak and temporary, because electrons tend to redistribute themselves at different instances.

FIGURE 9.2 Temporary dipoles giving rise to intermolecular attractions (dispersion forces)

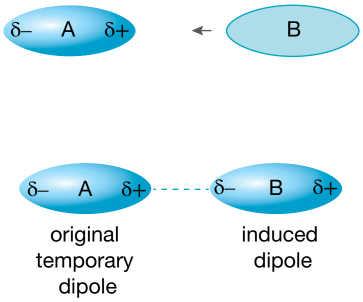


FIGURE 9.3 Candle wax consists of long hydrocarbon molecules held together by dispersion forces. The strength of dispersion forces increases with molecular size.

Dipole–dipole attractions

Molecules such as HCl, HBr and CH_3Cl are polar and have permanent dipoles. The partial positive charge on one molecule is electrostatically attracted to the partial negative charge on a neighbouring molecule. Dipole–dipole attractions are stronger intermolecular forces than dispersion forces.

Hydrogen bonding

When hydrogen forms a bond with one of fluorine, oxygen or nitrogen (highly electronegative atoms), its electrons move slightly toward that atom. This causes the hydrogen nucleus to be exposed or unshielded. The molecule that forms is a dipole. Hydrogen bonding occurs between this dipole and another molecule that must also contain an electronegative atom, such as oxygen or nitrogen.

Hydrogen bonds are *stronger* intermolecular forces than both dispersion forces and dipole–dipole attractions. Hydrogen bonding occurs between water molecules and also between organic compounds such as alcohols (e.g. methanol, CH_3OH), carboxylic acids (e.g. ethanoic acid, CH_3COOH) and organic amines (e.g. methylamine, CH_3NH_2).

Hydrogen bonding is stronger than dipole–dipole attractions due to the larger dipole moment that exists within these molecules and because of the small size of the hydrogen atom involved. This allows the molecules to get closer to each other than in dipole–dipole attractions, thus increasing the force of attraction.

Hydrogen bonding is stronger than dipole–dipole attraction, which is stronger than dispersion forces.

on Resources

Video eLesson Hydrogen bonding (eles-2483)

9.2.2 Physical properties

Physical properties are measurable and used to describe how a substance behaves and exists without changing its chemical composition. For example, physical states such as solid (s), liquid (l) and gas (g), density and colour are observable and measurable. There are many physical properties associated with chemical substances, but boiling point, **viscosity** and **flashpoint** are examined in detail below.

Boiling point

Standard boiling points are the temperatures at which liquids can vaporise at atmospheric pressure. For a liquid to boil, it must overcome the pressure of the atmosphere. This means when the air pressure varies so does a substance's boiling point. Kinetic energy of the particles causes an outward pressure and, if larger than atmospheric pressure, particles vaporise. At high altitudes with less air and therefore less air pressure, liquids need less energy to boil. For example, it is difficult to hard boil an egg on Mount Everest because water boils at around 71 °C at that altitude.

An increase in intermolecular forces makes it harder to separate particles and therefore they need higher temperatures to boil.

FIGURE 9.4 Honey is a viscose liquid because of strong intermolecular forces.

Viscosity

Viscosity is the resistance to flow of a liquid, and it is affected by intermolecular forces and the shapes of the molecules. Honey has high viscosity and water has low viscosity. The increased number of intermolecular forces in larger molecules, together with the possibility of branched molecules becoming tangled, results in higher viscosity. Viscosity decreases as the temperature increases because the molecules attain enough energy to overcome the forces holding the molecules together.

Flashpoint

Organic chemicals can be classified as flammable or combustible according to their flashpoints. The flashpoint of a volatile liquid is the lowest temperature at which the liquid gives off enough vapour to start burning at its surface on application of an ignition source. Below the flashpoint, there is not enough vapour available to support combustion. A flammable liquid is any liquid with a flashpoint below 37.8 °C. Liquids classified as combustible are harder to ignite and have a flashpoint of 37.8 °C and above.

Flammable liquids ignite and burn easily at lower temperatures. Combustible liquids can burn at temperatures that are usually above room temperature. It is not actually the liquid that burns, but rather the mixture of its vapours in the oxygen in the air. Smaller hydrocarbons have weaker intermolecular forces and are more easily vaporised, therefore they have lower flashpoints and are more flammable. The vaporisation rate increases as the temperature increases. This means that flammable and combustible liquids are more hazardous at temperatures higher than room temperature. If a fuel has a flashpoint below room temperature, such as petrol and alcohol, it is a safety hazard, because a spark could cause immediate ignition. It is this property that allows ethanol poured over Christmas puddings to be ignited in a celebratory display of flame. The pudding is not burned because the alcohol used is approximately half water, and the evaporating water keeps the temperature low. The oxygen in the alcohol causes it to completely combust with a blue flame, as distinct from the yellow flame observed when burning hydrocarbons in candle wax.

FIGURE 9.5 The low flashpoint of ethanol allows its ignition on a Christmas pudding.

9.2.3 Trends in homologous series

Within a homologous series, trends in physical properties are apparent. In the alkanes, the melting and boiling points increase with the size of the hydrocarbon. Their solubility in water is virtually non-existent due to the non-polar nature of hydrocarbons and the weak dispersion forces between molecules.

The presence of functional groups containing atoms other than hydrogen affects the properties of organic compounds. For example, the existence of a halogen in an organic molecule can result in a polar molecule. This would increase the strength of the intermolecular forces because dipole–dipole attractions would be present in addition to dispersion forces. When oxygen, fluorine or nitrogen is involved, hydrogen bonding will also be present.

Hydrocarbons

The alkane, alkene and alkyne homologous series' have similar physical properties. Alkanes are colourless compounds that are less dense than water and have weaker intermolecular attractive forces. Alkanes consist of non-polar molecules. The first four in the series are gases. As the size of the molecule increases, so does the influence of the dispersion forces, therefore, the melting and boiling points increase.

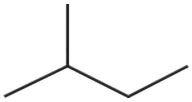
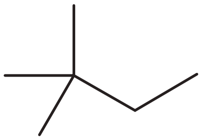
TABLE 9.1 The melting and boiling points of alkanes increase with increasing molecular size.

Alkane	Formula	Semi-structural formula	Melting point (°C)	Boiling point (°C)	State
Methane	CH_4	CH_4	−183	−164	gas
Ethane	C_2H_6	CH_3CH_3	−182	−87	gas
Propane	C_3H_8	$CH_3CH_2CH_3$	−190	−42	gas
Butane	C_4H_{10}	$CH_3(CH_2)_2CH_3$	−135	−1	gas
Pentane	C_5H_{12}	$CH_3(CH_2)_3CH_3$	−130	36	liquid
Hexane	C_6H_{14}	$CH_3(CH_2)_4CH_3$	−94	68	liquid
Heptane	C_7H_{16}	$CH_3(CH_2)_5CH_3$	−90	98	liquid
Octane	C_8H_{18}	$CH_3(CH_2)_6CH_3$	−57	126	liquid

Effect of side-chains or branching

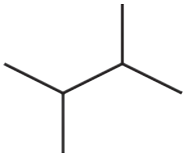
The degree of branching affects the boiling point; as the amount of branching increases, the boiling point decreases. This is due to the inability of molecules to get closer to each other. The dispersion forces operate over a small distance only, so the attraction is diminished. However, a higher degree of symmetrical branching has the opposite effect on melting point.

TABLE 9.2 Physical properties of branched butane isomers

Name	Skeletal structure	Melting point (°C)	Boiling point (°C)	Flashpoint (°C)
2-methylbutane		–159.8	27.8	–51
2,2-dimethylbutane		–99.9	49.7	–47.8

(continued)

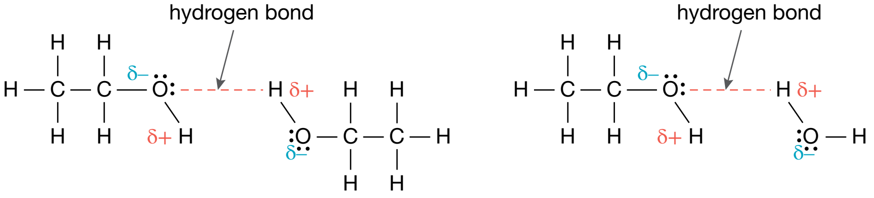
TABLE 9.2 Physical properties of branched butane isomers *(continued)*

Name	Skeletal structure	Melting point (°C)	Boiling point (°C)	Flashpoint (°C)
2,3-dimethylbutane		–128.8	57.9	–28.9

The hydroxyl functional group

The hydroxyl group in alcohols has a significant effect on properties. It can form hydrogen bonds with other alcohol or water molecules. Consequently, alcohols have a higher boiling point than corresponding alkanes, and smaller alcohols (three or fewer carbon atoms) are soluble in water. The boiling point of primary alcohols increases with increasing chain length due to the increasing number of dispersion forces, whereas the solubility decreases with increasing chain length due to the increasing length of the non-polar (hydrophobic) section of the molecules. The effect of the increased number of dispersion forces explains why volatility (tendency to vaporise) decreases with molecular size whereas viscosity increases.

FIGURE 9.6 Alcohols can form hydrogen bonds with other alcohol molecules or water.



two ethanol molecules

ethanol and water molecules

Many alcohols are highly flammable (with flashpoints below 37.8 °C), especially methanol (11 °C) and ethanol (17 °C). The flammability of alcohols decreases as the molecules increase in size and mass due to the increased strength of attraction between the molecules. Volatility also decreases as the size of the molecule increases.

FIGURE 9.7 This bar is made almost entirely of ice. The alcoholic drinks do not freeze even though they are served in ice vessels because alcohol has a lower freezing point than water.

The carboxyl functional group

Like the alcohols, the first few members of the carboxylic acid homologous series are very soluble in water due to their capacity for strong hydrogen bonding with water molecules. Carboxylic acids have much higher boiling points than the previously discussed homologous series because carboxylic acid molecules can form two hydrogen bonds with each other.

Carboxylic acids are weak acids that only partially ionise in water. They are still stronger acids than their corresponding alcohols because the —OH group is more polarised in the —COOH group by the presence of the highly electronegative O atom of C=O. This double-bonded O atom attracts the electrons away from the —OH group. Therefore, the H (from the hydroxyl group) is more weakly bonded to O and is more easily donated.

FIGURE 9.8 A dimer (a pair of molecules) is formed by carboxylic acid molecules.

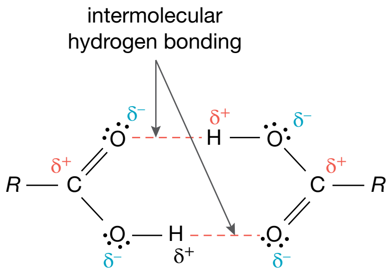


FIGURE 9.9 Polarisation of the −OH group in a carboxylic acid and an alcohol.

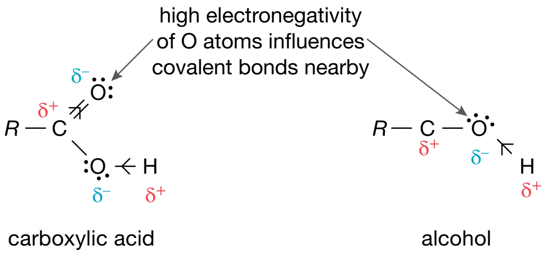
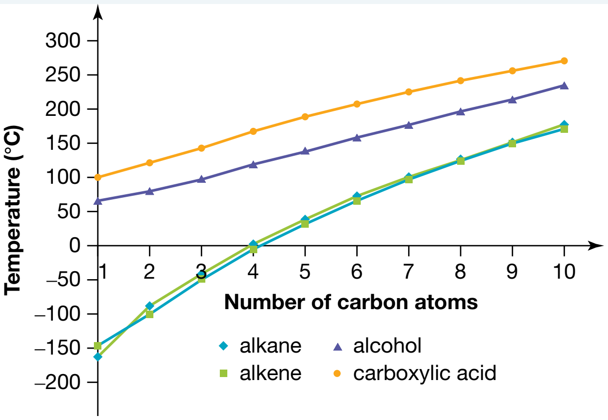


FIGURE 9.10 A graph showing the relative boiling points of the homologous series of alkanes, alkenes, alcohols and carboxylic acids



Aldehydes, ketones and esters

Aldehydes and ketones are volatile compounds and are commonly found in perfumes and flavourings. Smaller molecules of these compounds are soluble because they can form hydrogen bonds with water, but solubility decreases with increasing length of the non-polar chain. These molecules cannot hydrogen bond with each other, but the polarity of the molecule means that the boiling point is higher than for similar-sized alkanes but lower than for alcohols and carboxylic acids, which have hydrogen bonding between hydroxyl groups.

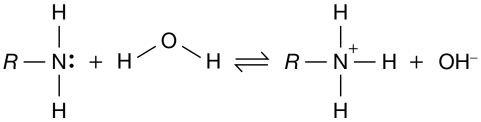
Esters are commonly found in plants and are responsible for many distinctive odours and flavours. Esters have lower boiling points than carboxylic acids because esters cannot form hydrogen bonds with each other (they do not have an O—H bond). Esters with very short carbon chains are soluble in water, whereas those with longer chains are less soluble.

Amines and amides

Amines are stable compounds that generally have strong or unpleasant odours, similar to rotting fish. They are weak bases because they can accept a proton (see figure 9.11).

Hydrogen bonding is possible in amines (due to the presence of N—H bonds) but their boiling points are lower than the corresponding alcohols. The first two members of the homologous series are gases at room temperature, whereas the larger members are liquids. As with the other polar compounds containing hydrogen bonding, the solubility decreases with chain length.

FIGURE 9.11 Amines are weak bases.



$$R{-}NH_2 + H_2O \rightleftharpoons R{-}NH_3^+ + OH^-$$

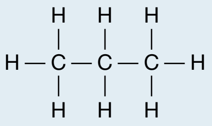
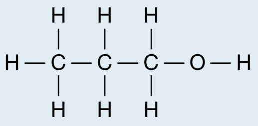
Amides have higher melting and boiling temperatures than similar-sized organic compounds due to their capacity to form multiple hydrogen bonds between molecules. Methanamide is a liquid at room temperature, but larger amides are solids because of the increased number of dispersion forces. Smaller amides are soluble but less soluble than comparable amines and carboxylic acids; their solubility is similar to that of esters.

TIP: **When explaining physical properties, ensure the structure of the molecule is used to justify the type of intermolecular forces existing and how the difference in strength of the intermolecular results in the different properties.**

SAMPLE PROBLEM 1

Propane has a boiling point of –42 °C whereas the boiling point of propan-1-ol is 97 °C. Explain this difference by referring to the intermolecular forces in both compounds.

Teacher-led video: SP1 (tlvd-0709)

THINK	**WRITE**
1. Draw the structures of propane and propan-1-ol.	Propane:  $H-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-H$ Propan-1-ol:  $H-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-O-H$
2. Consider the type of intermolecular forces that exist between molecules with the O–H functional group compared to hydrocarbons.	Propane: intermolecular forces are dispersion forces only. These forces are weak and temporary. As a result it doesn't take a lot of energy in the form of heat to vaporise the liquid. Propan-1-ol: intermolecular forces have hydrogen bonds due to the polar hydroxyl functional group on one end of the molecule.
3. Explain how the different intermolecular forces affect boiling point.	Hydrogen bonds are much stronger than dispersion forces so significantly more heat is required to vaporise propan-1-ol than propane.

PRACTICE PROBLEM 1

By referring to intermolecular forces, explain the difference in the boiling point of 1-chloropropane (46.6 °C) and propane (–42 °C).

on Resources

Digital document Experiment 9.1 Comparing physical properties of alkanes, haloalkanes, alcohols and esters (doc-31270)

9.2 EXERCISE

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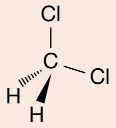
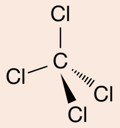
1. Describe the intramolecular and intermolecular bonding that exists in hydrocarbons.
2. Identify the types of intermolecular forces (dispersion forces, dipole–dipole attraction or hydrogen bonding) acting between molecules of the following compounds.
   (a) CH_3OH
   (b) CH_3CH_3
   (c) CH_3CH_2Cl
   (d) CH_3NH_2
3. (a) Explain why the flashpoint of propan-1-ol is higher than the flashpoint of propan-2-ol.
   (b) Predict whether propan-1-ol or propan-2-ol has the higher boiling point.
4. Explain why methane and ethane are insoluble in water whereas methanol and ethanol are soluble.
5. Explain which has the higher boiling point: butanamide, $CH_3CH_2CH_2CONH_2$, or ethyl ethanoate, $CH_3COOCH_2CH_3$.
6. Candles can be made from a variety of compounds including soy, and bee and paraffin waxes. Paraffin contains a mixture of alkanes and is a solid at room temperature and melts at 50–60 °C.
   (a) What does the solid state of paraffin candles suggest about the size of the mix of alkanes used to make it?
   (b) Why are essential oils, used to add scent to a candle, able to be mixed with paraffin wax?
7. Hexane is often used as an industrial solvent. Explain why each of the following is or is not an appropriate use of hexane.
   (a) Removing salt from water
   (b) Removing oil from soy beans
   (c) Removing oil contaminants in water
8. The structures of dichloromethane and carbon tetrachloride are shown.

dichloromethane



carbon tetrachloride



Explain the table of physical properties below based on the two structures.

Physical property	Dichloromethane	Carbon tetrachloride
Boiling point	39.6 °C	76.7 °C
Solubility in water at SLC	17.5 g L^{-1}	0.81 g L^{-1}

9. Two compounds have the molecular formula C_2H_6O. Use the data below to draw the structures of Compound A and Compound B.

Physical property	Compound A	Compound B
Boiling point	–24 °C	78 °C
Solubility in water at SLC	71 g L^{-1}	miscible

10. Explain why ethyl ethanoate has a higher solubility in water but a lower boiling point than ethyl butanoate.

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9.3 Organic reactions

KEY CONCEPTS

- Organic reactions, including appropriate equations and reagents, for addition reactions of alkenes, for substitution reactions of haloalkanes, for the oxidation of primary and secondary alcohols, for the esterification reaction between an alcohol and a carboxylic acid, the condensation reaction between an amine and a carboxylic acid, for hydrolysis reactions of esters
- The pathways used to synthesise primary haloalkanes, primary alcohols and carboxylic acids

As described in subtopic 9.2, functional groups influence physical properties, but they also influence chemical properties and the types of reactions they participate in. Common reaction types are addition, substitution, condensation, hydrolysis, redox and organic acid-base.

9.3.1 Addition reactions of alkenes

Alkenes are more reactive than alkanes. They are unsaturated hydrocarbons and undergo **addition reactions** in which the C=C bond is broken and new single bonds are formed. This is because the energy required to break the double bond is less than the energy released in the formation of two single bonds. For example, hydrogenation of ethene produces ethane and releases energy.

$$H_2C{=}CH_2(g) + H_2O(g) \xrightarrow{\text{catalyst}} H_3CCH_3(g)$$

Substances that undergo addition reactions with alkenes include hydrogen (H_2), chlorine (Cl_2), bromine (Br_2), hydrochloric acid (HCl), hydrogen bromide (HBr) and hydrogen iodide (HI). Addition of H_2 requires the presence of a catalyst, such as finely divided platinum (Pt), palladium (Pd) or nickel (Ni). The others react without the need for catalysis.

The following equations are examples of addition reactions with alkenes. Note that the reactants Br_2, HCl and H_2 in these reactions add *across* the double bond. Therefore, 1,2-dibromopropane is the only product.

$$\underset{\text{propene}}{H_2C{=}CHCH_3} \quad + \quad \underset{\text{bromine}}{Br_2} \quad \longrightarrow \quad \underset{\text{1,2-dibromopropane}}{CH_2BrCHBrCH_3}$$

$$\underset{\text{ethene}}{H_2C{=}CH_2} \quad + \quad \underset{\text{hydrogen chloride}}{HCl} \quad \longrightarrow \quad \underset{\text{chloroethane}}{CH_3CH_2Cl}$$

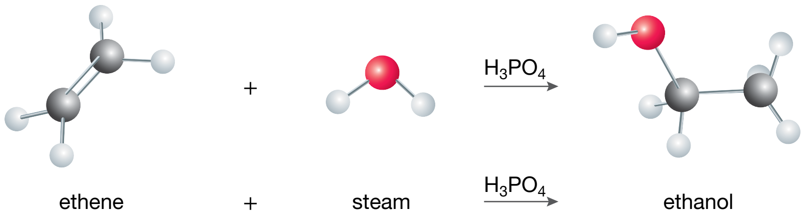
$$\underset{\text{but-1-ene}}{H_2C{=}CH{-}CH_2{-}CH_3} \quad + \quad \underset{\text{hydrogen}}{H_2} \quad \xrightarrow{\text{Pd}} \quad \underset{\text{butane}}{CH_3CH_2CH_2CH_3}$$

The reaction of an alkene with bromine is used as a test for unsaturation. When red-brown bromine water is shaken with an unsaturated hydrocarbon, the reaction mixture becomes colourless due to the formation of the dibromo derivative.

Ethene is used as a raw material in a fast method to produce the large amounts of ethanol needed for industrial use. Ethene is mixed with steam and passed over a phosphoric acid catalyst at 330 °C. The reaction of the direct catalytic hydration of ethene in the vapour phase is an addition reaction. This reaction is demonstrated using molecular models in figure 9.12.

$$\underset{\text{ethene}}{H_2C{=}CH_2(g)} \quad + \quad \underset{\text{steam}}{H_2O(g)} \quad \xrightarrow{H_3PO_4} \quad \underset{\text{ethanol}}{CH_3CH_2OH(g)}$$

FIGURE 9.12 Model equation for the direct hydration of ethene to form ethanol



on Resources

Video eLessons Addition reactions of alkenes (med-0352)

Catalysis: hydrogenation of ethylene (eles-1673)

Bromination of ethylene (eles-1674)

Indirect hydration of ethylene (eles-1677)

9.3.2 Substitution reactions

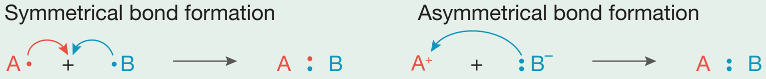
Substitution reactions occur when one or more atoms on a molecule are replaced by others as opposed to being added in like those in addition reactions. The types of atoms or groups involved in these reactions generally depend on the atoms they replace on the molecule. Electron rich, electron deficient and neutral groups participate in substitution reactions. Halogens are very good at substituting, as are polar functional molecules or groups with lone pairs of electrons, such as H_2O and NH_3.

REACTION MECHANISMS

Reaction mechanisms describe the way bonds are broken and formed. Many of the reactions and pathways explored in this topic are caused because of radical and polar reactions.

Bond breaking can be symmetrical (radical formation) or unsymmetrical (polar formation).

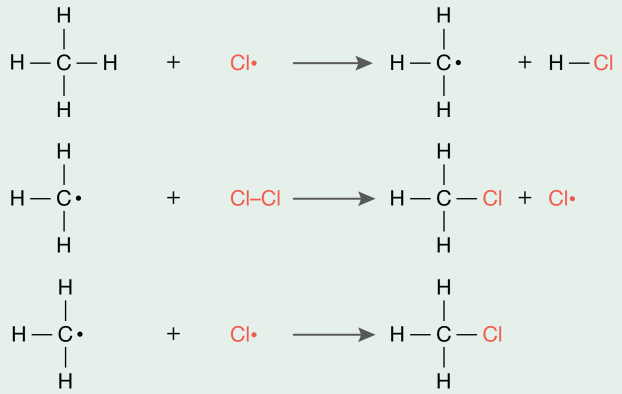
Bonds can be made symmetrically where each reactant contributes one electron to the covalent bond, or they can be unsymmetrical where one reactant contributes both electrons in a covalent bond.



Radical reactions

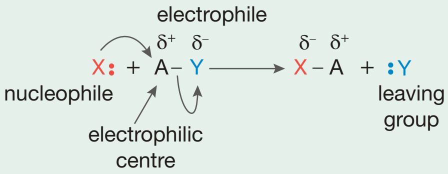
Radical reactions involve symmetrical bond formation and bond breaking. Reactions that involve asymmetrical bond formation and breaking are called polar reactions. Radicals are very reactive because they have an atom without a stable octet of outer shell electrons. They can achieve the stable octet of valence electrons by first taking an atom and its valence electron causing the formation of a new radical, and then adding across a C=C double bond, taking one electron from the double bond and forming a new radical.

The formation of chloromethane from methane involves a radical substitution. UV light provides the energy for the formation of two chlorine radicals from Cl_2 that has undergone symmetrical bond breaking (in a process called initiation). Then the Cl• radicals begin the process by taking a hydrogen atom and its electron from methane to form HCl and a $CH_3\bullet$ radical (UV light is not required for this to occur). Further radical processes take place to form CH_3Cl as outlined below.



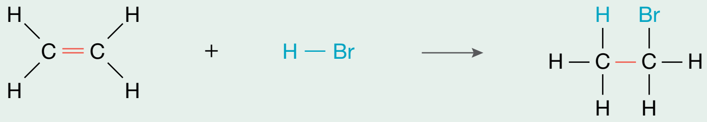
Polar reactions

Polar reactions occur because of the positive and negative attractions between centres and functional groups. This can be achieved by polarising molecules using chemicals such as acids. Negatively polarised groups or negative ions will be attracted to positively polarised groups or positive ions and the two form new covalent bonds. Negatively polarised groups or ions are called nucleophiles and positively polarised atoms, centres or ions are called electrophiles.



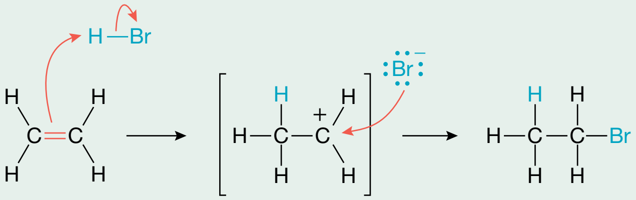
Ions or polar groups that can act as bases (accept protons) make good nucleophiles while acids make good electrophiles (donate protons). The terms nucleophile and electrophile are used when they are involved in bonds with carbon.

The addition of hydrogen bromide to ethene can be shown as:



ethene (nucleophile) hydrogen bromide (electrophile) bromoethane

However, it is an example of nucleophile and electrophile interactions requiring two steps to complete.



reaction intermediate

Substitution reactions of alkanes

The alkanes undergo substitution reactions with the halogens in which the halogen atoms replace hydrogen. For example, the successive chlorination of methane to form chloromethanes occurs as follows.

$$CH_4 + Cl_2 \xrightarrow{\text{UV light}} \underset{\text{chloromethane}}{CH_3Cl} + HCl$$

$$CH_3Cl + Cl_2 \xrightarrow{\text{UV light}} \underset{\text{dichloromethane}}{CH_2Cl_2} + HCl$$

$$CH_2Cl_2 + Cl_2 \xrightarrow{\text{UV light}} \underset{\substack{\text{trichloromethane} \\ \text{(chloroform)}}}{CHCl_3} + HCl$$

$$CH_2Cl_3 + Cl_2 \xrightarrow{\text{UV light}} \underset{\substack{\text{tetrachloromethane} \\ \text{(carbon tetrachloride)}}}{CCl_4} + HCl$$

These reactions require energy in the form of UV light to catalyse the reaction. The UV light breaks the covalent bond between the chlorine atoms to produce unstable chlorine free radicals. In general when exposed to light:

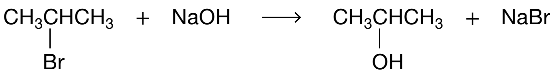
$$R\text{–}H + X_2 \xrightarrow{\text{UV light}} R\text{–}X + HX$$

Substitution reactions of haloalkanes

Haloalkanes are widely used but most do not occur naturally and must be produced synthetically. One of the first haloalkanes used was chloroform. It was used during the American Civil War (1861–65) as an anaesthetic for amputations and treatment of soldiers. Now, haloalkanes are widely used in medicine, agriculture and production of polymers.

Although haloalkanes have a number of uses in their own right, they are particularly useful as precursors to the preparation of further substances. Alcohols can be prepared from haloalkanes in substitution reactions by reacting them with dilute solutions of either sodium or potassium hydroxide. For example, propan-2-ol can be made by reacting either 2-chloropropane or 2-bromopropane with dilute sodium hydroxide.

FIGURE 9.13 Coral secretes natural haloalkanes to deter starfish like the Crown of Thorns from feeding on it.



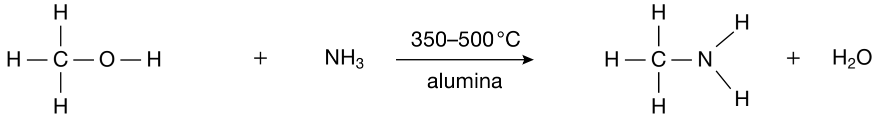
$$CH_3\underset{\substack{| \\ Br}}{C}HCH_3 + NaOH \longrightarrow CH_3\underset{\substack{| \\ OH}}{C}HCH_3 + NaBr$$

Either 1-chloropropane or 1-bromopropane could be used to make propan-1-ol.

$$CH_3CH_2CH_2Cl + NaOH \longrightarrow CH_3CH_2CH_2OH + NaCl$$

Polar group substitution

Polar groups can be substituted with other polar groups. For example, R—OH can be substituted to R—NH_2. Substitutions like this are controlled by the reagents and solvents used. NH_3 is added with a catalyst (such as alumina) and increased temperature (350–500 °C) and pressure (3000 kPa) facilitate the reaction.



Resources

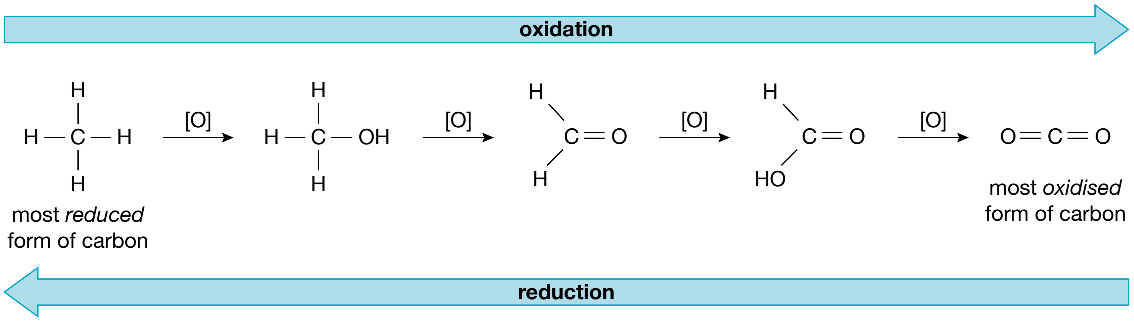
Interactivity Comparing substitution and addition reactions (int-1235)

9.3.3 Reactions of alcohols

Primary alcohols

Primary alcohols are easily oxidised in the laboratory, first to aldehydes and then to carboxylic acids, using either acidified permanganate,H^+/MnO_4^- (aq), or acidified dichromate,$H^+/Cr_2O_7^{2-}$ (aq), or another oxidising agent. [O] is the symbol for an oxidising agent.

FIGURE 9.14 Stages of oxidation of carbon compounds. Notice the increase in oxidation number of carbon from left to right.



In these oxidation reactions in figure 9.14, there is an increase in the oxygen to hydrogen ratio; that is, there is more oxygen and less hydrogen. The product of these reactions is a carboxylic acid. For example, propan-1-ol can be converted into propanoic acid as shown below.

$$CH_3CH_2CH_2OH \xrightarrow{H^+/Cr_2O_7^{2-}} CH_3CH_2COOH$$

The oxidation of ethanol in wine takes place when it is left exposed to air for some time. Such wine has a sour taste of ethanoic acid, commonly known as acetic acid. The oxidation reaction that takes place is:

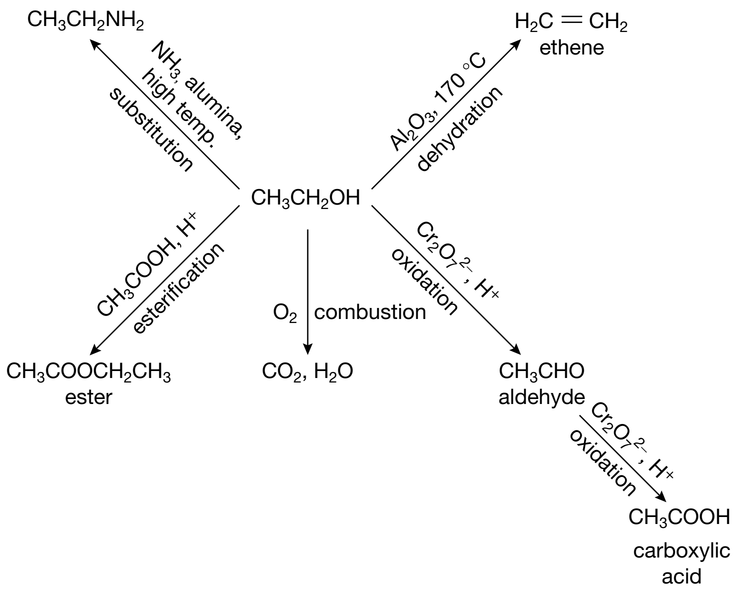
$$C_2H_5(aq) + O_2(g) \rightarrow CH_3COOH(aq) + H_2O(I)$$

The reaction is catalysed by the presence of the micro-organism *Acetobacter aceti* in the exposed wine.

As described in topic 1, all alcohols are flammable and burn in air to produce carbon dioxide and water. For this reason, ethanol is added to petrol to produce various ethanol blends.

$$CH_3CH_2OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(g)$$

FIGURE 9.15 Ethanol demonstrating the reactions of primary alcohols



Secondary alcohols

Secondary alcohols are oxidised to ketones, which do not undergo further oxidation.

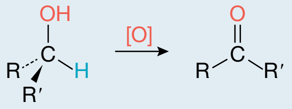
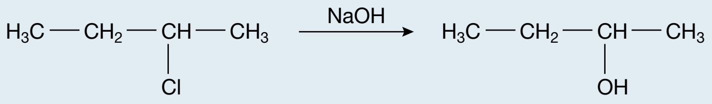
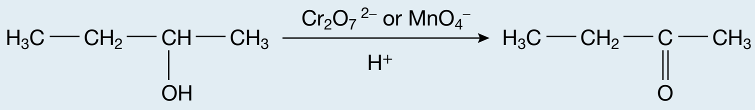
For example, propan-2-ol is oxidised to propanone.

$$CH_3CHOHCH_3 \xrightarrow{H^+/Cr_2O_7^{2-}} CH_3COCH_3$$

SAMPLE PROBLEM 2

Write the reaction steps and reagents used to make the ketone butan-2-one (butanone) from 2-chlorobutane.

Teacher-led video: SP2 (tlvd-0710)

THINK	WRITE
1. Recall ketones can be made by oxidising secondary alcohols.	
2. Draw the structure of 2-chlorobutane. What reagents are required to convert it into a secondary alcohol? −OH ions will substitute with the chlorine atom to form a secondary alcohol.	 $H_3C-CH_2-CH(Cl)-CH_3 \xrightarrow{NaOH} H_3C-CH_2-CH(OH)-CH_3$
3. What reagents and conditions are used to oxidise alcohols? Acidified dichromate or permanganate are used to oxidise primary and secondary alcohols.	 $H_3C-CH_2-CH(OH)-CH_3 \xrightarrow[H^+]{Cr_2O_7^{2-} \text{ or } MnO_4^-} H_3C-CH_2-C(=O)-CH_3$

PRACTICE PROBLEM 2

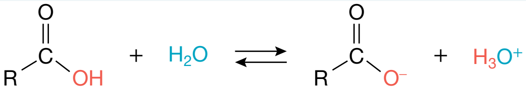
Write the reaction steps and reagents used to make hexan-2-one from a chloroalkane.

9.3.4 Reactions of carboxylic acids

Acid–base reactions

As the name implies, carboxylic acids act as proton donors with the hydrogen ion being donated from the —OH part of the carboxyl (—COOH) functional group. They slightly dissociate in water and have pH <7.

FIGURE 9.16 Dissociation of carboxylic acid in water



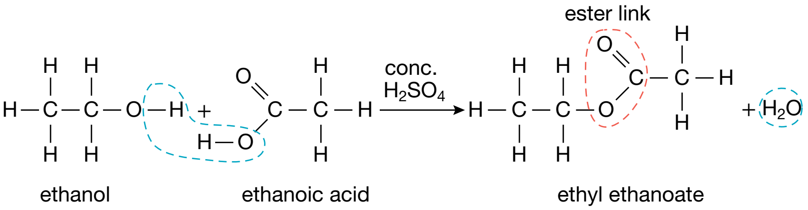
Carboxylic acids are much stronger acids than alcohols. This is because the carboxylate ion (COO^-) has the electron left behind shared evenly between the two oxygen atoms. In other words, it is delocalised. This provides extra stability so the equilibrium favours the product far better than when alcohols are deprotonated. We draw the negative charge on the single bonded oxygen of the conjugate base of the carboxylic acid.

Condensation with primary alcohols

Carboxylic acids undergo **condensation reactions** with alcohols to produce esters. A typical **esterification** reaction (the process of ester formation) is the formation of ethyl ethanoate, $CH_3COOCH_2CH_3$, by heating ethanol, C_2H_5OH, and ethanoic acid, CH_3COOH, in the presence of an acid such as concentrated sulfuric acid. During the condensation reaction, a water molecule is produced. The ester formed is partially insoluble in water and can be purified by mixing it with cold water. The ester forms a sweet-smelling insoluble layer on top of the water, while sulfuric acid and unreacted ethanol and ethanoic acid dissolve.

FIGURE 9.17 The acid present in vinegar is ethanoic acid, CH_3COOH, commonly known as acetic acid.

FIGURE 9.18 A typical esterification reaction



The process is called a condensation reaction because a small molecule (water) is split off as the two molecules join together. In general:

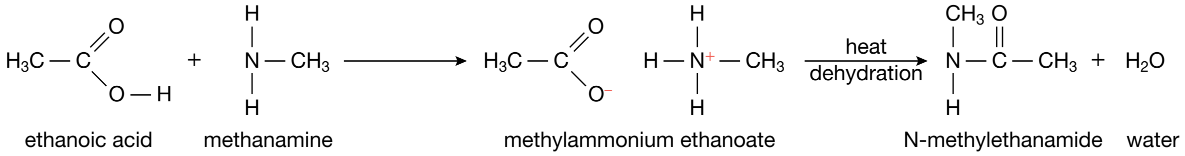
$R'OH$	+	RCOOH	→	$RCOOR'$	+	H_2O
alcohol	+	carboxylic acid	→	ester	+	water

TIP: When writing condensation reactions it is important to specify that the acid acting as a catalyst is concentrated and not in aqueous form.

Reaction with amines

Small amines react in a similar manner to ammonia, which is a weak base. Therefore, carboxylic acids can donate a proton to a primary amine. An example is the acid–base reaction of ethanoic acid with methanamine to produce the salt methylammonium ethanoate. This salt is heated to over 100 °C, water is removed and an amide is formed.

FIGURE 9.19 Reaction of a carboxylic acid with an amine



$$\text{carboxylic acid} + \text{amine} \longrightarrow \text{ammonium salt} \xrightarrow[\text{dehydration}]{\text{heat}} \text{amide} + \text{water}$$

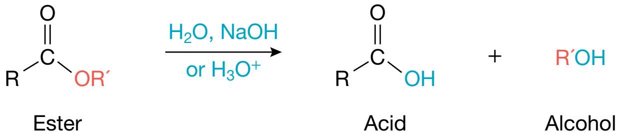
on Resources

Video eLessons	Esterification (eles-1668) Ester formation (med-0353) Acid–base reaction of an amine with a carboxylic acid (eles-1667)
Digital document	Experiment 9.2 Esterification (doc-31271)
Teacher-led video	Experiment 9.2 Esterification (tlvd-0757)

9.3.5 Hydrolysis reactions of esters

Esters undergo hydrolysis in aqueous acids or bases to reverse the condensation reaction. The products are carboxylic acids and alcohols.

FIGURE 9.20 Hydrolysis of an ester



Ester hydrolysis in alkaline solutions is also known as saponification, from the Latin word *sapo* meaning ‘soap’. The ester linkages in fats are hydrolysed in basic solutions to make soap.

FIGURE 9.21 Soaps are manufactured through ester hydrolysis.

POLYESTERS

Polyesters are synthetic fibres used as a substitute for cotton and wool and are formed as a result of ester linkages between monomers to form the polymer. A common polyester is terylene, which is poly(ethane-1, 2-diylbenzene-1,4-dicarboxylate). This polyester is made by the esterification of ethane-1,2-diol (also known as ethylene glycol) and benzene-1,4-dicarboxylic acid (also known as terephthalic acid). The structures of these molecules are shown in figure 9.22. These monomer units are joined together to form polyester as shown in figure 9.23.

FIGURE 9.22 Monomers used to form the polyester terylene

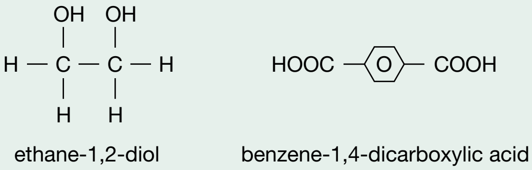
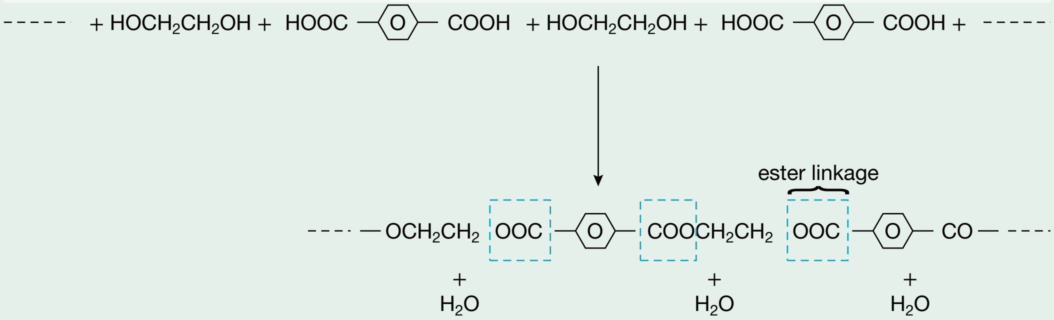


FIGURE 9.23 Esterification to form terylene



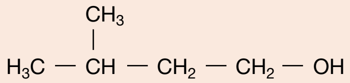
Polyesters have great tensile strength and are used as the bonding resin in glass fibre plastics. They have a wide variety of uses in the textile industry. Many yachts have sails made of polyester because it is stronger than natural fibres and does not rot. Polyesters are mixed with cotton to make fabric for clothing. They are crease resistant and do not shrink or stretch. The oven bags used for roasting are also made of polyester because it can withstand high temperatures.

FIGURE 9.24 Most sails today are made of polyester.

9.3 EXERCISE

To answer questions online and to receive **immediate feedback** and **sample responses** for every question go to your learnON title at www.jacplus.com.au.

1. Explain how you would make 1,1-dichloroethane from ethane.
2. Write the structural equations for the reactions of chlorine, hydrogen and hydrogen chloride with propene. Name the compounds formed.
3. Red bromine, Br_2, liquid is decolourised in an addition reaction with an alkene. With reference to ethane and ethene, explain how this reaction could demonstrate which substance is unsaturated.
4. (a) Name the following alcohol.



$$H_3C - \overset{\displaystyle CH_3 \atop |}{CH} - CH_2 - CH_2 - OH$$

   (b) Give the name and structure of the product formed by the complete oxidation of this alcohol by acidified potassium dichromate.
5. Why can't secondary alcohols be used to make carboxylic acids?
6. Write the equation representing the reaction between aqueous solutions of ethanoic acid and potassium hydroxide.
7. Draw the structures formed when ethanoic acid is reacted with:
   (a) butan-1-ol in the presence of $H_2SO_4(l)$
   (b) propan-1-amine followed by dehydration.
8. List the conditions and reagents required to convert ethene into:
   (a) ethane
   (b) ethanol
   (c) chloroethane
   (d) ethanamine
   (e) propyl ethanoate.
9. Write equations for the oxidation of:
   (a) pentan-1-ol
   (b) pentan-2-ol.
10. Explain the difference between ester hydrolysis and ester formation. What are the reactants and products?

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9.4 Reaction pathways

KEY CONCEPT

- 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.

Reaction pathways are important in synthetic chemistry. Chemists are looking to save time and money while reducing waste and maximising the yields from reactions. Subtopic 9.3 covered some of the steps and reagents to produce a host of chemicals, but this subtopic is looking at multi-step procedures for making these chemicals from a variety of starting materials and being able to calculate the yield and atom economy as means of measuring the efficiency of these reactions.

9.4.1 Measuring reaction efficiency

There are a number of ways of evaluating the efficiency of a chemical process. Factors that could be considered include energy consumption, cost of chemicals and equipment, and environmental impact. Traditionally, the efficiency of a reaction has been determined by calculating the **percentage yield**.

Percentage yield

Sometimes when chemical reactions are performed, not all of the reactants are converted into the desired products. This could be due to many factors including:

1. the reaction being an equilibrium reaction and not going to completion
2. losses when transferring liquids between containers
3. losses when filtering
4. losses when heating
5. presence of unreactive impurities
6. decomposition of product
7. some liquid lost due to evaporation
8. other side reactions.

Chemical processes have been designed to manufacture the maximum amount of product from a given amount of raw materials. This is called the yield of a reaction and can be calculated by finding the percentage of the mass of the product actually made compared to the theoretical mass of a product that could be made. The theoretical mass of the product is calculated using the given amount of the limiting reactant in the reaction.

$$\%\text{ yield} = \frac{\text{actual yield}}{\text{theoretical yield}} \times \frac{100}{1}$$

TIP: The % yield formula can be found in table 3 of the VCE Chemistry Data Book.

SAMPLE PROBLEM 3

2.18 g of ethanol, C_2H_5OH, is reacted with excess oxygen to produce 3.63 g of carbon dioxide according to the equation:

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

What is the percentage yield of this reaction?

Teacher-led video: SP3 (tlvd-0711)

THINK	WRITE
1. The percentage yield will be the mass of CO_2 actually produced (actual yield) divided by the theoretical mass of CO_2 expected to be produced (theoretical yield) according to the mole ratios in the equation and multiplied by 100.	$\%\text{ yield} = \frac{\text{actual yield}}{\text{theoretical yield}} \times \frac{100}{1}$

▶

2. Calculate the number of moles of ethanol by using the formula $n = \frac{m}{M}$.

$$\begin{aligned} n(C_2H_5OH) &= \frac{m}{M} \\ &= \frac{2.18\text{ g}}{(2 \times 12.0 + 6 \times 1.0 + 16.0)\text{ gmol}^{-1}} \\ &= 0.0474\text{ mol} \end{aligned}$$

3. Determine the number of CO_2 moles expected. From the equation given, one mole of ethanol produces two moles of carbon dioxide.

$$\begin{aligned} n(CO_2) &= 2 \times 0.0474 \\ &= 0.0948\text{ mol} \end{aligned}$$

4. Calculate the theoretical yield of CO_2 by rearranging the molar mass formula.

$$\begin{aligned} n &= \frac{m}{M} \\ m(CO_2) &= n \times M \\ &= 0.0948\text{ mol} \times (12.0 + 2 \times 16.0)\text{ g mol}^{-1} \\ &= 4.17\text{ g} \end{aligned}$$

5. Determine the % yield by dividing the actual yield by the theoretical yield and multiplying by 100. Express the answer to three significant figures and do not round answers at each step.
TIP: Formulas can be found in table 3 of the VCE Chemistry Data book.

$$\begin{aligned} \%\text{yield} &= \frac{3.63\text{g}}{4.17\text{g}} \times 100 \\ &= 87.0\% \end{aligned}$$

PRACTICE PROBLEM 3

2.5 g of methanol is reacted with excess oxygen to produce 3.1 g of carbon dioxide according to the following reaction.

$$2CH_3OH(l) + 5O_2(g) \rightarrow 2CO_2(g) + 4H_2O(g)$$

Calculate the percentage yield of carbon dioxide.

Atom economy

Calculating the percentage yield does not give an indication of how effectively the reactants have been used to generate the product with minimal waste. **Atom economy** is another method for measuring the efficiency of a reaction that takes into account the amount of waste produced.

$$\text{reactant (s)} \rightleftharpoons \text{desired product} + \text{waste products}$$

The atom economy of a reaction considers the amount of useful product produced from a particular amount of reactants. Measuring atom economy enables sustainable development by using fewer natural resources and minimising waste. The optimal situation is where the yield of a reaction is maximised, and as many atoms as possible of the reactants are incorporated into the final product. It is preferable to decrease the amount of waste produced rather than have to deal with it at the end of the process.

$$\%\text{ atom economy} = \frac{\text{molar mass of desired product}}{\text{molar mass of all reactants}} \times \frac{100}{1}$$

TIP: The % atom economy formula can be found in table 3 of the VCE Chemistry Data Book.

SAMPLE PROBLEM 4

What is the percentage atom economy for the synthesis of ethanamine from chloroethane?

$$C_2H_5Cl(g) + NH_3(g) \rightarrow C_2H_5NH_2(g) + HCl(g)$$

Teacher-led video: SP4 (tlvd-0712)

THINK	WRITE
1. Calculate relative molecular mass (M_r) of the product ethanamine.	$M_r(C_2H_5NH_2) = (2 \times 12) + (5 \times 1) + 14 + (2 \times 1)$ $= 45$
2. Calculate the M_r of the reactants and add them together.	$M_r(C_2H_5Cl) + M_r(NH_3) = (2 \times 12) + (5 \times 1) + 35.5 + 14 + (3 \times 1)$ $= 81.5$
3. Calculate the % atom economy by dividing the M_r of the desired product by the total M_r of the reactants and multiplying by 100%.	$\%\text{ atom economy} = \dfrac{\text{molar mass of desired product}}{\text{molar mass of all reactants}} \times \dfrac{100}{1}$ $= \dfrac{45}{81.5} \times 100$ $= 55\%$

PRACTICE PROBLEM 4

Calculate the percentage atom economy when methyl ethanoate is produced from the condensation of methanol and ethanoic acid.

TIP: Write ester functional group semi-structures as COO and not OCO.

9.4.2 Reaction pathway summary

Esters and amides from alkenes

Esters are produced from the condensation reaction between a primary alcohol and carboxylic acid using an acid catalyst. Alcohols are added in excess to favour the forward reaction and increase the yield of the ester.

The precursor to a carboxylic acid is a primary alcohol. Primary alcohols have the general formula R—O—H. These alcohols can be formed from the addition of steam to alkenes in the presence of an acid catalyst, or the substitution of an OH^- ion with a primary haloalkane. Haloalkanes can be prepared from the addition of HX, where X is a halogen, typically Cl or Br. Carboxylic acids are then produced by the oxidation of the primary alcohol using a strong oxidant in an acidified solution.

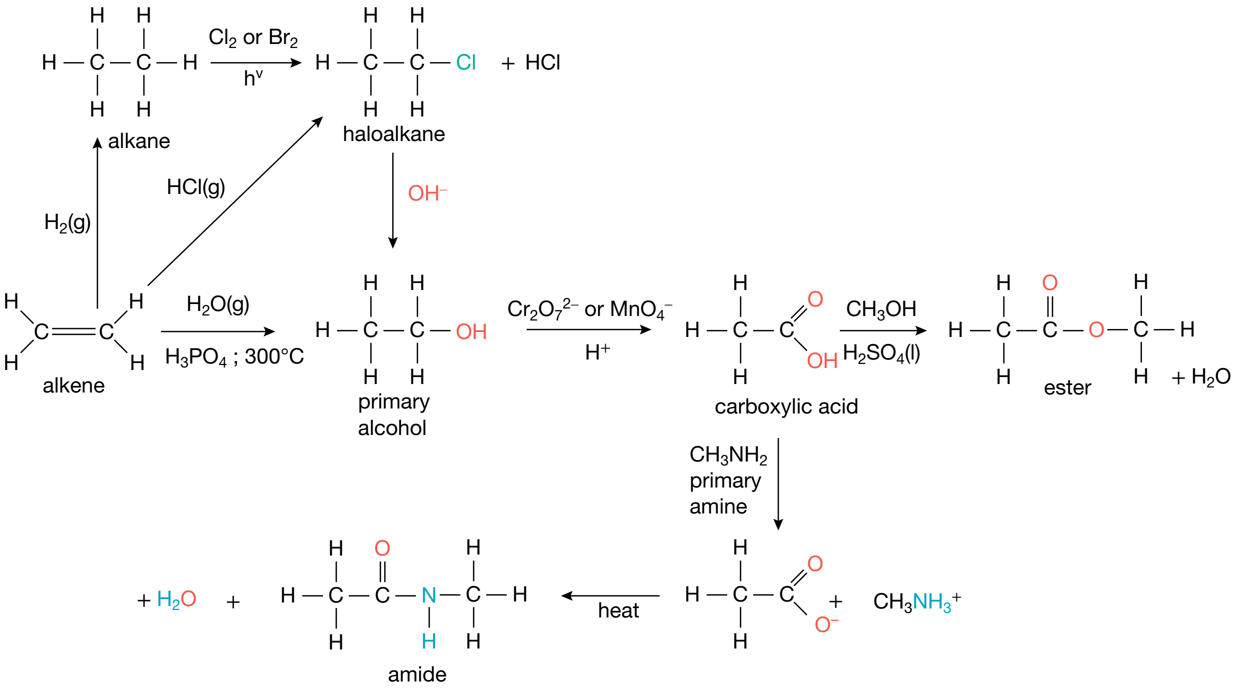
Amides can be made from the reaction between primary amines and the carboxylic acids.

Esters and amides from alkanes

To arrive at the carboxylic acid and primary alcohol reactants from alkanes, reactive haloalkanes are required as precursors. The further down the group a halogen is, the faster the rate of reaction when OH^- replaces it. For example, part of a primary haloalkane, Br, is 500 times more reactive than Cl, which means it is a lot easier to substitute OH^- for Br^- than it is Cl^-. Nonetheless, Cl can still readily leave the molecule and be replaced by OH^-. For tertiary haloalkanes, which are far more reactive than primary haloalkanes, the halogens are all reactive and are easily substituted out.

As seen earlier, substituted haloalkanes are prepared using diatomic halogens and UV light to catalyse the reaction.

FIGURE 9.25 Organic reactions pathways summary



on Resources

Interactivity Identifying compounds in reaction pathways (int-1236)

9.4 EXERCISE

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1. Ethanol is used in alcoholic drinks and as a fuel and a solvent. Write the structural equations for the chemical reactions involved in the three ways that ethanol can be produced.
2. Describe the steps involved in producing the flavouring ethyl ethanoate, commencing with ethane.
3. 30.3 g of ethanoic acid, CH_3COOH, is obtained from the oxidation of 26.8 g of ethanol, C_2H_5OH. What is the percentage yield?
4. The complete combustion of 82.2 g of propane produces a 73.2% yield. How many grams of CO_2 would be produced?
5. Ethanol is manufactured industrially by reacting ethene with steam.

$$H_2C{=}CH_2(g) + H_2O(g) \rightarrow CH_3CH_2OH(g)$$

What is the % atom economy for this reaction?

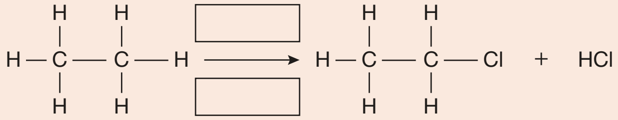
6. Two methods of producing hydrogen are shown below. Which has the higher % atom economy?

$$\text{Method 1: } CH_4(g) + H_2O(g) \rightarrow CO(g) + 3H_2(g)$$

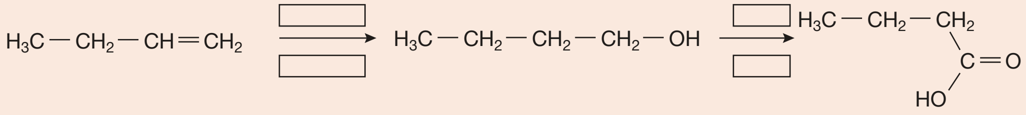
$$\text{Method 2: } C(s) + H_2O(g) \rightarrow CO(g) + H_2(g)$$

7. Starting with but-2-ene, draw a reaction pathway for the production of butanone.
8. Describe how 2-chloropropane could be used to synthesise:
   (a) propanone
   (b) propan-2-amine.
9. List the catalyst used in the following reactions:
   (a) chloroethane used to make ethanamine
   (b) propanal to make propanoic acid
   (c) propan-1-ol and ethanoic acid to make propyl ethanoate
   (d) prop-1-ene used to make propan-1-ol.
10. Fill in the boxes to complete the reaction pathways.

(a)



(b)



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9.5 Review

9.5.1 Summary

Overview

- Natural and synthetic pathways can range from single to multi-step procedures.
- Chemists and engineers are looking to reduce waste and improve materials by developing more efficient pathways.
- Many physical and chemical properties of materials and medicines can be altered using alternate structures and pathways.

Explaining trends in physical properties

- The boiling points and other physical properties of organic compounds are influenced by the size, shape, structure and degree of polarisation of their covalent bonds.
- The intermolecular forces involved are dispersion forces, dipole–dipole attractions and hydrogen bonding.
- Viscosity is a measure of how well liquids flow with higher values, meaning slower flow rate. Viscosity increases with molecular weight but decreases with increasing temperature.
- Flashpoint is the temperature at which there is a high enough concentration of vapours to support combustion of fuels. The weaker the intermolecular forces, the lower the flashpoint.

- General trends in a homologous series see an increase in boiling point, flashpoint and viscosity but decreased solubility in water as more carbon and hydrogen are added to the parent chain. Adding electronegative atoms to asymmetrical polarity increases solubility in water.
- Alkanes, alkenes and alkynes consist of non-polar molecules. Smaller molecular mass hydrocarbons are gases, and their boiling points increase with size due to the increased effect of dispersion forces.

  They are also insoluble in water but soluble in organic solvents. They are colourless and have low density.
- Alcohols are flammable and form hydrogen bonds with adjacent molecules. As a result, the smaller alcohols are liquids at room temperature and soluble in water. Solubility deceases with increasing chain length, whereas boiling point increases.
- Carboxylic acids form stronger hydrogen bonds than alcohols because their $-$OH group is more polarised due to the presence of the electron-withdrawing group C$=$O. The $-$COOH group is more acidic than the $-$OH group of alcohols, but carboxylic acids are much weaker acids than inorganic acids such as sulfuric acid.
- Aldehydes with lower molar mass have an unpleasant smell, but those with higher molar mass have a pleasant smell. Aldehydes and ketones have lower boiling points than alcohols because, although the C$=$O (carbonyl group) is polar, they do not have a hydroxyl group and so do not form hydrogen bonds between molecules.
- Esters are volatile liquids at room temperature. Smaller molecules are polar and soluble in water, but their solubility decreases with increased size.

Organic reactions

- All alkanes and alkenes undergo complete combustion with excess oxygen to produce carbon dioxide and water. The exothermic nature of these reactions is the reason for the use of these hydrocarbons as fuels.
- Alkanes undergo substitution reactions with halogens to produce a range of haloalkanes.
- Alkenes are more reactive than alkanes (because of the C$=$C double bond) and undergo addition reactions with a wide range of substances.
- Alcohols burn in air to form carbon dioxide and water. They undergo substitution reactions (e.g. with ammonia to form amines).
- Primary alcohols are oxidised to aldehydes and then to carboxylic acids using acidified dichromate or permanganate ions.
- Secondary alcohols are oxidised to ketones but do not undergo further oxidation. Tertiary alcohols cannot be oxidised.
- Carboxylic acids are weak acids that undergo reactions with metals, bases and metal carbonates.
- Carboxylic acids react with amines in acid–base reactions, followed by dehydration to form amides.
- Esters are formed by condensation reactions between alcohols and carboxylic acids in the presence of heat and an acid catalyst. A water molecule is eliminated in the process.

Reaction pathways

- The percentage yield is the amount of product produced from a given amount of raw materials. It is calculated using the formula:

$$\%\text{ yield} = \frac{\text{actual yield}}{\text{theoretical yield}} \times \frac{100}{1}$$

- Atom economy is another method of measuring the efficiency of a reaction that takes into account the amount of waste produced. It is a measure of the amount of reactants that become useful products. It is calculated using the formula:

$$\%\text{ atom economy} = \frac{\text{molar mass of desired product}}{\text{molar mass of all reactants}} \times \frac{100}{1}$$

- Pathways you should be familiar with are:
  - synthesis of primary alcohols, aldehydes and carboxylic acids from alkanes and alkenes
  - synthesis of ketones from haloalkanes
  - synthesis of esters from alkanes and alkenes
  - synthesis of amides from carboxylic acids.

Resources

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9.5.2 Key terms

addition reactions reactions in which one molecule bonds covalently with another molecule without losing any other atoms

atom economy measurement of the efficiency of a reaction that considers the amount of waste produced by calculating the percentage of the molar mass of the desired product compared to the molar mass of all reactants

condensation reactions reactions in which molecules react and link together by covalent bonding with the elimination of a small molecule, such as water or hydrogen chloride, from the bond that is formed

esterification the process of ester formation

flashpoint the temperature at which a particular organic compound gives off sufficient vapour to ignite in air

percentage yield measurement of the efficiency of a reaction by calculating the percentage of the actual yield compared to the theoretical yield

primary alcohols alcohols in which the carbon atom that carries the —OH group is attached to only one alkyl group

secondary alcohols alcohols in which the carbon atom that carries the —OH group attached is joined directly to two alkyl groups, which may be the same or different

substitution reactions reactions in which one or more atoms of a molecule are replaced by different atoms

viscosity a measure of a fluid's resistance to flow

Resources

Digital documents Key terms glossary – Topic 9 (doc-31415)

9.5.3 Practical work and experiments

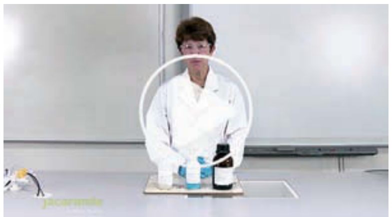
Experiment 9.2

Esterification

Aim: To prepare a small amount of the ester ethyl ethanoate from ethanol and ethanoic acid

Digital document: doc-31271

Teacher-led video: tlvd-0757



on Resources

Digital documents Practical investigation logbook (doc-31416)

Experiment 9.1 Comparing physical properties of alkanes, haloalkanes, alcohols and esters (doc-31270)

9.5 Exercises

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9.5 Exercise 1: Multiple choice questions

1. Which properties are generally characteristic of hydrocarbons?
   - A. Low melting point and soluble in polar solvents
   - B. High melting point and soluble in polar solvents
   - C. Low melting point and insoluble in polar solvents
   - D. High melting point and insoluble in nonpolar solvents
2. Which of the following alkanes would you expect to have the lowest melting point?
   - A. Octane
   - B. Propane
   - C. Pentane
   - D. Butane
3. The lowest temperature at which a material produces a flammable vapour describes:
   - A. auto ignition temperature
   - B. flashpoint
   - C. fire point
   - D. ignition temperature.
4. Which of the following is the most soluble in water?
   - A. $CH_3CH_2CH_2OH$
   - B. CH_3CH_2OH
   - C. $CH_3CH_2CH_3$
   - D. CH_3CH_3Cl
5. Which of the following compounds can form hydrogen bonds between its molecules?
   - A. $CH_3CH_2OCH_2CH_3$
   - B. $CH_3CH_2CH_2F$
   - C. $CH_3CH_2N(CH_3)_2$
   - D. $CH_3CH_2CH_2OH$
6. Which of the following has the greatest solubility in octane?
   - A. Octanol
   - B. Propylamine
   - C. Pentane
   - D. Ethanoic acid
7. What is the following reaction is an example of?

$$CH_2CH_2 + HCl \rightarrow CH_3CH_2Cl$$

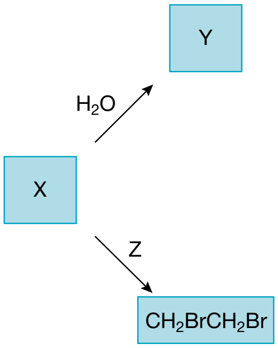
   - A. An addition reaction
   - B. A substitution reaction
   - C. A condensation reaction
   - D. A combustion reaction

8. If a secondary alcohol is oxidised it produces:
   - A. a ketone
   - B. an aldehyde
   - C. a carboxylic acid
   - D. initially an aldehyde that reacts further to form a carboxylic acid.
9. Which of the following reaction pathways used to produce ethanamine has the greatest percentage atom economy?
   - A. $C_2H_4 + H_2O \rightarrow C_2H_5OH$
     $C_2H_5OH + NH_3 \rightarrow C_2H_5NH_2 + H_2O$
   - B. $C_2H_5Cl + NH_3 \rightarrow C_2H_5NH_2 + HCl$
   - C. $C_2H_6 + Cl_2 \rightarrow C_2H_5Cl + HCl$
     $C_2H_5Cl + NH_3 \rightarrow C_2H_5NH_2 + HCl$
   - D. $C_2H_5Cl + NaOH \rightarrow C_2H_5OH + NaCl$
     $C_2H_5OH + NH_3 \rightarrow C_2H_5NH_2 + H_2O$
10. If the theoretical yield for a reaction to produce propanoic acid is 126 g and 95.0 g of the product is actually made, what is the percentage yield?
    - A. 132%
    - B. 32.6%
    - C. 75.4%
    - D. 24.6%

9.5 Exercise 2: Short answer questions

1. Describe the intermolecular forces acting between the following molecules.
   - a. CH_3Cl
   - b. CH_3OCH_3
   - c. CBr_4
   - d. $CH_3CH_2NH_2$
   - e. H_2CCH_2
   - f. $CH_3CH_2CH_2CH_2CH_2CHO$
   - g. *cis*–CH_2Cl_2
   - h. HCOOH
2. The molar masses of propan-1-ol and butane are similar. Which would you expect to have the higher boiling point? Explain your answer.
3. What is a substitution reaction? Write the equations of methane reacting with bromine and all the possible products formed.
4. Write equations for the reactions between:
   - a. ethene and HI
   - b. propene and H_2 (Pt catalyst)
   - c. ethene and Br_2
   - d. but-1-ene and Cl_2
   - e. methane and excess O_2
   - f. ethane and Cl_2
   - g. ethene and H_2O
   - h. but-2-ene and H_2.

5. Write the formulas for substances X, Y and Z shown in the following diagram.



6. What type of reaction is the esterification process? What are the reactants and products?
7. Carboxylic acids can be made from alkanes. Describe the stages and products formed in the conversion of ethane to ethanoic acid. Draw structures and name the products at each stage.
8. When 11.5 g of methanol was treated with excess acidified permanganate, 13.2 g of methanoic acid was obtained. Balance the following equation by first balancing the relevant half-equations, and then calculate the percentage yield.

$$CH_3OH + MnO_4^- \rightarrow HCOOH + Mn^{2+}$$

9. 2-methylpropan-1-ol can be used to manufacture diesel and jet fuel. The first step in the process is the production of 2-methylpropene (C_4H_8).

$$\underset{\text{2-methylpropan-1-ol}}{C_4H_{10}O(l)} \rightarrow \underset{\text{2-methylpropene}}{C_4H_8(g)} + H_2O(g)$$

Calculate the % atom economy for this reaction.

10. Explain why the atom economy of the following reaction is 100%.

$$H_2C{=}CH_2 + H_2O \rightarrow CH_3CH_2OH$$

9.5 Exercise 3: Exam practice questions

Question 1 (1 mark)

Which of the following would not distinguish between the colourless and odourless butan-1-ol and butan-2-ol?

A. Reaction with acidified $KMnO_4$ and then pH test
B. Boiling point
C. Flashpoint
D. Electrical conductivity

Question 2 (1 mark)

Which of the following compounds will be produced by the reaction between $CH_3CH_2CH_2OH$ and HCOOH in the presence of concentrated sulfuric acid?

A. Propanone
B. Propyl methanoate
C. Methyl propanaoate
D. Propanal

Use the following information to answer questions **3** *and* **4**.

A student decided to test the flammability of two esters. The student took a 50.0 g sample of each liquid, placed them on a hot plate and heated them gradually until they ignited in the air when a flame was passed over each sample. The first ester was methyl methanoate and the second was pentyl pentanoate.

Question 3 (1 mark)

Which of the following statements is not true?

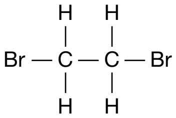
A. The student is measuring the flashpoint of each liquid.
B. The independent variable is the temperature at which the fuel ignites.
C. The methyl methanoate will ignite at a lower temperature.
D. Methyl methanoate is more volatile than pentyl pentanoate.

Question 4 (1 mark)

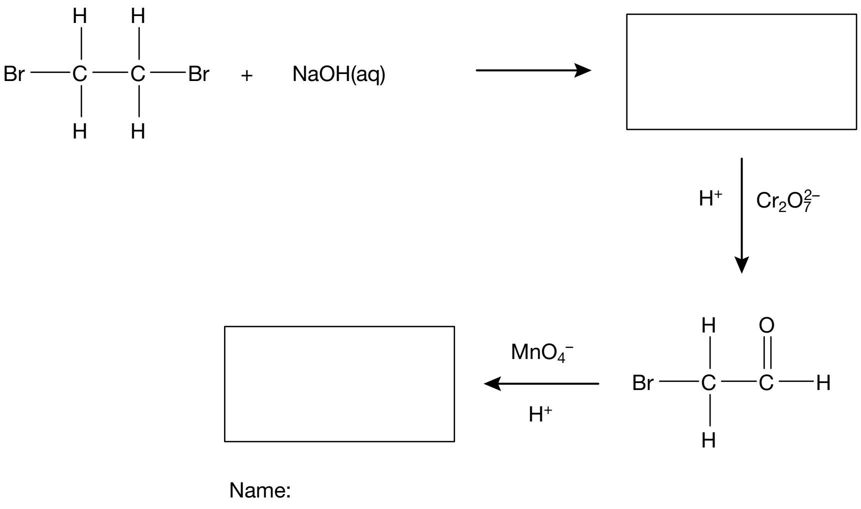
Calculate the mass of CO_2 produced when 50.0 g of methyl methanoate is completely combusted.

Question 5 (8 marks)

Haloalkanes have many uses ranging from solvents to fumigants. One particular haloalkane used to control termites is shown below.



a. Write equations to show the production of the haloalkane using ethane as a starting material. **2 marks**
b. Write the IUPAC name of the haloalkane used to control termites. **1 mark**
c. What is the percentage atom economy from the production of the haloalkane from ethane? **1 mark**
d. Write a chemical equation for the production of the haloalkane that would result in a 100% atom economy. **1 mark**
e. Haloalkanes also make excellent starting materials for the production of other chemicals used in industry.
  i. Complete the following reaction pathway by drawing the structures of molecules in the empty boxes. **2 marks**



  ii. Give the IUPAC name of the final product. **1 mark**

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10 Analysis of organic compounds

10.1 Overview

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10.1.1 Introduction

FIGURE 10.1 MRI is based on the principles of NMR, a spectroscopic technique used to study the structure of molecules.

The advances in our ability to qualitatively and quantitatively analyse chemical compounds have allowed research and technology to progress at an extraordinary pace. We are able to take advantage of the interactions between electromagnetic radiation and matter as well as the different interactions between matter itself. Doctors use magnetic resonance imaging (MRI) to investigate physical disorders without surgery. Images are created by a signal from flipping proton spins (hydrogen nuclei) in water molecules or fat molecules using a magnetic field and radio waves. As our bodies are 60 to 70% water, water-containing tissue appears white in an MRI, whereas bones with lower water content are much darker. MRI is based on the principles of NMR, a spectroscopic technique often used to obtain information about the structure of molecules.

The analysis of organic compounds in this topic covers qualitative spectroscopic techniques and analysis by chromatography and titration. You will revisit HPLC and acid-base titration analysis as well as learn about new techniques such as nuclear magnetic resonance (NMR), and infrared (IR) and mass spectroscopy (MS). The power of the instrumental techniques in combination allows for the identification of organic compounds and the amounts present in samples. These techniques are commonly used in the medical, food and pharmaceutical industries as well as forensics.

You will learn how to deduce the structure of simple organic compounds containing groups such as the amino, hydroxyl and carbonyl from spectra, and investigate how matter responds to different types of electromagnetic radiation. Chromatography and acid-base and redox titration will be used for quantitative analysis of organic compounds. In the case of HPLC, retention time will be used to identify the presence of chemicals in a mixture.

10.1.2 What you will learn

KEY KNOWLEDGE

In this topic, you will investigate:

- the principles and applications of mass spectroscopy (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 spectroscopy (IR) (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 spectroscopy (NMR) (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 peak and peak splitting patterns (excluding coupling constants) and application of the n+1 rule
- determination of the structures of simple organic compounds are determined using a combination of mass spectrometry (MS), infrared spectroscopy (IR) and proton and carbon-13 nuclear magnetic resonance spectroscopy (NMR) (limited to data analysis)
- 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
- how the concentration of an organic compound is determined by volumetric analysis, including the principles of direct acid-base and redox titrations (excluding back titrations).

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PRACTICAL WORK AND INVESTIGATIONS

Practical work is a central component of learning and assessment. Experiments and investigations, supported by a **Practical investigation logbook** and **Teacher-led videos**, are included in this topic to provide opportunities to undertake investigations and communicate findings.

on Resources

Digital documents Key science skills (doc-30903)
Key terms glossary – Topic 10 (doc-31429)
Practical investigation logbook (doc-31430)

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10.2 Mass spectrometry

KEY CONCEPT

- The principles and applications of mass spectroscopy (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

10.2.1 Principles of mass spectroscopy

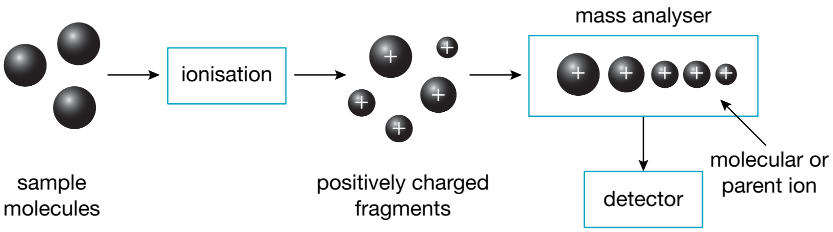
Mass spectrometry is a technique that can be used to determine the structures of molecules, and its applications are numerous. Mass spectrometry can be used to determine the structures of biomolecules, and detect drugs, explosives, toxins in seafood, oil deposits in rocks and impurities in steel, in space exploration and radiocarbon dating of fossils.

Mass spectrometry is not strictly **spectroscopy** because it does not use electromagnetic radiation. Instead, molecules are bombarded by high-energy electrons, and the positive ions formed in this process then undergo fragmentation. The output is a mass spectrum that plots the mass/charge ratio (*m/z*) versus the abundance of each fragment. The most abundant peak is assigned a value of 100%. Only milligrams of a sample are required for the analysis, but the sample is destroyed in the process.

Molecular ion formation and detection

A mass spectrometer detects ions formed from atoms and molecules to determine their mass and charge. It does this by detecting the path of the ionised substance through a magnetic field.

FIGURE 10.2 Fragmentation in a mass spectrometer



When a compound is analysed in a mass spectrometer, most of the molecule breaks up into smaller fragments, called fragment ions. Identification of the fragment ions can help determine the structure of the original molecule. The few remaining whole molecules produce ions with a peak at the relative molecular mass of the compound, even though this might be small due to extensive fragmentation. The ion represented by this peak is called the parent, or molecular, ion. Each line in the spectrum represents a positive ion with a specific *m/z* ratio.

$$\begin{aligned} M(\mathrm{g}) + \mathrm{e}^- &\rightarrow M^+(\mathrm{g}) + 2\mathrm{e}^- \\ M^+(\mathrm{g}) &\rightarrow P^+(\mathrm{g}) + Q\bullet(\mathrm{g}) \end{aligned}$$

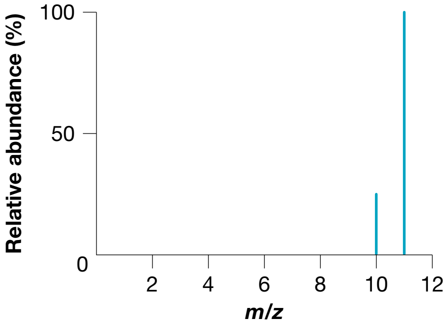
M^+ is the parent or **molecular ion**, which breaks down to P^+ and $Q\bullet$. The charged fragment, P^+, is detected in the mass spectrometer. The uncharged (free radical) fragment, $Q\bullet$, is not detected. Mass spectrometers can be used in conjunction with high-performance liquid chromatography (HPLC) to further identify a peak in a chromatogram.

The mass spectrum

The output of a mass spectrometer is a mass spectrum that generally looks like a bar graph. Each column represents an ion with a specific *m/z* ratio. The height of the column shows the relative abundance.

Although the horizontal scale is technically mass/charge, the bulk of the positive ions produced have a single positive charge (+1). This means that the horizontal axis is effectively a mass scale. Mass spectrometry can be used to identify isotopes of an element and to determine molecular structures. The mass spectrum in figure 10.3 shows that boron has two isotopes and that the heavier isotope is more abundant.

FIGURE 10.3 A mass spectrometer readout for boron



Consider the mass spectrum of propane (see figure 10.4b). Observe how each fragment ion produces a specific peak. The most abundant ion is known as the **base peak** and is usually assigned a height of 100%. This is the most common fragment, either because it is the most stable or because it can be formed in different ways. It is not always required to identify every peak in the spectrum.

FIGURE 10.4 (a) Structural formula and (b) mass spectrum for propane

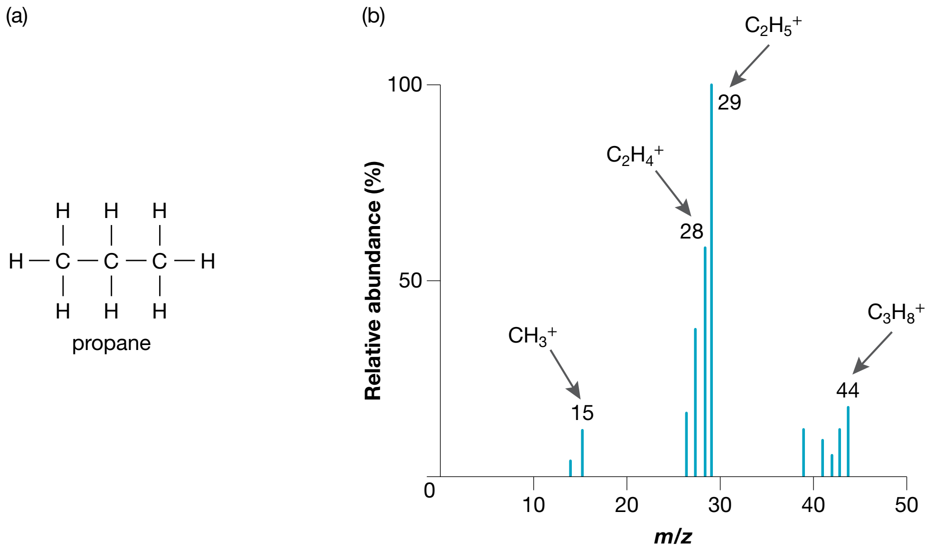


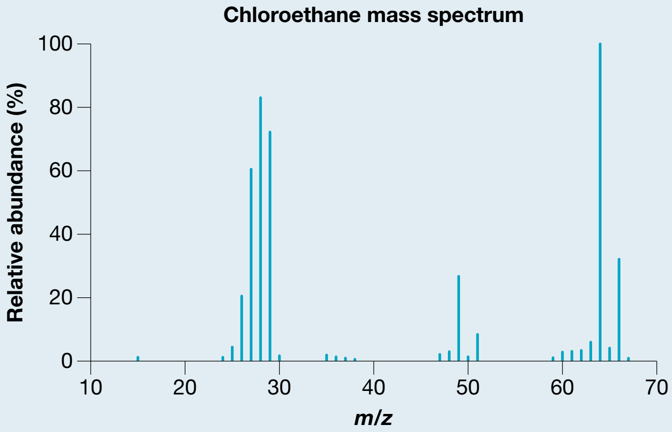
Table 10.1 shows *m/z* ratios for some small ions that may be observed in a mass spectrum. Sometimes, it is easier to determine the fragment by subtracting the fragment that is lost (e.g. subtracting 15 from the molecular mass suggests that a methyl group, CH_3, was part of the molecule).

TABLE 10.1 *m/z* values for small ions

m/z	Positively charged fragment
15	CH_3^+
17	OH^+
18	H_2O^+
19	H_3O^+, F^+
26	$C_2H_2^+$, CN^+
27	$C_2H_3^+$
28	$C_2H_4^+$, CO^+
29	$C_2H_5^+$, CHO^+
30	$CH_2NH_2^+$
31	CH_3O^+
35 (37)	$^{35}Cl^+$ ($^{37}Cl^+$)

SAMPLE PROBLEM 1

The following diagram shows the mass spectrum for chloroethane, C_2H_5Cl. What ions are responsible for the peaks at *m/z* = 66 and 64, 49 and 51, 29 and 28?

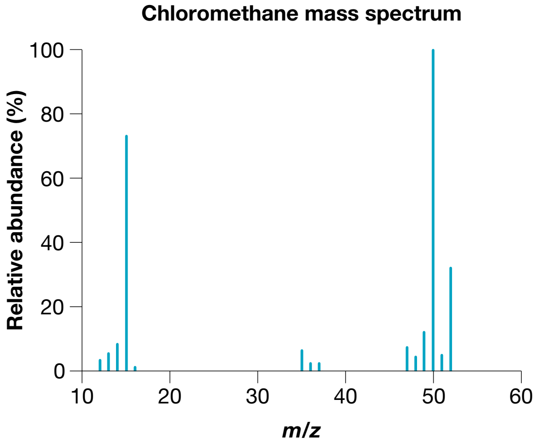


Teacher-led video: SP1 (tlvd-0713)

THINK	WRITE
1. Determine the molecular mass of chloroethane remembering chorine has two isotopes: ^{35}Cl and ^{37}Cl.	$M(C_2H_5{}^{35}Cl) = (2 \times 12.0) + (5 \times 1.0) + (35)$ $= 64$ $M(C_2H_5{}^{37}Cl) = (2 \times 12.0) + (5 \times 1.0) + (37)$ $= 66$
2. Check for isotope peaks (e.g. for carbon and chlorine).	The peak at $m/z = 64$ corresponds to $[C_2H_5{}^{35}Cl]^+$. The peak at $m/z = 66$ corresponds to $[C_2H_5{}^{37}Cl]^+$.
3. Look for gaps of 15 lost from the molecular ion, showing the loss of a methyl group, $[CH_3]$, to identify fragments.	$64 - 15 = 49$ corresponds to $[C_2H_5{}^{35}Cl]^+ - .CH_3 = [CH_2{}^{35}Cl]^+$. Hence, $[CH_2{}^{35}Cl]^+$ shows a peak at $m/z = 49$. $66 - 15 = 51$ corresponds to $[C_2H_5{}^{37}Cl]^+ - .CH_3 = [CH_2{}^{37}Cl]^+$. Hence, $[CH_2{}^{37}Cl]^+$ shows a peak at $m/z = 51$.
4. Identify any other fragments (table 10.1 may assist) and calculate the masses to confirm the peaks observed.	$[C_2H_5]^+$ occurs at $m/z = 29$, and the peak for $[C_2H_4]^+$ occurs at $m/z = 28$.
5. Write a concluding statement.	$m/z = 64$ corresponds to $[C_2H_5{}^{35}Cl]$ $m/z = 66$ corresponds to $[C_2H_5{}^{37}Cl]$ $m/z = 49$ corresponds to $[CH_2{}^{35}Cl]^+$ $m/z = 51$ corresponds to $[CH_2{}^{37}Cl]^+$ $m/z = 29$ corresponds to $[C_2H_5]^+$ $m/z = 28$ corresponds to $[C_2H_4]^+$

PRACTICE PROBLEM 1

The following spectrum is for chloromethane (CH_3Cl). What ions are responsible for the peaks at *m/z* = 52, 50 and 15?



TIP: When writing equations involving the production of ions in mass spectra, ensure detected ions have a positive charge and that the states in equations are gaseous (g).

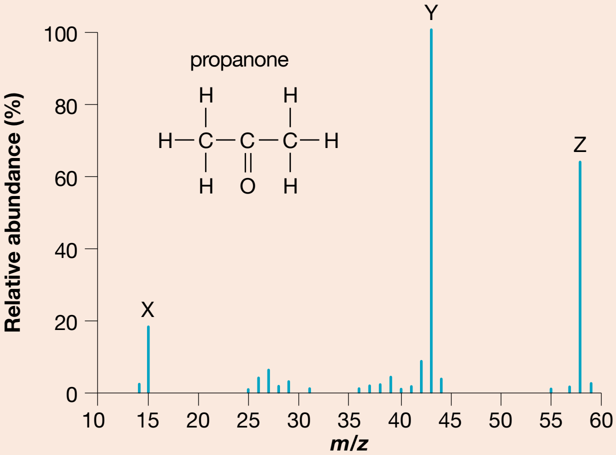
on Resources

Interactivity Interpreting a mass spectrum (int-1230)

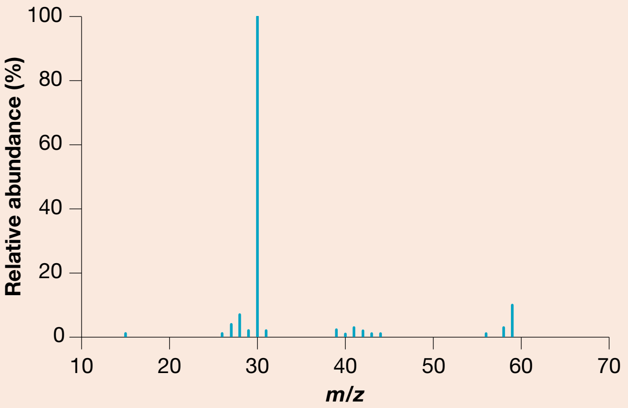
10.2 EXERCISE

To answer questions online and to receive **immediate feedback** and **sample responses** for every question go to your learnON title at www.jacplus.com.au.

1. Explain how mass spectra are produced.
2. What is the difference between the molecular ion peak and base peak?
3. If the relative intensity of the base peak is 100 and the molecular ion has a relative intensity of 50, what does this tell you about the abundance of each?
4. Why can the *m/z* ratio on a mass spectrum be thought of as a mass scale?
5. Write an equation for the molecular ion formation of ethanoic acid in a mass spectrometer.
6. Write an equation for the fragmentation of the ethanoic acid molecular ion into CH_3CO^+.
7. Propanone, commonly called acetone, CH_3COCH_3, is an important solvent in industry. In a mass spectrometer, propanone breaks down into a series of fragment ions.
   (a) Which peak corresponds to $CH_3{-}CO{-}CH_3{}^+$?
   (b) Identify which fragment ions correspond to the other labelled peaks.

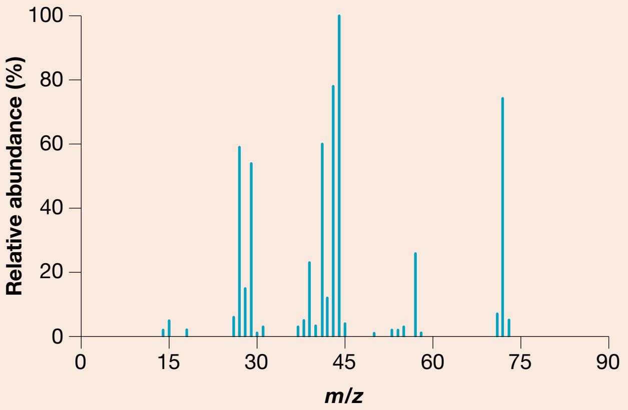


8. A molecule with the formula C_3H_9N produced the following mass spectrum.



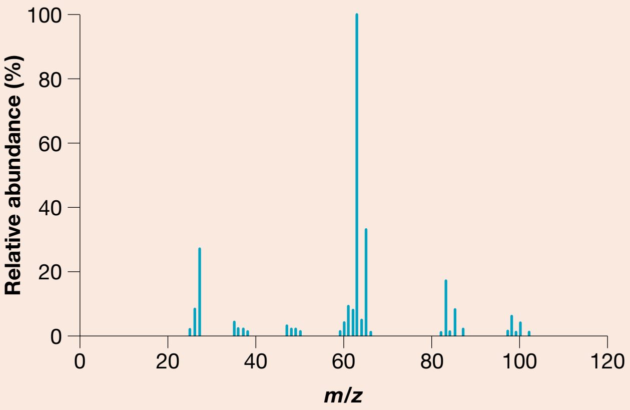
(a) What is the *m/z* ratio of the molecular ion?
(b) What is the *m/z* ratio of the base peak?
(c) Write the formula of the molecular ion.
(d) Write the formula of the fragment that produced the base peak.
(e) Write an equation for the formation of the base peak from the molecular ion.

9. The following mass spectrum is produced by an aldehyde.



(a) Write the *m/z* that would be caused by the aldehyde functional group.
(b) Write the formula of the fragment responsible for *m/z* = 43.
(c) What is the peak at *m/z* = 43 called?
(d) Name the aldehyde that produced this spectrum. Justify your answer by referring to peaks on the spectrum.

10. A compound with the empirical formula CH_2Cl produced the following spectrum.



(a) Write the molecular formula of the compound
(b) Explain the presence of three molecular ion peaks.
(c) Write an equation for the formation of the most abundant molecular ion.
(d) Draw the structure of the molecule that produced this spectrum. Justify your answer by referring to the mass spectrum.

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10.3 Infrared spectroscopy

KEY CONCEPT

- The principles and applications of infrared spectroscopy (IR) (excluding features of instrumentation and operation) and interpretation of qualitative and quantitative data including use of characteristic absorption bands to identify bonds

10.3.1 Principles of infrared spectroscopy

Infrared (IR) spectroscopy identifies the functional groups and single, double and triple bonds in organic molecules. This **qualitative analysis** method measures the characteristic amount of energy that the bonds between atoms in a molecule absorb when exposed to radiation in the infrared portion of the electromagnetic spectrum.

Covalent bonds can be likened to springs in that they can bend, stretch and vibrate in a number of different ways. These produce what are called vibrational energy levels. Just as the electrons in atoms have a number of allowed electronic energy levels, these vibrations have allowed vibrational energy levels. Therefore, it is possible to talk about 'ground-state' vibrational energy levels and 'excited-state' vibrational energy levels. A molecule can move from a lower to a higher vibrational energy level if it absorbs an amount of energy equal to the difference between levels. The region of the electromagnetic spectrum corresponding to such amounts of energy is the infrared region. All of this is affected by the type of bond. The amount of energy required for these transitions, and therefore the frequency (or wavelength), can give clues about the types of covalent bonds present.

One of the important pieces of information needed to identify an unknown organic compound is the type of functional groups within a molecule. Infrared spectroscopy can identify the following groups: $-\mathrm{CH}$ (alkyl groups), $-\mathrm{OH}$ (hydroxyl groups) and $\mathrm{C{=}O}$ (carbonyl groups). Infrared spectroscopy can also be used to determine if double or triple bonds are present in a molecule. Proteomics is the study of the structures and functions of proteins. Infrared spectroscopy was used to analyse proteins in human DNA as part of the Human Genome Project. The three-dimensional shapes of protein molecules can be easily and cheaply investigated by using infrared spectroscopy to study the $\mathrm{C{-}C}$ bonds, instead of using more complicated NMR spectroscopy.

INFRARED ASTRONOMY

This infrared photograph of the Trifid Nebula was taken by the Spitzer Space Telescope. The nebula is 5400 light-years away from Earth in the Sagittarius constellation. Visible-light telescopes cannot see into the nebula, but infrared cameras can detect infrared radiation coming from the nebula's interior, allowing us to 'see' what's inside it.

Infrared cameras take pictures using the infrared part of the electromagnetic spectrum. The differences in infrared wavelengths between parts of an object or between objects can be used to show different colours.

Infrared spectra

An IR spectrum looks upside down compared with a UV–visible or AAS spectrum. This is because it measures transmittance, which is the opposite of absorbance, on the vertical (y) axis. Unlike a UV–visible spectrum, which has a base line of zero absorbance running along the base of the graph, the IR spectrum has a base line of 100% transmittance running along the top of the graph, meaning that no light has been absorbed by the sample. A peak occurs in the UV–visible spectrum when energy is absorbed, whereas a dip appears in the IR spectrum when energy is absorbed. The IR spectrum measures wave number, which is the inverse of wavelength, on the horizontal (x) axis; wave number is proportional to frequency. As the wavelength increases, the wave number decreases. You studied these aspects of spectroscopy in Unit 2.

Nearly all molecules absorb IR radiation and it is largely a qualitative technique. The region above 1000 cm^{-1} can be used to identify the functional groups present. Tables exist to help identify peaks in this region and attribute them to certain types of bonds.

TABLE 10.2 Characteristic range for infrared absorption

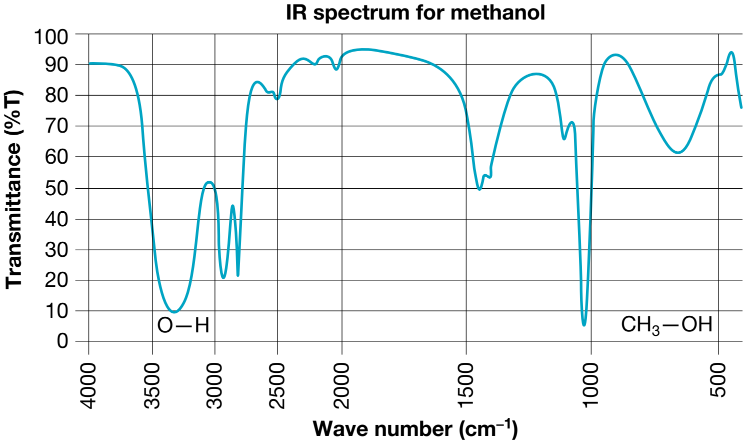
Bond	Wave number (cm^{-1})
C–C1 (chloroalkanes)	600–800
C–O (alcohols, esters, ethers)	1050–1410
C=C (alkenes)	1620–1680
C=O (amides)	1630–1680
C=O (aldehydes)	1660–1745
C=O (acids)	1680–1740
C=O (ketones)	1680–1850
C=O (esters)	1720–1840
C–H (alkanes, alkenes, arenes)	2850–3090
O–H (acids)	2500–3500
O–H (alcohols)	3200–3600
N–H (primary amines)	3350–3500

Source: VCAA 2018, *VCE Chemistry Data Book*, Version 2, June 2018, VCAA, Melbourne, table 14.

The IR spectrum for methanol in figure 10.5 shows characteristic peaks at 3300 cm^{-1} for –OH and 2950 cm^{-1} for –CH. The peak at 2950 cm^{-1}, indicating a C–H bond, is almost always present in organic molecules and is less helpful because it is not a characteristic identifier.

The lower end of an IR spectrum often looks like a series of peaks crowded together. This is called the **fingerprint region** of the spectrum. It is difficult to identify individual peaks caused by particular bonds, but the region is still useful in identifying the substance, because the region looks similar in any analysis of that substance.

FIGURE 10.5 This IR spectrum for methanol shows characteristic peaks at 3300 cm^{-1} for $-OH$ and 2950 cm^{-1} for $-CH$. The $-CH$ peak is almost always present in organic molecules and so is less helpful. Nearly every organic molecule has C—H bonds.



Most organic spectra contain peaks for C—H bonds in the same area, so how do we tell the different spectra apart?

Differences can be seen by comparing the spectra in figure 10.6 for ethanol, CH_3CH_2OH, and figure 10.7 for propan-1-ol, $CH_3CH_2CH_2OH$. The peaks for O—H at 3300 cm^{-1} and for C—H at 2900 cm^{-1} are clear in each of the spectra. However, there are many more peaks in the 1000–1100 cm^{-1} region for the longer molecule than the shorter molecule. This is because the C—H bonds adjacent to other C—H bonds, as in $CH_3CH_2CH_2OH$, affect each other. In addition to this, the electronegative oxygen atom affects the adjacent C—H bond, slightly polarising it towards the oxygen atom. This is because the oxygen atom draws the electrons in the C—O bond towards itself, making the carbon atom take on a slight positive charge. This partial, positive charge attracts the electrons in the C—H bond towards the C atom, making the C—H bond slightly polar. This alters the bond length and strength, making the bonds absorb and transmit IR at slightly different frequencies, so there are more peaks. The next C—H bond in the chain does not feel the same electrostatic attraction and so is not as affected.

FIGURE 10.6 IR spectrum for ethanol

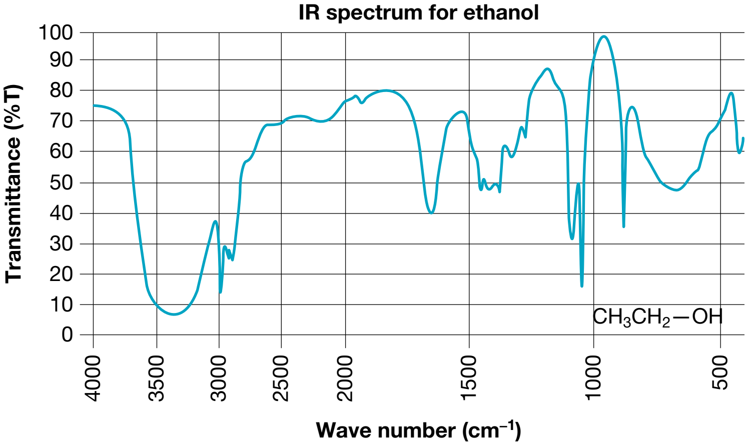


FIGURE 10.7 IR spectrum for propan-1-ol

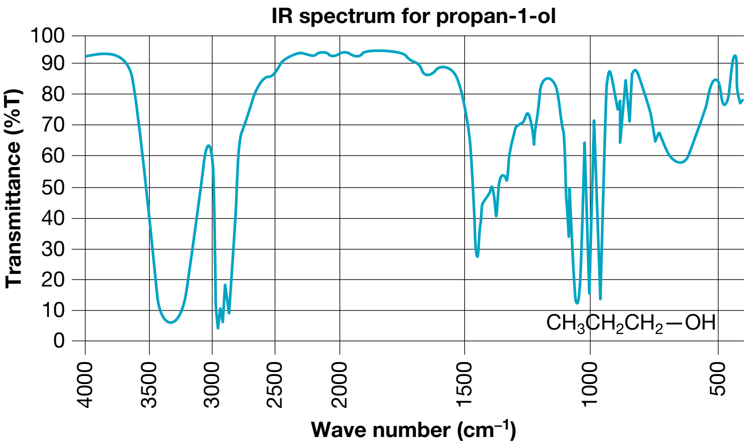


TABLE 10.3 Infrared band positions for selected functional groups

Functional group	–O–H (alcohols)	–O–H (carboxylic acids)	–C=O	–C–O–	–N–H
Infrared band position (cm^{-1})	3200–3550	2500–3300	1670–1750	1000–1300	3350–3500

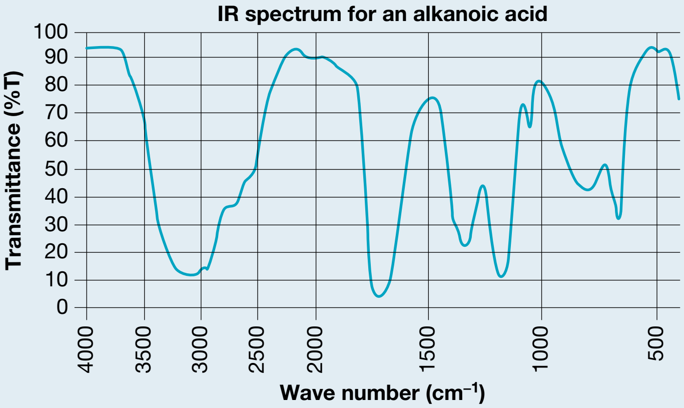
on Resources

Video eLesson Infrared spectroscopy (med-0349)

Interactivity Interpreting IR spectra (int-1229)

SAMPLE PROBLEM 2

Identify the major peaks in this IR spectrum for a molecule that has only one carbon atom in its molecular structure, and then identify the molecule.

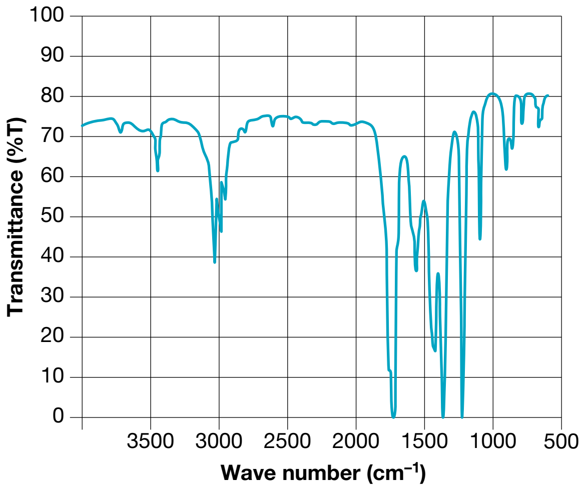


Teacher-led video: SP2 (tlvd-0714)

THINK	WRITE
1. Identify characteristic peaks caused by functional groups listed in table 14 of the VCE Chemistry Data Book.	The peak at approximately 1600–1750 cm^{-1} corresponds to C=O. The peak at approximately 2500–3200 cm^{-1} corresponds to O−H acids
2. Deduce a structure that must have both the C=O and O−H acid groups and contains one carbon atom only (as stated in the question).	Functional group must be −COOH.
3. Identify the molecule. The C atom in −COOH has one unbonded electron so it could be bonded to a H. The C−H peak at 2950 cm^{-1} is mostly hidden by the broad O−H peak. The structure is HCOOH.	The molecule must be HCOOH, methanoic acid.

PRACTICE PROBLEM 2

Identify the major peaks in this IR spectrum and deduce a structure for a molecule with the formula C_3H_6O.



TIP: O−H hydroxyl and O−H carboxyl are distinguished by OH(alcohols) and OH(acids) in the VCE Chemistry Data Book. When identifying −OH peaks you need to state which one you are referring to.

10.3 EXERCISE

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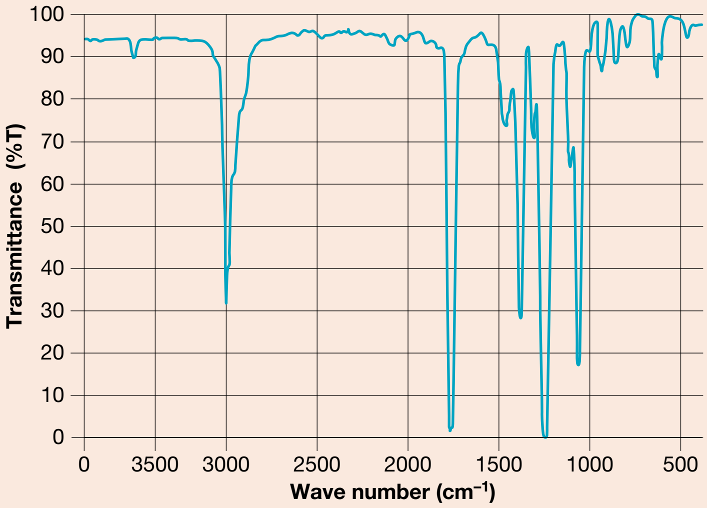
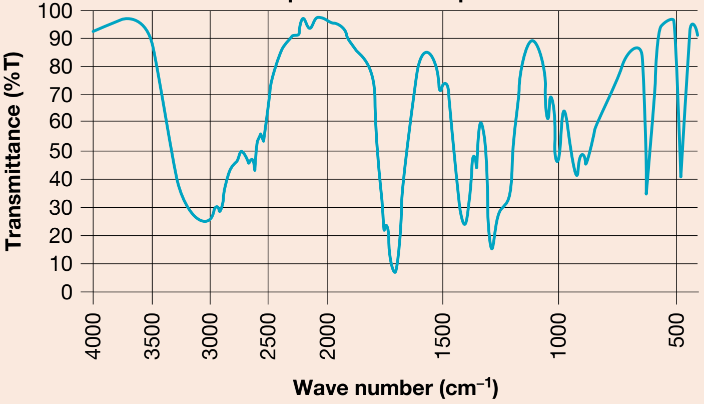
1. Describe the interaction between infrared light and covalent bonds.
2. With respect to the fingerprint region of an IR spectrum:
   (a) what trend would you observe in a homologous series?
   (b) how are fingerprint regions useful for identifying known substances?

3. The following infrared spectrum was produced by ethyl ethanoate. Identify the major peaks in the spectrum.

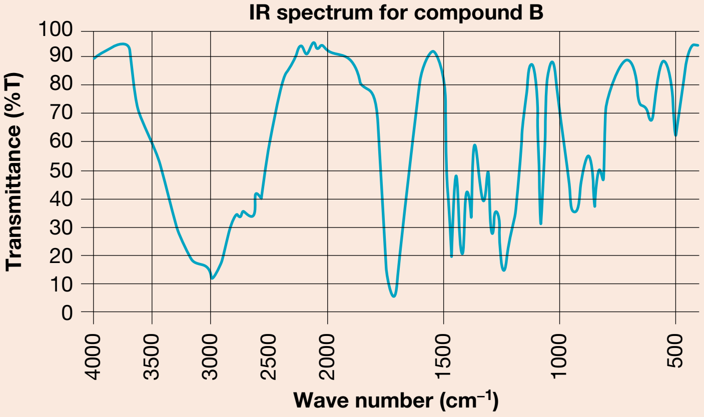


4. Examine the following IR spectra.

IR spectrum for compound A



IR spectrum for compound B

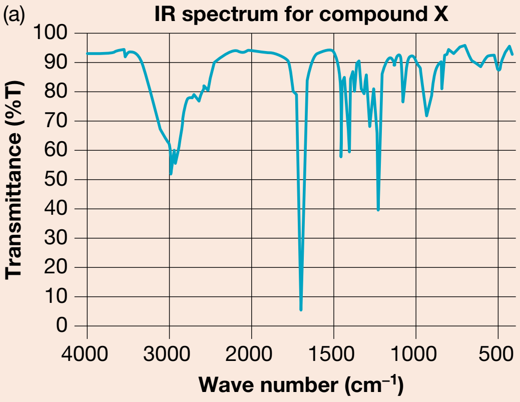


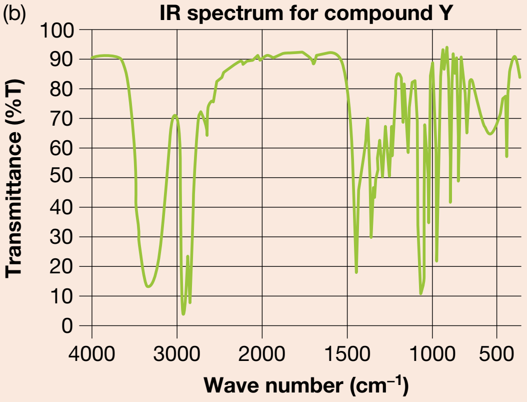
(a) Using table 10.2 or table 14 of the VCE Chemistry Data Book, identify the bonds responsible for the major peaks on each spectrum.

(b) By examining the peaks, determine which spectrum has the most C—H bonds.

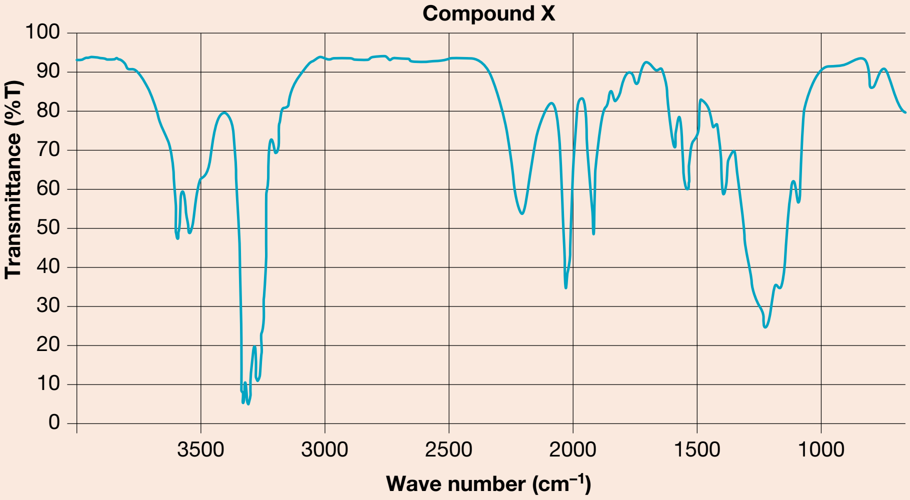
(c) Both substances were examined by mass spectrometry. The results confirmed that both of the molecules contained only carbon, hydrogen and oxygen. The molecular masses of the molecules were 60 and 74. Determine the possible molecular formulas of the two substances (i.e. deduce one possible molecular structure for each of the substances).

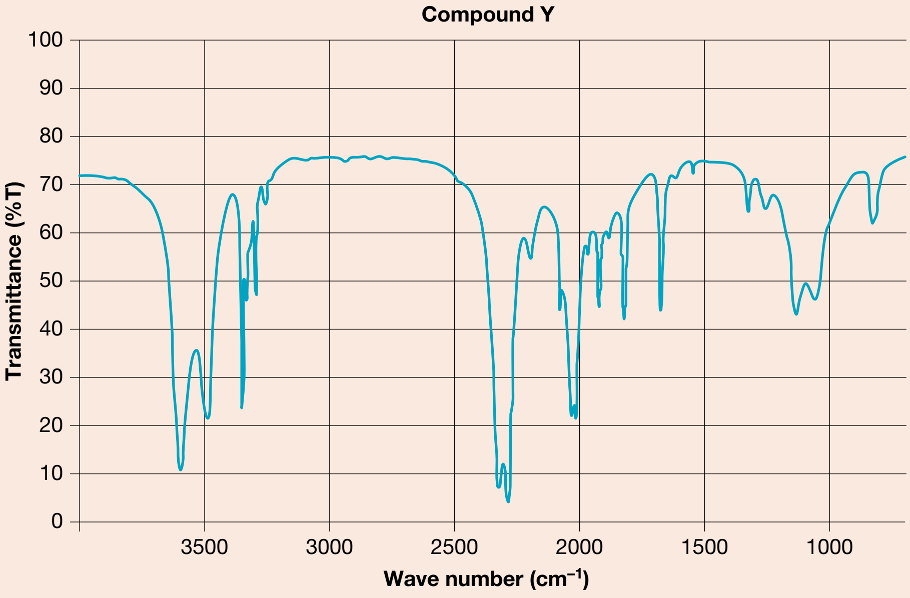
5. The following figure shows two infrared spectra for two different compounds, X and Y. Only one is a carboxylic acid; the other is an alcohol. Use table 10.2 to identify the spectrum corresponding to a carboxylic acid.





6. The following figure shows two IR spectra for two different compounds X and Y. Both compounds contain carbon, hydrogen and nitrogen but only one contains oxygen. Use table 10.2 or table 14 in the VCE Chemistry Data Book to identify the homologous series that compounds X and Y belong to.





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10.4 NMR spectroscopy

KEY CONCEPT

- The principles (including spin energy levels) and applications of proton and carbon-13 nuclear magnetic resonance spectroscopy (NMR) (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 peak and peak splitting patterns (excluding coupling constants) and application of the n+1 rule

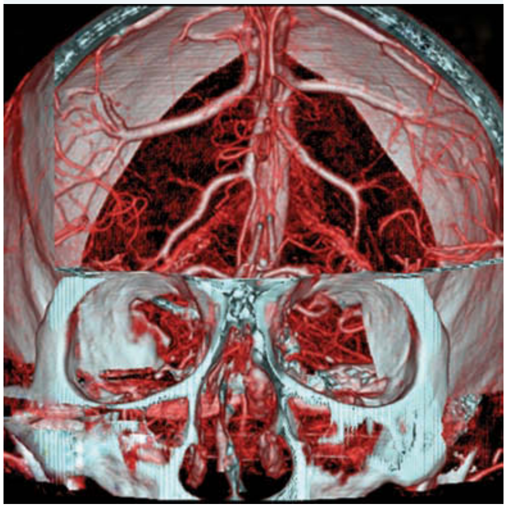
10.4.1 Principles of NMR spectroscopy

Nuclear magnetic resonance (NMR) images are called MRI scans in the medical field. MRI stands for magnetic resonance imaging. These images provide doctors with pictures of the soft tissues of the body. When NMR was introduced, many patients refused to have NMR scans because they thought it had something to do with being bombarded with radiation from a nuclear reactor. However, the word 'nuclear' in this case refers to the nucleus of an atom and how it interacts with a magnetic field. To alleviate patients' fears, NMR scanning is now called MRI.

Particles making up a nucleus exhibit properties called 'spin' and 'magnetic moment'. The combination of particular numbers of protons and neutrons give each nucleus an overall spin and magnetic moment, which responds to an applied magnetic field (see figure 10.9). NMR measures this response to give an indication of the connectivity of atoms in a molecule. It does this by recording the interaction of C and H nuclei with a magnetic field.

NMR is a qualitative analysis method. Some nuclei have two overall spin states and behave as if they are magnets spinning about their axes. ^{1}H and ^{13}C are two such nuclei. If a strong, external magnetic field is applied to such nuclei, these spinning magnets either align with the external field (to produce a slightly lower energy level) or align against it (to produce a slightly higher energy level). By absorbing the exact difference in energy between these two states, a nucleus can 'flip' between its lower and higher spin states. It then releases this same amount of energy when it 'relaxes' back to its lower state. The energy involved in these changes is in the radio frequency section of the electromagnetic spectrum. The energy difference between these two spin states depends on the strength of the external magnetic field that is 'felt' by the nucleus. This is not always the same as the external magnetic field because other atoms that surround a given nucleus can

FIGURE 10.8 A MRI scan showing the blood vessels in the brain



modify it in subtle, but important, ways. Therefore, the energy required for a nucleus to change its spin state depends on what is around it (its environment). The use of NMR can give valuable information about the connectivity of atoms in a molecule.

FIGURE 10.9 (a) Nuclear spin is random in the absence of a magnetic field B_0. (b) In the presence of a magnetic field, nuclear spin either aligns in the same direction as the magnetic field (red) or against the field (blue). The nuclei aligned with the magnetic field (lower energy) can absorb electromagnetic radiation of the correct frequency and flip to the higher energy state (against the magnetic field).

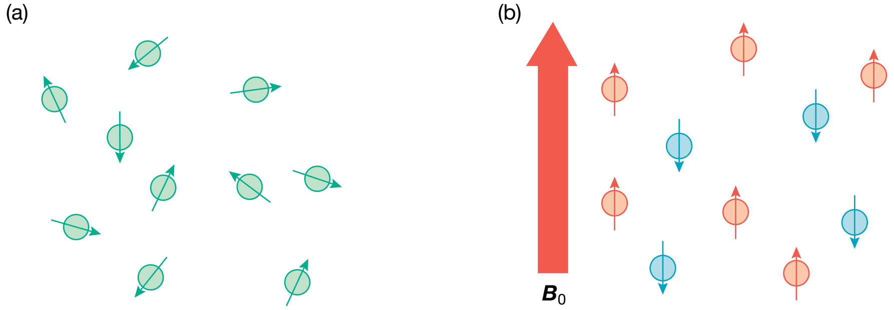
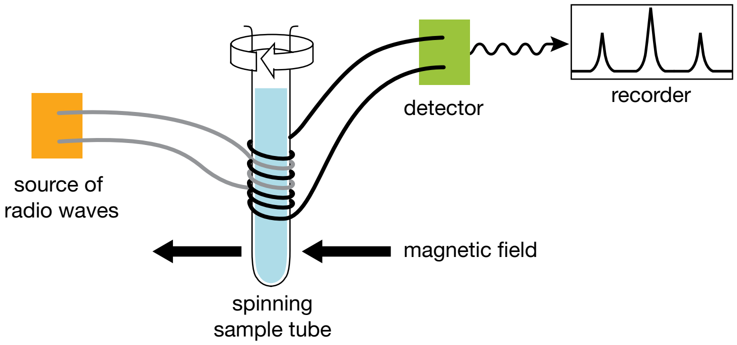


FIGURE 10.10 A schematic diagram of an NMR spectrometer



10.4.2 Chemical shift and NMR spectra

There are three main types of NMR spectra.

- Carbon-13 NMR (^{13}C)
- Low-resolution proton NMR (^{1}H)
- High-resolution proton NMR (^{1}H)

All of these produce spectra that show peak height versus chemical shift in ppm (parts per million). The horizontal scale is called '**chemical shift**' (δ); it starts from zero on the right and reads backwards. The zero reference point is taken from the chemical shift peak produced by tetramethylsilane, $(CH_3)_4Si$ or TMS, which is added to every sample; without this zero point, it would be impossible to know where to start the horizontal scale. The number of signals on the *x*-axis indicates the number of types of protons or carbons. The chemical shift or position of the peaks on the *x*-axis of the graph indicates the types of protons or carbons.

The two particles most commonly used in NMR analysis are carbon-13 atoms, ^{13}C, and protons, ^{1}H. Other atoms within an organic molecule can be analysed but examining the environments of the carbon atoms and protons reveals valuable information about the structure of the molecule under investigation.

Different functional groups are found at different characteristic chemical shifts on the NMR spectrum. Comparison with a table of the chemical shifts enables identification of the group. Either carbon or hydrogen may be the subject of the NMR scan, and each set of data lends different information to the analysis. Depending on the solvent used in the analysis, a signal may also be found for the carbon or hydrogen atoms in that solvent.

Chemical shift is influenced by the electrons surrounding the nucleus of an atom. Electrons surrounding a nucleus will somewhat shield the nuclei from the applied magnetic field of the NMR spectrometer. TMS is excellent at shielding its nuclei with electrons. Because of this, it takes a higher magnetic field strength at a particular radio frequency to flip the spin of nuclei in TMS. All other nuclei in organic molecules generally need less field strength than TMS at the same radio frequency to flip to the opposing spin.

Chemical shift for ^{1}H NMR occurs in the 0–13 ppm range downfield (lower strength) from the TMS reference. For ^{13}C NMR this range is from 0–220 ppm downfield. Electronegative atoms like nitrogen and oxygen will de-shield or expose the nuclei of neighbouring carbon and hydrogen atoms by attracting the electrons belonging to those atoms. This essentially results in a downfield shift required to achieve resonance of nuclei.

10.4.3 Applications of NMR spectroscopy

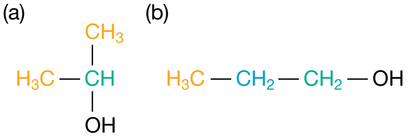
NMR is used extensively in organic synthesis. For example, in pharmaceutical manufacturing, NMR is used for quality control of medicines. It ensures that the drug molecule has been made with the correct atom–atom linkages and has the desired properties. Other uses include studying DNA, RNA and similar proteins in forensic analysis; the technique is not destructive so samples can be studied for weeks. NMR is also used in the petrochemical industry to identify oil and gas deposits, and other features of the rock sample in which deposits are contained. Although the scans seen in medical MRIs are like slices through the body that build up into a three-dimensional picture, simpler scans are effective when analysing most molecules.

10.4.4 ^{13}C NMR spectroscopy

To analyse an NMR spectrum we need to look at the chemical shift and the number of unique peaks (sets of peaks) on the spectrum. Peaks are unique if they are produced by nuclei in different electronic environments. That is, the effect of shielding electrons will be different for carbon atoms surrounded by different neighbours. Peaks will have the same chemical shift or environment if they have the same neighbouring groups of atoms.

Consider the carbon environments of propan-2-ol and propan-1-ol in figure 10.11. There are three carbon atoms in propan-2-ol but only two unique carbon environments. The CH_3 groups are both connected to the central carbon atom and nothing else. They both experience the same shielding and therefore will achieve resonance at the same chemical shift. The other carbon atom is in a different environment due it being connected to the two CH_3 groups and the OH group. Propan-1-ol has three unique carbon environments because each carbon atom in the structure has different connectivity or different neighbours.

FIGURE 10.11 Structures of (a) propan-2-ol and (b) propan-1-ol

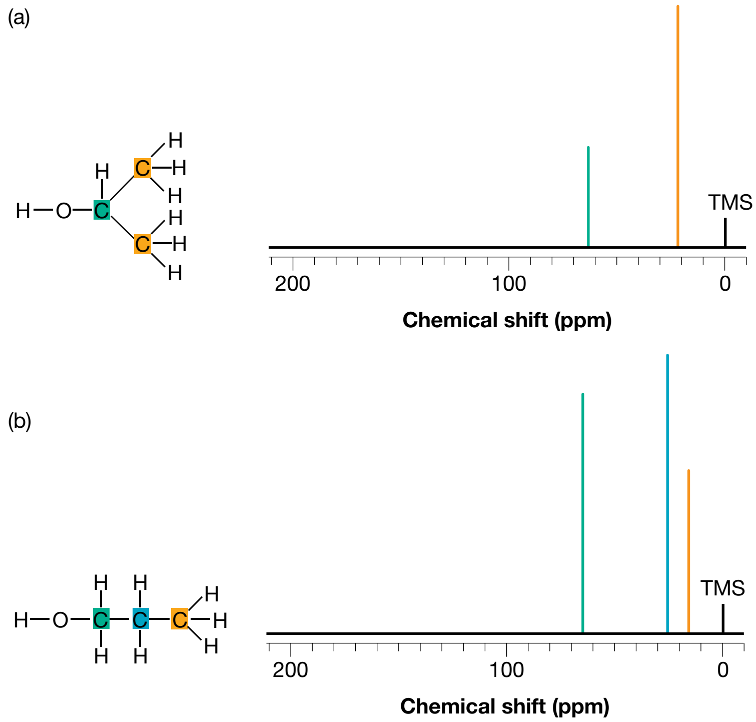


Identifying groups on a ^{13}C spectrum

If we examine the spectra propan-2-ol and propan-1-ol (see figure 10.12) we can see the difference in the chemical shift and the number of peaks visible on the spectra.

The carbon atoms attached to the OH in both molecules are shown downfield due to the de-shielding of the nuclei.

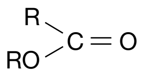
FIGURE 10.12 Spectra of (a) propan-2-ol and (b) propan-1-ol

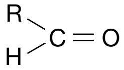


The CH_3 groups in propan-2-ol experience the same chemical shift from TMS to achieve resonance and show as one peak only. The CH_2 group in propan-1-ol is less shielded than the carbon atom in the neighbouring CH_3 group.

The ^{13}C NMR chemical shifts are summarised in table 10.4.

TABLE 10.4 ^{13}C NMR chemical shift data relative to TMS = 0

Type of carbon	Chemical shift (ppm)
$R–CH_3$	8–25
$R–CH_2–R$	20–45
$R_3–CH$	40–60
$R_4–C$	36–45
$R–CH_2–X$	15–80
$R_3C–NH_2$, $R_3C–NR$	35–70
$R–CH_2–OH$	50–90
$RC≡CR$	75–95
$R_2C=CR_2$	110–150
RCOOH	160–185
	165–175

Type of carbon	Chemical shift (ppm)
	190–200
$R_2C{=}O$	205–220

Source: VCAA 2018, *VCE Chemistry Data Book*, Version 2, June 2018, VCAA, Melbourne, table 15.

10.4.5 ^{1}H NMR spectroscopy

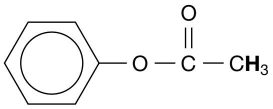
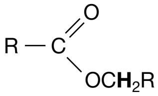
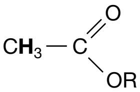
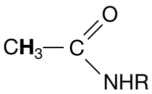
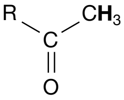
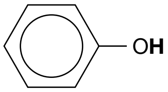
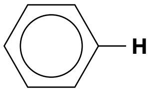
In ^{1}H NMR, the signal intensity (height) is statistically linked to the number of atoms for that signal. This is similar to the calibration graphs in other instrumental methods such as gas chromatography, HPLC, colorimetry, UV–visible spectroscopy and atomic absorption spectroscopy. An integral trace provides the relative area under each signal in ^{1}H spectra and indicates how many hydrogen atoms contribute to that signal. It is often indicated by a numeral written at the top of the integration curve (peak). For example, (3) indicates three H atoms.

The bonding electrons of each atom in a molecule experience a small but significant effect caused by the other atoms around them. A highly electronegative element, such as a halogen, affects the electrons of neighbouring atoms by slightly attracting their electrons towards it. An oxygen atom in an alcohol group not only affects the hydrogen atom bonded to it, but also affects the hydrogen atom bonded to the adjoining carbon atom. The distribution of electrons affects the magnetic field around each nucleus, enabling slight changes in electron distribution to be measured by NMR.

Identifying groups on a ^{1}H spectrum

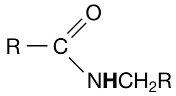
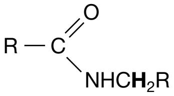
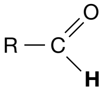
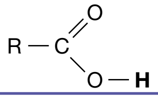
The chemical shifts for ^{1}H NMR spectra are summarised in table 10.5.

TABLE 10.5 ^{1}H NMR data

Type of proton	Chemical shift (ppm)	Type of proton	Chemical shift (ppm)
R–C**H**$_3$	0.9–1.0		2.3
R–C**H**$_2$–R	1.3–1.4		3.7–4.8
RCH=CH–C**H**$_3$	1.6–1.9	R–O–**H**	1–6 (varies under different conditions)
R$_3$–C**H**	1.5	R–N**H**$_2$	1–5
 or 	2.0	RHC=C**H**R	4.5–7.0
	2.1–2.7		4.0–12.0
R–C**H**$_2$–X (X = F, Cl, Br or I)	3.0–4.5		6.9–9.0

(continued)

TABLE 10.5 ^1H NMR data *(continued)*

Type of proton	Chemical shift (ppm)	Type of proton	Chemical shift (ppm)
$\mathrm{R{-}C\mathbf{H}_2{-}OH}$, $\mathrm{R_2{-}CH{-}OH}$	3.3–4.5	 $\mathrm{R{-}C({=}O)N\mathbf{H}CH_2R}$	8.1
 $\mathrm{R{-}C({=}O)NHC\mathbf{H}_2R}$	3.2	 $\mathrm{R{-}C({=}O)\mathbf{H}}$	9.4–10.0
$\mathrm{R{-}O{-}C\mathbf{H}_3}$ or $\mathrm{R{-}O{-}C\mathbf{H}_2R}$	3.3–3.7	 $\mathrm{R{-}C({=}O)O{-}\mathbf{H}}$	9.0–13.0

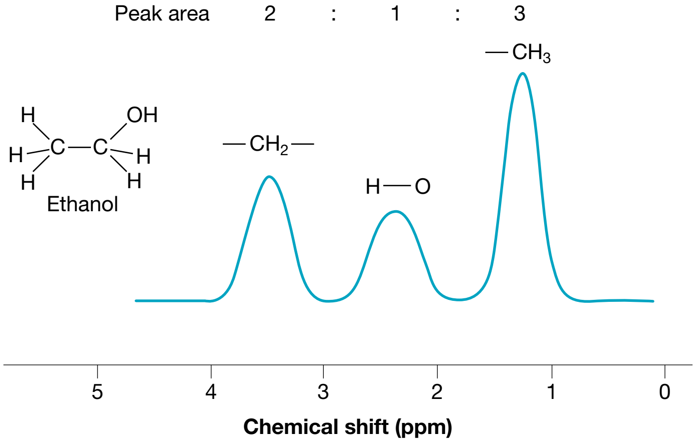
Source: VCAA 2018, *VCE Chemistry Data Book*, Version 2, June 2018, VCAA, Melbourne, table 16.

Low-resolution spectra

There are two different types of NMR spectrum: high resolution and low resolution. A low-resolution spectrum shows the unique types of environments of the hydrogen atom in the molecule; the ratio of the areas under the peaks shows the number of hydrogen atoms in that environment, and the chemical shift tells you important information about the type of bond involved.

In figure 10.13, the low-resolution ^1H NMR spectrum of ethanol, the size of the peaks are proportional to the number of hydrogen nuclei producing the signal.

FIGURE 10.13 Low-resolution ^1H NMR spectrum of ethanol



High-resolution spectra

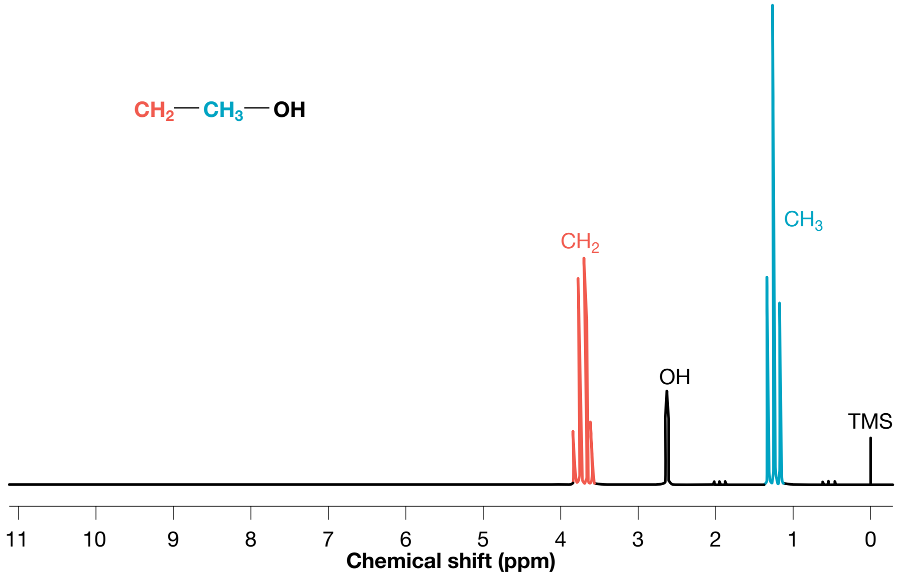
A high-resolution spectrum contains the same information as the low-resolution spectrum, but each signal in the low-resolution spectrum appears to have been split into several peaks.

^1H nuclei can interact with other ^1H nuclei near them. If the neighbours are chemically different, that interaction splits the NMR signal into a number of peaks. This happens because neighbouring nuclei have a small magnetic effect on each other, causing different signals depending on whether they are aligned with or against the applied magnetic field.

The number of peaks in the high-resolution spectrum tells you about the number of hydrogen atoms next to the hydrogen atom that has produced that signal. For simple molecules, the number of peaks is one more than the number of hydrogen atoms on the carbon atom next to that hydrogen atom and chemically different from that hydrogen atom. This splitting pattern is known as the **n+1 rule**.

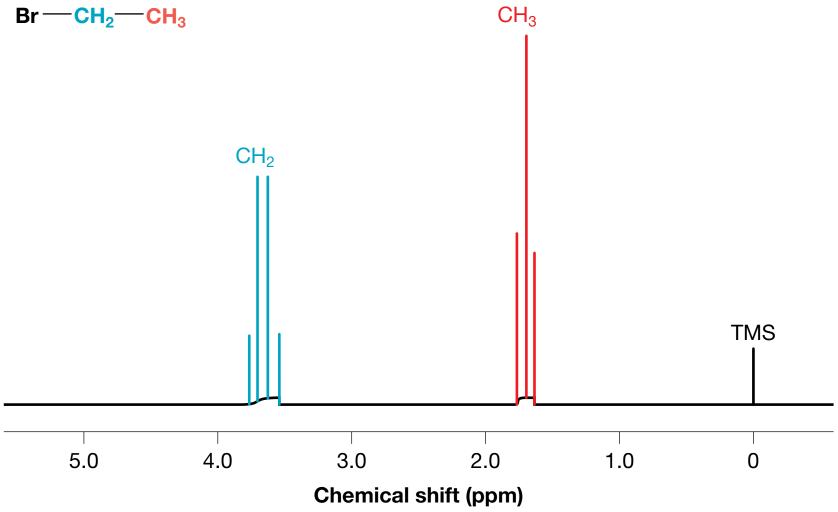
In the high-resolution spectrum of ethanol in figure 10.14, the signal of three peaks (triplet) indicates that there are two hydrogen atoms attached to the neighbouring carbon atom in the molecule. The set of four peaks (quartet) indicates that there are three neighbouring hydrogen atoms. O—H groups always present as a single peak (singlet) in high-resolution spectra.

FIGURE 10.14 The high-resolution spectrum of ethanol, C_2H_5OH, has peak heights proportional to the number of protons producing the signal and peak splitting according to the n + 1 rule. OH is always presents as a single peak.



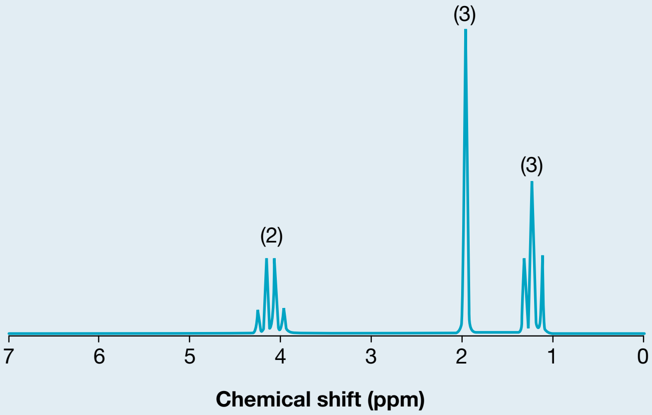
Let's also consider the spectrum of bromoethane in figure 10.15. The quartet is produced by the hydrogen atoms in the CH_2 group (due to the three hydrogen atoms on the neighbouring carbon). The chemical shift of 3.7 ppm is in the correct range for R–CH_2X (3.0–4.5 ppm) and is adjacent to a CH_3 group at 1.7 ppm. The CH_3 group produces the triplet because it is neighbouring the CH_2 group so the n+1 rule determines a set of three peaks.

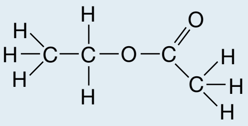
FIGURE 10.15 Spectrum of bromoethane



SAMPLE PROBLEM 3

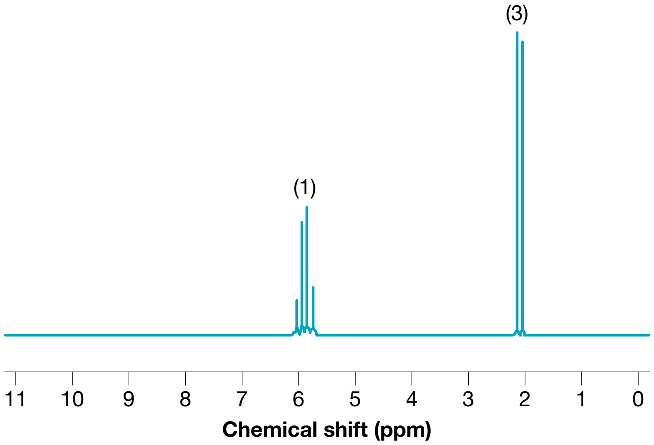
Analyse the following proton NMR spectrum and use table 10.5 (or table 16 in the VCE Chemistry Data Book) to identify the structure of the molecule. The molecular formula for the molecule is $C_4H_8O_2$.



THINK	WRITE
1. Identify the number of different hydrogen environments.	There are three different hydrogen environments.
2. Identify groups according to the splitting pattern and the number of hydrogens producing the signals by the numbers above the peaks.	The splitting patterns indicate there is a CH_3 group (1.2 ppm) next to a CH_2 group (4.1 ppm). The singlet at 2.0 ppm indicates there are no neighbouring hydrogen atoms but a chemical shift downfield indicates the presence of an electronegative atom. There are three hydrogen atoms producing this signal, indicating another CH_3 group.
3. Assemble the molecule that matches the number of peak sets, splitting patterns and chemical shifts.	

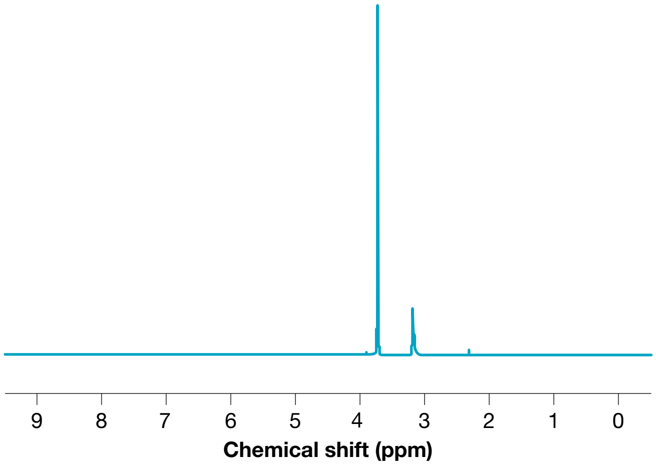
PRACTICE PROBLEM 3

Draw the structure of an isomer of $C_2H_4Cl_2$ that produced the following spectrum.



For hydrogen environments that are equivalent we don't see splitting. For example, 1,2-ethanediol, $HOCH_2CH_2OH$, produces two singlets because the CH_2 groups have equivalent hydrogen atoms and therefore no splitting occurs (see figure 10.16).

FIGURE 10.16 Spectrum for 1,2-ethanediol



on Resources

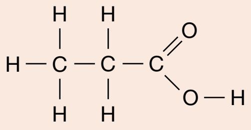
Video eLesson High-resolution proton NMR (med-0350)

Interactivity Predicting carbon and hydrogen environments in different compounds (int-1227)

10.4 EXERCISE

To answer questions online and to receive **immediate feedback** and **sample responses** for every question go to your learnON title at www.jacplus.com.au.

1. What determines the area under the peaks of NMR spectra?
2. What is meant by the term 'environment' in ^{13}C and ^{1}H NMR spectroscopy?
3. What is the major difference between low-resolution and high-resolution ^{1}H NMR spectra?
4. Why is TMS used as a reference for chemical shifts?
5. List possible chemical shifts in ppm observed in a ^{1}H NMR spectrum for CH_3CH_2Cl.
6. The molecule C_4H_{10} has two isomers. Sketch the isomers and examine the chemical environment of each carbon atom. Decide how many signals each isomer would produce in a ^{13}C NMR spectrum.
7. Draw the structural formulas of the two isomers of bromopropane and explain how ^{13}C NMR spectroscopy could be used to identify each.
8. How many different carbon environments are present in the compound 2-methylpropan-2-ol?
9. Propanoic acid is used as a preservative and anti-mould agent for animal feed and also in packaged food for human consumption. Complete the table by showing the hydrogen environment, splitting pattern, relative peak height and the chemical shift for each type of hydrogen atom in this molecule.



Hydrogen set or atom	Splitting pattern	Relative peak height	Chemical shift (ppm)
CH_3			

10. Describe and explain the differences you would expect to see in high-resolution ^{1}H NMR spectra for 1,1-dichloroethane and 1,2-dichloroethane.

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10.5 Combining spectroscopic techniques

KEY CONCEPT

- Determination of the structures of simple organic compounds using a combination of mass spectrometry (MS), infrared spectroscopy (IR) and proton and carbon-13 nuclear magnetic resonance spectroscopy (NMR) (limited to data analysis)

10.5.1 Combining spectroscopic techniques

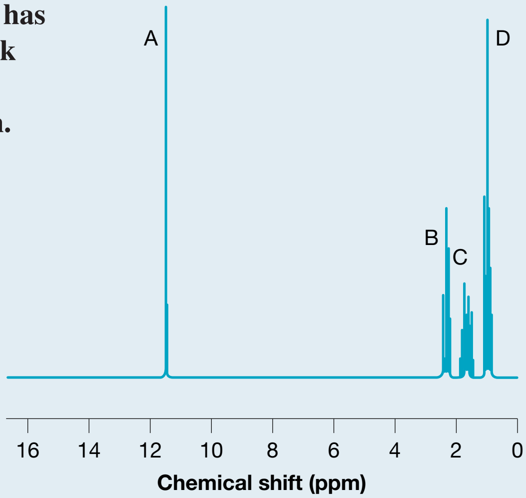
The previously described spectroscopic techniques are rarely used alone when determining the structure of unknown organic compounds. Typically, a combination of instrumental techniques is used for qualitative analysis. Mass spectroscopy is often used in conjunction with a chromatography and infrared analysis, while NMR spectroscopy can be used accurately for determining the structure of small molecules and biomolecules such as DNA and RNA.

In the VCE Chemistry course, you are exposed to using a combination of mass, infrared and NMR spectroscopy to determine the structure of small organic molecules, often with functional groups. For example, esters, carboxylic acids, amines, alcohols and haloalkanes are common analytes.

SAMPLE PROBLEM 4

Analysis of an unknown compound has revealed that it has an empirical formula C_2H_4O. Its MS has its parent peak at 88. The IR has significant peaks at 1700 cm^{-1} and a broad peak at 3000 cm^{-1}. The NMR spectrum is shown. Identify and name the compound.

Peak set	Number of split peaks	Relative area of peak set
A	1	1
B	3	2
C	multiple	2
D	3	3

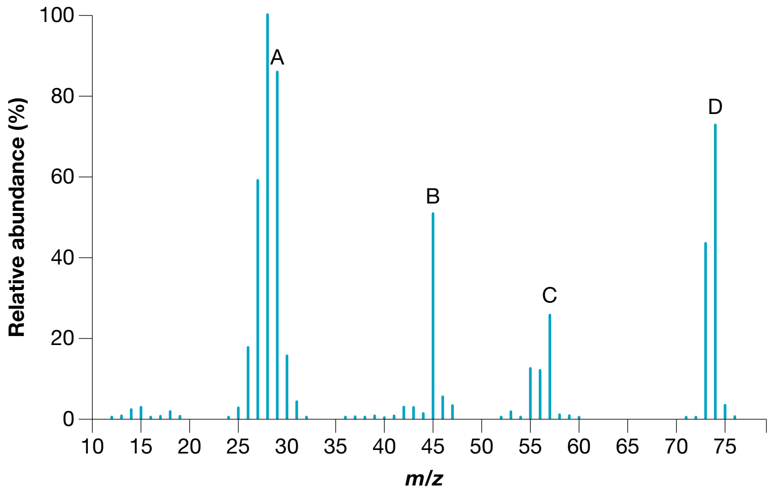


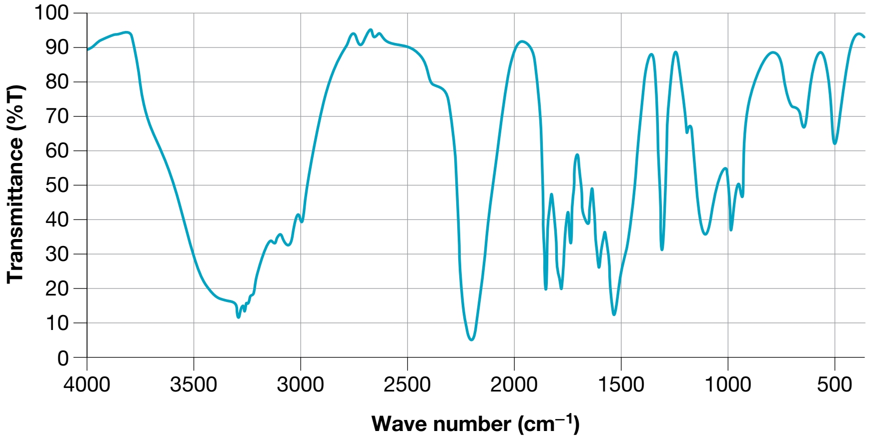
Teacher-led video: SP4 (tlvd-0716)

THINK	WRITE
1. Use the IR wave numbers to identify functional groups.	1700 cm^{-1} corresponds to a C=O bond and the broad peak at 3000 cm^{-1} could be the OH(acid) bond. This indicates the compound is likely to contain the COOH group and is most likely a carboxylic acid.
2. Consider the functional groups determined in step 1 and a molecular mass of 88 (which is twice the empirical formula given of $C_4H_4O_2$, which has a *Mr* of 44).	A carboxylic acid with a mass of 88 g mol^{-1} is butanoic acid, $CH_3CH_2CH_2COOH$.
3. Use the NMR data to confirm the correct order of groups and therefore the structure. Butanoic acid, $CH_3CH_2CH_2COOH$, has four unique hydrogen environments.	Four unique hydrogen environments can be seen confirmed in the NMR spectrum. • Two triplets produced by the CH_3(D) group and CH_2(B) group attached to the carboxyl group. • The carboxyl group (A) will present a singlet downfield in the range of 9.0–13.0 ppm. • The CH_2(C) group, R–CH_2–R, should be in a range of 1.3–1.4 ppm, which is close to the set of peaks seen on the spectrum. • This set should be split into a sextet (n+1) due to the five neighbouring hydrogen atoms. Peak areas confirm the structure as butanoic acid, $CH_3CH_2CH_2COOH$, because they correspond to the number of hydrogen atoms contributing to each signal.

PRACTICE PROBLEM 4

An organic compound has the empirical formula $C_3H_6O_2$. When sodium carbonate is added to this compound, bubbling is observed. The mass spectrum and infrared spectrum of the compound are shown.





a. **Determine the molecular formula of this compound.**

b. **Suggest the formulas of the fragments labelled A, B, C and D.**

c. **Identify the bonds responsible for the peaks at:**

  i. **3000 cm^{-1}**

  ii. **1720 cm^{-1}**

  iii. **1230 cm^{-1}.**

d. **Suggest a possible structure for this compound, giving reasons based on the spectra.**

e. **Name the compound.**

---

on Resources

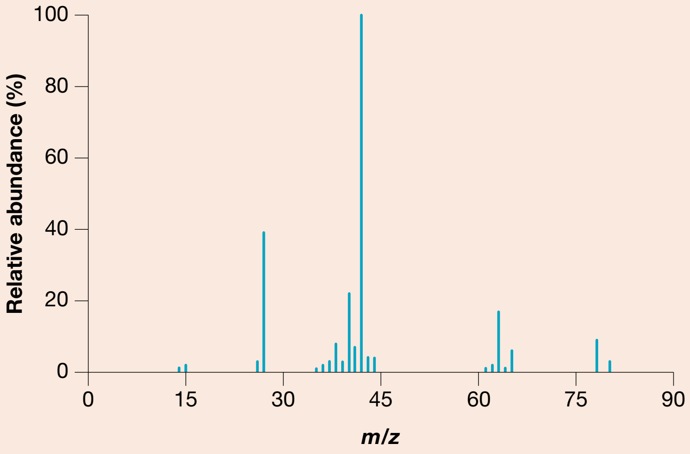
🎞 **Video eLesson** Combining spectroscopies (med-0351)

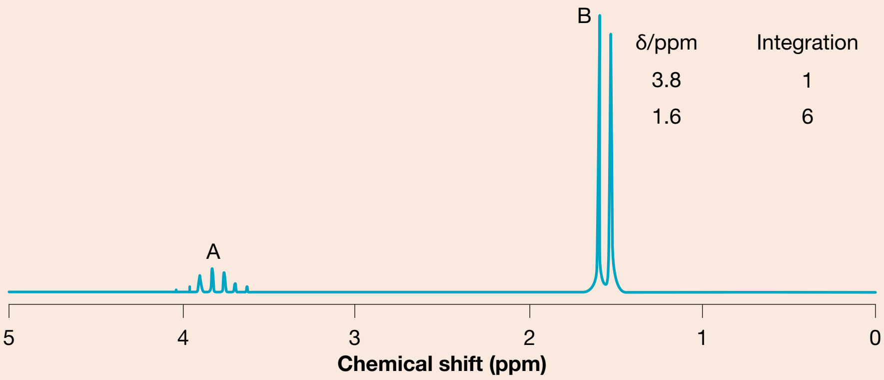
🗎 **Digital document** Experiment 10.1 Spectroscopy (doc-31272)

10.5 EXERCISE

To answer questions online and to receive **immediate feedback** and **sample responses** for every question go to your learnON title at www.jacplus.com.au.

1. Explain how you could use a mass spectrum and infrared spectrum together to distinguish between ethanol and butan-1-ol.
2. How would you use ^{1}H and ^{13}C NMR spectra to differentiate between ethanol and ethanal?
3. A compound has the empirical formula C_3H_7Cl. The mass spectrum and ^{1}H NMR spectrum are following.

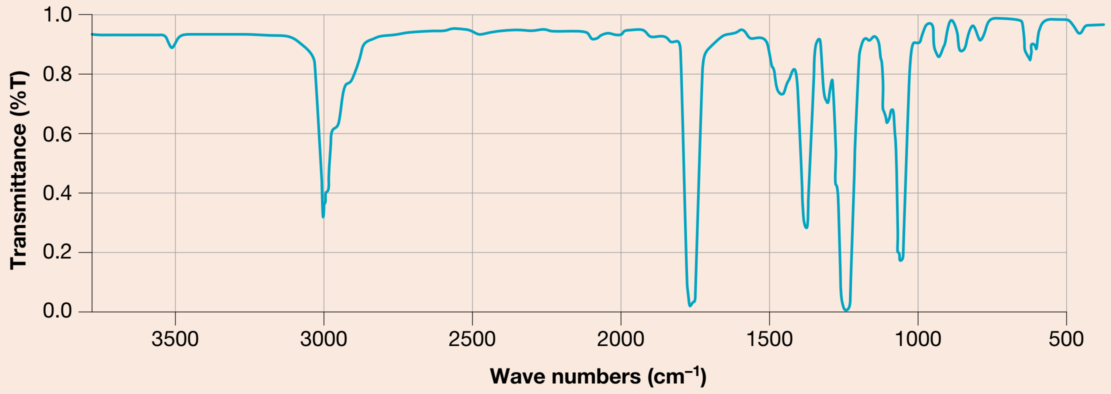


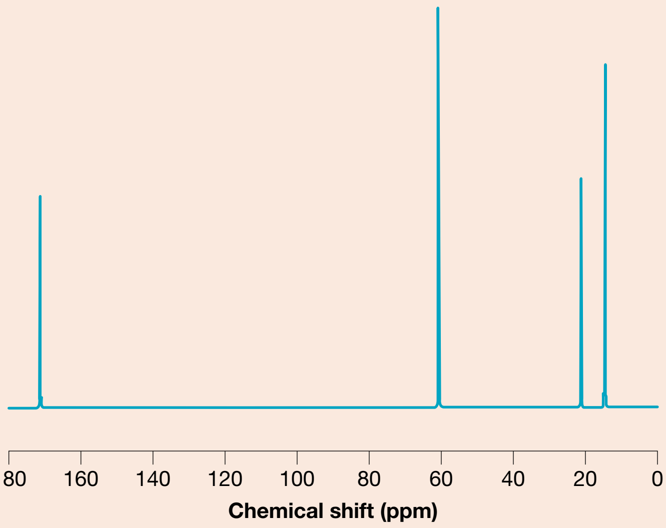


δ/ppm	Integration
3.8	1
1.6	6

(a) Explain why the mass spectrum shows two molecular ion peaks.
(b) What is the molecular formula of the compound?
(c) How many different ^1H environments are there?
(d) Explain why the septet is seen further downfield than the doublet at 1.6 ppm.
(e) Draw the structure of the compound.

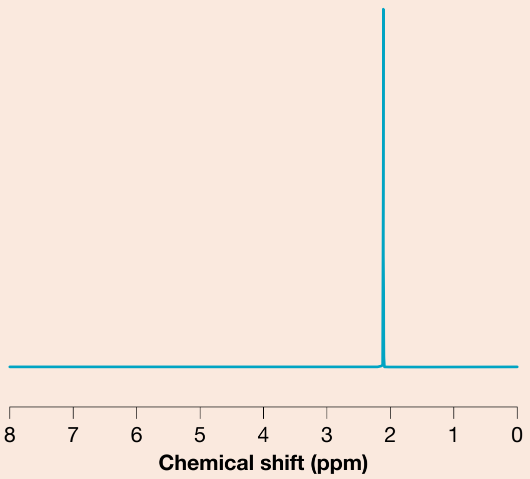
4. A compound with the molecular formula $C_4H_8O_2$ produced the following spectra.

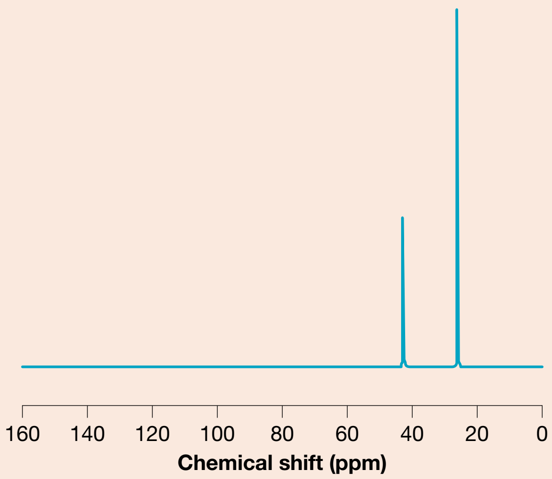




(a) What does the IR spectrum indicate about the functional group(s) present?
(b) What does the ^{13}C NMR spectrum indicate regarding the functional group(s) present?
(c) How many unique ^{13}C environments are there?
(d) Draw the structure of $C_4H_8O_2$.

5. Two different compounds with the molecular formula C_3H_9N produced one each of the following NMR spectra.





Draw the structures of the two molecules and explain how you used the spectra to deduce these structures.

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10.6 Chromatography

KEY CONCEPT

- 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

10.6.1 Principles of chromatography

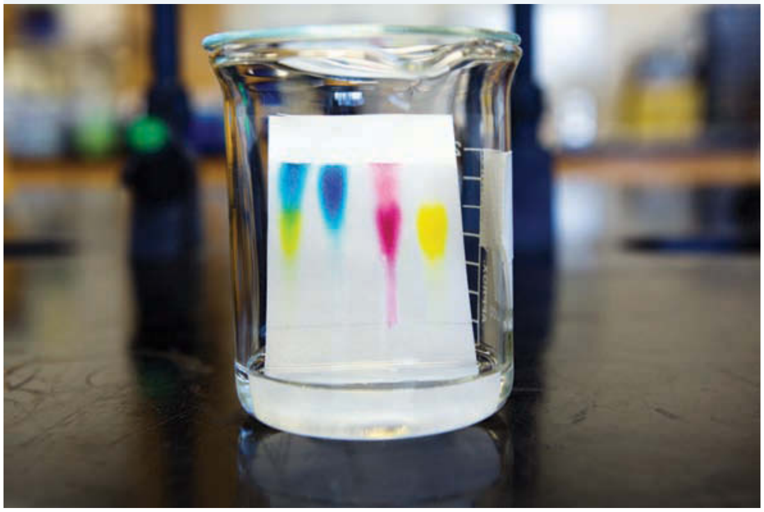
Chromatography is a technique that separates mixtures. In all forms of chromatography, a **mobile phase** passes over a **stationary phase**. The stationary phase is either a solid with a high surface area, or a finely divided solid coated with liquid. The mobile phase moves over or through the stationary phase and carries the mixture to be separated with it.

As the mixture being analysed is swept along in the mobile phase, some of its components ‘stick’ more strongly to the surface of the stationary solid phase than others. They then ‘unstick’ and move on. This results in the components travelling at different speeds, and so they separate.

Chromatography can be very simple (as in paper chromatography and thin-layer chromatography (TLC)) or very sophisticated (as in high-performance liquid chromatography (**HPLC**) and gas chromatography (GC)). In paper chromatography, the stationary phase is made up of cellulose fibres that are naturally coated with a thin layer of water. In thin-layer chromatography, a finely divided adsorbent material is coated onto either a glass slide or aluminium foil to form this phase. Liquids for the mobile phase can be any of a wide range of mixtures of solvents (including water). If you have ever seen ink separating into coloured bands as it rises up filter paper or chalk, you have witnessed chromatography.

The nature of the interactions that occur between the stationary and mobile phases can vary. However, a common interaction involves the processes of **adsorption** and **desorption**. The components of the sample adhere to the material in the stationary phase to differing extents. These interactions are then broken in the desorption process, allowing the substances to move on. The stronger these interactions, the slower a substance moves.

FIGURE 10.17 Thin-layer chromatography: we can see that the red and yellow dyes are more strongly attracted to the stationary phase than the blue dye because they have not travelled as far up the paper (stationary phase).



on Resources

Digital document Experiment 10.2 Separation of food dyes using chromatography (doc-31273)

10.6.2 High-performance liquid chromatography (HPLC)

You may recall from Unit 2 that HPLC is an adaption of the simple methods described in section 10.6.1. In HPLC, the most common stationary phase is a narrow diameter tube, called a column, which is packed tightly with a finely divided powder, commonly alumina or silica. The powder provides the large surface area required for the process. Particle sizes in the range of a few micrometres are typical, although these are now becoming even smaller and, when coupled with the higher-pressure pumps now becoming available, are leading to what is being called ultra-performance liquid chromatography (UPLC). The mobile phase is a liquid called an **eluent** and can be either a pure liquid or a mixture of liquids.

In operation, the substance to be analysed (called the **sample**) is injected onto the start of the column as a liquid. The eluent is then pumped through the column, taking the sample with it. As the mobile phase moves through the column, the process of adsorption and desorption results in the components of the sample (referred to as **analytes**) moving at different speeds and thus being separated from each other.

Separation by HPLC occurs due to interactions between the substances in the mobile phase and the stationary phase. The weaker these interactions with the stationary phase, the faster a substance moves through the column.

After passing through the column, the components in the sample exit the column and are detected by a suitable device. This is recorded as a series of peaks on a chart called a **chromatogram**. In many modern instruments, a computer can also present this information in tabular form, showing the **retention time** and area of each peak. The data can then be fed into programs for graph drawing or for further mathematical evaluation.

FIGURE 10.18 A schematic diagram of a high-performance liquid chromatography instrument

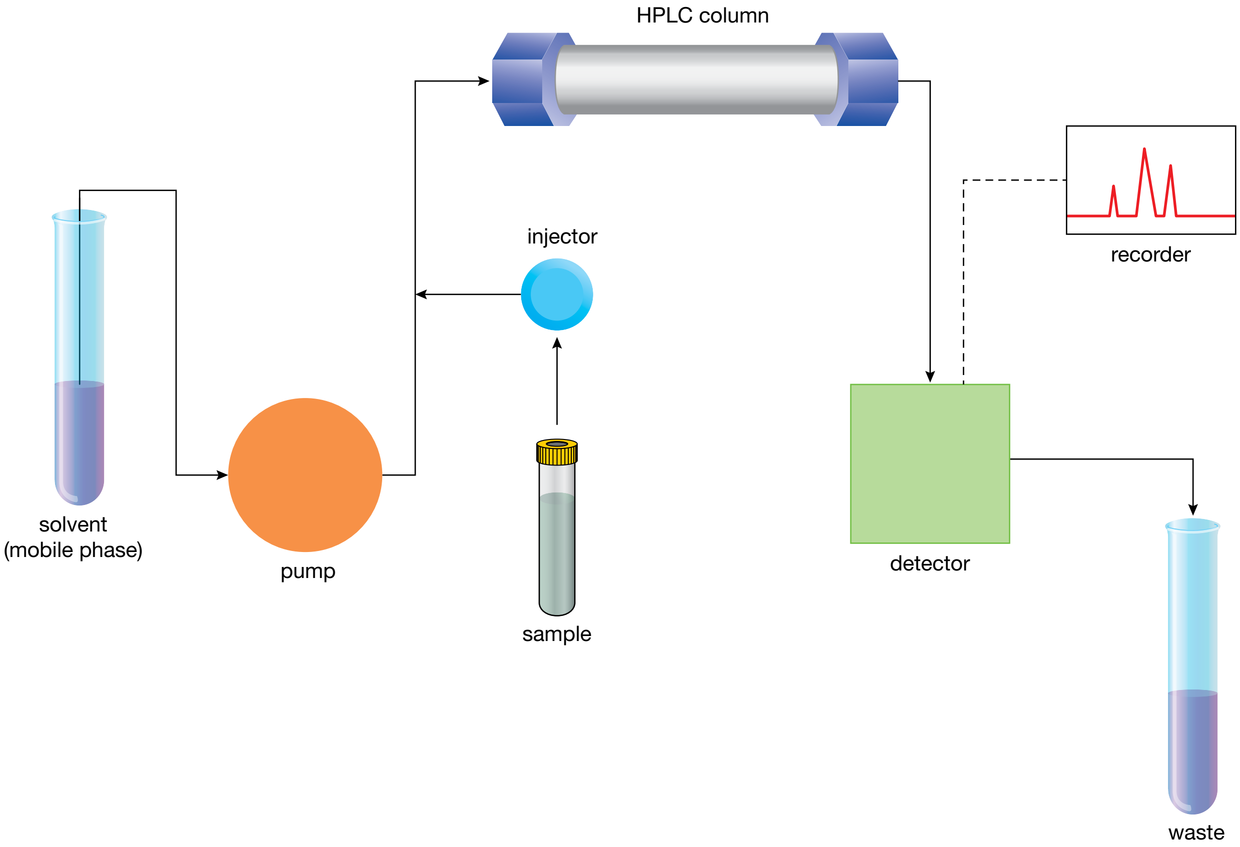
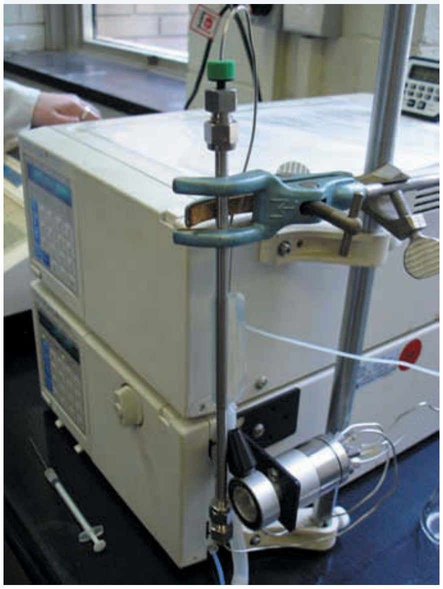


FIGURE 10.19 A high-performance liquid chromatography instrument



Developed in the 1960s, HPLC has developed into an extremely sensitive and widely-used technique. Detection of concentrations in parts per million and parts per billion levels is routine. Advanced instruments are now capable of detecting parts per trillion! Applications of HPLC include research, medicine, pharmaceutical science, forensic analysis, food analysis, drug detection in sport and environmental monitoring.

HPLC is often categorised according to the nature of stationary and mobile phases used. The two most common types are:

1. Normal-phase liquid chromatography (NPLC), where the material in the column is more polar than the mobile phase. Because of this, the more polar components in the sample adsorb more strongly to the column material and move more slowly through the column. Therefore, they have a longer retention time.
2. Reverse-phase liquid chromatography (RPLC), which is the opposite of NPLC, where the material inside the column is less polar than the liquid being pumped through it. The columns used often contain silica particles that have been coated with long hydrocarbon chains (C_8 and C_{18} are commonly used) to achieve a level of 'non-polarity'. This has the opposite effect on retention times. More polar molecules in the sample are not as strongly adsorbed to the column material and therefore move through it more quickly, thus displaying shortened retention times. RPLC is the most commonly used form of HPLC.

Besides these two types, there are other forms of HPLC that can be used in appropriate circumstances. These include ion-exchange chromatography and size-exclusion chromatography.

Resources

Video eLesson High-performance liquid chromatography (HPLC) (med-0347)

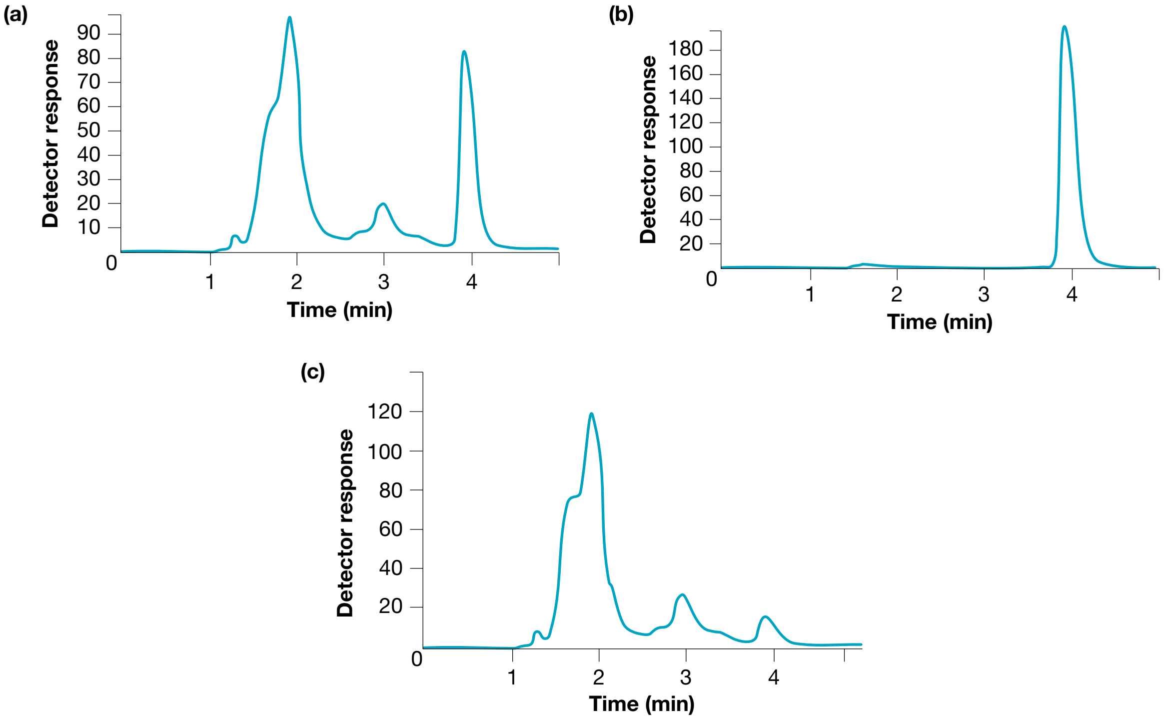
Weblink HPLC

Qualitative analysis

The time taken for each component of the sample to travel from the injection port to the end of the column where it is detected is referred to as its retention time, R_t. This corresponds to the position of the peak on the chromatogram. Retention time can be used to identify a component. The retention time for an unknown substance is compared with retention times for known substances under the same operating conditions.

Figure 10.20 shows results obtained from testing a brand of decaffeinated coffee. Note that a caffeine standard has been run through the instrument so that the potential caffeine peak on the chromatogram of the sample can be identified. Therefore, the reduction in the height of the peak due to caffeine becomes obvious when normal and decaffeinated coffee results are compared.

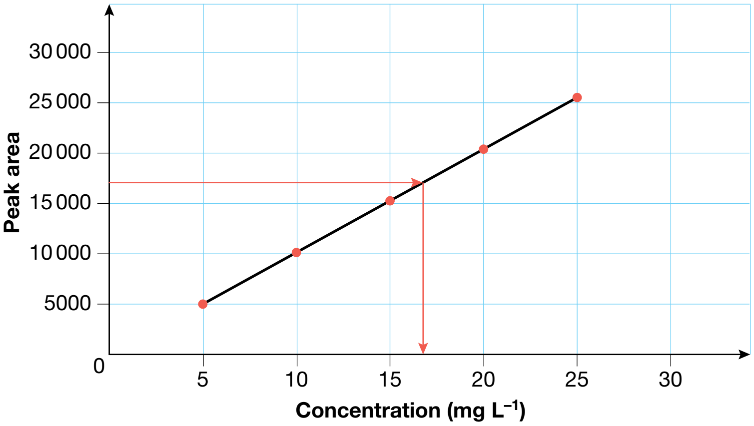
FIGURE 10.20 HPLC chromatograms for (a) normal coffee, (b) caffeine and (c) decaffeinated coffee



Quantitative analysis

The greater the amount of a component, the greater the area under the corresponding peak. This allows **quantitative analysis** of a substance. It should be noted that, when the peaks produced are narrow, the area measurement can be replaced by a measurement of the peak height. For a quantitative measurement of the amount of caffeine remaining in the sample, the height (or the area under the peak) could be measured and compared with a set of caffeine standards of known concentrations.

FIGURE 10.21 Using the calibration curve, the concentration of the unknown sample (shown by the red arrow) can be estimated as 16.8 mg L^{-1}.



Instruments must be accurately **calibrated**, using a set of standards, before any meaningful quantitative results can be obtained. This involves running a set of standards of *known concentration* through the instrument and noting the readings (usually either peak height or peak area). From these results, a graph of reading versus concentration can be drawn. These are known as **calibration curves**. It is then a matter of running the sample to be tested through the instrument and noting the reading. The calibration graph can then be used to obtain its concentration. (see figure 10.21).

Most modern instruments are programmed to do this automatically. They use statistical algorithms to determine the *equation of the line of best fit* using the calibration data. The test result for the unknown is then fed into this equation and the result displayed.

SAMPLE PROBLEM 5

Although it is usually done using gas chromatography (GC), the level of ethanol in wine can be determined using HPLC.

In one such analysis using HPLC, a set of six reference samples of known ethanol concentration were run through the instrument for the purpose of calibration. A sample of wine was then analysed under exactly the same conditions as the reference samples. A much more complicated chromatogram was obtained, from which the ethanol peak was identified.

The results obtained are shown in the following table.

Teacher-led video: SP5 (tlvd-0717)

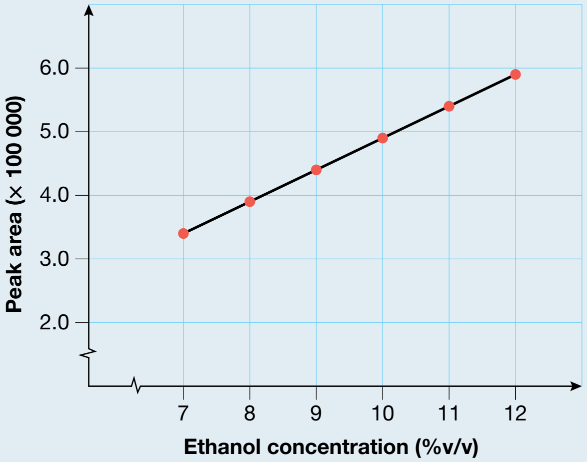
Standard concentration, %(v/v)	Peak area
7	342 401
8	391 318
9	440 230
10	489 136
11	538 058
12	586 970
Sample	450 012

a. **Using these results, plot a calibration curve of concentration versus peak area.**
b. **Use the graph to deduce the ethanol content in the sample of wine.**
c. **How was the ethanol peak identified from the pattern produced by the wine sample?**
d. **Explain why only one peak is produced in the chromatogram for each standard analysed.**

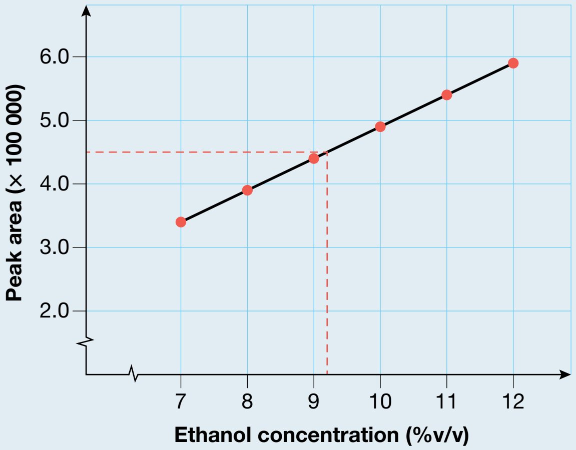
THINK | **WRITE**

a. To plot the graph, consider the scale required. For each percentage the peak area differs by approximately 50 000.

If required a line of best fit may be drawn.



b. Locate the peak area of the sample (450 012) and rule a straight line from it until you touch the graph. Drop straight down and read the corresponding percentage.



Reading from the calibration graph, the sample of wine gives an ethanol concentration of 9.2%.

c. As ethanol occurs in both the wine sample and in the ethanol standard, this can be used to identify the ethanol peak in the wine sample.

Each ethanol standard produces a peak at the same position on the chromatogram; in other words, they all have the same retention time. So it is just a matter of finding the peak from the chromatogram of the wine sample that corresponds to this retention time.

d. In a chromotagram, each peak corresponds to a particular substance.

Ethanol is the only substance present (apart from the solvent), so only one peak was produced.

PRACTICE PROBLEM 5

The ester methyl butanoate, $CH_3CH_2CH_2COOCH_3$, is used as a flavour additive and in perfumes. It has both a pleasant odour and taste. However, butanoic acid, from which it is made, has an extremely unpleasant odour. Therefore, it is desirable that residual butanoic acid levels be kept to a minimum in methyl butanoate preparations that are used for these purposes.

HPLC was used to measure the level of butanoic acid in a sample of food-grade methyl butanoate. A number of standards were run through the instrument, together with a sample of the methyl butanoate. The results are shown in the following table.

Concentration of butanoic acid (mg L^{-1})	Peak area
4.0	640
6.0	958
8.0	1280
10.0	1605
Sample	1150

a. Besides butanoic acid, what other organic compound is required to make methyl butanoate?
b. Plot the calibration curve for the data in the table.
c. Determine the concentration of butanoic acid in the sample tested.

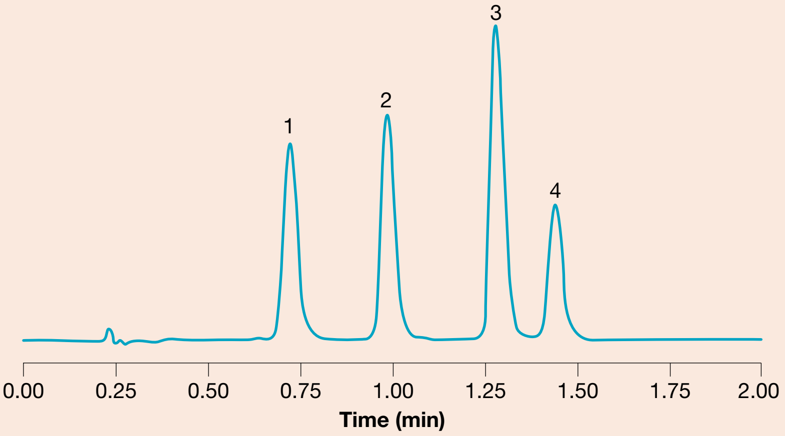
on Resources

Video eLesson Calibration curves (med-0348)
Digital document Experiment 10.3 Separating mixtures using column chromatography (doc-31274)

10.6 EXERCISE

To answer questions online and to receive **immediate feedback** and **sample responses** for every question go to your learnON title at www.jacplus.com.au.

1. Define the following terms.
   (a) Analyte
   (b) Stationary phase
   (c) Mobile phase
   (d) Retention time
   (e) Peak area
   (f) Chromatogram
   (g) Chromatograph
2. Explain the effect on the retention time of a polar compound through a NPLC column if:
   (a) the column length is increased from 25 m to 50 m
   (b) the mobile phase is pumped through with increased pressure
   (c) the temperature of the mobile phase is increased.
3. What do the terms ‘adsorb’ and ‘desorb’ mean with respect to HPLC?
4. In what sequence would the first four members of the carboxylic acid homologous series elute from a NPLC column? Explain your answer.
5. How does reverse-phase liquid chromatograpy (RPLC) differ from NPLC?
6. Which of pentane, pentanol and pentanoic acid would have the shortest retention time eluting from a RPLC column? Explain your answer.
7. A mixture of amino acids were separated using a polar HPLC column and the following chromatograph was produced. The mixture was thought to consist of leucine, isoleucine, phenylalanine and serine.



(a) Which of the four peaks (1–4) is most likely to be serine? Explain your answer.
(b) Explain how you would confirm the retention time of serine.
(c) Which of the peaks represents the highest concentration of an amino acid?
(d) Explain how you could determine concentration of serine in the sample.

8. Stanozolol is a performance-enhancing drug taken by athletes to build muscle tissue and increase power. Stanozolol can be analysed from urine samples using HPLC. A mobile phase mixture of methanol (90%) and water (10%) is pumped through a non-polar RPLC column.

One particular urine analysis required the preparation of stanozolol standards of 1.0, 2.0, 3.0 and 4.0 mgL^{-1}. The peak areas are shown in the following table.

Retention time (minutes)	Stanozolol standard (mgL^{-1})	Peak area (× 10 000)
4.1	1.0	5.0
4.1	2.0	9.8
4.1	3.0	15.2
4.1	4.0	20.0

A 20 μL sample of undiluted urine was run through the chromatograph under the same conditions.
(a) Explain how this procedure can be used for the qualitative analysis of stanozolol in urine.
(b) Explain how it could be used for the quantitative analysis of stanozolol in urine.
(c) What is the stanozolol concentration in a urine sample that returned a peak at R_t 4.1 minutes with an area of 125 000?
(d) Explain why an athlete with a suspected stanozolol concentration of 5.0 mg per litre of urine could not be reliably tested using this method.
(e) Suggest an alteration to the procedure above so that an athlete suspected of having a stanozolol concentration above 5.0 mg per litre of urine could be tested.

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10.7 Volumetric analysis by titration

KEY CONCEPT

- Determination of the concentration of an organic compound by volumetric analysis, including the principles of direct acid-base and redox titrations (excluding back titrations).

10.7.1 Volumetric analysis procedure

Volumetric analysis is a quantitative technique that involves reactions in solution. The concentration of a solution can be determined using accurately measured volumes and reacting it with another solution of (accurately) known concentration or, in some cases, by making it up directly from a primary **standard solution**.

The procedure involves measuring an accurate volume of one of the solutions with a **pipette** (this volume is called an **aliquot**) and pouring it into a conical flask. The other solution (called a **titrant**) is then added carefully from a **burette** until the reaction is just complete (as predicted by the stoichiometry of the equation). By knowing the volumes involved and the concentration of one of the solutions, the concentration of the other solution can be determined. This procedure is called **titration**. The volume of the titrant delivered is known as the **titre**.

Two common types of reactions encountered in volumetric analysis are acid–base reactions and redox reactions.

The correct use of burettes and pipettes, as well as other important aspects of volumetric analysis has already been covered in Unit 2. Some of the more important points of this technique are revisited in this subtopic.

FIGURE 10.22 Volumetric flasks, conical flasks, pipettes, burettes and various beakers are used in volumetric analysis.

Standard solutions

A standard solution is one whose concentration is accurately known. There are usually two methods by which a solution can have its concentration determined accurately. These are:

1. by reacting it with another solution whose concentration is known accurately. This is called standardisation.
2. by taking a substance called a **primary standard** and dissolving it in a known volume of water. Primary standards are pure substances that satisfy a special list of criteria.

To qualify as a primary standard, a substance must have a number of the following properties.

- It must have a high state of purity.
- It must have an accurately-known formula.
- It must be stable (its composition or formula must not change over time, which can happen as a result of storage or reaction with the atmosphere).
- It should be cheap and readily available.
- It should have a relatively high molar mass so that weighing errors are minimised.

Not all substances are suitable for use as primary standards. For example, sodium hydroxide is unsuitable for use as a primary standard for the following reasons.

1. It absorbs moisture from the atmosphere (is *deliquescent*) as it is being weighed out. Therefore, the precise mass of sodium hydroxide is uncertain because of the absorbed water.
2. As a typical hydroxide, it reacts with carbon dioxide in the atmosphere to produce sodium carbonate. Thus, there are doubts about its purity.

Hydrated sodium carbonate, $Na_2CO_3{\cdot}10H_2O$, is also unsuitable, but for a different reason. This substance is *efflorescent*, which means that it loses water to the atmosphere as it is being weighed out. This water comes from the crystal structure and is known as 'water of crystallisation'. As a result, the precise formula is unknown. However, if hydrated sodium carbonate is heated, these weakly bonded water molecules can be driven off. Eventually, anhydrous sodium carbonate, Na_2CO_3, is formed, which makes an excellent primary standard.

To prepare a primary standard, chemists use special flasks called *volumetric flasks*. These flasks are filled to a previously calibrated etched line on their necks, so that the volume of their contents is accurately known.

on Resources

Video eLesson Preparing primary standards and standard solutions (med-0345)

Glassware and rinsing

Table 10.6 summarises the glassware, use and rinsing methods for titration.

TABLE 10.6 Summary of glassware used for titration

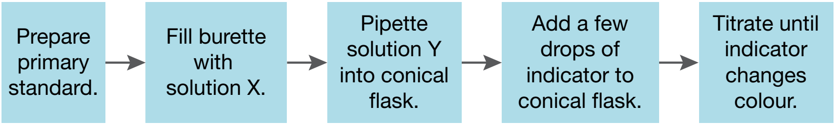
Glassware	Use	Rinsed with
Burette	Delivers the titrant or analyte. Readings from a burette should take place at the bottom of the meniscus formed by solution, ideally to two decimal places.	The solution it will deliver. A few mL of the solution is placed in the bottom and burette is inverted 2–3 times before the liquid is expelled using the tap.
Pipette	Used to deliver an aliquot of titrant and analyte directly to a conical flask or into a volumetric flask for dilution.	The solution it will deliver. A partial or full aliquot can be used to rinse a pipette as long as all of its inner surface has been rinsed.
Volumetric flask	Used to dilute aliquots. Commonly used are 50, 100 and 250 mL sizes.	Distilled water. The aliquots added to a volumetric flask will be diluted with distilled water and the number of moles from the pipette is unchanged.
Conical flask	Used to hold the analyte or titrant that is not in the burette. If it is a titration that needs an indicator, this will also be added.	Distilled water. Does not change the moles of analyte or titrant delivered by the pipette and burette.

Performing a titration

In volumetric analysis, the calculations require that a titration be stopped when one substance has *just finished* reacting with the other one. This point is called the **equivalence point**. Detection of this point is critical to the success of a volumetric procedure.

In some situations, a reaction may be self-indicating. This is often true in redox titrations where a substance involved in the analysis may have conjugate forms that display distinctly different colours. An example is in a titration involving the permanganate ion, MnO_4^-, which is bright purple, because an indicator is not required due to the reduced form, Mn^{2+}, being almost colourless.

FIGURE 10.23 Some typical steps in a volumetric procedure



In either type of titration, (acid–base or redox) we usually depend on a colour change to tell us when to stop. This is called the **end point**. Because this occurs only after a slight excess is added, we often do not have the true equivalence point. Thus, we can say that the *end point is an approximation to the equivalence point*. However, in a carefully designed procedure with a carefully chosen indicator, these two points should be very close together.

on Resources

Video eLessons Volumetric techniques (med-0820)
Simple (direct) titrations (med-0821)

Concordant titres

Although it may appear tedious and time consuming to produce the required solutions and to prepare the necessary equipment, a big advantage of volumetric analysis is that it is subsequently very easy to perform repeat titrations. Such repetition reduces the effect of random errors.

When performing repeat titrations, one usually aims for **concordant** titres. These are titres that are within a defined volume of each other, with 0.10 and 0.05 mL being commonly accepted values. 0.05 mL is an exacting standard, and requires very careful attention to detail and excellent technique because it represents approximately one drop. However, in many situations, including school laboratories, titres within ±0.10 mL of each other is a more realistic standard. On this basis, if a titration produces results of 19.25, 19.20, 19.40 and 19.20 mL, all except the third value can be considered concordant. Note that the volume of a titre is rounded to the nearest 0.05 mL.

Errors in titration

Volumetric analysis involves a number of steps, a number of different skills and a number of different measurements. Mistakes, uncertainties and poor technique throughout this process can accumulate to produce errors and uncertainties in the final result. Due care and diligence must be applied throughout all stages. It is important not only to understand the method and to practise the technical skills involved, but also to be able to predict the effect that a particular error will have on the final result. In this way, the cause of unexpected results can be traced and subsequently rectified to improve the accuracy of the analysis. Table 10.7 shows some general areas in which mistakes could be made and what effects these mistakes have on the final result.

TABLE 10.7 Effect on the calculated result of some possible mistakes during volumetric analysis

	Effect if substance under analysis is in the. . .		
Situation	**burette**	**titration flask**	**Comments**
Rinsing water left in burette	Underestimated	Overestimated	The burette solution is diluted with water, so more is used.
Rinsing water left in pipette	Overestimated	Underestimated	The solution aliquot in the titration flask is diluted.
Indicator chosen changes colour too soon	Overestimated	Underestimated	The choice of indicator can be critical.
Water in titration flask	No effect	No effect	All necessary measurements are made before the chemicals are mixed with this water.
Concentration of standard solution lower than calculated	Overestimated	Overestimated	Fewer moles of the standard solution than expected will be used; the substance being analysed will appear to have a higher concentration.
Concentration of standard solution higher than calculated	Underestimated	Underestimated	More moles of the standard solution than expected will be used; the substance being analysed will appear to have a lower concentration.
Random errors	Variable	Variable	Random errors can be minimised by repetition. It is easy to obtain multiple results with volumetric analysis.

10.7.2 Acid–base titration

In acid–base titrations, the solutions and their products are usually colourless, and identification of the equivalence point would therefore be quite difficult. To overcome this problem, a few drops of a suitable acid–base **indicator** are usually added. Such indicators work because they are either weak acids or bases themselves and, when they change into their conjugate form, a distinct colour change occurs. The pH at which such colour changes occur varies from one indicator to another. Therefore, a key step in a particular titration is to choose an indicator that changes colour at the pH of the equivalence point.

Choosing indicators

The equivalence point of a titration occurs when the correct stoichiometric amounts are present. At this point, the pH of the solution is not always 7, due to the acid–base properties of the conjugate products that might be formed. It is important to choose an indicator that changes colour close to the correct pH value for the titration concerned. A further consideration is how quickly the pH changes around the point at which the indicator changes colour. This determines whether the end point is sharp and easily detected. Table 10.8 shows the pH values at which various indicators change colour.

FIGURE 10.24 Phenolphthalein is used as an indicator in some acid–base titrations.

TABLE 10.8 Some common acid–base indicators

Indicator	Colour at lower pH	Colour at higher pH	pH range for colour change
Methyl orange	Red	Yellow	3.1–4.4
Methyl red	Red	Yellow	4.2–6.3
Litmus	Red	Blue	5.0–9.0
Bromothymol blue	Yellow	Blue	6.0–7.6
Phenolphthalein	Colourless	Crimson	8.3–10.0

on Resources

Interactivity: Simulation of an acid-base titration (int-1224)

Titration curves

A **titration curve** is a graph of the volume added from a burette versus the pH of the solution in the titration flask. The graphs in figure 10.25 show titration curves for three different scenarios, including:

- a solution of strong acid being reacted with a solution of strong base
- a solution of strong base being reacted with a solution of weak acid
- a solution of strong acid being reacted with a solution of weak base.

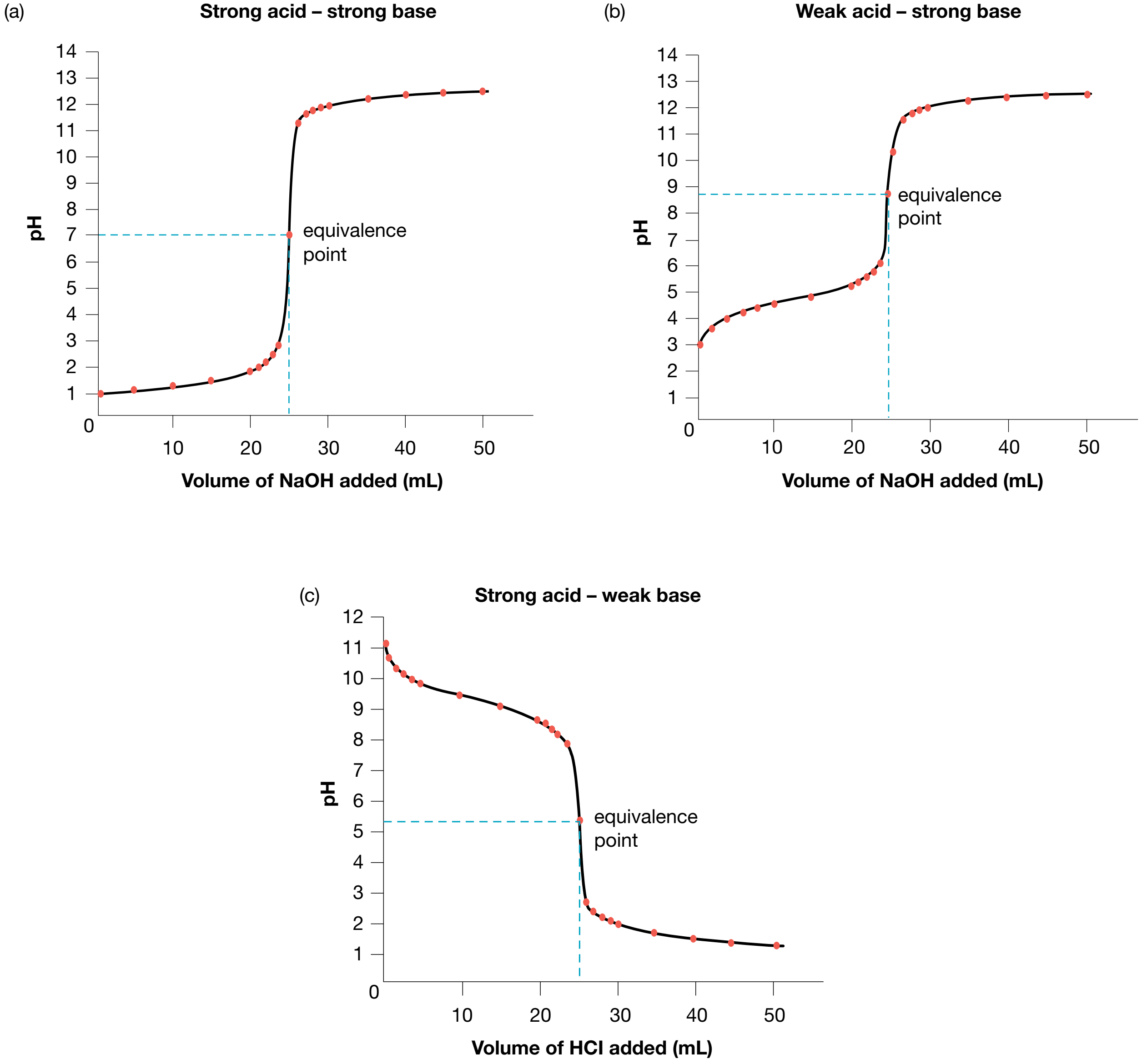
In figure 10.25a, note that all the indicators from table 10.8 change colour in the steep portion of its graph. The steepness of this section is such that the volume over which it occurs could be as little as one drop. Therefore, there is a wide choice of indicators that might be used, each one giving a sharp end point that is close to the correct pH.

In figures 10.25b and c, the situation is more complicated. In both cases, some indicators do not even change colour at the correct pH. In figure 10.25b, methyl red does not change colour at the correct pH and litmus would also be unsuitable because it begins to change colour before the steep section of the graph. Therefore, the end point occurs over a volume range that is too wide. In other words, it is not ‘sharp’. A good choice of indicator for this case would be phenolphthalein. Methyl red would be a good choice in figure 10.25c.

Examination of the titration curves in figure 10.25 also yields the following important points.

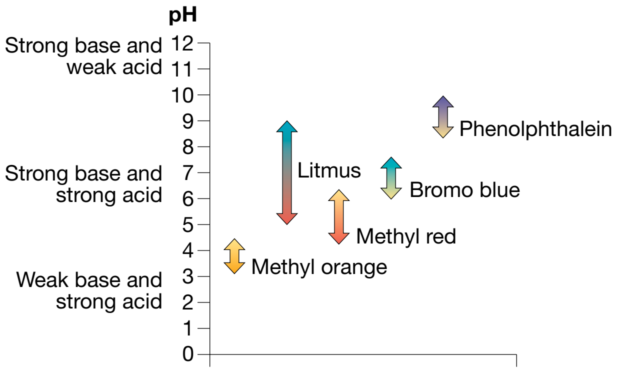
- The pH at the start of the titration depends on what is present in the flask at the start. Likewise, the pH at the end of the titration depends on what is present in excess at the end of the titration.

FIGURE 10.25 Three titration curves



- The pH at the equivalence point for the strong acid/strong base combination is 7. This is because the conjugate species present at this point are weak species and cancel each other out.
- When there is a weak species involved, the conjugate is appreciably stronger and this affects the pH at the equivalence point. For example, if a weak acid is involved, its (stronger) conjugate base is present at equivalence, thus raising the pH at this point.

FIGURE 10.26 Indicator colour changes



Some redox reactions are self-indicating but there are occasions where an indicator is required. An example of an indicator used in redox titrations is starch. Starch is used to detect the presence of iodine, I_2, which is formed in titrations from the oxidation of iodide ions, I^-. Starch is dark blue in the presence of iodine. Another indicator suitable for redox titrations is methylene blue, which is blue in the presence of an oxidising agent and colourless in the presence of a reducing agent.

on Resources

Digital document Experiment 10.4 Standardisation of hydrochloric acid (doc-31275)
Teacher-led video Experiment 10.4 Standardisation of hydrochloric acid (tlvd-0761)

Analysis of organic compounds using acid–base titration

Volumetric analysis can be used to analyse compounds with distinct acid–base properties, such as carboxylic acids and amines, as well as those that have redox properties, such as alcohols and aldehydes. Variations to the basic method of titration have evolved, all aimed at taking into account the properties of the substances involved. As a result, volumetric analysis can be performed using simple (or direct) titration where one reactant is added to the other until the correct stoichiometric proportions are present, as well as by more sophisticated variations.

Once concordant titres have been obtained, the average volume of the titres (in litres) is used to calculate the number of moles of either the analyte or titrant added to the conical flask from the burette.

The basic steps of any stoichiometric calculation include:

- writing a balanced chemical equation
- converting the known information into amounts (in moles)
- calculating amounts (in moles) of a second substance
- changing amounts (in moles) of this substance to the type of information required.

TIP:

- **Because solutions are involved, the formula $n = cV$ is frequently used.**
- **Due to the necessities of experimental procedure, dilution often takes place and must be considered, so the formula $c_1V_1 = c_2V_2$ may be useful.**

SAMPLE PROBLEM 6

Propanoic acid is used as a preservative in animal feeds. It is sold as a range of solutions that contain between 10 and 100% (m/v) propanoic acid.

In the analysis of one such solution, a 25.00 mL sample was carefully diluted to 250.0 mL in a volumetric flask. 25.00 mL aliquots of this diluted solution were then reacted with 0.2500 M sodium hydroxide. The average of the concordant titres obtained was 32.10 mL.

Calculate the percentage (%m/v) of propanoic acid in the original solution.

THINK	WRITE
1. Write the balanced chemical equation between propanoic acid and sodium hydroxide to obtain the mole ratios of the reactants.	$CH_3CH_2COOH(aq) + NaOH(aq) \rightarrow CH_3CH_2COONa(aq) + H_2O(l)$
2. Calculate the number of moles of the substance with the known concentration (titrant), NaOH by first identifying the variables and checking the units required. Volume is required in litres; convert mL to L.	$c(\text{NaOH}) = 0.2500\text{ M}$ $V(\text{NaOH}) = \frac{32.10}{1000}$ $n(\text{NaOH})_{\text{used}} = cV$ $= 0.25 \times \frac{32.10}{1000}$ $= 0.008\,025\text{ mol}$

▶

3. Use the mole ratio from the equation to calculate the number of moles of the analyte in the diluted sample.

$$n(\text{NaOH})_{\text{used}} = n(\text{CH}_3\text{CH}_2\text{COOH})_{\text{diluted}}$$
$$\therefore n(\text{CH}_3\text{CH}_2\text{COOH})_{\text{diluted}} = 0.008\,025 \text{ mol}$$

4. To determine the number of moles of propanoic acid in the original aliquot, multiply the calculated number of moles in the diluted sample by volume of the volumetric flask and then divide it by the volume of the undiluted sample.

$$n(\text{CH}_3\text{CH}_2\text{COOH}_{\text{original}}) \text{ in } 25.00 \text{ mL} = \frac{0.008025 \times 250.0}{25.00}$$
$$= 0.08025 \text{ mol}$$

5. To calculate the percentage (%m/v) of propanoic acid in the original solution, the mass of propanoic acid must first be determined by applying the formula $n = \frac{m}{M}$.

$$m(\text{CH}_3\text{CH}_2\text{COOH}) \text{ in } 25.00 \text{ mL} = n \times M$$
$$= 0.08025 \times 74.0$$
$$= 5.94 \text{ g}$$

6. The percentage (%m/v) of propanoic acid can be calculated using the mass from step **5** and the volume (mL) of the undiluted sample. Express answer to the correct number of significant figures.

$$\%(\text{m/v}) = \frac{5.94}{25.00} \times 100$$
$$= 23.8\%$$

PRACTICE PROBLEM 6

Ethylamine is widely used as a precursor to many herbicides. A chemist investigating the production of herbicides wished to check the claim on a newly purchased bottle that it contains between 68 and 72%(m/v) ethylamine dissolved in water.

After carefully diluting 10.00 mL of the amine solution to 1000 mL in a volumetric flask, 20.00 mL aliquots of this diluted solution were taken and titrated against a 0.197 M hydrochloric acid solution. Using methyl orange as the indicator, an average titre of 15.80 mL was obtained.

Do the contents of the bottle fall within the specifications shown on the label?

10.7.3 Redox titration

In some situations, a reaction can be self-indicating. This is often true in redox titrations where a substance involved in the analysis may have conjugate forms that display distinctly different colours. An example is in a titration involving the permanganate ion, MnO_4^-, which is bright purple, because an indicator is not required due to the reduced form, Mn^{2+}, being almost colourless. The permanganate ion, as well as the orange-coloured dichromate ion, $Cr_2O_7^{2-}$, are both strong oxidants and the various oxidation states of chromium and manganese ionic compounds are useful for redox reactions.

FIGURE 10.27 The presence of a starch-iodine complex indicates the end point of this redox titration.

Another well-known redox titration is the use of iodine and starch as an indicator. When iodine, I_2, is mixed with starch, a blue/black colour is observed. The appearance, or disappearance, of the blue colour formed in the presence of iodine with starch signals the end point of the titration.

on Resources

Interactivity Simulation of a redox titration (int-1225)

SAMPLE PROBLEM 7

The ethanol content in wine can be determined by a redox titration using potassium dichromate. The ethanol in the wine is oxidised to ethanoic acid, while the orange dichromate ions, $Cr_2O_7^{2-}$, are reduced to green Cr^{3+} ions. The reaction is therefore self-indicating. The equation for the reaction is:

$$2Cr_2O_7^{2-}(aq) + 3CH_3CH_2OH(aq) + 16H^+(aq) \rightarrow 4Cr^{3+}(aq) + 3CH_3COOH(aq) + 11H_2O(l)$$

In a particular analysis, a 25.00 mL sample of wine was poured into a volumetric flask and carefully diluted to 250.0 mL. 20.00 mL aliquots were then titrated against 0.150 M potassium dichromate solution. The average titre obtained was 17.50 mL.

Calculate the concentration of ethanol (in M) of the tested wine.

Teacher-led video: SP7 (tlvd-0719)

THINK	WRITE
1. Calculate the number of moles of the reactant of known concentration using $n = cV$. In this case, it is the number of moles of dichromate added from the burette. Remember to check the units required. Concentration is required in moles and volume in litres so convert mL to L.	$n(Cr_2O_7^{2-})_{used} = cV$ $= 0.150 \times \frac{17.50}{1000}$ $= 0.0026325\ \text{mol}$
2. Using the mole ratios from the equation given calculate the number of moles of the diluted reactant (ethanol) in each 20.00 mL aliquot.	$\frac{n(C_2H_5OH)}{n(Cr_2O_7^{2-})} = \frac{3}{2}$ $n(C_2H_5OH) = \frac{3 \times 0.002625}{2}$ $= 0.0039375\ \text{mol}$
3. Calculate the ethanol concentration of the dilute ethanol by dividing the number of moles by the aliquot volume (0.02000 L). This is the same concentration of the entire contents of the volumetric flask.	$n = cV$ $c = \frac{n}{V}$ $[C_2H_5OH_{diluted}] = \frac{0.0039375\ \text{mol}}{0.020000\ \text{L}}$ $= 0.19688\ \text{M}$
4. To determine the original concentration of the ethanol in moles per litre (M), apply the formula $c_1V_1 = c_2V_2$ where c_1 is the original concentration, V_1 is the original volume, c_2 is the dilute concentration and V_2 is the dilute volume.	$c_1V_1 = c_2V_2$ $[C_2H_5OH_{wine}] = \frac{c_2V_2}{V_1}$ $[C_2H_5OH_{wine}] = \frac{0.19688 \times 250.0}{25.00}$ $= 1.97\ \text{M}$

PRACTICE PROBLEM 7

A solution of ethanal (C_2H_4O) was standardised using 0.0557 M potassium permanganate. A 20.00 mL aliquot of ethanal was placed into a 250.0 mL volumetric flask and made up to the mark with distilled water.

Three 20.00 mL aliquots of the diluted ethanal were placed in conical flasks and titrated against the permanganate solution. The average titre was 18.50 mL.

Calculate the molarity of the ethanal solution.

10.7 EXERCISE

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1. Which piece of glassware would be used to:
   (a) deliver an aliquot
   (b) deliver a titre
   (c) react the analyte and titrant?
2. State what you would rinse the following items with before a titration.
   (a) Burette
   (b) Pipette
   (c) Conical flask
   (d) Volumetric flask
3. Name an indicator suitable for the titration of an unknown concentration of ethanoic acid in a conical flask against standard 0.10 M NaOH.
4. Explain why a redox titration with $K_2Cr_2O_7$ and ethanol doesn't require an indicator.
5. The substance potassium hydrogen phthalate, $KH(C_8H_4O_4)$, is frequently used as a primary standard for acid–base determinations. Calculate the concentration of a solution that is made by weighing out 10.19 g of this substance and accurately dissolving it in 500 mL of water.
6. A student standardised a solution of sodium hydroxide as follows: 20.00 mL of the hydroxide solution was titrated with 0.0921 M hydrochloric acid, using methyl orange as indicator. Titres of 18.67 mL, 18.73 mL and 18.64 mL were obtained.
   (a) Write the equation for the reaction occurring during this titration.
   (b) Calculate the molarity of the sodium hydroxide solution from the given data.
   (c) Why is the methyl orange indicator necessary in this experiment?
   (d) Once its concentration is determined, can the sodium hydroxide solution be called a standard solution? Explain.
7. A student standardised a hydrochloric acid solution as follows: 20.00 mL of a 0.0592 M sodium carbonate solution was pipetted into a conical flask. When the acid was added from the burette, 19.15 mL was required to reach the end point.

   Given that the equation for the reaction is:

   $$Na_2CO_3(aq) + 2HCl(aq) \rightarrow 2NaCl(aq) + CO_2(g) + H_2O(l)$$

   calculate the accurate concentration of the hydrochloric acid.
8. To analyse a sample of vinegar for its ethanoic acid content, a student began by accurately diluting a 20.00 mL sample of the vinegar to 250.0 mL in a volumetric flask. The student then placed 20.00 mL samples of this diluted vinegar in conical flasks and titrated them against a 0.0500 M solution of sodium hydroxide. The average titre obtained was 21.55 mL.

   Assuming that ethanoic acid is the only acid present in the vinegar, calculate the concentration of the ethanoic acid in the vinegar (in g L^{-1}).
9. A student was standardising a solution of sodium hydroxide using diprotic 0.100 M oxalic acid. First the student rinsed the burette and conical flask with water. Next, she filled the burette with the sodium hydroxide solution. She then placed a 20.00 mL aliquot of 0.100 M oxalic acid in a conical flask with three drops of methyl orange indicator. She performed the titration and the solution in the conical flask changed from red to yellow after the addition of 9.50 mL of NaOH.

   The reaction between sodium hydroxide and oxalic acid is

$$C_2H_2O_4(aq) + 2NaOH(aq) \rightarrow Na_2C_2O_4(aq) + 2H_2O(l)$$

(a) Calculate the mass of oxalic acid powder needed to make 100 mL of standard 0.100 M oxalic acid.
(b) Calculate the concentration of sodium hydroxide.
(c) State two errors in the student's procedure and the effect they have on the calculated concentration of NaOH.
(d) How could the reliability of the student's titre volumes be improved?

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10.8 Review

10.8.1 Summary

Mass spectrometry

- Qualitative analysis finds what substances are present.
- Quantitative analysis measures the quantity of substance present.
- A mass spectrometer (MS) analyses compounds to determine their mass/charge (m/z) ratio. It does this by analysing the path of ionic fragments of molecules through a magnetic field.
- The output of a mass spectrometer is a mass spectrum that generally looks like a bar graph. Each column represents an ion with a specific m/z ratio. The height of the column shows the relative abundance of the ion. The highest peak is known as the base peak and is assigned a value of 100%. Most ions formed have a single positive charge, so the m/z value is usually equivalent to the mass.
- Another important peak in a mass spectrum of an organic compound is the parent peak (also called the molecular ion peak). This is the peak that represents the ion formed when an electron is knocked from the original molecule, leaving it with a positive charge. The relative molecular mass of the compound is therefore the same as this m/z value.

Infrared spectroscopy

- Infrared (IR) spectroscopy identifies the functional groups and single, double and triple bonds in organic molecules. This qualitative method measures the characteristic amount of energy that the bonds in molecules transmit when exposed to radiation in the infrared portion of the electromagnetic spectrum.
- The infrared spectrum measures % transmittance on the y-axis (vertical axis) and wave number (cm^{-1}) on the x-axis (horizontal axis). Wave number is the reciprocal of the wavelength. The spectrum runs along the top of the readout when 100% of the light is transmitted and dips down to make an inverted peak when light is absorbed. Different bonds in an organic molecule have characteristic wave numbers and produce dips or inverted peaks that allow them to be identified.
- IR spectra usually change scale at 2000 cm^{-1}. The scale runs backwards.
- The fingerprint region of the spectrum, below 1000 cm^{-1}, is a crowded series of peaks that can be used to identify a substance because it is identical in every analysis of that substance.
- In general, the more types of atoms there are in a molecule, the more peaks appear on the IR spectrum, because these atoms affect the bonding between each other and absorb at slightly different wave numbers.
- To distinguish between alcohols and carboxylic acids, look at two regions. Alcohols have a peak between 3200 and 3600 cm^{-1} but no peak near 1700 cm^{-1}; carboxylic acids have a very broad peak between 2500 and 3500 cm^{-1} and a strong narrow peak near 1700 cm^{-1}.

- To distinguish between esters and carboxylic acids, an ester has only one peak, between 1720 and 1840 cm^{-1}, but a carboxylic acid has two peaks.

NMR spectroscopy

- Uses of NMR include organic synthesis, quality control of medicines, forensic analysis of proteins, and identification of oil and gas deposits.
- An NMR spectrum is a two-dimensional graph of peak height versus chemical shift, δ (in ppm).
- Chemical shifts in ^{13}C NMR correspond to a carbon-13 atom in a particular environment within a molecule.
- Chemical shifts in ^{1}H NMR correspond to a hydrogen atom in a particular environment within a molecule.
- A signal in a low-resolution ^{1}H spectrum can be split into a set of peaks in the high-resolution spectrum. The number of peaks in the high-resolution spectrum indicates the number of hydrogen atoms adjacent to the hydrogen atom that has produced that signal. For simple molecules, the number of peaks is one more than the number of hydrogen atoms attached to the adjacent carbon atom of that hydrogen atom. This is often called the $n + 1$ rule.
- For the high-resolution ^{1}H NMR spectrum of ethanol (and other alcohols), even though the $-OH$ and $-CH_2$ groups are separated by four bonds, under most conditions the $-OH$ signal does not show splitting.
- ^{1}H nuclei can interact with other ^{1}H nuclei near them, and the effect can be measured by the number of peaks in the NMR spectrum.

Combining spectroscopic techniques

- The properties of a material have an important bearing on the method chosen to analyse it.

Chromatography

- In all forms of chromatography, separation is achieved when a mobile phase (consisting of the mixture to be analysed and a solvent) is made to move over a stationary phase. The stationary phase has a large surface area. Separation occurs due to interactions between the substances in the mobile phase and the stationary phase. The weaker these interactions, the faster a substance moves through the column.
- High-performance liquid chromatography (HPLC) is an instrumental technique that is based on the principles of chromatography.
- In HPLC, a high-pressure liquid (eluent) is pumped through a column that is packed with a finely divided solid. Many organic substances can be separated, identified and quantified using this method.
- Separation on HPLC occurs due to interactions between the substances in the mobile phase and the stationary phase. The weaker these interactions with the stationary phase, the faster a substance moves through the column.
- Retention time (of a component), R_t, is an important term associated with HPLC. It is the time from injection of the sample until the component is detected leaving the column. Components in a mixture can be identified by their retention times.
- When HPLC is used for quantitative analysis, it is necessary to use standards of known concentration. The readings produced by these standards are then graphed against their concentrations so that a graph called a calibration curve can be drawn. The concentration of an unknown sample can then be deduced from this graph by interpolation.
- HPLC can be used for both qualitative and quantitative analysis.

Volumetric analysis by titration

- Volumetric analysis is a quantitative technique that uses standard solutions and accurately known volumes to determine the concentration of a solution accurately.
- Common reactions in volumetric analysis are acid–base reactions and redox reactions.
- A standard solution is one whose concentration is accurately known.
- A primary standard is a substance with certain properties that enable it to be weighed and made up into a solution whose concentration is precisely known.

- A secondary standard is a solution that has been standardised using another standard.
- Titration is the process by which burettes and pipettes are used in the procedure of volumetric analysis.
- The equivalence point of a titration occurs when the correct stoichiometric amounts of the reactants involved are mixed in the titration vessel.
- The end point of a titration is the stage at which the chosen indicator changes colour. An indicator is selected so that its end point approximates the equivalence point of the reaction.

Summary of the applications of instrumental analysis

Instrument	Type of radiation	Basis of analysis	Method of analysis	Type of analysis
Mass spectrometer	–	Mass/charge ratio of atoms or groups of atoms	Mass spectrum analysis	Identification of molecular mass, molecular fragments and structures
IR spectrometer	Infrared light	Change in vibration of molecules when they absorb IR radiation	Infrared absorption spectrum analysis	Identification of double bonds, triple bonds and functional groups in organic molecules
NMR spectrometer	Radio waves	Change in nuclear spin of nuclei of some atoms when they absorb or emit radio waves	NMR spectrum analysis	Identification of structural relationships within organic molecules
HPLC	–	Adsorption to stationary phase and solubility in mobile phase	Chromatogram	Separation, identification and quantification of organic compounds

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10.8.2 Key terms

adsorption the adhesion of atoms, ions or molecules from a gas, liquid or dissolved solid to a surface
aliquot the liquid from a pipette
analytes the components of a sample
base peak the most abundant ion in a mass spectrum
burette a graduated glass tube for delivering known volumes of a liquid, especially in titrations
calibrated ensure an instrument's accuracy
calibration curves a graph of reading versus concentration
chemical shift the horizontal scale on a NMR spectra
chromatogram a chart that results from analysis by chromatography
concordant describes titres that are within a defined volume of each other, such as 0.10 mL
desorption the removal of a substance from or through a surface; the opposite of adsorption
eluent a substance used as a solvent in separating materials
end point the experimentally determined equivalence point at which the indicator just changes colour or the pH curve becomes vertical
equivalence point where two reactants have reacted in their correct mole proportions in a titration
fingerprint region the lower end of the infrared spectrum
HPLC high-performance liquid chromatography; method used to separate the components of a mixture

indicator a chemical compound that changes color and structure when exposed to certain conditions and is therefore useful for chemical tests

infrared (IR) describes spectroscopy that deals with the infrared region of the electromagnetic spectrum

mass spectrometry the investigation and measurement of the masses of isotopes, molecules and molecular fragments by ionising them and determining their trajectories in electric and magnetic fields

mobile phase the liquid or gas that flows through a chromatography system, moving the materials to be separated at different rates over the stationary phase

molecular ion whole molecules that produce ions with a peak at the relative molecular mass of the compound

n+1 rule for simple molecules; the number of peaks is one more than the number of hydrogen atoms on the carbon atom next to that hydrogen atom and chemically different from that hydrogen atom

pipette a slender tube for transferring or measuring small quantities of liquid

primary standard a substance used in volumetric analysis that is of such high purity and stability that it can be used to prepare a solution of accurately known concentration

qualitative analysis an investigation used to identify the presence or absence of elements, ions or molecules in a sample

quantitative analysis an investigation used to determine the amount of a given element or compound in a known weight or volume of material

retention time the time taken for each component of a sample to travel from the injection port to the end of the column

sample a substance to be analysed

spectroscopy the investigation and measurement of spectra produced when matter interacts with or emits electromagnetic radiation

standard solution a solution that has a precisely known concentration

stationary phase a solid with a high surface area, or a finely divided solid coated with liquid. It shows different affinities for various components of a sample mixture when separating them by chromatography.

titrant a solution of known concentration

titration curve curve used to measure the volume of a titrant against pH

titration process used to determine the concentration of a substance by using a pipette to deliver one substance and a burette to deliver another substance until they have reacted exactly in their mole ratios

titre the volume delivered by a burette

volumetric analysis determination of the concentration, by volume, of a substance in a solution, such as by titration

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Digital document Key terms glossary – Topic 10 (doc-31429)

10.8.3 Practical work and experiments

Experiment 10.4

Standardisation of hydrochloric acid

Aim: To determine the accurate concentration of a solution of hydrochloric acid

Digital document: doc-31275

Teacher-led video: tlvd-0761

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Digital documents Practical investigation logbook (doc-31430)
Experiment 10.1 Spectroscopy (doc-31272)
Experiment 10.2 Separation of food dyes using chromatography (doc-31273)
Experiment 10.3 Separating mixtures using column chromatography (doc-31274)

10.8 Exercises

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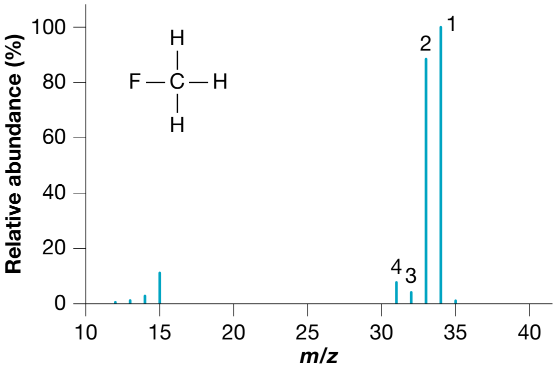
10.8 Exercise 1: Multiple choice questions

1. The tallest peak in a mass spectrum is called the:
   - **A.** molecular ion
   - **B.** parent peak
   - **C.** base peak
   - **D.** calibration peak.
2. In the following spectrum, which peak corresponds to the $[CH_2F]^+$ fragment?



   - **A.** 1
   - **B.** 2
   - **C.** 3
   - **D.** 4
3. The difference between the infrared spectra of an alcohol and a carboxylic acid is that the alcohol spectrum:
   - **A.** has a peak near 3200–3600 cm^{-1} and a peak near 1700 cm^{-1}
   - **B.** has a peak near 3200–3600 cm^{-1} but no peak near 1700 cm^{-1}
   - **C.** has a peak near 1700 cm^{-1} but no peak near 3200–3600 cm^{-1}
   - **D.** does not have a peak near 3200–3600 cm^{-1} or near 1700 cm^{-1}.
4. The proton NMR spectrum of chloroethane consists of:
   - **A.** a singlet and a doublet
   - **B.** a doublet and a triplet
   - **C.** a triplet and a quartet
   - **D.** a doublet and a quartet.
5. How many signals does the carboxylic acid $(CH_3)_2CHCOOH$ have in its ^1H NMR and ^{13}C NMR spectra?
   - **A.** Three ^1H signals and three ^{13}C signals
   - **B.** Three ^1H signals and four ^{13}C signals
   - **C.** Four ^1H signals and four ^{13}C signals
   - **D.** Five ^1H signals and three ^{13}C signals
6. Which of the following instrumental techniques would be most helpful to identify and quantify the presence of a known impurity in an illegal drug?
   - **A.** MS
   - **B.** IR
   - **C.** NMR
   - **D.** HPLC

7. Which feature of a chromatogram is most useful in qualitatively analysing the components of a mixture?
   - A. The time after injection at which the peaks occur
   - B. The heights of the peaks
   - C. The wavelengths at which the peaks appear
   - D. The widths of the peaks
8. Some typical steps for part of a volumetric analysis are shown below in jumbled order.
   - a. Fill burette with required solution.
   - b. Rinse burette with water.
   - c. Perform titration and record final volume.
   - d. Rinse burette with a small amount of the solution that it is to contain.
   - e. Take an initial reading.

   The only correct order for these steps is:
   - A. d, a, e, c, b
   - B. b, d, a, e, c
   - C. d, b, a, e, c
   - D. b, d, e, a, c.

Use the following information to answer questions **9** *and* **10**.

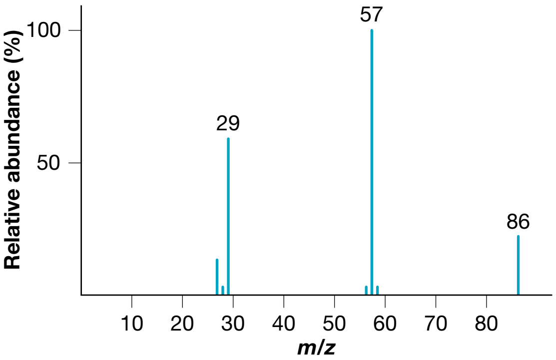
In a titration to determine the concentration of some hydrochloric acid, a student pours the acid into a burette and titrates it against some standardised sodium carbonate solution.

9. If a small amount of water was left in the titration flask before the aliquot of sodium carbonate solution was added, what effect would this have on the calculated concentration of the hydrochloric acid solution?
   - A. The answer would depend on the amount of water left in the flask.
   - B. The concentration would appear to be higher.
   - C. The concentration would appear to be lower.
   - D. There would be no effect on the calculated concentration.
10. After completing this experiment, the student compares her result with those obtained by other members of her class. She discovers that her result is significantly higher.

    A possible reason for this is that:
    - A. there was still some water in the burette when she filled it with the hydrochloric acid solution
    - B. she mistakenly used hydrated sodium carbonate instead of anhydrous sodium carbonate to prepare the standard solution
    - C. she mistakenly wrote down an initial burette reading of 10.09 mL instead of 10.90 mL
    - D. she used too many drops of the indicator solution.

10.8 Exercise 2: Short answer questions

1. Consider the following mass spectrum of a ketone, and answer the following questions.

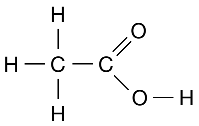


   - a. What is the *m/z* value for the parent ion?
   - b. What is the *m/z* value for the base peak?

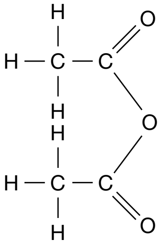
c. The peak at $m/z = 57$ represents the loss of what possible fragment from the molecule?

d. Suggest a possible structure for the compound.

2. The production of the painkiller aspirin involves the reaction of a hydroxyl group in salicylic acid with ethanoic acid. However, because this reaction is so slow, another compound, ethanoic anhydride, is used. The structures of ethanoic acid and ethanoic anhydride are shown below. Refer to particular bonds and wave numbers to explain how these two compounds could be distinguished using IR spectroscopy.

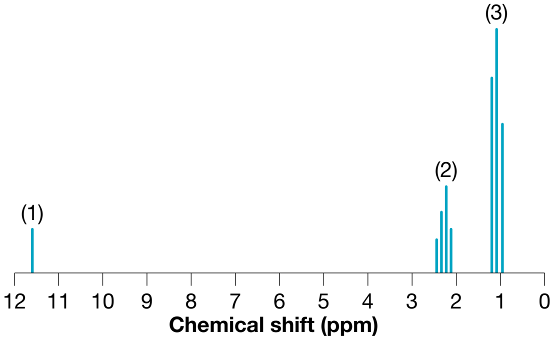


ethanoic acid



ethanoic anhydride

3. Shown below is an NMR spectrum of a molecule with the molecular formula $C_3H_6O_2$.



a. Identify the peaks using the table of chemical shifts (table 10.5).

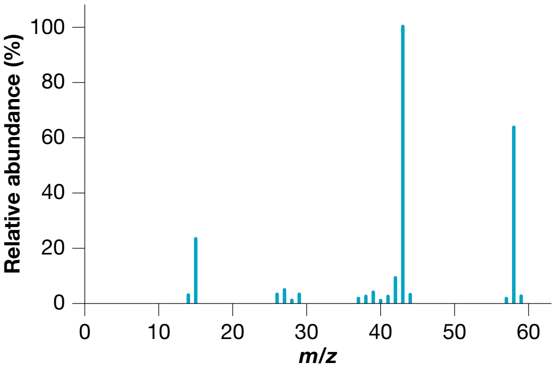
b. How many peaks would you most likely find in the set of peaks for the CH_2 group?

c. Sketch the structure of the molecule.

4. Compound A has the molecular formula C_3H_8O.

a. Draw the structural isomers represented by this formula.

Compound A reacts with acidified potassium dichromate solution to form compound B, which has the molecular formula C_3H_6O. The proton NMR spectrum of compound B shows only one peak, and its mass spectrum is shown below.



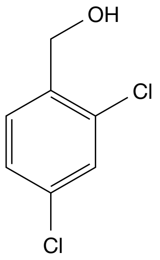
b. Name and draw the structure of compound B. Justify your answer by referring to the NMR information and mass spectrum.

c. Identify the fragment with $m/z = 43$.

d. Write an equation showing the formation of the fragment at $m/z = 15$.

e. How many peaks would you expect in the ^{13}C NMR spectrum of compound B?

5. In chromatography, why is it important that the stationary phase has a large surface area?
6. A sample containing a complex mixture of substances is analysed using HPLC. A peak of interest appears at retention time 5.3 minutes. When a control sample of substance X is injected, a peak appears at 5.3 minutes. Can we say for certain that the original mixture contains substance X? Explain why or why not.
7. A new brand of throat lozenges called ‘Throat Eze’ makes the claim that each lozenge contains 1.2 mg of dichlorobenzyl alcohol.



Dichlorobenzyl alcohol

To test this claim, a government analyst dissolved the lozenge in a solvent made from water and ethanol and made it up to 500 mL. A small sample was then injected into a high-performance liquid chromatograph. A chromatogram containing a large number of peaks was obtained.

The operator then ran a series of dichlorobenzyl alcohol standards of known concentration through the instrument. Chromatograms for each standard were obtained, as well as a measure of the area under each of the reference peaks.

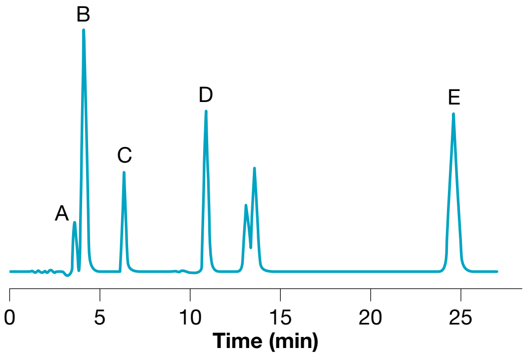
a. Explain how the standards would allow the dichlorobenzyl alcohol peak from the original chromatogram to be identified.
b. What is the purpose of using a set of standards as described and subsequently obtaining the area under their peaks?
c. The following table shows the results from the standards, together with a measurement for the area under the peak that was identified as dichlorobenzyl alcohol from the original chromatogram.

Is the claim made by the manufacturer true?

Results from HPLC analysis of dichlorobenzyl alcohol

Concentration of standard (mgL^{-1})	Area under peak (arbitrary units)
1.0	83
2.0	160
3.0	241
4.0	315
Lozenge extract	193

8. The following HPLC was obtained when a sample of a mixture was analysed.



a. Which compound spent the most time in the stationary phase?
b. Which compound was the least concentrated?

9. Aspirin, $CH_3COOC_6H_4COOH$, is also known as acetylsalicylic acid. It is a medication used to treat pain and fever.

a. Write the equation for its reaction with sodium hydroxide.
b. A sample of aspirin is analysed using standardised 0.105 M sodium hydroxide with phenolphthalein as an indicator. Calculate the mass of aspirin required to give a titration of 22.80 mL of sodium hydroxide.

10. The level of vitamin C (ascorbic acid) in citrus fruits can be determined by titration. The preferred method involves a redox titration using iodine. Acid–base titration is not used due to the presence of other acids, most notably citric acid.

The reaction involved produces dehydroacsorbic acid and iodide ions as its products, and starch is used as an indicator. The equation for this reaction is:

$$C_6H_8O_6(aq) + I_2(aq) \rightarrow C_6H_6O_6(aq) + 2I^-(aq) + 2H^+(aq)$$

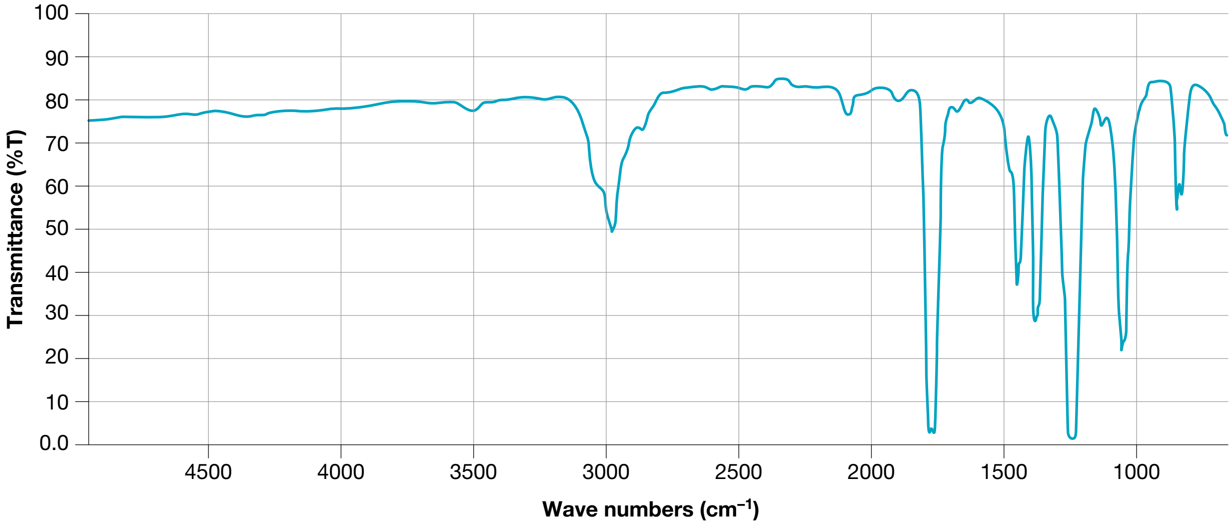
In an experiment to determine the level of vitamin C in oranges, the juice from a 210 g orange was carefully collected and strained into a 100.0 mL volumetric flask. It was then made up to the mark with water. 20.00 mL aliquots of this solution were titrated against a standardised 0.00500 M iodine solution. The average titre required was 24.80 mL.

a. Calculate the concentration (in M) of vitamin C in the diluted orange juice.
b. Calculate the mass of vitamin C in the volumetric flask.
c. Calculate the level of vitamin C in the orange tested. Express your answer as mg/100 g of fruit.

10.8 Exercise 3: Exam practice questions

Use the following information to answer questions **1** *and* **2**.

Esters are produced by the reaction between alcohols and carboxylic acids. One particular ester was distilled to purify it and remove waste products and unused reactants. The purified mixture was placed into an infrared spectrometer and produced the following spectrum.



Question 1 (1 mark)

The peak at approximately 1300 cm^{-1} is caused by:

A. C–H
B. C=O
C. O–H
D. C–O.

Question 2 (1 mark)

Which of the following statements is correct?

A. The ester is pure.
B. The ester is impure because the presence of a carboxylic acid is shown.
C. The ester is impure because the presence of an alcohol is shown.
D. The ester is impure because both an alcohol and carboxylic acid are shown.

Question 3 (1 mark)

The number of unique ^{13}C NMR environments produced by $(CH_3)_2CHClCH_3$ is:

A. 1
B. 2
C. 3
D. 4

Question 4 (1 mark)

Which of the following would be seen in a ^{1}H NMR spectrum of $(CH_3)_2CClCH_3$?

A. Two unique hydrogen environments
B. Two doublets with integration areas in the ratio 6:3
C. A set of seven peaks
D. A singlet

Question 5 (7 marks)

Malic acid, $C_4H_6O_5$, is used to impart the sour taste in candy. A 10.0 g candy sample was melted and placed in a 250.0 mL volumetric flask, which was made up to the mark with distilled water. A 25.00 mL aliquot of the candy/water mixture was placed in a conical flask.

A burette was then filled with 0.0100 M $KMnO_4$ solution and titrated into the dilute candy mixture until the end point was reached. This was repeated three times until concordant titres were obtained according to the following reaction.

$$2\,MnO_4^-(aq) + 5\,C_4H_6O_5(aq) + 6\,H^+(aq) \rightarrow 2\,Mn^{2+}(aq) + 5\,C_4H_4O_5(aq) + 8\,H_2O(l)$$

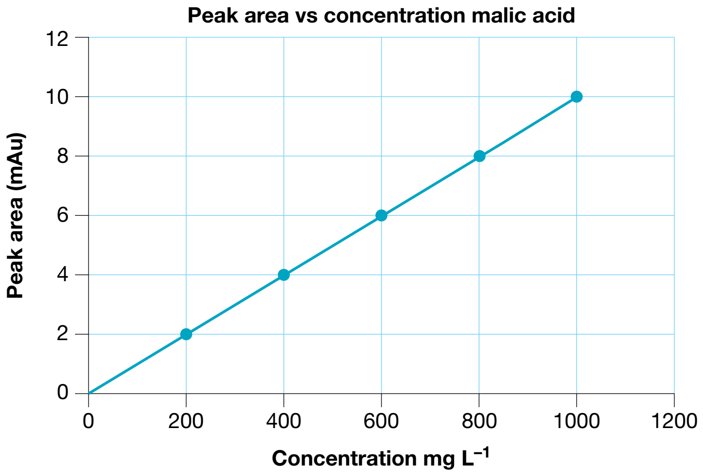
The average titre was 15.50 mL.

a. Calculate the average amount, in mol, of malic acid in the 25.00 mL aliquot. **1 mark**

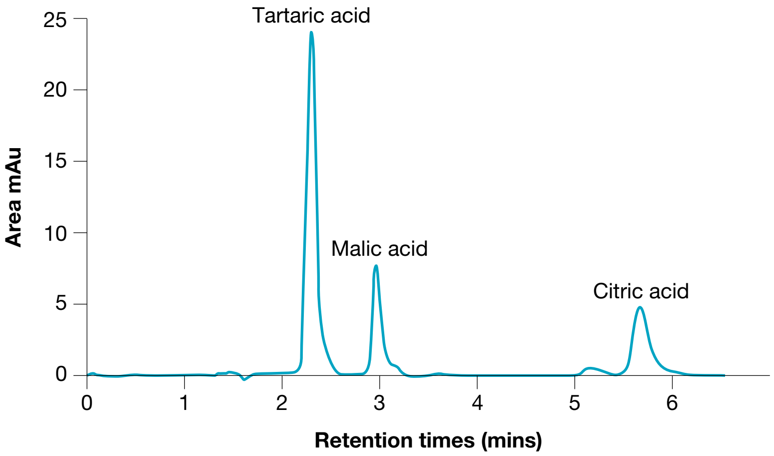
b. Calculate the percentage mass (m/m) of malic acid in the 10.0 g sample. **1 mark**

c. Another 10.0 g candy sample was quantitatively analysed for its malic acid content using HPLC. A suitable procedure was then used to liquefy the entire candy sample into a 50.0 mL volume.

A series of malic acid standards were run through the chromatograph and the peak area at R_t of 3 minutes was recorded and used to produce the following calibration graph.



The sample was then run through the column and produced the following chromatogram.



i. What is the concentration of malic acid in the 50.0 mL sample? **1 mark**

ii. What is the percentage mass of malic acid in the 10.0 g candy sample? **2 marks**

iii. Suggest and justify a reason as to why the results from the titration and HPLC analysis are quite different. **2 marks**

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AREA OF STUDY 1 How can the diversity of carbon compounds be explained and categorised?

OUTCOME 1

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.

PRACTICE EXAMINATION

STRUCTURE OF PRACTICE EXAMINATION		
Section	**Number of questions**	**Number of marks**
A	20	20
B	3	30
	Total	**50**

Duration: 50 minutes

Information:

- This practice examination consists of two parts. You must answer all question sections.
- Pens, pencils, highlighters, erasers, rulers and a scientific calculator are permitted.
- You may use the VCE Chemistry Data Book for this task.

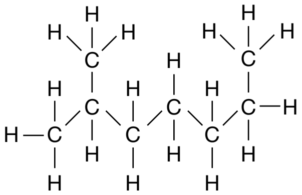
on Resources

Weblink VCE Chemistry Data Book

SECTION A — Multiple choice questions

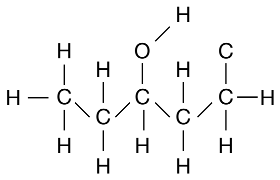
All correct answers are work 1 mark each; an incorrect answer is worth 0.

1. What is the name of the following molecule?



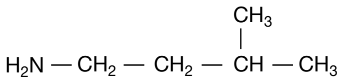
A. 1,6-dimethylhexane
B. 2,6-dimethylhaxane
C. 2-methylheptane
D. 6-methylheptane

2. What is the correct semi-structural formula for the following molecule?



A. $CH_3CH_2C(HOH)CH_2CH_3$
B. $CH_3CH_2CH(OH)CH_2CH_3$
C. $CH_3CH_2HCOHCH_2CH_3$
D. $CH_3CH_2HC(OH)CH_2CH_3$

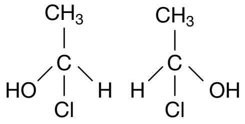
3. The compound below is:



$H_2N-CH_2-CH_2-CH(CH_3)-CH_3$

A. An amino acid
B. An amide
C. An amine
D. A nitroalkane.

4. What type of isomerism is shown?



A. Chain isomerism
B. Optical isomerism
C. Stereoisomerism
D. Functional isomerism

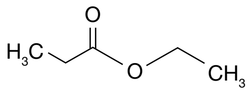
5. Which of the following is a tertiary alcohol?

A. Pentan-3-ol
B. Pent-2-en-1-ol
C. Propan-2-ol
D. 2-methylpropan-2-ol

6. What is the correct semi-structural formula of 2,4-dimethylpentane?

A. $CH_3CH(CH_3)CH_2CH_2CH(CH_3)CH_3$
B. $CH_2(CH_3)CH_2CH(CH_3)CH_3$
C. $CH_3CH(CH_3)CH_2CH(CH_3)CH_3$
D. $CH_3CH(CH_3)CHCH(CH_3)CH_3$

7. What is the correct name for the following molecule?



A. Methyl methanoate
B. Methyl ethanoate
C. Ethyl ethanoate
D. Ethyl propanoate

8. Which of the following can be described as being able to form stereoisomers?

A. Ethene
B. Propene
C. But-1-ene
D. But-2-ene

9. What is the correct name of the molecule with the semi-structural formula $CH_3CH_2CH_2CHO$?

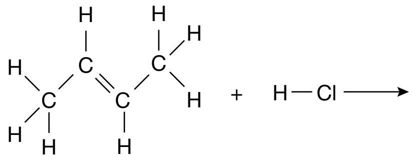
A. Butan-1-one

B. Butanoic acid

C. Butan-1-ol

D. Butanal

10.



For the reaction shown, the reaction type and products are, respectively:

A. Addition, 2,3-dichlorobutane

B. Addition, 2-chlorobutane

C. Substitution, 2-chlorobutane

D. Substitution, 2,3-dichlorobutane.

11. Which of the following is likely to be the most soluble in water?

A. Propanoic acid

B. Propanone

C. Methyl methanoate

D. Butan-1-amine

12. 18.6 g of butan-2-one, $CH_3COCH_2CH_3$, is obtained from the oxidation of 22.5 g of butan-2-ol, $CH_3CH(OH)CH_2CH_3$.

The percentage yield is closest to:

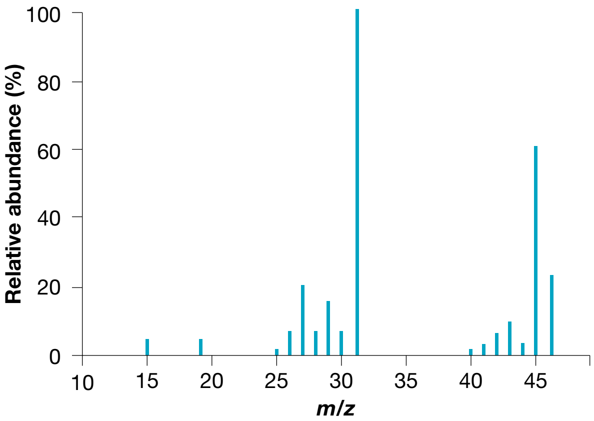
A. 82.6%

B. 95.9%

C. 87.3%

D. 86.1%.

13. A mass spectrum is shown below. What molecule is it likely to be produced by?



A. Methanoic acid

B. Ethanol

C. Ethanal

D. Propane

14. A molecule has the molecular formula $C_3H_6O_2$. Information about the ^1H NMR spectrum for the molecule is shown below.

Chemical shift (ppm)	Relative peak area	Peak splitting
1.3	3	triplet (3)
4.2	2	quartet (4)
9.0	1	single (1)

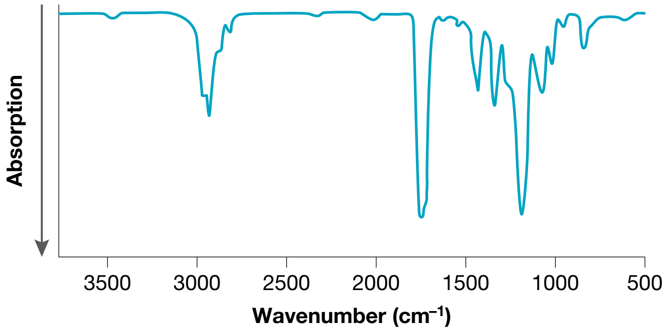
Based on this information, the molecule is likely to be:

A. Methyl ethanoate
B. Ethyl methanoate
C. Propanoic acid
D. Propan-1,2-diol.

15. How many peaks would be seen on a ^{13}C NMR spectrum for 1-chlorobutane?

A. 1
B. 2
C. 3
D. 4

16. The infrared spectrum for a molecule is shown below. The molecule is most likely to be:



A. An alcohol
B. An ester
C. An amine
D. A carboxylic acid.

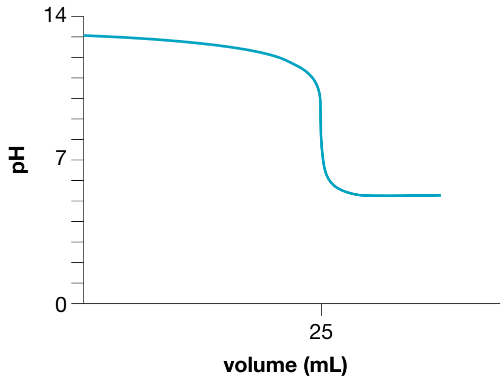
17. Ethanoic acid and methanamine are combined and then heated to 100 °C. The product is:

A. Methylethanamide + water
B. Ethlymethylamide + water
C. Ethanamine + water
D. Aminoethane + water.

18. The peak area in a HPLC chromatogram can be used to determine:

A. The retention time
B. The concentration of the analyte
C. The amount of analyte
D. The polarity of the analyte.

19. A titration curve is shown below. Which would be the best indicator to use for this titration and what colour change would be observed?



A. Bromophenol blue, yellow to blue
B. Bromophenol blue, blue to yellow
C. Phenolphthalein, colourless to pink
D. Phenolphthalein, pink to colourless

20. A student carried out a redox titration to determine the amount of vitamin C in lemon juice. They standardised an iodine solution and then titrated this against a diluted lemon juice sample. If the student rinsed their burette with deionised water, the implication would be:

A. The amount of lemon juice would be calculate too high
B. The amount of lemon juice would be calculated too low
C. There would be no effect on the calculated amount of lemon juice
D. 5.0 mL more lemon juice would be needed to rectify the error.

SECTION B — Short answer questions

Question 1 (12 marks)

Propanone and propan-2-ol both contain three carbon atoms and one oxygen atom.

a. Draw the structural formula of:
  - **i.** Propanone **1 mark**
  - **ii.** Propan-2-ol. **1 mark**

b. How many peaks would you expect to see on a ^{13}C NMR spectrum for:
  - **i.** Propanone **1 mark**
  - **ii.** Propan-2-ol? **1 mark**

c. Explain how many peaks (the splitting pattern) you would expect to see on a ^{1}H NMR spectrum for:
  - **i.** The R–CH_3 in propanone **2 marks**
  - **ii.** The R–CH_3 in propan-2-ol. **2 marks**

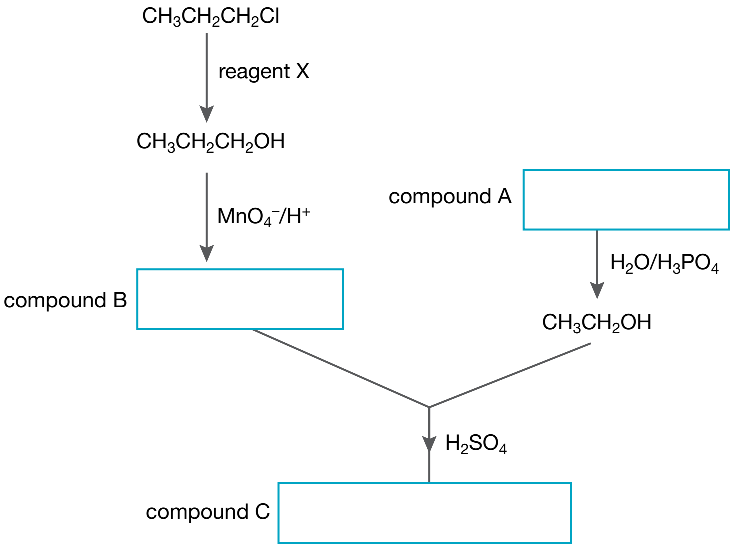
d. Describe the key difference expected in the IR spectrum of propanone compared to that of propan-2-ol. **2 marks**

e. Identify the peak at $m/z = 43$ for propanone. **1 mark**

f. A student has a bottle labelled ‘P’ that contains either propanone or propan-2-ol. When they react their unknown compound with acidified dichromate ions, they note a change in odour. Identify the compound in the bottle labelled ‘P’. **1 mark**

Question 2 (11 marks)

Consider the following reaction pathway.



a. **i.** Identify reagent X. **1 mark**

ii. Identify the type of reaction occurring to convert $CH_3CH_2CH_2Cl$ into $CH_3CH_2CH_2OH$. **1 mark**

iii. Identify the by-product of the reaction forming $CH_3CH_2CH_2OH$. **1 mark**

iv. Calculate the atom economy for this reaction. **1 mark**

b. **i.** Write the semi-structural formula of compound A. **1 mark**

ii. Identify the type of reaction occurring to convert compound A into CH_3CH_2OH. **1 mark**

c. **i.** Name the type of reaction that produces compound B. **1 mark**

ii. Name compound B. **1 mark**

d. **i.** Draw the skeletal formula of compound C. **1 mark**

ii. Calculate the atom economy for the production of compound C. **1 mark**

iii. Draw the structural formula of the other product formed when compound C is formed. **1 mark**

Question 3 (7 marks)

A student wished to determine the ethanoic acid, CH_3COOH, concentration of a sample of vinegar.

They took a 10.0 mL sample of vinegar and diluted it to 250.0 mL in a volumetric flask. They then took 20.0 mL samples of this solution and titrated them against a 0.0240 M standardised solution of sodium hydroxide, NaOH, solution. Their average titre was 21.80 mL.

a. Write the chemical equation for the reaction of ethanoic acid with sodium hydroxide. **1 mark**

b. Assuming that ethanoic acid is the only acid present in vinegar, calculate the concentration of ethanoic acid in the undiluted sample as % v/v. The density of ethanoic acid is 1.049 g mL^{-1}. **6 marks**

ASSESSMENT task – Data analysis

In this task you will analyse chromatogram, peak area data and mass spectra for a sample of vinegar.

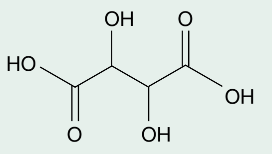
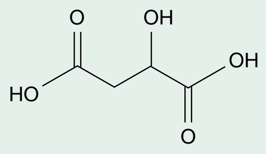
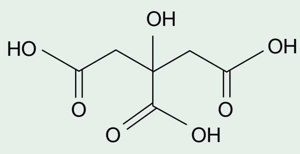
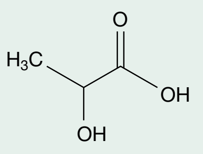
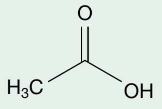
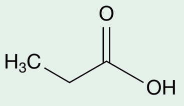
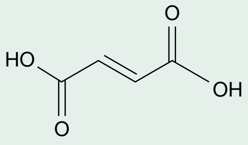
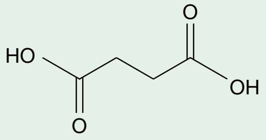
- Students are permitted to use pens, pencils, highlighters, erasers, rulers and a scientific calculator.
- Students may use the VCE Chemistry Data Book for this task.

Total time: 50 minutes
Total marks: 27 marks

Analysis of secondary qualitative and quantitative data

Vinegar is a popular condiment produced from the double fermentation of fruit. The first fermentation converts sugars into ethanol and the further fermentation produces the ethanoic acid that gives vinegar its sour taste. Spirit vinegars are typically between 5.0 and 20.0% v/v ethanoic acid.

Other organic acids can be formed during the fermentation process and these impart their own characteristics on the overall flavor, depending on the concentrations. Possible organic acids in spirit vinegars are shown below.

			
Tartaric acid	Malic acid	Citric acid	Lactic acid
			
Ethanoic acid	Propanoic acid	Fumaric acid	Succinic acid

Vinegar producers send their spirit vinegar samples to laboratories for qualitative and quantitative analysis using a technique known as LC–MS (Liquid chromatography–mass spectrometry).

LC–MS is a technique used to determine what is in a mixture when the components are similar. LC works the same way as HPLC except the mobile phase is not pumped through under high pressure. This slower flow rate of the mobile phase allows the mass spectrometer to function with high accuracy. The chromatograph separates the acids in the vinegar, while the mass spectrometer acts as the detector and identifies each component as it passes through.

One particular vinegar analysis used 20 μL vinegar samples injected onto a reverse-phase liquid chromatography (RPLC) column at 50 °C. The mobile phase was a mixture of water and methanol with a flow rate of 1.0 mL/min. The following chromatogram, peak area data and mass spectra were produced.

FIGURE 1 Vinegar sample chromatogram

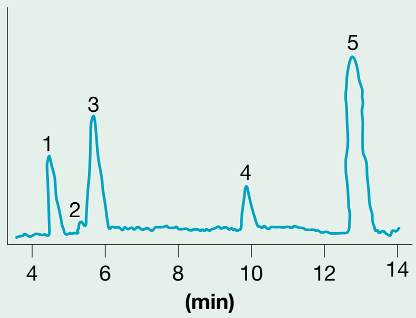


TABLE 1 Vinegar sample peak area data

Peak	Peak area ×10 000	Retention time (mins)
1	5.50	4.7
2	0.68	5.6
3	9.95	5.9
4	3.65	9.7
5	24.40	13.0

FIGURE 2 Vinegar sample Peak 1 mass spectrum

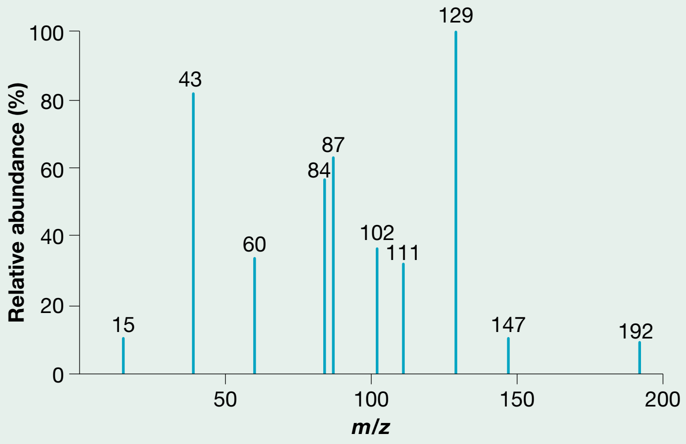


FIGURE 3 Vinegar sample Peak 2 mass spectrum

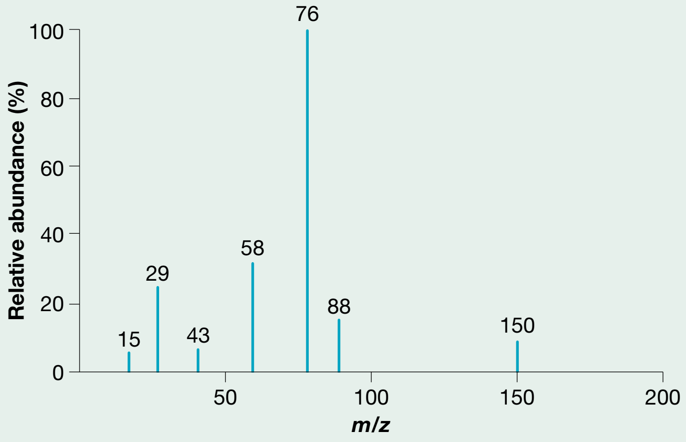


FIGURE 4 Vinegar sample Peak 3 mass spectrum

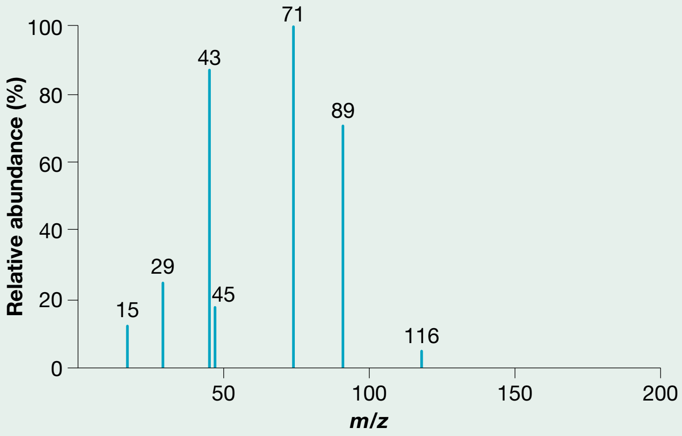


FIGURE 5 Vinegar sample Peak 4 mass spectrum

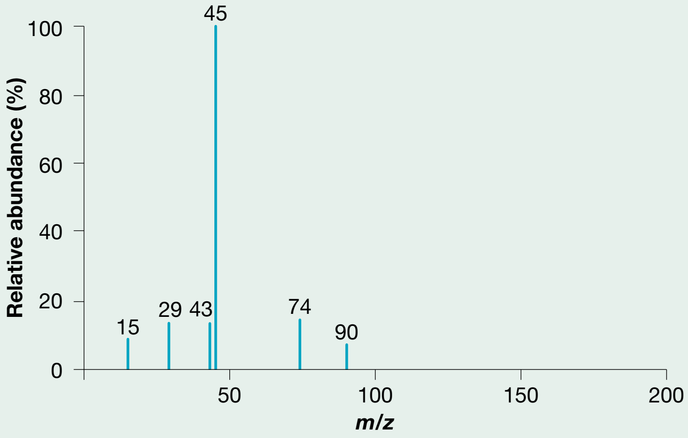
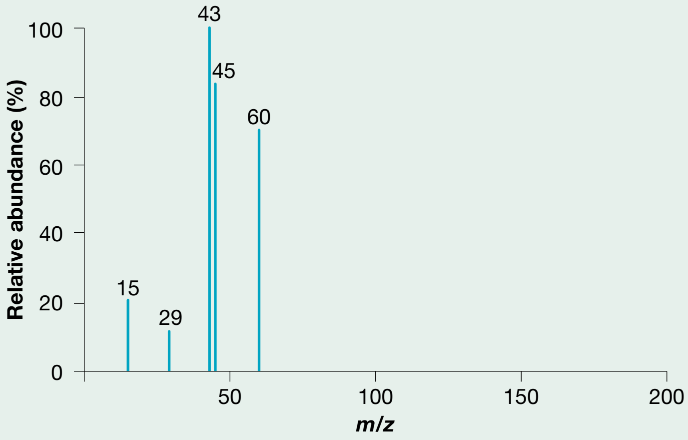


FIGURE 6 Vinegar sample Peak 5 mass spectrum



Analyse the data given to answer the following questions.

1. Using the principles of chromatography, explain how the mixture of organic acids was able to be separated in this reverse-phase chromatograph.
2. What is the difference between normal-phase and reverse-phase chromatography? What would happen to the retention times of the organic acids if NPLC was used instead?
3. Explain how mass spectrometry can be used as a qualitative technique and how the peaks on a mass spectrum are formed.
4. Using the mass spectra, name the two organic acids that were the first and last peaks detected on the chromatogram. Write equations to show the formation of both molecular ions of the two organic acids.
5. Which of the listed acids could not produce the mass spectrum corresponding to Peak 3 on the chromatogram? Justify your answer.
6. How would you change the experimental conditions, chromatograph or procedure to:
   (a) Separate Peaks 2 and 3 on the chromatogram
   (b) Accurately determine the identity of Peak 4?
7. If propanoic acid was detected, relative to other peaks and their retention times, where on the chromatogram would you expect it to be shown? Justify your answer.
8. Outline changes and additions you would make to this RPLC procedure to determine the percentage by volume (% v/v) of ethanoic acid in this sample of spirit vinegar. Include any changes you would make to the sample. Comment on the data to be collected and show how you would use it to calculate the percentage by volume (% v/v) of ethanoic acid in the spirit vinegar.

on Resources

Digital document U4AOS1 School-assessed coursework (doc-32007)

11 Key food molecules

11.1 Overview

Numerous **videos** and **interactivities** are available just where you need them, at the point of learning, in your digital formats, learnON and eBookPLUS at www.jacplus.com.au.

11.1.1 Introduction

FIGURE 11.1 In the future, insects could supply protein in a balanced diet.

Sharing food with family and friends is one of the joys of life. But what are we really eating? We know that a balanced diet enables us to stay active and healthy, providing energy for daily activity, and to allow growth, repair and regulation of our organs and body processes. The term ‘diet’ is referred to as the daily food that is usually eaten by a person, but what makes up a balanced diet?

Everything we eat is a chemical, so what happens to food molecules when we consume a meal? The proteins we eat are essential building blocks for an enormous number of compounds involved in growth and repair of cells and, if required, energy. They are usually obtained from animal sources but there are plant sources too. Most of our carbohydrates come from plants, which provide a source of energy for the many processes occurring in the body. ‘Lipid’ is a general term for fats and oils, which are energy storage compounds. Proteins and carbohydrates are polymers, large molecules that are made up of repeating units of small molecules called monomers. Although lipids are relatively large molecules, they are not polymers. The many reactions that occur between these organic compounds depend on how the molecular structures and various functional groups interact, and the conditions in the particular part of the body. The structure of the major food molecules is examined in this topic and the digestion of these molecules is discussed in topic 12.

11.1.2 What you will learn

KEY KNOWLEDGE

In this topic, you will investigate:

- proteins: formation of dipeptides and polypeptides as condensation polymers of 2-amino acids; primary (including peptide links), secondary, tertiary and quaternary structure 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 nonessential 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.

PRACTICAL WORK AND INVESTIGATIONS

Practical work is a central component of learning and assessment. Experiments and investigations, supported by a **Practical investigation logbook** and **Teacher-led videos**, are included in this topic to provide opportunities to undertake investigations and communicate findings.

on Resources

Digital documents	Key science skills (doc-30903)
	Key terms glossary – Topic 11 (doc-31418)
	Practical investigation logbook (doc-31419)

studyon

To access key concept summaries and past VCAA exam questions download and print the **studyON: Revision and practice exam question booklet** (doc-31420).

11.2 Proteins

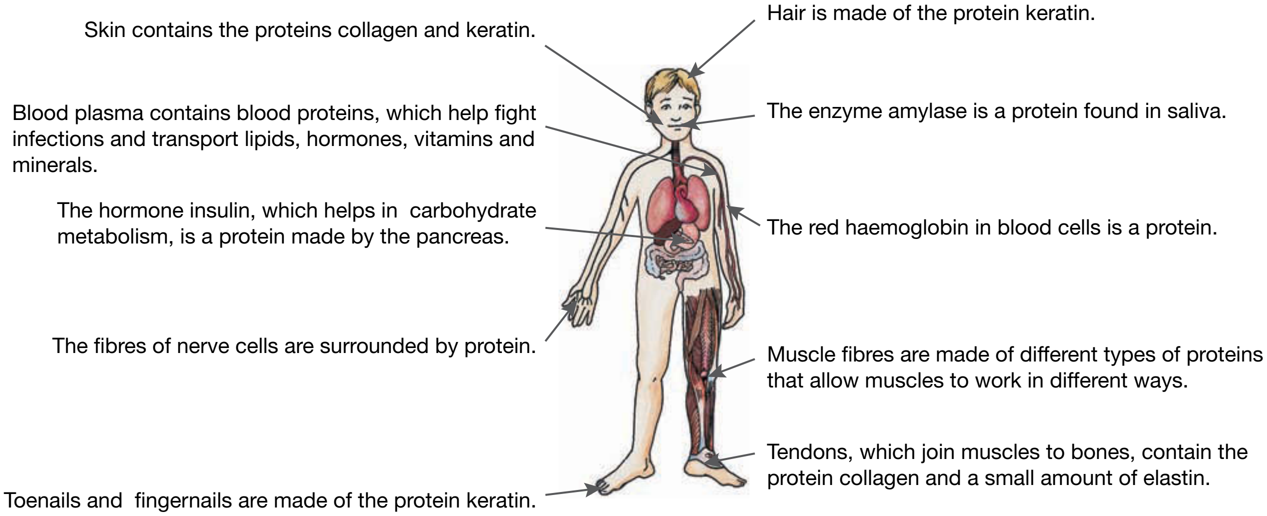
KEY CONCEPT

- Proteins: formation of dipeptides and polypeptides as condensation polymers of 2-amino acids; primary (including peptide links), secondary, tertiary and quaternary structure and bonding; distinction between essential and non-essential amino acids as dietary components

11.2.1 What are proteins?

Virtually all body structures and activities depend on **proteins**, and eating protein is not just about building muscles, it provides the raw materials for many structural and functional components in the body. As enzymes, proteins act as catalysts and have many other roles in the body. Some are antibodies to prevent infection, some assist with the formation of new molecules by interpreting the genetic information stored in DNA, and others act as hormones and transmit signals to coordinate biological processes between different cells, tissues and organs. Proteins provide structural components for cells, they form muscle fibres, which assist in movement, and they carry atoms and small molecules around the body.

FIGURE 11.2 Examples of proteins in the body



All protein molecules contain carbon, hydrogen, oxygen and nitrogen. Some also contain phosphorus and sulfur. Plants can make proteins from inorganic compounds such as nitrates, water and carbon dioxide. Animals cannot make their own proteins directly from the same inorganic starting materials that plants do; they depend on plants or other animals in their food supply for organic compounds that enable them to obtain or synthesise their own protein. Sources of protein include meat, fish, poultry, eggs, dairy products, soy products and beans. The thousands of proteins in our body are polymers made up of 20 different **amino acids**.

FIGURE 11.3 Sources of protein

11.2.2 Formation of dipeptides and polypeptides

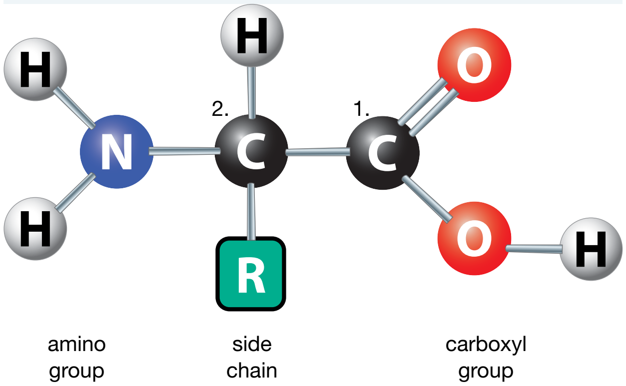
Amino acids: the building blocks of proteins

Proteins are polymers built from monomers called amino acids. These amino acids are compounds that contain amino ($-NH_2$) and carboxyl ($-COOH$) functional groups.

Most amino acids have four groups bonded to a central carbon atom. These are:

- a carboxyl group ($-COOH$)
- an amino group, $-NH_2$
- a R group (the amino acid side chain)
- a hydrogen atom.

FIGURE 11.4 General structure of an amino acid



Amino acids used to make proteins are named 2-amino acids because the amino group is attached to the second carbon counting from the carboxyl group (see figure 11.4). They are also called α-amino acids ('alpha amino acids'). α-amino acids contain an α-carbon, which is the first carbon atom (C1) directly bonded to a functional group, in this case, a carboxyl group.

TIP: Do not confuse the amino functional group ($-NH_2$) with the amide group ($-CONH-$).

on Resources

Interactivity Classifying properties of amino acids (int-1237)

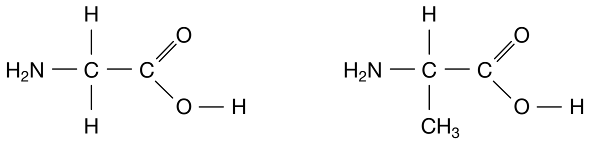
Differences between amino acids

Amino acids differ in the structure of the R side group and it is the nature of the R side group that forms the classification of 2-amino acids. The R side groups can be one or more of the following.

- Non-polar (hydrophobic)
  - Alkyl, for example $-CH_3$ in alanine
  - Aromatic, for example, cyclic hydrocarbon in phenylalanine
- Polar (hydrophilic)
  - Neutral, for example $-CH_2OH$ in serine
  - Acidic (proton donors), for example the acidic carboxyl group $-CH_2COOH$ in aspartic acid
  - Basic (proton acceptors), for example the basic $-CH_2CH_2CH_2CH_2NH_2$ in lysine.

The simplest 2-amino acids are glycine, where the R group is just a hydrogen atom, and alanine, where the R group is a methyl group (see figure 11.5).

FIGURE 11.5 Structures of glycine and alanine



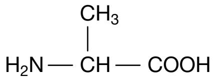
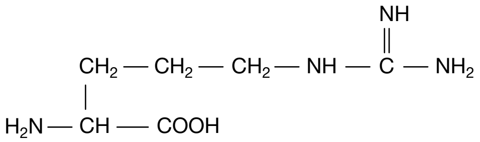
Glycine (Gly)(G)
non-polar
$C_2H_5NO_2$

Alanine (Ala)(A)
non-polar
$C_3H_7NO_2$

Hundreds of amino acids are known, but only 20 have been found in proteins in the human body. These 2-amino acids are the building blocks of thousands of proteins and are shown in table 11.1, with the three-letter abbreviation for their names. Amino acids can also be identified by a single letter but this is not used in VCE Chemistry.

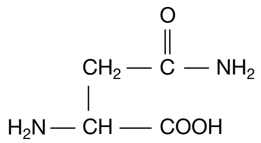
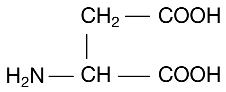
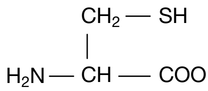
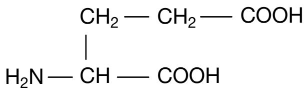
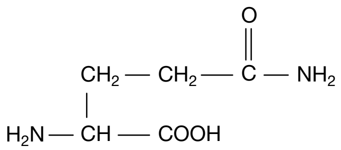
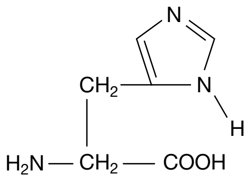
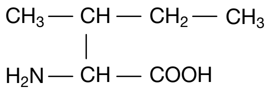
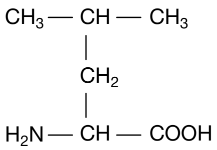
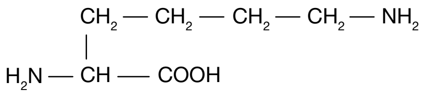
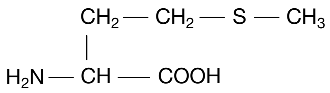
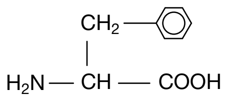
Amino acids are the monomers that form a protein polymer.

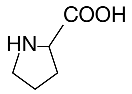
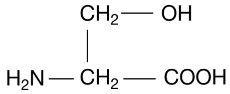
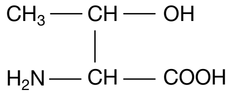
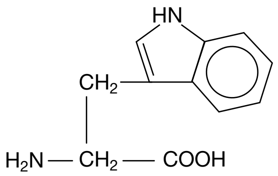
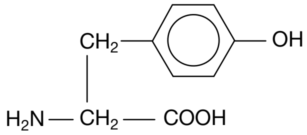
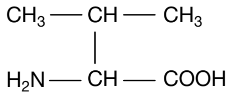
TABLE 11.1 2-amino acids (α-amino acids)

Name	Symbol	Structure
Alanine	Ala	 $H_2N-CH(CH_3)-COOH$
Arginine	Arg	 $H_2N-CH(CH_2-CH_2-CH_2-NH-C(=NH)-NH_2)-COOH$

(continued)

TABLE 11.1 2-amino acids (α-amino acids) *(continued)*

Name	Symbol	Structure
Asparagine	Asn	 $H_2N-CH(CH_2-C(=O)-NH_2)-COOH$
Aspartic acid	Asp	 $H_2N-CH(CH_2-COOH)-COOH$
Cysteine	Cys	 $H_2N-CH(CH_2-SH)-COOH$
Glutamic acid	Glu	 $H_2N-CH(CH_2-CH_2-COOH)-COOH$
Glutamine	Gln	 $H_2N-CH(CH_2-CH_2-C(=O)-NH_2)-COOH$
Glycine	Gly	H_2N-CH_2-COOH
Histidine	His	
Isoleucine	Ile	 $H_2N-CH(CH_3-CH-CH_2-CH_3)-COOH$
Leucine	Leu	 $H_2N-CH(CH_2-CH(CH_3)-CH_3)-COOH$
Lysine	Lys	 $H_2N-CH(CH_2-CH_2-CH_2-CH_2-NH_2)-COOH$
Methionine	Met	 $H_2N-CH(CH_2-CH_2-S-CH_3)-COOH$
Phenylalanine	Phe	

Proline	Pro	
Serine	Ser	 $\begin{array}{ccccc} & & CH_2 & - & OH \\ & & \vert & & \\ H_2N & - & CH_2 & - & COOH \end{array}$
Threonine	Thr	 $\begin{array}{ccccc} CH_3 & - & CH & - & OH \\ & & \vert & & \\ H_2N & - & CH & - & COOH \end{array}$
Trytophan	Trp	
Tyrosine	Tyr	
Valine	Val	 $\begin{array}{ccccc} CH_3 & - & CH & - & CH_3 \\ & & \vert & & \\ H_2N & - & CH & - & COOH \end{array}$

Source: VCE Chemistry Written Examination Data book (2018) extracts © VCAA; reproduced by permission.

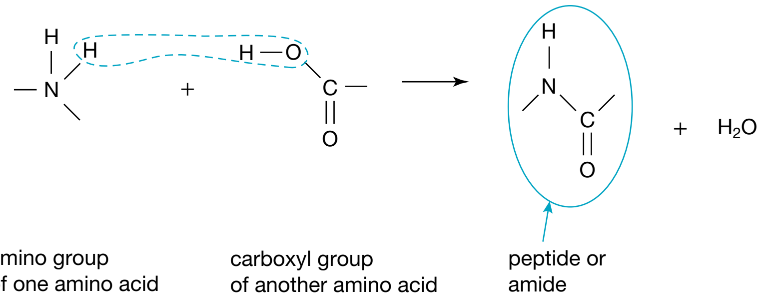
TIP: The name, symbol and structure of the 2-amino acids can be found in table 17 of the VCE Chemistry Data Book.

Dipeptides and polypeptides

Amino acids react to form **peptides**. The *carboxyl group* of one molecule reacts in a **condensation polymerisation** reaction with the *amino group* of another amino acid molecule to form a peptide or **amide link** between them. This link is called a peptide link if it is in a peptide or protein. The general term ‘amide link’ can be used for any compound that contains the $-CONH-$ link.

Water is produced when a **peptide link** is formed, so this reaction between amino acids to form peptides is an example of a condensation reaction. When two or more amino acids combine to form a peptide, what remains of each amino acid in the peptide is called an amino-acid **residue**.

FIGURE 11.6 Formation of a peptide link



Amino acids combine to form peptides in a condensation reaction.

When two amino acids combine, a **dipeptide** is produced. Two possible dipeptides can be made depending on the initial alignment of the amino acids. Glycine and alanine can combine in two ways.

The end of the peptide that has a free amino group is described as the **N-terminal**. This is usually drawn on the left. The end with a free carboxyl group is called the **C-terminal**. This is important because Ala-Gly has a different structure from Gly-Ala, as shown in figure 11.8.

FIGURE 11.7 Two amino acid residues

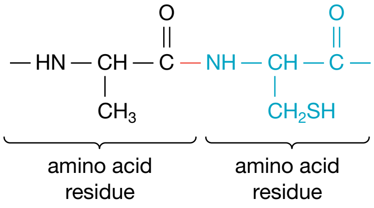
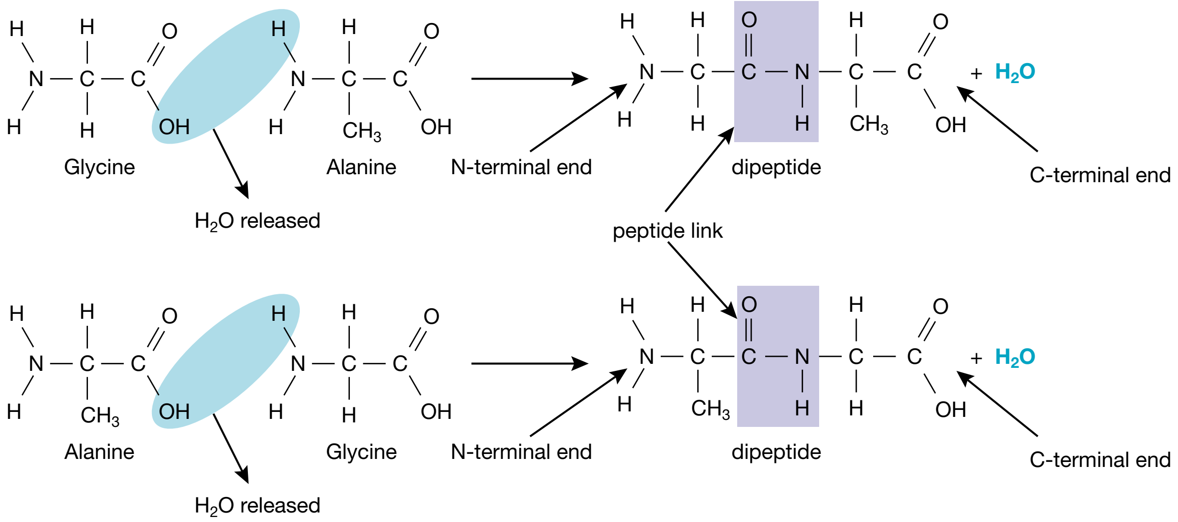


FIGURE 11.8 Two different dipeptides produced during the condensation reaction between glycine and alanine

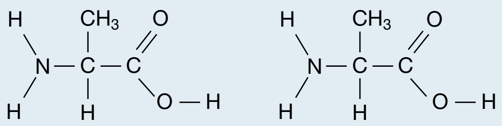
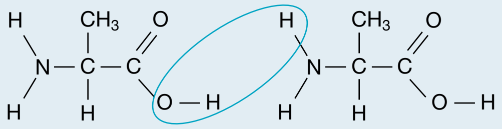


TIP: **Remember to include the water molecule as a product when writing equations for condensation reactions**

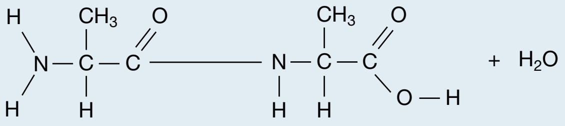
SAMPLE PROBLEM 1

Show the structure of the dipeptide formed from the condensation reaction of two alanine molecules.

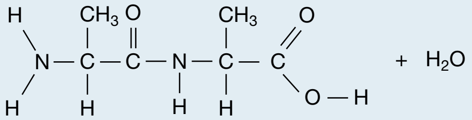
Teacher-led video: SP1 (tlvd-0720)

THINK	**WRITE**
1. Draw the two alanine molecules, with the carboxyl functional group of one molecule next to the amino functional group of the other.	
2. Circle the –O–H of the carboxyl group and the –H from the amine group. This is the water molecule that is removed in the condensation reaction.	

3. Join the remaining half bonds between the carbon atom and the nitrogen atom.



4. Draw the structure of the dipeptide with the double bond to the oxygen and the single bond from the hydrogen to the nitrogen vertically. Include the water molecule produced if an equation is required.
Check that a peptide link has been formed (−CONH−).



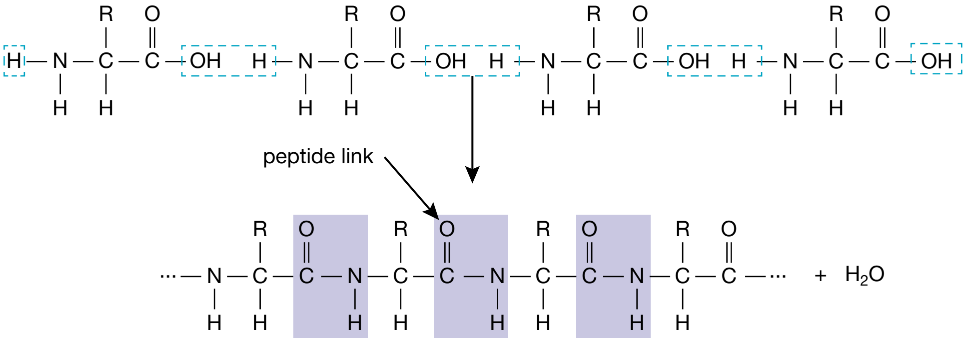
PRACTICE PROBLEM 1

Show the structure of a dipeptide formed from the condensation reaction of a serine and valine molecule.

Depending on the number of amino acid residues per molecule, the peptides formed from the condensation reactions of amino acids are known as dipeptides, tripeptides and so on until we reach **polypeptides**, which are the result of condensation polymerisation reactions. Note that, when drawing segments of proteins, it is necessary to show the open bonds at each end by using dashes where the next amino acid residue would be attached. Peptides of molar mass up to about 5000 g mol^{-1} (about 50 amino acid units) are known as polypeptides; even larger peptides are called proteins. The peptide chain of covalently bonded nitrogen and carbon atoms is referred to as the **backbone**, and the R-groups are described as **side chains**.

Amino acids combine in condensation reactions to form polypeptides.

FIGURE 11.9 Formation of a polypeptide



TIP: **Remember to use open bonds on each end when drawing a section of a polymer.**

on Resources

Video eLesson Condensation of amino acids (med-0354)

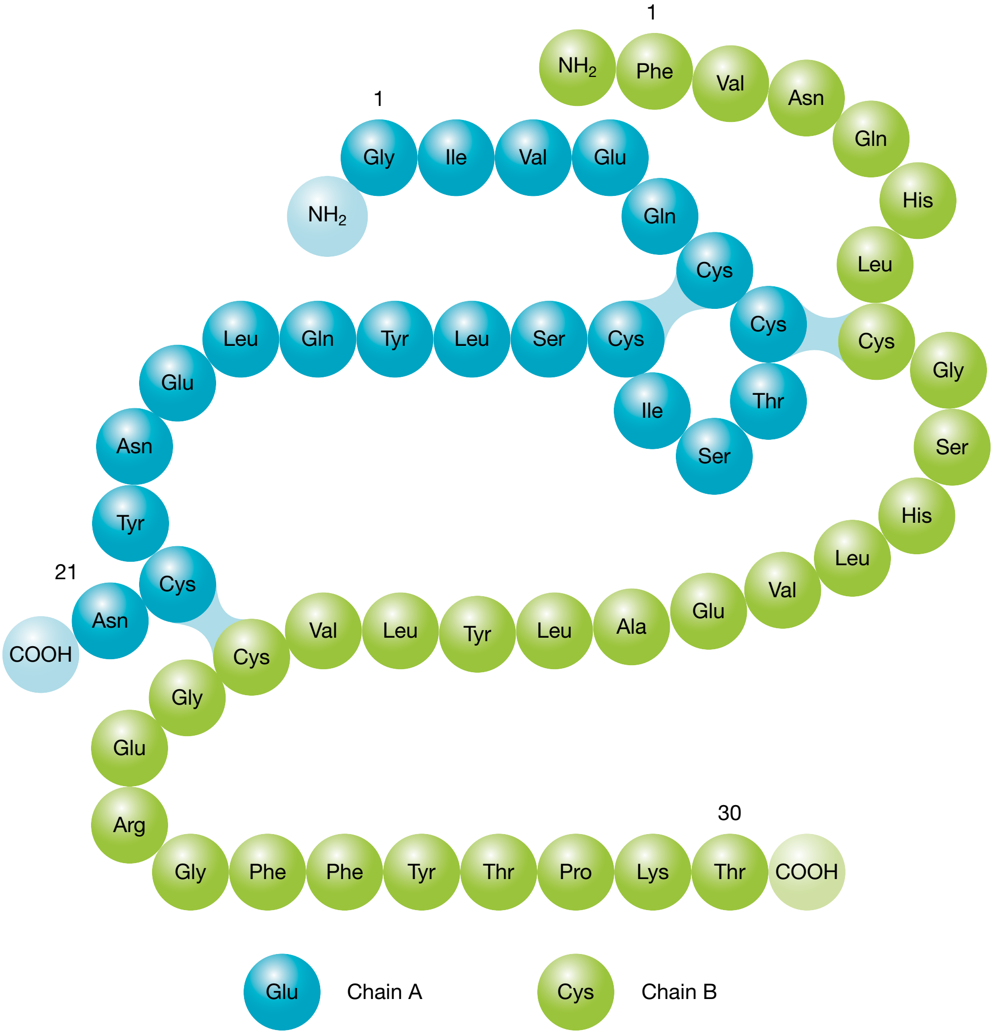
11.2.3 Structure of proteins

The structure of a protein is critical to its function. There are four levels of organisation that contribute to a protein's structure: primary, secondary, tertiary and quaternary.

Primary structure of proteins

The simplest level of protein structure is the order of amino acids in a polypeptide chain and is referred to as its **primary structure**. This is composed of the amino acid residues covalently bonded with peptide links. This sequence is unique for each particular protein and determines how the chain will be arranged in the next level of structure. For example, insulin consists of two amino acid chains: chain A has 21 amino acids and chain B has 30 amino acids. Insulin is a hormone produced by the pancreas that helps the cells in the body receive glucose from the blood and use it for providing energy.

FIGURE 11.10 Primary structure showing the order of amino acids in human insulin



The primary structure of proteins is the order of the amino acid residues covalently bonded in a polypeptitde chain. The amino acid residues are covalently bonded with the peptide links.

Secondary structure of proteins

Hydrogen bonds play a significant part in the **secondary structure** of proteins. The secondary structure of proteins refers to sections where the amino acid chain is organised into folded arrangements, usually **α-helices** and **β-pleated sheets**.

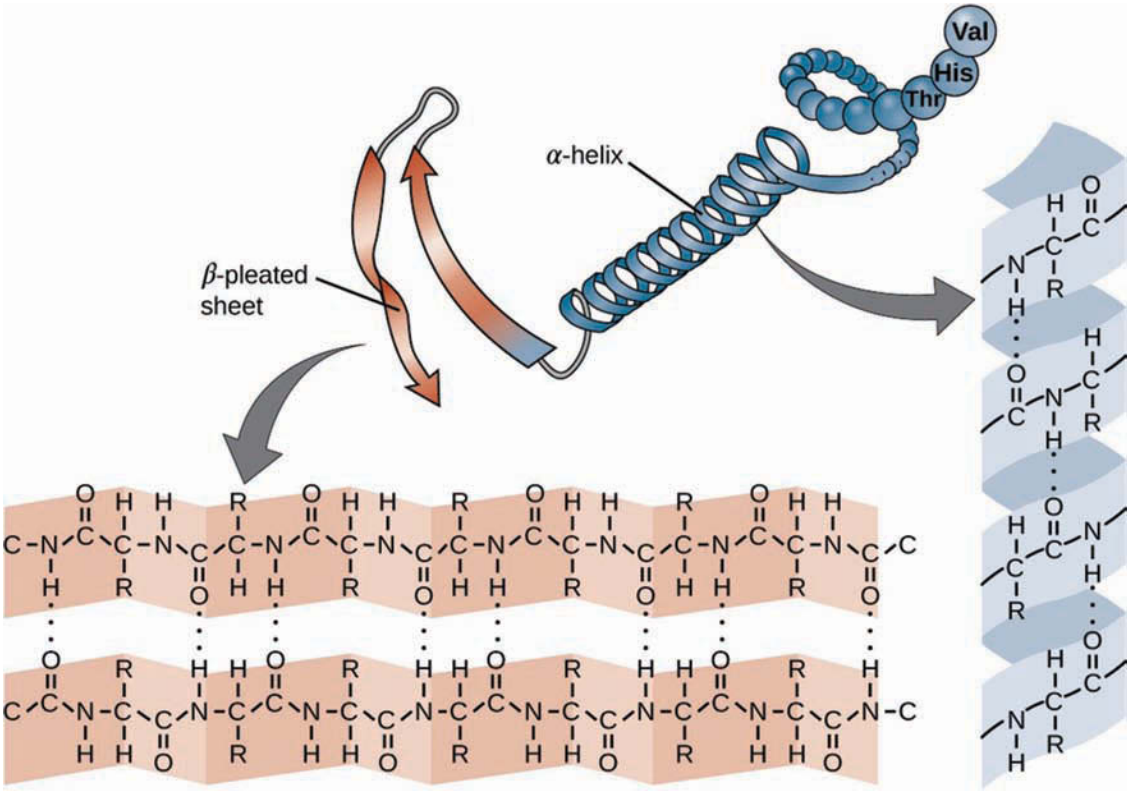
In α-helices, hydrogen bonds are formed between an oxygen atom of a C=O bond and a hydrogen atom of a N—H bond that is four amino acids away on the same chain (see figure 11.11). All C=O and N—H bonds are involved but R-groups are not included. A rigid, stable coiled structure is formed with the R-groups pointing to the outside. For example, these long thin protein structures make up the protein keratin, which is found in hair, skin and nails.

With β-pleated sheets, two sections of the peptide chain line up and are held together in a sheet-like structure by hydrogen bonds between one oxygen atom of a C=O bond and a hydrogen atom of a N—H bond in the parallel or anti-parallel sheet (see figure 11.11). The arrows at the ends of the ribbons point towards the carboxyl end of the chain. Silk thread has been shown to consist of a **fibrous** protein with a significant proportion of β-sheets.

Even though they are not involved in this level of structure, the R-groups influence the type of arrangements because of their size and shape. Amino acid residues with ring structures in side groups are more likely to be found in sheets because more space is available.

Some protein structures consist of more than a thousand atoms in complex arrangements with a multitude of intermolecular interactions, so they are sometimes represented by computer generated models, such as figure 11.11, The sections of α-helices and β-pleated sheets are linked by thin sections showing random coils and loops.

FIGURE 11.11 Secondary structure of a protein shown in a computer representation



The secondary structure of proteins is the arrangement of the amino acid chain into α-helices and β-sheets. These structures result from hydrogen bonding within the sequences.

Tertiary structure

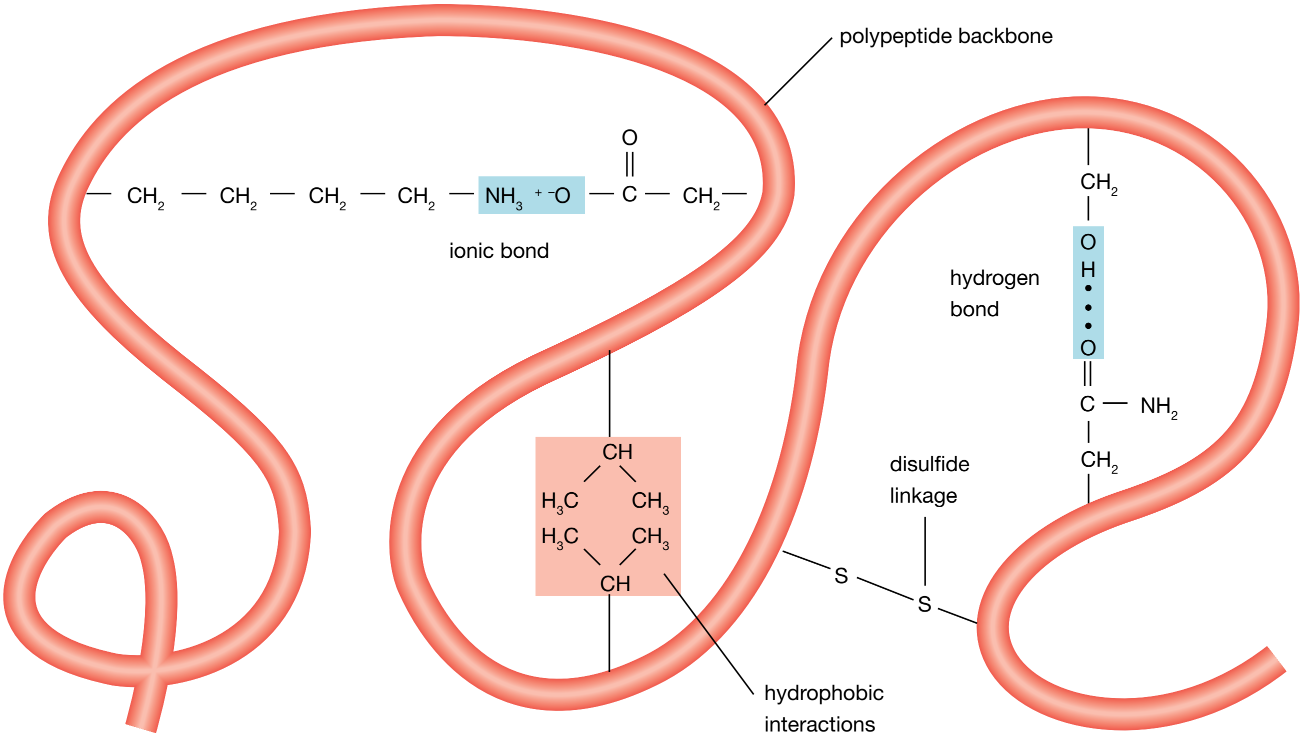
The three-dimensional structure of a protein is critical to its function and involves almost all common types of intermolecular interactions. Bonding between R-groups, the side chains, of the amino acids results in a complex three-dimensional shape called the **tertiary structure**. This may involve hydrogen bonding, ionic bonding or disulfide bridges. A covalent bond between two cysteine molecules is known as a disulfide bridge. These stabilise protein structures and keep them in particular conformations. Non-polar R-groups are **hydrophobic** and gather on the inside of the protein, leaving **hydrophilic** R-groups on the surface to interact with the aqueous environment in cells.

The tertiary structure involves interactions between R-groups as hydrogen bonding, ionic bonding or disulfide bridges.

Cysteine is the only amino acid that can form disulfide bonds.

TIP: Both the secondary and tertiary structures involve hydrogen bonding.
In the secondary structure the hydrogen bonds are within the same peptide chain.
In the tertiary structure the hydrogen bonding is between R-groups.

FIGURE 11.12 Types of bonding present in the tertiary structure of proteins



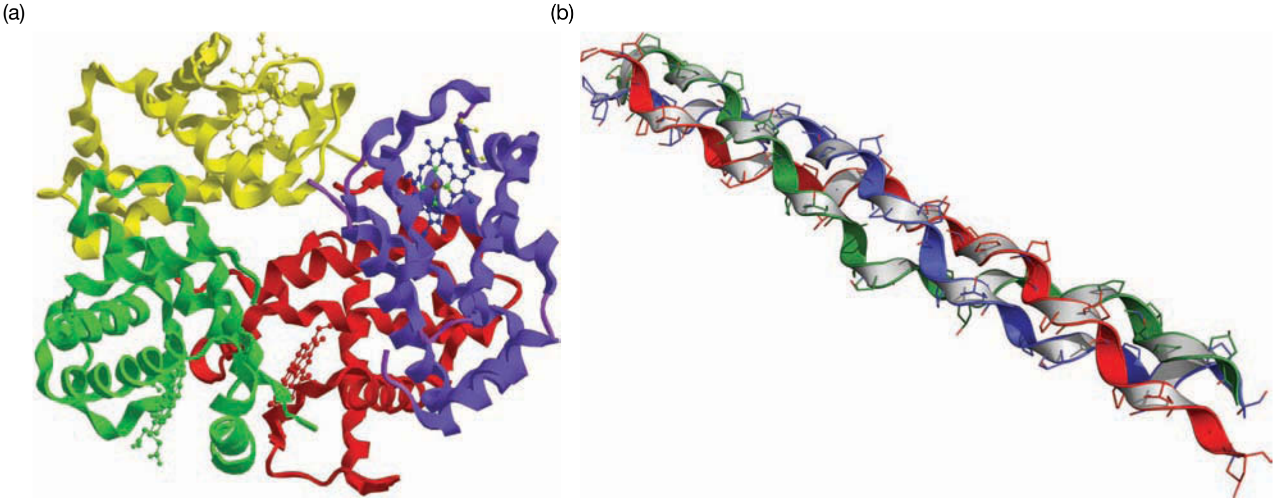
on Resources

Weblink Tertiary structure: the overall 3-dimensional shape of a protein

Quaternary structure

Some proteins consist of two or more folded peptide chains combined. When individual protein molecules link together in a particular spatial arrangement, a **quaternary structure** is formed. These proteins can be the same or different, and form a larger protein complex. This complex is stabilised by interactions similar to the tertiary structure, including hydrogen bonding, disulfide links and ionic attractions. An example is haemoglobin, the oxygen transport protein, which has four chains: two identical α chains and two identical β sheets (see figure 11.13a). Collagen, the main structural protein found in skin and tendons, has three polypeptide chains wound around each other (see figure 11.13b).

FIGURE 11.13 Models of (a) human haemoglobin molecule (globular) and (b) a collagen molecule (fibrous)



The quaternary structure refers to interactions between peptide chains.

on Resources

Weblink Human Complex DNA-binding protein 3D view

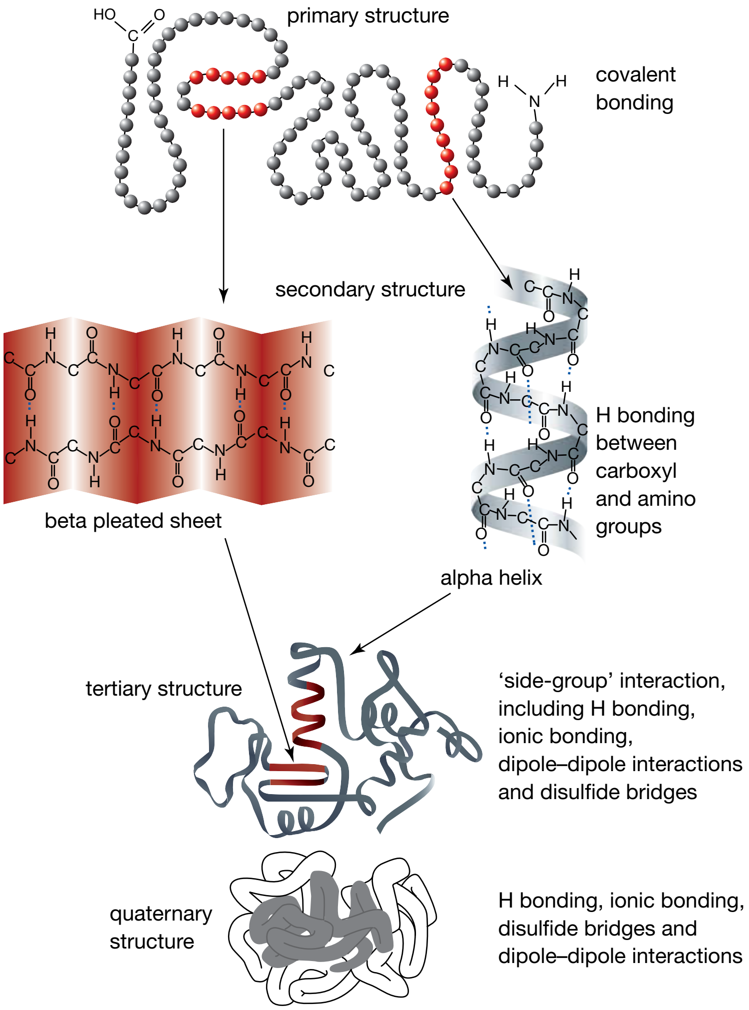
Summary of protein structures

Proteins contain four levels of structure.

- The primary structure is the sequence of amino acid in the molecule.
- The secondary structure is characterised by the hydrogen bonding between oxygen atoms in the C=O bond and the hydrogen atom in the N—H bond from the functional groups in a particular peptide chain.
- In the tertiary structure all of the main types of bonding between R-groups are involved in forming the 3D arrangement of the protein.
- The quaternary structure comprises the interactions between folded peptide chains for some proteins.

The four protein structures are visually presented in figure 11.14. The formation and performance of proteins within the human body results from energy generated at the cellular level. The proteins formed can be fibrous (keratin, collagen) or **globular** (haemoglobin, most enzymes) in structure. Fibrous proteins are long, narrow strands and are insoluble in water. They are structural proteins. Globular proteins have a compact rounded shape and are usually soluble.

FIGURE 11.14 Four levels of protein structure



11.2.4 Essential and non-essential amino acids

Humans can only produce 11 of the 20 amino acids necessary to make proteins. These proteins made in the body are classified as **non-essential amino acids**. Amino acids found in proteins that *cannot* be synthesised by animals from the other materials in their diets and must therefore be supplied directly in the diet are known as **essential amino acids**. Unlike carbohydrates and fats, amino acids cannot be stored in the body and must be obtained from daily food intake. High-protein food is necessary in animal diets so that all of the amino acids necessary for the body to manufacture protein can be obtained. Essential amino acids vary from species to species. Essential and non-essential amino acids for humans are shown in table 11.2.

TABLE 11.2 Essential and non-essential amino acids

Essential	Non-essential
1. Histidine	1. Alanine
2. Isoleucine	2. Arginine
3. Leucine	3. Asparagine
4. Lysine	4. Aspartic acid
5. Methionine	5. Cysteine

6. Phenylalanine	6. Glutamic acid
7. Threonine	7. Glutamine
8. Tryptophan	8. Glycine
9. Valine	9. Proline
	10. Serine
	11. Tyrosine

Protein sourced from animal-based food (meat) contain all the essential amino acids, but plant-based proteins, with the exception of quinoa and soy, do not include all essential amino acids. While it is not necessary to eat essential and non-essential proteins at every meal, our bodies' inability to make essential amino acids means it is important to have a balanced intake each day. Vegetarians and vegans are able to consume all of the necessary amino acids by including foods from a variety of plant sources (including legumes, soy products, grains, nuts and seeds) as part of a their daily intake. Particular care is required to ensure adequate intake of lysine and methionine because these are found in smaller quantities in some plant foods. Tempeh, tofu, lentils and legumes are good sources of lysine, and grains, Brazil nuts and seeds supply methionine.

FIGURE 11.15 Quinoa supplies the essential amino acids

11.2 EXERCISE

To answer questions online and to receive **immediate feedback** and **sample responses** for every question go to your learnON title at www.jacplus.com.au.

1. (a) Name three foods that have a high protein content.
   (b) State three functions of proteins in the body.
2. Which structure defines the three-dimensional shape of a protein?
3. Name and draw the structures of the two functional groups present in amino acids.
4. State two examples of amino acids with basic side chains.
5. (a) Draw a possible dipeptide formed between alanine and aspartic acid.
   (b) Circle the peptide link.
   (c) Name the type of reaction.
   (d) Use the appropriate three-letter abbreviations to label these dipeptides.
   (e) Calculate the molar mass of the dipeptide formed.
6. Refer to the insulin molecule in figure 11.10.
   (a) State the abbreviations for the first three amino acids.
   (b) Name the first three amino acids in chain A.
   (c) State the name of the link (bond) and type of bonding that is present between these amino acids
   (d) State the name of the link (bond) and type of bonding occurring between the cysteine residues.
7. How many distinct tripeptides can be formed from one valine molecule, one alanine molecule and one glycine molecule?
8. Which type of bonding is found in both the secondary and tertiary structures of proteins?

9. What type of intermolecular attraction could involve two residues of glutamic acid spaced along a polypeptide chain?
10. (a) Explain the difference between essential and non-essential amino acids.
    (b) Give an example of an essential and a non-essential amino acid.

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11.3 Carbohydrates

KEY CONCEPT

- 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

Athletes sometimes use sports drinks to give them a boost of energy while exercising or playing sport. Vigorous exercising can result in the rapid loss of fluids, particularly if the weather is hot; sports drinks can help replace the lost water, sugar and salt. Research tells us that ordinary water provides adequate hydration for everyone except elite athletes, but sports drinks continue to be popular despite problems with excess sugar intake. What is in these sports drinks that is absorbed quickly and readily provides energy?

FIGURE 11.16 Energy drinks contain the sugar, glucose

11.3.1 Introduction to carbohydrates

The sugar in sports drinks and in so many other foods helps replace the fuel that your body uses during exercise. The sugar is a simple carbohydrate, **glucose**, that is stored in the liver or muscles. It is readily available because it requires less oxygen to react than either protein or fat. **Carbohydrates** are molecules made up of carbon, hydrogen and oxygen. Their general formula can be represented as $C_x(H_2O)_y$.

Most carbohydrates in our food originate from plants, in the form of glucose, and are produced through the process of photosynthesis.

$$6CO_2\,(g) + 6H_2O\,(l) \xrightarrow[\text{sunlight}]{\text{chlorophyll}} C_6H_{12}O_6\,(aq) + 6O_2\,(g) \qquad \Delta H = +2820 \text{ kJ mol}^{-1}$$

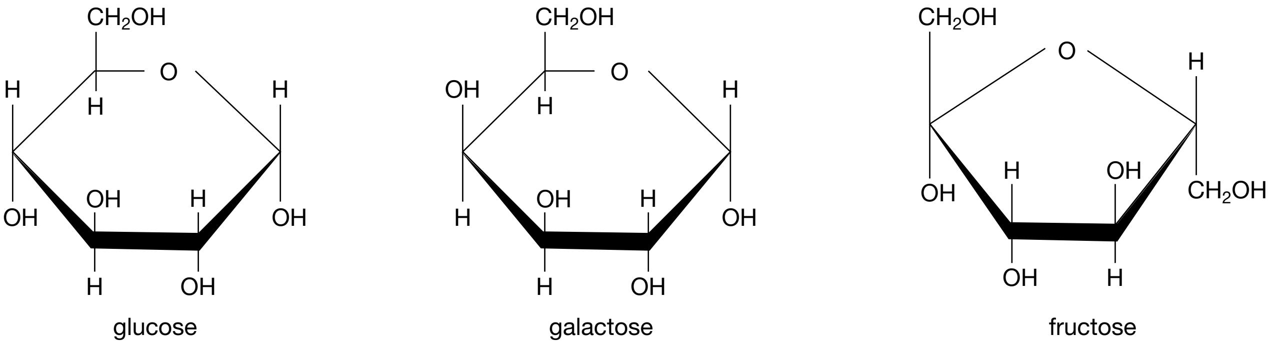
The glucose formed during photosynthesis can be used by the plant to form complex carbohydrates through polymerisation reactions. When an animal eats a plant, it can use the plant's carbohydrates as an energy source. Carbohydrates provide the greatest proportion of energy in the diets of most humans. The energy is required for muscle movement and the functioning of the central nervous system. Carbohydrates are also essential parts of other important molecules such as DNA. In addition, they have a number of beneficial effects on the taste and texture of foods.

FIGURE 11.17 Sources of carbohydrates

11.3.2 Formation of disaccharides from monosaccharides

Carbohydrates are classified into three groups according to their molecular structure: **monosaccharides**, **disaccharides** and **polysaccharides**. Monosaccharides (sometimes called simple sugars) are the basic building blocks of all carbohydrates. The most important monosaccharides are those containing five carbon atoms (pentoses) and those containing six carbon atoms (hexoses). They are not broken-down during digestion.

FIGURE 11.18 Structures of some common monosaccharides



Monosaccharides are white crystalline solids that are soluble in water. Their solubility is due to the presence of several polar hydroxyl (—OH) groups in the molecular structures. These can form hydrogen bonds with water molecules and are also strong reducing agents.

Monosaccharides can be in straight-chain and cyclic forms. In aqueous solution, the cyclic form predominates. The most abundant and most important of these monosaccharides is glucose, which circulates in the blood — this is why it is known as blood sugar. It is readily available as an energy source and provides fuel for the body, especially the brain.

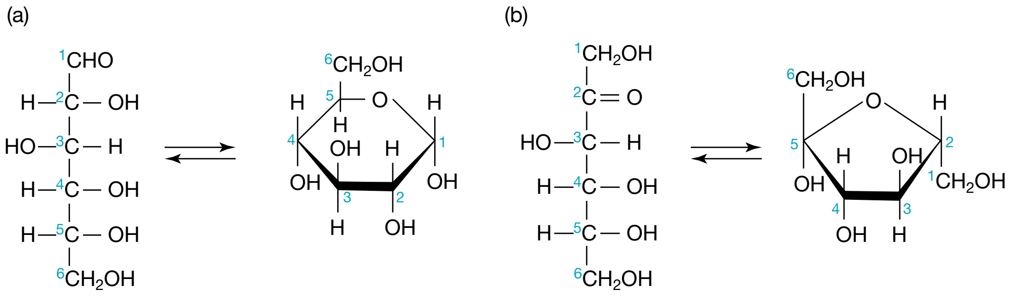
FIGURE 11.19 Fructose is a monosaccharide and is the main carbohydrate in fruit

Formation of glucose

Glucose is found as a number of stereoisomers. The **D-glucose** molecule in figure 11.20a has four chiral centres. The isomer designated as the D-isomer occurs in nature, but the L-isomer, which is a mirror image, does not. Assigning an isomer as D- or L- is based on the arrangement of the groups in the molecule and not on the direction of rotation of polarised light. However, the two enantiomers rotate light in opposite directions by the same amount.

The naturally occurring sugars discussed in this topic are D-isomers so when glucose is discussed from this point on remember that it is the D-isomer that is being referred to.

FIGURE 11.20 Straight-chain and cyclic forms of (a) D-glucose and (b) D-fructose

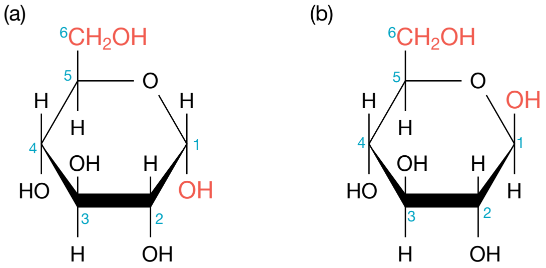


The formation of glucose ring structures from straight-chain glucose, the CH_2OH group on C5, ends up above the plane of the ring (see figure 11.21). As the ring closes, a new chiral centre is produced at C1, with −OH adopting one of two possible orientations:

- −OH below the plane of the ring (i.e. on the opposite side of the ring to CH_2OH) ⇒ α-glucose (α-D-glucose) (see figure 11.21a)
- −OH above the plane of the ring (i.e. on the same side of the ring as CH_2OH) ⇒ β-glucose (β-D-glucose) (see figure 11.21b).

The orientation of the hydroxyl group on C1 differentiates the two molecules.

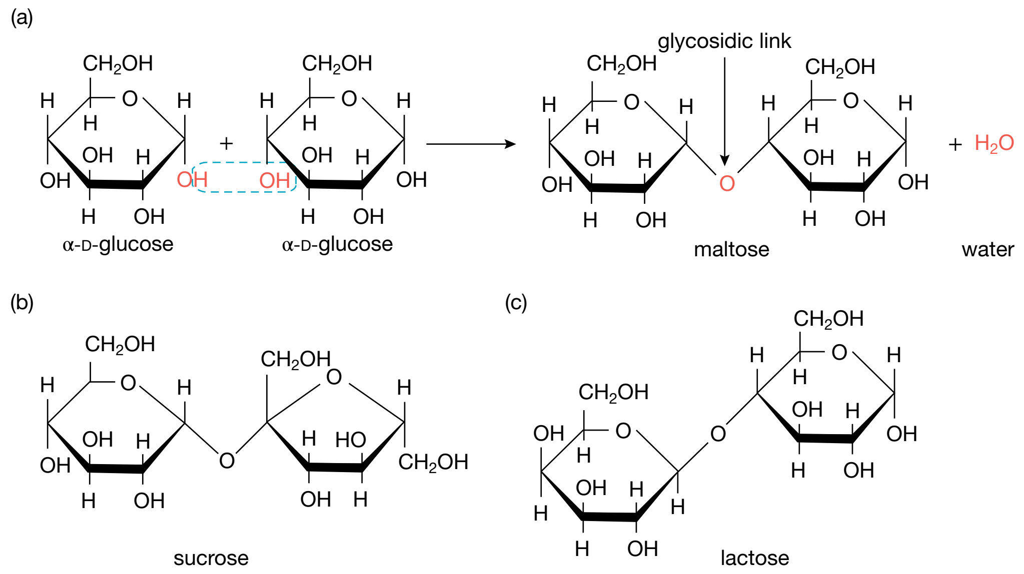
FIGURE 11.21 Structure of (a) α-glucose and (b) β-glucose



The carbohydrates in food are commonly made up of one or more of three simple monosaccharides: glucose, galactose and fructose. Monosaccharides can be joined to form disaccharides (two monosaccharides), **oligosaccharides** (from three to about ten monosaccharides) or polysaccharides (up to thousands of monosaccharides). Carbohydrates containing fewer than five monosaccharides are sometimes called *simple carbohydrates* while polysaccharides may be called *complex carbohydrates*.

Polysaccharides are polymers made up from monosaccharide or disaccharide monomers.

FIGURE 11.22 Two monosaccharides can form a disaccharide in a condensation reaction; water is produced as a by-product



Disaccharides are made of two monosaccharides through a condensation reaction that occurs between the hydroxyl group on C1 of one glucose molecule and the hydroxyl group on C4 of an adjacent glucose molecule. A molecule of water is eliminated as a **glycosidic link** (a special case of ether link), is formed. The three disaccharides found most commonly in food are sucrose (found in fruits), maltose (the end-product in the malting of barley during beer manufacture and also in starch digestion in the human gut) and lactose (found in milk). Table sugar is actually the disaccharide sucrose. However, all of these small carbohydrates are classified as sugars, and their names have the suffix −*ose*.

FIGURE 11.23 Sucrose (table sugar) is a disaccharide.

The glucose monomers in polysaccharides are held together by glycosidic links (−O−).

TIP: The formula of some biomolecules can be found in section 10 of the VCE Chemistry Data Book.

11.3.3 Polysaccharides

Polysaccharides are carbohydrates of high molar mass. Unlike monosaccharides and disaccharides, they are non-crystalline, generally insoluble and tasteless. Polysaccharides are polymers that consist of large numbers of monosaccharide monomers that have combined in condensation polymerisation reactions. They are sometimes called complex carbohydrates. **Starch**, **glycogen** and **cellulose** are important polysaccharides in plant and animal systems.

Starch

Starch is a white granular polysaccharide that is the major storage form of glucose for plants. It is found in corn, wheat, seeds and the fleshy part of vegetables and fruit, and is the second most common organic compound. Starch is a condensation polymer of α-glucose and is made up of two polymers: **amylose** and **amylopectin**. The proportion of each of these polymers present is dependent on the type of plant food.

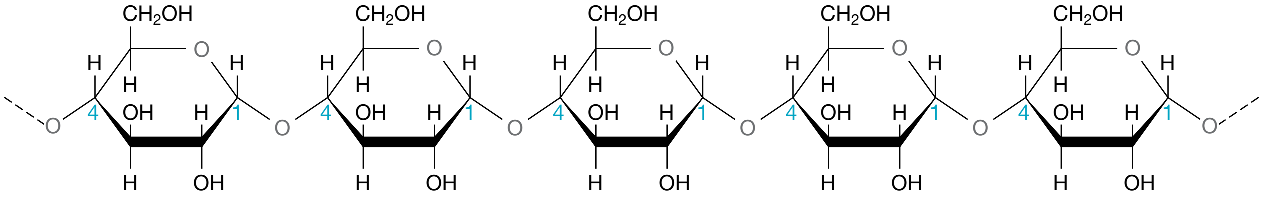
The three test tubes shown in figure 11.25 demonstrate a positive test for three different concentrations of starch solutions. Moving from left to right, the starch concentrations decrease by a factor of 10: they are 1%, 0.1% and 0.01%. The amylose portion of the starch molecule can trap iodine in its coiled structure. The iodine then appears to take on a purple colour, and even appears black at high concentrations.

FIGURE 11.24 Iodine can be used as a test for starch. The brown colour of iodine becomes blue/black in the presence of starch.

FIGURE 11.25 Testing different concentrations of starch solutions

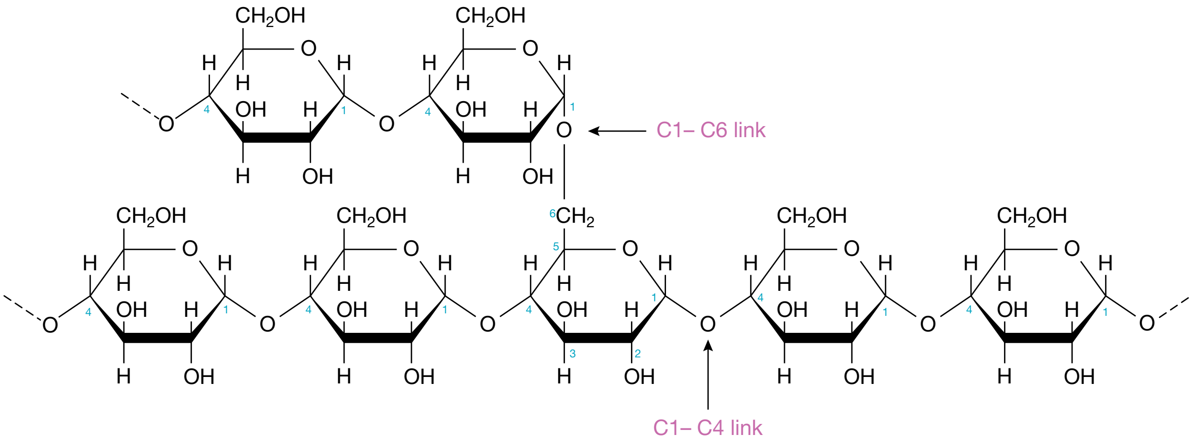
Amylose comprises about 20% of starch and consists of 50–300 α-glucose units in a continuous chain formed from C1–C4 linkages only. Because the hydroxyl groups on C1 and C4 are both below the plane of the ring and all the molecules are aligned the same way, polymerisation is straightforward. This results in a long chain molecule that forms tightly packed spirals due to hydrogen bonding along its length. Much of the hydrogen bonding is within the coil so fewer water molecules can form hydrogen bonds. This makes amylose insoluble in water.

FIGURE 11.26 Section of amylose polymer



Amylopectin is a polymer much larger and more loosely branched than amylose. It consists of 300–5000 α-glucose units. The branching occurs as a result of C1–C6 linking between smaller segments of the C1–C4-linked straight chain. Amylopectin is water soluble because the open branched structure allows hydrogen bonding with water. It has a more open and less rigid structure than amylose, and a reddish colour is seen when it is mixed with iodine.

FIGURE 11.27 Section of amylopectin polymer



Starch is the energy storage molecule in plants and consists of amylose and amylopectin polymers.

SAMPLE PROBLEM 2

Calculate the molar mass of a starch molecule made from 500 glucose monomers.

THINK	WRITE
1. Calculate the mass of 500 glucose monomers.	Molecular mass of glucose: $C_6H_{12}O_6 = (6 \times 12) + (12 \times 1) + (6 \times 16)$ $= 180\ \text{g mol}^{-1}$ Mass of 500 glucose monomers $= 500 \times 180$ $= 90\,000\ \text{g mol}^{-1}$
2. Determine how many water molecules are lost.	$500 - 1 = 499$ water molecules lost between 500 monomers in this condensation reaction.
3. Calculate mass of 499 water molecules.	Mass of 499 water molecules $= 499 \times 18.0$ $= 8982\ \text{g mol}^{-1}$
4. Calculate the molar mass of starch.	Molar mass of starch $= 90\,000 - 8982$ $= 81\,018$ $= 8.10 \times 10^4\ \text{g mol}^{-1}$

PRACTICE PROBLEM 2

Calculate the molar mass of a starch molecule made from 650 glucose monomers.

Resources

Digital document Experiment 11.1 Studying starch – starch in food (doc-31277)

Teacher-led video Experiment 11.1 Studying starch – starch in food (tlvd-0763)

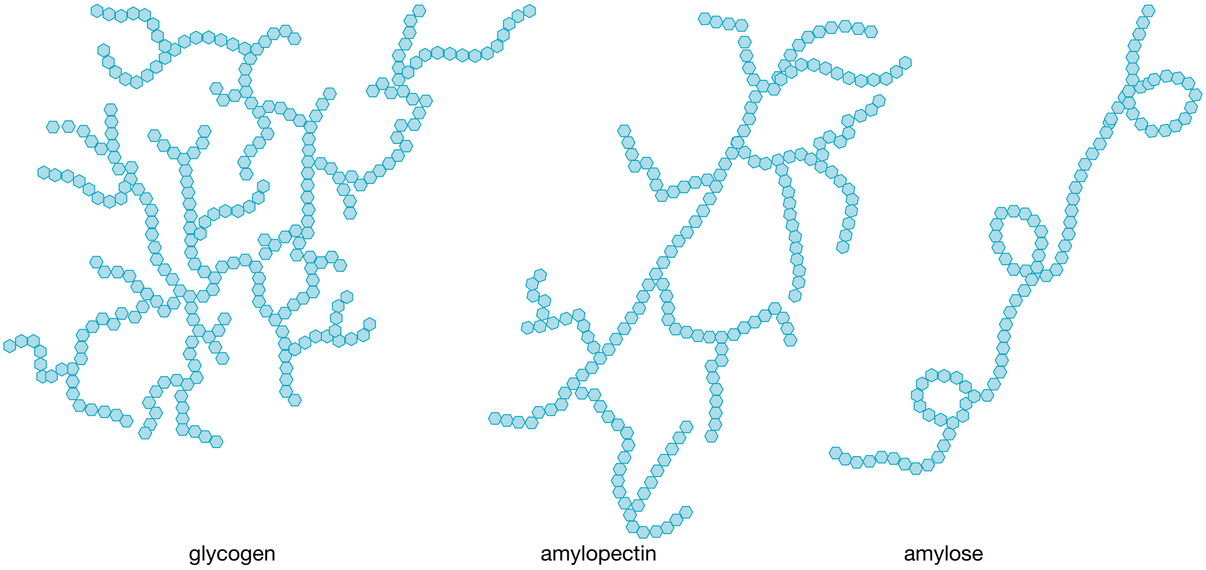
Glycogen

Three monosaccharides, glucose, fructose and galactose, are derived from the hydrolysis of carbohydrates and are absorbed from the digestive tract. They pass to the liver, which converts fructose and galactose to glucose, using specific enzymes. If glucose is not immediately required by the body as an energy source, it is stored in the liver (and, to a lesser extent, in the body tissues) as glycogen. The liver reconverts glycogen to glucose by hydrolysis for use by the body. In this way, the liver keeps the glucose concentration of the blood relatively constant. If the body needs energy in a hurry or when the body is not getting glucose from food, glycogen is broken down to provide the needed glucose.

Glycogen has a similar structure to amylopectin but is even more highly branched. In glycogen, as in amylopectin, the branching is due to C1–C6 linkages. However, in glycogen, these linkages occur approximately every 8–12 glucose units compared with every 25–30 glucose units in amylopectin. The many ends of the molecule are readily available to react and release energy during respiration.

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

FIGURE 11.28 Structures of polysaccharides



Glucose provides energy to animals. It is stored in the liver as glycogen if not immediately required and is reconverted to glucose by hydrolysis.

Cellulose

Cellulose is a natural polymer found in the cell walls of plant materials such as wood, paper, linen and cotton. Food sourced from plants including grains, vegetables, fruits, legumes and nuts all contain cellulose. Cellulose is the most abundant polysaccharide and is a linear polysaccharide also formed by condensation polymerisation of the β-glucose monomer. For the glycosidic bond to form between C1 and C4 in β-glucose, alternate glucose molecules must be inverted, which is the case for cellulose. As with starch, this reaction occurs in plants using the glucose they form during photosynthesis.

There is no branching in a cellulose molecule. The arrangement of β-glucose units and the extensive hydrogen bonding between the unbranched chains provides strength to the rigid cell walls in plants.

FIGURE 11.29 Structure of part of a cellulose polymer

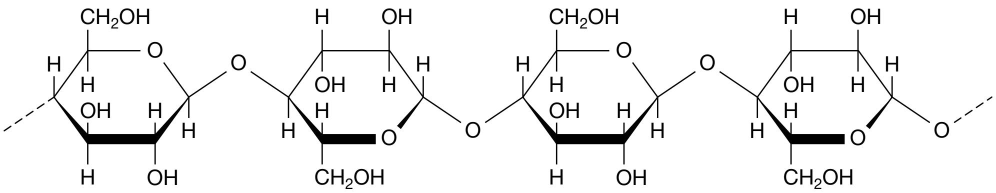
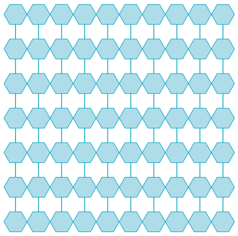


FIGURE 11.30 Arrangement of β-glucose units in cellulose



TIP: The monomer for cellulose is β-glucose but the monomer for starch and glycogen is α-glucose.

on Resources

Digital document Experiment 11.2 Constructing models of carbohydrates (doc-31278)

11.3.4 Structures and energy content

Simple sugars and artificial sweeteners

The simple sugars discussed in section 11.3.3 have different levels of sweetness and effects on blood glucose levels. The effect of a particular carbohydrate on blood glucose levels can be compared using the **glycaemic index (GI)**. Many people enjoy sweet food, but these foods contain mainly sugar and very few other nutrients. Eating excess sugar can lead to obesity and possibly diabetes, so many people have turned to artificial sweeteners, particularly in soft drinks.

One of the most commonly used artificial sweeteners is **aspartame**, which can be identified on food labels as additive 951. It is a white, odourless, soluble crystalline powder, a dipeptide methyl ester and chemically known as methyl l-α-aspartyl-l-phenylalaninate. A scientist who inadvertently licked his finger in the lab (a procedure that is definitely not recommended in a chemistry laboratory!) discovered it accidently. Aspartame is used extensively because it combines well with different foods. It can break down under conditions of high temperature or high pH, so it is not used for baking and the shelf life of foods containing aspartame is limited. A comparison of the relative sweetness of some simple sugars and aspartame is shown in table 11.3.

TABLE 11.3 Sweetness, energy and glycaemic index of sugars and aspartame

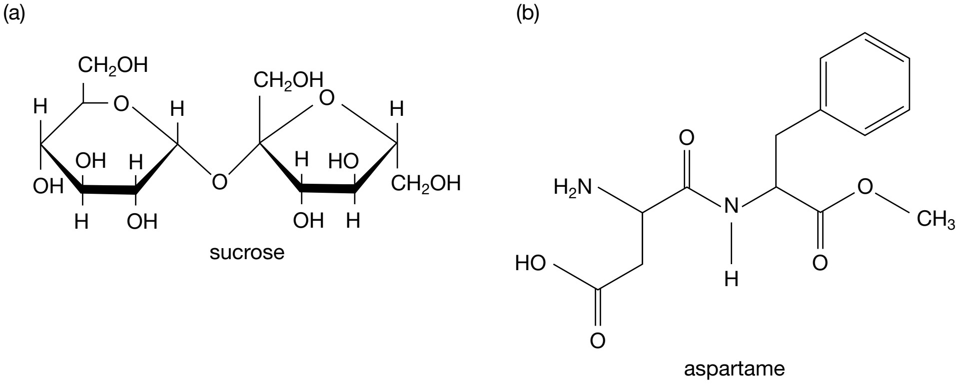
Sugar/sweetener	Notes	Relative sweetness	Energy	Glycaemic Index
Lactose	Disaccharide composed of glucose and galactose; naturally occurring sugar found in milk	0.15	16.7 kJ/g	45
Glucose	Monosaccharide also known as dextrose; can cause glucose levels in blood to rise quickly	0.74	16.7 kJ/g	100

(continued)

TABLE 11.3 Sweetness, energy and glycaemic index of sugars and aspartame *(continued)*

Sugar/sweetener	Notes	Relative sweetness	Energy	Glycaemic Index
Sucrose	Disaccharide composed of glucose and fructose; also known as table sugar, castor sugar, cane sugar and beet sugar	1.0	16.7 kJ/g	65
Fructose	Monosaccharide usually found combined with glucose in sucrose in honey and fruit juice; bees hydrolyse sucrose into glucose and fructose	1.6–1.9	16.7 kJ/g	19
Aspartame	An artificial, non-saccharide sweetener used as a substitute for sugar in some foods and drinks	150–250	16.7 kJ/g	0

FIGURE 11.31 Structures of (a) sucrose and (b) aspartame



TIP: **Make sure you can identify the functional groups in aspartame.**

Aspartame is about 200 times sweeter than sugar, which means that less aspartame than sucrose is needed to achieve the same level of sweetness. In the body, aspartame is hydrolysed to aspartic acid, phenylalanine and methanol. The effects of these products are minimal compared with the intake from other food sources.

- Aspartic acid is a non-essential amino acid, and is important as a component of DNA and in the production of urea. It also acts as a neurotransmitter in the brain. Neurotransmitters are chemicals that transfer impulses from one nerve cell to the next.
- Phenylalanine is an essential amino acid needed for the synthesis of some neurotransmitters and is involved in energy metabolism, although people with the genetic disorder phenylketonuria (PKU) cannot metabolise phenylalanine. Phenylketonuriacs need a special diet to avoid brain damage caused by the build-up of phenylalanine.
- Very small amounts of methanol are found in many foods and are poisonous only if consumed in large quantities. Methanol is absorbed and oxidised into methanal and then to methanoic acid.
- It is interesting to note that aspartame has two chiral carbon atoms, resulting in one isomer that is sweet and the other that is bitter.

FIGURE 11.32 Less aspartame is required to provide the same sweetness as sucrose.

STEVIA: ANOTHER SUGAR ALTERNATIVE

Stevia is also gaining popularity as a natural sweetener, which is derived from the leaves of the plant species *Stevia rebaudiana*. It has 30–50 times the sweetness of sugar and as the body cannot metabolise the glycosides it has both zero kilojoules and a zero glycaemic index.

11.3 EXERCISE

To answer questions online and to receive **immediate feedback** and **sample responses** for every question go to your learnON title at www.jacplus.com.au.

1. What is the molecular formula and molecular mass of glucose?
2. (a) List three sources of carbohydrates in the diet.
    (b) What is the major function of carbohydrates in the body?
3. (a) Identify the monosaccharides from which sucrose, maltose and lactose are formed.
    (b) Write a balanced equation (showing structural formulas) for the formation of maltose.
    (c) Name the type of reaction involved in the production of a disaccharide.
    (d) Name and label the link formed in the reaction between the two monosaccharides.
    (e) Name the functional groups taking part in the reaction.
4. Describe the similarities and differences between galactose and lactose.
5. Calculate the molar mass of two strands of cellulose each made from 400 glucose monomers.
6. Compare the structures of the three polysaccharides: glycogen, starch and cellulose.
7. Name the polysaccharide that matches each of the descriptions below.
    (a) It is the energy storage molecule in plants.
    (b) It is made from β-glucose monomer units.
    (c) If excess glucose is present in the body, it is first stored in muscle and the liver in this form.
    (d) It is made up of two polymers: one branched and the other unbranched.
    (e) It is the most abundant polysaccharide.
8. State and draw the functional groups that are present in:
    (a) glucose
    (b) sucrose
    (c) aspartame.
9. Aspartame has the same number of kilojoules per gram as sucrose, so why is it used in diet foods?
10. Aspartame is not a carbohydrate. What type of compound is it? Why is it used in diet foods?

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11.4 Fats and oils

KEY CONCEPT

- 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 nonessential fatty acids; and structural differences between omega-3 fatty acids and omega-6 fatty acids

11.4.1 Structural features of fats and oils

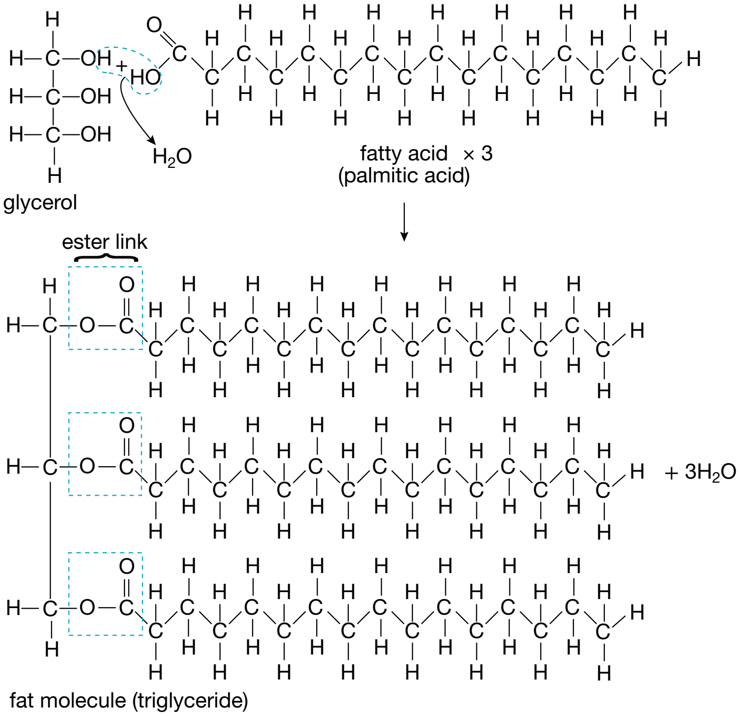
Fats and oils belong to a group of compounds called **lipids**, which also include a small number of other compounds such as waxes, fat-soluble vitamins, monoglycerides and diglycerides. Our bodies need lipids because, as well as their function as an energy store, they form components in cell membranes and are important for hormone production, insulation, protection of vital organs and transport of fat-soluble vitamins. Fats and oils contain the elements carbon, hydrogen and oxygen. In this respect, they are similar to carbohydrates, but fats and oils have a smaller percentage of oxygen and are not polymers. They are found in fish, dairy products, oils, fried foods, seeds and nuts.

FIGURE 11.33 Fats are solid at room temperature and oils are liquid

TIP: Fats contain a lower proportion of oxygen atoms than carbohydrates.

Fats and oils are called **triglycerides** because they are formed by a **condensation reaction** between **glycerol** and three **fatty acids**. The fatty acids can be the same or different. Glycerol is an alcohol, a non-toxic, colourless, clear, odorless and viscous liquid that is sweet-tasting and has the semi-structural formula $CH_2OHCH(OH)CH_2OH$. Fatty acids are long-chain carboxylic acids usually containing an even number of 12–20 carbon atoms. Examples of fatty acids include stearic acid and oleic acid, which have eighteen carbon atoms in their chains. The carboxyl groups in the fatty acids react with the three hydroxyl groups in the glycerol to form three ester links, $-COO-$, and water is a product of the reaction. Triglycerides are hydrophobic and less dense than water because of the large sections of non-polar, hydrophobic sections of the molecules.

FIGURE 11.34 Reaction of glycerol and three fatty acids to form a triglyceride



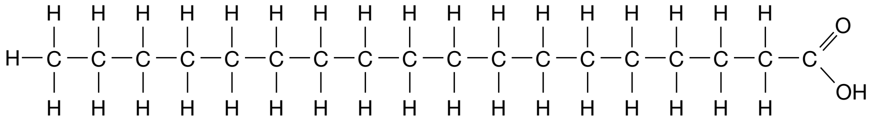
Fats and oils are formed by a condensation reaction between glycerol and three fatty acids.

Saturated and unsaturated fatty acids

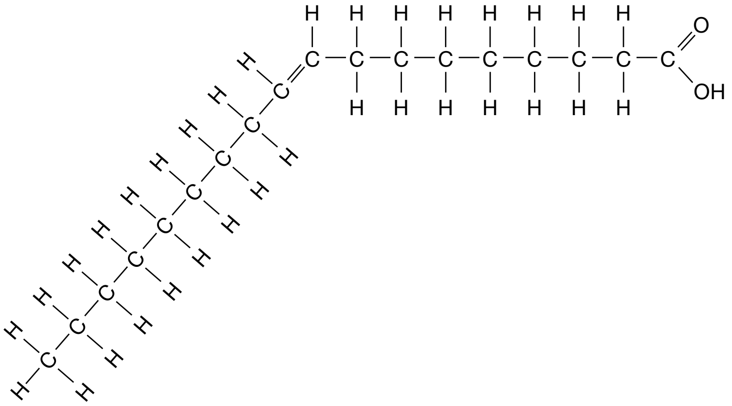
FIGURE 11.35 Sources of saturated fats

The presence of C=C double bonds affects the melting and boiling points of the triglycerides in fatty acids. Fatty acids can be classified as **saturated** or **unsaturated**. Saturated fatty acids have C—C single bonds and straight chains that pack close together to form saturated fats and allow dispersion forces to more effectively operate between the fatty acids and hold them together. Triglycerides that consist of mainly saturated fatty acids are usually solids at room temperature, 25 °C. Saturated fats are very stable and less likely to be oxidised. They generally originate from animal products including meat, butter and cheese. It is recommended that they be limited in our diet because they can increase blood cholesterol levels, one of the major factors in heart disease.

FIGURE 11.36 Example of a saturated and an unsaturated fatty acid



stearic acid (a saturated fatty acid)



oleic acid (a mono-unsaturated fatty acid)

Oils contain a higher proportion of unsaturated fatty acids than fats. Unsaturated fatty acids may contain **monounsaturated** fatty acids, with one C=C double bond, or **polyunsaturated** fatty acids with a number of C=C double bonds. The double bonds cause bends in the fatty acid chains, which disrupt the dispersion forces between the molecules and prevent close packing of these molecules. The consequence of this is that oils have a lower melting point and are liquid at room temperature. The hydrogen atoms and groups either side of a double bond can be found in the cis or trans configuration. Naturally-occurring fatty acids generally have the cis configuration. The structure of a trans-fat configuration is closer to a straight line.

FIGURE 11.37 Cis- and trans-fatty acids

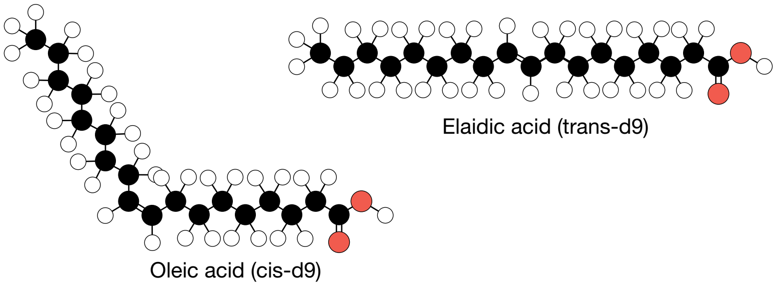


FIGURE 11.38 Weak interactions between long-chain branched lipids in olive oil means it is liquid at room temperature.

Naturally occurring fatty acids generally have the cis configuration.

TIPS:

- **Remember to refer to unsaturated fatty acids as having one or more carbon to carbon double bonds.**
- **Trans-fatty acids have a linear (non-bent) structure, which means that they have higher melting points than cis-fatty acids.**

Hydrogen can be reacted with unsaturated fatty acids to convert them to saturated fatty acids in a process called **hydrogenation** but this increases the amount of trans-fats, which are less healthy. The amount of hydrogen added determines the melting point of the triglyceride. Unsaturated triglycerides, whether monounsaturated or polyunsaturated, reduce cholesterol and so are preferable in the diet. The **iodine number** is used to measure the degree of unsaturation. The iodine number is the mass of iodine that reacts with 100 g of a fat or oil. Iodine reacts with the carbon to carbon double bonds so the more double bonds there are, the higher the iodine number.

TABLE 11.4 Some common carboxylic acids found in fats and oils

Common name	Number of carbon atoms	Semi-structural formula	Example of source	Degree of unsaturation
Palmitic acid	16	$CH_3(CH_2)_{14}COOH$	Palm oil	Saturated
Stearic acid	18	$CH_3(CH_2)_{16}COOH$	Animal fats	Saturated
Oleic acid	18	$CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH$	Peanut oil	Monounsaturated
Linoleic acid	18	$CH_3(CH_2)_4CH{=}CHCH_2CH{=}CH(CH_2)_7COOH$	Vegetable oils	Polyunsaturated

- **Saturated fatty acids have only single C—C bonds.**
- **Monounsaturated fatty acids contain one C=C bond.**
- **Polyunsaturated fatty acids contain more than one C=C bond.**

Essential and non-essential fatty acids

Normal functioning of the body requires some **essential fatty acids** (EFAs). Deficiency can affect the liver, kidneys, blood, immune system and condition of the skin. EFAs are fatty acids that must come from our diet because the body cannot produce them. They are often called omega fatty acids. Examples are alpha-linolenic acid (ALA) and linoleic acid (LA). ALA is found in flaxseed oil, canola oil, linseed, tuna, trout and salmon, whereas LA is present in oils such as soybean, sunflower, corn and safflower, as well as nuts and seeds. **Non-essential fatty acids** are still needed by humans but can be synthesised from foods. Examples of non-essential fatty acids include stearic acid and palmitic acid.

TIP: Take care recognising the two acids linolenic and linoleic acids. Their names are very similar.

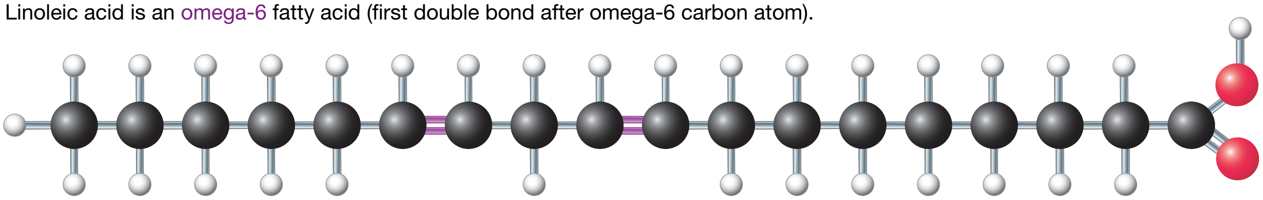
Structural differences between omega-3 and omega 6-fatty acids

Linolenic acid is an **omega-3 fatty acid**, and linoleic acid is an **omega-6 fatty acid**. The position of the double bond is critical to the function of the fatty acid because the body's enzymes cannot react with double bonds near the methyl end. The names arise from the number of the carbon atom in the double bond that is closest to the methyl end, rather than the carboxyl end. Omega (symbol ω) is the last letter of the Greek alphabet.

Humans can synthesise longer omega-3 and omega-6 fatty acids from LA and ALA. The human body can transform LA into other fatty acids including arachidonic acid (AA) and ALA into eicosapentaenoic acid (EPA), both of which contain 20 carbon atoms. These are important fatty acids that are needed to make chemicals for the process of inflammation and the nervous system.

FIGURE 11.39 Omega fatty acids

Linoleic acid is an omega-6 fatty acid (first double bond after omega-6 carbon atom).



Alpha-linolenic acid is an omega-3 fatty acid (first double bond after omega-3 carbon atom).

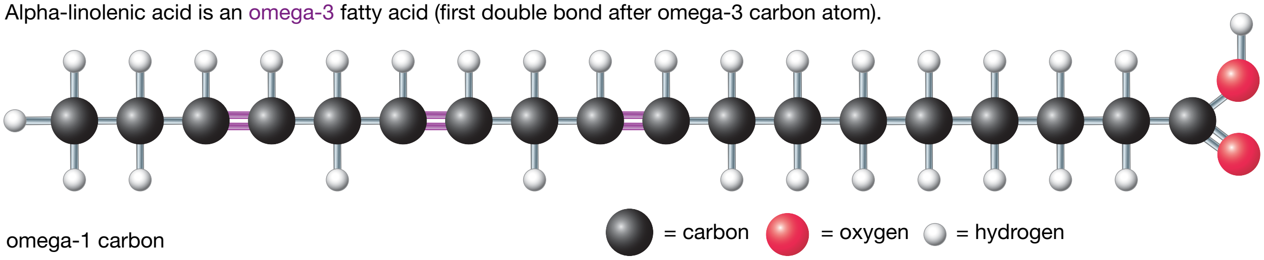


TABLE 11.5 Formulas of some fatty acids

Name	Formula	Semi-structural formula
Lauric	$C_{11}H_{23}COOH$	$CH_3(CH_2)_{10}COOH$
Myristic	$C_{13}H_{27}COOH$	$CH_3(CH_2)_{12}COOH$
Palmitic	$C_{15}H_{31}COOH$	$CH_3(CH_2)_{14}COOH$

(continued)

TABLE 11.5 Formulas of some fatty acids *(continued)*

Name	Formula	Semi-structural formula
Palmitoleic	$C_{15}H_{29}COOH$	$CH_3(CH_2)_4CH_2CH{=}CHCH_2(CH_2)_5CH_2COOH$
Stearic	$C_{17}H_{35}COOH$	$CH_3(CH_2)_{16}COOH$
Oleic	$C_{17}H_{33}COOH$	$CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH$
Linoleic	$C_{17}H_{31}COOH$	$CH_3(CH_2)_4(CH{=}CHCH_2)_2(CH_2)_6COOH$
Linolenic	$C_{17}H_{29}COOH$	$CH_3CH_2(CH{=}CHCH_2)_3(CH_2)_6COOH$
Arachidic	$C_{19}H_{39}COOH$	$CH_3(CH_2)_{17}CH_2COOH$
Arachidonic	$C_{19}H_{31}COOH$	$CH_3(CH_2)_4(CH{=}CHCH_2)_3CH{=}CH(CH_2)_3COOH$

TIP: The formulas of the fatty acids in table 11.5 can also be found in table 9 of the VCE Chemistry Data Book.

11.4 EXERCISE

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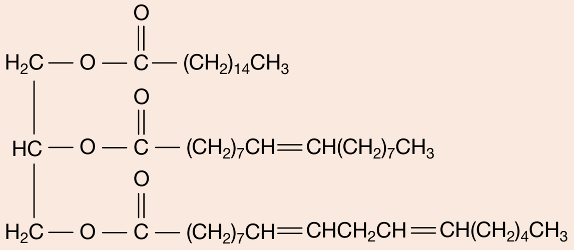
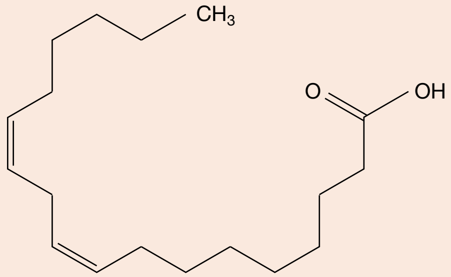
1. Refer to table 11.5 and give an example for each of the following.
   (a) Saturated fatty acid
   (b) Monounsaturated fatty acid
   (c) Polyunsaturated fatty acid
2. What is the molecular formula of:
   (a) glycerol
   (b) stearic acid?
3. Which fatty acid in table 11.5 contains the most double bonds?
4. Explain why ethanoic acid is soluble in water but myristic acid is not.
5. For each of the following pairs, explain which will have the higher melting point.
   (a) Cis- or trans-fatty acids
   (b) Saturated or unsaturated fatty acids
   (c) Longer or shorter fatty acids
6. Write names and formulas of fatty acids used to produce the following triglyceride.



7. (a) Write the molecular formula of a saturated fatty acid containing 12 carbon atoms.
   (b) Write the semi-structural formula of a polyunsaturated fatty acid containing 18 carbon atoms and two double carbon to carbon bonds.
8. Sketch the structural formula of a triglyceride formed from the reaction between glycerol, one molecule of stearic acid, one molecule of oleic acid and one molecule of myristic acid
9. Explain what an essential fatty acid is and provide an example.

10. Write the name for this omega fatty acid and say what type of omega acid it is.



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11.5 Vitamins

KEY CONCEPT

- 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.

11.5.1 Vital vitamins

Vitamins are organic compounds that are needed in minute quantities on a regular basis as part of a healthy diet. Thirteen vitamins are required but they cannot be synthesised by humans, except for vitamin D. However, if vitamins are present in excess or are deficient, diseases such as beriberi, scurvy, anaemia, rickets and skin disorders can occur. Some vitamins can act as coenzymes, which enable a particular enzyme to catalyse a reaction (see topic 13 for more about coenzymes). Vitamins can be divided into two groups: water-soluble and fat-soluble.

11.5.2 Water-soluble vitamins

Water-soluble vitamins include eight different B-group vitamins and vitamin C. They are absorbed directly into the bloodstream and generally operate in cells to help catalyse cellular reactions. These vitamins do not remain in the body and are excreted through the kidneys in urine if excessive amounts are consumed. They are also more easily destroyed by heat, oxygen and light, or lost in water when boiled than fat-soluble vitamins. Therefore, water-soluble vitamins must be obtained from food on a regular basis because they cannot be stored. They contain functional groups containing oxygen and nitrogen. This makes them polar molecules and explains their solubility; they can form hydrogen bonds with water. Other elements that may be present include sulfur; cobalt is found in vitamin B12.

The B-group vitamins assist in breaking down and releasing energy from food. They are required for healthy skin, hair, eyes and liver. The nervous system relies on B-group vitamins to function effectively. Chemical and various refining processes reduce the amount of these vitamins in food, which explains why brown sugar, rice and flour are more nutritious than their white forms. Vitamins play an essential part in metabolism in the body, often by combining with enzymes (protein catalysts) (see topic 12).

FIGURE 11.40 Sources and structure of vitamin C

Vitamin C (ascorbic acid)

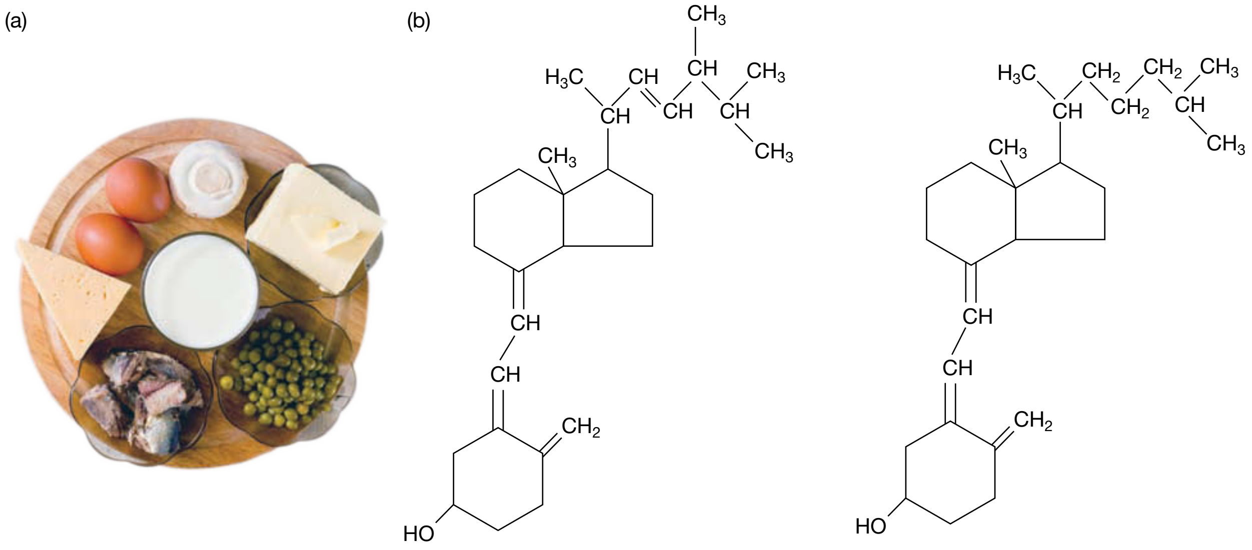
TABLE 11.6 Functions and sources of water-soluble vitamins

Vitamin	Function	Sources
B1 (thiamin)	Assists in breaking down and releasing energy from food; supports nerve function	Wholegrain cereals, seeds, nuts, pork
B2 (riboflavin)	Assists in releasing energy from food and red blood cell formation; supports healthy skin, eyes and nervous system	Dairy products, wholegrain breads and cereals, egg white, leafy vegetables, meat, yeast, liver and kidney
B3 (niacin)	Assists in energy production; supports skin health and nervous and digestive systems	Meats, fish, poultry, milk, eggs, wholegrain breads and cereals, nuts, mushrooms
B5 (pantothenic acid)	Metabolises food; assists in production of red blood cells and hormones	Liver, meats, milk, kidney beans, corn, legumes
B6 (pyroxidine)	Metabolises food; assists in production of red blood cells and hormones; supports nervous system and immunity	Poultry, meats, fish and shellfish, seeds and nuts, fish, liver, beans and legumes
B7 (biotin)	Assists in energy production; involved in metabolism of fat	Peanuts, leafy vegetables, egg, liver, chicken, yeast, mushrooms
B9 (folic acid)	Assists in production of red blood cells, development of foetal nervous system and DNA synthesis	Leafy vegetables, legumes, seeds, liver, poultry, eggs
B12 (cyanocobalamin)	Supports nervous system and production of DNA and red blood cells	Meat, liver, fish, cheese, eggs
C (ascorbic acid)	Maintains healthy immune system; assists in wound healing; helps production of collagen (protein in skin, cartilage, tendons, ligaments, teeth and blood vessels)	Red peppers, citrus fruits, kiwi fruit, cantaloupe, broccoli and Brussels sprouts

11.5.3 Fat-soluble vitamins

Fat-soluble vitamins include vitamins A, D, E and K. They can be absorbed in the intestines and moved via the lymphatic system, and are stored in fat deposits and within the liver, where they can accumulate. The body converts the antioxidant beta-carotene from orange or dark green vegetables into vitamin A, or it can be obtained from dairy products, fish or liver. Vitamin D is made by the enzyme-catalysed action of sunlight on cholesterol and can also be sourced from foods including fatty fish, cheese and eggs. Vitamin K can be produced in small amounts in the intestine by the action of bacteria. Fat-soluble vitamins mainly consist of carbon and hydrogen and consequently form non-polar molecules. This means they contain few, if any, polar groups and are more soluble in non-polar solvents such as fats and oils.

FIGURE 11.41 Some sources and the structures of vitamin D



Vitamin D_2 (ergocalciferol)

Vitamin D_3 (ergocalciferol)

TABLE 11.7 Functions and sources of fat-soluble vitamins

Vitamin	Function	Sources
A	Important for vision and immunity	Sweet potatoes, carrots, spinach, pumpkin, liver, fish
D	Helps calcium and phosphorus absorption	Sunshine, cod liver oil, salmon, sardines, milk, tuna, mushrooms
E	Cell membrane protection	Sunflower seeds, almonds, spinach, asparagus, avocado, peanuts, tofu
K	Helps blood clot	Kale, spinach, spring onions, Brussels sprouts, broccoli, parsley

ACTIVITY: A BERIBERI BAD EXPERIMENT

Christiaan Eijkman, a Dutch doctor living in Java, had a problem. The disease beriberi was becoming more common; it caused nerve damage in victims and eventually heart failure. His research involved injecting chickens with infected blood. Surprisingly, it was not just the injected chickens that died, but those in the control group as well. Thinking the whole area was contaminated, he moved new chickens to a different location and was pleased to observe that these chickens survived. He discovered that it was not the new location that improved the survival rate but that these chickens were being fed unpolished rice rather than the usual white rice. It was not until some years later that it was established that the water-soluble vitamin thiamin in the husks of the brown rice had improved the health of the chickens and provided protection from beriberi.

1. Describe one aspect of Dr. Eijkman's original experiment that was good practice.
2. What was the flaw in experimental technique for his second experiment that still led to a solution to his problem?
3. What is another name for thiamin?
4. What must be present in this vitamin for it to be described as water-soluble?
5. Describe what Dr. Eijkman might have done to improve the experimental design of this experiment.

FIGURE 11.42 Vitamins are found in the husks of brown rice

11.5 EXERCISE

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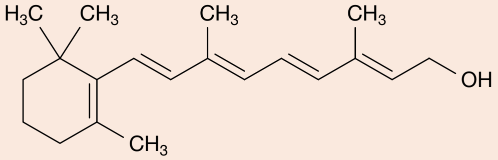
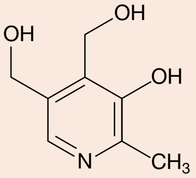
1. What are vitamins?
2. Why are vitamins essential in the human diet?
3. Name the vitamin that is able to be produced by humans.
4. State two food sources of:
   (a) vitamin C
   (b) vitamin D.
5. Why is it necessary to eat foods containing water-soluble vitamins every day, but not necessary for fat-soluble vitamins?
6. Explain why it is more likely that an excess of fat-soluble vitamins rather than water-soluble vitamins will cause health problems.
7. Compare the functional groups present in vitamin C and those present in vitamin D_2.
8. Are the following vitamins water-soluble or fat-soluble? Give reasons for your answers.
   (a)



   (b)



9. What is the molecular formula of vitamin C?
10. What is another name for vitamin C?

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11.6 Review

11.6.1 Summary

Proteins

- Proteins are made up of carbon, hydrogen, oxygen and nitrogen. Some also contain sulfur.
- Proteins are formed by the condensation polymerisation of amino acid units. The amino functional group of one amino acid reacts with the carboxyl functional group of another, and water is eliminated.
- Amino acids contain amino ($-NH_2$) and carboxyl ($-COOH$) functional groups together with a hydrogen atom and a R-group that identifies the amino acid.
- There are 20 amino acids in biological systems in the body.
- Essential amino acids cannot be synthesised by animals from other materials in their diet; they must be supplied by the diet.
- Non-essential amino acids can be synthesised within the body from other materials in the diet.
- Proteins have four structural levels.
  - Primary structure: the number, sequence and type of the amino acids in the chains. Only strong covalent bonds are involved.
  - Secondary structure: the helices, folds and pleats due to hydrogen bonding with non-R-group nitrogen and oxygen in small segments of the peptide chain
  - Tertiary structure: the three-dimensional shape of the protein, which is the result of interactions between different side-chain groups and involves dispersion forces, hydrogen bonding, ionic bonding and disulfide bridges
  - Quaternary structure: the way the constituent protein branches are held together in space when separate polypeptide chains interact with each other. This involves hydrogen bonding, disulfide bridges, ionic bonding and dipole–dipole interactions.

Carbohydrates

- Carbohydrates are made up of carbon, hydrogen and oxygen, and have the general formula $C_x(H_2O)_y$.
- Carbohydrates can be classified into three groups according to their molecular structures: monosaccharides, disaccharides and polysaccharides.
- Glucose is a monosaccharide that has a number of isomers including α-D-glucose and β-D-glucose. Naturally-occurring glucose is the D-form.
- In aqueous solution, monosaccharides can exist in equilibrium in both straight-chain and cyclic forms. It is the major energy source for the body.
- Glucose is formed from water and carbon dioxide during photosynthesis.
- Two monosaccharide units can undergo a condensation reaction to form a disaccharide. The hydroxyl ($-OH$) functional group from each monomer unit reacts to form water as a by-product.
- Aspartame is an artificial sweetener that is 200 times sweeter than sucrose.
- Starch is a polysaccharide formed from the condensation polymerisation of α-glucose from photosynthesis. It is the major storage form of glucose in plants, and is made up of amylose and amylopectin.
  - Amylose is smaller than amylopectin and consists of compacted linear chains arranged in a helical structure. It is not soluble in water.
  - Amylopectin is a longer, more loosely branched molecule that is soluble in water.
- Glycogen is the major storage form of glucose in animals. It is more highly branched than amylopectin. Excess glucose is stored in the liver as glycogen.
- Cellulose is a polysaccharide formed from the condensation polymerisation of β-glucose from photosynthesis in plants. Cellulose is the major structural component of cell walls in plants.
- Humans do not have the enzyme to digest cellulose.

Fats and oils

- Fats and oils are part of a group of nutrients called lipids; they are made up of carbon, hydrogen and oxygen.
- Fats and oils are large esters called triglycerides made from the condensation reaction of one molecule of glycerol and three long-chain carboxylic acids called fatty acids.
- Saturated fatty acids are long-chain carboxylic acids that do not contain a C=C double bond.
- Monounsaturated fatty acids contain one C=C double bond, and polyunsaturated fatty acids contain more than one C=C double bond.
- Unsaturated fats can be converted to saturated fats by the addition of hydrogen.

Vitamins

- Vitamins are a group of organic compounds that are essential for growth and nutrition and are required in small quantities in the diet because they cannot be synthesised by the body.
- Vitamins are categorised according to their solubility in water or fat; this is explained by the functional groups present.
- Water-soluble vitamins are the B-group vitamins and vitamin C. They cannot be stored in the body so need to be regularly ingested. They are unlikely to be toxic because they are excreted in urine. B-group vitamins can be converted to coenzymes.
- Fat-soluble vitamins, such as A, D, E and K, are stored in the liver. They can become toxic due to build up and are more stable to heat than water-soluble vitamins.

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11.6.2 Key terms

α-helices hydrogen bonds are formed between an oxygen atom of a C=O bond and a hydrogen atom of a N—H bond that is four amino acids away on the same chain

β-pleated sheets two sections of the peptide chain line up and are held together in a sheet-like structure by hydrogen bonds between one oxygen atom of a C=O bond and a hydrogen atom of a N—H bond in the parallel or anti-parallel sheet

amide link formed when a carboxyl group reacts with an amino group in a polymerisation reaction

amino acids molecules that contain an amine and a carboxyl group

amylopectin consists of 300–5000 α-glucose units; combines with amylose to form starch

amylose consists of 50–300 α-glucose units in a continuous chain formed from C1–C4 linkages only; combines with amylopectin to form starch

aspartame a common artificial sweetener

backbone a peptide chain of covalently bonded nitrogen and carbon atoms

C-terminal the end of a peptide chain with a free carboxyl group

carbohydrates general name for a class of carbon compounds that include sugars, starch and cellulose. Carbohydrates contain the elements carbon, hydrogen and oxygen.

cellulose the most common carbohydrate and a condensation polymer of β-glucose. Humans cannot hydrolyse cellulose, so it is not a source of energy.

condensation polymerisation step-growth polymerisation in which two monomers combine and a smaller molecule is eliminated

condensation reaction a reaction in which molecules react and link together by covalent bonding with the elimination of a small molecule, such as water or hydrogen chloride, from the bond that is formed

D-glucose an isomer that occurs in nature

dipeptide formed when two amino acids combine

disaccharides two sugar molecules (monosaccharides) bonded together
essential amino acids amino acids that cannot be synthesised by animals from materials in their diets and therefore must be supplied directly in the diet
essential fatty acids fatty acids that must come from our diet because the body cannot produce them; often called omega fatty acids
fatty acids long-chain carboxylic acids usually containing an even number of 12–20 carbon atoms
fibrous describes long fibres in proteins that serve a structural role in the body; insoluble in water
globular describes proteins with a compact rounded shape and are usually soluble
glucose a simple carbohydrate stored in the liver or muscles
glycaemic index (GI) a figure representing the relative ability of a carbohydrate food to increase the level of glucose in the blood
glycerol an alcohol; it is a non-toxic, colourless, clear, odorless and viscous liquid that is sweet-tasting and has the semi-structural formula $CH_2OHCH(OH)CH_2OH$
glycogen the storage form of glucose in animals. It has a similar structure to amylopectin but is even more highly branched
glycosidic link a particular type of ether bond
hydrogenation the addition of hydrogen to unsaturated compounds, such as fatty acids
hydrophilic describes a molecule more likely to interact with water and other polar substances
hydrophobic describes non-polar molecules that repel water molecules
iodine number used to measure the degree of unsaturation. The iodine number is the mass of iodine that reacts with 100 g of a fat or oil.
lipids substances such as a fat, oil or wax that dissolve in alcohol but not in water
monosaccharides the simplest form of carbohydrate, consisting of one sugar molecule
monounsaturated describes fatty acids containing only one double carbon to carbon bond
N-terminal the end of the peptide that has a free amino group
non-essential amino acid the 11 of the 20 amino acids necessary to make proteins that humans can produce
non-essential fatty acid fatty acids that humans can synthesise from food
oligosaccharides three to ten monosaccharides bonded together
omega-3 fatty acid polyunsaturated fatty acids with a carbon to carbon double bond on the third carbon from the methyl end
omega-6 fatty acid polyunsaturated fatty acids with a carbon to carbon double bond on the sixth carbon from the methyl end
peptide formed when amino acids react
peptide link formed when a carboxyl group reacts with an amino group in a polymerisation reaction
polypeptides many amino acid residues bonded together
polysaccharides more than 10 monosaccharides bonded together
polyunsaturated describes fatty acids containing more than one double carbon to carbon bond
primary structure the order of amino acids in a protein molecule
proteins large molecules composed of one or more long chains of amino acids
quaternary structure structure formed when individual protein molecules link together in a particular spatial arrangement
residue what remains when two or more amino acids combine to form a peptide
saturated describes fatty acids containing only single carbon to carbon bonds
secondary structure structure formed from hydrogen bonding between carboxyl and amino groups in a protein molecule
side chain R group attached to an amino acid
starch a condensation polymer of α-D-glucose that is made up of two polymers: amylose and amylopectin
tertiary structure structure formed from side-group interaction, including hydrogen bonding, ionic bonding, dipole–dipole interactions and disulfide bridges, in a protein molecule
triglycerides fats and oils formed by a condensation reaction between glycerol and three fatty acids
unsaturated compound containing one or more carbon to carbon double or triple bonds
vitamins organic compounds that are needed in minute quantities on a regular basis as part of a healthy diet

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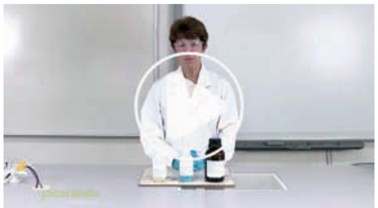
Digital document Key terms glossary – Topic 11 (doc-31418)

11.6.3 Practical work and investigations



Experiment 11.1

Studying starch

Aim: To test for starch in foods

Digital document: doc-31277

Teacher-led video: tlvd-0763

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Digital documents Practical investigation logbook (doc-31419)
Experiment 11.2 Constructing models of carbohydrates (doc-31278)

11.6 Exercises

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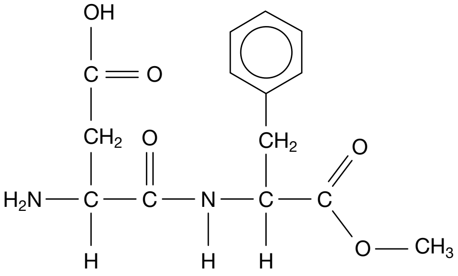
11.6 Exercise 1: Multiple choice questions

1. The $-NH_2$ functional group is:
   - A. an amino group
   - B. a hydroxyl group
   - C. a peptide group
   - D. an amide group.
2. Which functional groups are involved in forming peptide bonds?
   - A. The carboxyl group on two amino acids
   - B. The carboxyl group on one amino acid and the amino side chain on another
   - C. The amino group on both amino acids
   - D. The amino group on one amino acid and the carboxyl group on another
3. What does the primary structure of a protein refer to?
   - A. The covalent bonds that hold the protein in a particular shape
   - B. The hydrogen bonds between sections of the amino acid side chains
   - C. The amino acid sequence of the protein
   - D. Whether it is globular or fibrous
4. The most common covalent cross-links are sulfur–sulfur bonds that form between two amino acids. Which amino acid has this side chain?
   - A. Glycine
   - B. Methionine
   - C. Cysteine
   - D. Proline
5. Two 2-amino acids that contain sulfur atoms are:
   - A. cysteine and serine
   - B. cysteine and threonine
   - C. methionine and cysteine
   - D. methionine and serine.

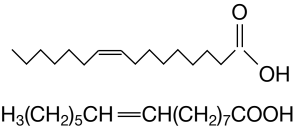
6. What is the strongest form of intermolecular bonding that could be formed involving the residue of the amino acid valine?
   - A. Ionic bond
   - B. Hydrogen bond
   - C. Dispersion forces
   - D. None of the above
7. Which of the following terms refers to the sequence of different amino acids in a protein?
   - A. Primary structure
   - B. Secondary structure
   - C. Tertiary structure
   - D. Quaternary structure
8. What is the main function of carbohydrates?
   - A. To repair body tissues
   - B. To fight infection
   - C. A source of energy
   - D. To speed up chemical reaction
9. Two monosaccharides are joined by a:
   - A. peptide bond
   - B. glycosidic bond
   - C. hydrogen bond
   - D. ester bond.
10. Starch consists of:
    - A. unbranched amylopectin and branched amylose
    - B. unbranched amylose and branched amylopectin
    - C. branched amylopectin and branched amylose
    - D. unbranched amylose and unbranched amylopectin.
11. Fatty acids without double carbon to carbon bonds are said to be:
    - A. saturated
    - B. monosaturated
    - C. polyunsaturated
    - D. unsaturated.
12. Lipids are formed by a condensation reaction between fatty acids and:
    - A. an alcohol
    - B. an amino acid
    - C. an ester
    - D. a monosaccharide.
13. Which of the following fatty acids would have the highest melting point?
    - A. Stearic acid
    - B. Linoleic acid
    - C. Oleic acid
    - D. Linolenic acid
14. Which group of compounds do triglycerides belong to?
    - A. Carboxylic acids
    - B. Alcohols
    - C. Ketones
    - D. Esters
15. Which reaction is used to convert an oil into a fat?
    - A. Esterification
    - B. Dehydration
    - C. Hydrogenation
    - D. Hydrolysis

11.6 Exercise 2: Short answer questions

1. What are the structural features of all amino acids found in naturally-occurring proteins?
2. Describe the differences in structure between glutamine and glutamic acid.
3. The amino acids cysteine and serine can react with each other to form a dipeptide.
   a. State the type of reaction occurring when amino acids react together, and identify the products of the reaction.
   b. Draw the structures of the two possible dipeptides formed in the reaction between one molecule each of cysteine and serine.
4. Polypeptides and proteins are formed by the condensation reactions of amino acids.
   a. Draw the structural formula of threonine, and label the carboxyl and amino groups.
   b. Give the structural formula of a dipeptide formed by the reaction of glycine and threonine. State the other substance formed during this reaction.
   c. State two functions of proteins in the body.
5. When many amino acid molecules react together, a protein is formed. These proteins have primary, secondary, tertiary and quaternary structures.
   a. State the type of intermolecular force responsible for maintaining the secondary structure.
   b. State two other ways in which the tertiary structure of the protein is maintained.
6. Suppose you want to synthesise tripeptides using the amino acids alanine, glycine and aspartic acid.
   a. How many different tripeptides can be prepared using each amino acid only once?
   b. How many different tripeptides can be prepared using any of the three amino acids in any of the three positions if you can use each more than once?
   c. Write a balanced equation for the formation of a tripeptide, indicating which functional groups react and which by-products are formed.
7. Draw the structural formula of the polar amino acid with formula $C_3H_7NO_3$ showing all bonds.
8. The molecular formula of glucose, a monosaccharide, is $C_6H_{12}O_6$. What is the molecular formula of maltose, a disaccharide formed from two molecules of glucose?
9. Starch is an important nutrient in the human diet. Describe the similarities and differences in the structures and properties of the two components that make up starch.
10. A cellulose molecule contains 640 glucose units. If the molar mass of glucose is 180 g mol^{-1}, what is the molar mass of the cellulose molecule?
11. Aspartame is soluble in water. Identify the atoms in the following structure that can form hydrogen bonds with water.



12. The structure of palmitoleic acid, a fatty acid found in olive oil, is shown below.

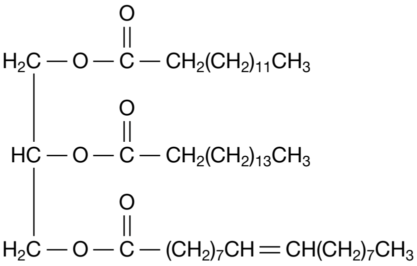


   a. Palmitoleic acid is described as a *monounsaturated fatty acid*. Explain how each of the three italicised words relates to the structure of palmitoleic acid.

b. Use structural formulas to show how three molecules of palmitoleic acid can form a triglyceride when reacted with one molecule of glycerol.

c. Why is the formation of a triglyceride often described as an esterification reaction?

13. Write an equation showing the hydrolysis of the following triglyceride.

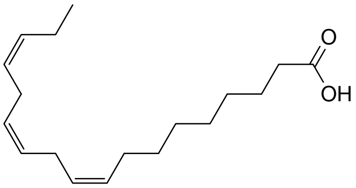


14. Explain, in terms of their chemical structures, the differences in solubility in water of carbohydrates and fats.

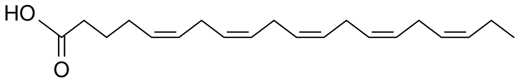
15. List the similarities and differences between the structures, properties and susceptibility to oxidation of saturated and unsaturated fatty acids.

16. An unsaturated fat can be converted into a saturated fat by reacting it with hydrogen gas using a metal catalyst. If 16.8 g of hydrogen gas reacts with 1.40 moles of the unsaturated fat, determine the number of carbon to carbon double bonds present in each molecule of the unsaturated fat.

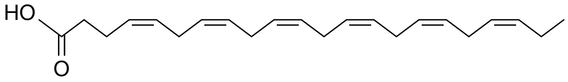
17. The following molecule is alpha-linolenic acid. It is described as an essential fatty acid and also an omega-3 fatty acid. Explain the reasons for this description.



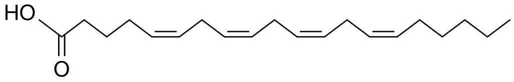
18. Indicate which of the following are omega-3 and which are omega-6 fatty acids. Explain your choices.



Eicosapentaenoic acid



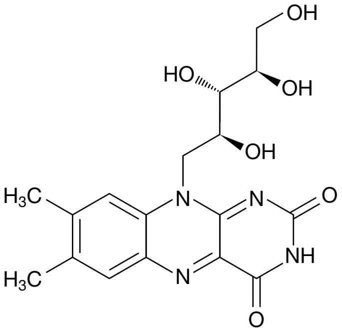
Docosahexaenoic acid



Arachidonic acid

19. Explain why vitamin C is soluble in water and why vitamin D is insoluble. What implications does this have on the possibility of deficiency or excess vitamins in the body?

20. Explain whether this vitamin would be soluble in water or fat.



11.6 Exercise 3: Exam practice questions

Question 1 (1 mark)

Amino acids can be formed in humans by the digestion of proteins in the food that is eaten. Which of the following is true of most amino acids?

- A. The amino acids found in the human body can all be classified as essential, rather than non-essential, amino acids.
- B. Amino acids can act as both acids and bases.
- C. Amino acids can undergo addition polymerisation, forming polypeptides.
- D. Amino acids are highly soluble in non-polar solvents.

Question 2 (1 mark)

The percentage of oxygen by mass in the amino acid glutamine is 32.9%. In a polypeptide formed from glutamine, the percentage of oxygen by mass is:

- A. 32.9%
- B. greater than 32.9%
- C. less than 32.9%
- D. unable to be determined from the information provided.

Question 3 (1 mark)

Sucrose is a disaccharide consisting of glucose and:

- A. fructose
- B. glucose
- C. maltose
- D. galactose.

Question 4 (1 mark)

Aspartame is an artificial sweetener. It contains:

- A. a hydroxyl group
- B. a lower energy content per gram than sugar
- C. a glycosidic link
- D. two chiral carbons.

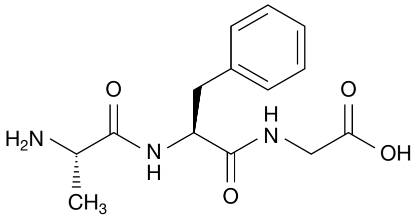
Question 5 (1 mark)

Vitamins are required in small amounts in a healthy diet. Vitamin C:

- A. is soluble in water
- B. is stored in the fatty tissues in the body
- C. can be obtained from eating meat and fish
- D. can be manufactured in the body.

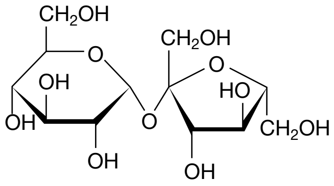
Question 6 (3 marks)

Circle and label the peptide links in the following structure, and name the amino acids used to produce the tripeptide.



Question 7 (7 marks)

The disaccharide sucrose is common table sugar, obtained from sugar cane and added to a wide range of foods. Most of us eat more than the recommended level. The structure of sucrose is shown below.



a.	Name the two monosaccharides that combine to form sucrose.	**1 mark**
b.	Draw the structure of the monosaccharide with the 5-carbon ring.	**1 mark**
c.	What type of reaction is involved in the formation of sucrose?	**1 mark**
d.	Name the other molecule that is produced in this reaction.	**1 mark**
e.	Name the types of functional groups present in sucrose.	**1 mark**
f.	How does the sweetness of sucrose compare with that of the two monosaccharides?	**1 mark**
g.	State the molecular formula of this disaccharide.	**1 mark**

Question 8 (2 marks)

A section of a starch molecule has a mass of 2.75×10^5 g mol^{-1}. Calculate the number of glucose residues that would be present.

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AREA OF STUDY 2
WHAT IS THE CHEMISTRY OF FOOD?

12 Metabolism of food in the human body

12.1 Overview

Numerous **videos** and **interactivities** are available just where you need them, at the point of learning, in your digital formats, eBookPLUS and learnON at www.jacplus.com.au.

12.1.1 Introduction

FIGURE 12.1 Enzymes help break down the proteins, carbohydrates, and fats and oils in this meal.

Our bodies are like a giant chemical laboratory with thousands of chemical reactions occurring at the same time. These reactions are referred to as the metabolism of food, and affect how nutrients are digested and how proteins, carbohydrates and fats and oils are broken down into their component parts. When we eat food, the body breaks down the large molecules into smaller molecules, which either provide energy or are built up into different substances that are required by the body.

This topic focuses on hydrolysis reactions as water is a reactant. Hydrolysis allows the breakdown of proteins to amino acids, and fats and oils to glycerol and fatty acids. The carbohydrate starch, when digested, is broken down into glucose monomers whereas cellulose, another polysaccharide, is unable to be digested by humans. An explanation for this and why some people are also unable to break down lactose are discussed. These reactions depend on the functional groups present, conditions in the particular part of the body, and often the presence of enzyme catalysts, that speed up reactions so they can occur in fractions of seconds. The effectiveness of enzymes can be limited by factors including temperature and pH, which can alter the shape, and therefore the function, of proteins. This process is referred to as denaturation and is different from hydrolysis.

12.1.2 What you will learn

KEY KNOWLEDGE

In this topic, you will investigate:

- 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 process 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).

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PRACTICAL WORK AND INVESTIGATIONS

Practical work is a central component of learning and assessment. Experiments and investigations, supported by a **Practical investigation logbook** and **Teacher-led videos**, are included in this topic to provide opportunities to undertake investigations and communicate findings.

on Resources

Digital documents Key science skills (doc-30903)
Key terms glossary – Topic 12 (doc-31421)
Practical investigation logbook (doc-31422)

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12.2 Metabolism of food

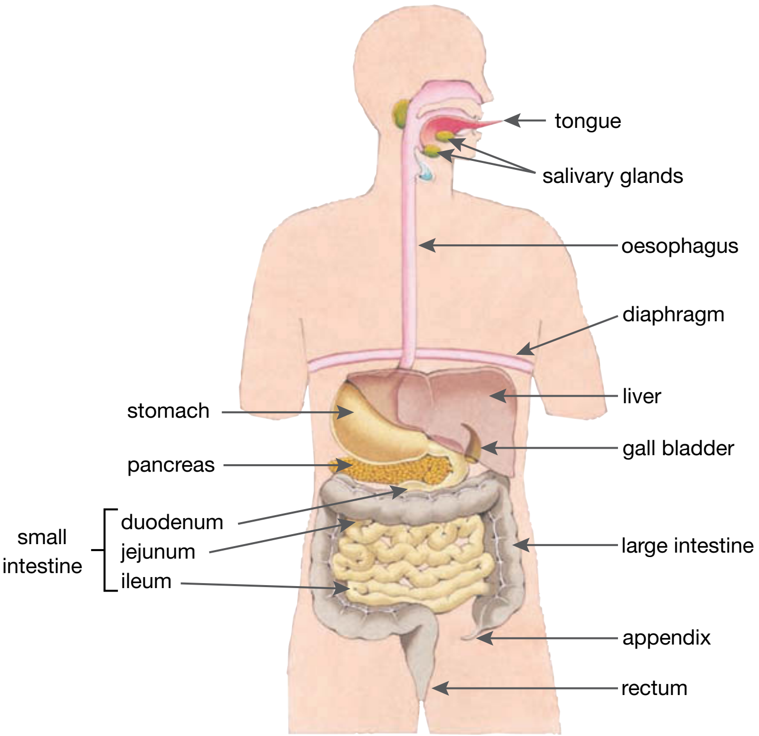
KEY CONCEPT

- 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.

12.2.1 Review of digestion

The digestion of food begins in the mouth where both mechanical and chemical breakdown occurs. Mechanical digestion is the physical break down of food, by teeth. Chemical digestion also commences in the mouth, where the mere thought of food causes enzymes to be released by salivary glands. This will begin the digestion of carbohydrates and some fats. The process of peristalsis pushes the food down the oesophagus to the stomach, where gastric enzymes and hydrochloric acid work together to break down protein and some fats. The partly digested food then travels to the alkaline conditions of the small intestine where more enzymes from the liver, pancreas and small intestine break the food molecules down further. Bile, produced in the liver, assists in the digestion of fats and oils. In the small intestine, food molecules have been sufficiently reduced in size to be absorbed into the bloodstream ready to be used to produce energy or be built up into the molecules body needs. Undigested food passes into the large intestine where water, minerals and some vitamins are absorbed.

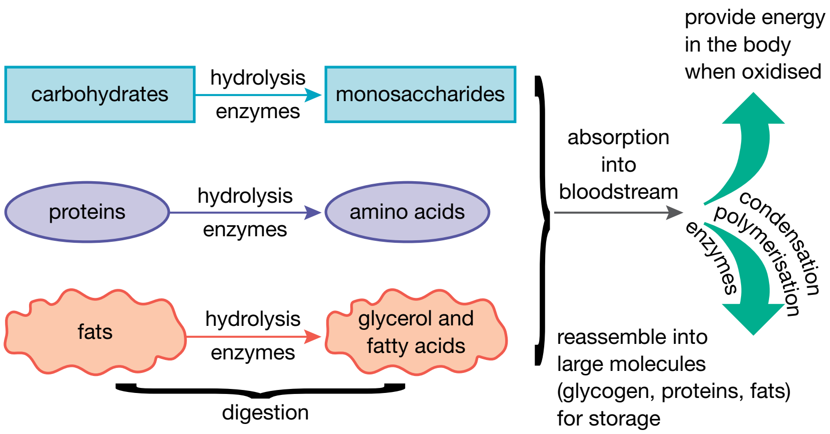
FIGURE 12.2 The human digestive system



12.2.2 The chemical process of digestion

In this section, we will examine the chemical breakdown (digestion) of the large biomolecules in the hamburger shown in figure 12.1 into smaller molecules, and the subsequent reassembly into larger molecules that the body needs to function effectively. These chemical processes are referred to collectively as **metabolism**. Each process is described in more detail in the following subtopics. The reactions in which complex carbohydrates, lipids and proteins are broken down into smaller molecules is **hydrolysis**, which can also be referred to as a hydrolytic reaction. In hydrolysis, water is a reactant and occurs in the presence of an enzyme. The products of these reactions are then synthesised by condensation reactions into large significant biological molecules that are required for general well-being.

FIGURE 12.3 Metabolism of food in the body



The bread in the hamburger is made from wheat and consequently has a high proportion of **starch**, which is a polysaccharide. During digestion, starch is hydrolysed to the disaccharide maltose and then hydrolysed to monosaccharides. The monosaccharides are converted to glucose, which is used as an energy source to power body cells including the brain, muscles and red blood cells. This process is called **respiration**, which uses the following equation.

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

Glucose that is not used immediately is converted into glycogen, $(C_6H_{10}O_5)_n$, another polysaccharide, in a **condensation polymerisation** reaction. Glycogen is stored in the liver (see subtopic 11.3.1).

Despite their bad publicity, fats and oils (lipids) have many essential roles in the body. In the hamburger, the fats in the cheese and meat are processed in various parts of the digestive system to hydrolyse them into the simpler molecules of glycerol and fatty acids. After these substances are passed through the wall of the small intestine they are resynthesised into triglycerides in condensation reactions and carried into the organs of the body through the lymphatic system, where they are stored for energy, and growth and development. Fats and oils store energy and are used when carbohydrates, which are easier to break down, are not available. Every cell membrane is made up of lipids, which also make up hormones, store vitamins and insulate and protect vital organs.

The hydrolysis of proteins in the cheese and meat in the hamburger begins in the stomach and produces a mixture of polypeptides. However, these polypeptides are still too large to be absorbed into the bloodstream at this point. After partial digestion in the stomach, proteins are further hydrolysed to form amino acids when they reach the small intestine. The amino acids then pass into the bloodstream and are carried to tissues where they can be reassembled to form new protein. The enzyme-catalysed hydrolysis reactions for the digestion of protein are the reverse of the condensation reactions by which they were formed originally.

- **Hydrolysis reactions occur when compounds are broken down by reaction with water.**
- **Proteins are digested by enzyme-catalysed hydrolysis reactions.**
- **These reactions are the reverse of the condensation reactions by which they were formed.**

12.2 EXERCISE

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1. Why do molecules of starch, protein and fat need to be digested?
2. Draw simplified flow charts to show the metabolism of each of the following food molecules. Where possible, include the type of reaction and state the main use of the final product.
   (a) Carbohydrates
   (b) Fats and oils
   (c) Protein
3. (a) What is a hydrolysis reaction? Give an example
   (b) What is condensation reaction? Give an example
4. Identify the following as either condensation or hydrolysis reactions.
   (a) Water produced
   (b) Disaccharide to polysaccharide
   (c) Dipeptide to amino acid
   (d) Glucose to starch
   (e) Maltose to glucose
   (f) Water consumed
   (g) Triglyceride to glycerol and fatty acids
5. What are the products of the hydrolysis of:
   (a) Fat
   (b) Starch
   (c) Protein
   (d) Maltose
   (e) Oil
   (f) Glycogen

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12.3 Enzymes as protein catalysts

KEY CONCEPT

- Enzymes as protein catalysts: active site; modelling of process 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.

12.3.1 What are enzymes?

Hydrolysis reactions and condensation reactions both require **enzymes** for the reactions to proceed. Most metabolic processes require enzymes to ensure that reactions occur fast enough to maintain life. Enzymes are proteins that act as biological catalysts. Catalysts are substances that increase the rate of a reaction without being changed in the reaction. In chemical reactions, for two molecules to react, they must collide with one another with the correct orientation and sufficient energy to overcome the energy barrier to the reaction. This is called the **activation energy**. Figure 12.4 shows how enzymes lower the activation energy of a reaction to enable the reaction to proceed. Like inorganic catalysts, enzymes speed up reactions by providing an alternative reaction pathway of lower activation energy (see topic 5).

Enzyme names usually end in *-ase*, except for pepsin, rennin and trypsin. For example, lactase breaks down **lactose**, which is a milk sugar, sucrase breaks down complex sugars, amylase breaks down starch, protease digests proteins, and lipase breaks down fats. Amazingly, reactions with enzymes occur up to millions of times faster than reactions without enzymes. They do this at body temperature, about 37 °C, and at a specific pH depending on the part of the body in which they function. Each enzyme catalyses a particular type of reaction so there are many different enzymes working in our bodies.

FIGURE 12.4 Activation energy profile for enzyme-catalysed and non-enzyme-catalysed reactions

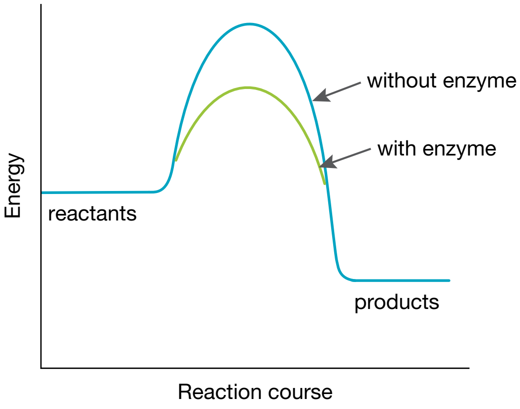


FIGURE 12.5 Pineapples contain bromelain, an enzyme that is used to digest proteins.

Most inorganic catalysts are not selective and can speed up many different chemical reactions, but enzymes are very specific. Each enzyme generally catalyses one specific reaction. The specificity lies in the shapes of the enzyme molecules. Like all catalysts, enzymes remain unchanged at the end of the reactions they catalyse. Enzymes alter the rates of reactions but not the position of the equilibrium. Bromelian is an example of an enzyme and is found in pineapples. It has a sweet taste and contains many minerals and vitamins. Bromelain is used as a meat tenderiser because it starts to break down the proteins in meat and makes it easier to digest.

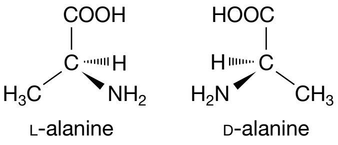
Enzymes lower the activation energy by providing an alternative pathway.

12.3.2 Enzymes and optical isomers

Every enzyme has a unique three-dimensional shape, which is determined by the nature of the bonding and side chains of the amino acid residues in the protein. As a result of their structure, many enzymes have an **active site**, which is a region into which the reactant molecule, called a **substrate**, is maneuvered.

The active site of each type of enzyme is unique, and is where the substrate is converted to product molecules. In addition, except for glycine, amino acids are enantiomers due to their chiral centres. This means that they are either the L- or D-form, according to the arrangement of groups around the chiral carbon atom. They are mirror images of each other and have different optical activity. It is remarkable, and as yet unexplained, that almost all plant and animal proteins are **L-amino acids**. This means that enzymes, which are proteins, catalyse reactions only between molecules with the appropriate **stereoisomerism**. The D-form is found in simple organisms, such as bacteria, and in some antibiotics that can destroy bacteria by interfering with the proteins required by the bacteria.

FIGURE 12.6 Enantiomers of alanine



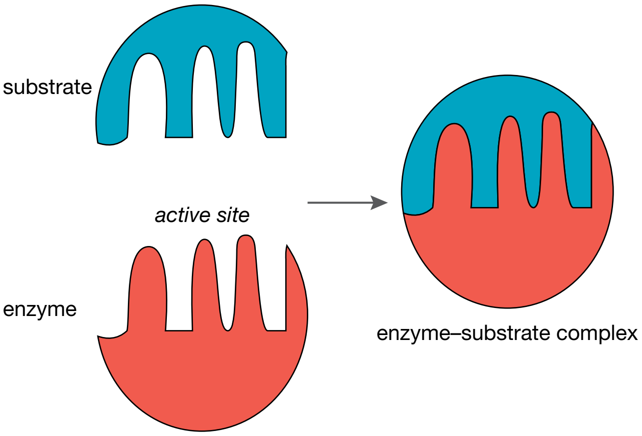
12.3.3 Enzyme models

There are two models proposed to explain the action of enzymes: the **lock-and-key model** and the **induced fit model**.

Lock-and-key model

In the lock-and-key model, only molecules with complementary shapes can react with the enzyme. The binding of the substrate to the enzyme is the result of reactions where bonds break in the substrate and are formed with the enzyme to create a enzyme–substrate complex, and then new products are released. The products move from the active site and the enzyme is unchanged at the end of the reaction. Enzyme action may be compared to a key fitting into a lock. Only a key with a particular shape can open the lock. It is important to remember that enzymes are three-dimensional and chiral, so they are highly stereoselective. Only one enantiomer can fit into the active site of the enzyme and react.

FIGURE 12.7 The lock-and-key model: the substrate and enzyme active site have complementary shapes.

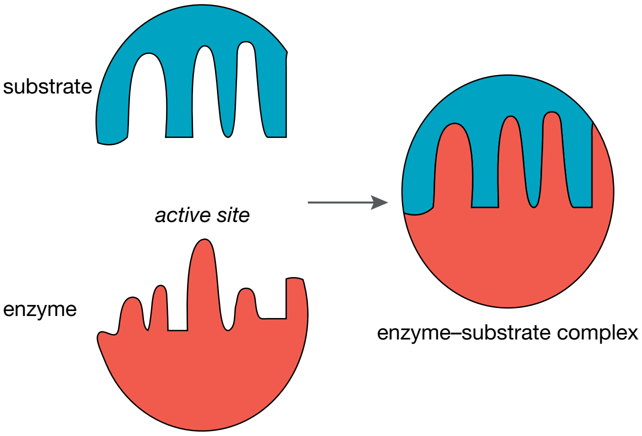


Enzyme catalysed reactions are stereospecific so only substrates with the correct shape will fit into the active site.

Induced fit model

The induced fit model was proposed because the lock-and-key model does not adequately explain all experimental evidence. The induced fit model suggests that the shape of the enzyme is more flexible and, in the presence of the substrate, the active site of the enzyme may change in order to fit the substrate's shape after the substrate and enzyme join. That is, the shape of the active site is not an exact match but may change shape in the presence of a specific substrate to become complementary. The enzyme-substrate complex formed may have better binding properties, but after the release of the products, the active site will return to its original shape.

FIGURE 12.8 Induced fit model: the enzyme active site forms a complementary shape to the substrate after binding.



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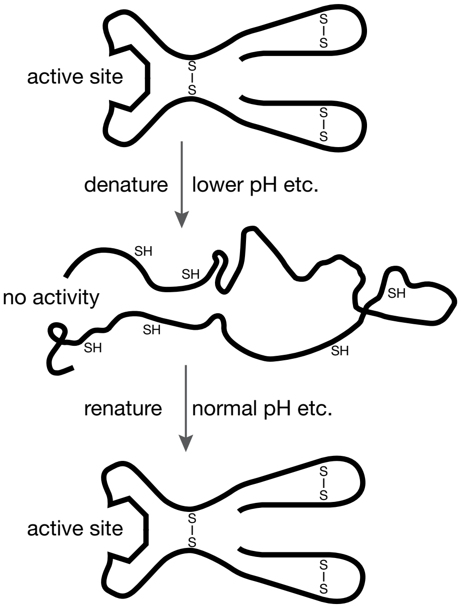
Digital document Experiment 12.1 Enzymes as protein catalysts (doc-31279)

12.3.4 Factors affecting denaturation and the function of enzymes

As already discussed, the structure of a protein is fundamental to its function and if this is altered it will become inactive. **Denaturation** of proteins refers to disruption of interactions in the secondary, tertiary and quaternary structures, where the α-helix and β-sheets uncoil and change their shape. The primary structure is not affected because covalent bonds are much stronger than hydrogen bonds and less easily broken. During denaturation, **coagulation** of the protein commonly occurs. You may have noticed this effect when cooking an egg. The 'white' of a raw egg is clear and runny, but after heating it becomes white and solid. This transformation shows that it has been denatured and the protein has formed different interactions when coagulating.

As well as heating, denaturation can also be caused by a change in pH. This alters the shape of an enzyme, thereby altering the enzyme's active site and destroying its catalytic activity. If the changes are mild and the original conditions restored, the protein may regain its former shape but this does not occur often. Some proteins are more susceptible to denaturation than others depending on the strength of the interactions. The type of disruption also impacts on the extent of the denaturation process — changing the pH will affect the interactions between acidic and basic groups but the disulfide links will not be disturbed.

FIGURE 12.9 Denaturing a protein, if mild, can be reversed.



Factors that affect enzyme activity include increased temperature and change in pH, substrate concentration, radiation or the presence of alcohol or heavy metal salts. The skin on curdled milk is caused by denaturing of milk protein by acidic conditions. Agitation can also have an effect (e.g. whipping cream or egg white).

TIP: Make sure you refer to the different levels by name when discussing protein structure

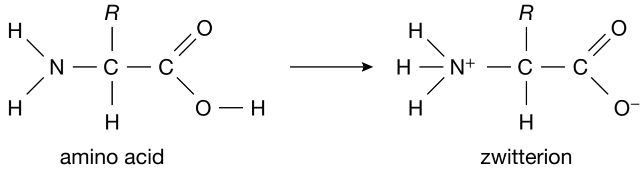
12.3.5 Effect of changes in pH on enzyme activity

Although amino acids are commonly shown as containing an amino group and a carboxyl group, $H_2NCH\mathbf{R}COOH$, certain physical and chemical properties, including melting points, solubilities and acid–base properties, are not consistent with this structure.

Zwitterions

The acid–base properties of carboxyl and amino groups have an effect on amino acid structure. The weakly acidic proton of the carboxyl group easily transfers to the amino group, forming a **zwitterion** or **dipolar ion**.

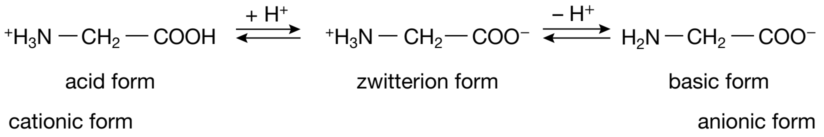
FIGURE 12.10 An amino acid and its corresponding zwitterion



A zwitterion is a molecule with a net charge of zero but negative and positive charges on individual atoms in its structure. In the pure solid state and in aqueous solutions with an approximately neutral pH, the amino acids exist almost completely as zwitterions.

Amino acids can behave as both acids and bases (that is, they are **amphoteric**) and can exist in several forms, depending on the pH of the solution. Consider glycine: it can lose or gain a H^+ ion. The form of glycine shown in the middle of figure 12.11 is a zwitterion because it has equal numbers of positive and negative groups, but its net charge is zero.

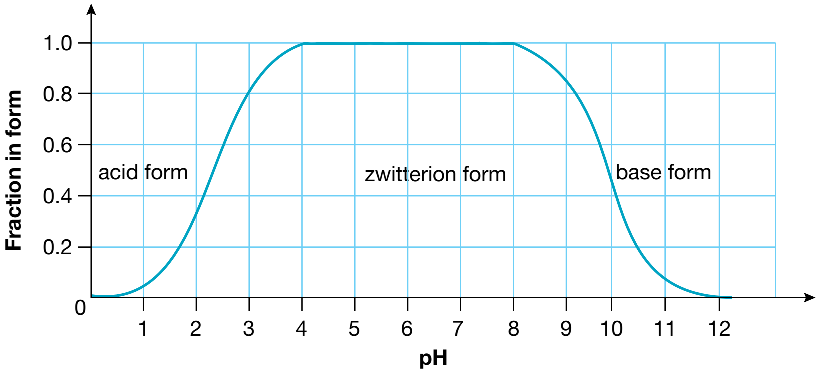
FIGURE 12.11 Glycine in solution



$$^{+}H_3N-CH_2-COOH \overset{+H^+}{\rightleftarrows} {}^{+}H_3N-CH_2-COO^- \overset{-H^+}{\rightleftarrows} H_2N-CH_2-COO^-$$

In an acidic environment, the zwitterion behaves as a base because the carboxyl groups combine with the increasing concentrations of H^+ to form uncharged $-COOH$ groups. The remaining ammonium group then gives the molecule a net positive charge (cationic form). In a basic environment, the zwitterion behaves as an acid because the ammonium group loses H^+ when the concentration of H^+ is lowered, leaving an uncharged amino group. The molecule then has a net negative charge from the remaining carboxyl group (anionic form).

FIGURE 12.12 The form of an amino acid varies with pH. This graph shows the fraction of glycine present as the zwitterion plotted against pH values. The fraction not present as a zwitterion exists as a cation in acidic solutions (left) and as an anion in basic solutions (right).



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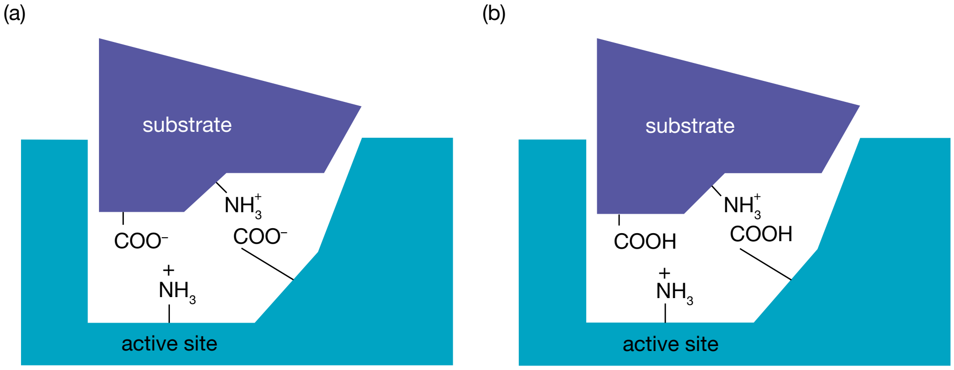
Video eLesson Glycine — amphoteric behavior (eles-2593)

Enzymes and pH

Enzymes are affected by pH due to uptake and release of protons (H^+), which influence whether they participate in hydrogen bonding. This changes the attractions between sections of the peptide chain. Changes in pH affect the interactions in both the enzyme and the substrate. Most enzymes have an **optimum pH** necessary for maintaining the structure of the enzyme.

Consider the example shown in figure 12.13. If the pH is at the optimal pH level the ionic interaction will occur between the $-COO^-$ and the $NH_3{}^+$ groups in the enzyme and the substrate as shown in figure (a). If the conditions become acidic, the pH will lower and the $-COO$ will accept a proton to become $-COOH$ as shown in figure (b). In this case, ionic bonds cannot form and the reaction will not be catalysed.

FIGURE 12.13 (a) At optimal pH, ionic interactions occur between the $-COO^-$ and the $NH_3{}^+$ groups. (b) In acidic conditions, ionic bonds cannot form between the substrate and the enzyme.



Different enzymes have different optimum pH levels because of the carboxyl or amino functional groups on the side chains of the amino acids present. Enzymes begin to denature if the pH of their environment goes outside their optimum range. For example, pepsin works best in the acid conditions of the stomach. Table 12.1 lists some of the enzymes in the digestive system and their different optimum pH values.

FIGURE 12.14 Different enzymes have different optimum pH levels

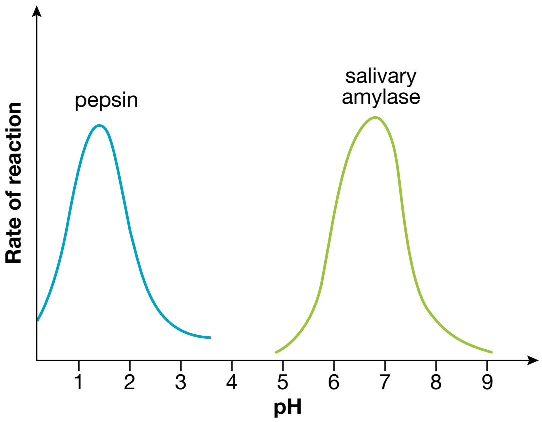


TABLE 12.1 Optimum pH levels for some enzymes in the digestive system.

Enzyme	Optimum pH
Lipase	8.0
Pancreatic protease (trypsin)	7.5–8.0
Salivary amylase	6.8
Stomach protease (pepsin)	1.5–2.0
Sucrase	6.2

Resources

Interactivity Classifying the effect of pH on amino acids (int-1238)

12.3.6 Effect of changes in temperature on enzyme activity

Enzymes can operate effectively only at body temperatures. Each enzyme has an optimum temperature and pH range for maximum activity. Below body temperature, the rate of reaction is very slow because of a low frequency of collisions between the particles. As temperature increases, reacting molecules gain more kinetic energy and increase their chances of successful collisions, thereby increasing the rate of a reaction. However, for an enzyme, there is a temperature at which it performs its catalytic activities most quickly. This is known as the **optimum temperature**.

For most enzymes in the human body, the optimum temperature is approximately 37.5 °C, but different organisms have different optimum temperatures depending on the environment in which they live. As the temperature continues to rise, the stronger vibrational energy increases a strain on the interactions holding the enzyme in its shape. When this happens, weak interactions such as hydrogen bonding and hydrophobic interactions are disrupted, and the secondary, tertiary and quaternary structures of the protein are destroyed. As demonstrated in figure 12.15, the rate of reaction starts to decline as the temperature rises above optimum temperature.

Denaturing can be irreversible, as in the case of frying an egg. The albumen protein in the egg white denatures and becomes insoluble when heated. Eggs are poached in water with vinegar added because the vinegar helps denature the protein on the egg surface to prevent it falling apart before it coagulates. Another example is when instruments are sterilised by heating them in boiling water. This denatures the proteins in any bacteria present.

FIGURE 12.15 Rate of reaction over different temperatures

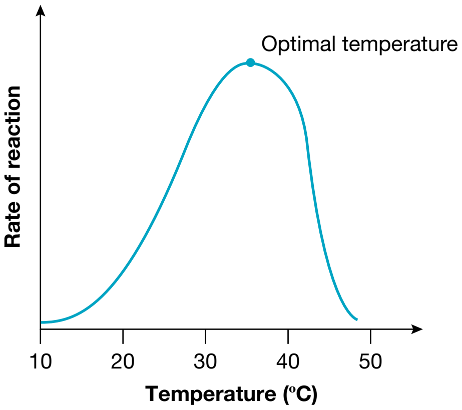
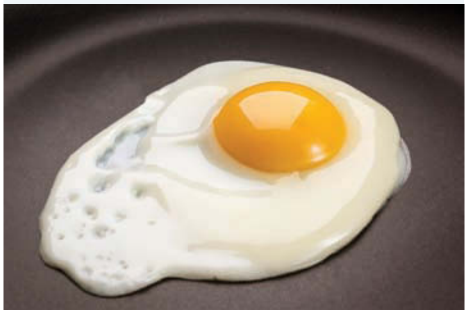


FIGURE 12.16 The protein in egg white is denatured when the egg is heated.



Low temperatures slow reaction rates and high temperatures can denature the enzyme.

on Resources

Digital document Experiment 12.2 Investigating proteins (doc-31280)

12.3.7 Use of reaction rates to measure enzyme activity

Investigating enzyme activity in the laboratory can help provide useful information about how they function. The rate of an enzyme-catalysed reaction can be observed by measuring the rate of disappearance of the substrate or appearance of the product over time. Laboratory investigations examining the factors previously discussed could involve changing the pH or temperature of the reaction as the independent variable. The dependent variable could include measuring the volume of gas produced over a given time or using simple observations, colour changes or colorimetry to measure a colour change over time. A glucose monitor that allows measurement of glucose levels within the blood is useful to obtain quantitative results. Some possible experiments are shown in table 12.2.

TABLE 12.2 Possible experiments to measure enzyme activity

Enzyme	Substrate	Products	Possible measurement
Amylase	Starch	Maltose and some glucose	Iodine (for starch) Benedict's solution Glucose test strips Glucose meter
Catalase	Hydrogen peroxide (H_2O_2): byproduct of respiration	Oxygen (O_2) and water (H_2O)	Count bubbles Gas syringe
Lactase	Lactose	Glucose and galactose	Benedict's solution Glucose test strips Glucose meter
Lipase	Lipid in milk	Fatty acids and glycerol	Phenolphthalein
Pectinase	Pectin	Simple sugars	Volume of liquid
Pepsin	Protein	Short polypeptides	Observation of egg white
Sucrase	Sucrose	Glucose and fructose	Benedict's solution Glucose test strips Glucose meter

MEASURING ENZYME ACTIVITY AND THE EFFECT OF pH AND TEMPERATURE

To measure the effect of pH on enzyme activity, an experiment might measure the reaction times of amylase and starch to determine the optimum pH of the reaction. The pH of the solution is varied by using two different concentrations of sodium carbonate solution (base) and ethanoic acid (acid). The presence of starch can be observed by using iodine, which changes to a blue-black colour in the presence of starch.

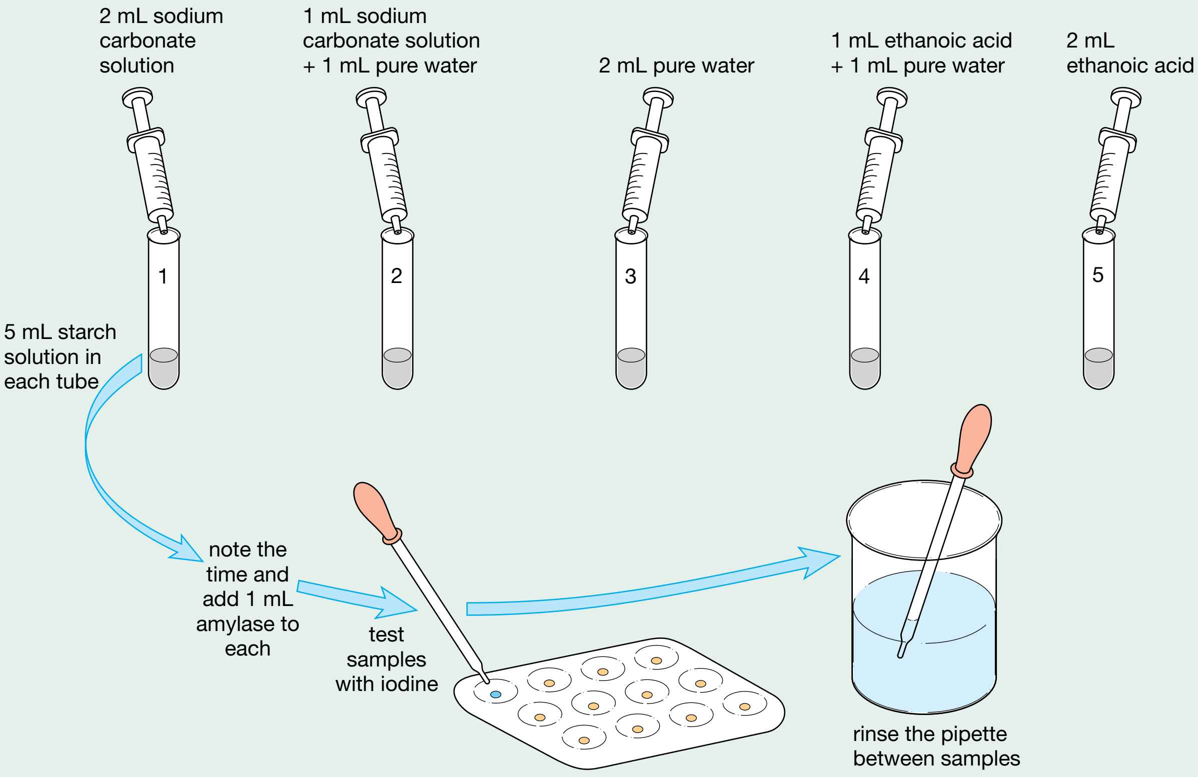
Independent variable: pH for colour change
Dependant variables: Time
Constants: Temperature, volumes and concentrations of enzyme (amalyse) and substrate

To begin the experiment, place two drops of iodine in each well of a tray. Place the 5 mL of starch in a test tube and add 2 mL of sodium carbonate solution. Start timing as 1 mL of amylase is added. Every 15 seconds remove a sample of the mixture using a clean dropping pipette and place in order in the tray.

The iodine will change colour to blue-black in the initial wells but at a particular time there will not be a change in colour. Note this time. If possible, repeat this experiment twice more, record the results in a table and determine an average time.

Repeat the procedure using clean equipment and solutions of different pH (e.g. ethanoic acid), including pure water as shown in figure 12.17. Observe the pH at which the reaction took place in the least amount of time to find out the optimum pH for this reaction to occur at the fastest rate.

FIGURE 12.17 Experiment to investigate the effect of pH on an enzyme reaction



This experiment could be repeated to find the effect of temperature on enzyme activity. By using the optimum pH as determined above, all solutions would be placed in a water bath for 10 minutes before mixing. The experiment would be carried out at different temperatures: at very low temperature, room temperature and then at higher temperatures. This variation would find the optimum temperature for enzyme effectiveness. All other factors must be kept constant.

Another experiment could measure the activity of catalase. The catalase reacts with hydrogen peroxide and produces oxygen bubbles, which can then be measured. This experiment would also be carried out using water baths at different temperatures. The rate of reaction is monitored by the rate of appearance of the product oxygen. Hydrogen peroxide is a by-product of many chemical reactions in the body but is toxic if it builds up in cells and so must be removed.

$$2H_2O_2\,(aq) \xrightarrow{\text{catalase}} 2H_2O\,(l) + O_2\,(g)$$

12.3 EXERCISE

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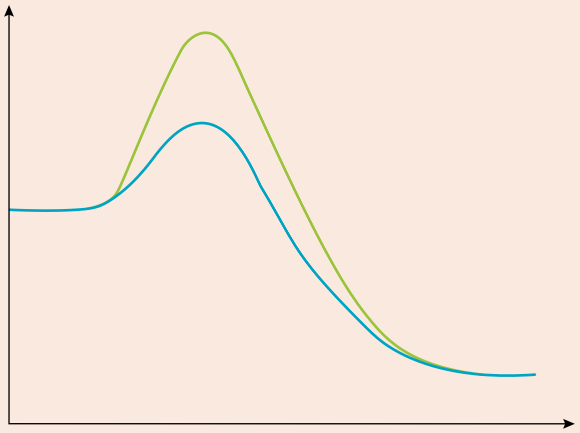
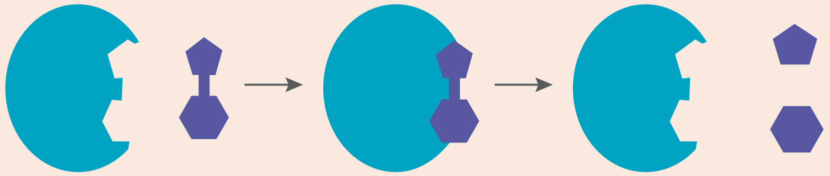
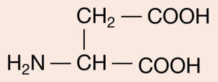
1. Enzymes affect the activation energy of a reaction. On the diagram, label the activation energy with an enzyme and the activation energy without the enzyme.



2. On the diagram, label the products, enzyme–substrate complex, active site, enzyme and substrate.

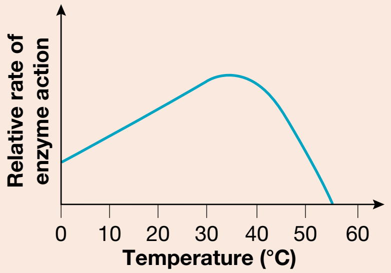


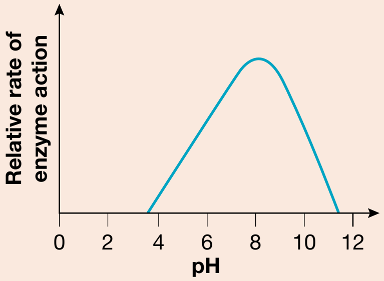
3. What type of interaction might occur between a $-CH_3$ group in a substrate and a functional group in an enzyme's active site?
4. Explain why glycine does not have an optical isomer.
5. Explain the difference between the lock-and-key model of enzyme action and the induced fit model.
6. (a) What is denaturation?
   (b) What conditions can cause a protein to be denatured?
7. Draw the structure of aspartic acid at a pH of 9.



$$\begin{array}{l} \qquad\quad\; CH_2-COOH \\ \qquad\quad\;\; | \\ H_2N-CH-COOH \end{array}$$

8. Why will a sample of amylase taken from the mouth not work effectively if placed in a solution of stomach juice but function in a solution of small intestine juice?
9. (a) What does the word 'optimum' mean when referring to enzyme temperature?
   (b) State the optimum temperature and pH of the enzyme shown in the graphs below.





10. Consider the experiments described in the green box 'Measuring enzyme activity and the effect of pH and temperature' in section 12.3.6.
    (a) Why is it important to repeat the experiment and find an average value for the time measurements?
    (b) In the experiment investigating the effect of pH on enzyme activity, identify the control.
    (c) Name the polymer in starch that reacts with the iodine to produce the colour change.
    (d) What factors must be controlled in the experiment measuring enzyme activity and temperature?
    (e) Explain what you would expect the value of the optimum temperature and optimum pH to be for amylase.

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12.4 Denaturation and hydrolysis of proteins

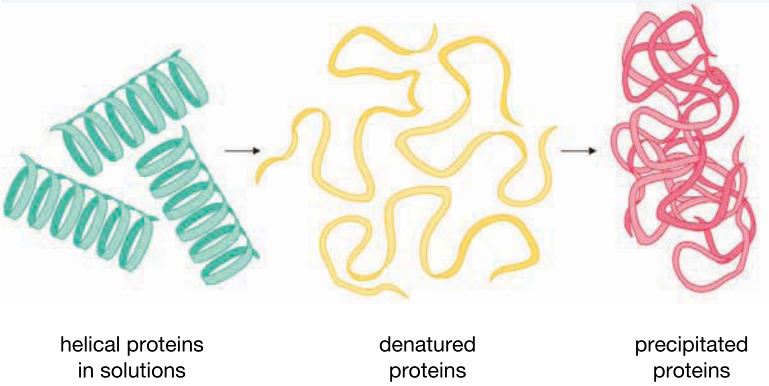
KEY CONCEPT

- The distinction between denaturation of a protein and hydrolysis of its primary structure

12.4.1 Denaturation and coagulation of proteins

As explained in subtopic 12.3, denaturation is the loss of biological activity of the protein by the action of heat, pH changes, radiation, presence of particular organic compounds, or heavy metal ions. Destruction of the secondary, tertiary or quaternary structure can occur by disrupting bonding interactions including hydrogen bonding, salt bridges, disulfide bonds, and non-polar hydrophobic interactions. The tertiary interactions are damaged and the protein uncoils to become just a long strand of amino acids again. However, the process of denaturation is not strong enough to break the peptide bonds in the primary structure and so it remains intact. When denaturation occurs, the unraveled protein strands can stick together, resulting in precipitation or coagulation of the protein.

FIGURE 12.18 Protein denaturation and coagulation



12.4.2 Hydrolysis of proteins

Digestion of proteins in the body requires both denaturation and hydrolysis.

This process occurs as follows:

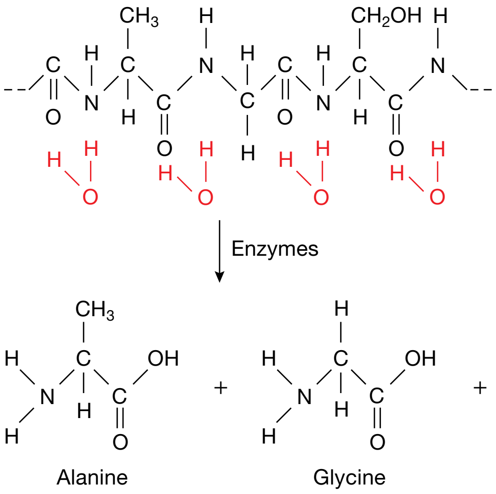
- Proteins are hydrolysed by an enzyme called pepsin. Unlike most protein-digesting enzymes, pepsin works efficiently in the acidic environment of the stomach.
- In this hydrolysis reaction, water is added across the peptide link, which breaks the covalent bonds between the amino acids in the primary structure.

FIGURE 12.19 Protein rich foods

- This denaturing and hydrolysis of the proteins occurs in the stomach and produces a mixture of polypeptides.
- Further hydrolysis occurs in the small intestines to break the polypeptides into amino acids. Pepsin becomes inactive in the alkaline environment of the intestine.
- These newly formed amino acids then pass into the bloodstream and are carried to tissues where they can be reassembled to form new protein.
- The enzyme-catalysed hydrolysis reactions for the digestion of protein are the reverse of the condensation reactions by which they were formed originally.

In summary, at the molecular level when hydrolysis occurs, the functional groups on the amino acid residues form covalent bonds with the atoms from the water, resulting in breakage of the peptide link to produce amino and carboxyl groups as shown in figure 12.20. If this hydrolysis was carried out in a laboratory it would be necessary to heat the protein with 6 M hydrochloric acid at over 100 °C for about 24 hours.

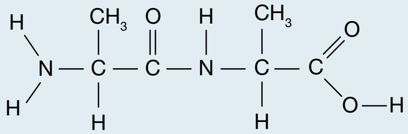
FIGURE 12.20 Enzyme-catalysed hydrolysis of proteins



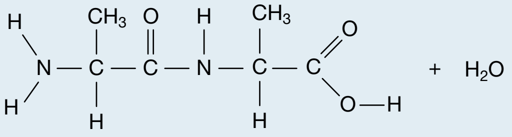
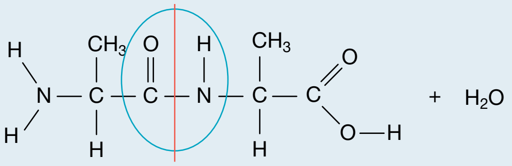
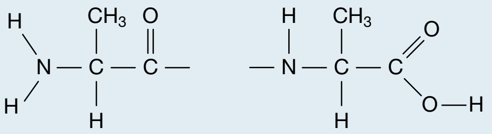
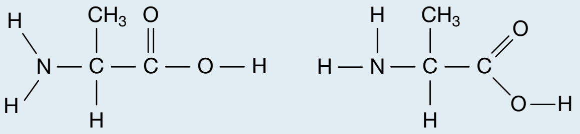
- **Denaturation can disrupt the secondary, tertiary and quaternary structures.**
- **Hydrolysis destroys the primary structure of a protein.**
- **The enzyme-catalysed hydrolysis reactions for the digestion of protein are the reverse of the condensation reactions by which they were formed originally.**

SAMPLE PROBLEM 1

Show the structure of the amino acids formed from the hydrolysis reaction of this dipeptide.

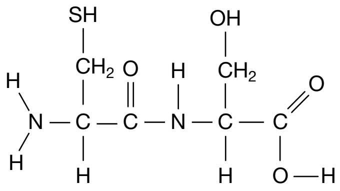


Teacher-led video: SP1 (tlvd-0722)

THINK	**WRITE**
1. A hydrolysis reaction requires water, so add water.	
2. Circle the peptide link and draw a vertical line through the middle to indicate separation of the two parts of the molecule.	
3. Separate the two parts of the molecule.	
4. Remember that each amino acid needs to have a carboxyl group and an amino group. The −O−H from the water is added to the C=O side and the −H from the water is attached to the nitrogen atom to form an amino group.	

PRACTICE PROBLEM 1

Show the structure of the amino acids formed from the hydrolysis reaction of this dipeptide.



Resources

Video eLesson Hydrolysis of proteins (med-0355)

12.4 EXERCISE

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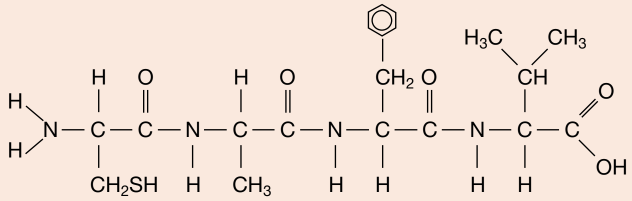
1. What types of interactions in proteins are disrupted by:
   (a) denaturation?
   (b) hydrolysis?
2. (a) Write an equation for the hydrolysis of the following polypeptide.



(b) Name the amino acids produced.

3. Describe the level of protein structure not disrupted when protein denaturation occurs. Explain why.
4. Name the functional group that is lost when a protein is hydrolysed.
5. Name the functional groups that are produced when a protein is hydrolysed.
6. What are the products of the complete hydrolysis of a protein?
7. For the following polypeptide Cys-Ala-Gly-Gly-Ala, state:
   (a) the number of peptide linkages present
   (b) the number of different amino acids produced by complete hydrolysis
   (c) the number of possible different dipeptides produced by partial hydrolysis
   (d) the number of possible different tripeptides produced by partial hydrolysis
   (e) the number of possible different tripeptides produced by denaturation.
8. Use an example to explain the process of coagulation.

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12.5 Carbohydrates

KEY CONCEPT

- 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

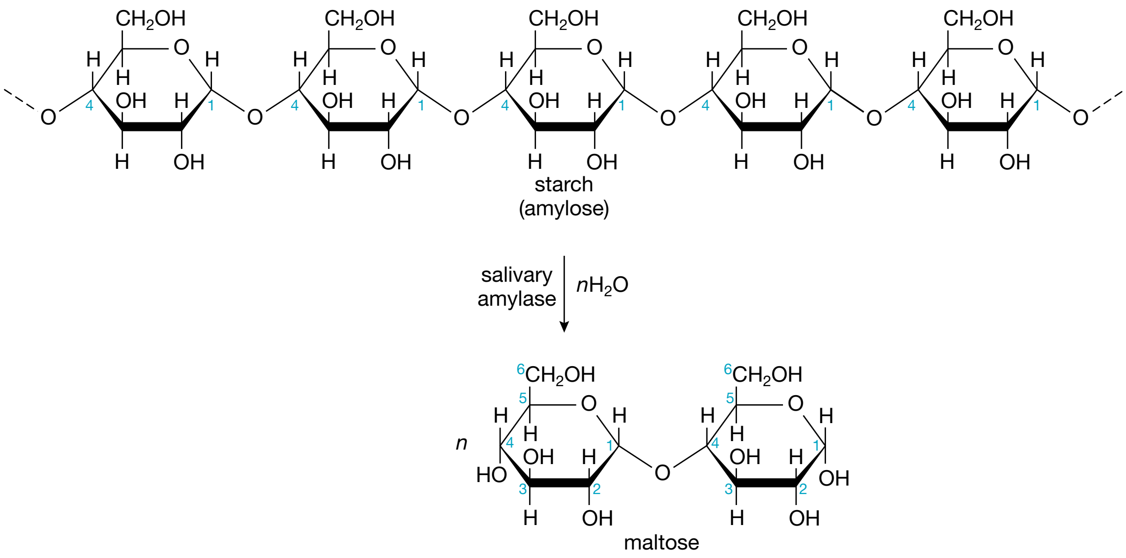
12.5.1 Starch and cellulose

Starch

The most important complex carbohydrate digested by humans is starch. Starch is initially hydrolysed in the mouth by an enzyme present in the saliva called salivary amylase. Salivary amylase does not completely hydrolyse starch to glucose, but it can split the bonds between every second pair of glucose units, producing maltose, a disaccharide. Hydroxyl functional groups form from the glycosidic (ether) linkages that are broken.

$$\underset{\text{starch}}{2(C_6H_{10}O_5)_n} + nH_2O \xrightarrow{\text{salivary amylase}} \underset{\text{maltose}}{nC_{12}H_{22}O_{11}}$$

FIGURE 12.21 Enzyme-catalysed hydrolysis of starch



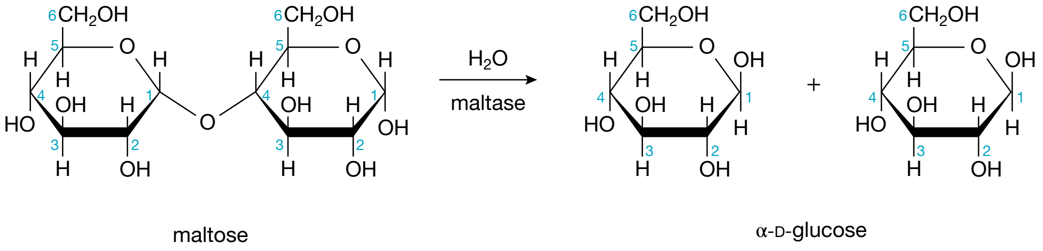
Food stays in the mouth for only a short time, so the salivary amylase has little chance to work there. Digestion by saliva continues in the stomach for about 20 minutes, until the action of the enzyme is stopped by the acidic gastric juices. The optimal pH for salivary amylase is about 6, whereas the pH in the stomach is about 1.5. This is a case of pH causing denaturation of the enzyme, so only a small percentage of the starch in food is digested by salivary amylase. The major enzyme for breaking down starches is pancreatic amylase, which can convert any unchanged starch (cooked or raw) to maltose.

Carbohydrate digestion is completed in the ileum (the last part of the small intestine) where the disaccharides maltose, lactose (milk sugar) and sucrose (cane sugar) are changed by the enzymes maltase, lactase and sucrase respectively, into their constituent glucose, fructose and galactose monosaccharides. These monosaccharides can then pass through the intestinal villi into the bloodstream. The equation for the hydrolysis of maltose to glucose by maltase is:

$$\underset{\text{maltase}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{\text{maltase}} \underset{\text{glucose}}{2C_6H_{12}O_6}$$

The formation of glucose eliminates the glycosidic linkages and creates two hydroxyl functional groups.

FIGURE 12.22 Enzyme-catalysed hydrolysis of maltose



TIP: The formulas for many biomolecules can be found in section 10 of the VCE Chemistry Data Book.

on Resources

Digital document 12.3 Studying starch - Hydrolysis of starch (doc-31281)
Teacher-led video Experiment 12.3 Studying starch - Hydrolysis of starch (tlvd-0767)

Cellulose

Cellulose, a polysaccharide, is the main structural component of the cell wall in plants. Brussels sprouts, cabbage, celery and kale are all high in cellulose. Both starch and cellulose are condensation polymers of glucose but in cellulose the monomer is β-glucose. This differs from α-glucose in that the C1 and C4 hydroxyl groups are on opposite sides of the ring plane (see figure 12.22). For the glycosidic link to form in β-glucose, alternate glucose molecules must be inverted. Humans cannot hydrolyse cellulose as we do not have the enzyme to hydrolyse the β-C1 to C4 glycosidic link, hence cellulose cannot be utilised as a source of energy for humans. Nevertheless, cellulose known as fibre or roughage is still important in the human diet because it assists the passage of food through the digestive system. Some herbivorous animals, such as cows, horses and koalas, have particular bacteria in their digestive systems to digest cellulose.

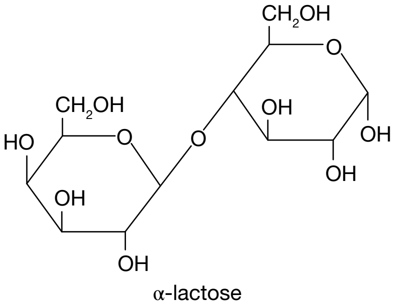
FIGURE 12.23 Green vegetables provide fibre, which is an important component of our diet.

12.5.2 Lactose intolerance

Milk is a source of many **nutrients** including proteins, lipids and carbohydrates; it also provides minerals and vitamins. These nutrients are important for strong bones and teeth and also play a part in nerve and muscle function, digestive enzymes and the immune system. For some people, milk can cause discomfort due to their inability to digest lactose, sometimes called milk sugar. Lactose, which is a disaccharide, is found in milk produced by mammals to feed their young. The lactose molecule consists of a molecule of galactose and a molecule of glucose.

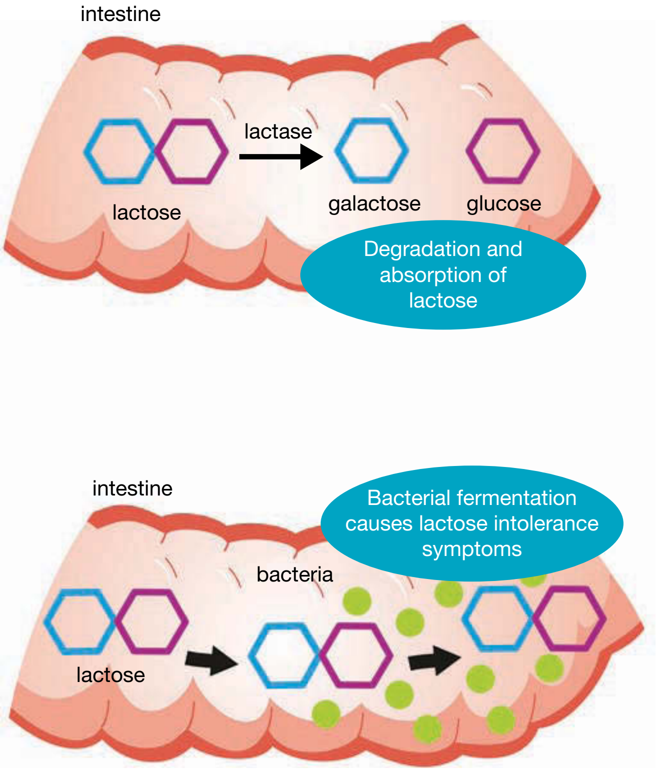
People who are lactose intolerant may have low levels of, or lack, the enzyme lactase, which is required in the hydrolysis of lactose. This deficiency means lactose cannot be absorbed into the bloodstream in the small intestine. The intolerance can be permanent or temporary as a result of certain digestive diseases. Undigested lactose passes into the large intestine, where anaerobic bacteria break down the lactose into small carboxylic acids and then to hydrogen, carbon dioxide and methane. The symptoms of lactose intolerance include cramps, diarrhoea, flatulence and nausea. Symptoms can be minimised by adapting the diet, or lactase enzyme tablets can be taken before meals. Lactose intolerant people can consume some products including yoghurt, which contains live bacteria, because the bacteria that converts milk to yogurt help digest the lactose.

FIGURE 12.24 Structure of the lactose molecule



Lactose intolerance is not an allergic reaction, because the immune system is not involved. The ability to produce lactase declines from childhood. People of Asian, African, South American, southern European and Australian Aboriginal heritage are more likely to become lactose intolerant than people of northern European descent. To test for lactose intolerance, blood glucose levels are measured every 15 minutes for two hours after having a lactose drink. Alternative methods of testing include measuring the amount of hydrogen in the breath or acidity in stools.

FIGURE 12.25 Lactose intolerance occurs when the small intestine lacks lactase.

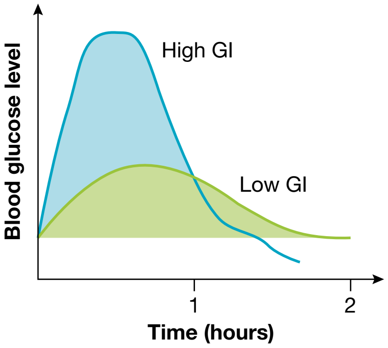


12.5.3 Glycaemic index of foods

Carbohydrates supply us with glucose (also known as blood sugar) to provide energy for our bodies to function and for physical activity, but some carbohydrates are more effective than others at providing energy. The most efficient carbohydrates come from fruits, vegetables and whole grains. Glucose levels rise and fall as we eat, exercise, rest and sleep. Optimal health requires a slow increase in glucose, rather than fluctuations to extreme levels.

The **glycaemic index (GI)** is used to indicate how quickly various carbohydrates influence glucose levels. Our bodies perform better when our blood sugar is kept relatively constant. Diets rich in high-GI foods, which include white bread, potatoes, white rice and sugary cereals, have been linked to an increased risk of diabetes, heart disease and obesity. Extremes in glucose levels can affect people differently. If the glucose level of a diabetic becomes too low (hypoglycaemia), they can have an increased heartbeat, feel dizzy and hungry, or even lapse into a coma. If it becomes too high (hyperglycaemia) more of the hormone insulin is released to lower the level, and the diabetic person can become thirsty or hungry, and have headaches and vision problems. If treatment is not sought, then more severe health issues will arise. All diets should be balanced and include a range of foods in moderation, but it is worth remembering that low-GI foods help you feel full for longer.

FIGURE 12.26 Changes in glucose levels brought about by high-GI and low-GI foods



The GI is determined by giving a group of people a particular mass of carbohydrate (usually 50 g) and measuring their glucose levels over three hours. These readings are then compared with eating pure glucose. Glucose is assigned a GI value of 100. The greater the GI, the greater the increase in blood glucose levels.

The glycaemic index (GI) is used to indicate how quickly carbohydrates influence glucose levels in the blood.

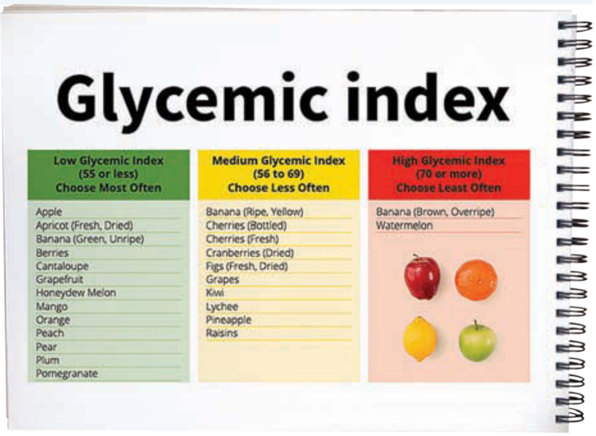
How quickly and easily food is digested depends on a number of factors. The factors include how refined the carbohydrate is, how well-cooked it is, and the chemical and physical structure of the carbohydrates. Processed food often has some or all of the fibre removed, which means cooking time is shorter and the food is also more easily broken down to glucose. The sugar in fruit, fructose, is not as easily digested as glucose and so has a lower GI. White bread has a relatively high GI because the high surface area of the flour used, together with the low density of the bread, results in easier digestion. Having fat or acid in the stomach also slows down digestion. Ripe fruit has a higher GI than fruit that is not ripe because some of the starch has already been converted to sugar. Other factors affecting the rate of digestion of carbohydrates are listed in table 12.3.

TABLE 12.3 Factors affecting the rate of digestion of carbohydrates

Factor	Explanation
Ripeness of fruit	Changes in the structure of starch as fruit ripens
Bran (the outer coating of wheat grains)	Limits the ability of enzymes to reach the starch
Fibre (cellulose)	Takes up space in the stomach and slows rate of digestion
Sugars	Have different ability to be hydrolysed; fructose has a lower GI than other sugars
Proteins, fats and oils	Slow down time for stomach to empty
Food processing	Smaller particles have greater surface area for reaction; bran is removed
Cooking method	Food swells and softens
Acidity of food	Acidic fruit slows down stomach emptying

Starch is the most important source of carbohydrates in our diet. It consists of amylose (20–30%) and amylopectin. Amylose is digested more slowly because it consists of closely packed linear chains of α-glucose monomers arranged in a helical structure, which is less available to the enzyme α-amylase. Amylopectin is a longer, more loosely branched molecule that has many free ends that can be easily hydrolysed. Therefore, foods with a greater amount of amylose have a lower GI. Foods that are high in amylose include seeds, nuts, legumes and some bread products. Foods like white rice and white potatoes contain more amylopectin and are digested faster. The chemical interactions in amylopectin are disrupted in the cooking process at high temperatures thus beginning digestion.

FIGURE 12.27 Glycaemic index of common fruits



Glycemic index

Low Glycemic Index (55 or less) Choose Most Often	Medium Glycemic Index (56 to 69) Choose Less Often	High Glycemic Index (70 or more) Choose Least Often
Apple	Banana (Ripe, Yellow)	Banana (Brown, Overripe)
Apricot (Fresh, Dried)	Cherries (Bottled)	Watermelon
Banana (Green, Unripe)	Cherries (Fresh)	
Berries	Cranberries (Dried)	
Cantaloupe	Figs (Fresh, Dried)	
Grapefruit	Grapes	
Honeydew Melon	Kiwi	
Mango	Lychee	
Orange	Pineapple	
Peach	Raisins	
Pear		
Plum		
Pomegranate		

Limitations on using the glycaemic index

The glycaemic index does not take into account the following factors:

- other nutrients present in the food
- the portion size
- the effect of eating different combinations of food
- foods with the same glycaemic index that produce different amounts of the hormone insulin, making the effects on health different.

Glycaemic load

Another measurement, glycaemic load (GL), takes into account how much carbohydrate a food contains. For example, carrots, bananas, watermelon and wholemeal bread have a high GI but a low glycaemic load because their available carbohydrate content is small. These foods have minimal effect on glucose levels. The available carbohydrate is the proportion of carbohydrate that can be hydrolysed by enzymes in our body and absorbed directly, supplying energy. The glycaemic load does not include fibre, which cannot be digested.

The glycaemic load is calculated by multiplying the number of grams of carbohydrate in a serving by the GI, and dividing by 100. For example, a 120 gserving of watermelon (GI = 72) has 6.0 g of available carbohydrate, so its glycaemic load is $6.0 \times \frac{72}{100} = 4.3$, which is quite low.

In a healthy diet, it is recommended that you eat moderate amounts of food, with a focus on foods that are high in fibre, low in kilojoules, naturally occurring and minimally processed. Use only small amounts of oils, drink lots of water, and enjoy the occasional treat. A healthy and varied diet includes the following nutrient groups in the approximate proportions:

- 30% grain foods
- 30% vegetables and legumes/beans
- 17% lean meats, poultry, fish, eggs, tofu, nuts and seeds and legumes/beans
- 13% dairy products
- 10% fruit.

CONTROLLING BLOOD SUGAR IN PEOPLE WITH DIABETES

Plants have an amazing ability: they can capture sunlight and use it to turn carbon dioxide and water into glucose, a molecule that is critical for life. Another name for glucose is blood sugar; it is an essential energy source not just for the muscles but also for the brain. Glucose levels vary during the day, but the body regulates the levels so that the change is not excessive.

After we eat, the glucose level in the blood rises and the pancreas releases a hormone, insulin, which is necessary to convert glucose to energy. Unhealthy levels of glucose in the blood can lead to health problems.

People with type 1 diabetes cannot produce insulin and need to carefully monitor their blood glucose levels. Only 10 to 15% of diabetics have type 1 diabetes. Type 2 diabetes develops with age and occurs when the body becomes resistant to the effects of insulin or loses the ability to produce enough insulin. While the cause of type 2 diabetes is unknown, it is associated with genetic predisposition and with risk factors such as high blood pressure, being overweight or obese, not enough physical activity or a poor diet.

Blood glucose levels, which are measured in mmol^{-1} (mM), can be controlled by taking insulin (either as an injection or through a pump), eating a healthy diet with accurate carbohydrate counts, and maintaining regular physical activity. Insulin cannot be taken as a tablet because it would be broken down before absorption. Excessively high glucose in the bloodstream is a condition called hyperglycaemia, whereas too little glucose is known as hypoglycaemia.

12.5 EXERCISE

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1. (a) Describe the similarities in structure between starch and cellulose.
   (b) Describe the differences in structure between starch and cellulose
2. Explain why cellulose is not able to be digested by humans but cows can digest cellulose in grass.
3. Write equations for the hydrolysis of maltose, lactose and sucrose. For these reactions include structural formulas and the enzymes required.
4. Lactose is a small and polar molecule.
   (a) Explain why it is more likely to be soluble in milk than in butter or cheese.
   (b) Write the molecular formula of lactose.
5. (a) What type of reaction results in the formation of two monosaccharides from lactose?
   (b) Name the two monosaccharides formed.
6. Explain why some people experience symptoms of cramps and bloating after drinking milk products.
7. What is the glycaemic index and how is it measured?
8. Suggest two reasons why low-GI foods are beneficial in the diet.
9. Explain why glucose is used as the standard when determining GI level.
10. The recommended glucose level is about 5.0 mM. Another unit used is mg dL^{-1} (1 decilitre (dL) = 100 mL). Calculate the recommended glucose level in mg dL^{-1}.

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12.6 Fats and oils

KEY CONCEPT

- 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

12.6.1 Hydrolysis of fats and oils

Digestion of lipids mostly takes place in the alkaline conditions of the small intestine, where the lipid is mixed with **bile**. Bile is made by the liver and released from the gall bladder. Lipids are insoluble so they clump together in an aqueous environment and bile is an **emulsifier**, which means that it increases the surface area of the fat by breaking it into smaller droplets (see figure 12.28). Bile molecules have a hydrophobic end that dissolves in fat and a hydrophilic end that dissolves in water and prevents the droplets from recombining. These droplets of fat combine with the **surfactant** bile molecules to form droplets of **micelles**, and it is the accompanying increase in surface area that helps fat react faster.

FIGURE 12.28 Bile breaks down fat globules into smaller droplets to enable faster digestion.

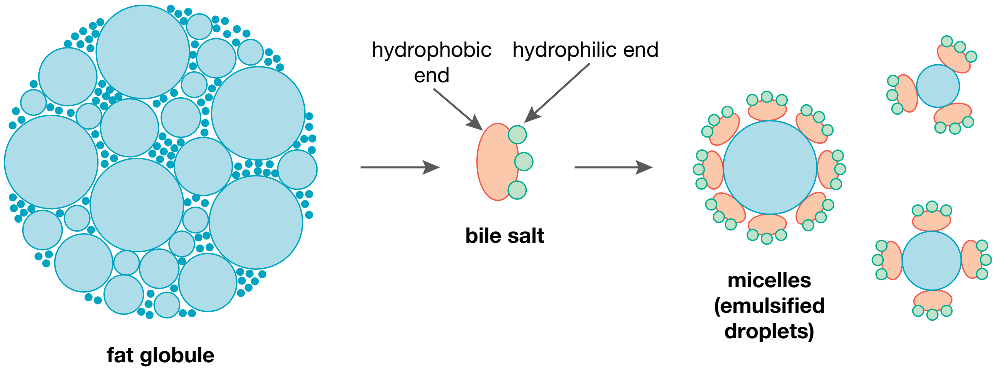
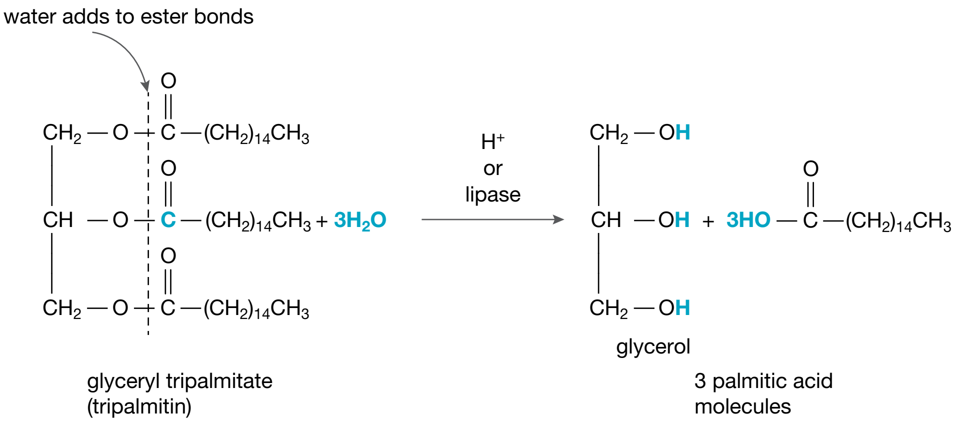


FIGURE 12.29 Triglycerides are hydrolysed to produce glycerol and three fatty acids



$$CH_2O\text{–}CO(CH_2)_{14}CH_3 / CH\,O\text{–}CO(CH_2)_{14}CH_3 / CH_2O\text{–}CO(CH_2)_{14}CH_3 + 3H_2O \xrightarrow[\text{lipase}]{H^+ \text{ or}} CH_2OH / CHOH / CH_2OH + 3HO\text{–}CO\text{–}(CH_2)_{14}CH_3$$

Once emulsified, the fat undergoes hydrolysis, catalysed by the water-soluble lipase enzymes from the pancreas. This produces glycerol, free fatty acids and monoglycerides, which are absorbed by cells lining the small intestine and converted back into triglycerides. These enter the body's lymphatic system and eventually the bloodstream for transport around the body. Excess fats not needed for energy production are stored as triglycerides in **adipose** tissues until needed as a source of energy.

FIGURE 12.30 In this X-ray of a finger, the subcutaneous fat layer is visible as the yellow layer under the skin and around the bone. This fat stores triglycerides.

12.6.2 Oxidative rancidity

You may have had the unfortunate experience of finding out that something that you were about to eat was ‘off’, the horrible smell emanating from the food confirming your realisation. This is what happens when some foods react with oxygen in the air. The presence of light, particularly UV radiation, can speed up the process.

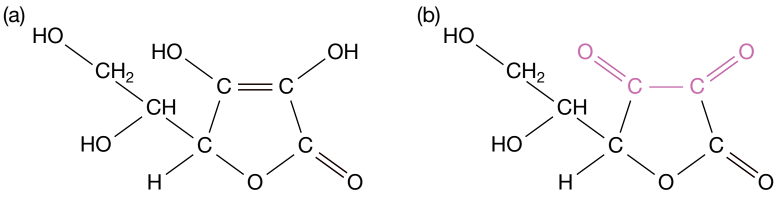
Oxidative rancidity is the deterioration of lipids by atmospheric oxygen. Unsaturated fats are less stable and are more susceptible to oxidation than saturated fats, because the oxygen reacts across the double bonds in unsaturated fats. This results in the food going rancid and becoming unpalatable. The more carbon-to-carbon double bonds there are, the faster the rate of rancidity.

When certain molecules interact with oxygen, they can form free radicals. These are atoms or groups of atoms with unpaired electrons, which make them very reactive. These free radicals can then start a chain of destructive chemical reactions. The smaller volatile molecules produced when food deteriorates, such as aldehydes, ketones and carboxylic acids, can give it unpleasant smells and flavours. For example, the flavour of rancid butter is due to the presence of butanoic acid.

Preventing rancidity

Antioxidants play an important part in slowing down oxidation and preventing food from spoiling. They can be natural or synthetic and are reducing agents, which means they are preferentially oxidised. An example of a natural antioxidant is vitamin C (ascorbic acid), which reacts to form dehydroascorbic acid by losing two hydrogen atoms from the ring section of the molecule (see figure 12.33).

FIGURE 12.31 (a) Vitamin C (ascorbic acid) and (b) dehydroascorbic acid



Citric acid and vitamin E are other natural antioxidants. Citric acid helps flavour food and increases the effectiveness of other antioxidants; vitamin E is a fat-soluble antioxidant found in seeds, nuts, whole grains, green leafy vegetables, soya beans and vegetable oils. Synthetic antioxidants, such as butylated hydroxytoluene (BHT), butylated hydroxyanisole (BHA) and propyl gallate, can be added to food to prevent deterioration. Bread, vegetable oils and cheese all have antioxidants added.

FIGURE 12.32 Potato chip packaging prevents light and moisture from entering. Nitrogen is pumped into the bags to eliminate oxygen.

Other methods of preventing rancidity include vacuum packaging or using nitrogen, filling containers up to the lid, storing food in the dark and cold places, and using dark containers or, in the case of the similar process of photoxidation, opaque containers.

12.6 EXERCISE

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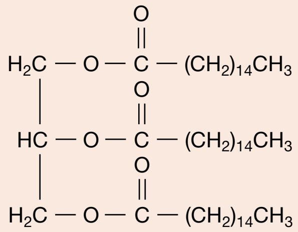
1. (a) Write the molecular, semi-structural and skeletal formula for glycerol.
   (b) What family of organic compounds does glycerol belong to?
2. (a) Provide a chemical equation for the hydrolysis of the fat with the following formula



   (b) Identify the functional groups involved in this reaction.
3. What is oxidative rancidity?
4. Explain why unsaturated fats are more susceptible to becoming rancid than saturated fats.
5. Name three types of molecules responsible for the unpleasant compounds formed as a result of rancidity and show the functional group present for each of them.
6. What are antioxidants? Give an example of a synthetic and natural antioxidant.
7. (a) Write the half-equation for the formation of dehydroascorbic acid, $C_6H_6O_6$, from ascorbic acid, $C_6H_8O_6$.
   (b) Explain whether this is an oxidation or reduction reaction.
   (c) Which functional groups are affected in ascorbic acid and what type of functional group is formed?
8. Explain why cooking oil should not be stored in clear, colourless bottles near the cooktop in the kitchen.
9. Describe three methods food manufacturers use to prevent foods from becoming rancid and explain why they are effective.

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12.7 Coenzymes

KEY CONCEPT

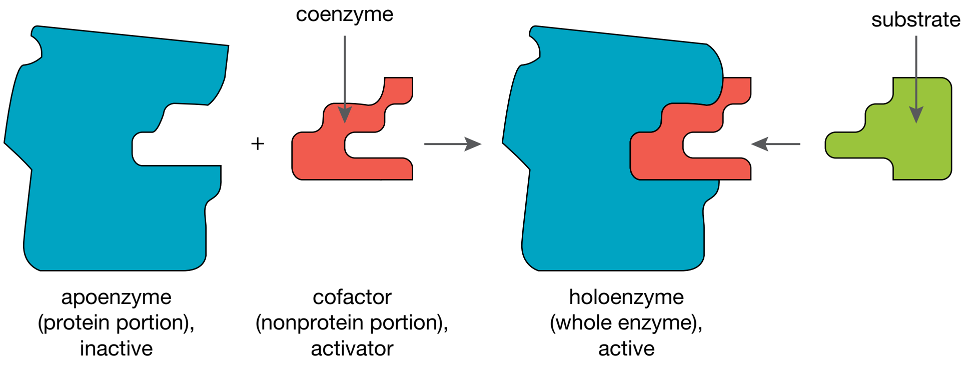
- The principles of the action of coenzymes (often derived from vitamins) as organic molecules that bind to the active site of an enzyme during catalysis, thereby changing the surface shape and hence the binding properties of the active site to enable function as intermediate carriers of electrons and/or groups of atoms (no specific cases required).

12.7.1 Coenzyme principles

Some enzymes need help in order to act as catalysts and this assistance is provided by **coenzymes**. Coenzymes are small, organic, non-protein molecules that are required to temporarily and loosely bind with the active site in the protein molecule (apoenzyme) to form the active enzyme (holoenzyme) and accommodate a substrate.

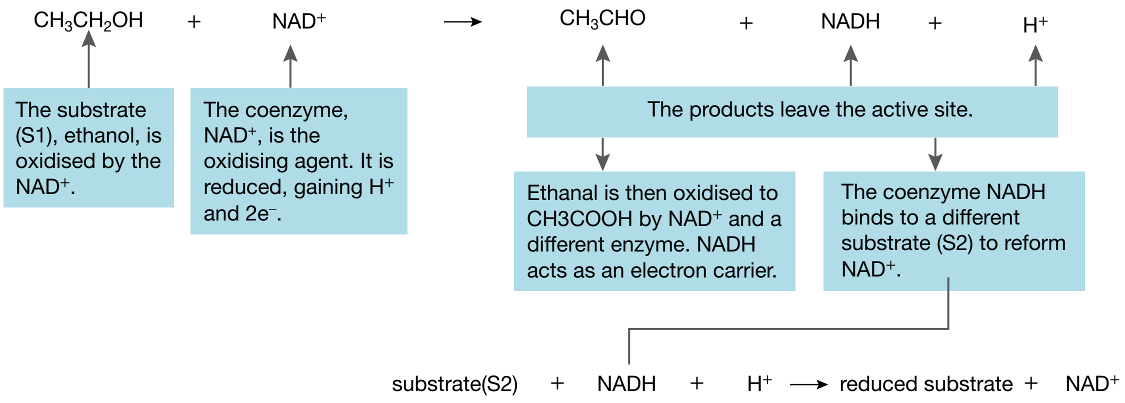
The removal or addition of electrons, atoms or groups can change the shape of the coenzyme, allowing it to bind to or be removed from an enzyme it is helping. Coenzymes are considered secondary substrates because they are changed by the reaction. Unlike primary substrates, they then reform and return to their initial structure in subsequent reactions and can be reused several times. They also act to transfer energy, as with ATP (adenine triphosphate), or act as intermediate transporters of electrons, particular atoms (such as H) or functional groups that are transferred in the final reaction. Once the reaction is completed, coenzymes detach and move away.

FIGURE 12.33 A coenzyme assists the enzyme in its role as a biological catalyst.



Consider the first stage in a series of reactions where ethanol is oxidised to ethanoic acid. The enzyme required is alcohol dehydrogenase. Both the coenzyme NAD^+ (nicotinamide adenine dinucleotide) and the ethanol substrate are bound together and to the active site of the enzyme. The overall effect is the transfer of electrons carried by NADH from substrate 1 (S1) to substrate 2 (S2).

FIGURE 12.34 A coenzyme acting as an electron carrier



The same coenzyme can be used by different enzymes. For example, NAD^+ is used by many enzymes. Most, but not all, coenzymes are derived from vitamins (see table 12.4).

TABLE 12.4 Examples of coenzymes and their sources

Vitamin	Coenzyme	Role
B1, thiamin	Thiamine pyrophosphate (TPP)	Transfers aldehydes
B2, riboflavin	Flavin adenine dinucleotide (FAD)	Oxidising agent (transfers electrons)
B3, niacin	Nicotinamide adenine dinucleotide (NAD^+)	Oxidising agent (transfers electrons)
B5, pantothenic acid	Coenzyme A (CoA)	Transfers acetyl group ($CH_3CO—$)
B12	Coenzyme B12	Transfers alkyl groups
	Adenosine triphosphate (ATP)	Transfers phosphate

Coenzymes are unable to function on their own and if an enzyme is denatured the coenzyme can no longer attach to the active site.

Coenzymes can have a number of roles. They:

- can alter the structural conformation of an enzyme to accommodate the shape of the substrate
- are able to transfer electrons, particular atoms or functional groups from one reaction to another
- can take part in redox reactions. For example, NAD^+ can act as an oxidising agent and undergo reduction to NADH by the addition of H^+ and 2 electrons
- act as antioxidants and prevent free radicals from damaging cells
- assist in the immediate transfer of energy within cells (ATP).

TABLE 12.5 Differences between an enzyme and a coenzyme

	Enzyme	Coenzyme
Type of compound	Mainly globular proteins	Non-protein organic molecule
Size of molecule	Large	Small
Derived from	Condensation of peptides	Many formed from vitamins but not all
Function	Biological catalyst	Binds to some enzymes to enable catalytic activity, acts as carrier
Is structure altered at the end of the reaction?	Maintains original structure	Structure is altered but is regenerated in subsequent reactions
Specificity	Specific to a particular reaction	Less specific
Interaction between enzyme and coenzyme	Loosely bound and easily removed	Loosely bound and easily removed
Example	Alcohol dehydrogenase	NAD^+
Stability	Disrupted by heat or high temperature	Stable to heat and/or temperature

12.7 EXERCISE

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1. What are coenzymes?
2. Explain how coenzymes work with enzymes to catalyse reactions.
3. Are coenzymes changed during the catalytic reaction?
4. Name a type of substance that is an important source of many coenzymes.
5. Name two examples of coenzymes.
6. Describe the differences in the general structure of enzymes and coenzymes.
7. Is NADH an oxidising or reducing agent? Explain.
8. State three examples of entities transferred by coenzymes.

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12.8 Review

12.8.1 Summary

Digestion of food

- Carbohydrates, proteins, and fats and oils are broken down into smaller molecules in the digestive system by enzyme-catalysed hydrolysis.
- Proteins are sensitive to extremes in pH, heat and some chemicals. Proteins denature by unfolding when subjected to changes in pH or extreme conditions. They can become insoluble or lose biological activity.

Enzymes as protein catalysts

- Enzymes are proteins that act as catalysts for the chemical reactions occurring in living things. They are highly specific, with each different type of enzyme catalysing only one type of chemical reaction.
- Each enzyme has an active site at which the reaction is facilitated.
- Amino acids form a dipolar ion called a zwitterion, due to the acid–base properties of the carboxylic acid and amino functional groups.
- A zwitterion is a molecule with a net charge of zero but negative and positive charges on individual atoms in its structure.
- Amino acids are amphoteric: they can behave either as an acid or as a base, depending on the pH of the solution. In aqueous solutions with an approximately neutral pH, amino acids exist as zwitterions.
- Enzymes operate in mild conditions. Extremes of temperature and pH denature the enzyme, altering the active site and leading to a loss of activity.
- Amino acids that form proteins are the L-form, so alternate optical isomers do not fit in the active site of enzymes in the body.
- There are two models proposed to explain the action of enzymes: the lock-and-key model and the induced fit model.

Denaturation and hydrolysis of proteins

- Digestion of proteins involves hydrolysis reactions where peptide bonds in the primary structure are broken.
- Denaturing involves the disruption of weak interactions present in the secondary, tertiary and quaternary structure of a protein.
- Denaturing does not affect the primary structure of a protein due to the strong covalent bonds in the polypeptide chain.

Carbohydrates

- Starch is a polysaccharide formed from the condensation polymerisation of α-glucose formed during photosynthesis.
- Starch is the major storage form of glucose in plants. It is made up of amylose and amylopectin.
  - Amylose is smaller than amylopectin and consists of compacted linear chains arranged in a helical structure and so is insoluble.
  - Amylopectin is a longer, more loosely branched molecule.
- Glycogen is the major storage form of glucose in animals. It is more highly branched than amylopectin.
- Excess glucose is stored in the liver as glycogen. It may also be converted to fat.
- Cellulose is a polysaccharide formed from the condensation polymerisation of β-glucose from photosynthesis.
- The arrangement of glucose monomers in cellulose is different from that in starch. Cellulose is the major structural component of cell walls in plants.
- Humans do not have the enzyme to digest cellulose.
- Lactose intolerance is caused by having insufficient enzyme lactase to hydrolyse the disaccharide lactose.

- The glycaemic index (GI) is a scale used to describe how quickly the carbohydrate in a food is broken down and absorbed into the bloodstream.

Fats and oils

- Saturated fatty acids are long-chain carboxylic acids that do not contain a C=C bond.
- Mono-unsaturated fatty acids contain one C=C bond, and polyunsaturated fatty acids contain more than one C=C bond.
- During digestion, fats and oils are hydrolysed to glycerol and fatty acids, which can be reassembled into triglycerides.
- Unsaturated fats are less stable and are more susceptible to oxidation.
- Antioxidants slow down the oxidation of food.
- Coenzymes are organic non-protein molecules that assist the functioning of enzymes. They are often derived from vitamins.

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12.8.2 Key terms

activation energy the minimum energy required by reactants in order to react
active site a region on an enzyme that binds to a reactant molecule (substrate) during a reaction
adipose a form of fatty tissue used to store energy
amphoteric describes amino acids that can behave as both acids and bases
antioxidants a substance that slows oxidation
bile a liquid produced by the liver to aid digestion through emulsification
cellulose the most common carbohydrate and a condensation polymer of D-glucose. Humans cannot hydrolyse cellulose, so it is not a source of energy.
coagulation the process of turning a liquid into a solid
coenzyme an organic non-protein molecule required to temporarily and loosely bind with the protein molecule to form an active enzyme
condensation polymerisation step-growth polymerisation in which two monomers combine and a smaller molecule is eliminated
denaturation change in the structure or function of a large molecule, such as a protein
dipolar ion an ion containing equal positive and negative charges
emulsifier a substance that increases the surface area of fat by breaking it into smaller droplets
enzymes proteins that catalyse chemical reactions
glycaemic index (GI) a figure representing the relative ability of a carbohydrate food to increase the level of glucose in the blood
hydrolysis a hydrolytic reaction; the chemical breakdown of a compound due to reaction with water
induced fit model a model of enzyme action where, in the presence of a substrate, the active site may change in order to fit the substrate's shape
lactose milk sugar
L-amino acids the stereoisomer of amino acids that is found in proteins in organisms. Enzyme-catalysed reactions occur only between molecules with this particular stereoisomerism
lock-and-key model model of enzyme action where only molecules with complementary shapes can react with the enzyme
metabolism the chemical processes that occur within a living organism in order to maintain life
micelle a group of surfactant molecules surrounding a fat droplet with the hydrophobic ends dissolved in the fat and polar ends dissolve in the water
nutrients food molecules that organisms need to make energy, grow, reproduce and maintain a healthy life. These are: proteins, vitamins, minerals, fats and carbohydrates.

▶

optimum pH the pH at which enzymes function best
optimum temperature the temperature at which enzymes function best
oxidative rancidity the deterioration of lipids by atmospheric oxygen
respiration when monosaccharides are converted to glucose, which is used as an energy source to power body cells including the brain, muscles and red blood cells
starch a condensation polymer of α-D-glucose that is made up of two polymers: amylose and amylopectin
stereoisomerism where two or more compounds differ only in the spatial arrangements of their atoms
surfactant molecule a molecule that has a polar (hydrophilic) and a non-polar (hydrophobic) end, for example, a detergent molecule
substrate the substance on which an enzyme acts
zwitterion a dipolar ion containing equal positive and negative charges

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Digital document: Key terms glossary – Topic 12 (doc-31421)

12.8.3 Practical work and investigations

Experiment 12.3

Studying starch - Hydrolysis of starch
Aim: To demonstrate the hydrolysis of starch by hydrochloric acid
Digital document: doc-31281
Teacher-led video: tlvd-0767

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Digital documents Practical investigation logbook (doc-31422)
Experiment 12.1 Enzymes as protein catalysts (doc-31279)
Experiment 12.2 Investigating proteins (doc-31280)

12.8 Exercises

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12.8 Exercise 1: Multiple choice questions

1. A balanced diet should:
   - A. include the 12 essential amino acids
   - B. contain large amounts of vitamins
   - C. provide essential carbohydrates
   - D. include essential fatty acids.

2. Foods that provide the requirements for metabolism are called:
   - **A.** proteins
   - **B.** vitamins
   - **C.** nutrients
   - **D.** enzymes.
3. The formation of carbohydrates, proteins and lipids in the human body requires numerous enzymes. Which of the following statements about enzymes is **incorrect**?
   - **A.** Enzymes operate within narrow pH ranges.
   - **B.** The catalytic action of enzymes increases with increasing temperatures up to 100 °C.
   - **C.** Enzymes specifically catalyse particular chemical reactions.
   - **D.** Enzymes are proteins.
4. Select the best definition of an enzyme.
   - **A.** An enzyme is an amino acid that speeds up chemical reactions.
   - **B.** An enzyme is a protein that is consumed in the diet and aids in chemical reactions.
   - **C.** Enzymes are proteins that speed up metabolic reaction and are consumed in the process.
   - **D.** Enzymes are proteins that speed up metabolic reaction but are not consumed in the process.
5. All of the following interactions occur in proteins. Which interaction is significantly stronger than the others?
   - **A.** hydrogen bonds
   - **B.** dispersion forces
   - **C.** ionic interactions
   - **D.** peptide bonds.
6. A protein with an α-helix secondary structure was mixed with orange juice and formed clumps. The change in the protein structure is due to:
   - **A.** oxidation
   - **B.** hydrolysis
   - **C.** denaturation
   - **D.** polymerisation.
7. Identify the **incorrect** statement about protein denaturation.
   - **A.** It is a shape change.
   - **B.** It is always irreversible.
   - **C.** It can be caused by a pH change.
   - **D.** It could result from a temperature change.
8. Which process causes the primary structure of a protein to be destroyed?
   - **A.** Hydrolysis
   - **B.** Denaturation
   - **C.** Polymerisation
   - **D.** Condensation
9. Hydrolysis of proteins using a catalyst involves:
   - **A.** adding water to amino acids to form proteins
   - **B.** adding water to proteins to form amino acids
   - **C.** water forming hydrogen bonds in the secondary structure of proteins
   - **D.** water forming hydrogen bonds in the tertiary structure of proteins.
10. When an egg is hard boiled the protein in the egg white, ovalbumin, is denatured. Which of the following is **least** changed?
   - **A.** The primary structure of ovalbumin.
   - **B.** The secondary structure of ovalbumin.
   - **C.** The tertiary structure of ovalbumin.
   - **D.** The quaternary structure of ovalbumin.

11. Which enzyme is missing in the small intestine of a person who is lactose intolerant?
   - A. Dipeptidase
   - B. Lipase
   - C. Lactase
   - D. Maltase

12. Which one of the following is a correct statement about the hydrolysis of a protein?
   - A. Hydrolysis is characterised by the combining of amino acids.
   - B. Water is a product of hydrolysis.
   - C. Hydrolysis involves disruption of only bonds in the tertiary structure.
   - D. The primary structure is disrupted when hydrolysis occurs.

13. Symptoms of lactose intolerance include:
   - A. coughing
   - B. intestinal gas
   - C. a runny nose
   - D. rashes.

14. Lactose intolerance:
   - A. is common in most people of all ages, from newborn to adulthood
   - B. is most common in people of northern European descent
   - C. is an allergic reaction
   - D. is not a problem if drinking soy milk.

15. The glycaemic index indicates the:
   - A. amount of nutrients in food
   - B. amount of fats in food
   - C. effect of food on blood glucose levels
   - D. glycogen stores in the body.

16. Which of the following would have the lowest glycaemic index?
   - A. Greek yoghurt
   - B. A banana
   - C. Kidney beans
   - D. Chocolate

17. In the process of oxidative rancidity:
   - A. saturated compounds are more likely to be involved than unsaturated compounds
   - B. oxygen attacks the double bond in a compound
   - C. less volatile compounds are produced
   - D. light is never involved.

18. A water-soluble vitamin that is also an antioxidant is:
   - A. vitamin B
   - B. vitamin C
   - C. vitamin D
   - D. vitamin E.

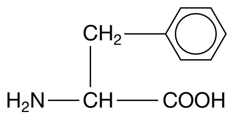
19. Coenzymes are:
   - A. proteins that assist in enzyme function
   - B. organic compounds that catalyse specific reactions
   - C. proteins that catalyse specific reactions
   - D. organic compounds that assist in enzyme function.

20. A function of coenzymes during cellular metabolism is to:
   - A. accept electrons and pass them to other molecules
   - B. catalyse chemical reactions
   - C. emulsify fats
   - D. denature proteins.

12.8 Exercise 2: Short answer questions

1. Enzymes are organic catalysts that operate in living things to facilitate chemical reactions essential to life. They are often referred to as 'biological catalysts'. List the differences between enzymes and inorganic catalysts. Include reference to influence on rate of reaction, specificity and the conditions under which they are employed.

2. Newborn babies are tested for phenylketonuria (PKU), which is a genetic disorder that prevents the breakdown of the amino acid phenylalanine, which then builds up in the body. Brain development can be limited if treatment is not provided. The structure of the phenylalanine molecule is:



- **a.** Draw the structure of phenylalanine in a solution of pH 3.
- **b.** Draw the structure of phenylalanine in a solution of pH 10.
- **c.** At a pH of about 5.9 phenylalanine is ionised but is not attracted to either the positive or negative electrodes of an electrolytic cell. Draw the structure of phenylalanine at pH 5.9.

3. Define the following terms.

- **a.** Enzyme
- **b.** Enzyme specificity
- **c.** Active site
- **d.** Coenzyme

4. **a.** Explain why the mechanism of action of an enzyme is sometimes referred to as a 'lock-and-key' mode of operation.

- **b.** Imagine you want to use a catalyst to speed up the reaction: A + B → C + D. Draw a diagram that shows how an enzyme can facilitate this reaction. Label the substrate and active site.

5. Define the term 'denaturation'.

6. Describe two ways in which an enzyme may be denatured.

7. Milk that has gone past its use-by date curdles and develops a sour taste. This is caused by the production of lactic acid by the lactose-fermenting bacteria naturally present in milk. This increased acid production leads to a decrease in pH, which causes the milk protein caseinogen to first denature and then coagulate.

- **a.** Explain how caseinogen is denatured.
- **b.** Explain why the secondary structure of caseinogen is affected whereas the primary structure is unaffected.

8. Digestive enzymes can be incorporated into washing powders. Instructions recommend that clothes are allowed to soak overnight in cool water and that hot water should be avoided.

- **a.** Explain the reason for the recommendation regarding effective use of the powder.
- **b.** Explain why digestive enzymes would be used.
- **c.** Describe the action of an enzyme.

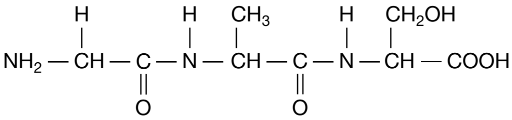
9. Why can fresh bloodstains be easily removed in cold water but not in hot water?

10. Meat and fish can be marinated (soaked) in fruit juices such as lime or pineapple juice to make them more tender.

- **a.** Explain how some fruit juices can tenderise meat.
- **b.** Suggest why the juice from canned pineapples does not tenderise meat.

11. List the variables that need to be considered when designing an experiment to measure enzyme activity.

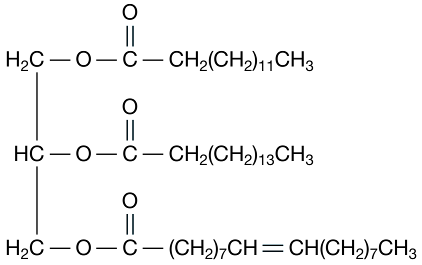
12. Write an equation showing the hydrolysis of the following peptide.



$$NH_2-\overset{\displaystyle H}{\overset{|}{CH}}-\underset{\displaystyle O}{\underset{\|}{C}}-\overset{\displaystyle H}{\overset{|}{N}}-\overset{\displaystyle CH_3}{\overset{|}{CH}}-\underset{\displaystyle O}{\underset{\|}{C}}-\overset{\displaystyle H}{\overset{|}{N}}-\overset{\displaystyle CH_2OH}{\overset{|}{CH}}-COOH$$

13. Starch is an important nutrient in the human diet. Describe the similarities and differences in the structures and properties of the two components that make up starch.

14. The percentage of amylose in food A is 28% and percentage of amylopectin 72%. In food B the percentage of amylose is 16% and percentage of amylopectin is 84%. Explain what GI is and explain which of the two foods would have the higher GI value.
15. A student comments that, after ingestion of dairy products, he experiences bloating, cramps and sometimes diarrhoea. With this information, it is reasonable to think that the student is intolerant to lactose. What is lactose intolerance and which age group and population are more likely to be lactose intolerant?
16. Describe the chemical structure of cellulose and explain why humans cannot digest it. Why is it still necessary in the human diet?
17. Write an equation showing the hydrolysis of this triglyceride.



18. List the similarities and differences between the structures and susceptibility to oxidation of saturated and unsaturated fatty acids.
19. a. What is rancidity?
    b. What name is given to compounds that limit oxidative rancidity in foods?
    c. Canola oil contains vitamin E as a natural component. Explain how this prevents the oil becoming rancid.
    d. Explain three other methods of limiting oxidation of foods.
20. Describe the differences between enzymes and coenzymes.

12.8 Exercise 3: Exam practice questions

Question 1 (1 mark)

Humans cannot digest cellulose because:

A. cellulose is insoluble in water
B. humans lack the necessary enzymes
C. cellulose is too branched
D. no organisms can digest cellulose.

Question 2 (1 mark)

Foods with a high glycaemic index would have a high proportion of:

A. sugars
B. fats
C. polysaccharides
D. cellulose.

Question 3 (4 marks)

Nicotinamide adenine dinucleotide (NAD^+) is an important coenzyme found in cells. It is essential for energy production and is involved in the conversion of ethanol, CH_3CH_2OH, to ethanal, CH_3CHO. NAD^+ is converted to NADH.

a. Write the half-equation for the oxidation reaction. **1 mark**
b. Write the half-equation for the reduction reaction. **1 mark**
c. The ethanal is then converted into ethanoic acid. Write the half-equation for this reaction. **1 mark**
d. A different enzyme is used for the reaction in question 3c. Explain why this is the case. **1 mark**

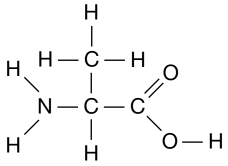
Question 4 (10 marks)

Lipase is an enzyme mainly produced in the pancreas and is important in the body because it catalyses the hydrolysis of fats and oils into their components. Lipase is soluble in water but the lipid molecules from food form clumps in aqueous solutions. When a sample of lipase is heated to more than 60 °C this enzyme is no longer effective.

a. Explain the process that occurs in the digestion of fats and oils that enables them to be digested in aqueous solution by lipase. **2 marks**
b. Name the products of the digestion of fats and oils. **2 marks**
c. What is the function of the lipase enzyme? **1 mark**
d. Explain why lipase is ineffective at high temperatures. **2 marks**
e. Why is the functioning of lipase closely related to its tertiary structure? **1 mark**
f. Lipase and co-lipase combine to catalyse a reaction. Describe how this occurs. **2 marks**

Question 5 (2 marks)

Explain why alanine is described as an enantiomer.



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13 Energy content of food

13.1 Overview

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13.1.1 Introduction

The food we eat supplies the energy we need to power all of the billions of chemical reactions happening in our bodies every second. Where does this energy come from, how do we get it and how can we measure the energy in food?

The energy in food can be traced back to the sun, where the process of photosynthesis converts the sun's energy into simple carbohydrates like glucose. Through condensation reactions these glucose molecules are turned into starch, a carbohydrate, and cellulose. Carbohydrates, fats and proteins in the food we eat provide the energy our bodies need. Carbohydrates are broken down to provide glucose, which releases energy in the process of respiration. The amount of energy a person needs depends on how active the individual is and whether the person is still growing. This energy is used for digestion, maintaining the heartbeat, breathing, brain function, nervous system movement, heat generation and maintaining constant body conditions. But how much energy is supplied by each food type and how readily available is it?

FIGURE 13.1 When exercising, muscles convert glucose into energy using oxygen in the blood in the process of respiration.

This topic explores the amount of energy in major food groups and demonstrates how the energy in foods can be measured using a process of calorimetry. Simple solution calorimeters will be investigated, as will bomb calorimeters. Associated calculations to measure energy content will be explained.

13.1.2 What you will learn

KEY KNOWLEDGE

In this topic, you will investigate:

- 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

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PRACTICAL WORK AND INVESTIGATIONS

Practical work is a central component of learning and assessment. Experiments and investigations, supported by a **Practical investigation logbook** and **Teacher-led videos**, are included in this topic to provide opportunities to undertake investigations and communicate findings.

on Resources

Digital documents Key science skills (doc-30903)
Key terms glossary – Topic 13 (doc-31424)
Practical investigation logbook (doc-31425)

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To access key concept summaries and past VCAA exam questions download and print the **studyON: Revision and practice exam question booklet** (doc-31426).

13.2 Energy values of carbohydrates, proteins and fats and oils

KEY CONCEPT

- The comparison of energy values of carbohydrates, proteins and fats and oils

13.2.1 Comparing energy values of foods

The food and drinks that we consume provide energy. In Australia, this energy is measured in **kilojoules (kJ)**. Another measurement that you may see on labels is **calories**.

$$1 \text{ calorie (cal)} = 4.184 \text{ Joule}$$

The energy that we obtain from food depends on the amount of carbohydrates, proteins and fats and oils in the meal and how much of each nutrient is eaten. Different nutrients have different energy values. The available energy content when used in the body is measured in kilojoules per gram.

The energy values of food are:

- **carbohydrate: 16 kJ g^{-1}**
- **protein: 17 kJ g^{-1}**
- **fat: 37 kJ g^{-1}.**

Not all of the energy in the food ingested is available to the body because it is not completely digested and absorbed, and some is converted to heat. The energy values given above have been adjusted to reflect this. Not all food molecules are a source of energy, including water, minerals, vitamins and fibre, but they are all necessary for good health. While carbohydrates, fats and proteins *are* a source of energy, some produce energy more readily than others. Carbohydrates are easily broken down to glucose, which is converted into energy using oxygen in the blood. Excess carbohydrates are stored as glycogen (see topic 12). Once all carbohydrates in the body, including glycogen, are consumed, the body starts to break down fat. Fat is not as efficient at providing energy as carbohydrates. Protein is not stored and is usually only used as an energy source in situations of starvation. The body can break down excess amino acids to produce glucose or fat if required.

FIGURE 13.2 What type of foods provide the most energy? What else must be considered when choosing food?

Not all energy in food is available for bodily functions because some food is not completely digested or absorbed, or not oxidised, and some energy is converted to heat.

Fats provide about 80% of the body's energy storage in adipose (fatty) tissue. They are used when food is scarce, when you haven't eaten for a while or when you are ill and don't feel like eating. While the brain is dependent on glucose, the liver, muscle and fat cells derive their energy from fat.

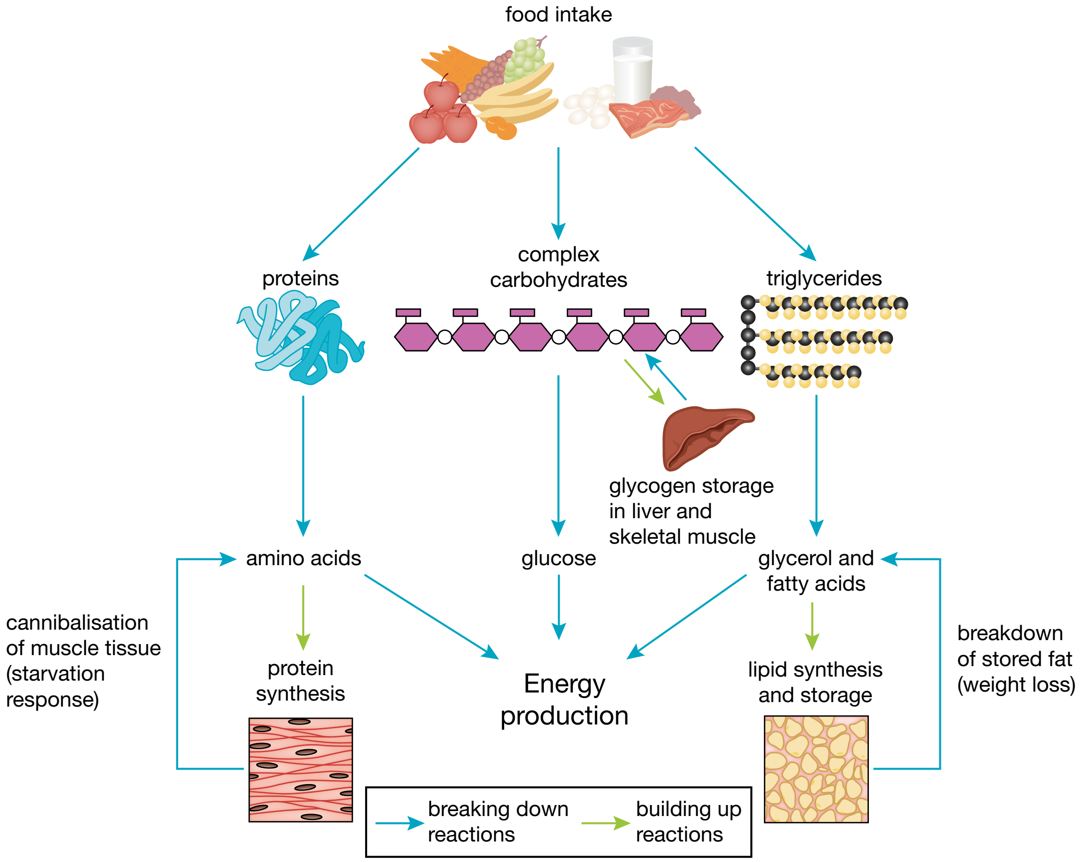
Fats are broken down in a complex series of steps that break the bonds in the long fatty acid carbon chains and separate the oxygen atoms in the oxygen molecules; the atoms then recombine to produce carbon dioxide and water. The overall reaction is an **exothermic** oxidation process in which the fats react with oxygen to produce carbon dioxide and water. This reaction is similar to a **combustion** reaction. An example would be the oxidation of linoleic acid (LA), a polyunsaturated omega-6 fatty acid.

$$C_{17}H_{31}COOH + 25O_2 \rightarrow 18CO_2 + 16H_2O \qquad \Delta H = -8382\ \text{kJ mol}^{-1}$$

TIP: Always check that the oxygen atoms are equal on both sides of the equation. There are 2 oxygen atoms in the fatty acid. If you require half an oxygen molecule on balancing an oxidation reaction, just double all coefficients.

Fats are a more concentrated energy reserve than carbohydrates but do not break down as easily. To break down fat molecules, more oxygen and more time is required than to break down carbohydrates, but more energy is released per gram. You can find out the energy in different foods by checking the nutrition labels on packaged foods.

FIGURE 13.3 Energy production from food molecules



Nutrition labels

All packaged foods must feature a nutrition label, which lists how much of each nutrient is present in the food. The ingredients on nutrition labels are listed in descending order according to mass. The overall value of food energy stated on packaging is obtained by multiplying the energy values by the mass of protein, fat and carbohydrate, and then adding all these results together.

For example, the ingredients for 100 g of tomato sauce are:

$$\begin{aligned}\text{Protein:}\quad & 1.6\,\text{g}\\ \text{Fat:}\quad & 0.20\,\text{g}\\ \text{Carbohydrate:}\quad & 30.2\,\text{g}.\end{aligned}$$

Therefore, the energy content per 100 g of the sauce is:

$$\begin{aligned}\text{Protein:}\quad & 1.6\,\text{g}\times 17 = 27.2\,\text{kJ}\\ \text{Fat:}\quad & 0.20\,\text{g}\times 37 = 7.4\,\text{kJ}\\ \text{Carbohydrate:}\quad & 30.2\,\text{g}\times 16 = 483.2\,\text{kJ}\\ \text{Total energy in } 100\,\text{g} &= 517.8\,\text{kJ}\end{aligned}$$

A **serving size** is how much of a food the manufacturer recommends consuming in a serving, but it is important to remember that these are often not based on dietary recommendations and may not be the amount that you consume. It is better to compare the quantity per 100 g when making food choices. Official standard serves vary depending on the type of food but in general you should aim for:

- less than 10 g of total fat, which includes all of the different types of fats (it is healthier to choose less saturated fat where possible)
- less than 10 g of sugar. The total carbohydrate figure includes starches and sugars, but be aware that sugars may be listed under other names, often ending in *-ose*. Foods with no added sugar could contain a large amount of natural sugar, and low-fat foods can also contain large quantities of sugar.
- less than 400 mg salt
- 3–6 g of fibre in breads and cereals.

FIGURE 13.4 Learning how to read and understand food labels can help you make healthier choices.

13.2 EXERCISE

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1. List five uses of the energy that is received by the body from cellular respiration.
2. In 100 g of tomato sauce, the energy was determined to be 548.0 kJ. The suggested average serve is 15 g. Calculate the amount of energy supplied in this serving.

Questions 3 to 7 refer to the ingredients of a nut bar containing 27.1 g protein, 25.7 g fat and 30.6 g carbohydrate per 100 g.

3. Calculate the total energy provided per 100 g.
4. Included in the fat component in the ingredients list is 5.0 g of saturated fat. Explain what a saturated fat is and give an example.
5. Also present is 10.3 grams of dietary fibre. Name the compound most likely to be contributing to this ingredient.

6. The carbohydrate ingredients include 11.7 g sugar. What type of compounds would be included in this 11.7 grams?
7. (a) On the front of the packet is a label stating that the sugar content is less than 4 g per bar. Confirm if this is a correct statement, given that each bar is 33 g.
   (b) A similar product includes berries in the bar and contains 24.1 g protein, 29.8 g fat and 28.6 g carbohydrate per 100 g. How does the energy content of this bar compare with that in the original bar?
8. A food that is a solid has the following composition per 100 g: 0.5 g protein, 78.0 g fat and 0.6 g carbohydrate.
   (a) Suggest what food it might be.
   (b) The sum of these masses does not amount to 100 g. What could account for the remaining mass?
9. Oleic acid makes up 55–83% of olive oil, and is also found in many other animal and vegetable fats and oils. Its chemical formula is $C_{18}H_{34}O_2$.
   (a) It is described as a monounsaturated fatty acid. Explain the meaning of this term.
   (b) Explain why olive oil is a liquid rather than a solid.
   (c) Write a balanced equation showing the full oxidation of oleic acid.
10. Michael eats a hamburger for lunch. The amount of energy supplied by the hamburger is about 3020 kJ. Going for a run uses about 48 kJ per minute. How long would Michael need to run to use up the energy supplied by the hamburger?

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13.3 Glucose—the primary energy source

KEY CONCEPT

- Glucose as the primary energy source, including a balanced thermochemical equation for cellular respiration

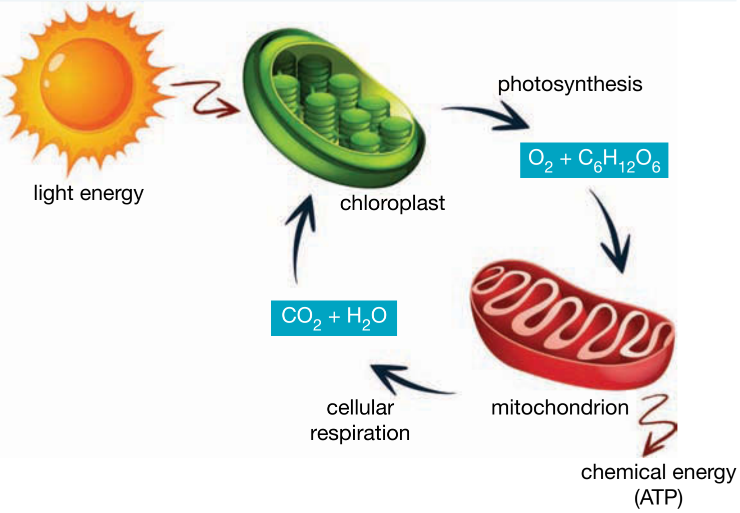
13.3.1 Cellular respiration

As described in topics 11 and 12, our main source of energy is glucose. The brain is the most energy-demanding organ, consuming about half the glucose in the body. The huge task of controlling all of the body's functions, including thinking, memory and learning, all rely on glucose levels and how the brain utilises this monosaccharide. Although the brain needs a good supply of glucose, too much can cause cognitive problems and other health issues, including diabetes. Muscles also demand a large amount of energy but unlike the brain, which cannot store glucose, muscles have some stored energy for their own use. Glucose is obtained through the catalysed hydrolysis of glycogen and starch. The glucose passes from the digestive system into the blood and then to the cells of the liver and other tissues.

FIGURE 13.5 The brain uses more energy than any other organ in the body.

The process by which energy is obtained from glucose is a remarkable and complicated series of biochemical steps and is called **cellular respiration**. This occurs in the cells of all living organisms. The cells release energy from the chemical bonds of food molecules, providing energy for the essential processes of life. In chemical terms it is an exothermic, redox reaction and is similar to a combustion reaction where glucose reacts with oxygen to form carbon dioxide and water. It is also an aerobic process because oxygen is required. The energy released in this process is 2860 kJ mol^{-1}.

FIGURE 13.6 Cellular respiration



The overall **thermochemical equation** for cellular respiration is:

$$C_6H_{12}O_6(aq) + 6O_2(g) \rightarrow 6CO_2(g) + 6H_2O(l) \qquad \Delta H = -2860\,\text{kJ mol}^{-1}$$

This equation is the reverse of the equation for photosynthesis although the chemical pathway involved is very different.

Remember to include the ΔH value and sign when asked to write a thermochemical equation.

Anaerobic respiration occurs when there is no oxygen present, and results in less energy being obtained. This occurs in tissues where there is a high demand for fast energy, such as in working muscles, but there is a shortage of oxygen to satisfy the energy needed by just using aerobic respiration. The product of anaerobic respiration is **lactic acid**, which must be oxidised to carbon dioxide and water at a later stage so that it doesn't build up. Lactic acid can cause muscle soreness because the cells cannot process waste products fast enough. The oxygen must be replaced and that is why you breathe deeply after exercise.

FIGURE 13.7 The burning, cramping pain felt in muscles during intense exercise is caused by a build-up of lactic acid.

The chemical equation for anaerobic respiration is:

$$C_6H_{12}O_6(aq) \rightarrow 2CH_3CH(OH)COOH(aq)$$

Anaerobic respiration also occurs in plant cells and some microorganisms. This process is called fermentation. Anaerobic respiration in yeast is used during brewing and bread-making, where sugars are broken down into ethanol and carbon dioxide.

$$C_6H_{12}O_6(aq) \rightarrow 2C_2H_5OH(aq) + 2CO_2(g)$$

Ethanol is the alcohol used in beer and wine production, and is also added to petrol to be used as a fuel. In bread-making, bubbles of carbon dioxide gas form in the dough and cause the bread to rise.

Aerobic respiration occurs in the presence of oxygen and anaerobic respiration occurs in the absence of oxygen.

13.3 EXERCISE

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1. (a) Name and write the formula for the monosaccharide that is referred to as 'blood sugar'.
   (b) Where is it stored in the body?
   (c) In what form is it stored?
2. When glucose is low, which part of the body will be affected first?
3. How much energy is provided by 1.00 g of glucose?
4. What type of reaction is occurring as glucose is broken down to carbon dioxide?
5. What functional group(s) is/are found in monosaccharides such as glucose?
6. Draw the structure of lactic acid ($CH_3CH(OH)COOH$) and label the functional groups.
7. An athlete is running on a treadmill. After running for some time, the athlete's legs started to cramp. What is the possible cause of this discomfort? Provide an equation to support your answer.
8. (a) Write the balanced equation showing anaerobic respiration of glucose to ethanol.
   (b) What is the name of this process?
   (c) How is anaerobic respiration useful in bread-making?

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13.4 Principles of calorimetry

KEY CONCEPT

- 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

13.4.1 Measuring the energy content of food

The amount of energy produced by a food can be measured by a process called **calorimetry**. This is the measurement of the amount of heat released or absorbed in a chemical reaction, change of state or formation of a solution. The change in temperature in a **calorimeter** can be related to the heat generated by first **calibrating** the calorimeter.

A simple method of measuring the heat content in food is to ignite a weighed sample of food and use it as a fuel to heat a particular volume of water, and measure its increase in temperature. The **specific heat capacity (*c*)** of water can then be used to determine the heat energy provided by the food sample. The specific heat capacity (c) is the energy needed to raise the temperature of 1 g of a substance by 1 °C. The energy being transferred to the water can be calculated using the heat energy released in the combustion of fuel equation. This can be found in table 3 of the VCE Chemistry Data Book.

Energy = mass of water × specific heat capacity of water × temperature increase

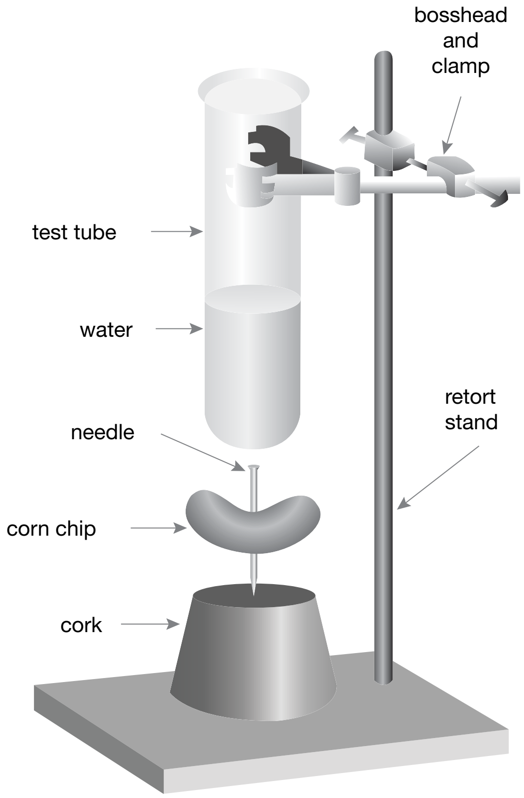
$$q = mc\Delta T$$

where:

- **q is the energy measured in Joule (J)**
- **m is the mass of water (not the food) in grams (g)**
- **c is the specific heat capacity of water, 4.18 J°$g^{-1}C^{-1}$**
- **ΔT is the change in temperature in °C.**

The apparatus used to measure the heat content in food is shown in figure 13.8. If a larger volume of water is required, a can may be used instead of a test tube. The food sources should be burnt at a constant distance from the water to ensure reliability of results.

FIGURE 13.8 Measuring the energy in food



This method is very inaccurate because of the considerable heat loss from the flame and the water container to the environment, but it can be used to do a comparison of the heat content of different foods. Increased accuracy can be obtained by using a heat shield around the apparatus to confine the heat produced. A solution or bomb calorimeter can provide more accurate results, but they must be calibrated so that the energy content can be calculated using the temperature changes.

To compare the energy obtained from different foods per gram:

$$\textbf{Energy released from food per gram (J)} = \frac{\textbf{mass of water (g)} \times \textbf{4.18} \times \textbf{temperature rise (°C)}}{\textbf{mass of food sample (g)}}$$

TIP: **If the volume of water is provided, the mass can be calculated using the density formula $d = \frac{m}{V}$. The density of water is 0.997 g mL^{-1}.**

SAMPLE PROBLEM 1

A 1.71 g sample of a food is burned, heating 50.0 g of water. The temperature increased from 20.0 °C to 59.0 °C. Calculate the energy transferred to the water, and then estimate the energy present per gram of food.

THINK	WRITE
1. Calculate the energy that is going into the water using the equation $q = mc\Delta T$ and substituting the specific heat capacity of water ($c = 4.18$ J°$g^{-1}C^{-1}$) and mass of the water. **TIP:** Take care to use the mass of the water to calculate the energy going into the water, not the mass of the food.	$q = mc\Delta T$ $= 50.0 \times 4.18 \times (59.0 - 20.0)$ $= 8151$ J
2. Convert to kilojoules.	$8151 \text{ J} = 8.15 \times 10^3 \text{ J}$ $= 8.15$ kJ
3. To calculate the energy per gram of food, divide the energy by the mass of food.	Energy per gram of food $= \frac{8.15}{1.71}$ $= 4.77 \text{ kJ g}^{-1}$

PRACTICE PROBLEM 1

A 1.08 g sample of almonds is completely burned, heating 150.0 g of water. The temperature increased from 20.0 °C to 33.0 °C. Calculate the energy transferred to the water, and then estimate the energy present per gram of almonds in kJ g^{-1}.

This method is very inaccurate because of the considerable heat loss from the flame and the water container to the environment but it can be used to do a comparison of the heat content of different foods. Increased accuracy can be obtained by using insulated containers to confine the heat produced. A solution or bomb calorimeter can provide more accurate results, but they must be calibrated so that the energy content may be calculated using the temperature changes.

A calorimeter is an instrument used to measure energy changes in chemical reactions.

on Resources

Digital document Experiment 13.1 Calculating the energy in food (doc-31282)

13.4.2 Calibrating a calorimeter

As explained in topic 2, the **enthalpy** or heat content (H) is the total energy in a substance. The change in enthalpy in a chemical reaction is known as the heat of reaction, and it is denoted by the symbol ΔH.

A calorimeter is an instrument that can be used to determine the energy changes that occur when a chemical reaction, such as burning food, takes place. There are different types of calorimeters, including **solution calorimeters** and **bomb calorimeters**. Because the temperature rise for a reaction depends on the substance itself, the amount of substance used and the nature of the immediate surroundings, the value of the conversion factor, called the calibration factor, must be established for each calorimeter before determining an enthalpy change. The calibration factor must be calculated for individual calorimeters before heat of reaction is calculated.

In all calorimeters, a reaction takes place inside an insulated container with a fixed amount of liquid (usually water), and the temperature rise or fall is recorded using an accurate thermometer. This temperature change (in °C) must be converted to an energy change (in J or kJ) before a value of energy or ΔH can be determined.

on Resources

Interactivity Calibrating a calorimeter (int-1253)

Electrical calibration

Electric calibration is achieved by calibrating the calorimeter using an electrically heated coil to supply a measured quantity of electrical energy, which is converted to heat energy. The heat energy is transferred to a known mass of a substance, usually water, and then measuring the temperature rise.

The energy released to the calorimeter is given by:

$$E = VIt$$

where:

E **= energy released (joules)**
V **= potential difference (volts)**
I **= current (amps)**
t **= time (s).**

If a current of I amps flows for t seconds at a potential difference of V volts, the calibration factor may be calculated as follows.

$$\text{Calibration factor (CF)} = \frac{\text{energy released during calibration}}{\text{temperature rise}} = \frac{VIt}{\Delta T_c}$$

The calibration factor (CF) is measured in joules per degree, J °C^{-1}.
The temperature rise (ΔT_c) during calibration is: Final temperature (T_f) – Initial temperature (T_i).

SAMPLE PROBLEM 2

A calorimeter is filled with 100 mL of water and its temperature recorded as 19.50 °C. A current of 2.52 A at a potential difference of 5.68 V is passed through the water for 2.00 minutes. The final temperature was measured at 24.25 °C.

Teacher-led video: SP2 (tlvd-0724)

THINK	WRITE
1. Calculate the electrical energy that is going into the water using the equation $E = VIt$. Remember to convert time from minutes to seconds.	$E = VIt$ $= 5.68 \times 2.52 \times 120$ $= 1.72 \times 10^3$ J
2. Calculate the calibration factor (CF) by dividing the energy released by the change in temperature using the equation $\Delta T_c = T_f - T_i$ **TIP:** The calibration factor equation can be found in table 3 of the VCE Chemistry Data Book. Give your answer to the smallest number of significant figures in the question.	$\text{CF} = \frac{energy}{\Delta T_c}$ $= \frac{1.72 \times 10^3}{24.25 - 19.50}$ $= 362\ \text{J}\ {}^\circ\text{C}^{-1}$

PRACTICE PROBLEM 2

Tim calibrates a calorimeter for an experiment he is about to perform. He uses 100 mL of water in an electrical calibration. The current supplied was 1.80 A and the voltage was 5.60 V over a period of 150 seconds. The temperature rose from 20.00 °C to 24.56 °C. Determine the calibration factor of the calorimeter in J $^\circ\text{C}^{-1}$.

Remember 'Rules in Joules'. Both rules $q = mc\Delta T$ and $E = VIt$ give answers in joules so care must be taken with units if answers are required in kilojoules.

13.4.3 Solution calorimetry

A solution calorimeter is the simplest type of calorimeter and is used to find the energy change occurring in aqueous solutions. This type of calorimeter consists of an insulated container and lid. Inserted through the lid is a stirrer to ensure even distribution of heat energy, a thermometer to measure changes in temperature and a heating coil to allow electrical energy to be converted to thermal energy for calibration.

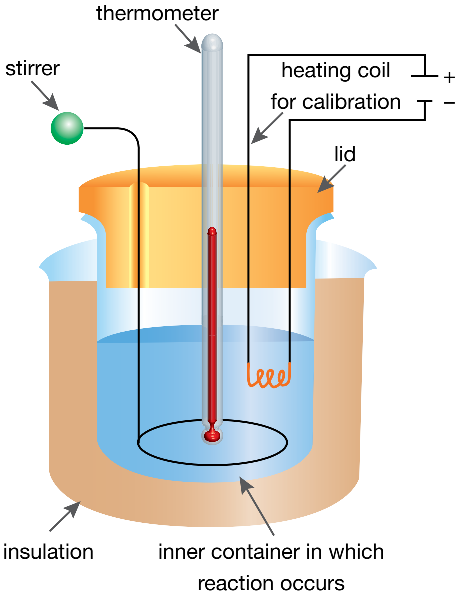
The steps for using a calorimeter are:

1. Calibrate the calorimeter (this step can also be done at the completion of the reaction).
2. Measure the masses or volumes of the chemicals that are required for the reaction, ensuring that the volume of water or solutions used is the same as the volume used for calibration.
3. Measure the temperature of the water or solutions.
4. Add the solid or solutions to the calorimeter.
5. Record the highest or lowest temperature reached.
6. Perform the calculations.
7. If ΔH is required, remember to use the appropriate sign.

The heat of solution (when 1 mole of any substance dissolves in water) and the heat of neutralisation (when an acid reacts with a base) for a reaction may be determined using a solution calorimeter.

In an *exothermic reaction*, the heat produced by the reaction is *released into* the solution, which increases its temperature.

FIGURE 13.9 In a solution calorimeter, experiments are usually carried out in aqueous solution.



In an *endothermic reaction*, the heat required is *absorbed from* the thermal energy of the solution, which decreases its temperature.

In a solution calorimeter, experiments are usually carried out in aqueous solution. The change in temperature caused by the reaction (ΔT_r) is measured and then multiplied by the calibration factor to determine the heat change for the reaction.

In solution calorimetry, the energy change is calculated using the equation:

$$\text{Energy change} = \text{CF} \times \Delta T_r$$

The ΔH is the energy change per mole. To find the ΔH divide the energy change by the number of mole, n.

$$\Delta H = \frac{\text{energy change}}{n}$$

TIPS:

- **Make sure that you label the temperature change in the calibration as ΔT_c and the temperature change for the reaction as ΔT_r so that you are not confused about which temperature to use.**
- **The equation $\Delta H = \frac{\text{energy change}}{n}$ can also be adapted from table 3 of the VCE Chemistry Data Book, utilising the equation for the enthalpy of combustion, $\Delta H = \frac{q}{n}$, because q is the variable for energy and n is the number of mole.**

SAMPLE PROBLEM 3

A pure sample of sulfuric acid with a mass of 0.231 g was combined with 100 mL of pure water in a solution calorimeter. The temperature increased from 19.90 °C to 20.42 °C. The calorimeter was previously calibrated with 100 mL of water and found to have a calibration factor of 463 J $°\text{C}^{-1}$. Calculate the ΔH and write the thermochemical equation of the reaction.

Teacher-led video: SP3 (tlvd-0725)

THINK	WRITE
1. The calibration factor is provided so it does not need to be calculated.	$\text{CF} = 463\ \text{J}\ °\text{C}^{-1}$
2. Calculate the energy change by multiplying the calibration factor (CF) by the temperature change of the reaction (ΔT_r).	$\text{Energy change} = \text{CF} \times \Delta T_r$ $= 463 \times (20.42° - 19.90°)$ $= 241\ \text{J}$
3. Find the number of mole (n) of H_2SO_4 by using the equation $n = \frac{m}{M}$.	$n\,(H_2SO_4) = \frac{0.231}{98.1}$ $= 2.35 \times 10^{-3}\ \text{mol}$
4. ΔH is the energy change divided by the number of mole using the equation: $\Delta H = \frac{\text{energy change}}{n}$.	$\Delta H = \frac{241\ \text{J}}{2.35 \times 10^{-3}}$ $= 1.02 \times 10^{5}\ \text{J mol}^{-1}$ $= 102\ \text{kJ mol}^{-1}$

▶

5. Write the thermochemical equation. Remember that it is an exothermic reaction so the sign of ΔH is negative.	$H_2SO_4(l) \rightarrow H_2SO_4(aq) \quad \Delta H = -102 \text{ kJ mol}^{-1}$

PRACTICE PROBLEM 3

A sample of potassium nitrate with a mass of 5.378 g was combined with 100 mL of pure water in a solution calorimeter. The temperature decreased from 20.34 °C to 20.10 °C. The calorimeter was previously calibrated with 100 mL of water and found to have a calibration factor of 620 J $°C^{-1}$. Calculate the ΔH of the reaction.

TIP: If there are quantaties provided for two reactants it is necessary to use the moles of the *limiting reactant* to calculate ΔH.

SAMPLE PROBLEM 4

A solution calorimeter containing 100 mL of water was calibrated by passing a 4.00 A current through the instrument for 35.0 s at a potential difference of 3.00 V. The temperature rose by 0.700 °C. When 6.60 g of calcium chloride hexahydrate, $CaCl_2 \cdot 6H_2O$, was added to the calorimeter and dissolved by rapid stirring, the temperature dropped by 0.895 °C.

Determine ΔH for the reaction:

$$CaCl_2 \cdot 6H_2O(s) \xrightarrow{H_2O} Ca^{2+}(aq) + 2Cl^{-}(aq)$$

Teacher-led video: SP4 (tlvd-0726)

THINK	WRITE
1. Calculate the calibration factor for the calorimeter from the relationship using $CF = \frac{VIt}{\Delta T_c}$.	$CF = \frac{VIt}{\Delta T_c}$ $= \frac{3.00 \times 4.00 \times 35.0}{0.700}$ $= 600 \text{ J°C}^{-1}$
2. Calculate the energy change during the reaction by applying the equation: Energy change = $CF \times \Delta T_r$	Energy change $= CF \times \Delta T_r$ $= 600 \times 0.895$ $= 537 \text{ J}$
3. To calculate the energy per mole first find the number of moles using $n = \frac{m}{M}$, where $M(CaCl_2 \cdot 6H_2O) = 219.1 \text{ g mol}^{-1}$	$n\,(CaCl_2 \cdot 6H_2O) = \frac{m}{M}$ $= \frac{6.60}{219.1}$ $= 0.0301 \text{ mol}$
4. The energy per mole can be calculated using $\Delta H = \frac{\text{energy change}}{n}$	$\Delta H = \frac{\text{energy change}}{n}$ $= \frac{537}{0.0301}$ $= 17819 \text{ J}$ $= 17.8 \text{ kJ}$

5. Because energy was absorbed during the reaction, the reaction is endothermic and the sign of the ΔH value is positive. Write the thermochemical equation, converting the ΔH value to kilojoules.

$$\mathrm{CaCl_2 \cdot 6H_2O(s)} \xrightarrow{\mathrm{H_2O}} \mathrm{Ca^{2+}(aq)} + 2\mathrm{Cl^-(aq)}$$
$$\Delta H = +17.8\ \mathrm{kJ\ mol^{-1}}$$

PRACTICE PROBLEM 4

A calorimeter was calibrated electrically. The potential difference through the heating coil was 5.23 V, producing a current of 1.83 A for 2.00 minutes. During this time the temperature rose from 19.40 °C to 22.85 °C. Then, 5.10 g of sodium hydroxide was added and the temperature rose to 37.33 °C. Determine ΔH for the reaction:

$$\mathbf{NaOH(s)} \xrightarrow{\mathbf{H_2O}} \mathbf{Na^+(aq) + OH^-(aq)}$$

on Resources

Digital document Experiment 13.2 Solution calorimetry (doc-31283)

Teacher-led video Experiment 13.2 Solution calorimetry (tlvd-0769)

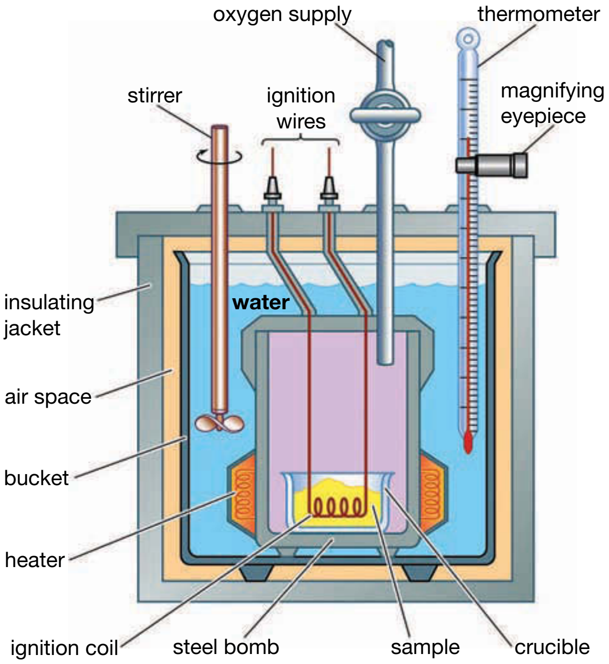
13.4.4 Bomb calorimetry

A solution calorimeter cannot be used to measure the energy obtained from foods or reactions involving gases. The heat of combustion (when a substance burns in oxygen, according to a particular equation) for a reaction in these situations may be determined using a bomb calorimeter. The ‘bomb’ is a container that is designed to withstand high pressure; its volume does not change, and it has valves for adding gases and an ignition source for combustion reactions. It can be used to measure enthalpy of combustion of other chemicals, such as fuels, as well as food samples.

Use of bomb calorimeters follows this sequence:

1. The calorimeter is calibrated as described in section 13.4.2 or by chemical calibration (as described following practice problem 5).
2. The mass of the sample compound is measured and then the sample placed in the inner chamber of the calorimeter.
3. This chamber (the ‘bomb’) is filled with oxygen at high pressure. A wire leads into the sample from outside the calorimeter and an electrical discharge is sent through the ignition wires.
4. The sample is ignited and reacts with oxygen. The heat from this reaction passes through the walls of the chamber into the water in the reservoir, which is stirred constantly. A thermometer measures the change in temperature of the water in the insulated water bath. This temperature change is then used to calculate the heat of combustion of the sample.

FIGURE 13.10 Features of a bomb calorimeter



The combustion of food is chemically similar to breaking down food in cellular respiration, and this combustion reaction involves oxygen. However, the reaction occurs more quickly in a bomb calorimeter compared to a solution calorimeter, and the energy content of a food, as determined by bomb calorimetry, usually differs from its energy content from a nutritional point of view. Less energy is available in the body because fruits and vegetables contain indigestible carbohydrates in the form of cellulose, and some energy is converted to heat in the body. Bomb calorimeters may be used to measure the energy content of foods. In the human body, energy is obtained from the combustion of glucose using the equation:

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

When the combustion of glucose reaction is carried out in a bomb calorimeter, it is found that 1 mole of glucose evolves 2083 kJ of heat in a rapid reaction. However, in the body glucose reacts in a sequence of steps to produce a slower release of energy. This gives the cells in the body a continual supply of energy for their needs. When calculating the energy in food it is necessary to calculate the energy per gram because food is a mixture of components and as such does not have a unique molar mass.

SAMPLE PROBLEM 5

A bomb calorimeter was calibrated by passing a current of 3.55 A at a potential difference of 6.40 V through a heating coil for 123.7 s. The temperature of the calorimeter rose from 21.82 °C to 26.13 °C.

After calorimeter had cooled, a dried biscuit weighing 2.34 g was then burned in the calorimeter in the presence of excess oxygen. The temperature of the calorimeter rose from 22.75 °C to 24.98 °C. Calculate the energy content of the biscuit in J g^{-1}.

Teacher-led video: SP5 (tlvd-0727)

THINK	WRITE
1. To find calibration factor, first calculate the electrical energy input using $E = VIt$.	$E = VIt$ $= 6.40 \times 3.55 \times 123.7$ $= 2810\ \text{J}$
2. Find the temperature change for calibration using $\Delta T_c = T_\text{f} - T_\text{i}$	$\Delta T_c = 26.13 - 21.82$ $= 4.31\,°\text{C}$
3. Calculate the calibration factor using $\text{CF} = \frac{VIt}{\Delta T_c}$	$\text{CF} = \frac{VIt}{\Delta T_c}$ $= \frac{6.40 \times 3.55 \times 123.7}{4.31}$ $= 652\ \text{J°C}^{-1}$
4. The change in temperature due to combustion of the biscuit is $\Delta T_r = T_f - T_i$	$\Delta T_r = 24.98 - 22.75$ $= 2.23\ °\text{C}$
5. The energy released by the biscuit is determined by Energy change = $\text{CF} \times \Delta T_r$	Energy from biscuit $= \text{CF} \times \Delta T_r$ $= 652 \times 2.23$ $= 1454\ \text{J}$
6. The energy content per gram of the biscuit is determined by the total energy of the biscuit divided by the biscuit's mass.	Energy per g $\frac{\text{energy}}{\text{mass of food (g)}} = \frac{1454}{2.34}$ $= 621\ \text{J g}^{-1}$

PRACTICE PROBLEM 5

A bomb calorimeter was calibrated by passing 1.35 A through the electric heater for 60.0 s at a potential difference of 6.44 V. The temperature of the water in the calorimeter rose from 22.85 °C to 23.30 °C.

A 2.25 g piece of Margarita pizza was completely burned in the calorimeter in excess oxygen. The temperature of the calorimeter rose from 22.30 °C to 39.68 °C. Calculate the energy content of the pizza in kJ g^{-1}.

Chemical calibration

Chemical calibration uses a combustion reaction with a known ΔH. This means that, instead of electrical energy, chemical energy is converted to thermal energy. Tablets of benzoic acid are widely used for this purpose because benzoic acid is readily available, stable, not **hygroscopic** and has an accurately known value of molar heat of combustion. The molar heat of combustion of benzoic acid at constant pressure is 3227 kJ mol^{-1}, that is, $\Delta H = -3227$ kJ mol^{-1}.

SAMPLE PROBLEM 6

When a sample of benzoic acid, C_6H_5COOH, with a mass of 1.18 g was ignited in a bomb calorimeter, it produced a temperature rise of 2.43 °C. Given that ΔH(benzoic acid) = –3227 kJ mol^{-1} and $M(C_6H_5COOH) = 122.0$ g mol^{-1}, calculate the calibration factor of the calorimeter in kJ $°C^{-1}$.

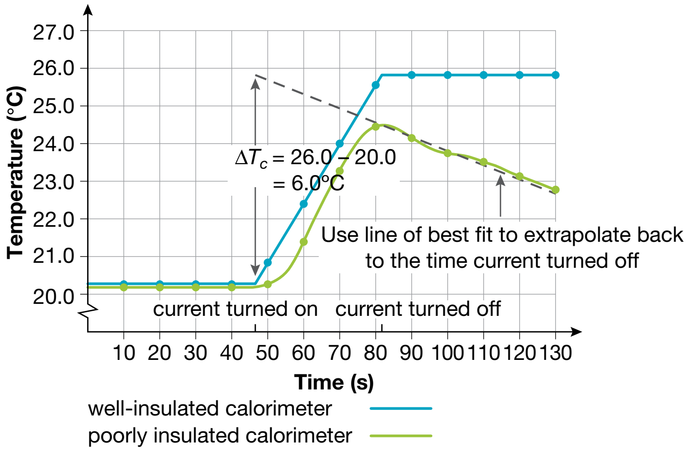
THINK	WRITE
1. Find the moles of benzoic acid using $n = \frac{m}{M}$.	$n(C_6H_5COOH) = \frac{m}{M} = \frac{1.18}{122.0}$ $= 0.00967$ mol
2. Calculate the energy produced by this amount of benzoic acid. Remember that ΔH(benzoic acid) = –3227 kJ mol^{-1}.	Energy change $= n \times \Delta H$ $= 0.00967 \times 3227$ $= 31.2$ kJ
3. To determine the CF, the temperature change must be calculated using $\Delta T_c = T_f - T_i$.	$\Delta T_c = T_f - T_i$ $= 2.43°C$
4. Calculate the calibration factor	$CF = \frac{energy}{\Delta T_c}$ $= \frac{31.2}{2.43}$ $= 12.8$ kJ $°C^{-1}$

PRACTICE QUESTION 6

A 2.48 g sample of benzoic acid was placed in a calorimeter and ignited. The initial temperature was 18.50 °C and a temperature of 27.37 °C was reached after combustion. Given that ΔH(benzoic acid) = –3227 kJ mol^{-1} and $M(C_6H_5COOH) = 122.0$ g mol^{-1}. calculate the calibration factor of the calorimeter in kJ $°C^{-1}$.

13.4.5 Temperature–time graphs

FIGURE 13.11 Determining ΔT_c for a poorly insulated calorimeter



Using a bomb calorimeter delivers very accurate results. If a calorimeter is well-insulated, there is little heat loss, and the temperature of the contents decreases slowly. This is demonstrated by figure 13.11, which is a plot of temperature against time as the reaction proceeds. Temperature–time graphs can be used to obtain a more accurate temperature change (ΔT_c) for a poorly insulated calorimeter.

In solution calorimetry we assume that there is a negligible heat loss and that all of the heat from the reaction is used to heat the water. However, a small amount of heat may be lost through poor insulation, a poor fitting lid, through holes for the thermometer and stirrer, or absorbed by parts of the calorimeter. In a perfectly insulated calorimeter, the final temperature remains constant after the current is turned off (as demonstrated by the blue line in figure 13.11). However, in a poorly insulated calorimeter, the temperature rise would be less than that in a well-insulated calorimeter. While the current is flowing in a poorly insulated calorimeter there would be heat loss throughout that time and once the current is turned off, the temperature would fall rather than remain stable. This is demonstrated by the green line in figure 13.11. The theoretical ΔH for the reaction can be calculated by extrapolating the graph to when the reaction commenced. The temperature change (ΔT_c) is the measurement from when the current was turned off in the calibration to the extrapolated line. This compensates for the error caused by loss of heat from the water to the surroundings during the time when the current was turned on.

Temperature–time graphs can be used to obtain a more accurate temperature change (ΔT_c) for a poorly insulated calorimeter.

13.4 EXERCISE

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1. Calculate the energy, in kJ, required to heat 1.00 L of water from room temperature (25.0 °C) to boiling point (100 °C) given the density of water is 0.997 g mL^{-1}.
2. (a) Consider the apparatus shown in figure 13.8, which was used to measure the energy in a corn chip. Imagine that the test tube was replaced by a can containing 250 g of water. A biscuit of mass 2.55 g was burnt, leaving a mass of ash of 2.25 g and a temperature increase from 21.32 °C to 27.23 °C. Estimate the energy of the biscuit in kJ g^{-1}.
   (b) A large amount of heat escapes using this set up of apparatus. Suggest a modification to improve the accuracy of this experimental design.
   (c) Explain why the answer is given in kJ g^{-1} and not kJ mol^{-1}
3. (a) What is calorimetry?
   (b) Why do calorimeters need to be calibrated?
   (c) Explain the difference there would be to the calibration factor, if any, if kelvin (K) was used instead of °C.
   (d) Explain the difference there would be to the calibration factor, if any, if 50.0 mL of water was used for calibration instead of 100.0 mL.

4. Determine the temperature change in a solution calorimeter when 5.00 g of $CaCl_2 \cdot 6H_2O$ dissolves in 200 mL of water according to the equation:

$$CaCl_2 \cdot 6H_2O\,(s) \xrightarrow{H_2O\,(l)} Ca^{2+}(aq) + 2Cl^-(aq) \quad \Delta H = +17.8\,\text{kJ mol}^{-1}$$

The calibration factor for the calorimeter under these conditions was found to be 825 J $°C^{-1}$.

5. A student used a simple calorimeter to determine the heat of neutralisation of a strong acid with a strong base according to the reaction:

$$H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$$

After calibrating the calorimeter, the student calculated the calibration factor to be 343 J $°C^{-1}$. The student then carefully added 50.0 mL of 0.100 M HCl to 50.0 mL of 0.110 M NaOH in the calorimeter. The temperature in the calorimeter rose from 20.4 °C to a maximum of 21.2 °C.
   (a) Explain how the student determined the calibration factor.
   (b) Calculate the heat of neutralisation for the reaction.
   (c) Suggest why a higher concentration of base than acid was used.
   (d) How would the heat of neutralisation have been affected if the student had added 50.0 mL of 0.100 M NaOH to 50.0 mL of 0.110 M HCl in the calorimeter?
   (e) Identify the sources of error in the experiment and suggest how these could be minimised.

6. (a) In what circumstances would a bomb calorimeter be used instead of a solution calorimeter?
   (b) Describe the features that are found in a bomb calorimeter to cater for these differences in use.

7. Daniel calibrated a bomb calorimeter by passing a current of 3.20 A at a potential difference of 5.40 V through a heating coil for 1 minute and 15 seconds. The temperature of the calorimeter rose from 19.4 °C to 20.5 °C. A sample of breakfast cereal weighing 1.37 g was then burned in the calorimeter in the presence of excess oxygen. The temperature of the contents of the calorimeter rose from 19.2 °C to 22.7 °C.
   (a) Calculate the calibration factor.
   (b) Calculate the heat content of the breakfast cereal in J g^{-1}.
   (c) Explain why this experiment was performed in a bomb calorimeter rather than a solution calorimeter.
   (d) Why is the energy content calculated per gram instead of per mole?

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13.5 Review

13.5.1 Summary

Energy values of carbohydrates, proteins and fats and oils

- On average, proteins and carbohydrates provide 17 kJ g^{-1}, and fats provide 37 kJ g^{-1} of energy.
- Fats provide more energy but take longer to breakdown.
- Water, minerals, vitamins and fibre are *not* sources of energy.
- Glucose is the primary energy source and provides 2860 kJ mol^{-1}.
- Not all of the energy in food is available for bodily functions because some food is not completely digested or absorbed, or not oxidised, and some energy is converted to heat.
- The brain is dependent on glucose; the liver, muscles and fat cells get energy from fat.
- Fats are broken down in an exothermic oxidation process, similar to combustion, producing carbon dioxide and water.
- Energy content on nutrition labels is calculated by multiplying the mass of proteins by 17 kJ g^{-1}, carbohydrates by 16 kJ g^{-1} and fats by 37 kJ g^{-1}.

Glucose—the primary energy source

- Glucose is obtained through the catalysed hydrolysis of glycogen or starch.
- Cellular respiration is how energy is obtained from glucose. It occurs in the cells of all living organisms.
- Cellular respiration is an exothermic, redox reaction, similar to combustion, where oxygen reacts with glucose to form carbon dioixde, water and energy.
- The reaction of cellular respiration is:

$$C_6H_{12}O_6(aq) + 6O_2(g) \rightarrow 6CO_2(g) + 6H_2O(l) \qquad \Delta H = -2860\,\text{kJ mol}^{-1}$$

- Anaerobic respiration breaks down glucose in the absence of oxygen, producing lactic acid and less energy than cellular respiration. The reaction of anaerobic respiration is:

$$C_6H_{12}O_6(aq) \rightarrow 2CH_3CH(OH)COOH(aq)$$

Principles of calorimetry

- Calorimetry is the measurement of the amount of heat released or absorbed in a chemical reaction, change of state or formation of a solution.
- A simple device to measure heat content in food uses the heat capacity of water.
- Energy = mass of water × specific heat capacity of water × temperature increase:

$$q = mc\Delta T$$

- If the volume of water is provided, the mass can be calculated using the density formula $d = \frac{m}{V}$. The density of water is 0.997 g mL^{-1}.
- A calorimeter is an instrument that can be used to determine the energy changes that occur when a chemical reaction takes place.
- The energy released to the calorimeter is given by $E = VIt$, where: E = energy released (joules), V = potential difference (volts), I = current (amps) and t = time (s)
- A calibration constant (called a calibration factor) for a calorimeter may be calculated by electrical calibration according to:

$$\text{Calibration factor (CF)} = \frac{\text{energy released during calibration}}{\text{temperature rise}} = \frac{VIt}{\Delta T_c}$$

- Enthalpy of reaction can be calculated using Energy = CF × ΔT_r
- To find ΔH use $\Delta H = \frac{\text{Energy change}}{n}$, where n is the number of mole.
- Solution calorimeters can be used to determine the energy changes occurring in aqueous solutions.
- Bomb calorimeters can be used to determine energy changes determined for combustion reactions.
- A calibration factor for a calorimeter may also be calculated by chemical means using a reaction with a known ΔH.
- A temperature–time graph can be used to improve accuracy of measurement when using a poorly insulated calorimeter.

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13.5.2 Key terms

anaerobic respiration breakdown of glucose in the absence of oxygen
bomb calorimeter an insulated steel container enclosed in water used to perform measurements of heat of combustion
calibrating finding a relationship between two quantities
calorie a measurement of heat energy needed to raise 1 g of water. 1 °C = 4.18 joule
calorimeter apparatus used to measure heat changes during a chemical reaction or change of state
calorimetry a method used to determine the changes in energy of a system by measuring heat exchanges with the surroundings
carbohydrate general name for compounds including sugars, starch and cellulose
cellular respiration process that occurs in cells to oxidise glucose in the presence of oxygen to carbon dioxide, water and energy
chemical calibration calibration of a calorimeter using a combustion reaction with a known ΔH
combustion rapid reaction of a compound with oxygen
electric calibration calibration of a calorimeter by supplying a known quantity of electricity
enthalpy heat content; the total energy in a substance
ethanol an alcohol with two carbons produced from fermentation of glucose by yeast
exothermic a reaction or process where heat is released to the surroundings
fat a triglyceride formed from glycerol and three fatty acids
hygroscopic something that absorbs moisture from the air
kilojoule (kJ) a unit of energy
lactic acid organic acid, $C_3H_6O_3$, present in muscle tissue as a by-product of anaerobic respiration
protein large molecule consisting of one or more chains of amino acids
serving size recommended amount of food on nutrition label for one serving
solution calorimetry an insulated device used to measure heat changes in a solution, for example, heat of dissolution and neutralisation reactions
specific heat capacity (c) energy needed to change the temperature of 1 g of a substance by 1 °C
thermochemical equations chemical equations that include the ΔH value

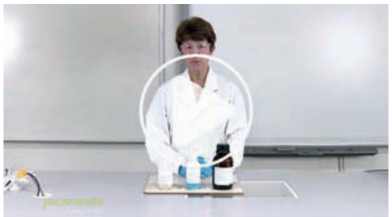
Resources

Digital document Key terms – glossary Topic 13 (doc-31424)

13.5.3 Practical work and investigations

Experiment 13.2

Solution calorimetry
Aim: Part A: To determine the calibration factor of a solution calorimeter
Part B: To determine the heat of reaction for zinc metal and copper ions
Digital document: doc-18832
Teacher-led video: tlvd-0769



Resources

Digital documents Practical investigation logbook (doc-31425)
Experiment 13.1 Calculating the energy in food (doc-31282)

13.5 Exercises

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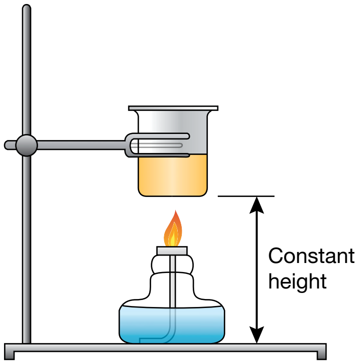
13.5 Exercise 1: Multiple choice questions

1. A can of chicken noodle soup provides 10 g of protein, 14 g of carbohydrate and 5 g of fat. The total number of kilojoules provided by one can of soup is:
   - A. 659
   - B. 827
   - C. 692
   - D. 579
2. Excess energy from the diet is most likely to be stored in the body as:
   - A. fat
   - B. fibre
   - C. salt
   - D. sugar.
3. Glucose is a monosaccharide that is essential in metabolism because it:
   - A. is formed in anaerobic respiration
   - B. polymerises in the body to form starch
   - C. is produced by the reaction of CO_2 and H_2O, releasing energy
   - D. is readily available to react with oxygen to provide energy.
4. Which one of the following statements concerning glucose is incorrect? Glucose:
   - A. polymerises to form proteins
   - B. releases energy when it reacts with oxygen to form CO_2 and H_2O
   - C. is the main energy source for all living organisms
   - D. is a monomer of cellulose.
5. Lipids in the diet can be:
   - A. hydrolysed to glycerol and fatty acids
   - B. broken down into energy for the body
   - C. stored as triglycerides for later use
   - D. all of the above.
6. Annabel measured the heat of combustion of ethanol by burning some ethanol in a spirit burner and a can containing 250 g of water as shown below. She used the ethanol to heat the water until the temperature rose 20 °C. The heat absorbed by the water was calculated and then Annabel used this calculation and the mass of ethanol used to determine the heat of combustion of the ethanol. The result was less than the value stated in the VCE Chemistry Data Book. Which of the following alternatives could NOT account for this result?



   - A. Some of the ethanol evaporated
   - B. Heat escaped into the atmosphere
   - C. Heat was absorbed by the can and thermometer
   - D. The mass of the water was 240 g, not 250 g
7. Bomb calorimeters can be used to measure the energy released by burning a small piece of food. Before the bomb calorimeter can be used to determine heat of combustion of any compound, it must be calibrated. The following steps in random order are taken to perform the calibration.

   Step 1. Supply a measured amount of electricity to the calorimeter for a particular time interval.
   Step 2. Record the highest temperature obtained.

Step 3. Fill the calorimeter with a measured volume of water.
Step 4. Connect the calorimeter to a power source.
Step 5. Measure the initial temperature.
Which of the following presents an appropriate sequence of steps?

- **A.** Steps 5, 1, 3, 2, 4
- **B.** Steps 3, 1, 5, 4, 2
- **C.** Steps 3, 4, 5, 1, 2
- **D.** Steps 4, 3, 1, 5, 2

8. 2.31×10^{-2} mol of a compound is burned in a bomb calorimeter. The calorimeter factor is 4700 J $°C^{-1}$, and the temperature of the calorimeter increases by 5.75 °C when the compound is burned. Calculate the molar heat of combustion of the compound in J mol^{-1}.

- **A.** +18.9
- **B.** –18.9
- **C.** 1.17×10^6
- **D.** -1.17×10^6

9. A bomb calorimeter measures the energy:

- **A.** released in a reaction in solution
- **B.** absorbed in a reaction in solution
- **C.** released by a combustion reaction
- **D.** absorbed by a combustion reaction.

10. The temperature rises from 25.00 °C to 27.90 °C when 2.55 g of sucrose undergoes combustion in a bomb calorimeter. Calculate the molar enthalpy of combustion of sucrose. The calibration factor of the calorimeter is 4.90 kJ $°C^{-1}$. The molar mass of sugar is 342.0 g mol^{-1}.

- **A.** 1.91×10^3 kJ mol^{-1}
- **B.** -1.91×10^3 kJ mol^{-1}
- **C.** -1.51×10^0 kJ mol^{-1}
- **D.** 1.45×10^1 kJ mol^{-1}

13.5 Exercise 2: Short answer questions

1. Calculate the energy content of one slice of bread with a tablespoon of peanut butter on it which contains 17 g carbohydrate, 7.0 g protein and 9.0 g fat.
2. ‘Mates’ savoury biscuits contain 14.7 g carbohydrate in 11 biscuits (25 g), which is described as a standard serve. What is the energy available from 100 g of biscuits?
3. Name the type of chemical reaction that produces the major part of the energy used by the body.
4. Describe one similarity and one difference between the way in which fats and carbohydrates provide energy in the body.
5. The thermochemical equation for the combustion of glucose is:

$$C_6H_{12}O_6(s) + 6O_2(g) \rightarrow 6CO_2(g) + 6H_2O(l) \qquad \Delta H = -2860\,\text{kJ mol}^{-1}[1]$$

The thermochemical equation for the combustion of ethanol is:

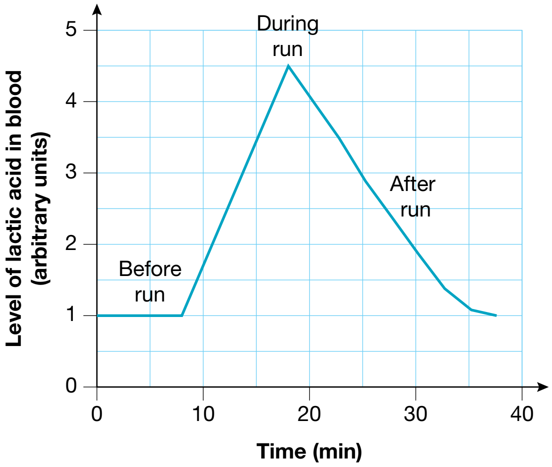
$$C_2H_5OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l) \qquad \Delta H = -1360\,\text{kJ mol}^{-1}[2]$$

Use this information to calculate ΔH for the fermentation of glucose:

$$C_6H_{12}O_6(s) \rightarrow 2C_2H_5OH(l) + 2CO_2(g)$$

6. The heat of combustion of lauric acid, $C_{11}H_{23}COOH$, can be determined by burning it in a bomb calorimeter. Write an equation for the complete combustion of lauric acid in excess oxygen.

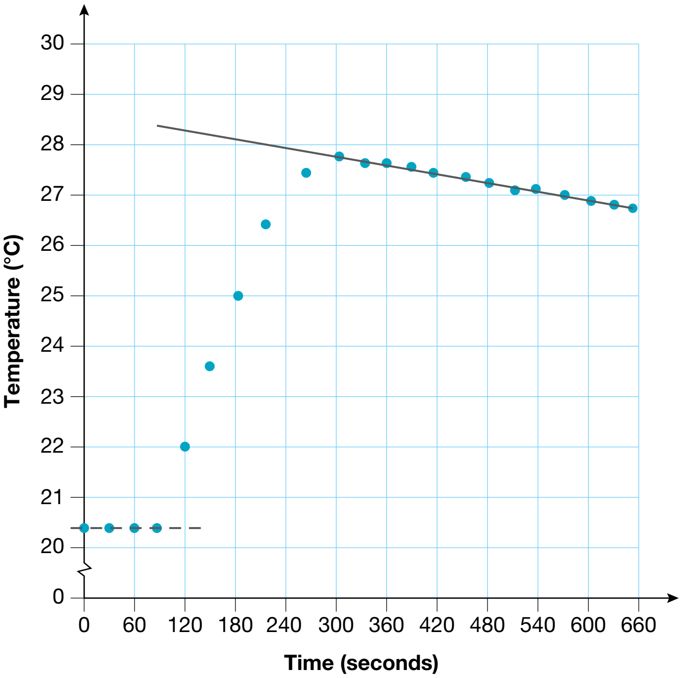
7. The molar heat of combustion of glucose is 2860 kJ mol^{-1}. Estimate the approximate heat of combustion of sucrose and explain how you arrived at your answer.
8. The graph below displays the lactic acid level in an athlete's blood while doing a training run for a race.



Use the graph to describe and explain the changes in the athlete's blood.

9. A solution calorimeter containing 100 mL of water was electrically calibrated by recording the stabilised temperature for 90 seconds and then turning on the current recording the temperature every 30 seconds for 210 seconds. The current was then turned off while still continuing to record the temperature. The temperature–time graph below was obtained.

   The potential difference applied was 6.30 V and the current recorded was 3.55 A. Calculate the calibration factor for this calorimeter.



10. A calorimeter was calibrated by passing an electrical current through a heater and measuring the rise in temperature that resulted. When a current of 133 mA from a 23.1 V source was passed through the heater for 264 s, the temperature of the calorimeter rose by 2.65 °C. Determine the calibration factor of the calorimeter.

11. A simple calorimeter was used in a school laboratory to determine the heat of reaction when magnesium filings were added to hydrochloric acid according to the equation:

$$2HCl(aq) + Mg(s) \rightarrow MgCl_2(aq) + H_2(g)$$

The calorimeter was calibrated by filling it with 100 mL of deionised water and then passing a current of 1.85 A at a voltage of 4.70 V through a heating coil for 1 minute and 17 seconds. The temperature rose by 3.8 °C. The calorimeter was then emptied and 0.766 g of magnesium filings was added to it. Subsequently, 100 mL of 2.00 M HCl was added to reach the 100 mL calibration mark in the calorimeter. The temperature in the calorimeter rose from 19.8 °C to a maximum of 21.1 °C.
    a. Calculate the calibration factor for the calorimeter.
    b. Calculate the heat of reaction.
    c. The experimentally determined heat of reaction in question b is much lower than the actual heat of reaction. Suggest reasons for this discrepancy.
    d. What assumptions are made in this experiment?

12. A bomb calorimeter is used to measure the energy content of a 'Crispy' biscuit. The calibration factor of the calorimeter is 2.03 kJ $°C^{-1}$. When 2.50 g of the biscuit was burned in the calorimeter, the temperature of the water rose from 24.2 °C to 45.5 °C.
    a. Calculate the heat energy in kJ g^{-1} of the biscuit.
    b. Why is the energy measured in kJ g^{-1} and not kJ mol^{-1}?
    c. The energy obtained by the body is actually less than this calculated value. Excluding experimental error, what might be the reason for this?

13.5 Exercise 3: Exam practice questions

Question 1 (4 marks)

A brand of processed meat is advertised as being 85% fat free. One hundred grams of this meat provides 1.25×10^3 kJ of energy.

a. Calculate the mass of fat in 100 g of the meat. **1 mark**
b. How many kilojoules are provided by this fat? **1 mark**
c. Assuming that protein is the only other nutrient present, what mass of protein is present in 100 g of this meat? **1 mark**
d. What mass is remaining and what substance might account for the remaining mass of the meat? **1 mark**

Question 2 (6 marks)

Palmitic acid is a very common fatty acid that is used to produce soaps and cosmetics. It has a heat of combustion of 1.00×10^4 kJ mol^{-1}.

a. Write a thermochemical equation showing the oxidation of palmitic acid, $M(CH_3(CH_2)_{14}COOH) = 256.4$ g mol^{-1} **2 marks**
b. Is palmitic acid a saturated or unsaturated fatty acid? **1 mark**
c. Calculate the energy released by the combustion of 20.0 g of palmitic acid. **2 marks**
d. Calculate the mass of glycerol ($M(C_3H_8O_3) = 92.0$ g mol^{-1}) required to form a triglyceride using 20.00 g of palmitic acid. **1 mark**

Question 3 (3 marks)

Two almonds of total mass 2.41 g are burned. The heat released raises the temperature of a 100 g sample of water from 19.5 °C to 33.4 °C. The mass of the almonds remaining after burning is 1.83 g. Calculate the energy content of the two almonds in joules per gram. Assume that the water is only able to absorb 30% of the heat released by the burning almonds.

Question 4 (2 marks)

The calibration factor of a bomb calorimeter was determined to be 26.3 kJ $°C^{-1}$. When a marshmallow weighing 0.870 g was placed in the calorimeter with excess oxygen and ignited, the temperature of the water bath increased by 1.32 °C. Calculate the heat of combustion of the marshmallow in kJ g^{-1}.

Question 5 (6 marks)

A bomb calorimeter was calibrated by passing a current of 4.15 A at a potential difference of 3.680 V through a heating coil for 2 minutes and 15 seconds. The temperature of the calorimeter rose from 21.5 °C to 23.7 °C. A sample of a high-energy bar weighing 2.50 g was then burned in the calorimeter in the presence of excess oxygen. The temperature of the contents of the calorimeter rose from 20.9 °C to 35.2 °C.

a. Calculate the heat content of the bar in J g^{-1}. **3 marks**

b. Identify the sources of error in the experiment, explaining how they may have affected the results. **3 marks**

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AREA OF STUDY 2 What is the chemistry of food?

OUTCOME 2

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.

PRACTICE EXAMINATION

STRUCTURE OF PRACTICE EXAMINATION		
Section	**Number of questions**	**Number of marks**
A	20	20
B	6	29
	Total	**49**

Duration: 50 minutes
Information:

- This practice examination consists of two parts. You must answer all question sections.
- Pens, pencils, highlighters, erasers, rulers and a scientific calculator are permitted.
- You may use the VCE Chemistry Data Book for this task.

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Weblink VCE Chemistry Data Book

SECTION A – Multiple choice questions

All correct answers are work 1 mark each; an incorrect answer is worth 0.

1. Diagrams of amino acid structures can be found in the VCE Chemistry Data Book. In the pure solid state with an approximately neutral pH, the amino acids exist almost completely:
A. As uncharged molecules
B. As zwitterions
C. In cationic form
D. In anionic form.

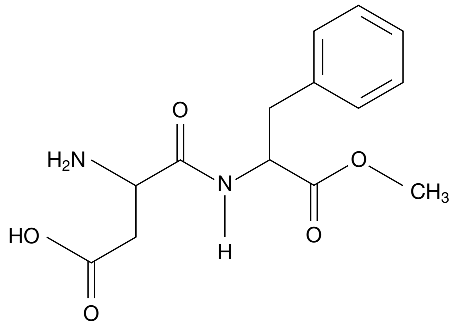
2. Which amino acid does *not* form an optical isomer?
A. Alanine
B. Phenylalanine
C. Glutamine
D. Glycine

3. A coenzyme is an organic non-protein molecule. It assists with the functioning of enzymes by:
A. Binding to the active site of the enzyme. The coenzymes are unaltered as a consequence the reaction.
B. Binding to the active site of the enzyme. The coenzymes are altered as a consequence of the reaction.
C. Binding to the substrate. The coenzymes are unaltered as a consequence the reaction.
D. Binding to the substrate. The coenzymes are altered as a consequence the reaction.

4. Select the *incorrect* statement. Denaturation of enzymes is the result of the breaking of bonds in the:
   A. primary structure
   B. secondary structure
   C. tertiary structure
   D. quaternary structure.

5. A protein chain is made up of 146 amino acids. What mass of water is released when 1.00×10^{-3} mol of this protein is formed?
   A. 0.018 g
   B. 0.146 g
   C. 2.61 g
   D. 2.63 g

6. The structural formula of aspartame is shown. The functional groups present in aspartame are:



   A. Carboxyl, amine, carbonyl, ester
   B. Carboxyl, amine, amide, ester
   C. Carboxyl, amine, amide, ester, methyl
   D. Carbonyl, hydroxyl, carbonyl, amine, ester.

7. Select the correct statement. Sucrose is a:
   A. Monosaccharide
   B. Disaccharide of glucose and galactose
   C. Disaccharide of two glucose molecules
   D. Disaccharide of glucose and fructose.

8. Cellulose is the most common carbohydrate. It provides strength to cell walls and roughage to the diet, known as fibre. Cellulose is able to form strong cell walls because:
   A. There is extensive branching in cellulose polysaccharide chains
   B. There is cross-linking between cellulose polysaccharide chains
   C. There is extensive hydrogen bonding between cellulose polysaccharide chains
   D. The glycosidic links between the glucose monomers are very strong.

9. A triglyceride formed from which of the fatty acids listed has the lowest iodine number (mass of iodine that reacts with 100 g of substance)?
   A. Palmitoleic
   B. Stearic
   C. Oleic
   D. Linoleic

10. Which of the following is true of the formation of a molecule of fat?
   A. A water molecule is produced in the reaction.
   B. The fat produced is always a solid.
   C. The reaction is between a fatty acid and glycerol.
   D. An ester linkage forms between the hydroxyl groups and carboxylic acid groups.

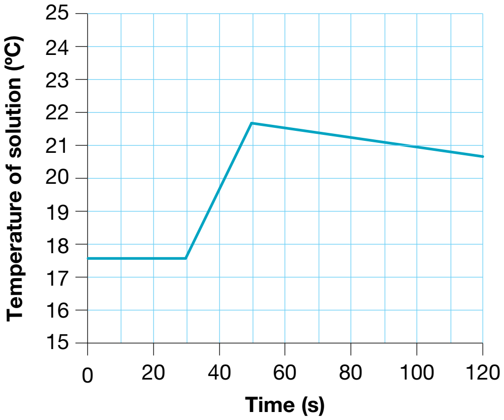
11. What is glycaemic index a measure of?

A. The amount of sugar present in a food
B. The proportion of a carbohydrate that is sugar
C. How readily the carbohydrate is broken down to glucose and absorbed
D. The ratio of amylopectin : amylose

12. Which of the following is an omega-6 fatty acid?

A. Linolenic
B. Palmitoleic
C. Linoleic
D. Arachidic

13. The following graph was obtained for a reaction that took place in a solution calorimeter.



Which of the following statements are consistent with the information in the graph?

I. The change in temperature was 4 °C.
II. The calorimeter was not very well insulted.
III. The current was turned off after 50 seconds.

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

14. Which of the following amino acid combinations can form hydrogen bonds with one another when part of a polypeptide chain?

A. Alanine and arginine
B. Asparagine and leucine
C. Cysteine and glutamic acid
D. Asparagine and serine

15. The correct equation for the complete combustion of sucrose is:

A. $2C_{12}H_{22}O_{11} + 70O_2 \rightarrow 24CO_2 + 22H_2O$
B. $C_{12}H_{22}O_{11} + 12O_2 \rightarrow 12CO_2 + 11H_2O$
C. $C_{14}H_{24}O_{11} + 40O_2 \rightarrow 14CO_2 + 12H_2O$
D. $2C_{14}H_{24}O_{11} + 29O_2 \rightarrow 28CO_2 + 24H_2O$

16. Cellular respiration is represented by the following thermochemical equation. What is the energy value of a teaspoon (5.0 g) of glucose?

$$C_6H_{12}O_6(s) + 6O_2(g) \rightarrow 6CO_2(g) + 6H_2O(l) \qquad \Delta H = -2816 \text{ kJ mol}^{-1}$$

A. 7.8×10^4 J
B. 782 kJ
C. 7.82 MJ
D. 7.82 kJ

17. A student calibrated a bomb calibrator by passing a current of 3.2 A at a voltage of 5.8 V through the heater for 2 minutes 45 seconds. The temperature rose by 3.65 °C. What is the calibration factor for the calorimeter?

A. 747.5 J $°C^{-1}$

B. 747.5 kJ $°C^{-1}$

C. 839.0 J $°C^{-1}$

D. 839.0 kJ $°C^{-1}$

18. The label on a loaf of bread says that a slice of bread is 33 g, with 2 g of that being fat, 17 g carbohydrate and 3 g protein. How many slices of bread would a person need to eat to meet their daily recommended intake of 8700 kJ?

A. 11 slices

B. 12 slices

C. 21 slices

D. 22 slices

19. Which of the following statements about enzymes are correct?

I. Changing pH can change the shape of the enzyme and its active site, reducing its activity.

II. Enzymes cannot be used again; once they have been used they are denatured.

III. The induced fit model illustrates that enzymes can temporarily change the shape of their active site.

A. I and II

B. I and III

C. II and III

D. I, II and III

20. Determine the temperature change in a calorimeter when 1.2 g of naphthalene, $C_{10}H_8$, is burned in a calorimeter with a calibration factor of 9560 J $°C^{-1}$. The molar heat of combustion of naphthalene was found to be 5575 kJ mol^{-1}.

A. 5.5 °C

B. 0.7 °C

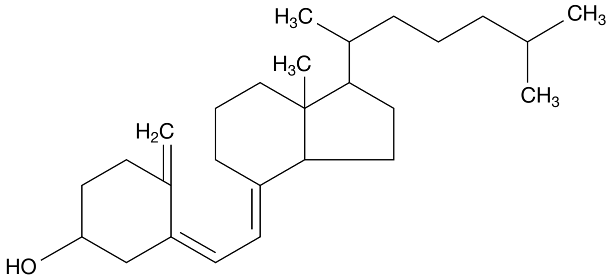
C. 62 °C

D. 16.5 °C

SECTION B – Short answer questions

Question 1 (4 marks)

The structure of Vitamin D_3 is shown below. The structure of Vitamin C can be found in the VCE Chemistry Data Book.



Vitamin D

a. Is Vitamin D_3 soluble in water? Give reasoning. **2 marks**

b. Explain why foods containing Vitamin C must be eaten every day. **2 marks**

Question 2 (2 marks)

Starch is made up of two polymers: amylopectin and amylose.

For the same percentage of starch in total, state and explain the difference in solubility of a food higher in amylose than amylopectin compared to one that contains equal amounts of each.

Question 3 (4 marks)

Many people choose to keep butter out of the fridge because it is more spreadable at warmer temperatures. The label on a packet of butter suggests that it be stored in an airtight container in the fridge. Explain why these suggestions are made using ideas about the chemical content of butter and the reactions that it can undergo.

Question 4 (5 marks)

Competitive enzyme inhibition occurs when a molecule similar to the substrate, but unable to be acted on by the enzyme, competes with the substrate for the enzyme's active site.

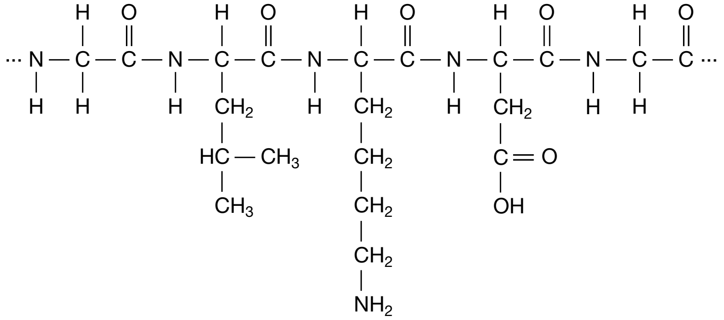
Using ideas about the lock and key model, explain:

a. How an enzyme works to increase the rate of reaction. You may use annotated diagrams to help you. **3 marks**

b. How this inhibition may affect the rate of reaction. **2 marks**

Question 5 (8 marks)

A section of a protein chain is shown.



a. On the diagram, circle a peptide bond. **1 mark**

b. Using their symbols, identify the amino acids in the chain from left to right. **1 mark**

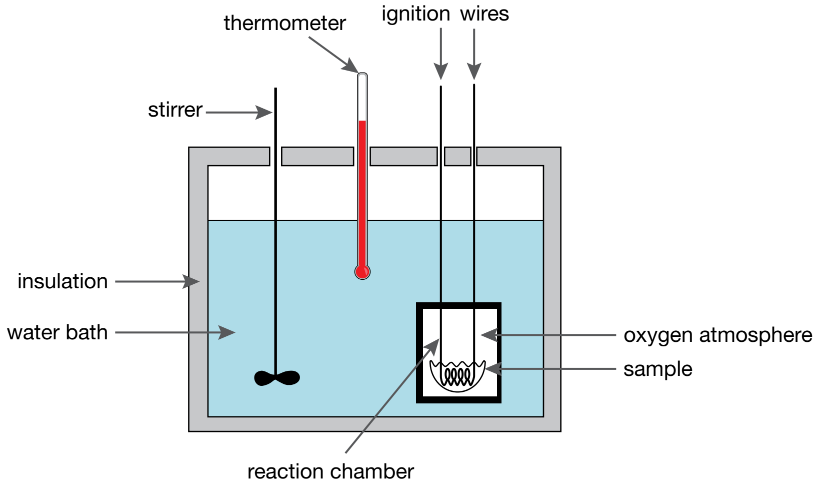
c. Identify the functional groups responsible for the secondary structure of the protein. **2 marks**

d. Based on the amino acids present, what type of bonding would be expected in the tertiary structure of this protein? **2 marks**

e. Explain what would happen if the protein were subject to high temperatures. **2 marks**

Question 6 (6 marks)

A VCE student calibrated a bomb calorimeter. Their apparatus set up is shown below. They calibrated the calorimeter by igniting benzoic acid, $\Delta H = -3227$ kJ mol^{-1} and $M(C_6H_5COOH) = 122$ g mol^{-1}, in the calorimeter. When 2.05 g of benzoic acid is ignited, a temperature rise of 3.32 °C was recorded.



a. Calculate the calibration factor of the calorimeter **3 marks**

b. A 1.50 g sample of biscuit was burned in the calorimeter in excess oxygen. The temperature of the contents of the calorimeter then rose from 21.6 °C to 24.7 °C. Calculate the heat content of the biscuit in J g^{-1}. **3 marks**

PRACTICE SCHOOL-ASSESSED COURSEWORK

ASSESSMENT task – Investigating molecular models

In this task you will analyse four models of key food molecules.

- You will be provided with four models by your teacher and must use these as the basis for your comparison.
- Students are permitted to use pens, pencils, highlighters, erasers, rulers and a scientific calculator.

Total time: 50 minutes (Time may be allocated before writing time for students to explore the provided models in test conditions.)

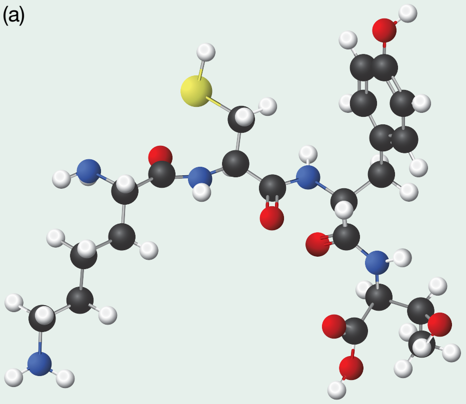
Total marks: 70 marks

A comparison of food molecules

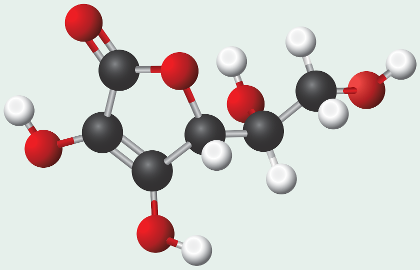
Part A – Investigating models

Examine the following diagrams (you may wish to construct these using modelling kits). These represent the four different key food molecules you will investigate.

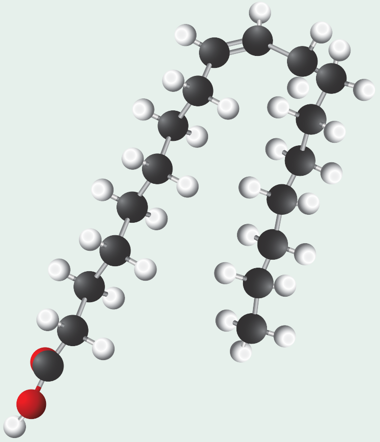
(a)



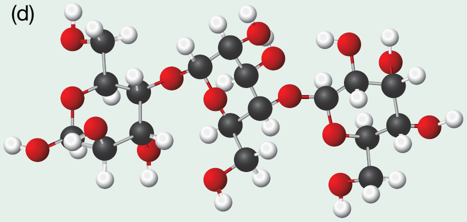
(b)



(c)



(d)



1. Draw a table and complete the following tasks for *each model* (you should have four tables in total), clearly labelled (a), (b), (c) and (d) as shown.
   Each table should have the following sections.
   (a) Identification of the type of molecule
   (b) Molecular drawing of the model, with clear labels of functional groups and bonds

(c) Drawing and the name of a monomer of this molecule (if any)
(d) Explanation of how this molecule would be metabolised in the body and broken down (including the key chemical reactions)
(e) Explanation of how larger molecules of this category would be synthesised from smaller subunits (included the detail of the bonding)
(f) Key properties expected of the molecule formed by the model shown
(g) Five examples of molecules within this category
(h) List of chemical elements found in molecules of this type
(i) General use of the class of molecule by the body

Part B – Analysing food molecules

2. Proteins have four different structures: primary, secondary, tertiary and quaternary. Describe the differences between these structures, and identify and describe the types of structures shown in the model of the protein you investigated.
3. Fatty acids can be classed as either saturated or unsaturated. Explain the difference between these and identify the type of fatty acid in the model you investigated.
4. Excess glucose from carbohydrates is stored in the body. Identify how it is stored and how this molecule is created.
5. There are both essential and non-essential vitamins, amino acids and fatty acids. Define the term ‘essential’ in this context and provide an example of:
   (a) An essential amino acid
   (b) An essential fatty acid
   (c) An essential vitamin.
6. Proteins and carbohydrates are known to have monomers, whereas lipids and vitamins do not. Comment on this statement, explaining the differences between the different food molecules regarding their structure.
7. Explain the structure of enzymes in relation to food molecules and describe how they are used in the breakdown of carbohydrates, proteins and fatty acids.
8. Explain the role of vitamins as coenzymes.
9. Identify the differences in the energy values of carbohydrates, proteins and fats and oils. Explain, with reference to structure, why these differences are observed.
10. A molecule is found to have the chemical formula $C_{40}H_{80}O_2$. What category of food molecule is this likely to be? Justify your response.

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Digital document U4AOS2 School-assessed coursework (doc-32008)

AREA OF STUDY 3
PRACTICAL INVESTIGATION

14 Practical investigation

14.1 Overview

Numerous **videos** and **interactivities** are available just where you need them, at the point of learning, in your digital formats, learnON and eBookPLUS at www.jacplus.com.au.

14.1.1 Introduction

Performing practical investigations and writing clear and concise reports are essential skills in chemistry. As part of Unit 4 in VCE chemistry, you will conduct a practical investigation related to energy and food. Energy is vital for life and the way in which this is gained from food is vital for our survival. Conducting investigations allows questions to be investigated and answered, and conclusions to be drawn and. In this topic, you will find guidelines for carrying out practical tasks safely and preparing thorough reports and scientific posters using appropriate scientific conventions. You will learn how to develop a question, plan a methodology and present, analyse and evaluate data obtained using appropriate chemical terminology.

FIGURE 14.1 A student conducting a scientific investigation in the classroom

14.1.2 What you will learn

KEY KNOWLEDGE

In this topic, you will investigate:

- independent, dependent and controlled variables
- chemical concepts specific to the investigation and their significance, including definitions of key terms, and chemical representations
- the characteristics of scientific research methodologies and techniques of primary qualitative and quantitative data collection relevant to the selected investigation: volumetric analysis, instrumental analysis, calorimetry and/or construction of electrochemical cells; precision, accuracy, reliability and validity of data; and minimisation of experimental bias
- ethics of and concerns with research including identification and application of relevant health and safety guidelines
- methods of organising, analysing and evaluating primary data to identify patterns and relationships including sources of error and uncertainty, and limitations of data and methodologies
- models and theories and their use in organising and understanding observed phenomena and chemical concepts including their limitations
- the nature of evidence that supports or refutes a hypothesis, model or theory
- the key findings of the selected investigation and their relationship to thermochemical, equilibrium and/or organic structure and bonding concepts
- the conventions of scientific report writing and scientific poster presentation including chemical terminology and representations, symbols, chemical equations, formulas, units of measurement, significant figures, standard abbreviations and acknowledgment of references.

KEY SCIENCE SKILLS

- Develop aims and questions, formulate hypotheses and make predictions
- Plan and undertake investigations
- Comply with safety and ethical guidelines

- Conduct investigations to collect and record data
- Analyse and evaluate data, methods and scientific models
- Draw evidence-based conclusions
- Communicate and explain scientific ideas

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Digital documents Key science skills (doc-30903)
Key terms glossary – Topic 14 (doc-31427)

14.2 Key science skills in chemistry

KEY CONCEPTS

- Independent, dependent and controlled variables
- Chemical concepts specific to the investigation and their significance

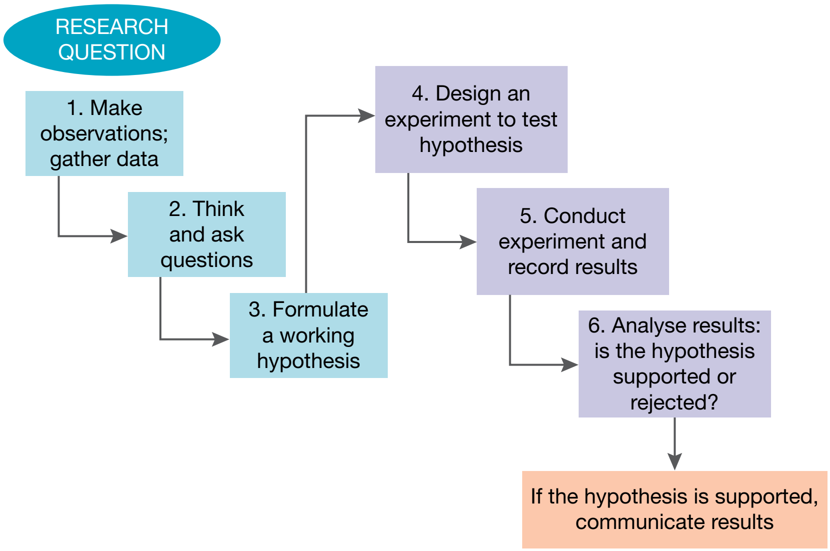
KEY SCIENCE SKILLS

- Develop aims and questions, formulate hypotheses and make predictions
- Plan and undertake investigations
- Comply with safety and ethical guidelines
- Conduct investigations to collect and record data

14.2.1 The scientific method: why do we conduct investigations?

In Unit 4, you will be required to conduct an investigation to explore the links between energy and food. This will require you to present methodologies, evaluate results and draw conclusions in your logbook and present this as a scientific poster. You will be conducting a practical investigation that uses laboratory or fieldwork to respond to a question. A practical investigation involves considerable planning, expertise in working scientifically and time to be appropriately conducted. Figure 14.2 summarises this process of practical investigations and **scientific method**.

FIGURE 14.2 The scientific method



This investigation will draw upon a number of the key skills and key knowledge that you gained in Units 1 and 2 and have been developing in Units 3 and 4. You will have the opportunity to show your skill and imagination in experimental design, commitment to a task and your communication ability in explaining your **results**. You will need to develop a question, plan actions to answer this question, undertake an investigation and interpret the data to form a conclusion.

This Unit 4 Outcome 3 task requires four to six hours of class time, allowing time to both conduct the investigation and communicate your findings. Table 14.1 will assist with your planning. The timeline may be different depending on your school. Your teacher may also have set checkpoints regarding when you are required to submit work and what specific components need to be included.

FIGURE 14.3 This investigation will rely on both skills and key knowledge.

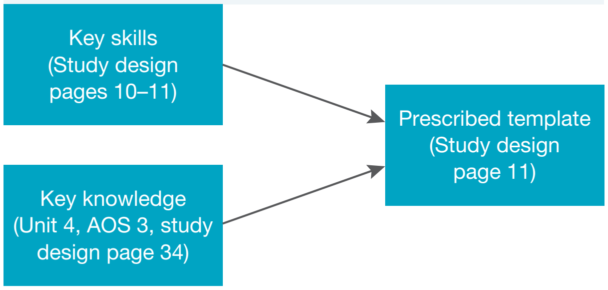


TABLE 14.1 Investigation planning with sample schedule

Task	Due date
• Introduction of task and expectations by teacher • Brainstorm topics around the idea of energy and food • Construct a choice of topics of investigation for your teacher	About two weeks before formal experimentation begins
• You return your list of possible topics for approval by your teacher, who then provides feedback, recommendations and final approval.	A few days later
• Submission of your detailed research proposal for your approved topic	At the beginning of the week before your experiment begins
• Submit your completed and signed risk assessment (this also must be signed by your teacher)	By the end of the week before your experiment begins
• Your requested equipment is assembled by the teacher and lab technician.	By the end of the week before your experiment begins
Your investigation begins. • Set up equipment • Collect preliminary data • Troubleshoot any issues with equipment • Collect data and measurements, graph your results and evaluate trends • Adjust and refine method	Week 1
• Continue the cycle of measurements and data analysis, leading to a review of progress and further more detailed measurements.	Week 2
• Finalise writing the sections of your report and paste them into a poster template. • Submit your logbook and finished poster.	Week 3

14.2.2 Using a logbook

As part of your scientific investigation (as well as all practical experiments throughout the year), it is a requirement to keep a logbook. Usually this logbook is a bound exercise book, but your teacher may request a digital logbook instead. It is vital to show all aspects of your practical investigation within your logbook using the scientific approach.

Your logbook will be assessed by your teacher. You must date all work that is completed in your logbook to show when it was completed and assist in validating your work.

TABLE 14.2 Components of a logbook

Component	Explanation
Chosen question and title	Information about your topic and how you chose it, and the question you have selected from this
Introductory material	Background data on your topic, diagrams, notes and tables, information about key terms and past experiments that were similar to that which you are conducting
Hypothesis and aim	A clear hypothesis and aim should be recorded outlining what you are investigating and why, and what you believe will happen.
Planning a method	Show all equipment you plan to use and a clear method you plan to follow, with detailed steps that could be reproducible by someone else
Experimental results	Observe and record results in an appropriate form — tables are particularly useful for this
Discussing and analysing results	Refer to your results and carefully evaluate these, referring back to your hypothesis and questions. You may have set discussion questions to answer to help scaffold your thoughts and ideas.
Thoughts and questions	Note down any concerns or questions you have about your investigation and research the answer to this.
Conclusion	Relates to the aim and hypothesis, and summarises the findings of the investigation

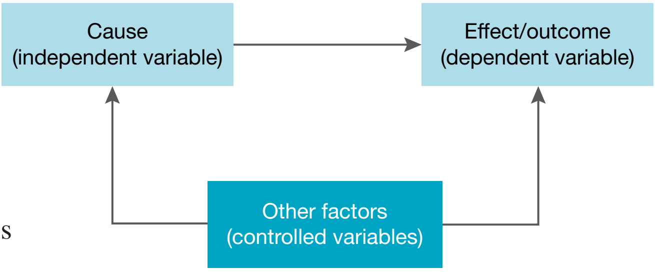
FIGURE 14.4 All observations should be recorded in a logbook.

14.2.3 Variables

Independent, dependent and controlled variables

In an experiment, a variable is any factor that the researcher can control or change or measure. Three kinds of variables are commonly recognised (see figure 14.5). For some variables you will set the value at the start of each experiment, others will be determined by your experiment, and sometimes there will be variables that you calculate using your measurements.

FIGURE 14.5 The relationships between variables in an experiment



- An **independent variable** (IV) is a factor that is deliberately manipulated by the investigator and affects the dependent variable. For example, you may be comparing the different energy content of various brands of cereal. The independent variable is the type of cereal.

  When graphing results, the independent variable is always placed on the horizontal axis.
- A **dependent variable** (DV) is the factor that the investigator measures. The dependent variable is affected by the independent variable. In the cereal brand investigation, the dependent variable would be the energy content.

  The dependent variable is always placed on the vertical axis of a graph.
- **Controlled variables** are all the other factors that the investigator must maintain at constant values through the course of an experiment. If these factors are not kept constant, they can confound the experimental results because they can cause changes in the dependent variable. In the cereal brand investigation, controlled variables would include the amount of each cereal used, the storage of the cereal and the instrument used to record data. Controlled variables should also include environmental factors such as humidity and air temperature, but these are harder to control.

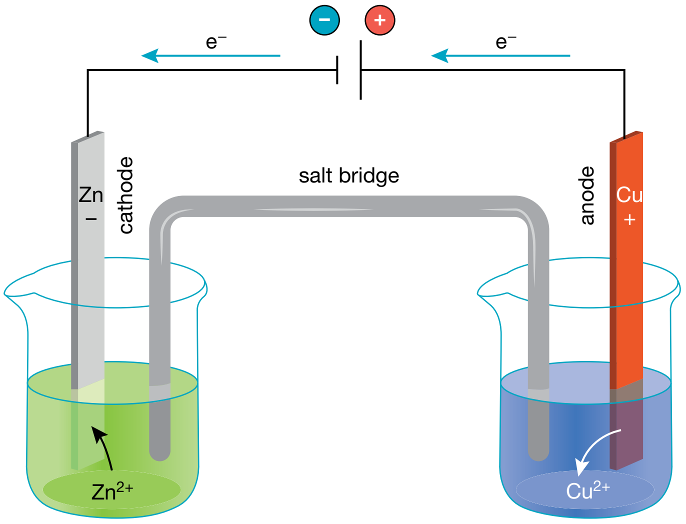
In summary:

- the independent variable is what an investigator changes
- the dependent variable is what an investigator observes and measures
- controlled variables are what the investigator keeps constant.

The following is an example for identifying variables.

Allira and Hunter are investigating the use of different combinations of metals for the anodes and cathodes in constructing galvanic cells. They plan to measure and record the cell voltage.

FIGURE 14.6 A galvanic cell



- *Independent variable:* The factor that is being manipulated is *the metals used in the galvanic cell*
- *Dependent variable:* The factor that is being measured is the *cell voltage*
- *Controlled variables:* The factors that are kept consistent are the same amount of solution in beakers, same type of salt bridge, same voltmeter used for all setups, same size beakers, and same laboratory conditions

Variables can also be classified as numerical (quantitative) or categorical (qualitative). Refer to section 14.4.2 for further detail on this.

on Resources

Interactivity Variables (int-7731)

14.2.4 Developing aims and questions

Coming up with a topic

Choosing a topic is not an immediate process — it takes time and careful consideration. It is important you don't just pick a topic that sounds interesting, but that you pick one that is reasonable to complete in the provided time frame and using the available resources.

The topic of your investigation needs to be around food and energy, so review the work you completed in Units 3 and 4 to help brainstorm ideas.

You may wish to create a mind map or a diagram outlining the various types of food and different ways that you measure each of these. Research the time this will take and what other research you could conduct. Plan what types of food you might investigate — figure 14.7 might give you some ideas. This will help you get your head around the different topics and what requirements there would be.

FIGURE 14.7 There are many different foods that can be explored in this investigation

Some examples of topics may be:

- Comparing the energy values between different types of oils
- Checking the accuracy of nutritional information on different brands of chips
- Exploring how differences in pH affect the enzymatic breakdown of starch by amylase

Creating a question

Turning the topic into a question focuses your mind on what you want to find out. The question needs to be:

- one that can be investigated through scientific method
- practicable, given your knowledge, time and the school resources
- asked in a way that indicates what you will do.

The following is an example of formulating a question from a topic:

Topic: Comparing the energy found in carbohydrates and fats.

Question: Do fruits high in fats and oils such as avocados have more energy than fruits high in carbohydrates such as oranges?

OR

Question: How does the energy content differ between fats and carbohydrates when examined using solution calorimeter?

There are many ways of formulating a question from a topic. Just make sure it is something that can be measured, explored and answered in the scope of your practical investigation.

Developing an aim

Often, developing an **aim** of an investigation is done at the same time as formulating a question from your topic. The aim outlines the purpose or the key objective of the investigation. It outlines what you are trying to achieve in order to answer your question and either support or not support your hypothesis.

There are two different ways that you can format your aim.

1. To [determine/investigate/compare] how the **dependent variable** is affected by the **independent variable**
2. To [determine/investigate/compare] how the **independent variable** affects the **dependent variable**

Your aim must:

- Be no more than two lines
- Be linked to your question
- Link the independent and dependent variables.

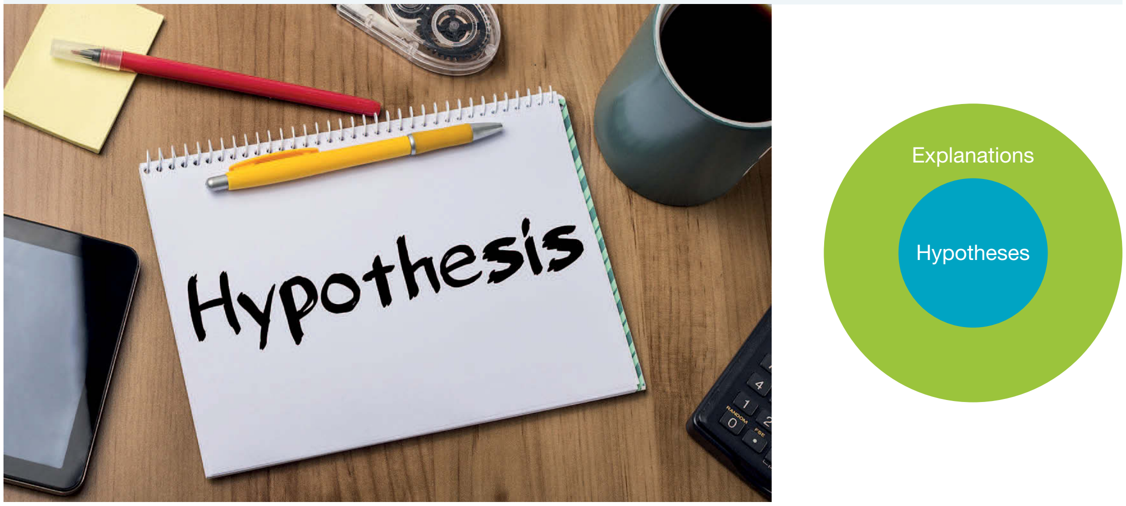
Examples of aims include:

- To use solution calorimetry to find the enthalpy change of different concentrations of sugar solutions.
- To investigate what variety of bread has the highest energy content per gram.
- To compare the energy content of peanuts and baked beans.
- To observe if changing the temperature of amylase affects the rate of starch breakdown.
- To explore if different types of oil have the same energy content.

14.2.5 Formulating hypotheses and making predictions

Formulating a **hypothesis** is an important step in the scientific method.

FIGURE 14.8 A hypothesis is a testable explanation for a concept.



A hypothesis is a tentative, testable and falsifiable statement for an observed phenomenon, which predicts the relationship between two variables or predicts the outcome of an investigation.

Testable means that a hypothesis can be easily tested by observations and/or experiments.

Falsifiable means that there has to be a way to be prove the hypothesis wrong.

A hypothesis usually predicts the relationship between two kinds of variables: an independent and a dependent variable.

> **To write a hypothesis, a good tip is to use the following format:**
> **If *[statement involving independent variable],* then *[prediction involving dependent variable].***

Typically, a scientific hypothesis starts with the tentative explanation and includes a prediction by which the hypothesis can be tested.

TABLE 14.3 Example of a good working hypothesis

IF	THEN
IF a straw is used to blow bubbles of carbon dioxide into a glass of water	THEN the pH will increase due to the production of carbonic acid.
IF the number of double bonds decreases the melting temperature of a molecule	THEN unsaturated fats such as linoleic acid will have a lower melting point than saturated fats such as palmitic acid.

FIGURE 14.9 What would you hypothesise if bubbles were blown through a straw?

FIGURE 14.10 Oils are liquid at room temperature and fats are solid. Which would you expect to have more double bonds?

Now consider the following statements and decide if each is an example of a well-formatted hypothesis:

- Statement 1: 'Small ice cubes melt faster.'
  No. This is simply a testable prediction. It does not include a tentative explanation.
- Statement 2: 'If an ice cube has a smaller volume, then it will melt faster when left at room temperature'.
  No. This does not identify a tentative explanation. The statement shows a method and a predicted outcome.
- Statement 3: 'If an ice cube has a smaller volume, particles will gain energy at an increased rate, causing it to melt faster at room temperature compared to an ice cube with a larger volume.'
  Yes. This identifies a tentative hypothesis (explanation) and a predicted outcome by which the hypothesis can be tested.

on Resources

Interactivity Formatting a hypothesis (int-7732)

SAMPLE PROBLEM 1

Polly is putting the kettle on. Polly is very curious about science and wants to see how she can change the speed the water boils. She has heard rumours that salt causes water to boil faster. She has four different types of salts in her house: table salt, sea salt, Himalayan pink salt and chicken salt.

Write an appropriate research question, aim and hypothesis for the scenario listed above:

Teacher-led video: SP1 (tlvd-0107)

THINK	WRITE
1. Determine the variables to help write an aim, hypothesis and research question. The factor that Polly is manipulating (the independent variable) is the type of salt. The factor that Polly is measuring (the dependent variable) is the time it takes for the water to boil.	The IV is the salt type The DV is the time it takes for the water to boil.
2. Create a research question based on Polly’s problem. Make sure that the question is one that is testable and clearly outlines what is occuring in the investigation?	Does the type of salt added to water impact the time it takes for water to boil?
3. Write an aim that clearly outlinesthe purpose of the investigation. Be sure to link the IV and DV.	To determine if different types of salts impact the time it takes for water to boil.
4. Write a hypothesis in the ’IF ... THEN’ format. Remember, a hypothesis needs to link the IV and DV. Your hypothesis may not be correct, but it must be testable (you may also specify which salt you think would do this best).	If table salt, sea salt, Himalayan salt or chicken salt is added to water, then the time taken for the water to boil will decrease with pure table salt causing the largest decrease in time.

PRACTICE PROBLEM 1

Jack wants to know if changing the material of the clothing that Jill is wearing will impact the speed at which she rolls down the hill.

Write an appropriate research question, aim and hypothesis for the scenario listed above.

14.2.6 Planning and undertaking experiments

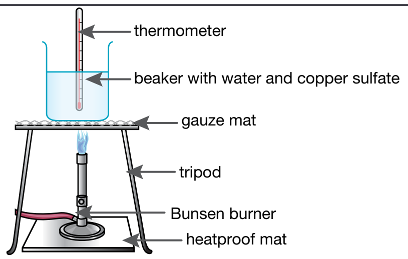
Planning experiments

Once your teacher has approved your topic, and you have written a question, aim and hypothesis, the real work begins. One way that planning may begin is through the use of a practical proposal.

At the end of your planning, you should be able to produce three written documents. These should be in your logbook and include the following.

- A risk analysis based on the hazards that you have identified (refer to section 14.5.2 for detail on risk assessments).
- A detailed list of equipment required, along with quantities (refer to section 14.4.3 for detail about different equipment used in chemistry).
- An explicit, step-by-step method that takes all of your planning into consideration, including diagrams if relevant. Setting this up as a Practical Investigation proposal as seen in figure 14.11 may be useful.

FIGURE 14.11 A practical investigation proposal

Practical investigation proposal	
Name:	Jill
Partner's name: (optional)	Jack
Title of your investigation	Exploring the solubility of copper sulfate in water at various temperatures
Briefly describe its purpose: *(A brief sentence, but it needs to be precise)*	To determine if the solubility of copper sulfate in water changes at varying temperatures.
Write down three starting questions you want to answer. *(These are to help focus your planning.)*	1. Is there an optimal temperature for copper sulfate solubility in water? 2. Is copper sulfate soluble at all temperatures? 3. What is the solubility of copper sulfate at room temperature?
List your independent variable as well as dependent variables. *(This enables your teacher to see if you have thought of all the obvious variables.)*	Independent: Temperature of the water Dependent: Solubility of copper sulfate, mass of copper sulfate able to dissolve, colour of solution
List the chemistry concepts and relationships that you expect to use in your investigation. *(This will give your teacher an indication of the extent of your understanding of the topic)*	Solubility is the extent to which a solute dissolves in a solvent All sulfates are soluble in water except those formed with silver, lead, calcium, strontium and barium. In water, copper sulfate dissociates as follows: $CuSO_4\ (s) \rightarrow Cu^{2+}\ (aq) + SO_4^{2+}\ (aq)$ The solubility of copper sulfate is known to be 20.5 g per 100 g of water at 20 °C
List the equipment and measuring instruments that you plan to use. *(This is for your teacher to see whether you have the right tools for the task.)*	• Copper sulfate solid • Watch glass • Spatula and stirring rod • Scales • Bunsen burner, heatproof mat, gauze mat and tripod • Thermometer • 200 mL beaker • Deionised water
Sketch your experimental set up. *(This will ensure the first day of your investigation runs smoothly and your teacher may be able to suggest refinements.)*	
List the steps in your experimental design. *(This is an important stage in your planning and it will enable your teacher to see if there is anything you have forgotten.)*	1. Fill the beaker with 100 mL of water 2. Place copper sulfate on a watch glass and weigh it 3. Record the temperature of the room 4. Slowly add copper sulfate into the water, mixing with a stirring rod 5. Determine when no more copper sulfate can be dissolved and record the mass 6. Fill another beaker with 100mL of water and heat to 40 °C and repeat step 4 and 5. 7. Repeat step 6 at 60 °C, 80 °C and 100 °C
Any special requests (E.g. equipment may need to be left set up between classes, or access at lunchtime or after school may be needed.)	Will need a container to dispose of copper sulfate solution

Conducting investigations

When conducting investigations, it is vital to:

- follow all health and safety protocols
- make sure you know how to use any chosen equipment correctly to minimise **errors**.
- carefully follow your methods, and if any changes are required, note these down in your logbook.
- control variables outside your independent variable to keep your results accurate and precise.
- clearly record any results obtained, along with the date. This includes any results that did not go according to plan and any results for both control and experimental groups.
- carefully pack up equipment after use. If equipment is required to be set up for a few days, leave it in a location where it cannot be impacted by other individuals or environmental factors.
- if time allows, repeat your experiment to improve accuracy and reliability.

14.2 EXERCISE

To answer questions online and to receive **immediate feedback** and **sample responses** for every question go to your learnON title at www.jacplus.com.au

1. Using the following topics, create a testable question that could be used for a practical investigation.
   (a) Comparing the electrolysis of different electrodes in potassium nitrate solution.
   (b) Exploring the boiling point of different hydrocarbons.
   (c) Using the specific heat capacity of water to determine the heat energy released by different fuels.
2. What is the purpose of a logbook in practical investigations?
3. Describe the difference between a dependent and an independent variable.
4. Why is it important to control variables in an investigation?
5. A student conducted an experiment to measure the effect of changing temperature on the rate of the combustion of a certain type of fuel.
   Test 1: 0.01 mol at 10 °C
   Test 2: 0.02 mol at 20 °C
   Test 3: 0.03 mol at 30 °C
   The results from each trial were then analysed to produce an overall conclusion.
   (a) State the independent and the dependent variables in this experiment.
   (b) What were the controlled variables in this experiment?
   (c) Describe any improvements you would make to the experimental method.
6. The following is an excerpt from a report describing the method for an experiment on determining the temperature change of water when burning different brands of bread.

   > *Five brands of bread were chosen to be examined. Three slices of bread were selected from each packet of bread and broken down into pieces that were the same size and mass. All bread was baked on the same day and kept in the same conditions before the investigation was conducted. The pieces of bread were then burnt underneath a test tube of water and the change in temperature was recorded*.

   (a) What is the independent variable in this experiment?
   (b) What is the dependent variable?
   (c) State as many controlled variables as you can think of for this experiment.
7. Select which of the following is an acceptable hypothesis.
   A. Does cordial have a higher pH than water?
   B. If the amount of hydrogen ions is higher in cordial compared to water, then the cordial is more acidic and will be recorded at a lower pH.
   C. If cordial is more acidic, it will have a lower pH recorded.
8. Testing a scientific question by experiment involves a number of stages. These are shown by the statements below. Use the letters to put these stages into their correct order.
   A. Formulate the hypothesis.
   B. Decide on the question.
   C. Analyse the results.
   D. Communicate the results.
   E. Plan the experiment.
   F. Carry out the experiment.

9. After some preliminary reading, a student has become intrigued by the possibility that hydrocarbons with double bonds (alkenes) have lower boiling points than those with single bonds (alkanes). Therefore, she proposes the questions: Do alkanes and alkenes have different boiling points?
   (a) Write a reasonable hypothesis that she could test experimentally based on this question.
   (b) Which of the following is a characteristic of a good hypothesis?
      A. It must be proven true.
      B. It must be testable by observation or an experiment.
      C. It must be based on experiments done by other scientists.

Fully worked solutions and sample responses are available in your digital formats.

on Resources

Interactivity Variables (int-7731)

14.3 Concepts specific to investigations

KEY CONCEPT
- Chemical concepts specific to the investigation and their significance, including definitions of key terms, and chemical representations

KEY SCIENCE SKILL
- Communicate and explain scientific ideas

14.3.1 Concepts specific to investigations

As part of an investigation, it is vital to link key chemistry concepts that are relevant and clearly explain their significance. This shows a clear link of your understanding for an investigation, and allows others to see the connection between theory and practical applications.

Background knowledge

Concepts should be researched prior to commencing your investigation, recorded in your logbook and referenced. This background information also will form part of your introduction in your poster.

Concepts that are relevant to your investigation include:
- explanations of key formulae
- definitions of key terms
- detail about the theories being examined
- information about other practical investigations exploring similar concepts.

An example of this may be investigating the heat energy released in the combustion of a fuel. In your background information, it would be important to:
- describe the fuels you are looking at in the investigation and their chemical formulas
- discuss previous investigations and experiments conducted, by yourself and by other researchers
- describe key theoretical ideas to provide the reader with knowledge to understand the key concepts (e.g. linking to thermochemical factors)
- defining key terminology relating to the investigation
- explaining key formula (such as $\Delta H = \frac{q}{n}$), including identifying the symbols used.

14.3.2 Key terms

It is vital in practical investigations to define any key terminology. This can be done in two ways:
- within the report itself
- as part of an appendix or glossary at the end of the report.

The following excerpt shows an introduction from a scientific report written by a student. This investigation was conducted to explore different types of hydrocarbons.

> *Hydrocarbons are organic compounds that are composed solely of carbon and hydrogen, used in a variety of different roles, including as fuels. Two types of hydrocarbons are being explored in this investigation: alkanes, which only contain single carbon bonds and are saturated, and alkenes, which contain one or more double bonds between carbon atoms.*

This student has clearly defined key terms as part of their introduction within their report itself. What terms have they defined?

Read the following excerpt of an introduction from a scientific report written by a different student, investigating the same practical.

> *In this investigation, different types of* ***hydrocarbons*** *are being compared, with a particular focus on their use as fuels. Two groups of hydrocarbons are being investigated:* ***alkanes*** *and* ***alkenes****.*

In this situation, the student has not defined the terms in their introduction itself, but has bolded key words that later appeared in their glossary as shown below:

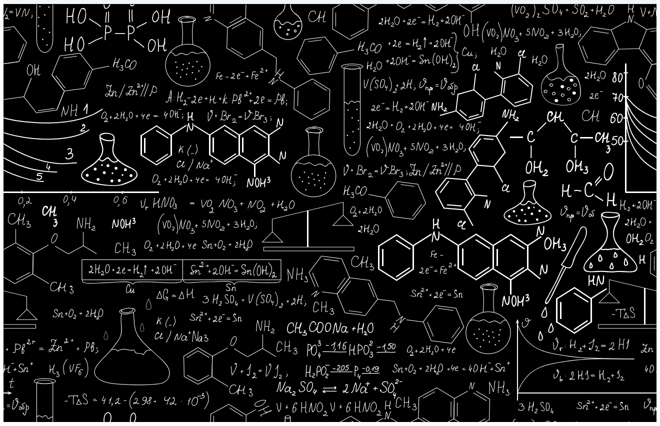
> *Glossary of key terms:*
> ***Hydrocarbons:*** *organic compounds that are composed solely of carbon and hydrogen*
> ***Alkanes:*** *hydrocarbons that contain only single bonds between carbon atoms*
> ***Alkenes:*** *hydrocarbons that contain one double bond between carbon atoms*

Both of these formats are valid methods to define key terms. The method used depends on the format of the report or personal preference. Be sure to check which method is most suitable for the practical investigation you are conducting with your teacher.

14.3.3 Chemical representations

A variety of representations are used in chemistry. They include the use of models, sketches, graphs, equations, formulae, symbols and diagrams. As well as this, there are many vital conventions into the use of numerical data, including significant figures and scientific notation. Perhaps the most common chemical representation is the use of chemical formulas. Care should be taken with capital letters and subscripts and superscripts when representing atoms and ions. For example, CO is carbon monoxide, while Co is the metal cobalt.

FIGURE 14.12 Representations form a vital part of chemistry reporting



Formulas that demonstrate structure

Structures are often drawn in a skeletal form in chemistry, particularly in organic chemistry.

Lines between atoms represent the number of bonds present. Sometimes we can shorten these representations even further, as shown in the skeletal formulas for the benzene ring and dodecane in figure 14.15. Skeletal formulas do not show specific carbon and hydrogen atoms or the bonds connecting them.

FIGURE 14.13 Different representations of methane: (a) Ball-and-stick model, (b) diagram showing bond angles, (c) valence structure and (d) shape diagram

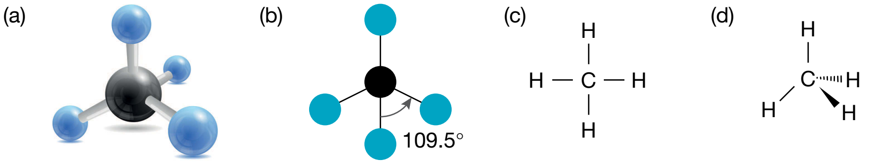


FIGURE 14.14 Some common structural formulas representing various molecules

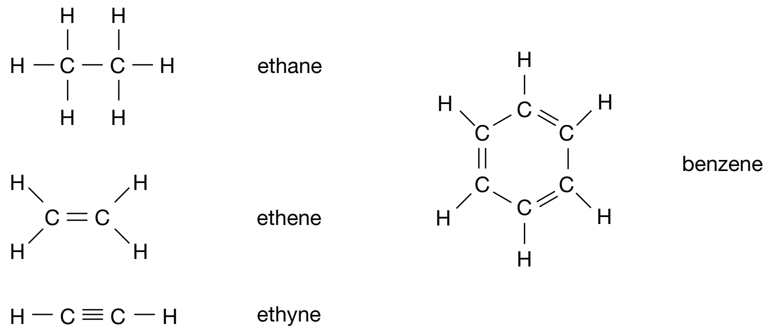
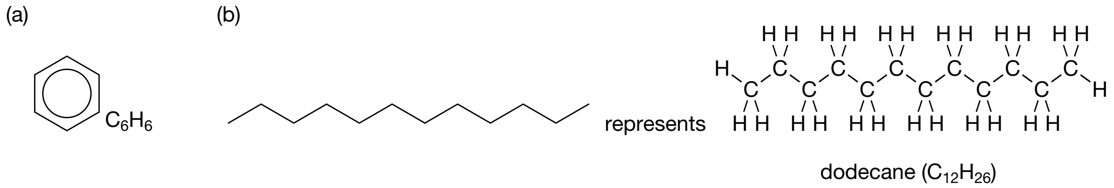


FIGURE 14.15 Skeletal formulas of different molecules: (a) benzene and (b) dodecane.



Scientific notation

Very large and very small quantities can be more conveniently expressed in scientific notation. In scientific notation, a quantity is expressed as a number between one and ten multiplied by a power of ten. In chemistry, scientific notation is generally used for numbers less than 0.01 and greater than 1000.

To write in scientific notation, follow the form $N \times 10^a$, where N is a number between one and ten and 'a' is an integer (positive or negative).

When converting numbers into scientific notation the following steps should be followed:

1. Determine where the decimal point needs to go so that N is between 1 and 10.
2. Count the number of places the decimal point is moved to determine a (the power of 10 or the exponent). If the decimal point was moved to the left, a will be positive, if it was moved to the right, a will be negative.
3. Write the number in scientific notation.

For example, the average distance between the Earth and the moon is 380 000 000 m. This is more conveniently expressed as 3.8×10^8 m in which the decimal point was moved 8 places to the left. The radius of a lead atom in metres is 0.000 000 000 175. This is more conveniently expressed as 1.75×10^{-10} m, in which the decimal point was moved 10 places to the right.

As you can see, very large numbers will have a positive exponent (a), whereas very small numbers will have a negative exponent. 5×10^{-3} for example, can be written as 0.005, whereas 5×10^3 can be written as 5000.

Quantities in scientific notation can be entered into your calculator using the EXP button or ^ button.

SAMPLE PROBLEM 2

a. The average distance between Earth and Sun is 149 600 000 kilometres. Write this in scientific notation.

b. The mass of a proton is 0.000 000 000 000 000 000 000 001 67 g. Write this in scientific notation

Teacher-led video: SP2 (tlvd-0103)

THINK	WRITE
a. 1. Determine the position of the decimal point in order for the number to be between 1 and 10 and remove any 0s that are not between non zero digits. The decimal point would need to go between 1 and 4 to form 1.496	1.496
2. Determine the exponent by establishing the number of places the decimal point was moved. If the decimal point was moved to the left to convert to scientific notation, the exponent should be positive, if the point was moved to the right, the exponent should be negative. The decimal point was moved 8 spots to the left so the exponent is 8.	10^8
3. Write the number in scientific notation, remembering to include the units.	1.496×10^8 km
a. 1. Determine the position of the decimal point in order for the number to be between 1 and 10 and remove any 0s that are not between non zero digits. The decimal point would need to go between 1 and 6 to form 1.67.	1.67
2. Determine the exponent by establishing the number of places the decimal point was moved. If the decimal point was moved to the left to convert to scientific notation, the exponent should be positive, if the decimal point was moved to the right, the exponent should be negative. The decimal point was moved 24 spots to the right so the exponent is −24.	10^{-24}.
3. Write the number in scientific notation, remembering to include the units.	1.67×10^{-24} g

PRACTICE PROBLEM 2

Express the following quantities in scientific notation.

a. The distance from the Earth to the Sun is 149 600 000 km.

b. The radius of a potassium atom is 0.000000028 m.

c. There are an estimated 900 000 000 dogs in the world.

14.3 EXERCISE

To answer questions online and to receive **immediate feedback** and **sample responses** for every question go to your learnON title at www.jacplus.com.au

1. Show two ways that key terms can be defined in your report, by writing a short paragraph defining the terms ‘aim’ and ‘hypothesis’.
2. Why are representations useful in scientific reporting?
3. Express the following quantities in scientific notation.
   (a) The mass of a grain of sand that is 0.000667 g.
   (b) The diameter of the nucleus of uranium is 0.000000000000015 m
   (c) The approximate number of new skin cells produced in a month is 900 000.
4. Convert each of the following numbers from scientific notation to an ordinary number (the full number).
   (a) 6.524×10^{-4}
   (b) 5.1234×10^{5}
   (c) 1.54×10^{1}
   (d) 12.01×10^{-3}

(e) 4.5×10^{2}
(f) 2.457×10^{-6}
(g) 9.024×10^{-5}

Fully worked solutions and sample responses are available in your digital formats.

14.4 Scientific research methodologies and techniques

KEY CONCEPTS

- The characteristics of scientific research methodologies and techniques of primary qualitative and quantitative data collection relevant to the investigation: volumetric analysis, instrumental analysis, calorimetry and/or construction of electrochemical cells; precision, accuracy, reliability and validity of data; and minimisation of experimental bias
- Methods of organising, analysing and evaluating primary data to identify patterns and relationships including identification of sources of error and uncertainty, and of limitations of data and methodologies

KEY SCIENCE SKILLS

- Conduct investigations to collect and record data
- Analyse and evaluate data, methods and scientific models

14.4.1 Characteristics of scientific research methodologies

Carefully following **scientific research methodology** when conducting practical investigations is important to ensure that your results are as precise, accurate, reliable and valid. This includes minimising errors and uncertainties in data in order to draw **conclusions** in relation to your question.

Each type of research method has its specific purposes, procedures, advantages and limitations. The researcher's choice depends on which method is most appropriate for the specific topic of research interest and hypothesis being tested.

There are different types of scientific inquiry and research methods that can be used. These are shown in table 14.4.

TABLE 14.4 Types of scientific inquiry

Method	Use
Controlled experiment	Determining the relationship between an independent and dependent variable. All other variables are controlled. For example, testing the melting temperatures of different metals.
Single variable investigation	Exploring how a variable can change over time and understanding causes of the observations and how other factors impact it. For example, investigating how an element decays over time.
Identification	Investigating if objects or events belong to specific sets or are part of new sets. For example, understanding if a new element is a metal or non-metal.
Designing	Designing a device using scientific knowledge. For example, designing, constructing, testing and evaluating a device that can be used to treat and purify water.
Investigating models	Exploring everyday phenomena and collecting evidence to test the model For example, devising an investigation to test the law of conservation of mass.

In all scientific inquiries, various processes are followed. These include:

- formulating a question and hypothesis to be tested
- controlling variables
- completing a logbook outlining the introduction, methodology, results, **discussion** and conclusion of an investigation
- ensuring that methods are being taken to allow for validity, accuracy, precision and reliability
- ensuring that methods are being used that reduce uncertainties and errors
- collecting data accurately in an appropriate form that best suits the question being investigated
- where possible, having a **control group** (not exposed to an independent variable to act as a baseline) and numerous **experimental groups** (exposed to the independent variable).

Control groups

Usually, if the identification of controlled variables is complex, or many are present, it can be simpler to include a control group. A scientific control is an experiment or observation that involves all variables except the independent variable. For example, a scientist may be trying to measure the absorbance of light by various concentrations of cobalt chloride solutions. The independent variable in such an investigation would be the concentration of cobalt chloride, and the dependent variable would be the absorbance reading obtained. However, there are a number of other variables that may affect the result. These include the nature of the solvent, the type of glass that the containers holding the solutions are made from, the distance the light has to travel (especially through the solution) before it is measured, the temperature of the solution and so on. A convenient way to control all these variables, and maybe even some that you aren't aware of, is to use a control. Everything about the control, from the way it is prepared to how it is manipulated and measured in the experiment, is the same as for the test solutions containing cobalt chloride. The only difference is that there is no cobalt chloride (the controlled variable) in the control. This allows the scientist to isolate the amount of absorption in each reading that is due to the cobalt chloride alone because it is the only variable left that is responsible for any differences in absorbance readings.

Another example of control and experimental groups being used may occur in a practical investigation exploring the conductivity of different concentrations of sodium chloride (NaCl) solution.

The experimental groups would be the different concentrations of sodium chloride being tested.

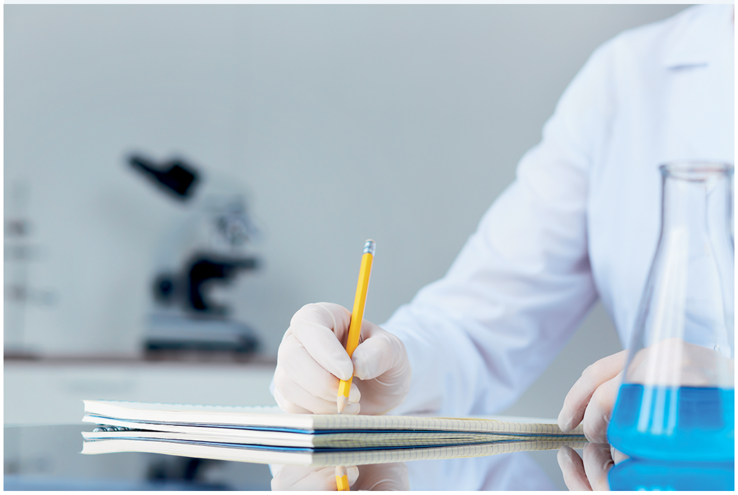
The control group would be testing with pure water (0% sodium chloride), to examine the conductivity when there is no NaCl present.

14.4.2 Techniques of primary qualitative and quantitative data collection

Data is a set of facts that are collected, observed or generated. Data that you gather may come from primary sources or from secondary sources. Typically, data that you collect is raw data that must later be analysed and interpreted to produce useful information.

Primary sources of data provide direct or firsthand evidence about some phenomenon, such as a research investigation. Your completed logbook will be a primary source of data about pursuing an investigation into your research question.

FIGURE 14.16 Recording data is vital in investigations



Secondary sources of data are comments on, or summaries and interpretations of, primary data. Sources of secondary data include review articles in newspapers and popular science magazines in which other individuals summarise and comment on the research of others.

Qualitative and quantitative data

Qualitative data (or **categorical data**) is expressed in words. It is descriptive and not numerical and can be easily observed but not measured. Bar graphs or pie graphs are often used to display the frequencies of categorical variables.

There are two types of categorical data.

1. *Ordinal data* can be ordered or ranked such as ionisation energies (1st, 2nd, 3rd) or opinion polls (strongly agree, agree, disagree, strongly disagree)
2. *Nominal data* cannot be organised in a logical sequence such as the types of sub-atomic particles (proton, neutron or electron) and the colour litmus paper turns when exposed to an acid or base.

Quantitative data (or **numerical data**) can be precisely measured and have values that are expressed in numbers. Line graphs or scatterplots are often used to display the frequencies of numerical variables.

There are two types of numerical data.

1. *Continuous data* can take any numerical value, such as the temperature of a substance or the concentration of a solution.
2. *Discrete data* can only take on set values that can be counted, such as the number of protons in an atom or the number of electron shells.

Table 14.5 shows examples of how some attributes can be expressed both qualitatively and quantitatively.

TABLE 14.5 Examples of data types

Attribute	Qualitative	Quantitative
Length of pendulum	Long	52 cm
Colour	Green	520 nm
Sound	Loud	85 decibels
Speed	Fast	120 kph
Temperature	Hot	100 °C
Gravitational force	Strong	$9.807\ m/s^{-2}$

When collecting data, it is vital to consider what is most appropriate for your investigation. Normally, the best evidence is primary quantitative data, and for a majority of your investigations this is what should be collected and recorded. However, while preferred, it is sometimes not always possible to collect quantitative data. In this case qualitative data can be collected instead. Qualitative data can be quite subjective or open to interpretation (one student may say dark, another may say dark blue and a third student may say black), so it is important to make sure that the data you collect and record is clear and as detailed as possible.

In terms of primary data collection, it is important that results are carefully checked to make sure that recorded data is correct. Many people interpret measurements slightly differently, or use the wrong units, so make sure you are double checking data. All your collected data should be recorded in your logbook — note down all observations (usually in a table). You may find noting down both the qualitative and quantitative data gives the clearest detail for your investigation.

14.4.3 Choosing techniques relevant to an investigation

It is important to select techniques that will best suit your investigation. You should consider the techniques used in experiments investigating topics similar to your own, and the construction and evaluation of devices used in these experiments.

When selecting appropriate techniques, it is important to ensure the following:

- the technique can be performed in an appropriate time frame
- the technique is appropriate to your investigation and serves a purpose to answering the question and supporting or rejected your hypothesis
- the data is easily recorded, measured and interpreted, with a particular emphasis on quantitative data
- the technique can be safely performed. This is particularly important in a school where health and safety restrictions are closely regulated.
- the equipment used in the technique is available and cost effective — if it is not available in a school, can it be used with permission at other locations?
- the technique allows for the control of other variables — if there are too many factors that cannot be controlled, the technique is not a good choice for an investigation.

Selecting your measuring instruments

You should consider the most appropriate equipment to use for the purposes of your investigation. For example, if a liquid volume of 25 mL is required, what would be the most appropriate piece of equipment to measure it? If a high-precision measurement is required (i.e. a lower uncertainty), a 25.00 mL pipette would probably be used. However, if this level is not required, a measuring cylinder or even a 100 mL beaker might be more appropriate.

Your school will have a range of measuring instruments, which will vary in precision and ease of use. You won’t always need to use the most accurate instrument. A simple instrument that allows for quick measurements will be enough more often than not. Sometimes a simple stopwatch is just as good as an electronic timer, or a voltmeter may compare well to a more accurate multimeter.

FIGURE 14.17 Different types of measuring equipment vary in precision

Some instruments that you might consider are as follows, listed based on what they measure.

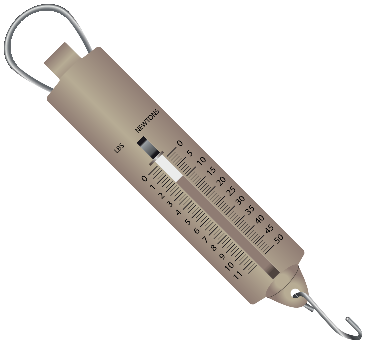
Mass

- *Beam balance:* accurate with a large range of values; can be time-consuming to measure several masses

FIGURE 14.18 Beam balance

- *Spring balance:* quick to use; covers a large range of masses; not very accurate

FIGURE 14.19 Spring balance



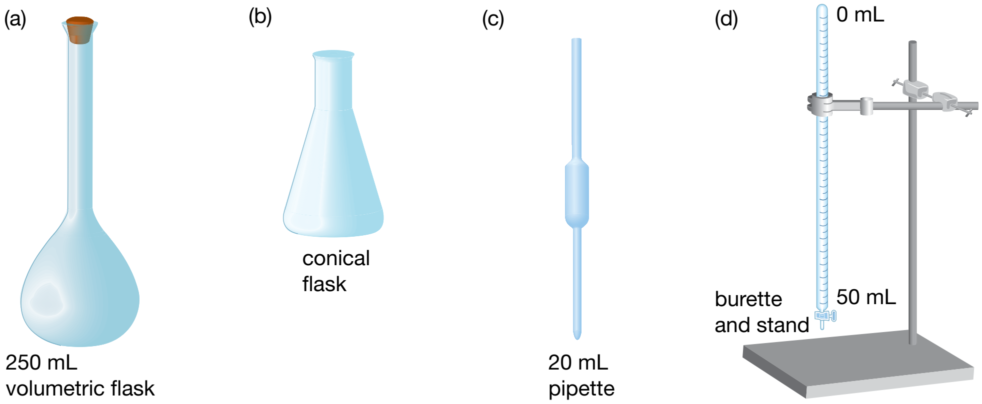
- *Top-loading balance:* very accurate; very good for small masses; simple to use. With equipment set up above the balance, it can be used to measure small variations in attractive and repulsive forces such as magnetic force, electric force and surface tension. If the balance sits on a laboratory jack, force against distance can be easily measured.

FIGURE 14.20 Top-loading balance

pH and concentrations

- *Titrations:* determine the concentration of a solution, particularly through acid-base titrations

FIGURE 14.21 Equipment used in titrations. (a) A volumetric flask is used to prepare a standard solution. (b) A conical flask holds the solution of unknown concentration. (c) A pipette is used to add the unknown solution to the conical flask. (d) The burette holds the standard solution, which is added ot the conical flask.



- *pH meter:* Measures pH accurately, but can easily break if not maintained or stored correctly.
- *Litmus paper:* Allows for a quick visual to determine if a solution is acidic or alkaline
- *Universal indicator:* Allows for an easy visual representation to determine the approximate pH of a solution.

Time

- *Stopwatch:* simple to use; accurate down to your response time; not reliable for short time intervals
- *Electronic timer:* requires some instruction; very accurate; best suited for short time intervals; can be used with electrical contacts and photogates

Electrical

- *Meters:* includes voltmeters, ammeters, galvanometers, etc; easy to set up, but care is needed to ensure the meter is wired into the circuit correctly, otherwise the meter can be damaged; large range of values; usually analogue displays

FIGURE 14.22 Voltmeter

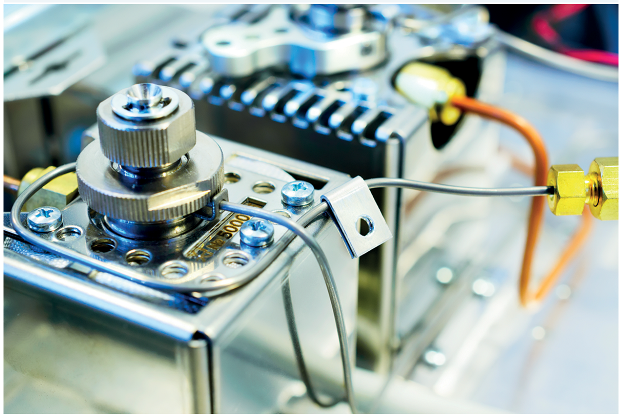
- *Multimeters:* easy to set up; more tolerant of incorrect use, but can be damaged if incorrectly connected to a high current; large range of values; usually digital displays

Specialised equipment

You may also have access to some specialised equipment, which you may use in your practical investigation. These are unlikely to be available in a general school laboratory, but it is important to note that the following equipment is all highly accurate and precise. Discuss with your teacher if any of these are available for use at your school or nearby. Alternatively, you may wish to explore these as a point of discussion when discussing uncertainties and possible errors in the data and results you obtained.

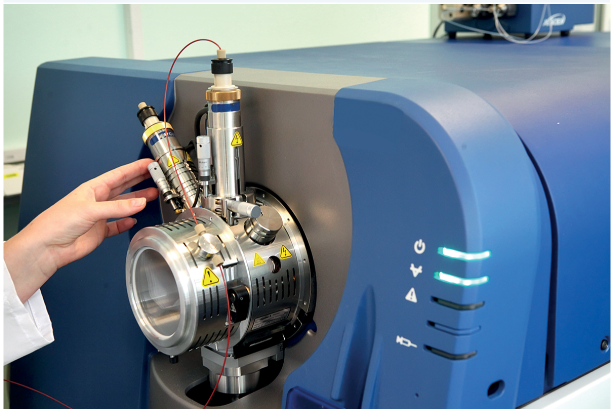
- *Gas chromatograph:* a sample is injected and it measures the content of various components in a sample

FIGURE 14.23 Gas chromatograph



- *Mass spectrometer:* an analytical instrument that determines the relative isotopic masses of the different isotopes of an element and abundance

FIGURE 14.24 Mass spectrometer

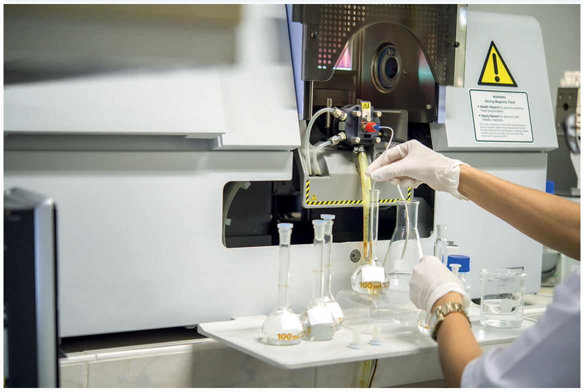


- *Solution calorimeter:* used to find energy change occurring in aqueous solutions

FIGURE 14.25 Solution calorimeter

- *Bomb calorimeter:* used to determine the energy change for reactions involving gases
- *Atomic absorption spectrometer:* absorption of light to measure concentrations of metal ions.

FIGURE 14.26 Atomic absorption spectrometer



- *HPLC (high-pressure liquid chromatography):* used to measure the concentration of organic substances.

FIGURE 14.27 HPLC

14.4.4 Precision, accuracy, reliability and validity

For your investigation, it is important to carefully consider the data you obtain and the confidence you can have in the conclusions drawn. Understanding the precision and accuracy of your data is important to ensure your findings are both reliable and valid.

Precision

Precision refers to how close multiple measurements of the same investigation are to each other. Results that are precise may not be accurate. It is often difficult to have completely precise results due to random error.

Table 14.6 shows two investigations by different students. Student 1 has more precise results, because the range of their measurements is much smaller when compared to Student 2.

TABLE 14.6 Two investigations by different students measuring the point in which water boils.

Investigation by student 1		Investigation by student 2	
	Temperature (°C)		Temperature (°C)
Trial 1	98.5	Trial 1	100
Trial 2	98.6	Trial 2	102
Trial 3	99	Trial 3	95
Trial 4	98	Trial 4	99
Trial 5	99.2	Trial 5	106

FIGURE 14.28 Results vary in precision when recording temperature

Accuracy

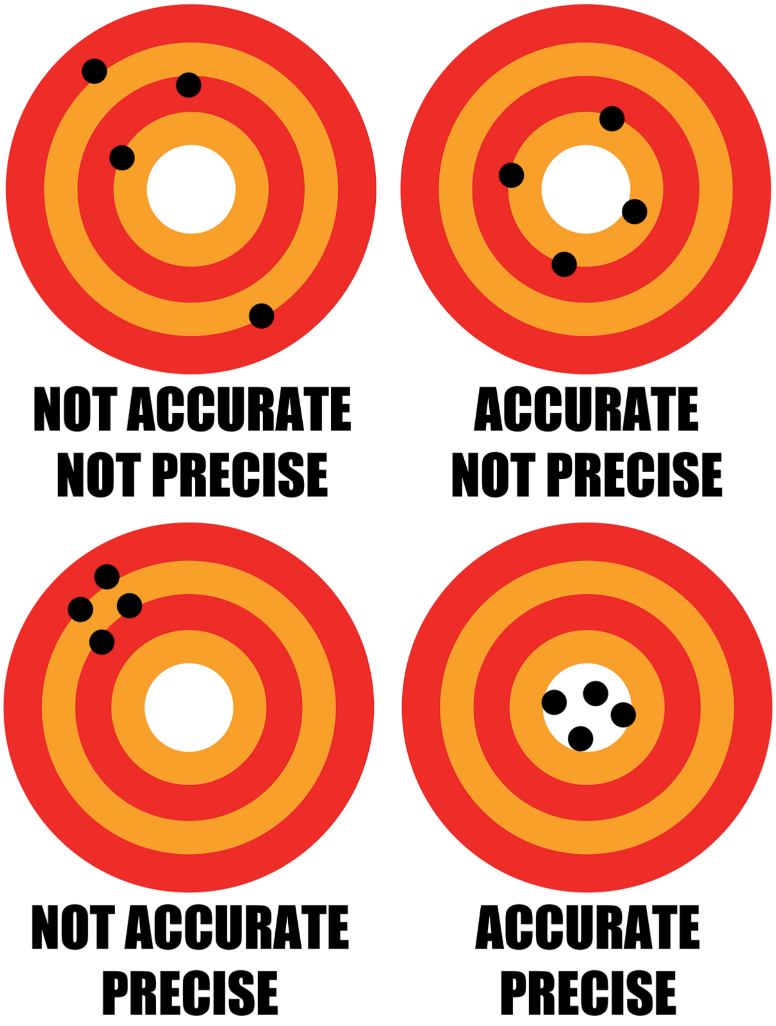
Accuracy refers to how close an experimental measurement is to a known value. If an archer is accurate, their arrows hit close to the target. Consider an experimental calculation of the boiling point of water, which is known to be 100 °C. A student who obtained a experimental value of 99 °C is more accurate than a student who obtains a value of 105 °C.

TABLE 14.7 Two investigations by different students to determine the boiling point of water.

Investigation by student 1		**Investigation by student 2**	
	Temperature (°C)		Temperature (°C)
Trial 1	100	Trial 1	95
Trial 2	102	Trial 2	94.8

In table 14.7, student 1 has the most accurate result. However, Student 2 has the most precise results. In order to obtain the best experimental data, we want results that are both accurate and precise.

FIGURE 14.29 Comparing precision and accuracy



SAMPLE PROBLEM 3

Students conducted an experiment to determine the temperature of a substance as it changed from a solid to a liquid. They repeated the experiment 4 times and achieved the following results:

Student 1: 56.5 °C; 58.0 °C; 60.0 °C; 55.0 °C
Student 2: 60.5 °C; 61.0 °C; 60.5 °C; 62.0 °C
Student 3: 56.5 °C; 58.5 °C; 57.0 °C; 56.0 °C

Students were then provided with the exact value of the melting temperature of the substance, which was found to be 56.48 °C.

a. **Which student had the least accurate data?**
b. **Which student had the least precise data?**
c. **Was the student with the most precise data also the student with the most accurate data? Explain your answer.**

Teacher-led video: SP3 (tlvd-0218)

THINK	**WRITE**
a. **1.** Review what accuracy means.	Accuracy refers to how close a measurement is to a known value.
2. Explore the data of the three students.	Student 1 had data 1.48 °C lower and 3.52 °C higher than the actual data Student 2 had data that was up to 5.52 °C higher Student 3 had data that was 0.48 °C lower and data that was 2.02 °C higher
3. Determine which student had the least accurate data	Student 2 had the least accurate data, as their values were the furthest away from the actual value
b. **1.** Review what precision means.	Precision refers to how close multiple measurements of the same investigation are to each other.
2. Explore the data of the three students.	Student 1 had a data range of 5.0 °C Student 2 had a data range of 1.5 °C Student 3 had a data range of 2.5 °C
3. Determine which student had the least precise data	Student 1 had the least precise data
c. **1.** Identify the students with the most accurate and most precise data	Using the results from **a.** and **b.** it can be seen that Student 3 had the most accurate data and Student 2 had the most precise data
2. Respond to the question and explain your answer	The student who had the most precise data was not the same student who had the most accurate data. Students may have measurements very close together (precise), but it may not be accurate. This may be to errors in their measuring device or their interpretation of the melting point (when the solid is a liquid). Data may also be accurate without being precise- you can be close to the target, but the readings are inconsistent. For reliable and valid results, data should be both accurate and precise.

PRACTICE PROBLEM 3

Students conducted an experiment to determine the temperature of a substance as it changed from a liquid to a gas. They repeated the experiment 4 times and achieved the following results:

Student 1: 85.4 °C; 92.0 °C; 82.0 °C; 75.5 °C
Student 2: 83.5 °C; 85.0 °C; 85.5 °C; 86.5 °C
Student 3: 85.5 °C; 90.0 °C; 89.50 °C; 81.0 °C

Students were then provided with the exact value of the boiling temperature of the substance, which was found to be 85.4 °C.

a. **Which student had the least accurate data?**
b. **Which student had the least precise data?**
c. **Was the student with the most precise data also the student with the most accurate data? Explain your answer.**

Reliability

Reliability refers to whether or not another researcher could repeat your investigation by following your method and obtain similar results. As well as this, the more times an experiment is replicated, the more reliable the results are considered to be.

Experiments that are reliable shouldn't just be able to be carried out by the investigator, but also by a third party. If a test is reliable, it usually has both accuracy and precision, because errors are reduced through repetition.

Validity

Validity refers to the credibility of the research results from experiments or from observations. Validity factors in both experimental design and implementation. Experiments that are valid are usually using the results from one manipulated variable, where other variables are controlled. It is also impacted by factors such as experimental bias.

Validity applies more to biology and psychology, where precise measurement is more difficult (and the misinterpretation of data is higher) and there is the risk of bias on the part of the researcher. In physics and chemistry, the variables are quantifiable and physically measurable.

If your experimental method clearly relates to the purpose of the investigation and you take care to be precise in your measurements and thorough in your analysis, your results should be valid and meaningful. Measurements that are valid must also be reliable, and therefore must have accuracy and precision.

Validity can be:

- *Internal:* Internal validity focuses on if the results can be believed and haven't been impacted by other variables (as they were properly controlled). Did the experiment measure the variable that was being examined in the experimental question and outlined in the hypothesis?
- *External:* This does not often apply in chemistry, but is the idea that results obtained when using a sample should be indicative of the results expected for the entire population. This is often more prevalent in drug trials and making sure that a varied and large sample size is used.

Measurements that are valid must also be reliable, and therefore must have accuracy and precision.

14.4.5 Minimisation of experimental bias

Bias is an intentional or unintentional influence on a research investigation as a result of systematic errors introduced by the researcher into the sampling or the testing procedures of an experiment. These biases will prejudice the research findings and raise questions about their validity and reliability.

There are numerous types of bias in experiments, some of which apply more to chemistry compared to others. These include:

- *Measurement bias* occurs when experimenters manipulate results in order to get a desirable outcome. Sometimes this can be unintentional (if an experimenter consistently records the boiling point earlier than they should, leading to a lower recorded temperature), but often it is through the deliberate actions of an individual.
- *Selection bias* can arise when test subjects are not randomly assigned to the experimental and control groups.

  An example of selection bias is in clinical trials of a new synthetic drug. A doctor may choose their family members to receive a drug being tested and have individuals they don't know receive a placebo. Selection bias can be minimised by randomly and equally allocating subjects to each group.
- *Sampling bias* can arise if the subjects chosen for the study are not representative of the target population. If this occurs, the research results cannot be generalised to that population.

  For example, the average height of students at a school is calculated, but due to time constraints only 50 out of the 600 students are measured. If only Year 7 students were measured, the results will not be representative of the target population and is an example of sampling bias. Sampling bias can be minimised by ensuring that the participants in the study are a reasonable representation of the target population.
- *Response bias* arises when only certain members of the target population respond to an invitation to participate in the clinical trial, resulting in an unrepresentative sample of the larger population.

  Similarly to sampling bias, response bias can be minimised by ensuring that the subjects in the study are a reasonable representation of the target population.

FIGURE 14.30 Selection bias

FIGURE 14.31 Sampling bias

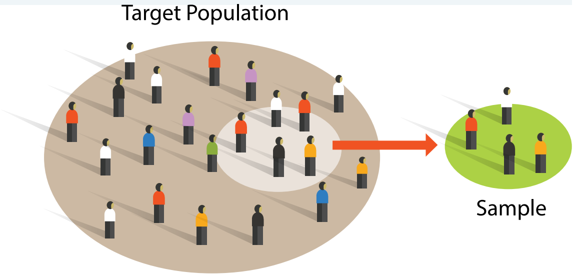


FIGURE 14.32 Response bias

14.4 EXERCISE

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1. Distinguish between validity and reliability.
2. Is it essential that the results of an experiment can be replicated in order for the experiment to be considered reliable? Explain your answer.
3. Give an example of when results would not be considered reliable.
4. Under what circumstances can it be said that the conclusions or findings of research are valid?
5. List two procedures that could adversely impact on the internal validity of an experiment.

6. Explain, how an experiment can be reliable but not valid, and why an experiment that is valid must also be reliable.
7. Explain, with examples, the difference between precision and accuracy.
8. Give an example of a strength and a weakness of quantitative and qualitative data.

Fully worked solutions and sample responses are available in your digital formats.

14.5 Ethics, and health and safety guidelines

KEY CONCEPT

- Ethics of and concerns with research, including identification and application of relevant health and safety guidelines

KEY SCIENCE SKILL

- Comply with safety and ethical guidelines

14.5.1 Ethics

Ethics determine acceptable and moral conduct. They do not just apply to scientific investigations, but also to many aspects of life, guiding us between what ‘right’ and what is ‘wrong’.

Science interacts with ethics in several ways, including:

- The way an experiment is conducted
- Confidentiality and conduct with research
- Conflicts with religious and personal beliefs.

Ethical standards and considerations also apply to any type of research or data collection method involving people or animals. They are particularly obvious in drug trials, using both animal testing and human trials. It is important that individuals involved in drug trials give permission and know of all possible side effects and risks associated with treatments. The confidentiality of participant answers must also be ensured when individuals are taking part in a survey.

It is important to be mindful of individuals with regard to personal beliefs. While drug trials have minimum ethical standards for the use of animals in trials, for some individuals, differing personal beliefs may impact experimentation and interpretation of data. This is an ethical consideration that needs to be evaluated and understood when teaching and reporting on these topics.

FIGURE 14.33 Ethics are involved in moral choice

14.5.2 Health and safety guidelines

Part of the enjoyment of a practical investigation is that the topic may be unconventional or use an innovative method. However, such situations can present some risk, so special care needs to be taken to ensure the safety of yourself and others.

General safety rules

Some general safety precautions will help to ensure that you and others are not injured in the laboratory.

- Wear protective clothing. This might include a laboratory coat, safety glasses and gloves.
- Be aware of the position of safety equipment such as the fire blanket, fire extinguisher, safety shower and eye wash.
- Ask your teacher if you are unsure how to operate equipment or how to use apparatus.
- Read labels carefully to confirm contents and concentration of chemicals.
- Clean and return all equipment to the correct places ensuring lids are placed back on containers when not in use.
- Check for the correct disposal of equipment and chemicals, including damaged equipment (i.e. broken glassware).
- Read instructions carefully before commencing an experiment.
- Prepare a **risk assessment** for required chemicals and equipment.
- Do the investigation as outlined in your approved plan. Don’t vary your plan without approval from your teacher.
- Don’t do experimental work unsupervised unless you have prior approval from your teacher.
- When first setting up electrical experiments, ask your teacher to check the circuit.
- Don’t interfere with the equipment set-up of others.

It is important to address health and safety concerns through the use of a risk assessment. This is a procedure for identifying hazardous chemicals, what the risks are and how to work safely with them. It also assesses potential hazards with equipment being used and standard handling procedures to ensure health and safety of individuals and the environment.

Risk assessments should also take into consideration the correct disposal of equipment and chemicals to adhere to safety and bioethical guidelines. Many chemicals are harmful to the environment, so correct disposal is paramount. Table 14.8 lists the usual requirements for a written risk assessment.

TABLE 14.8 Requirements for a written risk assessment

Section	Details
Outline of investigation	Title, date and location of task
Summary of method	Brief list of steps indicating how the chemicals and equipment will be used
Equipment/chemicals used	List of materials used in the experiment
Equipment/chemical risk and hazards	List of hazards associated with the equipment
Risk control measures	General precautions taken to limit risks

An example of a risk assessment is shown in figure 14.34.

FIGURE 14.34 (a) Risk assessment (b) GHS pictograms that can be found through risk assessments to visually show any possible hazards

ACTIVITY	Cross-linking an addition polymer to make slime

SUMMARY OF EXPERIMENT	
AIM	To investigate how the properties of a linear polymer may be altered by the introduction of weak cross-linking between its chains.
METHOD	1. Pour the polyvinyl alcohol into the beaker and add a few drops of the food dye (optional). 2. Add the borax solution and stir with the paddle pop stick. It will take a few minutes for the slime to appear. 3. Perform tests on the product that will enable you to describe its properties and how these are different to the original polymer.

PROTECTIVE MEASURES

GLASSES	GLOVES	DUST MASK	LAB COAT	FUME HOOD
x	x		x	

SAFETY INFORMATION

REACTANT

Polyvinyl alcohol (solution, 6%)

Hazards	Safety precautions
• Flammable • Irritating to the eyes 	• Wear gloves, safety glasses and a lab coat • Keep away from sources of ignition • Use in well-ventilated areas

FIRST AID	
SWALLOWED	Rinse mouth out with water immediately and repeat until all traces are removed. Seek medical attention.
EYE	Flush out with water. Seek medical attention if pain or irritation persists
SKIN	Wash with soap and water
INHALED	Move into fresh air, give oxygen if required. Seek medical attention if breathing is difficult

REACTANT

Borax (sodium tetraborate, solution, 4%)

Hazards	Safety precautions
• Not classified as hazardous substance at the concentration used • However, at concentrations above 4.5%, may damage fertility and unborn child 	• Wear gloves, safety glasses and a lab coat • Should not be handled by pregnant women. Those of reproductive age should also avoid the chemical. • Wash hands after use, even if gloves were worn

FIRST AID	
SWALLOWED	Rinse mouth out with water immediately and repeat until all traces are removed. Seek medical attention.
EYE	Flush out with water. Seek medical attention if painor irritation persists
SKIN	Wash with soap and water. Seek medical attention if pain or irritation persists
INHALED	Move into fresh air, give oxygen if required. Seek medical attention if breathing if difficult

EQUIPMENT

Beaker

Hazards	Safety precautions
• Glass may break leading to cuts and damage to eyes and skin	• Do not use damaged or cracked equipment • Sweep up any broken glass, being aware of any chemical residue

CONCLUSION

- Wear glasses, gloves and a lab coat for the duration of this experiment
- Ensure all equipment has been maintained and checked for damage before use
- Make sure that the area is well-ventilated

Signed: ______________________________

Date: _______________________

14.5 EXERCISE

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1. Research and identify possible hazards and suggest safety precautions for the following equipment and chemicals.
   (a) 0.5 mol L^{-1} of sodium hydroxide
   (b) Beaker
   (c) Methane
   (d) Bunsen burner
2. Provide two examples of when ethics may be important in a chemistry investigation.
3. List three purposes of a risk assessment.
4. What other things do you think should be added to a risk assessment?
5. Look around your laboratory and note its safety features and equipment.
   (a) Draw a plan of your laboratory and label the positions of safety equipment.
   (b) Does it have any foam fire extinguishers? How are these identified? On what types of fire can these be used and on what types of fire should they not be used?
   (c) Does it have any dry chemical or dry powder extinguishers? How are these identified? On what types of fire can these be used and on what types of fire should they not be used?
   (d) Are then any other fire extinguishers you can see? What are they used for?
   (e) Where is/are the fire blanket(s) located? Describe a scenario in which a fire blanket would be used and how you would use it.
   (f) Where are the master (emergency) shut-offs for gas and electricity located?
6. The Safety Data Sheet (SDS) for a chemical to be used in an experiment contains the following risk phrases.
   - Irritating to eyes/skin
   - Flammable
   - Vapours may cause dizziness

   Suggest appropriate methods to reduce these risks.

Fully worked solutions and sample responses are available in your digital formats.

14.6 Methods of organising, analysing and evaluating primary data

KEY CONCEPT

- Methods of organising, analysing and evaluating primary data to identify patterns and relationships including identification of sources of error and uncertainty, and of limitations of data and methodologies

KEY SCIENCE SKILLS

- Conduct investigations to collect and record data
- Analyse and evaluate data and methods

14.6.1 Organising primary data

Scientists gather raw data or plain facts from their observations, and this data must be recorded at the time in a suitable form (e.g. text entries, sketches, tables and diagrams in logbooks or in field notebooks). These may be supplemented by audio and video recordings.

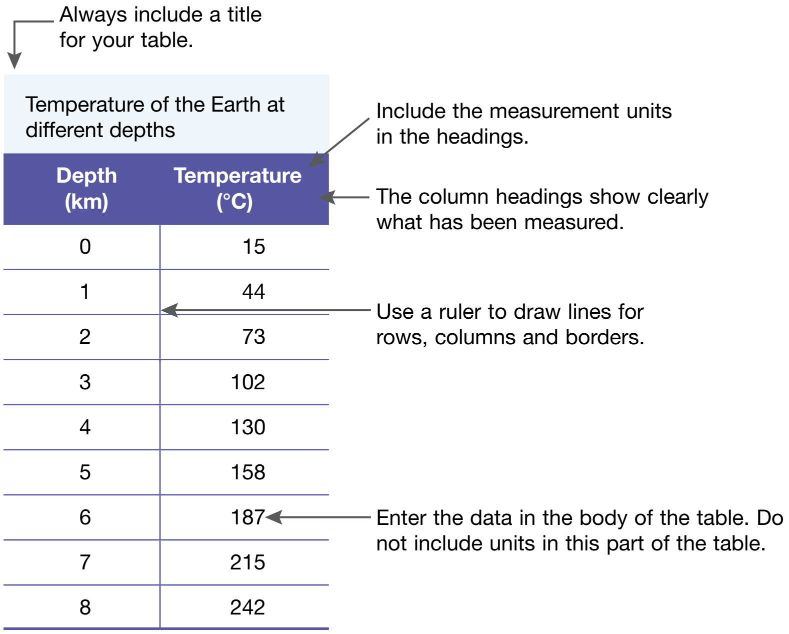
FIGURE 14.35 Using logbooks is an easy way to organise data

Using a table

Tables should be used when you initially record data to help separate and organise your information. All tables should:

- have a heading
- display the data clearly, with the independent variable in the first column and the dependent variable in later columns.
- include units in the column headings and not with every data point
- be designed to be easy to read. If a table becomes too complicated, it is better to break it down into a number of smaller tables.

FIGURE 14.36 Format on a scientific table



Always include a title for your table.

Temperature of the Earth at different depths

Depth (km)	Temperature (°C)
0	15
1	44
2	73
3	102
4	130
5	158
6	187
7	215
8	242

Include the measurement units in the headings.

The column headings show clearly what has been measured.

Use a ruler to draw lines for rows, columns and borders.

Enter the data in the body of the table. Do not include units in this part of the table.

Using a graph

Presenting results as a graph makes it easier to see patterns and trends in your data, allowing more accurate result analysis. While you will usually use a table to record results in your logbook, displaying your data as a graph is preferred on your scientific poster.

When drawing graphs:

- decide on the type of graph to be used. Different types of information are better suited to different types of graphs. If both the independent and dependent variables are quantitative, a line graph or scatterplot is preferred. Bar graphs are used when one piece of data is qualitative and the other is quantitative. Histograms are used when intervals and frequency are being explored.
- include a title — this should link the dependent and independent variables that are shown in the graph.
- in most graph types (excluding pie graphs), the independent variable should be on the horizontal (x) axis, and the dependent variable on the vertical (y) axis.
- axes should be ruled and clearly labelled. Those displaying numerical variables should have a clearly marked scale and units.
- make sure your scale is suitable and the numbers are evenly distributed
- use a line (or curve) of best fit as required. This is a smooth curve or line that passes as close as possible to all the plotted points.
- include the origin, the zero value for the variables, on both axes. If required, you can use a an axis break symbol if all the values you are plotting are clustered around high value, as seen in figure 14.37a.

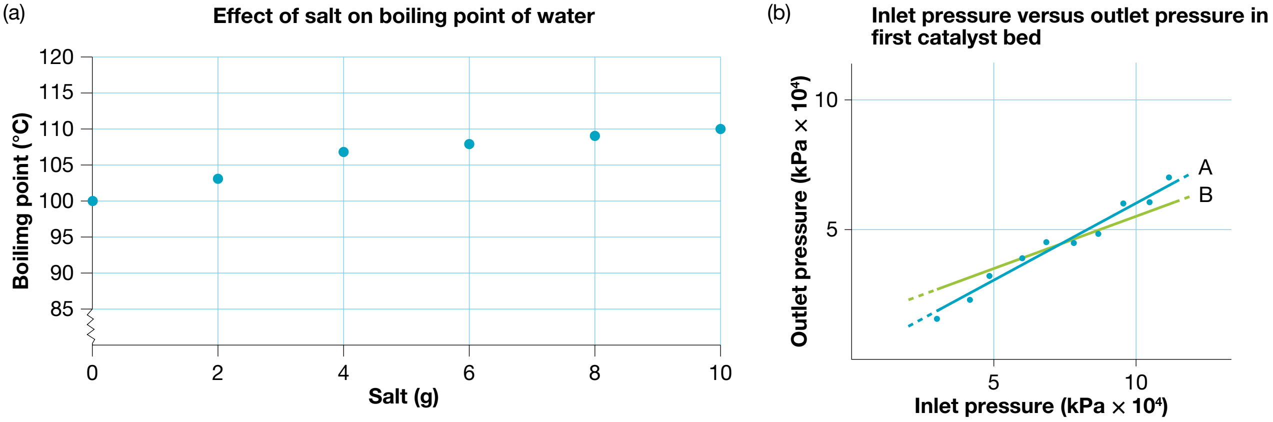
The most common graphs you will use in chemistry include:

- scatterplots
- bar/column graphs
- line graphs
- histograms.

Scatterplots

Scatterplots require both sets of data to be numerical. Each dot represents one observation, recorded in regards to the independent and dependent variable. A scatterplot can easily show trends between data sets, and correlations can be seen.

FIGURE 14.37 (a) Example of a scatterplot and (b) a scatterplot with a line of best fit



DRAWING A LINE OF BEST FIT

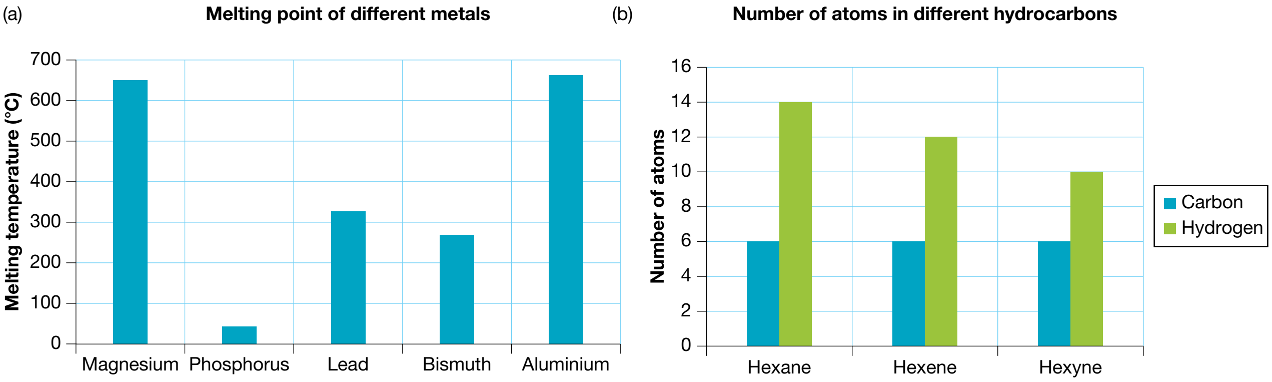
A **line of best fit** can be used to show the general trend of data and provides a quick summary. Figure 14.37b shows that line A, although not passing through any points, is a better fit than line B.

The line of best fit doesn't need to pass through each data point. Although you should try to draw the line through each error bar if possible, you may not be able to go through all of them. As a general rule, try to have as many data points above your line as you have below. Don't assume your line must pass through the origin. For some data, a curve of best fit may be more appropriate.

Bar graphs

Bar (or **column**) **graphs** are often used when one piece of data is qualitative and the other is quantitative. The bars are separated from each other. The horizontal axis has no scale because it simply shows categories. The vertical axis has a scale showing the units of measurements. Bar graphs can also be used to compare two sets of data by using side-by-side bars, as shown in figure 14.38b.

FIGURE 14.38 (a) Bar graph showing differences in melting points of different metals and (b) a side-by-side bar chart comparing the number of hydrogen and carbon atoms

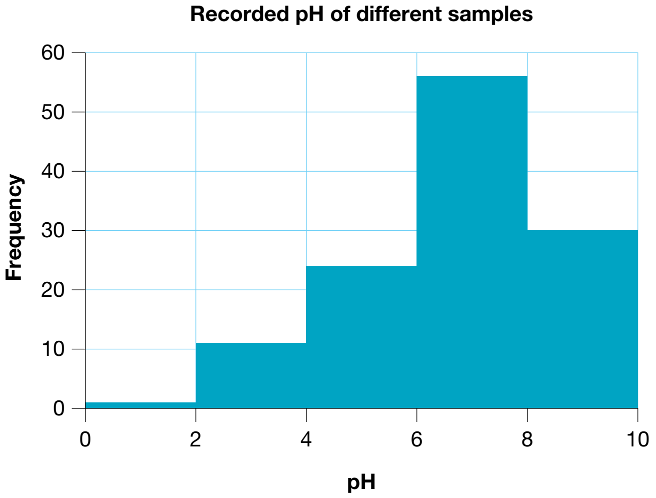


Historgams

Histograms are a special kind of bar graph that show continuous categories, and are often used when examining frequency. The bars are not separated.

In figure 14.39, the exact values cannot be determined, because data is displayed in intervals. It can be seen that there were 30 samples that had a pH between 8 and 10 but we do not know what specific values these are.

FIGURE 14.39 Histogram showing frequency of pH of different samples



Line graphs

Line graphs involve a series of dots that represent the values of a variable. The dots are usually joined using a straight line (this is different to a line of best fit, in which the line is straight and does not have to go through each point), but sometimes the line is curved.

Line graphs are often used to show changes over a continuous period of time, or over space. In particular, line graphs can identify patterns, trends and turning points in a dataset.

FIGURE 14.40 Setting up a line graph

1. Grid

Graphs should always be drawn on grid paper so values are accurately placed. Drawing freehand on lined or plain paper is not accurate enough for most graphs.

2. Title

Tell the reader what the graph is about! The title describes the results of the investigation or the relationship between variables.

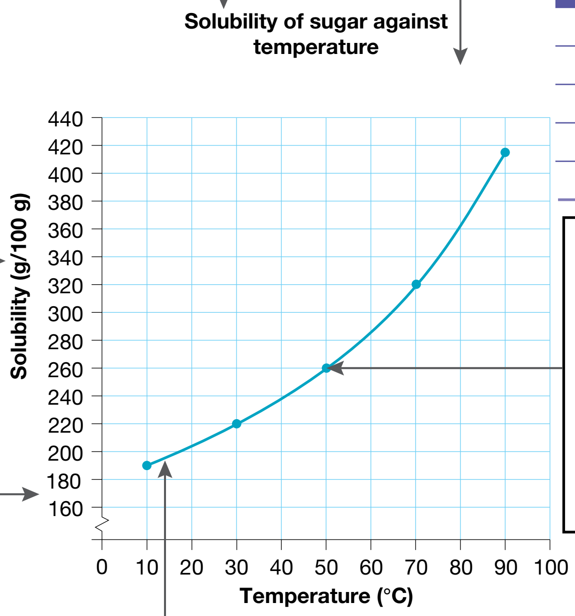
3. Setting up and labelling the axes

Graphs represent a relationship between two variables. When choosing which variable to put on each axis, remember that there is usually an independent variable (which the investigator chooses) and a dependent variable. For example, if students wish to find how solubility of sugar changes with temperature, they may choose to measure the solubility (in g/100g) every 20°. The temperature of each measurement was chosen by the students and is the independent variable. The solubility measured is therefore the dependent variable. Usually the independent variable is plotted on the *x*-axis and the dependent variable on the vertical *y*-axis.

After deciding on the variable for each axis, you must clearly label the axes with the variable and its units. The unit is written in brackets after the name of the variable.

Data table

Temperature (°C)	Solubility (g/100 g)
10	190
30	220
50	260
70	320
90	415



4. Setting up the scales

Each axis should be marked into units that cover the entire range of the measurement. For example, if the solubility ranges from 0 to 415 g/100 g then 0 and 440 g/100 g could be the lowest and highest values on the vertical scale. If measurements start above zero, as per the solubility measurements on the vertical axis, an axis-break symbol can be used. The distance between the top and bottom values is then broken up into equal divisions and marked. The horizontal axis must also have its own range of values and uniform scale (which does not have to be the same scale as the vertical axis). The most important points about the scales are:

- they must show the entire range of measurements (have an axis-break symbol if required).
- they must be uniform, that is, show equal divisions for equal increases in value.

5. Putting in the values

A point is made for each pair of values (the meeting point of two imaginary lines from each axis). The points should be clearly visible. Include a point for (0, 0) only if you have the data for this point.

6. Drawing the line

A line is then drawn through the points.

A line that follows the general direction of the points is called a 'line of best fit' because it best fits the data. It should be on or as close to as many points as possible. Some points follow the shape of a curve, rather than a straight line. A curved line that either touches all the points or conforms to a best fit can then be used.

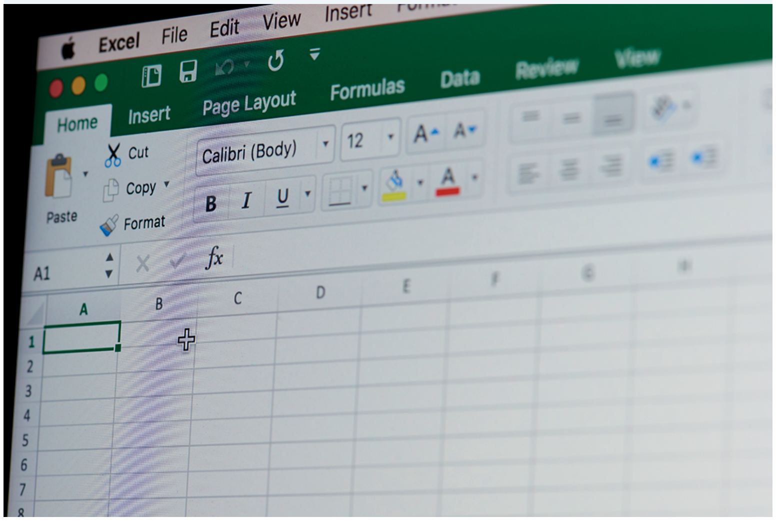
The type of data you graph may lead you to expect either a straight line or a curve. For example, you might expect the increase in temperature of water being boiled to be a straight line because the temperature increases at a steady rate. In this example, the solubility of a sugar with increasing temperature is a curve. Inspecting the data will help you decide whether your line should be straight or smooth and curved.

Using Microsoft Excel

While you may very carefully hand-draw your graph, being able to create digital graphs is important, especially for neat presentation on your poster. Excel is extremely helpful for this. It can:

- calculate any derived physical quantities, such as speed and acceleration of a parachute or the percentage of energy lost by a bouncing ball. The ‘Fill down’ command is a time saver.
- be a powerful graphing tool, but must be controlled by the user. You will have to select the type of graph, what aspects of your graph you want to show and the scale on the axis. You will also have to decide what label you want on your axis and whether you want the data displayed on the graphed points.
- generate a line of best fit. If you right-click on any data point, a window pops up with the option ‘Add Trendline’. This is the Excel command to create a line of best fit. Once selected, you have several choices. If your graph looks like a straight line, choose ‘Linear’.
- create error bars (in Excel all error bars are usually the same for each data point, rather than calculated separately which is the usual protocol).

FIGURE 14.41 Excel is a useful data tool



Resources

Interactivity Selecting a graph (int-7733)

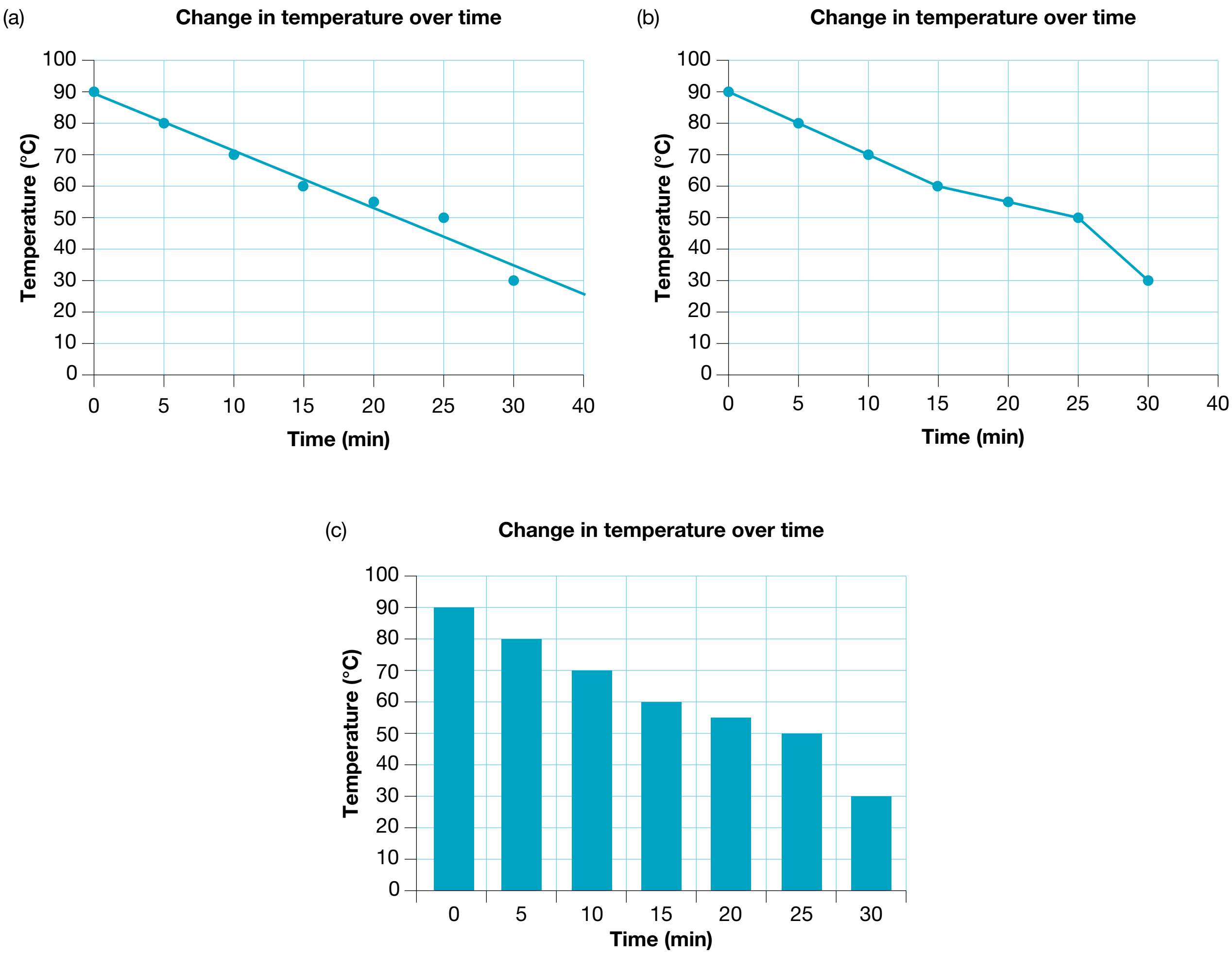
14.6.2 Analysing primary data

When analysing primary data, it is important to explore trends and patterns that can be seen. This may involve asking questions such as:

- Is there a clear positive or negative correlation in data? (One variable increasing in response to another increasing shows positive correlation, whereas one variable decreasing in response to another increasing is negative correlation).
- Are there any outliers (unusual data)?
- What results would you expect for specific data that you didn’t observe experimentally?
- Can you calculate the average for your data?

Analysis of your data often depends on the type of graph selected, because it alters the way trends and patterns are seen. The graphs in figure 14.42 show the same data presented in three ways.

FIGURE 14.42 Various graphs showing temperature change over time: (a) a scatterplot using a line of best fit, (b) a line graph and (c) a bar graph



Each of the graphs in figure 14.42 will be analysed in slightly different ways. From these graphs, you might draw the following information:

- Graph (a): There is a clear downwards trend (negative correlation) in data, as temperature decreases over time. However, at 25 minutes, the temperature is slightly higher than expected based on the line of best fit, and at 30 minutes, the temperature is slightly lower than expected.
- Graph (b): There is a clear downwards trend in data (negative correlation), as temperature decreases over time. The rate of temperature drop slows after 15 minutes, before the rate increases again between 25 and 30 minutes.
- Graph (c): There is a clear downwards trend in data (negative correlation), as temperature decreases over time. The temperature is lowest at 30 minutes, where it is half the temperature seen at 15 minutes.

The right graph is fundamental for data analysis. In this case, the representation of the data in Graphs a and b is far more powerful than that obtained from Graph c. Regardless, it is important to note down any clear trends and patterns seen in the data, and note down any outliers that can be seen.

Graph analysis can also be used to predict and make assumptions about data that was not gathered experimentally, but through interpolation (predicting data points within the data set that were not measured) or extrapolation (predicting data points outside data set based on predicted relationship). Based on the graphs you might estimate:

- The temperature at 35 minutes
- The temperature at 13 minutes
- The time that the temperature was 45 °C.

The estimation you make can vary greatly between all the graphs, so it is important to carefully consider which graph you use.

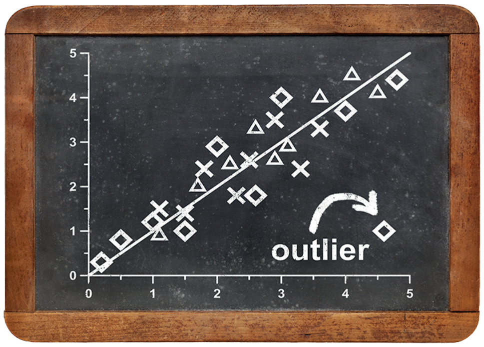
TABLE 14.9 Analysing data from different graph types

	Graph (a)	Graph (b)	Graph (c)
Temperature at 35 minutes (°C)	25	15	20
Temperature at 13 minutes (°C)	65	62	66
Time the temperature was 45 °C (mins)	24	27	26

Outliers

Outliers are results that are a long way from other results and seen as unusual. They should be accounted for and analysed, but are often not included when calculating averages.

FIGURE 14.43 Outliers in data are unusual results.



14.6.3 Evaluating primary data

When you evaluate your data, it is important to link back to the initial question of your investigation. It is important that you can explain and justify your data evaluation in relation to your question.

- Does the data provide an answer to the question?
- Does the data support or refute your hypothesis?
- If there are any outliers, errors or uncertainty in your data, why may these have occurred?
- Does your data link to correctly supported models and theories?
- Are there further improvements that you could make to improve your data in future investigations that may reduce errors or limitations?

The following are two examples of data evaluation by two different students, based on figure 14.42.

> *Student 1: The results show that temperature decreased.*
>
> *Student 2: Table 2 shows a clear decrease in temperature over time, dropping from an initial temperature of 90 °C to a final recorded temperature of 30 °C. While there is a clear trend in temperature decreasing over time, the rate of decrease was inconsistent, particularly between 25 and 30 minutes. This may be due to a decrease in external air temperature, causing the rate of heat loss through convection to change.*

It is clear that student 2 provided a more detailed response and based their evaluation on evidence and a link to theory. What else should they add?

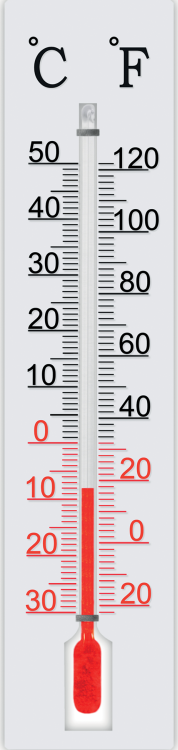
14.6.4 Sources of uncertainty and error

Understanding sources of **uncertainty** and error is vital in scientific reporting, accounting for the fact that the conclusions are being drawn from data that is not perfectly accurate or precise. Uncertainty and errors can appear in any experiment. Uncertainty is acknowledging that no matter how precise an instrument might be, there is a limit to that precision. The uncertainty is a range within which a measurement lies. An error bar is a way of representing that uncertainty graphically.

Errors, on the other hand, are differences between a measurement taken and the true value that is expected; errors lead to a reduction in the accuracy of the investigation.

Every instrument has a limit to how precisely it measures. The scale or digital display imposes a constraint on how many digits you can record, and also reveals the tolerance of the measurement. For example, there are both errors and uncertainties associated with using thermometers. Two individuals might look at it and not get the exact same result as they might have been standing at different angles or interpret the reading slightly differently. Or results might not be identical between two different thermometers. The thermometer only gives measurements to the accuracy of 1 °C and not decimal values. However, through careful observation, 0.5 °C can usually be observed by looking at the gaps between markings.

FIGURE 14.44 Thermometers can have issues with precision and accuracy.



Sources of error

Sources of error are the causes of errors found in experiments. Some of these are listed below.

- **Systematic errors** affect the accuracy of a measurement that cannot be improved by repeating an experiment. They are usually due to equipment or system errors and produce measurements that are consistently too high or too low. They include:
  - instrumental errors that arise because an instrument, such as a weighing balance, is uncalibrated and incorrectly set to zero
  - environmental errors that arise because of malfunctions, such as a power outage, that affect the conditions under which an experiment is being conducted.
- **Random errors**: Random errors are chance variations in measurements that affect the precision of measurements and are always present in measurements of continuous data.

  An example of a random error is an error of judgement when reading the smallest division on the scale of a measuring instrument, such as a ruler. Unlike systematic errors, this can usually be resolved with repetition of measurements.

It should be noted that so-called 'human errors' are not errors but mistakes that result from carelessness. Examples include gross misreading of an instrument, and writing the wrong result in your logbook, such as 40 instead of 4.0.

Measuring errors

It is important to consider the instrument you are using when you consider uncertainties and errors.

Reading measuring cylinders

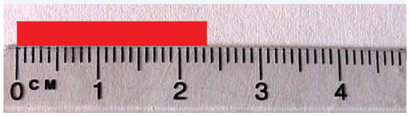
When measuring liquids, it is important to record from the bottom of the dip (the meniscus). What is the measurement in figure 14.45? Would every single individual correctly record this data?

FIGURE 14.45 Liquids should be measured from the bottom of the dip

Reading rulers

A metre ruler has lines to mark each millimetre, but there is space between these lines. You could measure a length to the nearest millimetre, but because of the space between the lines, if you look carefully, you can measure to a higher precision — to the nearest 0.5 mm.

FIGURE 14.46 Errors in rulers



The best estimate for the length of the red line in figure 14.46 is 2.35 cm. The actual length is closer to 2.35 cm than it is to either 2.30 cm or 2.40 cm. The measurement of 2.35 cm says the actual length is somewhere between 2.325 cm and 2.375 cm. The way to write this is:

$$\text{The length of the red line} = 2.35 \pm 0.025\,\text{cm}$$

The 0.025 represents the tolerance or uncertainty in the measurement (half of the precision that can be recorded).

Reading top-loading balances

If the reading on a digital scale is 8.94 g the mass is not 8.93 g nor 8.95 g. The actual mass is somewhere between 8.935 and 8.945 grams. In this example, the smallest unit of measurement is 0.01 g. Therefore the tolerance is half of this (0.005 g), as the measurement can be 0.005 g below or above the recorded measurement. The way to write this is:

$$\text{Mass} = 8.94 \pm 0.005\,\text{g}$$

FIGURE 14.47 Top-loading balances measure to a certain number of significant figures.

FIGURE 14.48 What is the tolerance in these measuring instruments?

SAMPLE PROBLEM 4

a. Record the reading on the scales shown in Figure 14.48(a) including the tolerance.
b. Record the reading on the thermometer shown in Figure 14.48(b) including the tolerance

Teacher-led video: SP4 (tlvd-0104)

THINK	WRITE
a. 1. Determine the reading on the scale	128.93
2. Determine the range of the measurement	The measurement can be between 128.925 and 128.935.
3. Determine the tolerance. One way to calculate the tolerance is to halve the smallest unit that can be measured.	0.01 g is smallest measurement possible. $\frac{0.01\text{g}}{2} = 0.005$
4. Record the reading including the tolerance.	128.93 ± 0.005 g
b. 1. Determine the reading on the scale.	47 °C
2. Determine the range of the measurement. In this case, you can tell if the thermometer is a 0.5 increment due to the gaps in the thermometer, so our range is smaller.	The measurement can be between 46.75 and 47.25
3. Determine the tolerance. The tolerance is half of the smallest unit that can be measured. The smallest unit is 0.5 °C.	$\frac{0.5\,°\text{C}}{2} = 0.25\,°\text{C}$
4. Record the reading, including the tolerance.	47 ± 0.25 °C

PRACTICE PROBLEM 4

a. Record the reading on scales, including the tolerance, that show a reading of 0.12 g.
b. Record the reading on scales, including the tolerance, that show a reading of 0.195 g.

Repeated measurements

Measurements of independent variables are usually precise and careful, so one measurement should be enough. However, measurements of the dependent variables are often prone to some variation.

Whether the variation is caused by the human reaction time when using a stopwatch, judging the rebound height of a basketball or, in the case of a parachute, the unpredictable way the canopy will open each time, each reading may be different. Therefore, it is sensible to take several readings to obtain an average. Three to five measurements would be needed, but more than five is generally unnecessary.

The following example comes from physics, but the graphing techniques equally apply to chemistry. If your partner dropped a basketball from a height of 80.0 cm, and you judged the rebound height of the ball for five trials as 68 cm, 69.5 cm, 68.5 cm, 68.5 cm and 69.5 cm, the average is 68.8 cm. You would round this to the nearest 0.5 cm because of the difficulty of judging a moving ball and achieve an average of 69 cm. This set of measurements would then be written as 69 ± 1 cm (the 1 cm is the furthest the measurement is from the average).

Graphing error bars

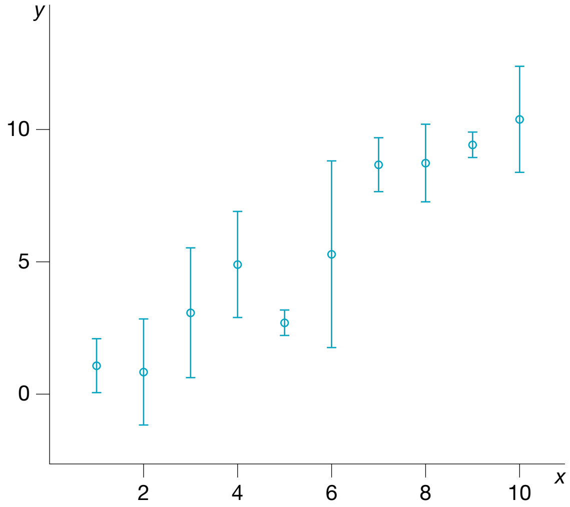
You can show variations in measurement on graphs using errors bars. These are lines above and below the graphed point so show the average variation — that is, the margin for error.

For the basketball experiment previously discussed, you will plot 69 cm on your graph. To represent the '±1 cm' variation, you can draw a line through the point, up 1 cm and down 1 cm, with a short line across the top and bottom of the line to make the ends evident.

Calculating error bars

Rather than graphing rebound height against drop height, it is more revealing of the physics of the situation to calculate and graph the ratio of the rebound height to drop height against drop height. The ratio is a measure of how much of the original gravitational potential energy is restored.

FIGURE 14.49 Error bars



In this case, the ratio would be $\frac{69}{80.0} = 0.8625$, but how many digits are we entitled to use and how big should the error bar be? The first question is reasonably straightforward. The number of digits in your answer should equal the smallest number of digits in the data you used in the calculation. In this instance, the average height has two digits, so the answer would be written as 0.86. You are not justified in including more digits because you don't know the original data accurately enough.

Working out the size of an error bar takes more effort. If the two pieces of data are 69 ± 1 cm and 80.0 ± 0.3 cm, we can just add the uncertainties to get ± 1.3 cm, but that doesn't make sense when the calculated value is 0.86. Dividing the uncertainties would produce another unusual result.

The method used is to first express the uncertainty for each data value as a percentage. For example:

$$\text{Percentage error of } 69 \pm 1\text{ cm} = \left(\frac{1}{69}\right) \times 100 = 1.4\%$$

$$\text{Percentage error of } 80.0 \pm 0.3\text{ cm} = \left(\frac{0.3}{80}\right) \times 100 = 0.4\%$$

Now add the two percentage errors together.

$$\text{Total percentage error} = 1.4\% + 0.4\% = 1.8\%$$

Use this total percentage error to find the error in the calculated answer.

$$\text{Error} = 0.86 \times 1.8\% = 0.016$$

This would be rounded to one digit as 0.02.

Therefore, the full calculated answer would be 0.86 ± 0.02.

on Resources

Video eLesson Calculating error (eles-2560)

14.6.5 Limitations of data and methodology

The data that is gathered from the experimental results will have **limitations**. Limitations arise from several sources that can affect the quality of the data.

- Experiments create artificial situations that do not necessarily represent real-life situations.
- While every effort may be made to identify controlled variables and keep them constant throughout the course of an experiment, it is not always possible to identify and control every one of this type of variable.
- The degree on which results obtained in the laboratory can be generalised to other situations and applied in the real world is limited.

It is important to consider limitations when analysing and drawing conclusions from data. Limitations should be factors that are out of your control, but need to be discussed in regards to how they might impact your results. As part of your practical investigation, you need to clearly outline limitations and possible suggestion on improvements to the method or data collection to avoid these.

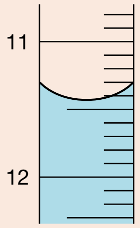
14.6 EXERCISE

To answer questions online and to receive **immediate feedback** and **sample responses** for every question go to your learnON title at www.jacplus.com.au

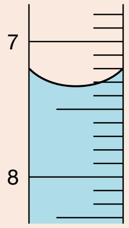
1. Describe the difference between a random and systematic error and provide two examples of each.
2. List two ways that you can minimise uncertainty in an investigation.
3. Identify which graph type would be most appropriate for the following investigations. Justify your choice:
   (a) Comparing the pH of different household liquids
   (b) Showing how pH changes with temperature
   (c) Measuring the temperature inside a car every 5 minutes for an hour
   (d) Showing the frequencies of different test mark intervals for 400 students
4. Using the provided data, construct an appropriate graph.

Time (mins)	Volume of ice cube (cm^3)
0	30
5	25
10	21
15	18
20	14
25	10

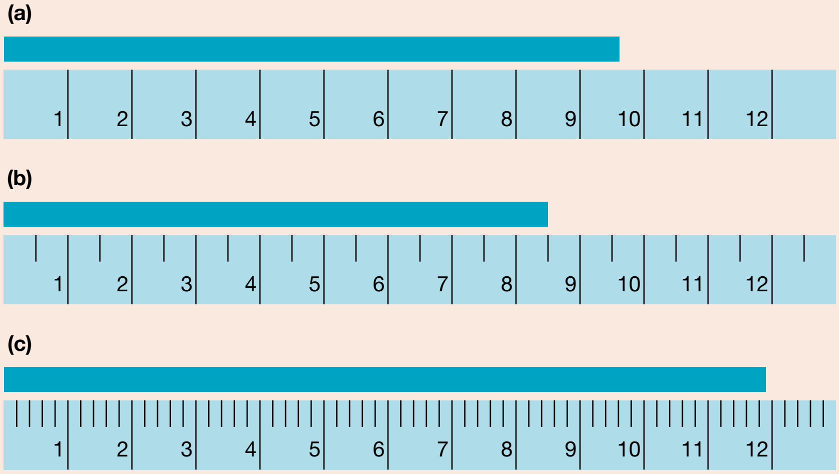
   Once you construct the graph, analyse and evaluate the data shown.
5. Describe how an outlier should be treated when analysing and evaluating data.
6. Record the reading on the burette in this diagram (remember the measurements on a burette go downwards, unlike in a measuring cylinder).



7. Explain why a student reading this burette as 8.67 mL is incorrect.



8. Determine the length of each line in the following diagram, showing the tolerance in each case.



9. A student is designing an experiment that involves measuring liquid volumes at various stages. A number of glassware items are available for this purpose, as shown in the following table.

	Item	Uncertainty (mL)
A	Volumetric flask (250 mL)	±0.1
B	Beaker (100 mL)	±10
C	Measuring cylinder (100 mL)	±0.1
D	Burette (50 mL)	±0.02
E	Conical flask (250 mL)	±25

Which item(s) would be most appropriate for:

(a) rinsing a burette with 10 mL of water

(b) producing 250 mL of a solution of accurately known concentration

(c) producing 250 mL of a solution of approximately known concentration.

Fully worked solutions and sample responses are available in your digital formats.

14.7 Models and theories to understand observed phenomena

KEY CONCEPT

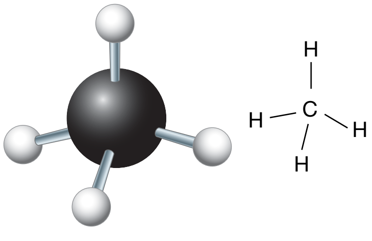
- Models and theories and their use in organising and understanding observed phenomena and chemical concepts including their limitations

Limitations exist in the models and theories that we use in chemistry. It is important to be able to use models and theories to allow us to understand a variety of observed phenomena, but to also understand the limitations in models and theories and that they may change over time.

14.7.1 Models

Models are representations of ideas, phenomena or scientific processes. They can be physical models, mathematical models or conceptual models. Models can provide a framework that explains observed phenomena and helps with the understanding of abstract concept. In chemistry, many concepts are hard to visualise, so models help contextualise the idea on a smaller and simpler scale.

FIGURE 14.50 Different models of methane, a gas involved the greenhouse effect. How do you think this differs from a 'real' methane molecule?

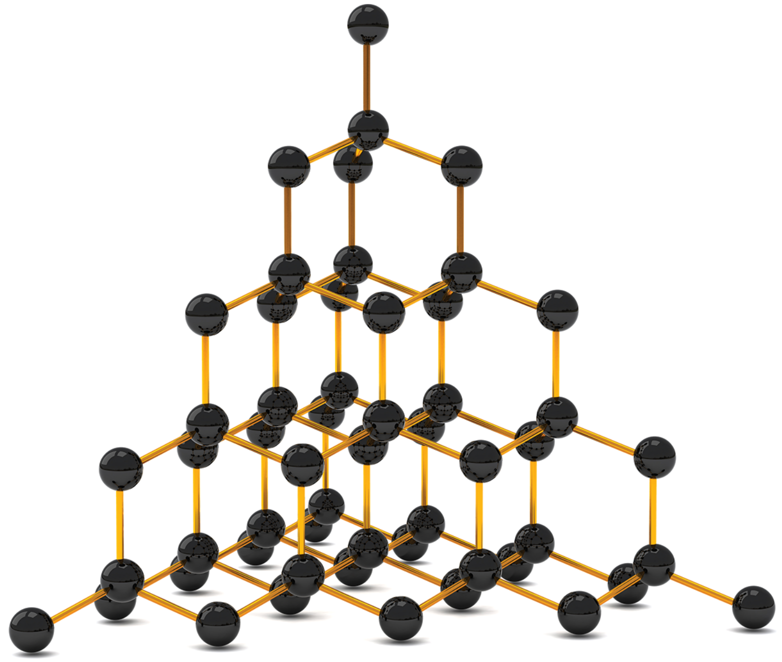


CH_4, methane

While they are very useful, models have their limitations. These include:

- Models cannot include all the details of the processes or the things that they represent because of the complexity of the processes
- Models are only approximations of the real world. For example, we can use ideal gas laws to make predictions about the behavior of gases, but this model is constrained by certain conditions, such as specific pressure and temperature. The model's predictions would not always match what happens in real-world situations. We can also model various lattices (as seen in figure 14.51) or bonding, but we often assume ideal conditions for temperature and pressure, which is not always a realistic model.
- Models have some limits in their accuracy and are often simplified and stylised. For example, a ball and stick model of methane (see figure 14.50) is useful, but it is a very highly simplified and stylised representation that reduces covalent bonds to sticks and atoms to solid balls.
- Models are based off current observations and knowledge at the time. This means that they aren't definite and can change as new observations and experiments allow for different ideas evolve. Models that we currently believe to be accurate will be disproven in the future.

FIGURE 14.51 A model showing the lattice of diamond



14.7.2 Theories

A **theory** is a well-supported explanation of a phenomena. It is based on the interpretation of facts that have been obtained through investigations, research and observations.

There are limitations that can exist with theories. These include:

- A reliance on theories rather than observations made during practical investigations. Often, individuals manipulate results to match a theory, failing to realise the power of observations. Often, theories are treated as perfect, when in fact, they are able to be disproven as new observations and evidence come to light.
- Theories often rely on a specific set of conditions to be met. For example, the Law of Conservation of Mass cannot be used in systems that are open systems (not isolated) or systems that involve very large amounts of energy.
- Often, a phenomenon needs to be described using multiple theories. Sometimes, aspects of theories contradict each other.

FIGURE 14.52 The flat Earth theory has been replaced by the idea that the Earth is spherical.

Theories can change seemingly overnight or can take a very long time to change. Theories that were once popular and widely accepted can be discarded when too much evidence builds up against them. They are replaced by a theory that better fits the observations.

Some examples of theories that have been superseded by other theories are:

- Miasma theory of disease — the idea that diseases were caused by bad air
- The Sun and planets orbit around the Earth (geocentrism)
- The flat Earth theory

How do refinements of existing theory come about?

Refinements of existing theory come about in a number of ways. These include:

- carefully planned laboratory-based or field-based experiments designed to support or refute a particular hypothesis
- critical reinterpretation of previously accepted facts, producing a new framework
- collection and analysis of new data
- identification and exploration of patterns or anomalies
- new technologies that allow for changes to understanding and more depth of knowledge.

14.7 EXERCISE

To answer questions online and to receive **immediate feedback** and **sample responses** for every question go to your learnON title at www.jacplus.com.au

1. Describe three ways in which models can be useful.
2. Describe three limitations of models.
3. What is the difference between a model and a theory?
4. How can theories help us understand phenomena?

Fully worked solutions and sample responses are available in your digital formats.

14.8 Nature of evidence and key findings of investigations

KEY CONCEPTS

- The nature of evidence that supports or refutes a hypothesis, model or theory
- The key findings of the selected investigation and their relationship to thermochemical, equilibrium and/or organic structure and bonding concepts

KEY SCIENCE SKILLS

- Analyse and evaluate data, methods and scientific models
- Draw evidence-based conclusions
- Communicate and explain scientific ideas

14.8.1 Nature of evidence — supporting or refuting a hypothesis, model or theory

Evaluating a hypothesis, model or theory uses the evidence from the results obtained in an investigation. In your investigation, it is important to understand how to best use evidence in order to correctly support or refute your hypothesis.

Evidence can be strong or weak, as summarised in table 14.10. It is vital that the evidence you choose allows the provision of strong and clear conclusions.

Strong evidence should:

- be based on facts derived from studies with high validity and minimal bias
- use data to support conclusions
- clearly link to the aim and hypothesis of an experiment
- be obtained from an investigation that has a reproducible and reliable method.

If the prediction from your hypothesis was validated by your experimental results, you should evaluate your hypothesis as ‘supported’; if your hypothesis was not supported by results, it is ‘rejected’ or ‘not supported’.

Remember: a scientific hypothesis can be rejected (or not supported), but it can *never be proven true*; it can only be supported. This is because the nature of evidence is that as new technologies and information become available, evidence can change and be interpreted in different ways. This may than disprove a previously made hypothesis.

TABLE 14.10 Examples of results that can support or disprove a hypothesis

Observation	Hypothesis	Test of hypothesis	Result	Conclusion
The toaster has stopped working	The power point is faulty	Use a different power point	The toaster works in the different power point	Hypothesis supported
The car won’t turn on	The battery is empty	Replace the battery	The car still won’t turn on	Hypothesis not supported
The measurement on the scales is too high	The scales weren’t set to zero before use	Set the scales back to zero	The reading is more accurate	Hypothesis supported

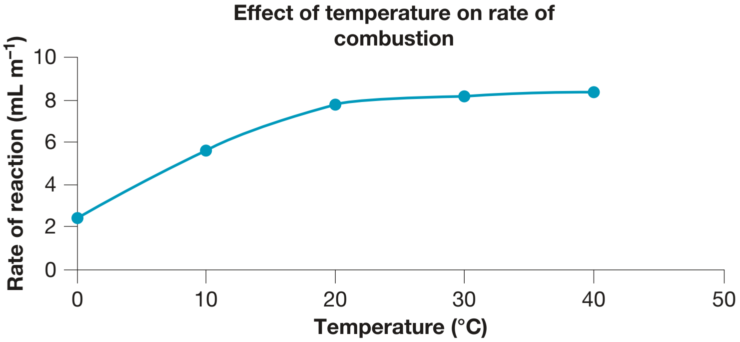
14.8.2 The key findings of investigations

For your investigation, you wrote a question and a hypothesis, created a clear reproducible methodology, conducted an experiment, and collected and analysed data. Once these steps are complete it is important to determine the key findings of your investigation.

Your key findings should include:

- information about the data obtained in the practical investigation and any patterns and trends
- the relationship of your findings to chemical concepts including thermochemical, equilibrium and/or organic structure and bonding concepts
- an answer to the question of your investigation.

FIGURE 14.53 Heat of combustion based on different molar mass of alcohols



For example, you might be investigating the question: How does the molar mass affect the heat of combustion of alcohols? You could use the graph in figure 14.53 to link this data to thermochemical ideas and develop your key findings.

> *Many alcohols are commonly used as fuels due to their high heat of combustion, which measures the heat energy released when the fuel burns completely in oxygen.*
>
> *Five main alcohols were examined in this investigation, and the heat of combustion was recorded. The chosen alcohols were methanol, ethanol, propanol, butanol and pentanol. These were graphed in accordance with their molar mass, in order to allow for quantitative data to be examined.*
>
> *From the graph shown, it can be observed that as the molar mass of an alcohol increases, the heat of combustion also increases. This is because the heat energy released would be higher. Because there are more bonds in the larger molecules, there is more energy already present, and therefore more energy is released in the process of combustion.*
>
> *There appears to be a positive correlation between molar mass and heat of combustion, and generally a linear trend with some minor deviations. Therefore, it is clear that the size and number of atoms and, in turn, the molar mass impact the heat of combustion, supporting the hypothesis of the investigation.*

14.8 EXERCISE

To answer questions online and to receive **immediate feedback** and **sample responses** for every question go to your learnON title at www.jacplus.com.au

1. Why do we say that we ‘support’ a hypothesis rather than ‘prove’ it?
2. Provide three examples of strong evidence.
3. Describe what key findings you should communicate in a discussion.
4. Why is it important to show the relationship of your results to concepts such as solubility and concentration?

Fully worked solutions and sample responses are available in your digital formats.

14.9 Conventions of scientific report writing and scientific poster presentation

KEY CONCEPT

- The conventions of scientific report writing including chemical terminology and representations, symbols, chemical equations, formulas, units of measurement, significant figures, standard abbreviations and acknowledgement of references.

KEY SCIENCE SKILLS

- Communicate and explain scientific ideas

14.9.1 Conventions of report writing

It is vital to follow the set structure in scientific report writing and scientific poster presentation to follow the protocols of scientific written communication (see table 14.11).

TABLE 14.11 Aspects of a written report

Section	Description
Title	A precise and complete description of what you investigated
Abstract	An optional section to outline the key findings and information.
Introduction	A paragraph explaining the relevant chemical and background concepts and relationships and how they apply to this investigation. It should explore any prior investigations conducted on this topic. This should also include a clear aim and hypothesis.
Methodology	A detailed section that describes your selection of equipment and measuring instruments, and your step-by-step method. This may include diagrams and photos. Refer to how you controlled variables, achieved the desired accuracy, and overcame, avoided or anticipated difficulties. It should be clear enough for someone else (at your level) to repeat your experiment. Do not forget to highlight how the relevant ethical and safety concerns have been addressed.
Results	A clear representation of your results, including your data and graphs. If there is too much data, refer to your logbook for the full set. Make sure you present your results in an organised and clear manner, following accepted conventions (such as numbering sequentially). Make sure you include the appropriate units and use the correct number of significant figures. Try to organise this in such a way that any patterns or relationships start to become obvious, thus making it easier to analyse in the next section. Show sample calculations if required.
Discussion	A detailed analysis and evaluation of your results. How does your data support your initial intentions and link to relevant chemistry concepts? What trends and relationships are apparent as a result of your investigation? How much of your analysis is limited by uncertainties? Were there any outliers in your investigation and how were they treated? What limitations and sources of error were present in your investigations and how would you improve this in future repetitions? What would be your next steps in the investigation if you had more time?
Conclusion	This should relate to the aim and must be based entirely on the evidence obtained in the experiment. It should state whether the hypothesis is supported, and summarise the meaning of your results in response to your question. No new information should be included.
References and acknowledgements	You should quote the sources of any content that you include that is not your own original work. Unaltered tables, diagrams and graphs are examples that fit this description, as are direct quotes. In your introduction, you may have mentioned previous work that your investigation is based on. This also needs to be acknowledged, along with any sources that inform your discussion of concepts and theory in a more general sense. This section is not counted in your final word count.

It is important to remember that your assessed practical investigation is based on both your scientific poster and your logbook. The information you will be marked on may be in either your poster or your logbook, or it may appear in both. It is important that all information is presented.

There are some other important points to remember when writing your scientific report or poster. These include:

- try to avoid subjective language — where possible, use third-person (he, she, they, etc)
- don't just record the data you believe supports your hypothesis — you should also include any errors, uncertainties and outliers
- if you used any calculations, show your working out
- use subheadings throughout your report to make it clear to read
- provide headings for all graphs, tables and figures, and label them sequentially (graph 1, graph 2, etc).

14.9.2 Terminology and representations

Throughout your report, it is important to use clear and concise terminology relevant to the related chemistry concept. The use of key terms was covered in section 14.3.2.

Furthermore, chemical representations are required to be accurate and use common conventions. These representations were discussed in section 14.3.3. There may be other representations used that are appropriate to your specific investigation. These should be used consistently in both your logbook and your poster.

14.9.3 Symbols

Symbols are commonly used in chemistry to represent specific variables, different elements and measurements, among other things. There are many also many symbols that are specific to drawing the skeletal structure of molecules. Symbols are often letters but, due to the sheer quantity of variables we have to represent, it is important to note that the capital and lowercase letter usually represent different things. As well as that, sometimes the same symbol is used to represent different variables.

μ can be used to represent:

- the statistical mean
- micro in measurement.

C can be used to represent:

- carbon (C)
- concentration (c).

It is important to know various symbols, including those used in equations, and to use them correctly and carefully in your report to minimise confusion. Table 14.12 shows some commonly used symbols in chemistry.

TABLE 14.12 Some common symbols used in chemistry

Symbol	Representation
Δ	Change in variable
$\rightleftharpoons$	Equilibrium arrow
N_A	Avogadro's Constant
N	Number of particles
n	Amount in mole
M	Molar mass
m	Mass

Symbol	Representation
c	Concentration
V	Volume
V_m	Molar volume
e^-	Electron
(g)	Gas (used in chemical formulas)
(aq)	Aqueous (used in chemical formulas)
(l)	Liquid (used in chemical formulas)
(S)	Solid (used in chemical formulas)

14.9.4 Equations and formulas

During your exam you will be provided with a data book, which will contain physical constants, formulas and data that will help you answer many questions. When using equations and formulas in your scientific investigation, it is important to:

- define all variables
- provide any figures for constants (e.g. Avogadro's number).

Some key formulas in chemistry are included here, and many of which can be found in your VCE Chemistry Data Book. You should become very familiar with this data book prior to your exam as it contains a huge amount of useful information which you do not need to memorise.

Determining the number of moles *(n)*

- $n = \dfrac{\text{mass}}{\text{molar mass}} = \dfrac{m}{M}$
- $n = \dfrac{\text{number of particles}}{6.02 \times 10^{23}} = \dfrac{N}{N_A}$
- $n = \text{concentration} \times \text{volume} = cV$
- $n = \dfrac{\text{volume}}{\text{molar volume}} = \dfrac{V}{V_m}$

Chemical relationships

- Universal gas equation: $pV = nRT$
- Heat energy released from combustion: $q = mc\Delta T$
- Enthalpy of combustion: $\Delta H = \dfrac{q}{n}$
- Calibration factor for bomb calorimetry: $\text{CF} = \dfrac{VIt}{\Delta T}$
- Number of moles of electrons: $n(e^-) = \dfrac{Q}{F}$
- % yield: $\dfrac{\text{actual yield}}{\text{theoretical yield}} \times \dfrac{100}{1}$
- % atom economy: $\dfrac{\text{molar mass of desired products}}{\text{molar mass of all reactants}} \times \dfrac{100}{1}$
- Electric charge: $Q = It$

14.9.5 Units of measurement

In chemistry, it is vital to use the correct unit of measurement for accurate and clear scientific communication.

Prefixes

Prefixes are used at the start of measurements to denote how large or small a value is. These values are from a base unit. Examples of base units include meter, seconds or grams. These base units have the value of 10^0 (or 1). All other prefixes are compared to this base unit.

TABLE 14.13 Prefixes for units of measurement

Pico p	Nano n	Micro μ	Milli m	Centi c	Deci d	Kilo k	Mega M	Giga G
10^{-12}	10^{-9}	10^{-6}	10^{-3}	10^{-2}	10^{-1}	10^3	10^6	10^9

Understanding the different prefixes allows the correct units to be used in practical investigations, and also allows for easy conversion between different units.

$$\frac{\text{initial unit }\ (10^a)}{\text{changed unit }\ (10^b)} \times \text{value}$$

SAMPLE PROBLEM 5

Convert:

a. 12.412 millilitres to microlitres

b. 26 153 milligram to decigram

c. 8.7 metres to nanometres

Teacher-led video: SP5 (tlvd-0105)

THINK	WRITE
a. 1. Determine the conversion between the units $\frac{\text{millilitres}}{\text{microlitres}}$	$\frac{10^{-3}}{10^{-6}} = 10^3$
2. Multiply this by the value to be converted.	$10^3 \times 12.412 \text{ mL} = 12\,412$
3. Add the new unit.	$12\,412\ \mu\text{L}$
b. 1. Determine the conversion between the units $\frac{\text{milligram}}{\text{decigram}}$	$\frac{10^{-3}}{10^{-1}} = 10^{-2}$
2. Multiply this by the value to be converted.	$10^{-2} \times 26\,153 \text{ mg} = 261.53$
3. Add the new unit.	261.53 dg
c. 1. Determine the conversion between the units $\frac{\text{metre}}{\text{nanometre}}$ *Note:* We use 10^0 for metres as it is our standard unit, so is equal to 1.	$\frac{10^0}{10^{-9}} = 10^9$
2. Multiply this by the value to be converted.	$10^9 \times 8.7 \text{ m} = 8\,700\,000\,000$
3. Add the new unit (round if required).	$8\,700\,000\,000 \text{ nm}$

PRACTICE PROBLEM 5

Convert:

a. 738.3 micromole into nanomole

b. 8233 centimetres into kilometres.

SI units of measurement

SI units (or Système Internationale) are our metric system of measurements. It is an internationally standardised system.

TABLE 14.14 Common SI units used in chemistry

Quantity	Unit	Symbol
Length	metre	m
Mass	kilogram	kg
Time	second	s
Temperature	kelvin	K
Electric current	ampere	A
Amount of substance	mole	mol
Energy	electron volt	eV

Derived units

Derived units are units of measurements derived from the SI units.

Speed is an example of a quantity that is measured in derived SI units. The unit of enthalpy change is kilojoule per mole, derived from the SI unit of energy (joule) and SI unit mole which measures the number of particles in a given substance. Enthalpy is written as kJ/mol, or with a negative index, as kJ mol^{-1}.

TABLE 14.15 Commonly used derived units used in chemistry

Quantity	Unit	Symbol	Unit in terms of other units
Molar mass	Amu	M	g mol^{-1}
Enthalpy change		ΔH	kJ mol^{-1}
Energy and work	Joule	J	N m
Pressure	Pascal	Pa	N m^{-2}
Temperature	Degrees Celsius	°C	+273.15 K
Density		*d*	kg m^{-3}
Radiation dose	Sievert	Sv	J kg^{-1}

14.9.6 Significant figures

There is a degree of uncertainty in any physical measurement. The uncertainty can be due to an error or to the limitations of the measuring instrument.

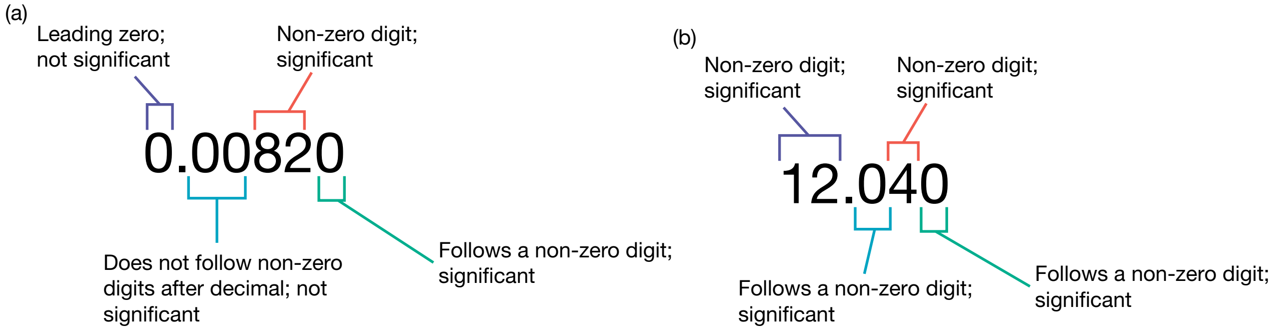
In most physical measurements, the last significant figure shows a small degree of uncertainty. For example, the length of an Olympic competition swimming pool is correctly expressed as 50.00 m. The last zero has a small degree of uncertainty.

Complicated by zeros

Two simple rules can be used to help you decide if zeros are significant.

- Zeros before the decimal point are significant if they are between non-zero digits. For example, all of the zeros in the numbers 4506, 27 034 and 602 007 are significant. Therefore, the numbers have four, five and six significant figures respectively. The zero in the number 0.56 is not significant.
- Zeros after the decimal point are significant if they follow a non-zero digit. For example, in the number 28.00, the two zeros are significant. The number has four significant figures. However, in the number 0.0028, the zeros are not significant (the one before the decimal point and the two after the decimal point). They do not follow a non-zero digit and are present only to indicate the position of the decimal point. Therefore, this number has only two significant figures. The number 0.002 80 has three significant figures.

FIGURE 14.54 Examples of significant figures: (a) has three significant figures and (b) has five significant figures



Calculating significant figures

When multiplying or dividing, the answer is written to the least number of significant digits.

For example, if you knew a substance had a mass of 7.6 g and a molar mass of 18.5 g mol^{-1}, the amount in mol would be given by:

$$\begin{aligned}\text{mol} &= \frac{\text{mass}}{\text{molar mass}}\\ &= \frac{7.6}{18.5}\\ &= 0.4108108\ \text{mol}\\ &= 0.41\ \text{mol}\end{aligned}$$

We can be confident of the result up to two significant figures as this is the least number of significant figures on which the calculation was based. Hence, the result should be rounded to two significant figures.

When quantities are added or subtracted, the result should be expressed to the minimum number of decimal places used in the data. For example, if you measured three consecutive volumes of 23.4 mL, 24.63 mL and 20.123 mL, the total volume measured would be given by:

$$\begin{aligned}23.4 + 24.63 + 20.123 &= 68.153\\ &= 68.2\ \text{mL}\end{aligned}$$

The result should be rounded off to one decimal place because this was the minimum number of decimal places provided in the data.

SAMPLE PROBLEM 6

In determining the density of a particular liquid, a student measured the volume of a sample as 8.3 mL. She then weighed the same sample and obtained a mass of 7.2136 g. Calculate the density to the correct level of significant figures.

Teacher-led video: SP6 (tlvd-0106)

THINK	WRITE
a. 1. Determine the number of significant figures provided.	7.2136 = 5 significant figures 8.3 = 2 significant figures
2. Determine the least number of significant figures. This will be the number of significant figures in the final result.	2 significant figures
3. Calculate the density $\text{density} = \dfrac{\text{mass}}{\text{volume}}$	$\text{Density} = \dfrac{7.2136}{8.3} = 0.8691$
4. Round down to the appropriate number of significant figures. In this case, 0.8691 needs to be rounded down to significant figures.	$= 0.87\ \text{g mL}^{-1}$

PRACTICE PROBLEM 6

Sodium has a molar mass of 22.989 g mol^{-1}. A sample was found to have a mass of 6.65381 g. What is the amount in mole of sodium?

on Resources

Video eLesson Determining significant figures (eles-2559)

14.9.7 Standard abbreviations

Writing out terms in each instance can make a scientific report bulky and hard to follow. Therefore, it is often appropriate to abbreviate frequently repeated terms.

In chemistry, we often shorten formulas instead of writing them out in full. This is particularly true with molecules such as water, for which the abbreviation H_2O is universally known.

Some common abbreviations used in chemistry are:

- IUPAC: International Union of Pure and Applied Chemistry
- pH: Potential of hydrogen
- UV: Ultraviolet
- AAS: Atomic absorption spectroscopy
- HPLC: High performance liquid chromatography
- ppm: Parts per million
- ppb: Parts per billion
- CF: Calibration factor
- IR: Infrared spectroscopy
- MS: Mass spectrometry
- NMR: Nuclear magnetic resonance
- SLC: Standard laboratory conditions

When using an abbreviation, write the word out in full on the first appearance followed by its abbreviation in brackets and then the abbreviation can be used in subsequent appearances.

For example:

> *Atomic absorption spectroscopy (AAS) was developed in Australia. In AAS, the concentrations of metal ions are detected.*

14.9.8 Acknowledgement of references

An in-depth scientific report requires a depth of research for concepts relating to the investigation. This could include:

- using other sources for definitions and background material
- finding examples of similar investigations
- research on the obtained results to link to scientific understanding.

If you use any material that is the work of another person, you *must* acknowledge its source. Do not claim it as your own work. Acknowledgments come in two formats: a short version when it occurs in the body of your report or poster, and a longer version when it occurs in the *Reference and Acknowledgments* section at the end of your poster or scientific investigation.

There are many ways to make such acknowledgments, and various institutions and publications use different systems. Details of these systems can be found online and can be quite complicated. You should check with your teacher about which system they want you to use. Remember, you cannot mix systems so all your references, both in-text and in the References and Acknowledgments, must follow the same style.

Acknowledging sources within your report: In-text referencing

An in-text reference is an abbreviated form of a reference and should be used in the body of your report in the location the sourced information is referred to. It is used not just for direct quotes, but also for tables, images and any information that has been paraphrased.

There are numerous ways to use in-text references and these depends on what style you are using.

Author–date system

The author-date style of in-text referencing is the most commonly used, particularly in the APA and Harvard systems of referencing. As well as the shortened in-text referencing, a full reference is included in the reference list.

Text that has been sourced has the in-text reference at the end of the information being used. For example:

> *... over the past 10 years, the number of eligible children has increased (Kringle, 2008) and a need has therefore developed for sleighs to travel faster to meet the required delivery schedule. More efficient fuels are required for this purpose.*

Tables, diagrams and graphs that are being inserted without being substantially altered can often be acknowledged by stating the details directly underneath them. Table 14.16 shows an example.

TABLE 14.16 Energy content of commonly available sleigh fuels

Fuel	Energy content (kJ L^{-1})
Rudolphene	45
Polar plus	29
Super sleigh	53

(Claus, 2016, p. 45)

There are some points to remember about in-text referencing using the author–date system. These include:

- if the online article is undated, put (n. d.) in place of the date
- if there is no author, use the title in place of the author's name
- if there are up to three authors, list them all
- if there are more than three authors, only use the name of the first author and follow it with the phrase 'et al', which means 'and others'
- if you quote directly from an author or cite a specific idea or piece of information from the source, you need to include the page number of the quote in your in-text reference.

Footnotes system

The footnotes system of in-text referencing is usually used in the Chicago and Vancouver systems. In this style, the citation is denoted by a superscript number showing the point in which a reference have been used. For example:

> *... over the past 10 years, the number of eligible children has increased*[5] *and a need has therefore developed for sleighs to travel faster to meet the required delivery schedule. More efficient fuels are required for this purpose.*

In the footnotes section of the page (depending on the format of the report) the work is referenced with the corresponding number, and is then included again in the reference list.

Acknowledging sources at the end of your report: Reference list

At the end of a scientific report or poster, a reference list is included. If you are using the author-date systems, your references should be listed alphabetically. If you are using the footnotes system, references should be listed in order of footnote number.

Following are examples showing references using the Harvard (author–date) system.

Book

Author surname(s), initial(s) (Year published). *Title*. Edition (if applicable). Place of publication: publisher.

Example:

Langley, P & Jones, M (2013) *The search for Richard III: The king's grave.* London: John Murray.

Do not use et al. in your reference list. This is only appropriate in your in-text referencing.

Journal

Author surname(s), initial(s) (Year published). *Title of article*. Title of Journal. Volume number. Page numbers.

Example:

Boiero, D & Bagaini, C (2018). *S-wave splitting intensity analysis and inversion.* Geographical Prospecting. Vol. 67(2). 362–378.

If available, you may also include the DOI (digital object identifier) after the page numbers. A DOI is a permanent identifier for a journal article and is often used in place of a URL.

TV programs

Title of program (date), (TV program) Channel identification.

Example:

Gene editing made simple (2016), (TV program), ABC Sydney.

Websites

Any websites you use in your report should be written for an academic target audience.

Author surname(s), initial(s) (Year published). *Title of page*. Name of website, date and website of retrieval

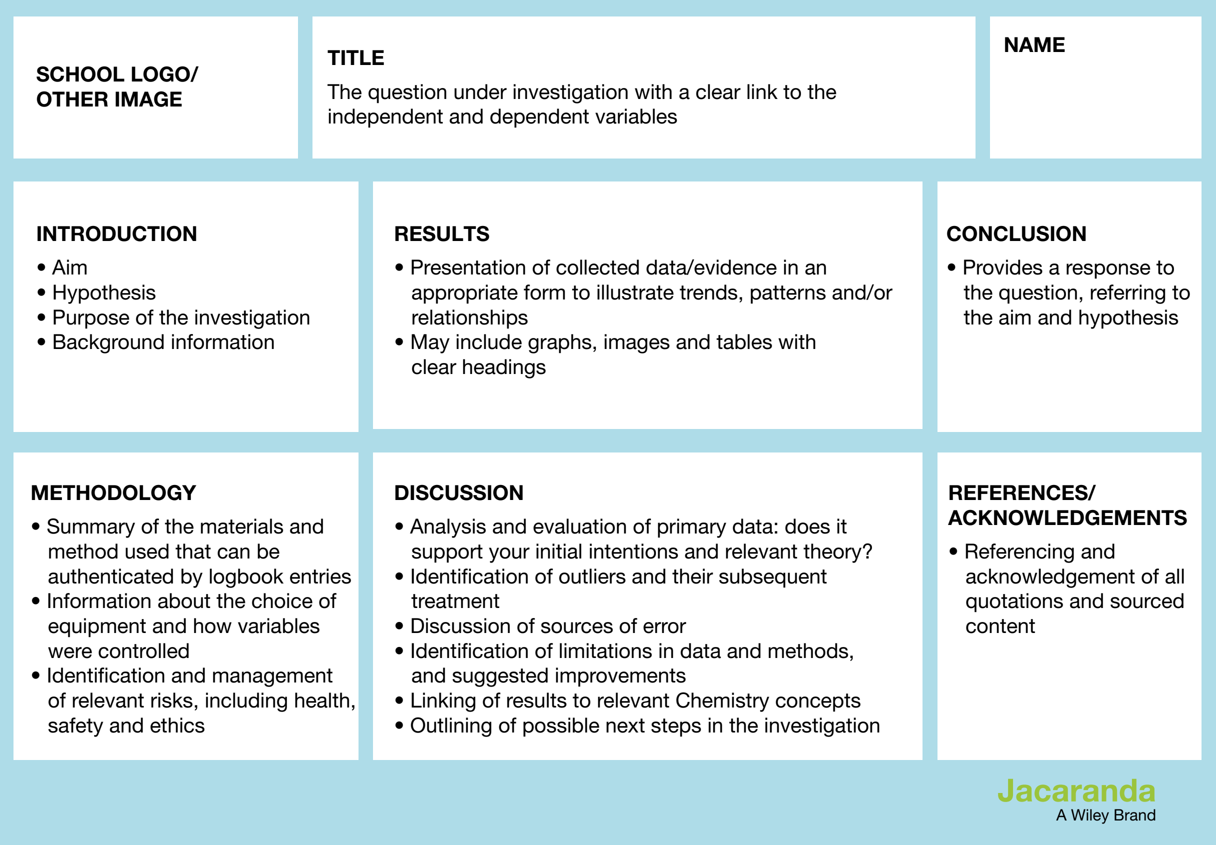
Example:

Fein, B 2011. *The Patriot Act is at war with the constitution*. The American view: God, family, republic, accessed 8 November 2011, <http://archive.theamericanview.com/index.php?id=1770>

14.9.9 Presenting a scientific poster

You will be assessed on two items: your logbook and your scientific poster. A sample format of the poster is shown in figure 14.55.

FIGURE 14.55 Format of scientific poster



SCHOOL LOGO/ OTHER IMAGE

TITLE

The question under investigation with a clear link to the independent and dependent variables

NAME

INTRODUCTION

- Aim
- Hypothesis
- Purpose of the investigation
- Background information

RESULTS

- Presentation of collected data/evidence in an appropriate form to illustrate trends, patterns and/or relationships
- May include graphs, images and tables with clear headings

CONCLUSION

- Provides a response to the question, referring to the aim and hypothesis

METHODOLOGY

- Summary of the materials and method used that can be authenticated by logbook entries
- Information about the choice of equipment and how variables were controlled
- Identification and management of relevant risks, including health, safety and ethics

DISCUSSION

- Analysis and evaluation of primary data: does it support your initial intentions and relevant theory?
- Identification of outliers and their subsequent treatment
- Discussion of sources of error
- Identification of limitations in data and methods, and suggested improvements
- Linking of results to relevant Chemistry concepts
- Outlining of possible next steps in the investigation

REFERENCES/ ACKNOWLEDGEMENTS

- Referencing and acknowledgement of all quotations and sourced content

Jacaranda
A Wiley Brand

14.9.10 Practical investigation checklist

Before you submit your report, use the following checklist to make sure you have included everything you need to.

☐ Your name, the title and the aim/hypothesis are listed.
☐ An introduction describes the purpose and outlines the investigation in a logical and concise manner. Key terms are defined and variables are stated clearly. Relevant theory is addressed.
☐ The method is outlined clearly in step form and includes a consideration of ethics, health and safety. A risk assessment is provided.
☐ Your logbook contains dates, headings and complete records.
☐ Any abbreviations are explained.
☐ Results are presented in an organised way, in a table if possible. All relevant measurements are recorded with appropriate accuracy and units.
☐ Observations are clear and concise, as are all diagrams, graphs and tables.
☐ Any calculations are shown.
☐ There is a concise summary and interpretation of key findings, including trends and any unexpected results with connection to theory.
☐ The experimental design is evaluated and possible improvements are included.
☐ There are suggestions for future investigations.
☐ The conclusion concisely summarises how your results support or contradict your original hypothesis.
☐ All sources are acknowledged and references correctly cited.
☐ The use of key terms, symbols and equations is appropriate.

A poster or other form of scientific report should address the sections outlined in table 14.11 without going into too much detail. For example, you would display only a subset of the data to convey your findings and accuracy. Similarly, not all your graphs need appear.

14.9 EXERCISE

To answer questions online and to receive **immediate feedback** and **sample responses** for every question go to your learnON title at www.jacplus.com.au

1. Convert the following units to the SI base unit shown.
   (a) 142 mL (to L)
   (b) 0.67 kg (to g)
   (c) 762 184 μm (to m)
2. Convert the following to the unit shown.
   (a) 1.67 kg (to mg)
   (b) 198 μmol (to mmol)
3. Describe the following aspects of a scientific report.
   (a) Introduction
   (b) Discussion
   (c) Conclusion
4. Write a reference in Harvard style for this textbook. Show both the in-text referencing and the full reference for the reference list.
5. How many significant figures are in the following?
   (a) 760.4
   (b) 0.0109
   (c) 1.200
   (d) 4.08
6. Calculate the following and express your answer in the appropriate number of significant figures.
   (a) $4 + 9$
   (b) $0.002 + 3.7$
   (c) $5.9 + 70.4134$
   (d) $0.80 - 0.2$
   (e) $840 - 612.03$
   (f) $62.098 + 6.72$
7. Solve the following problems using the correct number of significant figures.
   (a) density = 63.45 g / 1.2 mL
   (b) mass = 23.713 g + 11.1 g
   (c) moles = 1.4 mol L^{-1} × 2.05 L
   (d) m(Cu) = 1.8 mol × 63.5 g mol^{-1}

Fully worked solutions and sample responses are available in your digital formats.

14.10 Review

14.10.1 Summary

Key science skills in chemistry

- It is important to choose a topic that allows for the development of a question and observations to be made.
- Variables are factors that an investigator can control, change or measure.
- An independent variable is manipulated by the investigator (e.g. the type of metal examined).
- A dependent variable is measured by the investigator and is influenced by the independent variable (e.g. the melting temperature of a metal).
- A controlled variable is one that is kept the same in an investigation — there are usually numerous controlled variables in an experiment (e.g. the device used to record temperature, environmental factors such as air temperature and humidity, and the mass of the metal being investigated).

- It is important to control variables in order to examine one independent variable at a time to better understand its relationship to the dependent variable.
- An aim is a one to two sentence outline of the purpose the investigation, linking the dependent and independent variables.
- A hypothesis is a tentative, testable and falsifiable statement for an observed phenomenon and acts as a prediction for the investigation.
- Part of scientific method or process is designing an experiment, conducting the experiment and analysing the results.

Concepts specific to investigation

- Key terms can be defined as part of a scientific report or in a glossary.
- Key terms that are selected should be those that are vital to understand the investigation.
- There are various representations used in chemistry, including symbols, models, equations and formulas.
- Understanding various representations helps make communication easier and clearer.

Scientific research methodologies and techniques

- Primary sources of data are direct or firsthand evidence, often gained through practical investigations.
- Data can be quantitative (numerical) or qualitative.
- It is vital to carefully choose the best techniques and equipment for an investigation. These should be precise, accurate and easy to conduct within a school environment.
- In an investigation, it is vital to consider accuracy, precision, reliability and validity.
- Accuracy is how close a measurement is to a known value (like hitting the target on a bullseye).
- Precision is how close multiple measures are to each other (like hitting a six on a target three times in a row).
- Reliability shows that if an experiment is replicated (by oneself or another researcher), the results should be similar.
- Validity is how much credibility can be given to the results — do the results measure what they intended to and back up their claims?
- The best designed experiments are accurate, precise, reliable and valid, while minimising errors and uncertainties.

Ethics, and health and safety guidelines

- In an investigation, care must be taken to follow ethical, and health and safety guidelines.
- Ethics are involved in moral conduct, particularly when humans and animals are involved as test subjects — this does not tend to be an issue is chemistry compared with biology and psychology.
- Health and safety is often evaluated using a risk assessment, where different hazards are analysed and safety requirements are explained.

Methods of organising, analysing and evaluating primary data

- Data can be organised in a variety of ways, including through the use of tables and graphs.
- Scatterplots and line graphs are used when both variables are quantitative.
- Bar graphs are used when one piece of data is qualitative and the other is quantitative.
- Histograms are used when intervals and frequency are being explored.
- It is important to choose an appropriate method of organising data in order to effectively analyse trends, patterns and relationships.
- Graphs can be used to predict data outside of the investigated set.
- When evaluating data, it is important to link to scientific concepts, models and theories, link back to your aim and hypothesis, describe trends and patterns, and identify any outliers or limitations.
- Both errors and uncertainty can affect the results gained.
  - Errors are a measurement of the difference between a measured value and the true value (the accuracy).
  - Uncertainty is the limit to precision and the range of values that can be measured.

Model and theories to understand observed phenomena

- Models represent ideas, phenomena or scientific processes. They can be physical models, mathematical models or conceptual models.
- Limitations of models include an oversimplification of concepts, an inability to be completely accurate and being specific to a set of conditions, which may or may not reflect the real world.
- Theories are well-supported explanations of phenomena.
- Similar to models, theories are often oversimplifications of concepts, specific to a set of conditions and subject to change as new information becomes available.

Nature of evidence and the key findings of investigations

- Evidence can be used to support or reject a hypothesis. A hypothesis is not stated to be confirmed or proven true because new evidence can come to light, which later leads to its rejection.
- When reporting key findings, it is important to provide information about the data obtained in the practical investigation and any patterns and trends, show the relationship of your findings to chemistry concepts and provide an answer to the question of your investigation.

Conventions of scientific report writing and scientific poster presentation

- Both your logbook and scientific poster are forms of scientific reporting and combine for your mark for Unit 4 AOS 3.
- Components required in a scientific report are a title, date, name, introduction, aim, hypothesis, methodology (method and materials), results, discussion, conclusion and references.
- A variety of key symbols, formulas, equations, terminology, representations and abbreviations are used in chemistry and are required for effective communication.
- All sourced information must be correctly and clearly referenced using a style such as Harvard or APA.
- Your poster will not have every piece of information that your logbook will, but it will show the important and key points that will allow for a clear understanding of your investigation.

on Resources

Digital document Topic summary – Topic 14 (doc-31428)

14.10.2 Key terms

accuracy how close an experimental measurement is to a known value

aim a statement outlining the purpose of an investigation, linking the dependent and independent variables

bar graphs graphs in which data is represented by a series of bars. They are usually used when one variable is quantitative and the other is qualitative.

bias the intentional or unintentional influence on a research investigation

categorical data also known as qualitative data, this is when data has labels or names rather than a range of numerical quantities

column graphs see **bar graphs**

conclusion a section at the end of a report that relates back to the question, sums up key findings and states whether the hypothesis was supported or rejected

control group a group that is not affected by the independent variables, and is used as a baseline for comparison

controlled variables variables that are kept constant across different experimental groups

dependent variable the variable that is influenced by the independent variable. It is the variable that is measured.

discussion a detailed area of a report in which results are discussed, analysed and evaluated, relationships to concepts are made, errors, limitations and uncertainties are assessed, and suggestions for future improvements are made

error differences between a measurement taken and the true value that is expected; they lead to a reduction in the accuracy of the investigation

ethics acceptable and moral conduct determining what ‘right’ and what is ‘wrong’

experimental group test groups that are exposed to the independent variable

falsifiable there has to be a way to be prove the hypothesis wrong

histograms a graph in which data is sorted in intervals and frequency is examined. This is used when both pieces of data are quantitative. Columns are not separated in a histogram.

hypothesis a tentative, testable and falsifiable statement for an observed phenomenon that acts as a prediction for the investigation

independent variable the variable that is changed or manipulated by an investigator

limitations factors that have impacted the interpretation and/or collection of findings in a practical investigation

line graphs graphs in which points of data are joined by a connecting line. These are used when both pieces of data are quantitative (numerical).

line of best fit a trend line that is added to a scatterplot to best express the data shown. These are straight lines, and are not required to pass through all points.

models representations of ideas, phenomena or scientific processes; they can be physical models, mathematical models or conceptual models

numerical data also known as quantitative data, this is when data involves numbers and can be measured or counted

outlier results that are a long way from other results and seen as unusual

precision how close multiple measurements of the same investigation are to each other

primary source direct or firsthand evidence about some phenomenon

qualitative data categorical data that examines the quality of something (i.e. colour, gender), rather than numerical values

quantitative data numerical data that examines the quantity of something (i.e. length, time).

random errors chance variations in measurements

reliability whether or not another researcher could repeat your investigation by following your method and obtain similar results

results a section in a report in which all data obtained is recorded, usually in the form of tables and graphs

risk assessment a document that examines the different hazards in an investigation and suggests safety precautions

scatterplots graphs in which two quantitative variables are plotted as a series of dots

scientific method sometimes referred to as scientific process, this is the procedure that must be followed in scientific investigations that consists of questioning, researching, predicting, observing, experimenting and analysing

scientific research methodology the principles of research based on the scientific method

secondary source comments on or summaries and interpretations of primary data

systematic errors errors that affect the accuracy of a measurement, that cannot be improved by repeating an experiment. They are usually due to equipment or system errors.

theory a well-supported explanation of a phenomena, based on facts that have been obtained through investigations, research and observations

testable a hypothesis can be easily tested by observations and/or experiments

uncertainty a limit to the precision of equipment, it is a range within which a measurement lies

validity credibility of the research results from experiments or from observations. Validity shows how much results measure what they intend to and how well they show the claims they make.

on Resources

Digital document Key terms glossary – Topic 14 (doc-31427)

14.10 Exercises

To answer questions online and to receive **immediate feedback** and **sample responses** for every question go to your learnON title at www.jacplus.com.au

14.10 Exercise 1: Multiple choice questions

1. Belinda conducted an experiment to test the combustion of different types of fuel.
   In this experiment, type of fuel being tested is:
   A. the dependent variable
   B. the independent variable
   C. the controlled variable
   D. the control group.
2. Ben conducted an investigation to experimentally determine if the specific heat capacity of water is actually $4.18\ \text{J g}^{-1}\ \text{K}^{-1}$. His experimental results are shown:

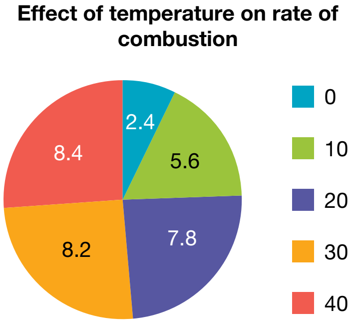
$$6.28\ \text{J g}^{-1}\ \text{K}^{-1}$$
$$6.24\ \text{J g}^{-1}\ \text{K}^{-1}$$
$$6.47\ \text{J g}^{-1}\ \text{K}^{-1}$$

   Which of the following statements is correct about his results?
   A. It was neither precise nor accurate.
   B. It was precise but not accurate.
   C. It was accurate but not precise.
   D. It was accurate and valid.
3. Paul was investigating how temperature impacted the rate of a reaction for the combustion of a fuel. He calculated this by determining the volume of carbon dioxide produced in the process. The results of his investigation are shown below.

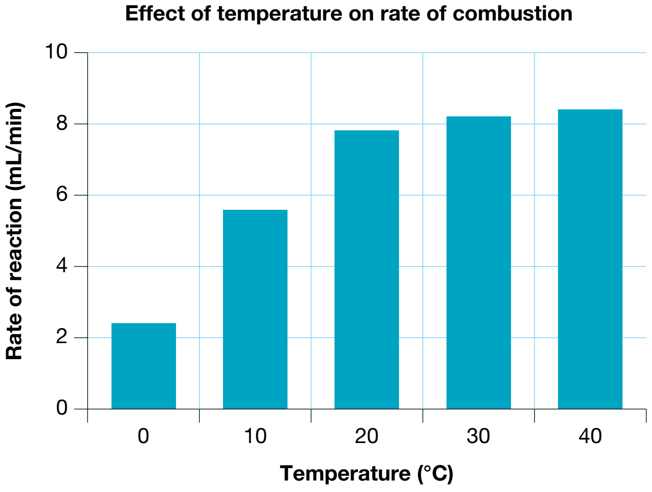
Temperature (°C)	Rate of reaction (mL of CO_2 per minute)
0	2.4
10	5.6
20	12.8
30	8.2
40	8.4

   The most appropriate graph to use to show and analyse trends in this data is:

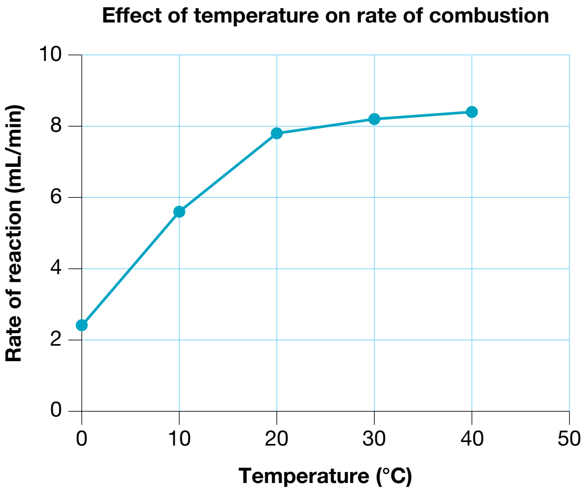
A.



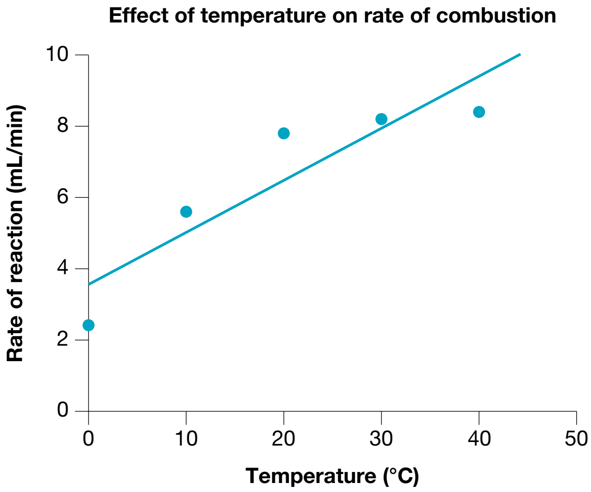
B.



C.

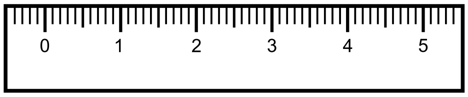


D.



4. In the formula $q = mc\Delta T$, ΔT represents:
- **A.** the change in temperature
- **B.** the change in time
- **C.** the initial temperature
- **D.** the final temperature.

5. A ruler is shown. The measure of uncertainty would be:



- **A.** 0.5 cm
- **B.** 0.1 cm
- **C.** 0.05 cm
- **D.** 0.025 cm.

6. One way to reduce systematic errors is to:
- **A.** repeat an experiment with the same piece of equipment
- **B.** make sure all equipment has been correctly calibrated
- **C.** make sure that the correct units are being recorded in results
- **D.** carefully follow practical instructions.

7. The difference between an aim and a hypothesis is:
- **A.** the aim of an experiment is a statement, but the hypothesis is a question
- **B.** the aim includes the dependent and independent variables, but the hypothesis doesn’t
- **C.** the aim explains the expected data, but the hypothesis explains how you will get the data
- **D.** the aim outlines the purpose of the investigation, but the hypothesis is a testable prediction.

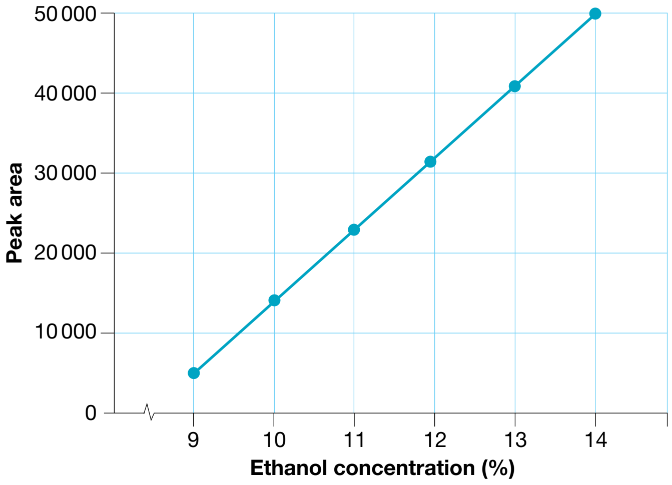
8. Vic and Dan both competed to see who could do 100 push-ups the fastest. In a very close finish, it was found that Dan was 4.50 seconds faster than Vic. Which of the following correct about this result?
- **A.** It is equal to 4500 milliseconds.
- **B.** It contains 2 significant figures.
- **C.** It can be written as 450×10^2 seconds.
- **D.** It is equal to 450 000 microseconds.

9. Theories are:
- **A.** concepts that were once accurate, but have now been rejected
- **B.** diagrammatic representations of abstract concepts
- **C.** ideas that are unable to be rejected due to the amount of evidence they have
- **D.** well-supported ideas where evidence has been gained from investigations, research and observations.

10. The conclusion section of a report should:
    - A. include new information that has not been covered in other sections of the report
    - B. include graphs that best outline the data
    - C. link the findings of the investigation back to the hypothesis and question of the investigation
    - D. describe any outliers and errors that occurred in the data.

14.10 Exercise 2: Short answer questions

1. An investigation was conducted to observe the differences in the energy content of carbohydrates, proteins and fats.
    - a. Identify two pieces of quantitative data that you could record and measure.
    - b. What instruments, if any, would you need to make these observations?
    - c. Identify two pieces of qualitative data that you could observe.
    - d. What instruments, if any, would you need to make these observations?
2. Identify a key difference between the members of the following pairs.
    - a. Independent and dependent variables
    - b. Models and theories
    - c. Systematic and random errors
    - d. Primary and secondary sources of data
    - e. Uncertainty and error
3. In an investigation conducted in class, Jayde recorded a temperature of 812.010 °C.
    - a. How many significant figures does this recorded temperature have?
    - b. Write this temperature in scientific notation.
4. Chris used gas chromatography (GC) to measure the ethanol content of some alcoholic beverages. GC works on a similar principle to high-performance liquid chromatography (HPLC). In both instruments, it is necessary to produce a calibration curve in addition to obtaining readings for the test samples. One such calibration curve is shown below.



    - a. Sample A produced a reading of 36 000 from the GC. Estimate the level of ethanol in this sample.
    - b. Sample B produced a reading of 50 500. Estimate the level of ethanol in this sample and comment on your answer.
    - c. Sample C produced a reading of 95 000. Is it possible to estimate the ethanol level in this sample? Explain why or why not.
    - d. Write a conclusion for this investigation.

5. The following is an extract from a student's logbook where the temperature was recorded at regular intervals during an experiment.

   Initial temperature = 15.0 °C

   Temperature every 30 seconds after initial recording in °C: 16.5, 18.1, 19.5, 20.8, 22.4, 23.7, 24.0, 23.9, 23.5, 23.2

   a. Using graph paper, plot the data on the most appropriate graph, including a scale and labels.
   b. Describe the trends and patterns in this graph.
   c. What conclusions would you make from this investigation?

14.10 Exercise 3: Exam practice questions

Question 1 (10 marks)

Vicki decided to investigate how the rate of reaction is affected by the concentration of acid. She weighed out 3.00 g of calcium carbonate powder and put it in a balloon. She put on some safety gloves and added 50 mL of 1.0 M hydrochloric acid to a flask. She then weighed the balloon and the flask and recorded her results. Vicki then stretched the balloon over the opening of the flask before mixing the two chemicals. When the bubbling stopped, she weighed the balloon and flask again. She repeated the experiment again using 3.00 g of calcium carbonate powder but used 50 mL of 2.0 M hydrochloric acid. She found that changing the concentration had little effect on the rate of reaction because there was hardly any change in mass.

a. Comment on the safety precautions taken. Do you think they were sufficient? **2 marks**
b. Identify the dependent variable in this investigation. **1 mark**
c. List two variables that need to be controlled in this investigation? **1 mark**
d. Describe what measuring equipment should be used in this investigation and identify **one** factor that could affect the accuracy of this piece of equipment **2 marks**
e. Vicki's method is flawed as it does not allow for the rate of the reaction to be measured as mass should be conserved (due to the conservation of mass). Write a clear experimental method for Vicki that shows how she can investigate how the concentration of hydrochloric acid affects the rate of a reaction. You may need to add to her method to make sure that more data is being collected and to ensure it is reproducible **4 marks**

Question 2 (10 marks)

An investigation was being conducted to examine how changing the pressure affects the volume of a gas.

a. Write a suitable aim for this investigation. **1 mark**
b. Identify the hypothesis for this investigation. **1 mark**
c. Describe **one** piece of qualitative data and **one** piece of quantitative data that may be collected in this investigation **2 marks**
d. Explain **two** factors that may lead to differences in results between different students **2 marks**
e. Design an investigation that could be used to test this **4 marks**

Question 3 (8 marks)

A student conducted an experiment, examining the rate of production of hydrogen gas and magnesium oxide from hydrochloric acid and magnesium. The student used the same amount of magnesium in all experiments, but altered the concentration of the pH.

The student recorded how long it took for hydrogen bubbles to first appear. The results from this investigation are shown below:

Concentration of HCl (mol L^{-1})	Time for hydrogen bubbles to appear (seconds)
0.5	10.2
1	8.2
2	5.3
3	3.0
4	1.5
5	0.8

a. Using the data provided:
  - **i.** Plot the graph, ensuring that the time is shown on the vertical axis (this is different compared to other line graphs you may have drawn)
  - **ii.** Label the graph and axes as appropriate
  - **iii.** Draw a straight line of best fit in one colour
  - **iv.** Draw a smooth line joining the points in another colour. **4 marks**

b. Describe the trends seen in your data. **2 marks**

c. Explain the differences between your line of best fit and your line joining the points. Which is better for this data? **2 marks**

Question 4 (8 marks)

Two students, Joe and Robert wanted to explore if the energy content of carbohydrates was 16.7 kilojoules per gram. They used a pack of corn chips to investigate this, each testing five corn chips.

Their results are shown in the table below:

	Joe	Robert
Sample number	Energy content (kJ g^{-1})	Energy content (kJ g^{-1})
1	14.2	10.1
2	12.9	10.5
3	16.2	9.90
4	11.1	11.1
5	15.6	12.0

a. Describe **one** error that may have occurred which reduced the accuracy of the data for both Joe and Robert and identify how this error may be avoided? **2 marks**

b. Calculate the average energy content recorded by Robert, using correct significant figures based on the data provided **2 marks**

c. Describe, with reference to the known value of the energy content of carbohydrates, why the results obtained by Joe are more accurate than those obtained by Robert. **2 marks**

d. It was found that the average energy content recorded by Joe was 14.0 kJ g^{-1}. Convert this to J g^{-1}. **2 marks**

Question 5 (12 marks)

A student conducted an investigation to explore the different boiling points of organic molecules containing 3 carbons.

The student's report is shown below:

> *Introduction: In this experiment, various 3-carbon organic compounds were investigated. The substances being explored were propanoic acid, propan-1-ol, propan-2-ol, propanone and propanal. This investigation was conducted in the laboratory and all substances were slowly heated to a maximum temperature of 100 °C and the boiling point was recorded. Propane was not included in this investigation as it was already a gas at room temperature.*
>
> *Aim: To examine if different carbon containing compounds have different boiling points.*
>
> *Hypothesis: If various three-carbon containing organic molecules are heated, then propanoic acid will have the highest boiling point.*
>
> *Method:*
>
> 1. *Set up 5 beakers. Label each with the organic compound.*
> 2. *Pour the organic compound into the appropriate beaker.*
> 3. *Place a thermometer in the liquid and record the initial temperature.*
> 4. *Place the first beaker above the bunsen burner, using a tripod and gauze mat.*
> 5. *Heat the liquid to 100 °C, recording the temperature of boiling.*
> 6. *Repeat with the next liquid.*

	Initial temperature	Boiling point
Propanoic acid	20.0 °C	>100 °C
Propan-1-ol	25.0 °C	95.0 °C
Propan-2-ol	24.0 °C	83.5 °C
Propanone	23.5 °C	59.0 °C
Propanal	23.5 °C	49.5 °C

a. Describe an issue with the hypothesis written by the student. How would you adjust this to make it testable? **2 marks**

b. In the experiment, the substances were only heated to a maximum of 100 °C. Explain why this may lead to errors in the data obtained. **2 marks**

c. Students were only able to use a thermometer in which temperature could only be measured to the nearest 0.5 °C. Identify the tolerance of this device and describe the uncertainty expected in the data. **2 marks**

d. Outline **two** limitations in the experimental method or data collection process that would affect the conclusions drawn? **2 marks**

e. Describe the most appropriate graph that the student should use to represent their data. Justify your choice. **2 marks**

f. Based on the student's results, write a conclusion for this investigation, linking back to the hypothesis. **2 marks**

Answers

1 Obtaining energy from fuels

1.2 Fossil fuels and biofuels

1.2 Exercise

1. There are several brown coal mines in Victoria (including Hazelwood, Loy Yang, Yallourn). The economics of using the lower quality fuel for on-site power generation outweighs the cost of transporting higher grade coal from interstate.
2. a. A fuel is an exothermic substance that releases energy, commonly in the form of heat.
   b. Examples could include all foods, petrol (if you have driven or have been driven anywhere), natural gas (if you have cooked on a gas stove), wood, oil and diesel.
   c. A fossil fuel is a non-renewable carbon-based energy source that was formed extremely slowly from the decaying remains of plants and animals that accumulated millions of years ago. Biofuel: renewable (short formation time), carbon-based energy source, formed primarily from plant matter.
3. a. Renewable fuels can be replaced by natural processes within a relatively short period of time. Non-renewable fuels are used more quickly than they can be produced.
   b. Yes, all biofuels are renewable because the rate of production can exceed the rate of consumptions.
   c. No. Renewable energy can come in many forms including solar, hydro-electric, tidal, geothermal and wave energy.
4. $CH_3(CH_2)_{14}COOH + CH_3OH \rightleftharpoons CH_3(CH_2)_{14}COOCH_3 + H_2O$
   Palmitic acid Methanol Methyl Palmitate Water

1.3 Combustion of fuels

Practice problem 1

% efficiency = 21%

1.3 Exercise

1. a. Endothermic
   b. Endothermic
   c. Exothermic
   d. Exothermic
   e. Exothermic
   f. Endothermic
2. % efficiency = 34.3%
3. $85\text{ MJ} = 8.5 \times 10\text{ kJ}^{-2}$
   $= 8.5 \times 10{-}5\text{ J}$ (2 significant figures)
4. Energy $= 1.7 \times 10^2$ MJ
5. $m(CO_2) = 0.266\text{ kg MJ}^{-1}$ (3 significant figures)

1.4 Thermochemical equations

Practice problem 2

a. $2CH_3OH(l) + 3O_2(g) \rightarrow 2H_2O(g) + CO_2(g)$
$\Delta H = -723.6\text{ kJ mol}^{-1}$

b. Amount of energy evolved = 179 MJ (3 significant figures)

Practice problem 3

Energy released = −809 kJ (3 significant figures)

Practice problem 4

$2C_2H_6(g) + 5O_2(g) \rightarrow 4CO(g) + 6H_2O(l)$
$\Delta H = -3120\text{ kJ mol}^{-1}$

or $C_2H_6(g) + 2O_2(g) \rightarrow C(s) + CO(g) + 3H_2O(l)$
$\Delta H = -1560\text{ kJ mol}^{-1}$

or $2C_2H_6(g) + 3O_2(g) \rightarrow 4C(g) + 6H_2O(l)$
$\Delta H = -3120\text{ kJ mol}^{-1}$

Practice problem 5

$2S(s) + 2O_2(g) \rightarrow 2SO_2(g) \qquad \Delta H = -546\text{ kJ mol}^{-1}$

1.4 Exercise

1. $2CH_3OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 4H_2O(g)$
   $\Delta H = -1454\text{ kJ mol}^{-1}$
2. 234 kJ of heat energy
3. a. Energy released $= 1.13 \times 10^3$ kJ
   b. Energy absorbed = 282 kJ
4. Energy $= 2.46 \times 10^6$ kJ
5. 607 kJ of heat energy
6. $m(CH_3OH) = 22.0\text{ g}$
7. a. Energy released $= 4.965 \times 10^3$ kJ
   b. $m(\text{octane}) = 51.8\text{ g}$
   The physical state of matter must be shown because changes of state require energy changes.
8. $\Delta H = -4.23 \times 10^3$ kJ
9. $\Delta H = -1.28 \times 10^3$ kJ

1.5 Gaseous fuels and the universal gas equation

Practice problem 6

a. $M = 44.0\text{ g mol}^{-1}$
b. Carbon dioxide

Practice problem 7

$V(CH_4) = 35\text{ L}$ (2 significant figures)

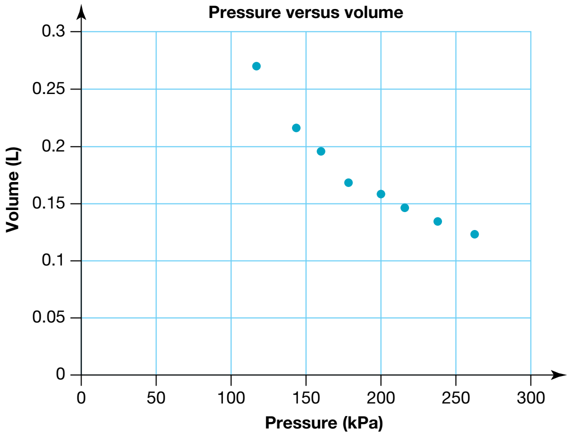
1.5 Exercise

1. a. 1.03 atm
   b. 4.0×10^5 Pa
   c. 1.33×10^5 Pa
   d. 167 k Pa
   e. 473 K
   f. 227 °C
   g. 3.0×10^3 L
   h. 2.5×10^5 mL
   i. 1.6 L
   j. 3×10^3 L
   k. $5 \times 10^{-3}\text{ m}^3$
   l. $6.00 \times 10^{-4}\text{ m}^3$

2. a.

Pressure (kPa)	$\frac{1}{p}$
120	8.33×10^{-3}
145	6.90×10^{-3}
162	6.17×10^{-3}
180	5.56×10^{-3}
200	5.00×10^{-3}
216	4.63×10^{-3}
240	4.17×10^{-3}
258	3.88×10^{-3}

b.



c. See figure at foot of the page.*

d. The first graph is non linear, with volume decreasing as pressure increased. The second graph shows a linear proportionality, where volume increases linearly as $\frac{1}{p}$ increases.

3. a. $n(O_2) = 0.60\,\text{mol}$
   b. $n(Cl_2) = 1.0\,\text{mol}$

4. a. $V(H_2) = 32.2\,\text{L}$
   b. $V(CH_4) = 5.58\,\text{L}$
   c. $V(Ar) = 0.22\,\text{L}$

5. a. $m(Ne) = 13.4\,\text{g}$
   b. $m(SO_2) = 2.71\,\text{g}$

6. $m(CO) = 0.9599\,\text{kg}$

7. $M(\text{gas}) = 83.3\,\text{g mol}^{-1}$
The gas is most likely Krypton (Kr), which has a molar mass of 83.8 g mol^{-1}.

8. a. $V(O_2) = 93.9\,\text{L}$
   b. $V(Ar) = 10\,\text{L}$
   c. $V(CO_2) = 6.1 \times 10^{-3}\,\text{L}$
   d. $V(He) = 0.010\,\text{L}$
   e. $V(Ne) = 0.24\,\text{L}$

9. a. $V = 21.8\,\text{L}$
   b. $T = 88.0\,°\text{C}$

10. a. $p = 1.3 \times 10^4\,\text{kPa}$
   b. 17.6 kJ.

1.6 Calculations related to the combustion of fuels

Practice problem 8

$m(C_6H_{14}) = 57.8\,\text{g}$

Practice problem 9

a. $V(O_2) = 50\,\text{mL}$
b. $V(CO_2) = 25\,\text{mL}$
c. $V(H_2O) = 50\,\text{mL}$

Practice problem 10

Energy required = 47.3 kJ.

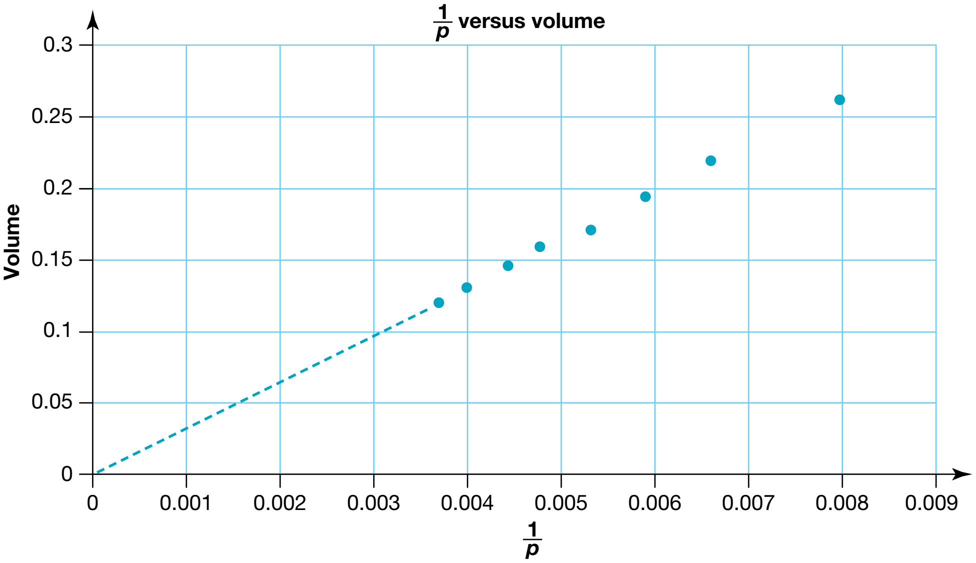
Practice problem 11

$M(C_2H_2) = 72.3\,\text{g}$

1.6 Exercise

1. $m(KNO_2) = 101\,\text{g}$
2. $m(Mg) = 0.059\,\text{g}$

2c*



3. **a.** $V(O_2) = 40$ mL

b. $V(\text{reactants}) = 60$ mL

c. $V(NO_2) = 40$ mL

d. Decrease in volume = 20 mL

4. **a.** Increase in mass = 224 g

b. % increase = 175%

c. If pressure and temperature are kept constant, $V(CH_4)$ consumed = $V(CO_2)$ produced, that is, there is no percentage change in volume. This contrasts significantly with the 175% increase when comparing masses.

5. $m(CO_2) = 64.7$ g

6. **a.** $m(CO_2) = 60.6$ g

b. $V(CO_2) = 34.2$ L

c. 1 MJ of energy produced by burning ethanol produces 64.5 g of carbon dioxide, while 1 MJ of energy released from burning methanol produces 60.7 g of carbon dioxide. Methanol has a slightly lower greenhouse gas emission per MJ of energy produced.

7. **a.** $m(CO_2) = 180$ g

b. $V(CO_2) = 101.1$ L

1.7 Calculating heat energy using the specific heat capacity of water

Practice problem 12

$c = 0.129\ \text{J}\ °\text{C}^{-1}\ \text{g}^{-1}$

1.7 Exercise

1. **a.**

Property	Ethanol	Candle wax	Butane
Mass of 'burner' before heating (g)	23.77	32.72	43.94
Mass of 'burner' after heating (g)	22.54	32.50	43.71
Mass of fuel used (g)	1.23	0.22	0.23
Mass of water (g)	200	200	200
Initial temperature of water (°C)	20.0	20.0	20.0
Highest temperature of water (°C)	35.0	30.0	29.0
Temperature rise (°C)	15.0	10.0	9.0
Molar mass (g mol^{-1})	46.0	282	58

b. Ethanol:
Energy per g = 10.2 kJ g^{-1}
Candle wax:
Energy per g = 38 kJ g^{-1}
Butane:
Energy per g = (32.6) 33 kJ g^{-1}

c. Ethanol: $\Delta H = -469$ kJ mol^{-1}
Candle wax: $\Delta H = -1.1 \times 10^4$ kJ mol^{-1}
Butane: $\Delta H = -1.9 \times 10^3$ kJ mol^{-1}

d. **i.** Exothermic.

ii. % efficiency = 34.5%

iii. Sample answer:
Sources of error: heat loss from the candle flame to the surrounding air; heat loss from the copper can; heat loss from the water in the can; incomplete combustion of the fuel.
Minimising errors: totally surround the flame with a heat-reflecting barrier; cover the side of the can with insulating material; place a lid on the can.

1.8 Review

1.8 Exercises

1.8 Exercise 1: Multiple choice questions

1. C.
2. C.
3. C.
4. A.
5. A.
6. D.
7. D.
8. A.
9. D.
10. C.
11. C.
12. B.
13. B.
14. C.
15. B.

1.8 Exercise 2: Short answer questions

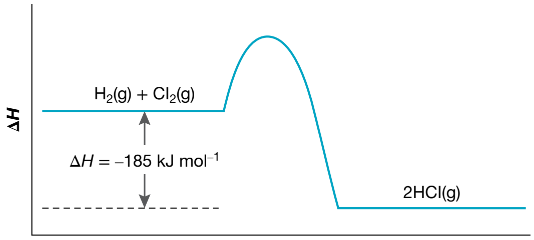
1. **a.** Exothermic

b. Endothermic

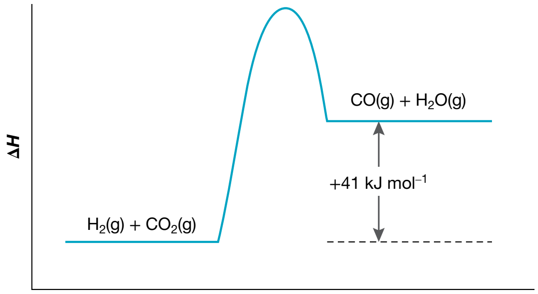
c. Endothermic

d. Exothermic

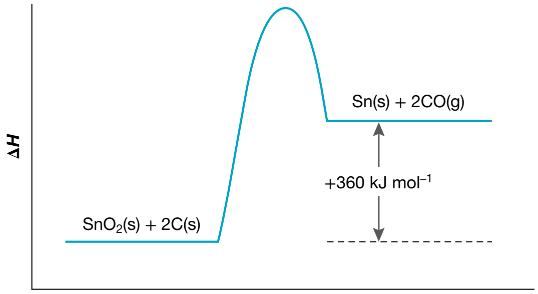
2. **a.**



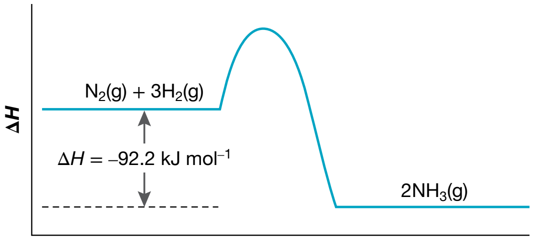
b.



c.



d.



3. a. $CH_3CH_2OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l)$
$\Delta H = -\ 1364\ kJ\ mol^{-1}$

b. $CH_3CH_2OH(l) + 2O_2(g) \rightarrow 2CO(g) + 3H_2O(l)$
$\Delta H = -\ 1192\ kJ\ mol^{-1}$

c. Carbon dioxide forms in plentiful air ($3O_2$) while carbon monoxide forms in limited air ($2O_2$).

d. $\Delta H = -168\ kJ\ mol^{-1}$

4. Ethane:
$2C_2H_6(g) + 7O_2(g) \rightarrow 4CO_2(g) + 6H_2O(l)$
$\Delta H = -3.12 \times 10^3\ kJ\ mol^{-1}$

Ethene:
$= -1.41 \times 10^3$
$C_2H_4(g) + 3O_2(g) \rightarrow 2CO_2(g) + 2H_2O(l)$
$\Delta H = -1.41 \times 10^3\ kJ\ mol^{-1}$

5. a. Gas particles move with continual random motion and, when doing so, collide with the walls of any container, producing the effect we know as pressure.

b. As temperature increases, gas particles move more rapidly. This results in an increase in the frequency of collisions of the gas particles with the walls of any container.

6. a. $1.34\ atm = 1.02 \times 10^3\ mmHg$
$= 136\ kPa$

b. $365\ mm\ Hg = 4.87 \times 10^4\ Pa$
$= 0.480\ atm$

c. $102\,576\ Pa = 1.01\ atm$
$= 770\ mmHg$

7. a. 300 K = 27 °C

b. 427 K = 154 °C

c. 173 K = −100 °C

d. 392 K = 119 °C

e. 73 K = −200 °C

8. a. $n(O_2) = 0.061\ mol$

b. $n(H_2) = 0.103\ mol$

c. $n(N_2) = 0.0101\ mol$

9. a. $V(H_2) = 37.9\ L$

b. $V(CH_4) = 21.1\ L$

c. $V(N_2) = 1.0 \times 10^8\ L$

10. a. $m(O_2) = 0.194\ g$

b. $m(CO_2) = 7.9\ g$

11. a. $T_2 = -267°C$

b. $T_2 = -93\ °C$

12. a. $n = 1.38\ mol$

b. $n = 12.7\ mol$

13. a. $V = 13.3\ L$

b. $V = 35.9\ L$

14. a. $n = 0.0433\ mol$

b. $N = 2.65 \times 10^{22}$

c. $T_2 = 333\ K = 60°C$

15. $M(gas) = 28\ g\ mol^{-1}$
The gas is most likely nitrogen (N_2).

16. $N(O_2) = 1.9 \times 10^{20}$ molecules

17. a. $m(H_2O) = 9.9\ g$

b. $V(CO_2) = 11\ L$

c. $V_2 = 15\ L$

d. $V\left(C_4H_{10}O\right) = 0.092\ mL$

18. a. $V(CO_2) = 4.41 \times 10^5\ L$

b. $m(CaCO_3) = 1.78 \times 10^6\ g$
$= 1.78$ tonne

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

b. $V(N_2) = 15\ m^3$

c. $V(NH_3) = 30\ m^3$

20. a. It includes the amount of heat absorbed by the reaction.

b. Energy absorbed = 0.5 kJ

c. Energy absorbed = 70.0 J

d. $m(Fe) = 4.24\ kg$.

e. $V(CO_2) = 2.83 \times 10^3\ L$

21. a. Energy released = 1.57×10^3 kJ

b. $V = 1.4 \times 10^7\ L$

22. a. m(propane) = 19.8 g

b. $m(CO_2) = 59.4$ g per MJ

c. m(octane) = 20.9 g

d. $m(CO_2) = 64.4\ g$

e. The net reduction of CO_2 emissions is 5.0 g MJ^{-1}

f. m(butane) = 20.2 g
$m(CO_2) = 61.2$ g per MJ
The net reduction of CO_2 emissions is 3.2 g MJ^{-1}.

g. V(propane) = 1.3 L

h. According to the calculations, LPG has a net reduction of CO_2 emission of 5.0 g MJ^{-1}, whereas petrol has a reduction of only 3.0 g MJ^{-1}. Therefore, LPG is the better fuel on this basis.

23. a. Heat produced per gram = 18.4 kJ

b. $\Delta H\,(CH_3CH_2OH) = -\ 846\ kJ\ mol^{-1}$

c. % accuracy = 62.0%

d. Sources of error include heat loss from the flame, heat absorbed by the can, heat loss from the water in the can, and incomplete combustion of the ethanol. An improved design could include a barrier surrounding the apparatus to mimimise radiated heat loss from the flame, using insulating material surrounding the can and placing a top on the can.

24. Heat is progressively lost at each energy transformation stage.

25. a. Chemical energy in the organic waste → chemical energy in the biogas → thermal energy (e.g. in furnaces) or electrical energy (e.g. for lighting).

b. Sample responses can be found in your digital formats.

c. Sample responses can be found in your digital formats.

1.8 Exercise 3: Exam practice questions

1. $V = 464\,\text{L}$
2. a. The heat is measured in kJ kg^{-1} rather than kJ mol^{-1} because kerosene is measured in industry in kilograms rather than moles.
   b. 5.52 cups.
3. a. m(methanol) = 44.2 g
   b. m(propan-1-ol) = 29.8 g
   c. The net mass reduction of CO_2 = 4.9 g MJ^{-1}.
   d. Net $V(CO_2)$ reduction = 2.62 L
4. a. $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$
   b. Methane is non-renewable when obtained from a fossil fuel (natural gas) but is renewable when obtained from a biofuel (biogas).
   c. Methane combustion in an insufficient supply of oxygen may produce carbon monoxide.
   d. $2CH_4(g) + 3O_2(g) \rightarrow 2CO(g) + 4H_2O(g)$
   e. Carbon monoxide is toxic.

2 Fuel choices

2.2 Comparing energy sources

2.2 Exercise

1. Brown coal: 16 kJ g^{-1}
   Biogas: 26 kJ g^{-1}
   Bioethanol: 30 kJ g^{-1}
   Black coal: 30 kJ g^{-1}
   Biodiesel: 42 kJ g^{-1}
   Petrol: 46 kJ g^{-1}
   Diesel: 48 kJ g^{-1}
   Natural gas: 56 kJ g^{-1}
2. The enhanced greenhouse effect is the accumulation of excess greenhouse gases in the atmosphere, causing more heat to be trapped in the atmosphere. By choosing sustainable fuels, we can limit the amount of greenhouse gases being released into the atmosphere and thereby reduce the impact of the enhanced greenhouse effect.
3. The combustion of fossil fuels puts carbon back into the environment (as carbon dioxide) that has been locked underground for millions of years. By comparison, biofuels are considered to be carbon neutral because the carbon released into the atmosphere was obtained relatively recently via photosynthesis.

2.3 Suitability of fuels for transport

2.3 Exercise

1. a. As population growth rate increases, the population increases rapidly. This increases the rate of fossil fuel use because there are more people to supply energy to.
   b. Community awareness can cause more people to think about and act on reducing the amount and types of energy they use.
   c. As alternative technologies and fuel sources are developed, fossil fuels can start to be replaced by more environmentally friendly sources. Therefore, the rate of fossil fuel consumption decreases.
   d. The rate of fossil fuel use might drop if fuel prices increase, or increase if fuel prices drop.
   e. Fossil fuel trade embargoes between nations could reduce fossil fuel use. This is a complex issue which will depend on the nature of the trade deals.
2. **a** and **b.**

Activities that require fossil fuels	Alternative energy supplies
Transport	Solar, wind or other renewable energy sources
Air conditioning/heating	Solar, wind or other renewable energy sources
Cooking (stove, oven, microwave, etc.)	Solar, wind or other renewable energy sources
TV/computer/phone use	Solar, wind or other renewable energy sources

   c. Answers will vary. Although fossil fuels currently provide the majority of Australia's energy, students may feel that renewable energy sources are more important because they will have to become the major energy sources of the future.
3. a. Sample responses can be found in your digital formats.
   b. Sample responses can be found in your digital formats.
4. a. Biodiesel comprises alkyl esters manufactured from vegetable oils or animals fats. Petrodiesel comprises long-chain alkanes obtained from the fractional distillation of petroleum.
   b. Sample answer: At low temperatures, biodiesel can gel and increase its viscosity, which can compromise engine life.
   c. Sample answer: Biodiesel is biodegradable, renewable resource that can replace the use of fossil fuels.
   d. Sample answer: Food crops for human consumption may be diverted into biodiesel manufacture.

2.4 Review

2.4 Exercises

2.4 Exercise 1: Multiple choice questions

1. A.
2. B.
3. D.
4. B.
5. A.

2.4 Exercise 2: Short answer questions

1. a. A fuel formed from the remains of living organisms, such as animals, trees and smaller plants that lived many years ago.
   b. Coal, petroleum and natural gas.
2. Sample responses can be found in your digital formats.
3. a. Biofuel: a fuel that is produced from renewable, organic resources, especially biomass (organic material).
   b. Bioethanol, biodiesel and biogas.

4.

	Advantages	**Disadvantages**
Ethanol	Environmentally friendlier Cheaper Higher octane rating	Absorbs water, which is bad for engine health and performance Less efficient
Petrol	More efficient Does not damage engines	Worse for the environment More expensive

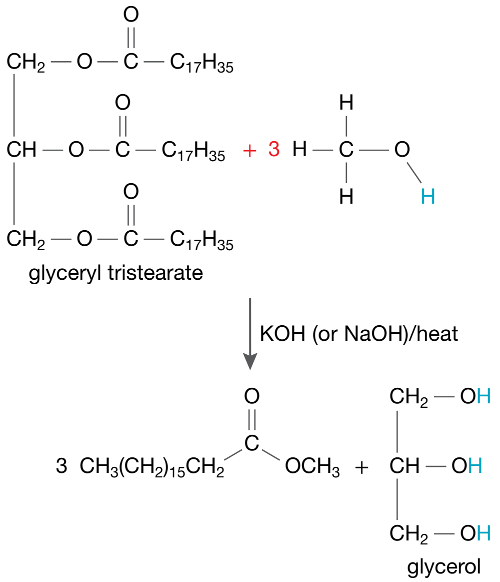
5.

	Advantages	**Disadvantages**
Biodiesel	Environmentally friendlier Fewer harmful emissions	Higher viscosity Less efficient
Petrodiesel	More efficient Lower viscosity	Worse for the environment

6. a. Non-renewable
   b. Coal seam gas is extracted by drilling wells into underground coal deposits.
   c. Methane gas
   d. Sample answer: possible pollution of underground water aquifers, and pollution from chemicals used in the fracking process
7. a. Electricity production by coal-fired power stations is an inefficient process because heat is lost when coal is burned and when steam is condensed back into water.
   b. Sample answer: Overuse of electrical appliances not turning appliances off at the wall
8. a. Answers will depend on electricity usage. An example for a household that uses 5000 kWh per year: $1.44 \times 5000 = 7200$ kg of carbon dioxide.
   b. Carbon dioxide is a greenhouse gas that contributes to the enhanced greenhouse effect which causes more heat to be trapped in the Earth's atmosphere, leading to environmental issues such as global warming.
   c. Sample answer:
      - installing solar panels or switching to any other form of sustainable energy
      - limiting electricity use
      - using public transport instead of driving
9. a. Cost of wasted fuel = 87 cents
   b. Cost of trip back = \$10.87
10. % efficiency = 37%

2.4 Exercise 3: Exam practice questions

1. a. Transesterification involves a chemical reaction where one type of ester is turned into another.
   b.



   c. $2C_{17}H_{35}COOCH_3(l) + 55O_2(g) \rightarrow 38CO_2(g) + 38H_2O(g)$
   d. Glycerol ($C_3H_8O_3$)
   e. Ester
   f. Sample answer: Advantages: renewable resource, carbon neutral
   Disadvantages: using crops for fuel rather than food production, deforestation to grow crops

3 Galvanic cells as a source of energy

3.2 Redox reactions and half-equations

Practice problem 1

Oxidation number of S = +4.

Practice problem 2

The oxidation number of tungsten has decreased (from +6 to 0), so it has been reduced. Similarly, the oxidation number of hydrogen has increased (from 0 to +1), indicating oxidation.

Therefore, this is a redox reaction. WO_3 is the oxidising agent and H_2 is the reducing agent.

Practice problem 3

Na(s)	**+**	**$H_2O(l)$**	**→**	**$NaOH_4(aq)$**	**+**	**$H_2(g)$**
Gets oxidised Acts as an reducing agent Forms a conjugate oxidising agent		$H_2O(l)$ gets reduced Acts as a oxidising agent Forms a conjugate reducing agent		Conjugate oxidising agent		Conjugate reducing agent

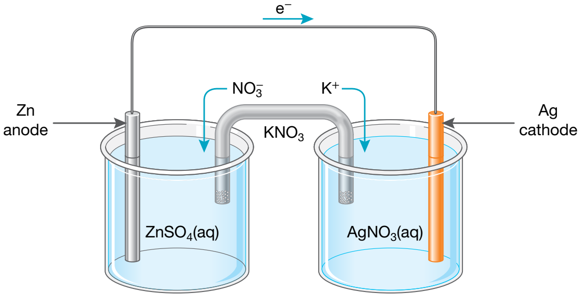
3.2 Exercise

1. a. H is $+1$. Br $= -1$.
   b. O is -2. Na $= +1$.
   c. H is $+1$. C $= -4$.
   d. O is -2. Na $= +1$. Cl $= +5$.
   e. O is -2. Al $= +3$
   f. O is -2. H is $+1$. P $= +5$.
2. a. $O_4 = -8$, $H_2 = +2$. S $= +6$
   b. $O_2 = -4$. S $= +4$
   c. $O_3 = -6$. S $= +6$
   d. $H_2 = +2$. S $= -2$
3. a. Cr $= +6$
   b. Cr $= +3$
   c. Cr $= +2$
4. a. H $= +1$. $(2 \times 1) + N = -1$. N $= -3$
   b. O $= -2$.
   Mn $= +7$
   c. H $= +1$; S $= -2$
   d. O $= -2$. V $= +4$
   e. O $= -2$. I $= +5$
   f. O $= -2$. P $= +5$
5. a. Fe is oxidised and Cl_2 is reduced.
   b. N (in NO) is oxidised and O_2 is reduced.
   c. C (in CO) is oxidised and O_2 is reduced.
   d. H_2 is oxidised and C (in C_2H_4) is reduced.
6. a. i. $CH_3CH_2OH \rightarrow CH_3CHO + 2H^+ + 2e^-$
      ii. $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$
      iii. $5CH_3CH_2OH(l) + 2MnO_4^-(aq) + 6H^+(aq) \rightarrow 5CH_3CHO(l) + 2Mn^{2+}(aq) + 8H_2O(l)$
      iv. CH_3CH_2OH is the reducing agent and MnO_4^- is the oxidising agent.
   b. i. $CH_3CHO + H_2O \rightarrow CH_3COOH + 2H^+ + 2e^-$
      ii. $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$
      iii. $5CH_3CHO(l) + 2MnO_4^-(aq) + 6H^+(aq) \rightarrow 5CH_3COOH(l) + 2Mn^{2+}(aq) + 3H_2O(l)$
7. $Cu(s) + 2NO_3^-(aq) + 4H^+(aq) \rightarrow Cu^{2+}(aq) + 2NO_2(g) + 2H_2O(l)$

3.3 Galvanic cells

Practice problem 4

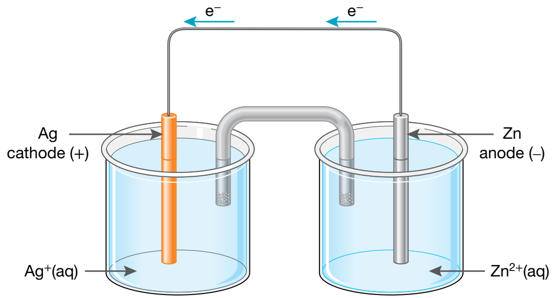
a, d and **e**



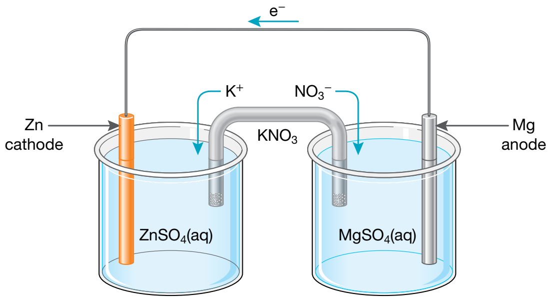
b. Oxidation: $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$
   Reduction: $Ag^+(aq) + e^- \rightarrow Ag(s)$
c. $Zn(s) + 2Ag^+(aq) \rightarrow Zn^{2+}(aq) + 2Ag(s)$

3.3 Exercise

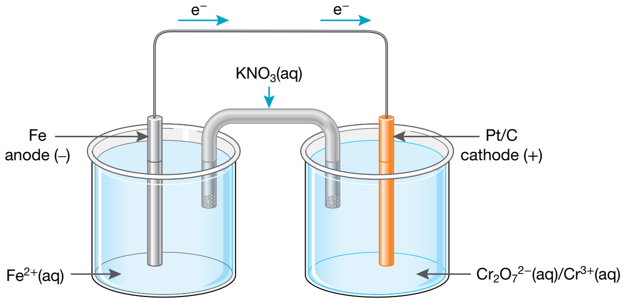
1. A salt bridge or porous barrier is need to connect the two half-cells because electrons cannot flow in the external circuit unless ions can move in the internal circuit. The circuit must be complete and the half-cells must be separated while still allowing the flow of charge through the salt bridge or porous barrier.
2. a. $Zn(s) + 2Ag^+(aq) \rightarrow Zn^{2+}(aq) + 2Ag(s)$
   b.



   c. Cathode: $Ag^+(aq) + e^- \rightarrow Ag(s)$
   Anode: $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$
   d. Not all of the chemical energy is transformed into electrical energy. Some of the chemical energy stored in the reactants is released as heat energy. This relationship increases as the temperature of the system increases.
3. **a–e**



   f and **g** Oxidation (at anode): $Mg(s) \rightarrow Mg^{2+}(aq) + 2e^-$
   Reduction (at cathode): $Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$
   h. Overall reaction: $Mg(s) + Zn^{2+}(aq) \rightarrow Mg^{2+}(aq) + Zn(s)$
   i. Zn^{2+} is the oxidising agent; Mg is the reducing agent.
4. **a** and **c**



   b. $Fe(s) \rightarrow Fe^{2+}(aq) + 2e^-$
   $Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$
   d. This reaction will not occur without $H^+(aq)$.

3.4 The electrochemical series

Practice problem 5

a. i. MnO_4^-
   ii. Al
   iii. Al^{3+}
   iv. Mn^{2+}

b. $Cl_2(g) + 2e^- \rightleftharpoons 2Cl^-(aq)$
$I_2(l) + 2e^- \rightleftharpoons 2I^-(aq)$
$Al^{3+}(aq) + 3e^- \rightleftharpoons Al(s)$
$MnO_4^- + 8H^+(aq) + 5e^- \rightleftharpoons Mn^{2+}(aq) + 4H_2O(l)$
$Pb^{2+}(aq) + 2e^- \rightleftharpoons Pb(s)$

Practice problem 6

Reduction (cathode): $Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq)$
Oxidation (anode): $Ni(s) \rightarrow Ni^{2+}(aq) + 2e^-$
Overall equation: $Ni(s) + 2Fe^{3+}(aq) \rightarrow Ni^{2+}(aq) + 2Fe^{2+}(aq)$
$E^0_{cell} = +1.00\ V$

3.4 Exercise

1. $Ag^+(aq) + 2e^- \rightarrow Ag(s)\ E^0 = +0.80\ V$
   $2Br^-(aq) \rightarrow Br_2(l)\ E^0 = -1.09\ V$
   It will be a non-spontaneous reaction because $Ag^+(aq)$ is the weaker of the two oxidising agents and $Br^-(aq)$ is the weaker of the two reducing agents.
2. **a.** $Cl_2(g) + Ni(s) \rightarrow 2Cl^-(aq) + Ni^{2+}(aq)$
   b. $2Al^{3+}(aq) + 3Mg(s) \rightarrow 2Al(s) + 3Mg^{2+}(aq)$
   c. $2MnO_4^- + 6H^+(aq) + 5ClO_3^-(aq) \rightarrow 2Mn^{2+}(aq) + 3H_2O(l) + 5ClO_4^-(aq)$
   d. $2MnO_4^- + 16H^+(aq) + 5Fe(s) \rightarrow 2Mn^{2+}(aq) + 8H_2O(l) + 5Fe^{2+}(aq)$
3. Predicted spontaneous redox reactions may not occur because the rate of reaction may be too slow to be observed initially or non-standard conditions may have been used, making the reaction less favourable/observable.
4. **a.** Anode: zinc, cathode: lead
   $E^0_{cell} = +0.63\ V$

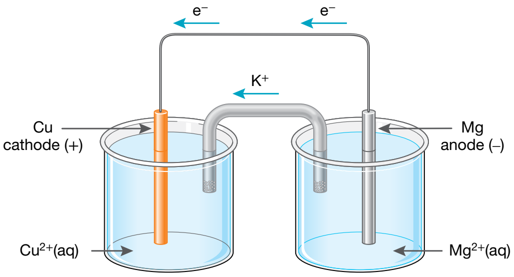
   $$Pb^{2+}(aq) + Zn(s) \rightarrow Pb(s) + Zn^{2+}(aq)$$
   $2e^-$

   b. Anode: platinum/carbon, cathode: silver
   $E^0_{cell} = +0.03\ V$

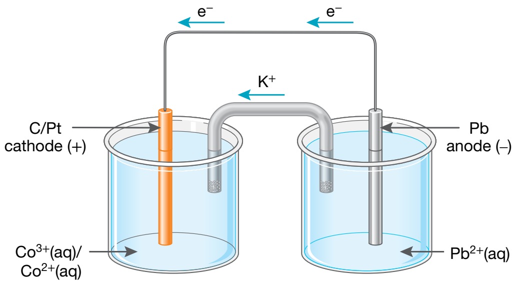
   $$Fe^{2+}(aq) + Ag^+(aq) \rightarrow Ag(s) + Fe^{3+}(aq)$$
   e^-

   c. Anode: iron, cathode: platinum/carbon
   $E^0_{cell} = +1.67\ V$

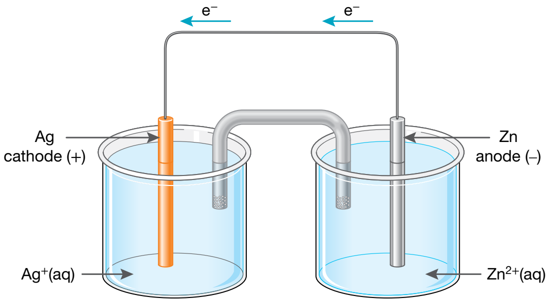
   $$O_2(g) + 4H^+(aq) + 2Fe(s) \rightarrow 2H_2O(l) + 2Fe^{2+}(aq)$$
   $4e^-$
5. **a.**



b.



6. A zero cell voltage may result from: the cell contents may be used up, the salt bridge may be dried out, or the electrical circuit may not be complete if ions from salt bridge precipitate with ions in the half-cell (the wrong electrolyte used in the salt bridge).
7. Primary cells are not rechargeable while secondary cells are rechargeable.
8. Zinc (Zn)
9. The oxidation number changes from + 4 in MnO_2 to + 3 in Mn_2O_3
10.



11. The oxidation number of oxygen has decreased from 0 to −2.
12. Lithium cells can produce a high cell voltage. They also last for a long time and have a high energy density.

3.5 Review

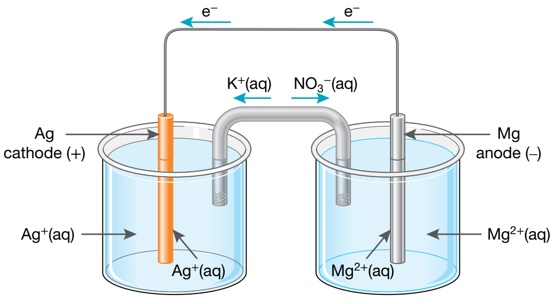
3.5 Exercises

3.5 Exercise 1: Multiple choice questions

1. B.
2. B.
3. D.
4. B.
5. B.
6. A.
7. B.
8. C.
9. C.
10. A.
11. B.
12. C.
13. B.
14. B.
15. A.

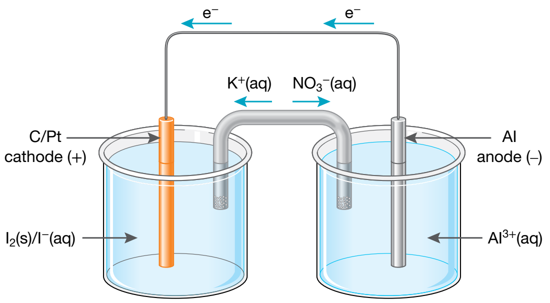
3.5 Exercise 2: Short answer questions

1. Answers will vary. Sample responses can be found in your digital formats.
2. a. Zn is oxidised; HCl is reduced.
   b. NO is oxidised; O_2 is reduced.
   c. Mg is oxidised; H_2SO_4 is reduced.
   d. Al is oxidised; Cl_2 is reduced.
3. a. Oxidising agent: Cl_2; reducing agent: I^-.
   b. Oxidising agent: Br_2; reducing agent: Cl^-.
   c. Oxidising agent: I_2; reducing agent: Br^-.
   d. Oxidising agent: Co^{3+}; reducing agent: Pb.
   e. Oxidising agent: Pb^{2+}; reducing agent: Fe
   f. Oxidising agent: H^+; reducing agent: Hg
   g. Oxidising agent: Cl_2; reducing agent: F.
4. a. $2Br^-(aq) + SO_4{}^{2-} + 4H^+(aq) \rightarrow Br_2(l) + SO_2(g) + 2H_2O(l)$
   b. $2Al(s) + 3Cl_2(g) \rightarrow 2AlCl_3(s)$
   c. $I_2(s) + H_2S(g) \rightarrow 2I^-(aq) + S(s) + 2H^+(aq)$
   d. $5Cu(s) + 2NO_3{}^-(aq) + 8H^+(aq) \rightarrow 5Cu^{2+}(aq) + 2NO(g) + 4H_2O(l)$
   e. $Cu(s) + 2NO_3{}^-(aq) + 4H^+(aq) \rightarrow Cu^{2+}(aq) + 2NO_2(g) + 2H_2O(l)$
   f. $3CuO(s) + 2NH_3(g) \rightarrow 3Cu(s) + 3H_2O(l) + N_2(g)$
   g. $PbS(s) + 4H_2O_2(l) \rightarrow PbSO_4(s) + 4H_2O(l)$
   h. $2Cr_2O_7{}^{2-}(aq) + 16H^+(aq) + 3CH_3CH_2OH(aq) \rightarrow 4Cr^{3+}(aq) + 11H_2O(l) + 3CH_3COOH(aq)$
5. a. $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$
   b. $Fe^{2+}(aq) + 2e^- \rightarrow Fe(s)$
   c. $Zn(s) + Fe^{2+}(aq) \rightarrow Zn^{2+}(aq) + Fe(s)$
6. a. Galvanic cell: An electrochemical cell that creates electrical energy from spontaneous redox reactions occurring within the cell.
   b. Internal circuit: The electrolyte in the two half-cells and the salt bridge.
   c. External circuit: The external wiring that connects the anode and cathode.
   d. Cathode: A solid conductive surface where reduction occurs.
   e. Anode: A solid conductive surface where oxidation occurs.
   f. Salt bridge: The electrolyte connecting the anode and cathode compartments.
   g. Inert electrode: An unreactive electrode, such as carbon or platinum, used as a conductive surface on which the redox half-reaction can occur.
7. a. Yes
   b. No
   c. Yes
   d. No
8. a.



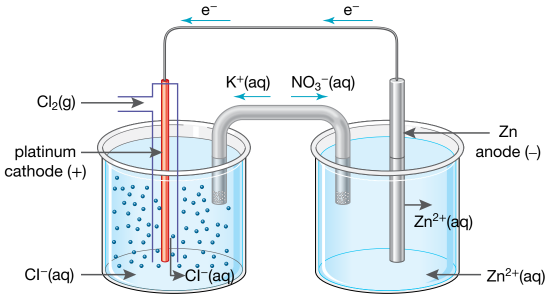
Cathode: $Ag^+(aq) + e^- \rightarrow Ag(s)$
Anode: $Mg(s) \rightarrow Mg^{2+}(aq) + 2e^-$

   b.



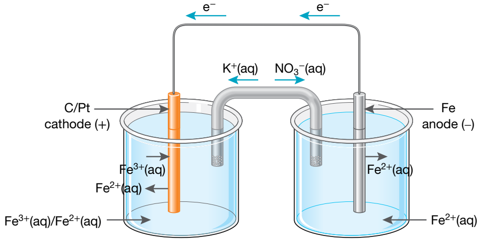
Cathode: $I_2(s) + 2e^- \rightarrow 2I^-(aq)$
Anode: $Al(s) \rightarrow Al^{3+}(aq) + 3e^-$

   c.



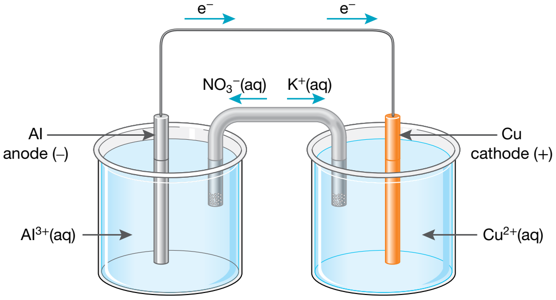
Cathode: $Cl_2(g) + 2e^- \rightarrow 2Cl^-(aq)$
Anode: $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$

   d.



Cathode: $Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(s)$
Anode: $Fe(s) \rightarrow Fe^{2+}(aq) + 2e^-$

9. a.



Reduction: $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$
Oxidation: $Al(s) \rightarrow Al^{3+}(aq) + 3e^-$
Overall: $3Cu^{2+}(aq) + 2Al(s) \rightarrow 3Cu(s) + 2Al^{3+}(aq)$

   b. There would be no electron flow — the transformation from chemical energy to electrical energy would stop.
   c. The intensity of the blue colour would slowly fade to become colourless as the Cu^{2+} ions react at the cathode.
10. Both Mg and Zn are stronger reducing agents than iron so, when iron is exposed to a corrosive environment (oxygen in the air/water from rain), the Mg or Zn will preferentially corrode, thus protecting the iron from corrosion.
11. Typically, a battery is a series connection of two or more cells, although it is common (but incorrect) to refer to single cells as batteries.

12. Commercial cells use an electrolyte paste to prevent the contents of the cell from mixing. They also use separators to prevent mixing of the anode and cathode compartments.

13. a. $4Al(s) + 3O_2(g) + 6H_2O(l) \rightarrow 4Al(OH)_3(s)$
    b. $2Al(s) + 6H_2O(l) \rightarrow 2Al(OH)_3(s)$

3.5 Exercise 3: Exam practice questions

1. a. The student noted the direction of electron flow. Electrons flow from the site of oxidation (the anode) to the site of reduction (the cathode).
   b. Electrons can flow from a reducing agent to an oxidising agent only if there is a difference in the half-cell reduction potential. In a copper–copper cell there is no difference in helf-cell reduction potential.
   c. $Ag(s) < Cu(s) < Ni(s) < Pb(s) < Fe(s) < Al(s) < Mg(s)$. The larger the voltage, the stronger the reducing agent strength.
2. a. $E^0_{cell} = +2.01\ V$
   b. The copper electrode would become larger because it would have an increasing layer of a salmon pink solid (copper) deposited on it (increase in mass). The colour intensity of the blue copper sulfate solution would fade over time.
   c. Positive
   d. *a*
   e. $Al(s) \rightarrow Al^{3+}(aq) + 3e^-$

4 Fuel cells as a source of energy

4.2 Fuel cells

4.2 Exercise

1. Electrochemical cells use stored chemical energy that they convert into electrical energy. Fuels cells require a continuous supply of fuel, which, when combusted with oxygen gas, converts chemical energy into electrical energy.
2. a.

	Equation
Anode (−) oxidation	$H_2(g) + 2OH^-(aq) \rightarrow 2H_2O(l) + 2e^-$ or $2H_2(g) + 4OH^-(aq) \rightarrow 4H_2O(l) + 4e^-$
Cathode (+) reduction	$\tfrac{1}{2}O_2(g) + H_2O(l) + 2e^- \rightarrow 2OH^-(aq)$ or $O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq)$
Overall	$H_2(g) + \tfrac{1}{2}O_2(g) \rightarrow H_2O(l)$ or $2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$

b.

	Equation
Anode (−) oxidation	$CH_4(g) + 2H_2O(l) \rightarrow 8H^+(aq) + 8e^- + CO_2(g)$
Cathode (+) reduction	$8H^+(aq) + 8e^- + 2O_2(g) \rightarrow 4H_2O(l)$
Overall	$CH_4(g) + 2O_2(g) \rightarrow 2H_2O(l) + CO_2(g)$

c.

	Equation
Anode (−) oxidation	$C_2H_5OH(l) + 3H_2O(l) \rightarrow 12H^+(aq) + 12e^- + 2CO_2(g)$
Cathode (+) reduction	$12H^+(aq) + 12e^- + 3O_2(g) \rightarrow 6H_2O(l)$
Overall	$C_2H_5OH(l) + 3O_2(g) \rightarrow 3H_2O(l) + 2CO_2(g)$

3. Any two of the following would be correct.
   - More efficient due to fewer energy transformations.
   - Fewer greenhouse gases produced in the overall manufacture/use of energy production.
   - Lower maintenance due to fewer moving parts
   - Lower running costs
   - Lower weight, which results in greater fuel economy.
4.
   - As a compressed gas in high-pressure tanks
   - As a liquid in tanks (stored at −253 °C)
   - As a solid by either absorbing or reacting with metals or chemical compounds, or storing in an alternative solid hydride compound.
5. Advantages include:
   - water is the only by-product (non-polluting and no carbon emissions)
   - greater efficiency.

   Disadvantages include:
   - hydrogen is difficult to store
   - hydrogen is difficult to initially manufacture and has a limited life cycle of H_2.

4.3 Review

4.3 Exercises

4.3 Exercise 1: Multiple choice questions

1. A.
2. A.
3. C.
4. D.
5. D.
6. A.
7. D.

4.3 Exercise 2: Short answer questions

1. a. A fuel cell is an electrochemical device that converts chemical energy into electricity without combustion as an intermediary step. There is also a continual supply of reactants.
   b. In fuel cells, operating and maintenance costs are lower because they can be used continually rather than being discarded when depleted. Fuel cells often need the supply of only one reagent, as oxygen can be readily sourced from the atmosphere.
2. a. Sample answer: In spacecraft, fuel cells are more advantageous than internal combustion engines due to: high energy conversion efficiency, easy maintenance and low temperature operation.
   b. Sample answer: Limitations of fuel cells include: expensive, not fully technologically developed, and

difficulties with the distribution, storage and transportation of fuels (particularly hydrogen gas).

3. a. $CH_4(g) + 2H_2O(l) \rightarrow CO_2(g) + 8H^+(aq) + 8e^-$
   b. $O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$
   c–f. See figure at foot of the page.*
4. a. $2C_8H_{18}(l) + 25O_2(g) \rightarrow 16CO_2(g) + 18H_2O(l)$
   b. Fuel cells are more efficient at transforming the chemical energy in the fuel. Also, they are more environmentally friendly because less carbon dioxide is released per unit of transformed energy.
   c. anode:
   $C_8H_{18}(l) + 16H_2O(l) \rightarrow 8CO_2(g) + 50H^+(aq) + 50e^-$
   cathode: $O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$
   d. $2C_8H_{18}(l) + 25O_2(g) \rightarrow 16CO_2(g) + 18H_2O(l)$
   While finding the overall equation, remember that the electrons in the half equations must be cancelled out. The answers to questions a and d are the same.
5. Fossil fuels are non-renewable and their use is a major contributor to global warming. Electrochemical cells, and fuel cells in particular, can use renewable fuels (e.g. hydrogen gas obtained from water using solar energy for electrolysis) and are therefore a sustainable alternative to fossil fuels.
6. Electricity produced from an electrochemical cell involves just one energy transformation (chemical energy to electrical energy) and has a relatively high level of efficiency. Both hydro-electricity schemes and coal-fired power stations produce electricity less efficiently because they involve multiple energy transformations.
   a. potential → kinetic → mechanical → electrical
   b. chemical → thermal (when combusted) → thermal (in steam) → mechanical → electrical

4.3 Exercise 3: Exam practice questions

1. a. $C_3H_8(g) + 6H_2O(l) \rightarrow 3CO_2(g) + 20H^+(aq) + 20e^-$
   b. $O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$ [1 mark]
   c. Sample answer: Using propane as a fuel in a fuel cell rather than combusing propane results in more efficient energy transformation and less CO_2 is evolved per unit of transformed energy.
   d. The electrodes of a fuel cell must be porous, and they must catalyse the half-cell reactions. Electrodes in primary cells are not catalysts, as the areas of oxidation and reduction are separated.
2. a. Cars powered by hydrogen would not be truly carbon neutral because the hydrogen gas to power the cars would need to be made in power stations (and potentially by burning fossil fuels) resulting in carbon dioxide formation/global warming/greenhouse gas emission/acid rain production and because manufacturing the hydrogen cars produces polluting gas.
   b. An advantage of using hydrogen instead of petrol is that combusting hydrogen will not produce carbon dioxide or sulfur dioxide pollutants.
   c. Advantages of storing hydrogen as a solid hydride rather than as a gas include:
      - hydrogen gas is very flammable and storing hydrogen as a solid hydride (MgH_2) is safer because it is not flammable [1 mark]
      - a solid will occupy a much smaller volume than a gas, saving weight and therefore increasing overall efficiency. [1 mark]

5 Rate of chemical reactions

5.2 How does a chemical reaction occur?

Practice problem 1

To increase the number of collisions:

- increase temperature
- increase concentration or pressure.

Sample responses can be found in your digital formats.

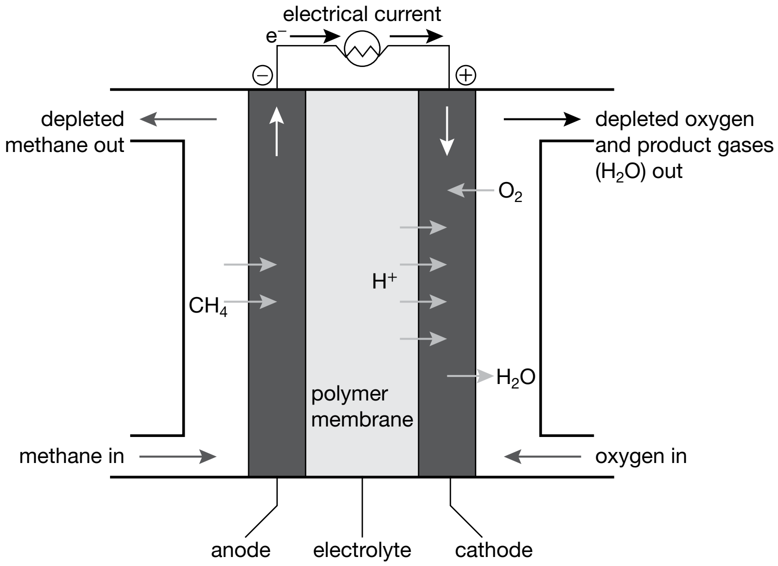
Practice problem 2

a. No change.
b. The graph will be stretched to the right.

5.2 Exercise

1. Reacting particles must collide, the collisions must have correct orientation, and collisions must possess the minimum amount of energy required to break bonds.
2. With increasing temperature, the graph will be stretched to the right and flatten slightly (a lower peak). An increase in concentration will cause no change to the graph.

c–f*



3. Increasing the temperature will increase the average kinetic energy of the particles, therefore, more particles will have a higher energy, resulting in the area under the graph at higher energies becoming larger.
4. The area under the graph becomes larger because there are now more particles in the sample. However, the position of the maximum peak will not shift because the distribution of particle energies will not have altered — there has been no change in temperature.
5. a. Collisions occur at random. Some of these will slow particles down, while others will speed particles up. This results in a range of velocities and energies.
   b. There will always be some particles in the tail of the Maxwell–Boltzmann distribution, at or above the activation energy of the reaction which possess enough energy to break bonds upon collision. However, this number may sometimes be so small that it is effectively negligible.
6. a. Both graphs will mimic the energy graph, however the 350 K graph will be shifted to the right because particles will have a higher average velocity at 350 K compared to 298 K.
   b. The graph for hydrogen gas will be stretched to the right to reflect the higher average velocities of the hydrogen molecules. Both samples are at the same temperature, therefore the average energies of the particles in both samples will be the same. However, because H_2 molecules are lighter than CH_4 molecules, they will need to move faster to achieve the same energy.
   c. The graphs will be the same. Both samples are at the same temperature and have particles of the same mass ($M_r = 44$ in both cases).

5.3 Exothermic and endothermic reactions

Practice problem 3

a. Exothermic (ΔH is negative)
b. 100 kJ mol^{-1}.

5.3 Exercise

1. a. Exothermic (ΔH is negative)
   b. i. $\Delta H = -30$ kJ mol^{-1}.
      ii. $E_a = 20$ kJ mol^{-1}.
      iii. $E_a = 20$ kJ mol^{-1}. This is the same as the minimum energy required to break the reactant bonds.
      iv. Energy released = 50 kJ mol^{-1}.
2. The activation energy must be low.
3. This is not possible because the products would have to have an enthalpy higher than that of the activated complex (transition state).
4. a. Forward reaction is lower than backward reaction
   b. Forward reaction is higher than backward reaction

5.4 Factors affecting the rate of a chemical reaction

Practice problem 4

Set A.

5.4 Exercise

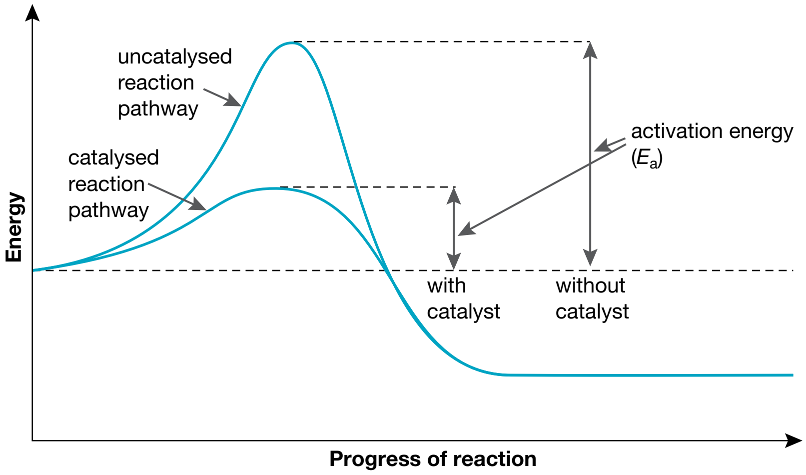
1. Increase temperature, increase concentration or pressure, increase surface area, use of a catalyst
2. Fireworks need their powder to react quickly with oxygen. A large surface area (powder) facilitates this.
3. Rate will increase due to a higher frequency of collisions caused by the particles being closer together.
4. a. Concentration of H_2CO_3 decreases as it is used up, which decreases the rate of CO_2 production.
   b. The rate of carbon dioxide production (and hence the rate of forward reaction) would be higher if the drink was warm.
5. Powdered coal has a higher surface area than the same amount of lump coal.
6. a. Powder, 2 M HCl and a hot water bath
   b. Strip, 0.5 M HCl and a cool water bath
7. a. The molecules in the gas/air mixture may not initially have enough energy to overcome the activation energy barrier and hence do not react. However, a spark provides enough energy for some of the molecules to do so and so the reaction starts.
   b. Following on from (**a**), energy is given out and this provides the energy for further molecules to overcome the activation energy barrier. This enables the reaction (explosion) to build up and continue.

5.5 Catalysts and reaction rates

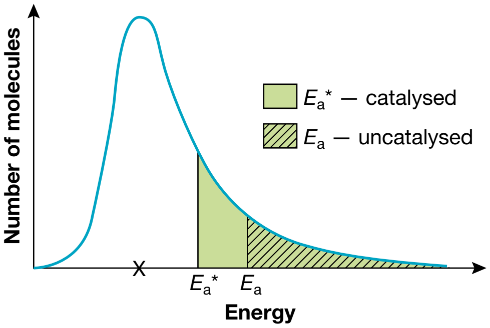
5.5 Exercise

1. No. A catalyst lowers the activation energy, it does not change the enthalpy of the reactants or the products, therefore ΔH will remain unchanged.
2. See figure at foot of the page.*

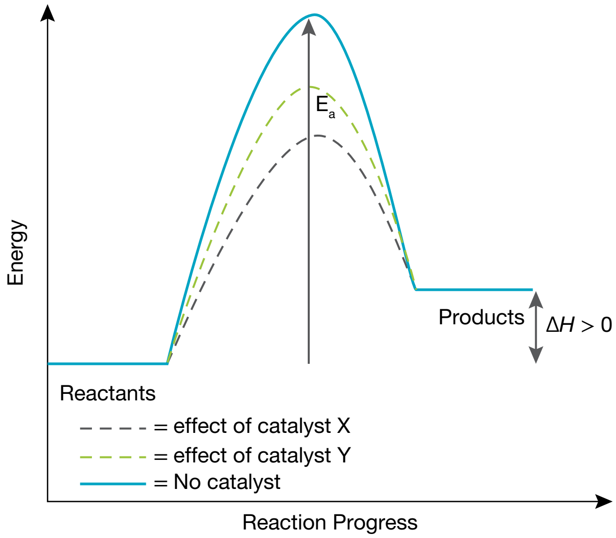
2*



3. A catalyst lowers the activation energy.



4.



5. a. Powdered form has more surface area.
   b. The temporary bonds between X and AB weaken the AB bond.
   c. The catalyst is improving the orientation for collisions to be successful.
   d. Once formed, molecules of CA leave the surface thus freeing it up to repeat the process with more molecules of AB.

5.6 Review

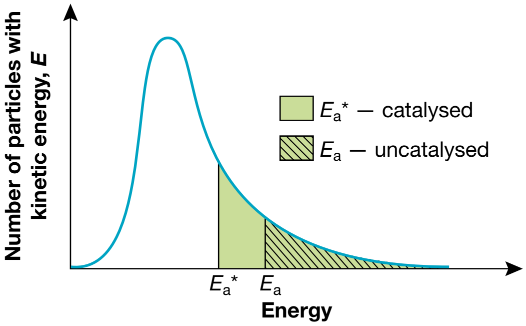
5.6 Exercises

5.6 Exercise 1: Multiple choice questions

1. B.
2. D.
3. A.
4. C.
5. D.
6. B.
7. B.
8. C.
9. B.
10. D.

5.6 Exercise 2: Short answer questions

1. a. Slow
   b. Fast
   c. Moderate
   d. Moderate
   e. Fast
   f. Moderate
2. A catalyst lowers the activation energy of a reaction; that is, it makes it easier to break the bonds in reactants. This is described as 'providing an alternative reaction pathway'.
3. Castor sugar is finely ground and has a much greater surface area than granulated sugar. Consequently, more castor sugar particles are exposed to the sulfuric acid molecules, resulting in an increased frequency of collision between the reacting particles.
4. Particles are continuously colliding with each other. All such collisions are elastic — energy is conserved; some particles will slow down and others will speed up, resulting in a wide range of velocities. The Maxwell–Boltzmann distribution curve represents this spread of energies.
5. a.

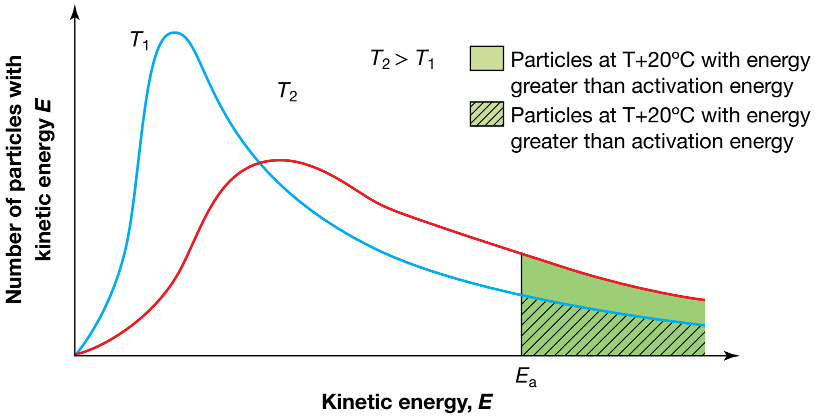


   Sample responses can be found in your digital formats.

   b. See figure at foot of the page.*

   When temperature is increased, there are more particles with an energy greater than the activation energy, and faster reaction rate results.
6. a. The necessary reactions happen at a quicker rate as the average energy of the colliding particles is greater and thus able to overcome the activation energy barrier.

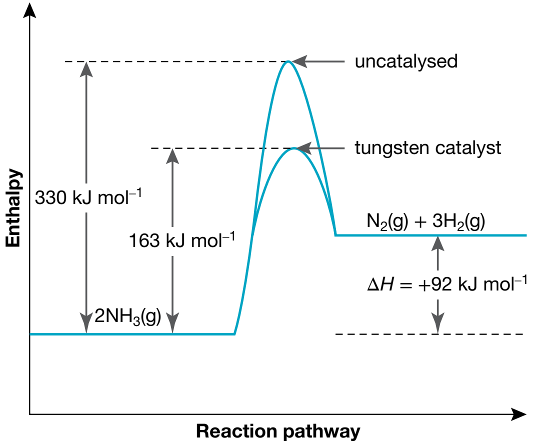
5b*



b. The steel wool has a greater surface area and hence is more exposed to the oxygen in the air.
c. The manganese dioxide is acting as a catalyst; allowing peroxide to decompose faster, producing oxygen continually.
d. Increased temperature causes a faster reaction due to particles colliding with more energy.
e. The reaction slows because the concentration of reactants decreases as they are used up.
f. The chemicals in the infrared film are sensitive to heat. With cooling during storage, the rate at which these chemicals react is lowered.

7. a. The reactant molecules are consumed; resulting in a progressive decrease in the frequency of successful collisions of reactant molecules.
b. Four reactant gas molecules are being converted into three product gas molecules.

8. a. A substance that increases the rate of a chemical reaction without being consumed. It provides an alternative reaction pathway with a lower activation energy.
b.



c. $E_a = 238$ kJ mol^{-1} (note: question is about reverse reaction)
d. $E_a = 71$ kJ mol^{-1} (note: question is about reverse reaction)

9. a. Lipase, an enzyme, acts as a catalyst, thereby lowering the activation energy.
b. It is the same because catalysts are not consumed in chemical reactions.

10. Increase in surface area for solid reactants, an increase in pressure for gas reactions, an increase in concentration for reactions occurring in solutions and using an appropriate catalyst.

5.6 Exercise 3: Exam practice questions

1. a. The rate of production of C be higher during the initial stages in both reactions because the reactant concentration is greatest at this stage in both scenarios.
b. Equal amounts of A and B are used, leading to equal amounts of C produced. A catalyst does not affect the nature of the products.
c. Y is a catalyst. The rate of reaction is increased. The concentration of Y stays the same.
d. Repeat experiment under identical conditions (except) without X present.

2. a. Endothermic
b. The new method is quicker.
c. Because the temperature and concentration is the same across both methods, these factors will not influence collision rate and hence rate of reaction.
In the new method, the greater surface area of B (and thus of contact between the two immiscible liquids) would lead to more collisions between A and B, and hence more successful collisions, and a faster rate of reaction.
d. As liquid B now interacts with liquid A for a longer time, the droplets of B in the spray will become coated with C as their reaction is a surface reaction. The collected C will not therefore be pure. This could be minimised by making the droplets in the spray as small as possible.
e. Increased temperature will result in more collisions between molecules of A and B. The contact time between the two liquidscan be reduced.

3. a. Increasing $S_2O_8^{2-}$(aq) concentration produces a faster rate in reaction 1.
Keeping I^-(aq) volume constant and doubling $S_2O_8^{2-}$(aq) volume results in a decrease in the time taken for the blue colour to appear; that is, the rate of reaction 1 is increased.
b. Comparing trials 1 and 3
Keeping $S_2O_8^{2-}$(aq) volume constant and doubling the I^-(aq) volume results in a decrease in the time taken for the blue colour to appear; that is, the rate of reaction 1 is increased.
c. The reaction times would increase
d. Adding water as indicated ensures concentration does not become another variable in the experiment, as this would vary the frequency of collisions between reacting particles and thus affect the rate of the reaction.
e. To identify when reaction 1 reaches the same stoichiometric point for each trial, the appearance of the blue colour is used to indicate when the same amount of $S_2O_3^{3-}$(aq) is used up, leaving I_2 in excess to react with starch.

6 Extent of chemical reactions

6.2 Reversible and irreversible reactions

6.2 Exercise

1. Irreversible reaction: the reactants form products that cannot be converted back into reactants. Only the forward reaction is possible. Reversible reaction: the reactants react to form products, the products can react to form reactants. Both the forward and backward reactions can occur.
2. The rate of a reaction measures how quickly reactants are converted into products. The extent of a reaction measures the quantity of reactants that are converted into products.
3. The rate at which the hydrogen peroxide decomposes (under normal conditions) is very slow.
4. Reaction I: type 4
Reaction II: type 1, type 2, type 3
Reaction III: type 2
Sample responses can be found in your digital formats.
5. The provision of more time or the addition of a catalyst would provide evidence for the isolation of type 2. Distinguishing between types 1 and 3 would prove more difficult. A more sensitive method for detecting any product may work.

6.3 Homogenous equilibria

Practice problem 1

a. The concentration of N_2O_4 at t_1 will be equal to its concentration at t_2.

b. N_2O_4 is increasing but at an ever slower rate until the reaction reaches equilibrium. After this its value stays constant.

6.3 Exercise

1. The dynamic nature of equilibrium refers to the fact that reaction is still taking place, it has not stopped. The rate of the forward reaction is equal to the rate of the reverse reaction. The result is that all amounts therefore stay constant.

2. Answers will vary. Sample responses can be found in your digital formats.

3. a. Static: Radioactive iodine would be found only in I_2.

b. Dynamic: Radioactive iodine will be distributed between I_2, I^- and I_3^-.

4. a. forward reaction > reverse reaction

b. forward reaction > reverse reaction

c. forward reaction = reverse reaction

d. forward reaction = reverse reaction.

5. a. There would be no further changes to any of the concentrations.

b. Z increases because there is a net forward reaction. It increases at 3 times the rate that Y decreases and at $\frac{3}{2}$ times the rate that X decreases (due to the stoichiometry of the reaction).

c. The concentration of X = 2.5, Y = 1.5 and Z = 1.

6. A reaction depends on successful collisions (see topic 5). Statistically, the more particles there are, the more successful collisions there will be. Reactions slow down as their reactants are being used up. When this occurs to a reaction, its reverse reaction will speed up as the number of its reactants have increased by the first reaction.

6.4 Calculations involving equilibrium systems

Practice problem 2

$$K_c = \frac{[CO_2]\,[H_2O]^2}{[CH_4]\,[O_2]^2}$$

Practice problem 3

$K_c = 31\,M^{-1}$

Practice problem 4

$K_c\,(2) = 0.00400\,M^{-1}$

Practice problem 5

$K_c = 1.2\,M$

Practice problem 6

$[NH_3] = 0.089\,M$

Practice problem 7

The reaction is not at equilibrium. As $Q > K_c$ there is a net backward reaction. The rate of the reverse reaction is faster than the rate of the forward reaction.

6.4 Exercise

1. a. The very high value of $K_c = 10^{140}$ suggests the reactants are completely converted into products.

b. No. The high equilibrium constant means this can be considered a complete reaction.

2. a. i. $K_c = \dfrac{[CIF_3]^2}{[Cl_2]\,[F_2]^3}$

ii. $K_c = \dfrac{[NO]^2}{[N_2]\,[O_2]}$

iii. $K_c = \dfrac{[H_2O]^2\,[Cl_2]^2}{[HCl]^4\,[O_2]}$

iv. $K_c = \dfrac{[CF_4]\,[CO_2]}{[COF_2]^2}$

v. $K_c = \dfrac{[PF_5]^4}{[P_4]\,[F_2]^{10}}$

b. i. K_c units = M^{-2}

ii. K_c units = no unit

iii. K_c units = M^{-1}

iv. K_c units = no unit

v. K_c units = M^{-7}

3. $2A + B \rightleftharpoons C + 2D$

4. $K_c = 4.0$

Note: There are no units.

5. a. $m(Z) = 17$ g (2 significant figures)

b. $K_c(\text{new}) = 3.57\,M^4$

6. a. $K_c(2) = 0.617$

b. $K_c(2) = 2.62$

7. $K_c = 31\,M^2$

8. a. There are no units (concentrations cancel out).

b. $K_c(2) = 0.16$

9. After evaluating the reaction quotient (Q) for each experiment, experiment 4 is the only one where $Q = K$. Therefore experiment 4 is at equilibrium.

Worked solutions can be found in your digital formats.

6.5 Measuring the efficiency of a reaction or process

Practice problem 8

% yield = 62.65%

Practice problem 9

% atom economy = 51.1%

6.5 Exercise

1. % yield = 86.3%

2. a. % atom economy = 17%

b. 100% (there will be no waste products — all atoms are used to make desired products)

3. % yield = 89.7%

6.6 Le Châtelier's principle

Practice problem 10

The reaction would partially oppose the removal of the hydrogen by attempting to replace some of it. This is achieved by the forward reaction becoming temporarily faster than the backward reaction. The 'position' of the equilibrium would, therefore, shift to the right. The forward reaction is favoured.

Practice problem 11

a. The addition of water immediately lowers the total concentration. The system responds by increasing the number of moles in an effort to compensate. The amount of I_3^- present would decrease.
b. If the volume was decreased the reactant $CaCO_3$ would increase. If the volume was increased, the the products CaO and CO_2 would increase.

Practice problem 12

The reaction is exothermic.

Practice problem 13

Oxygen transport in the body relies on an equilibrium reaction between haemoglobin and oxygen.
$Hb_4 + 4O_2 \rightleftharpoons Hb_4(O_2)_4$

In the lungs, the high concentration of O_2 forces this reaction to the right. Formation of $Hb_4(O_2)_4$ is favoured. On reaching the tissues, O_2 is being removed by respiration. This removal forces the reaction to the left. Decomposition of $Hb_4(O_2)_4$ is favoured thus releasing O_2 to the tissues. Upon return of the Hb_4 to the lungs, the cycle begins again.

6.6 Exercise

1. Temperature is the only variable where a change effects the position of the equilibrium. Exothermic and endothermic reactions are affected differently by temperature.
2. **a.** Produces a net forward reaction to partially replace the removed product
   b. Produces a net forward reaction to partially use up the added reactant
   c. Produces a net forward reaction that turns four molecules into two, thus partially countering the effect of the increased pressure
   d. A net backwards reaction
   e. No change.
3. The position of the equilibrium will be:
   a. Produces net back reaction.
   b. Reaction is unchanged
   c. Produces net back reaction
   d. Produces net forward reaction.
4. The student is correct in saying that an increase in pressure will cause the system to move to the right. However, assuming the temperature is kept constant, there will be no change in the value of the equilibrium constant.
5. **a.** High temperatures
   b. Low temperatures
   c. The ZnO/Cr_2O_3 catalyst allows a suitable rate to be achieved at a lower temperature. This lower temperature is preferable for maximising the extent/yield.
   d. Lower the temperature of the exit gases. Methanol, a polar molecule, will condense before both CO and H_2. Unreacted CO, H_2 can then be recycled.
   e. % atom efficiency = 100% (methanol is the only product)
6. **a.** The equilibrium constant for reaction II is greater than the equilibrium constant for reaction I.
   b. Respiration is effectively removing O_2, a reactant in the original equation. This forces the equilibrium to the left, favouring decomposition into Hb_4 and O_2.
   c. The reverse reaction of reaction II is not triggered by respiring cells because:
   1. the equilibrium constant is very high. Reaction is essentially irreversible.
   2. Respiring cells do not use up CO, so there is no removal of this from the equilibrium.
   d. So long as there is a critical but small amount of uncombined haemoglobin present, adding O_2 will drive the formation of oxyhaemoglobin to the right, i.e. will make more efficient use of the small number of uncombined haemoglobin that is present.
7. **a.** At t_1 there was a decrease in temperature.
   b. Between times t_1 and t_2 there is a net backward reaction.
   c. If substance D was added at t_3 there would be no effect.
8. **a.** The lines indicate a system at equilibrium.
   b. Increase in volume (water added)
   c. Additional substance A was added
   d. If a catalyst was added at t_3 the time between t_3 and t_4 would be decreased.
   e. All results would be the same
9. **a.** Endothermic
   b. New reaction is reverse of original reaction. The new K_c will therefore be the reciprocal of the original one.

$$K_c(2) = \frac{1}{6.25} \times 10^{-3}$$
$$= 160$$

10. **a.** Increased pressure will maximise the yield of methanol.
    b. Lowering the temperature will increase the yield of methanol.
    c. If carbon monoxide (CO) was added the yield of methanol would be increased.
    d. Changing temperature is the only way to change the value of the equilibrium constant.
11. **a.** It is a reaction between ammonia and oxygen to make nitrogen monoxide and water.
    b. The reaction is exothermic due to the negative energy value given in kJ mol^{-1}
    c. To obtain a high value for K_c (i.e. favour the forward reaction) the reaction should be carried out at low temperatures.
    d. The formation of products would be favoured by low pressure.

6.7 Review

6.7 Exercises

6.7 Exercise 1: Multiple choice questions

1. A
2. C.
3. C.
4. A.

5. D.

6. A.

7. B.

8. C.

9. D.

10. A. At time, *t*, we can see that the concentration of two substances decreases. This must correspond to the reactants A and B. The stoichiometry of the reaction indicates 2 mol B for every mole of A. Hence B is the middle line. At time, *t*, the concentration of one substance increases, which corresponds to substance C. Hence from top to bottom the graphs represent substances C, B, A.

6.7 Exercise 2: Short answer questions

1. Isla is correct.
Sample responses can be found in your digital formats.

2. $K_c = 4.2\,M^{-1}$

3. a. $[I_2] = 0.067$ M

b. The value of K_c is temperature dependent.

4. a. $Hb_4 + 4O_2 \rightleftharpoons Hb_4(O_2)_2$

b. $Hb_4 + 4CO \rightarrow Hb_4(CO)_4$. This reaction is extremely difficuilt to reverse.

c. $K_{(a)} = \dfrac{[Hb_4(O_2)_4]}{[Hb_4]\,[O_2]^4}, K_{(b)} = \dfrac{[Hb_4(CO)_4]}{[Hb_4]\,[CO]^4}$

d. $K_{(b)} >> K_{(a)}$

e. When CO is inhaled, it readily replaces O_2 in oxyhaemoglobin. Once formed, $Hb_4(CO)_4$ is very stable due to the high value of the equilibrium constant for the reaction shown in (b). The stability of $Hb_4(CO)_4$ prevents O_2 being carried to the cells, and cell death occurs relatively quickly.

5. a. Equilibrium has been achieved in experiments 2 and 5, as $Q = K_c = 4$.

b. A net forward reaction will occur in experiments 1, 3 and 6 as $Q < K$. A net back reaction will occur for experiment 4 as $Q > K$.

6. a. Exothermic reaction

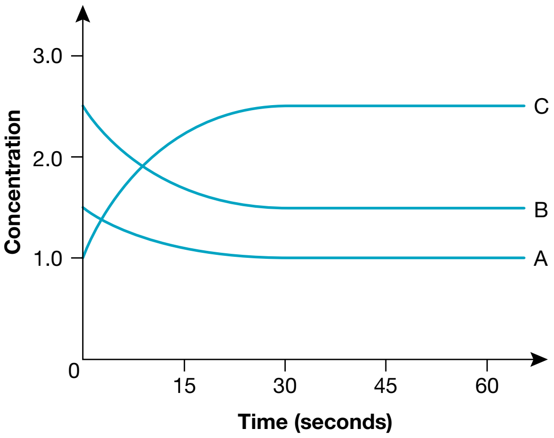
b. Fewer particles on the right-hand (product) side

7. a. $K_c = 1.85\,M^{-2}$

b. $p = 42.9T$ kPa

c. The amount of NH_3 would increase.

8. a.



b. Rate of forward reaction > rate of back reaction.

c. Rate of forward reaction = rate of back reaction.

d. $y = 2; z = 3$

e. $K_c = 6.9$

9. a. The system was in the process of reaching equilibrium.

b. The system was at equilibrium.

c. Some HI being removed

d. The spike in the graph indicates that some HI was added.

e. The volume was lowered.

f. No, because there are equal numbers of moles on each side of the equation.

10. $K_c = 1.7$

6.7 Exercise 3: Exam practice questions

1. a. Change 1: darken; Change 2: stay the same Change 3: lighten

b. Le Châtelier's principle states that if a change is made to a system at equilibrium it will partially oppose it (if possible).
Change 1: Adding KBr adds Br^- ions to the right-hand side. The system opposes this change with a net backward reaction and more Br_2 is produced making it darker.
Change 2: As NaCl is not involved in the reaction there would be no change.
Change 3: As the reaction is endothermic increasing the temperature would favour the forward reaction, consuming the brown $Br_2(g)$, resulting in the solution becoming lighter in colour.

2. a. $Q = 11.1\,M^{-1}$

b. $Q > K_c$ so rate of the backward reaction is greater than the rate of the forward reaction

c. $Q = 10\,M^{-1}$. Two rates being equal means the system is at equilibrium, hence $Q = K_c$.

d. The initial rate of the forward reaction (second experiment) will be greater than the initial rate of the forward reaction (first experiment).

e. The initial rate of the backward reaction (second experiment) will be greater than the initial rate of the backward reaction (first experiment).

f. $Q = 10\,M^{-1}$ System would be at equilibrium. A catalyst affects only the rate, nothing else.

3. a. At the right hand end of the graph, the top line is C and bottom two are A and B (already labelled).

b. $x = 2; y = 2$.

c. $K_c = 0.1$ M

d. Addition of C, shown by the sharp increase in the concentration of C, and the gradual equilibration of A, B and C.

e. Endothermic as K_c has increased with temperature. Alternatively, it could be explained that the reaction is endothermic because a net forward reaction has occurred after time t_2.

4. a. Sample asnwer: Safety concerns include: CO is highly toxic; HCN is highly toxic; H_2 is flammable. The toxicity of CO and HCN could be managed by, wearing a respirator/conducting experiment in a fume hood. H_2 gas risks can be minimised by ensuring production in small volumes only, and avoiding naked flames.

b. $K_c = \dfrac{[HCN]\,[CO_2]\,[H_2]}{[CO]^2\,[NH_3]}$

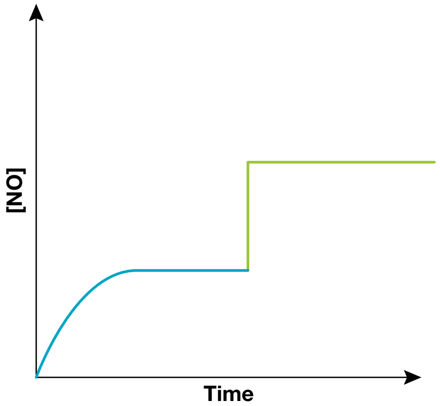
c. $[CO] = 0.0025\,M$
$[NH_3] = 0.0013\,M$
$[HCN] = 0.0042\,M$
$[HCN]_{eq} = [CO_2]_{eq} = [H_2]_{eq} = 0.0042$ M

d. $K_c = 9.3$
K_c has no units.

e. **i.** No change.
ii. Increased.

5. **a.** NO production is favoured because the necessary reactants, N_2 and O_2, are present in the air being used to burn the petrol and the temperature in the engine is sufficient to bring about NO production.

b.



c. As the reaction is endothermic ($\Delta H = 181$ kJ mol^{-1}) an increase in temperature will favour the forward reaction and more NO will be produced.

7 Production of chemicals by electrolysis and rechargeable batteries

7.2 What is electrolysis?

Practice problem 1

a. Cathode $K^+(l) + e^- \rightarrow K(l)$
Anode $2I^-(l) \rightarrow I_2(g) + 2e^-$
b. $2K^+(l) + 2I^-(l) \rightarrow 2K(l) + I_2(g)$

Practice problem 2

Cathode: K^+ ions and H_2O molecules
Anode: NO_3^- ions and H_2O molecules. The NO_3^- ions can be ignored because they are inert.

7.2 Exercise

1. Cathode: Potassium metal.
   Anode: Chlorine gas. Chloride ions will be oxidised at the anode forming chlorine gas. $2Cl^- \rightarrow Cl_2 + 2e^-$
   (The overall reaction would be: $2K^+ + 2Cl^- \rightarrow 2K(s) + Cl_2(g)$).
2. Sample answer:
   - hydrogen gas (bubbles) produced around the cathode
   - pH increases around the cathode (due to OH^- production)
   - blue colour around the anode (due to Cu^{2+} ions).
3. Pure water is a non-conductor because it does not contain any mobile ions. Adding a small amount of KNO_3 provides some mobile $K^+(aq)$ ions and some mobile $NO_3^-(aq)$ ions. Because there are charged particles that are free to move, the solution conducts electricity.
4. Positively charged (left) side of the apparatus: oxygen gas
   Negatively charged (right) side: hydrogen gas
   Sample responses can be found in your digital formats.
5. Electrodes must conduct electricity from their external circuit connections to their surfaces. Glass is a non-conductor.
6. **a.** The cathode has a negative charge because it is connected to the negative terminal of the power supply. It receives electrons from the external circuit. Electrons are removed from its surface by the process of reduction.
   b. The anode has a positive charge because it is connected to the positive terminal of the power supply. Electrons are added to its surface by the process of oxidation, and these flow back into the external circuit, towards the cathode.
7. Reactants in a galvanic cell would react spontaneously if they were placed in the same compartment. Reactants in an electrolytic cell do not react until a critical amount of energy is supplied, so a single compartment cell can be used.
8. Sample answer: The electrolysis of dilute sodium chloride: if the anode is inert, oxygen gas is produced. If the anode is copper, Cu^{2+} ions are produced.
9. Cathode: Li
   Anode: I_2
10. **a.** $K^+(l) + e^- \rightarrow K(l)$
    b. The cathode is negative (−).
    c. $2Br^-(l) \rightarrow Br_2(g) + 2e^-$.
    d. The anode is positive (+).
    e. $2K^+(l) + 2Br^-(l) \rightarrow 2K(l) + Br_2$

7.3 Predicting reactions that occur during electrolysis

Practice problem 3

Cathode: $Ag^+(aq) + e^- \rightarrow Ag(s)$. Silver metal will form.
Anode: $2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$. Oxygen gas will form.
Overall:
$Ag^+(aq) + 2H_2O(l) \rightarrow Ag(s) + O_2(g) + 4H^+(aq)$
Minimum voltage required: 0.43 V

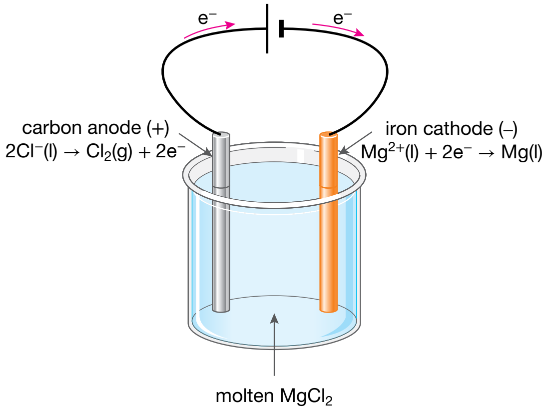
Practice problem 4

Cathode: $Pb^{2+}(aq) + 2e^- \rightarrow Pb(s)$ Lead metal will form.
Anode: $Fe(s) \rightarrow Fe^{2+}(aq) + 2e^-$. Fe^2+ will form.
Overall:
$Fe(s) + Pb^{2+}(aq) \rightarrow Pb(s) + Fe^{2+}(aq)$
Minimum voltage required: 0.31 V

7.3 Exercise

1. Cathode: $Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$
   Anode: $2Br^-(aq) \rightarrow Br_2(l) + 2e^-$
   Overall: $Zn^{2+}(aq) + 2Br^-(aq) \rightarrow Zn(s) + Br_2(l)$
2. **a.** Cathode: $2H^+(aq) + 2e^- \rightarrow H_2(g)$
   Anode: $Ag(s) \rightarrow Ag^+(aq) + e^-$
   Overall: $Ag(s) + 2H^+(aq) \rightarrow Ag^+(aq) + H_2(g)$
   b. This solution cannot be electrolysed using nickel electrodes because Ni and H^+ ions react spontaneously.

3. Cathode: $2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$
   Anode: $2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$
4. Cathode: water reacts in preference to Al^{3+}
   Anode: water reacts in preference to Cl^-
   Minimum cell voltage required: 2.06 V
5. a. Cathode: lead metal, Pb(s). Anode: chlorine gas, $Cl_2(g)$.
   b. Cathode: lead metal, Pb(s). Anode: O_2 and H^+.
6. a. Copper metal
   b. Lead metal
   c. Hydrogen gas and hydroxide ions
   Sample responses can be found in your digital formats.
7. a. Cathode: $Ni^{2+}(l) + 2e^- \rightarrow Ni(s)$
   Anode: $2I^-(l) \rightarrow I_2(g) + 2e^-$
   Overall: $Ni^{2+}(l) + 2I^-(l) \rightarrow Ni(s) + I_2(g)$
   b. Cathode: $Ni^{2+}(aq) + 2e^- \rightarrow Ni(s)$
   Anode: $2I^-(aq) \rightarrow I_2(aq) + 2e^-$
   Overall: $Ni^{2+}(aq) + 2I^-(aq) \rightarrow Ni(s) + I_2(aq)$
8. a. Iron can be used at the cathode because it cannot be reduced (iron does not accept electrons to produce negative ions). It is not used at the anode because it would be oxidised in preference to the chloride ions (Fe is a stronger reducing agent than Cl^- ions).
   b.

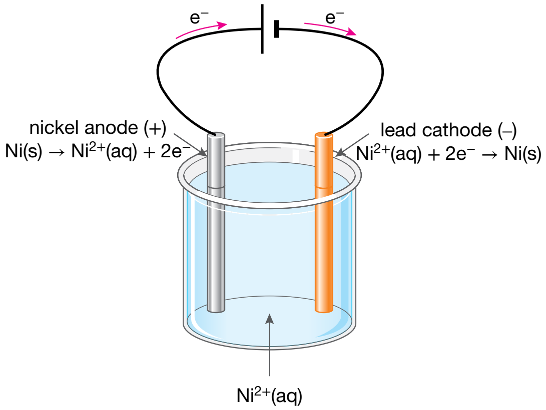


9. Ag, Zn and H_2.
10. a. Cathode: $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$
    Anode: $2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$
    b. The concentration of Cu^{2+} ions
    c. Cathode: $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$
    Anode: $Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$
    d. The concentration of Cu^{2+} ions will stay constant.
11. The electrolysis is not being performed at standard conditions.
12. This solution will react spontaneously to produce Sn^{4+} and Fe^{2+}.

7.4 Commercial applications of electrolysis

7.4 Exercise

1. Sodium hydroxide, chlorine gas and hydrogen gas
2. OH^- ions are formed at the cathode and will be attracted to the anode. Membranes impervious to OH^- ions ensure that they stay in the cathode compartment so that they can form sodium hydroxide.
3. Any metals that have an $E^0 < -0.83$ V, such as magnesium or potassium.
4. a. Aluminium can be produced at a lower temperature and therefore saves energy.
   b. Alumina does not dissolve in water, so cryolite is used as a solvent instead. Even if it alumina did dissolve in water, water would react preferentially at the cathode.
5. The electrolysis of water would cause oxygen to begin to be produced at the anode. If the dilution continued, eventually only oxygen would be produced.
6. Na^+ and F^- are extremely weak oxidising agents and reducing agents respectively and will therefore not interfere with the desired reactions at the cathode and anode.
7. Cathode: $Al^{3+}(l) + 3e^- \rightarrow Al(l)$
   Anode: $C(s) + 2O^{2-}(l) \rightarrow CO_2(g) + 4e^-$
   The carbon cathode acts as an inert electrode and therefore remains intact, whereas the carbon anode is consumed in the oxidation reaction that takes place.
8.



   Nickel will be oxidised at the anode and then will be reduced at the cathode to plate the lead cathode. Ni(s) is a stronger reducing agent and oxidising agent than water.
9. Reduction always takes place at the cathode according to the reaction: $M^{x+}(aq) + xe^- \rightarrow M(s)$.
10. a. Anode: nickel
    b. Electrolyte: nickel(II) solution

7.5 Comparing galvanic and electrolytic cells

7.5 Exercise

1. a. Energy into electrical energy.
   b. Electrical energy into chemical energy.
2. Sample responses can be found in your digital formats.
3. Sample responses can be found in your digital formats.

7.6 Calculations in electrolysis using Faraday's Laws

Practice problem 5

$n(X) = 0.0032\ \text{mol}\ (2\ \text{sig. figs})$

Practice problem 6

$n(W) = 0.027$ mol

Practice problem 7

a. $m(Cu) = 0.172\ g$
b. $V(O_2)_{SLC} = 0.0337\ L$ or $33.7\ mL$

Practice problem 8

The charge on the aluminium ion is 3+ (Al^{3+}).

Practice problem 9

$m(\text{Al}) = 80.6\,\text{kg}$ (2 sig. figs)

7.6 Exercise

1. $n(\text{Cr}) = 0.0073\,\text{mol}$
2. a. $m(\text{Ag}) = 0.805\,\text{g}$
   b. $V(O_2)_{\text{SLC}} = 0.0463\,\text{L}$ or $46.3\,\text{mL}$
3. The charge on the gold ion is 1 + (Au^+).
4. $t = 936\ s$
5. a. $m(\text{Al}) = 19.3\,\text{g}$
   b. $V(O_2) = 8.84\,\text{L}$
6. 36.3 minutes
7. 0 g
8. $t = 4.09$ days
9. i. a. $m(\text{Cu}) = 0.19$ g
      b. $V(O_2) = 37$ mL
   ii. a. $m(\text{Cu}) = 2.7$ g
      b. $V(O_2) = 0.52$ L
   iii. a. $m(\text{Cu}) = 10$ g
      b. $V(O_2) = 2.0$ L
   iv. a. $m(\text{Cu}) = 68$ g
      b. $V(O_2) = 13$ L
10. $t = 39.6$ s

7.7 Rechargeable batteries (secondary cells)

7.7 Exercise

1. The pH will fall.
2. The positive terminal of the battery is positive because electrons flow *into* it during discharge. To recharge the battery, the direction of electron flow needs to be reversed. To achieve this, the positive terminal must be connected to the positive of the charging device. This means that electrons will be *removed* (i.e. move in the opposite direction).
3. a. Cathode: $Cd(OH)_2(s) + 2e^- \rightarrow Cd(s) + 2OH^-(aq)$
   b. The negative terminal.
   c. $Cd(OH)_2(s) + 2Ni(OH)_2(s) \rightarrow Cd(s) + 2NiO(OH)(s) + 2H_2O(l)$
   d. Anode:
   $Ni(OH)_2(s) + OH^-(aq) \rightarrow NiO(OH)(s) + H_2O(l) + e^-$
4. a. $V^{2+}(aq) + VO_2{}^+(aq) + 2H^+(l) \rightarrow V^{3+}(aq) + VO^{2+}(aq) + H_2O(l)$
   b. $V^{3+}(aq) + VO^{2+}(aq) + H_2O(l) \rightarrow V^{2+}(aq) + VO_2{}^+(aq) + 2H^+(l)$
   c. Cathode: $V^{3+}(aq) + e^- \rightarrow V^{2+}(aq)$
   Anode: $VO^{2+}(aq) + H_2O(l) \rightarrow VO_2{}^+(aq) + 2H^+(aq) + e^-$
5. a. i. During discharge:
      Anode (−): $Fe(s) + 2OH^-(aq) \rightarrow Fe(OH)_2(s) + 2e^-$
      Cathode (+):
      $NiO(OH)(s) + H_2O(l) + e^- \rightarrow Ni(OH)_2(s) + OH^-(aq)$
   ii. During recharge:
      Cathode (−): $Fe(OH)_2(s) + 2e^- \rightarrow Fe(s) + 2OH^-(aq)$
      Anode (+):
      $Ni(OH)_2(s) + OH^-(aq) \rightarrow NiO(OH)(s) + H_2O(l) + e^-$
   b. Anode: Iron in contact with iron(II) hydroxide.
   Cathode: Inert electrode in contact with a mixture of nickel(III) oxyhydroxide and nickel(II) hydroxide.
   c. Fe is oxidised during discharge so this electrode is the anode. The NiO(OH) electrode undergoes reduction as the oxidation state of Ni decreases from +3 to +2.
   d. $Ni(OH)_2$ $Fe(OH)_2$

7.8 Review

7.8 Exercises

7.8 Exercise 1: Multiple choice questions

1. D.
2. D.
3. B.
4. D.
5. D.
6. C.
7. B.
8. C.
9. D.
10. A.
11. D.
12. C.
13. D.
14. B.
15. D.

7.8 Exercise 2: Short answer questions

1. See table at foot of the page*.
2. a. In the solid state, $Na^+(s)$ and $Cl^-(s)$ ions are held firmly in the ionic lattice ($Na^+(s)$ and $Cl^-(s)$ ions are not free to move, whereas, in the molten (or liquid) state, $Na^+(l)$ and $Cl^-(l)$ ions are free to move.
   b. It is only at the electrodes that electrons can be accepted in a reduction reaction (at the cathode) and lost in an oxidation reaction (at the anode), because electrons move freely though the metal/graphite but not through the molten solution.
   c. The external power supply drives the current flow in the external circuit, which in turn drives the ion flow in the internal circuit.
3. a. Cathode: sodium metal
   Anode: bromine gas
   The minimum cell voltage is 3.8 V.
   Overall:
   $2Na^+(l) + 2Br^-(l) \rightarrow 2Na(s) + Br_2(l)$
   b. Cathode: aluminium metal
   Anode: oxygen gas and water.
   The minimum cell voltage is 2.06 V.

1*

Electrolyte type	Electrodes	Reaction at	
		Anode(+)	Cathode(−)
Molten salt	Inert	$2Cl^-(l) \rightarrow Cl_2(g) + 2e^-$	$Na^+(l) + e^- \rightarrow Na(l)$
1 M aqueous salt solution	Inert	$2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$	$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$
6 M aqueous salt solution	Inert	$2Cl^-(aq) \rightarrow Cl_2(g) + 2e^-$	$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$

Overall:
$4Al^{3+}(l) + 12OH^{-}(l) \rightarrow 4Al(l) + 6H_2O(g) + 3O_2(g)$

c. Cathode: lead metal
Anode: chlorine gas.
The minimum cell voltage is 1.49 V.
Overall:
$Pb^{2+}(l) + 2Cl^{-}(l) \rightarrow Pb(l) + Cl_2(g)$

d. Cathode: magnesium metal
Anode: chlorine gas.
The minimum cell voltage is 3.73 V.
Overall:
$Mg^{2+}(l) + 2Cl^{-}(l) \rightarrow Mg(l) + Cl_2(g)$

4. a. Cathode: hydrogen gas and hydroxide ions.
Anode: oxygen gas and water
The minimum cell voltage is 1.23 V.
Overall:
$2H_2O(l) \rightarrow O_2(g) + 2H_2(g)$

b. Cathode: hydrogen gas and hydroxide ions.
Anode: oxygen gas and hydrogen ions
The minimum cell voltage is 2.06 V.
Overall:
$2H_2O(l) \rightarrow O_2(g) + 2H_2(g)$

c. Cathode: hydrogen gas and hydroxide ions.
Anode: oxygen gas and hydrogen ions
The minimum cell voltage is 2.06 V.
$2H_2O(l) \rightarrow 2H_2(g) + O_2(g)$

d. Cathode: zinc metal
Anode: bromine liquid
The minimum cell voltage is 1.85 V.
Overall:
$Zn^{2+}(aq) + 2Br^{-}(aq) \rightarrow Zn(s) + Br_2(l)$

e. Cathode: hydrogen gas and hydroxide ions.
Anode: iodine (aq)
The minimum cell voltage is 1.37 V.
Overall:
$2H_2O(l) + 2I^{-}(aq) \rightarrow H_2(g) + 2OH^{-}(aq) + I_2(l)$

f. Cathode: hydrogen gas
Anode: chlorine gas
The minimum cell voltage is 1.36 V.
Overall:
$2H^{+} + 2Cl^{-} \rightarrow H_2(g) + Cl_2(g)$

g. Cathode: hydrogen gas
Anode: oxygen gas and hydrogen ions
The minimum cell voltage is 1.23 V.
Overall:
$2H_2O(l) \rightarrow 2H_2(g) + O_2(g)$

5. a. i. Cathode: copper metal
Anode: oxygen gas and hydrogen ions
The minimum cell voltage is 0.89 V.
Overall:
$2Cu^{2+}(aq) + 2H_2O(l) \rightarrow 2Cu(s) + O_2(g) + 4H^{+}(aq)$

ii. Cathode: copper metal
Anode: copper ions
There is effectively no reaction at minimum cell voltage, just a transfer of copper.
Overall:
$Cu^{2+}(aq) + Cu(s) \rightarrow Cu(s) + Cu^{2+}(aq)$

b. i. Cathode: copper metal
Anode: oxygen gas and hydrogen ions
The minimum cell voltage is 0.89 V.
Overall:
$2Cu^{2+}(aq) + 2H_2O(l) \rightarrow 2Cu(s) + O_2(g) + 4H^{+}(aq)$

ii. There is effectively no reaction at minimum cell voltage, just a transfer of copper.
Overall:
$Cu^{2+}(aq) + Cu(s) \rightarrow Cu(s) + Cu^{2+}(aq)$
Note: The reactants and products are the same.

6. Similarities:

- Oxidation occurs at the anode and reduction occurs at the cathode.
- Anions migrate to the anode and cations migrate to the cathode.
- Circuit requires an electrolyte between the electrodes.
- Electrons move through the 'external circuit' and ions move through the 'internal circuit'.

Differences:
Galvanic cell

- Cell polarity is determined by the reactions occurring within the cell.
- Chemical energy is transformed into electrical energy.
- The anode is negative and the cathode is positive.

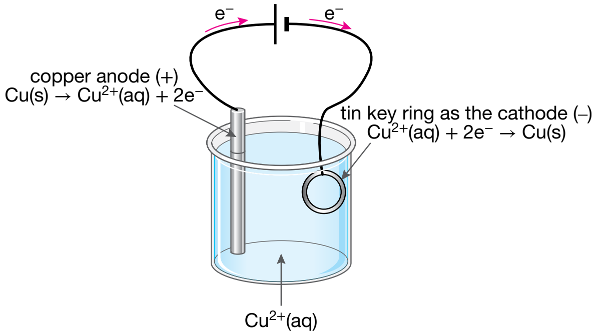
Electrolytic cell

- Cell polarity is determined by the external power source.
- Electrical energy is transformed into chemical energy.
- The anode is positive and the cathode is negative.

7. Lead–acid accumulators are secondary cells and, as such, can be recharged. When recharged, the chemical energy that is transformed from the electrical energy used in the charging process is stored until needed.

8. Option c. is the closest to such conditions.

9.



10. In each part of this question the number of faradays = $n(e^{-})$

a. 2.0 faradays
b. 5.0 faradays
c. 1.7 faradays
d. 0.23 faradays
e. 0.014 faradays

11. a. $Q = 289\,C$
b. $n(e^{-}) = 0.00300\,mol$
c. $n(Cr) = 0.00100\,mol$
d. The charge on the chromium ion is 3+.

12. $V(O_2) = 0.145$ L
$V(H_2) = 0.289$ L

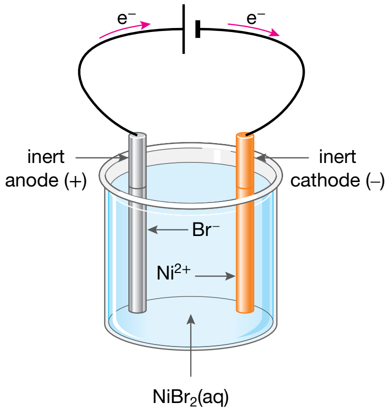
13. $t = 47$ minutes

14. a. $m(Sn) = 1.10$ g
b. No magnesium will be deposited.

15. $t = 1.28$ hours

7.8 Exercise 3: Exam practice questions

1. a.



   b. Anode: $2Br^-(aq) \rightarrow Br_2(l) + 2e^-$
   Cathode: $Ni^{2+}(aq) + 2e^- \rightarrow Ni(s)$
   Overall: $2Br^-(aq) + Ni^{2+}(aq) \rightarrow Br_2(l) + Ni(s)$
   c. The minimum cell voltage is 1.34 V.
   d. If nickel electrodes were used nickel ions would be the strongest oxidising agent and nickel metal would be the strongest reducing agent.
   Anode: $Ni(s) \rightarrow Ni^{2+}(aq) + 2e^-$
   Cathode: $Ni^{2+}(aq) + 2e^- \rightarrow Ni(s)$
2. a. $Q = 304\,C$
   b. $n(Cu) = 0.00157$ mol
   c. $n(e^-) = 0.00315$ mol
   d. 96 520 C
   e. $N_A = 6.0 \times 10^{23}$
3. $m(Cl_2)$ (90% efficiency) = 1.67 kg
4. a. The cathode is the negative electrode and the anode is the positive electrode.
   b. $2Cl^-(l) \rightarrow Cl_2(g) + 2e^-$
   c. $Na^+(l) + e^- \rightarrow Na(l)$
   d. The perforated iron plate keeps products apart, which prevents products reacting spontaneously.
   e. If an iron anode was used, the possibility of Fe being oxidised would need to be considered. Because Fe is a stronger reducing agent than Cl^- ions it will be preferentially oxidised to Fe^{2+} ions and Cl_2 would not be produced.
   f. Ca^{2+} ions are a weaker oxidising agent than Na^+ ions. Therefore, Na^+ ions are the preferred reactant. They are still able to undergo reduction to Na.
   g. $V(Cl_2)$ at SLC = 13.9 L
5. a. Cathode
   b. i. $Ag^+(aq) + e^- \rightarrow Ag(s)$
      ii. $Au^+(aq) + e^- \rightarrow Au(s)$
   c. i. $Ag(s) \rightarrow Ag^+(aq) + e^-$
      ii. $2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$
   d. Ag is a better reducing agent than H_2O, but Au is not.
   e. The concentration of silver ions does not drop because those consumed at one electrode are replaced at the other. Gold ions are consumed at the cathode but are not replaced at the anode.
   f. $m(Au) = 0.612$ g

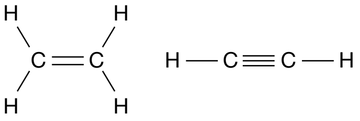
8 Structure and nomenclature of organic compounds

8.2 The carbon atom

Practice problem 1

$$\text{Energy} = 6624\,\text{kJ}$$
$$= 6.6 \times 10^3\,\text{kJ}$$

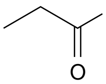
8.2 Exercise

1. C.
2. C=C bonds are stronger than C−C bonds because they have twice the number of electrons between the nuclei. This causes a shorter, stronger and more stable bond.
3. Energy = 1130 kJ
4. 
   The bond angles in C_2H_4 are 120° whereas in C_2H_2 they are 180°. The difference in bond angles is 60°.
5. 1812 kJ mol^{-1}.

8.3 Structure and naming of organic compounds

Practice problem 2

Semi-structure: $CH_3CH_2COCH_3$.
Skeletal structure:



Practice problem 3

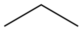
4-ethyl-2,3-dimethylhexane

Practice problem 4

a. The functional group is carboxyl (COOH). The homologous series is the carboxylic acids.
b. 2,4-dimethylpentanoic acid

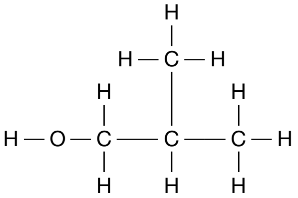
8.3 Exercise

1. $C_{18}H_{38}$
2. Molecular formula: C_3H_8
   Empirical formula: C_3H_8
   Semi-structural formula: $CH_3CH_2CH_3$
   Skeletal structure:

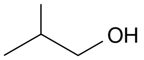


3. a. 4,5-dibromohex-2-ene
   b. $CH_3CHBrCHBrCHCHCH_3$ or $CH_3(CHBr)_2(CH)_2CH_3$
   c. $C_6H_{10}Br_2$
   d. C_3H_5Br

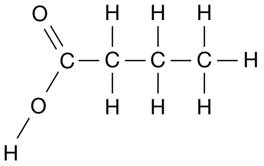
4. Structural diagram:



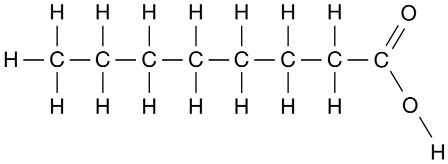
Semi-structural formula:
$CH_3CH(CH_3)CH_2OH$ or $(CH_3)_2CHCH_2OH$
Skeletal structure:



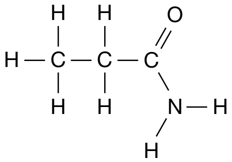
5. Butanoic acid:



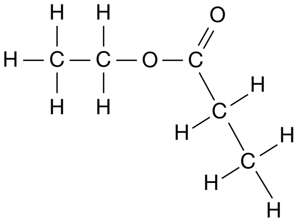
Octanoic acid:



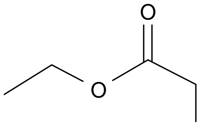
6. a. 3,3-dimethylpentan-2-amine
   b. cyclohexane
   c. cyclopropane
   d. benzene
   e. 4-chlorohex-2-yne
   f. methyl butanoate
7. The CO in the molecule is indicative of a ketone.
8.



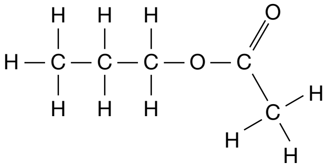
9. a. Ethylpropanoate
   Structural diagram:



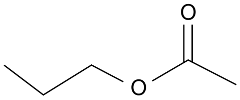
Semi-structural formula:
$CH_3CH_2COOCH_2CH_3$ or $CH_3CH_2OCOCH_2CH_3$
Skeletal structure:



b. Propylethanoate
Structural diagram:



Semi-structural formula:
$CH_3COOCH_2CH_2CH_3$ or $CH_3CH_2CH_2OCOCH_3$
Skeletal structure:



10. a. There are two methyl(CH_3) groups and one ethyl ($-CH_2CH_3$) group.
    b. 5-ethyl-3,3-dimethyloctane.

8.4 Functional groups and naming priority

Practice problem 5

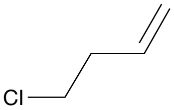
3-amino-2-methylpropanal

8.4 Exercise

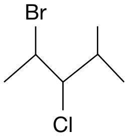
1.

Functional group	Name	Priority	Homologous series
COOH/CO_2H	Carboxyl	1	Carboxylic acids
C=O/CO	Carbonyl	4	Ketones
NH_2	Amino	6	Amines
OH	Hydroxyl	5	Alcohols
COO	Ester	2	Esters

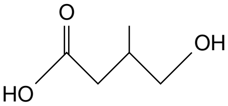
2. $CH_3CHNH_2(CH_2)_3OH$
3. i. a. 4-chlorobut-1-ene
      b. $CH_2CH(CH_2)_2Cl$ or $Cl(CH_2)_2CHCH_2$
      c.



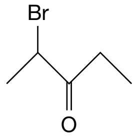
   ii. a. 2-bromo-3-chloro-4-methylpentane
       b. $CH_3CHBrCHClCH(CH_3)_2$ or $(CH_3)_2CHCHClCHBrCH_3$
       c.



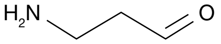
   iii. a. 4-hydroxy-3-methylbutanoic acid
        b. $CH_2OHCH(CH_3)CH_2COOH$ or $HOOCCH_2CH(CH_3)CH_2OH$
        c.



- **iv.** **a.** 2-bromopentan-3-one or 2-bromo-3-pentanone
  - **b.** $CH_3CHBrCOCH_2CH_3$ or $CH_3CH_2COCHBrCH_3$
  - **c.**

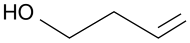


- **v.** **a.** 3-aminopropanal
  - **b.** $H_2N(CH_2)_2COH$ or $CHO(CH_2)_2NH_2$
  - **c.**

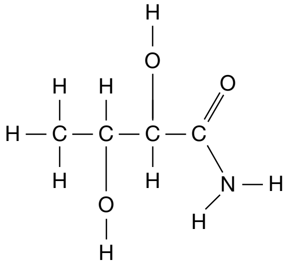


4. No. IUPAC name is 5-chlorohexan-2-amine because the amino functional group takes priority over hydrocarbons.

5.



6.

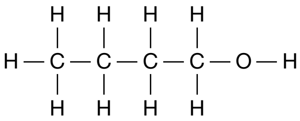


$CH_3(CHOH)_2CONH_2$ or $H_2NCO(CHOH)_2CH_3$.

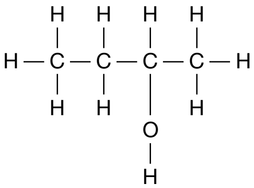
8.5 Isomers

Practice problem 6

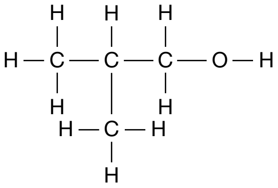
butan-1-ol



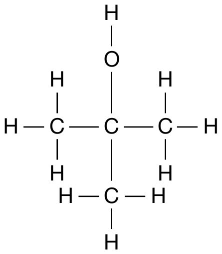
butan-2-ol



2-methylpropan-1-ol



2-methylpropan-2-ol

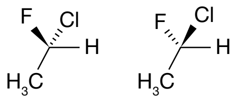


Practice problem 7

a. Answer B. CH_3CHBrF

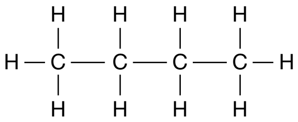
8.5 Exercise

1. Chiral carbons have bonds that result in no plane of symmetry and the molecule mirror images are non-superimposable. Achiral molecules have symmetry and their mirror images can be superimposed.
2. Enantiomers are called optical isomers because they will rotate plane-polarised light in opposite directions when it is passed through a sample of each one.
3. Stereoisomers are those where the atoms or groups have the same connectivity but different spatial arrangement. Structural isomers have different connectivity of atoms or groups.
4. Note the central chiral carbon has not been drawn in the structure.

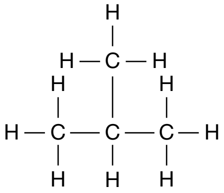


5. Butane only has two structural isomers: butane (n-butane) and 2-methylpropane.

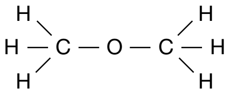
butane



2-methylpropane



6. Optical isomerism/stereoisomerism
7. The ether functional group R—O—R’ can be formed from C_2H_6O.



8. The geometric stereoisomer is *cis*-hex-3-ene.
9.

trans–pent–2–ene
(2E)–pent–2–ene

cis–pent–2–ene
(2Z)–pent–2–ene

10. See figure at foot of the page*.

8.6 Review

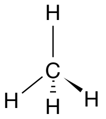
8.6 Exercises

8.6 Exercise 1: Multiple choice questions

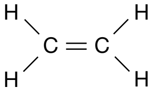
1. A.
2. C.
3. B.
4. B.
5. C.
6. B.
7. B.
8. B.
9. D.
10. B.

8.6 Exercise 2: Short answer questions

1. a.

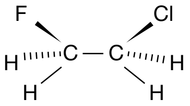


b.

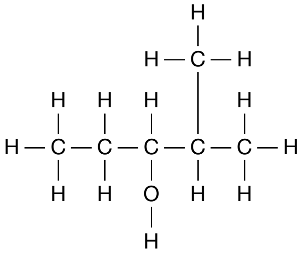


c. $H-C\equiv C-H$

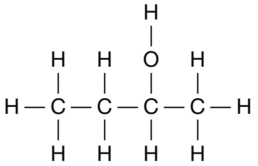
d.



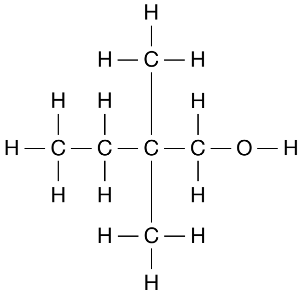
2. Triple bonds are shorter in bond length and have more electrons participating in the covalent bonds.
3. Bond energy = 168 kJ
4. a. A compound comprising only carbon and hydrogen atoms
   b. A family of carbon compounds where each member of the family differs from the preceding member by a $-CH_2-$ group
   c. A hydrocarbon containing only single $C-C$ covalent bonds
   d. A hydrocarbon containing one or more double $C=C$ or triple $C\equiv C$ covalent bonds
   e. Molecules with the same molecular formula but different structural formulas
5. An alkane is a hydrocarbon containing only single $C-C$ covalent bonds. An alkene is a hydrocarbon containing one or more double $C=C$ covalent bonds.
Sample responses can be found in your digital formats.
6. a. ent-2-ene
   b. chloroethene
   c. dichloro-difluoromethane
   d. ethanol
   e. 2,2-dimethylpropane
   f. hexan-2-ol
   g. 1,1-dibromo-2,2-dichloroethane
7. a.



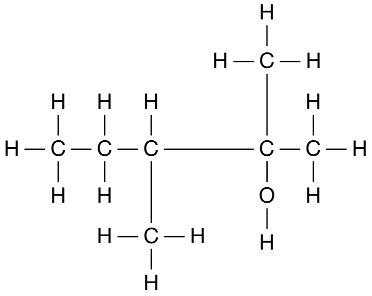
b.



c.



d.



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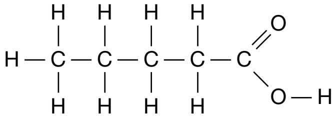

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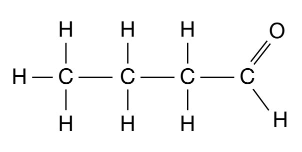
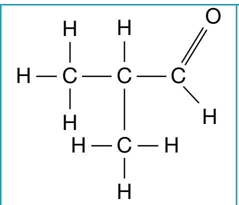
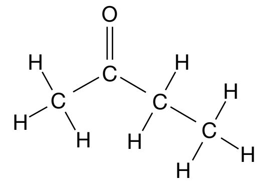
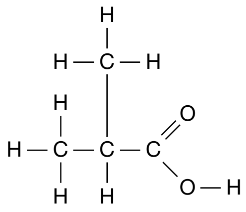
		
butanal	2-methylpropanal	butanone

f.



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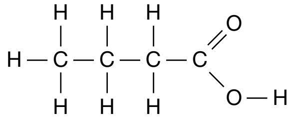

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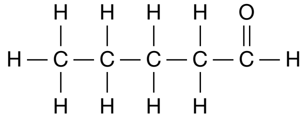
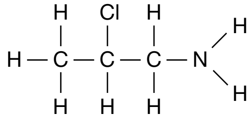


i.



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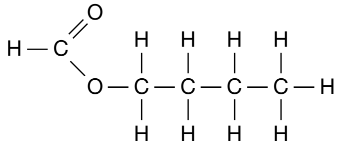

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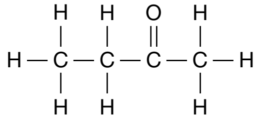

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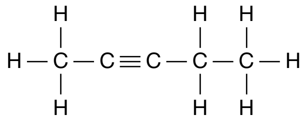
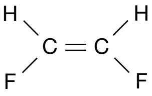
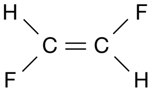


8. **a.** methylamine/methanamine
   b. 3-aminobutanal
   c. 3-hydroxypropanoic acid
   d. 1,3-dichloropropanone
9.



cis–CH_2CF_2

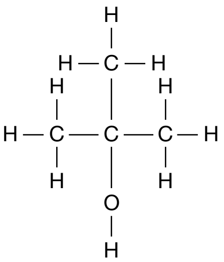


trans–CH_2CF_2

10. **a.** Stereoisomerism, therefore they are optical isomers.
    b. The type of isomerism present is stereoisomerism. These molecules are *cis–trans* isomers.
    c. Structural isomerism. These molecules contain the same atoms in different arrangements, therefore they are positional isomers.

8.6 Exercise 3: Exam practice questions

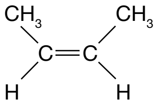
1. C.
2. D.
3. B.
4. A.
5. **a.** **i.**



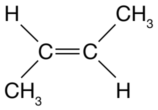
   ii. The functional group is a hydroxyl group.
   iii. This is a tertiary alcohol because the carbon bonded to the O—H group is attached to three other carbon atoms (alkyl groups).

   b. $CH_3CH_2COOCH_3$ / $CH_3(CH_2)_2COOCH_3$
   or
   $CH_3OOCCH_2CH_2CH_3$ / $CH_3OOC(CH_2)_2CH_3$

   c. **i.** *cis*-but-2-ene



   trans-but-2-ene



   ii. $C_4H_8(g) + 6O_2(g) \rightarrow 4CO_2(g) + 4H_2O(l)$
   iii. $V(CO_2) = 2.66 \times 10^3$ L
   Or using the universal gas equation:
   $V(CO_2) = 2.65 \times 10^3$ L

9 Categories, properties and reactions of organic compounds

9.2 Explaining trends in physical properties

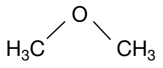
Practice problem 1

Propane is a symmetrical hydrocarbon with weak dispersion forces only operating between molecules. This results in it boiling at a relatively low temperature.
1-chloropropane has the electronegative Cl atom that causes the molecule to become polar. Permanent dipole–dipole attractions also exist between molecules, which are much stronger than the dispersion forces. This explains why its boiling point is considerably higher than that of propane.

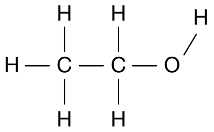
9.2 Exercise

1. The intermolecular forces are dispersions forces, also known as van der Waals forces. They are temporary dipole moments that form as electrons move around, creating attractions between neighbouring molecules with opposing temporary charges.
   The intramolecular forces are the forces within the molecule that hold it together. These are very strong covalent bonds.
2. **a.** CH_3OH: dispersion forces and hydrogen bonding
   b. CH_3CH_3: dispersion forces only
   c. CH_3CH_2Cl: dispersion forces and dipole–dipole
   d. CH_3NH_2: dispersion forces and hydrogen bonding

3. a. Propan-1-ol is a straight chain hydrocarbon with strong intermolecular forces (dispersion forces and hydrogen bonding). Propan-2-ol has a lower flashpoint because it is a branched chain alcohol resulting in weaker intermolecular forces between molecules.
   b. The forces between propan-1-ol molecules are stronger than the forces between propan-2-ol molecules, so propan-1-ol will have a higher boiling point.
4. Both methanol and ethanol are soluble in water because they can form hydrogen bonds with water molecules. Methane and ethane, as non-polar molecules, are unable to form hydrogen bonds with water molecules and are therefore insoluble.
5. Butanamide has a higher boiling point than ethyl ethanoate because it has hydrogen bonding between its molecules, while ethyl ethanoate has weaker dipole–dipole attraction between its molecules.
6. a. Candle wax is a solid at room temperature and melts at temperatures in a range of 50–60 °C suggests the alkane chains are long compared to those that exist in the gas and liquid states at SLC.
   b. Dispersion forces between the wax and oils allow miscibility. Sample responses can be found in your digital formats.
7. a. Hexane is not suitable for removing salt from water. Sample responses can be found in your digital formats.
   b. Hexane will be able to separate oil from soy beans. Sample responses can be found in your digital formats.
   c. Hexane will be able to remove oil contaminants in water. Sample responses can be found in your digital formats.
8. Carbon tetrachloride is non-polar reducing its ability to dissolve in water. Dichloromethane has permanent, unsymmetrical dipoles resulting in hgiher solubility. However, the smaller dichloromethane, collectively, has fewer intermolecular forces acting resulting in a lower boiling point.
   Sample responses can be found in your digital formats.
9.



Compound A



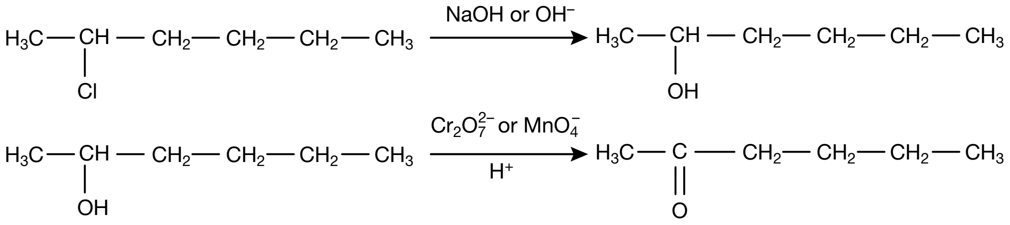
Compound B

Sample responses can be found in your digital formats.

10. Ethyl ethanoate and ethyl butanoate both have dipole–dipole attractions with water. Ethyl butanoate, with longer hydrocarbon sections results in fewer dispersion forces between themselves or with other non-polar molecules. As a result, it is easier for the smaller ethyl ethanoate to dissolve in water. The boiling point also increases as the size of the ester increases due to the number of intermolecular forces acting. We observe this trend in a homologous series.

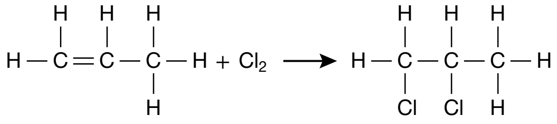
9.3 Organic reactions

Practice problem 2

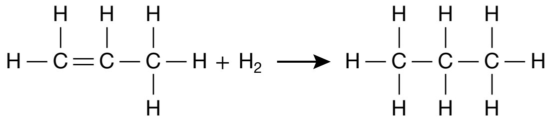


9.3 Exercise

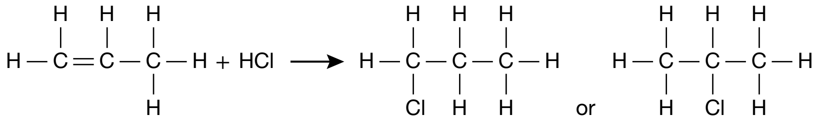
1. 1,1-dichloroethane would be made in two steps using chlorine gas and UV light to catalyse the reaction.
   Sample responses can be found in your digital formats.
2.



1,2-dichloropropane

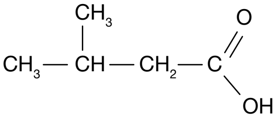


propane



1-chloropropane 2-chloropropane

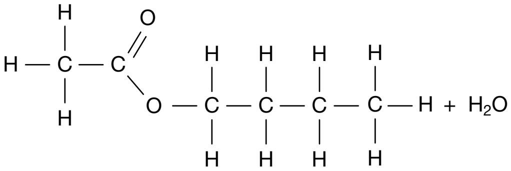
3. If bromine was added to ethane, the red colour of the bromine would remain because there would be no reaction. However, if bromine was added to ethene, the bromine would undergo an addition reaction with the ethene and the reaction mixture would turn colourless. Only unsaturated molecules react with the bromide.
4. a. 3-methylbutan-1-ol
   b. 3-methylbutanoic acid. Sample responses can be found in your digital formats.



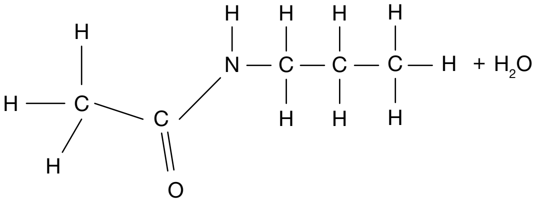
5. The O−H group needs to be on the end of a chain to be able to form the three covalent bonds with the two oxygen atoms in a carboxyl functional group.
6. $CH_3COOH(aq) + KOH(aq) \rightarrow CH_3COOK(aq) + H_2O(l)$

   or

   $CH_3COOH(aq) + OH^-(aq) \rightarrow CH_3COO^-(aq) + H_2O(l)$
7. a.



   b.



8. a. Hydrogen gas $H_2(g)$ needs to react with ethene in the presence of a metal catalyst such as Ni or Pt.
   b. Steam $H_2O(g)$, heat and an acid catalyst (e.g. H_3PO_4) are required.
   c. Chlorine gas $Cl_2(g)$ is required.
   d. First add HCl(g) to produce chloroethane then add $NH_3(g)$ with an aluminium catalyst.
   e. First add $H_2O(g)$, heat and H_3PO_4 to produce ethanol. Then add acidified $K_2Cr_2O_7$ to produce ethanoic acid. React this with propan-1-ol in the presence of concentrated H_2SO_4 to produce the ester.
9. a. $C_5H_{12}O \xrightarrow{[O]} C_5H_{10}O_2/CH_3CH_2CH_2CH_2CH_2OH \xrightarrow{[O]} CH_3CH_2CH_2CH_2COOH$
   b. $C_5H_{12}O \xrightarrow{[O]} C_5H_{10}O/CH_3CH_2CH_2CHOH\,CH_3 \xrightarrow{[O]} CH_3CH_2CH_2COCH_3$
10. Hydrolysis refers to the addition of water across the ester link. This causes the reformation of a carboxylic acid and alcohol. Acid or alkaline catalysts are required for the hydrolysis. Condensation between a carboxylic acid and alcohol eliminates water in the form of OH from the COOH and H from OH. The ester link is formed joining the two reactants in the presence of an acid catalyst.

9.4 Reaction pathways

Practice problem 3

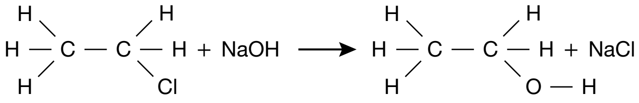
$\%\ \text{yield} = 91\%$

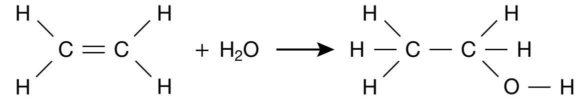
Practice problem 4

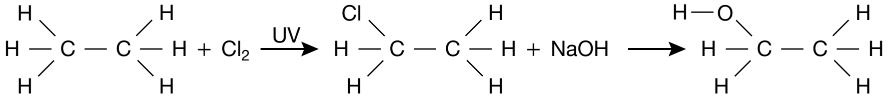
$\%\ \text{atom economy} = 80\%$

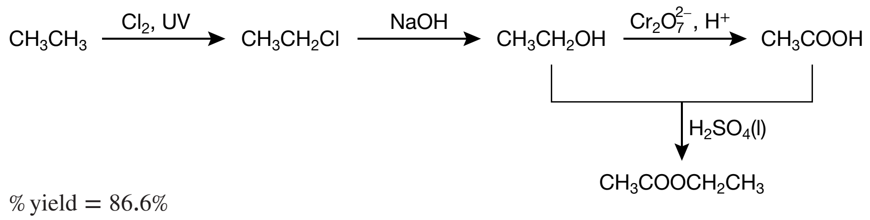
9.4 Exercise

1.





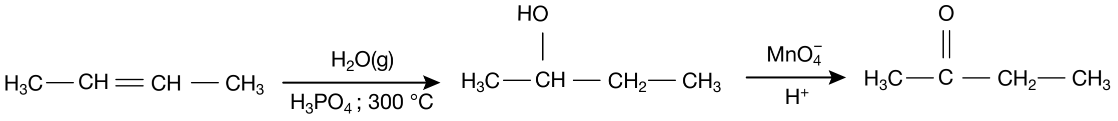


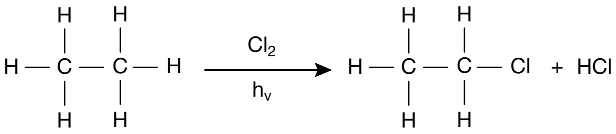
2. 

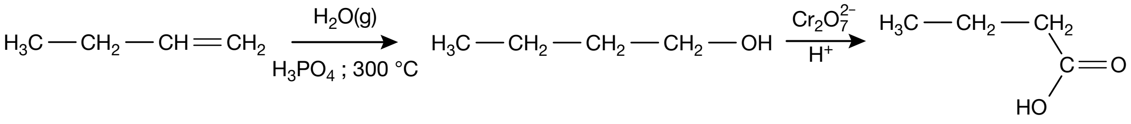
3. % yield = 86.6%
4. $m(CO_2)$ = 181 g
5. % atom economy = 100%
6. Method 1 has the higher atom economy for the production of hydrogen gas.

   $\%_{method1} = 17.6(18\%)$

   $\%_{method2} = 7\%$

7. 

8. a. Start with 2-chloropropane and react it with NaOH to produce propan-2-ol. Oxidise the secondary alcohol to the ketone using a strong oxidant in acid, such as potassium dichromate ($K_2Cr_2O_7$) or potassium permanganate ($KMnO_4$).
   b. React 2-chloropropane with $NH_3(g)$ in the presence of an aluminium catalyst such as Al_2O_3.
9. a. alumina, Al_2O_3
   b. acidified $Cr_2O_7^{2-}$, $K_2Cr_2O_7$, or MnO_4^-, $KMnO_4$
   c. $H_2SO_4(l)$
   d. H_3PO_4 on silica
10. a. 

    b. 

9.5 Review

9.5 Exercises

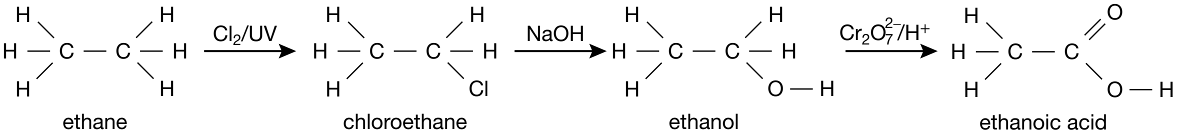
9.5 Exercise 1: Multiple choice questions

1. C.
2. B.
3. B.
4. B.
5. D.
6. C.
7. A.
8. A.
9. A.
10. C.

9.5 Exercise 2: Short answer questions

1. a. CH_3Cl: dispersion forces and dipole–dipole attractions
   b. CH_3OCH_3: dispersion forces and dipole–dipole attractions
   c. CBr_4: dispersion forces only
   d. $CH_3CH_2NH_2$: dispersion forces and hydrogen bonding
   e. H_2CCH_2: dispersion forces only
   f. $CH_3CH_2CH_2CH_2CH_2CHO$: dispersion forces and dipole–dipole attractions
   g. *cis*–CH_2Cl_2: dispersion forces and dipole–dipole attractions
   h. HCOOH: dispersions forces and hydrogen bonding

2. Propan-1-ol. Sample responses can be found in your digital formats.
3. A substitution reaction is a reaction in which an atom is replaced by another atom or group.
   Sample responses can be found in your digital formats.
4. a. $H_2C{=}CH_2 + HI \rightarrow CH_3CH_2I$
   b. $H_2C{=}CHCH_3 + H_2 \rightarrow CH_3CH_2CH_3$
   c. $H_2C{=}CH_2 + Br_2 \rightarrow CH_2BrCH_2Br$
   d. $H_2C{=}CHCH_2CH_3 + Cl_2 \rightarrow CH_2ClCHClCH_2CH_3$
   e. $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$
   f. $CH_3CH_3 + Cl_2 \rightarrow CH_3CH_2Cl + HCl$
   g. $H_2C{=}CH_2 + H_2O \rightarrow CH_3CH_2OH$
   h. $CH_3CH{=}CHCH_3 + H_2 \rightarrow CH_3CH_2CH_3CH_3$
5. $X = C_2H_4$, $Y = C_2H_5OH$ and $Z = Br_2$.
6. Esterification is a condensation reaction. The reactants are carboxylic acid and alcohol, and the products are an ester and water.
7.



8. % yield = 80.0%
9. % atom economy = 76%
10. Atom economy is a measure of how much of the mass of the reactants transfers into the desired product. As all of the atoms in the reactants are directly present in the product, the economy is 100%.

9.5 Exercise 3: Exam practice questions

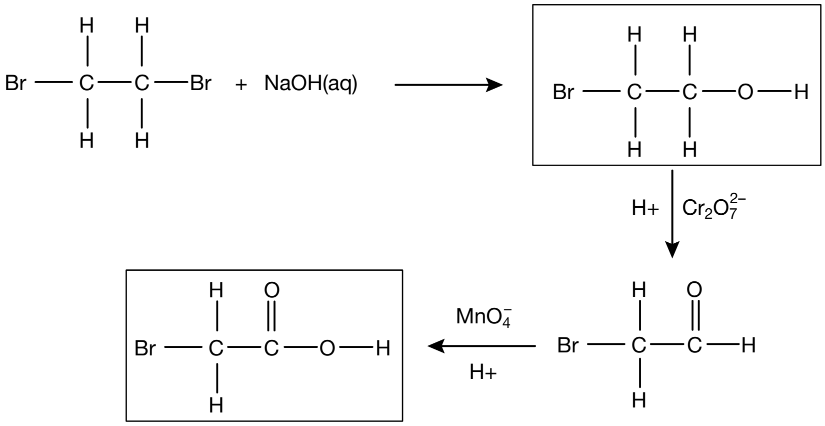
1. D.
2. B.
3. B.
4. $m(CO_2) = 73.3$ g
5. a. $C_2H_6(g) + Br_2(l) \xrightarrow{UVlight} C_2H_5Br(l) + HBr(g)$

   $C_2H_5Br(l) + Br_2(l) \xrightarrow{UVlight} C_2H_4Br_2(l) + HBr(g)$ [2 marks]

   OR

   $C_2H_6(g) + 2Br_2(l) \xrightarrow{UVlight} C_2H_4Br_2(l) + 2HBr(g)$

   b. 1,2-dibromoethane
   c. % atom economy = 53.4%
   d. $C_2H_4(g) + Br_2(l) \rightarrow C_2H_4Br_2(l)$
   All atoms from the reactants end up part of the desired product, therefore the atom economy is 100 per cent.
   e. i.



   ii. 2-bromoethanoic acid

10 Analysis of organic compounds

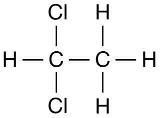
10.2 Mass spectrometry

Practice problem 1

The peak at $m/z = 50$ corresponds to $[CH_3{}^{35}Cl]^+$.
The peak at $m/z = 52$ corresponds to $[CH_3{}^{37}Cl]^+$.
The peak at $m/z = 15$ corresponds to $[CH_3]^+$

10.2 Exercise

1. Mass spectra are produced when positively charged ions are detected in a mass spectrometer. A beam of electrons knocks out an electron, causing the molecule to become positively charged. Sample responses can be found in your digital formats.
2. The molecular ion peak is caused by the ionisation of the whole molecule and its *m*/*z* ratio is equivalent to the molar mass. The base peak is the most abundant ion relative to the other fragments detected in the sample and is assigned a value of 100.
3. The abundance of other peaks are assigned values based on the proportion of them being detected.
4. The *m*/*z* ratio can be thought of as a mass scale because usually only one electron is removed per molecule in the spectrometer.
5. Any of:
   $C_2H_4O_2(g) + e^- \rightarrow C_2H_4O_2^+(g) + 2e^-$
   $C_2H_4O_2(g) + e^- \rightarrow [C_2H_4O_2]^+(g) + 2e^-$
   $C_2H_4O_2(g) \rightarrow C_2H_4O_2^+(g) + e^-$
6. $[C_2H_4O_2]^+(g) \rightarrow [CH_3CO]^+(g) + \bullet CHO(g)$
7. a. Peak Z
   b. Peak Y corresponds to CH_3CO^+
   Peak X corresponds to $CH_3{}^+$
8. a. 59
   b. 30
   c. $C_3H_9N^+$ or $[C_3H_9N]^+$
   d. CH_4N^+ or $[CH_4N]^+$ or $[CH_2NH_2]^+$
   e. $C_3H_9N^+(g) \rightarrow CH_4N^+(g) + \bullet C_2H_5(g)$
   $[C_3H_9N]^+(g) \rightarrow [CH_4N]^+(g) + \bullet C_2H_5(g)$
   $[CH_3CH_2CH_2NH_2]^+(g) \rightarrow [CH_2NH_2]^+(g) + \bullet CH_2CH_3(g)$
9. a. $m/z = 29$
   b. CH_2CHO^+ and/or $C_3H_7{}^+$. It is likely both, which explains it being the highest peak on the spectrum.
   c. It is called the base peak because it is the most abundant ion detected.
   d. Butanal, C^4H^8O. Sample responses can be found in your digital formats.
10. a. The peak at $m/z = 98$ indicates the two chlorine atoms are both ^{35}Cl isotopes while the peaks at 100 and 102 indicate $^{35}Cl/^{37}Cl$ and $^{37}Cl/^{37}Cl$ combinations.
    b. $C_2H_4{}^{35}Cl_2(g) \rightarrow [C_2H_4{}^{35}Cl_2]^+(g) + e^-$
    $C_2H_4{}^{35}Cl_2(g) + e^- \rightarrow [C_2H_4{}^{35}Cl_2]^+(g) + 2e^-$
    c.



$$\begin{array}{ccccccc} & & Cl & & H & & \\ & & | & & | & & \\ H & - & C & - & C & - & H \\ & & | & & | & & \\ & & Cl & & H & & \end{array}$$

The fragment at $m/z = 83$ suggests a loss of CH_3. This is absent from the 1,2-dichloroethane spectrum.

10.3 Infrared spectroscopy

Practice problem 2

C=O peak at 1670–1750 cm^{-1} corresponds to C=O.

Deduce a structure that has C=O and C−H bonds, with a molecular formula C_3H_6O. The molecule has the structural formula CH_3COCH_3.

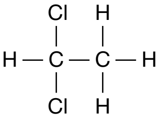
10.3 Exercise

1. Absorption of infrared radiation causes vibrational changes to the covalent bonds in molecules. The wave number at which parts of molecules absorb in proportion to the frequency or energy of the vibration gives clues about the types of covalent bonds present.Detield sample responses can be found in your digital formats.
2. a. In a homologous series, each member increases by CH_2, so there will be more peaks scattered throughout the fingerprint and other areas of the spectrum.
   b. A fingerprint region can be useful for identifying pure samples. As the bonding in a molecule is unique, so will be the infrared absorption wave numbers and number of peaks.
3. C=O (esters) at 1750 cm^{-1}
   C−O (esters) at 1230 cm^{-1}
   C−H at 2800–3150 cm^{-1}
4. a. C=O (acids) 1700 cm^{-1}; O−H (acids) 2500−3500 cm^{-1}
   b. Spectrum B
   c. Ethanoic acid, CH_3COOH, has a molar mass of 60 g mol^{-1} and propanoic acid, CH_3CH_2COOH, has a molar mass of 74 g mol^{-1}.
5. Compound X is the carboxylic acid. Compound Y is the alcohol.
6. Compound X is a primary amine.
   Compound Y is a primary amide.

10.4 NMR spectroscopy

Practice problem 3

1, 1-dichloroethane. (CH_3CHCl_2).



$$\begin{array}{ccccccc} & & Cl & & H & & \\ & & | & & | & & \\ H & - & C & - & C & - & H \\ & & | & & | & & \\ & & Cl & & H & & \end{array}$$

10.4 Exercise

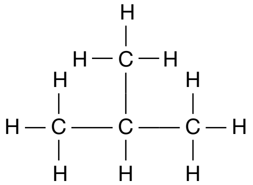
1. The area under the peaks is proportional to the number of nuclei contributing to the resonance.
2. Environment is a reference to the unique chemical shift because of the connectivity of atoms in a molecule and the field strength required to flip the spin of nuclei. Different connectivity will result in unique environments. Each peak or set of peaks represents a unique environment.
3. Low-resolution ^1H NMR spectra show unique environments and peak area to determine the number of hydrogen atoms contributing to the signal. High-resolution spectra show splitting, which allows the use of the n+1 rule to determine the number of adjacent hydrogen atoms to those producing the signal.
4. TMS is excellent at shielding its nuclei, which means its nuclei resonate at lower frequencies for a particular strength

of the applied magnetic field. TMS is inert and volatile, which makes it suitable to be recovered and it won't react with the sample.

5. CH_3CH_2Cl consists of $R-CH_3$, $R-CH_2-X$.

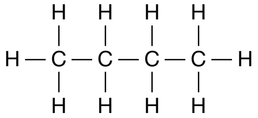
   The CH_3 group will produce a signal close in the 0.9−1.0 ppm range for a ^1H NMR spectrum and the $R-CH_2-X$ will produce a signal at the 3.0−4.5 ppm range.

6. Methyl propane:



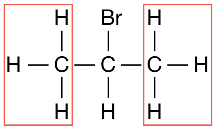
   The three CH_3 groups are in the same environment because they are all connected to the same carbon atom. There would be two peaks in the ratio of 3:1.

   Butane:

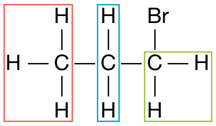


   Butane will also produce two peaks in a 1:1 ratio.

7. 1-bromopropane has three different carbon environments, therefore there will be three peaks on the spectrum. 2-bromopropane only has two environments due to the CH_3 groups being in identical environments and only producing one peak.

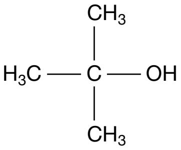


2-bromopropane, $(CH_3)_2CHBr$ (2 peaks)



1-bromopropane, $CH_3CH_2CH_2Br$ (3 peaks)

8. There are two different carbon environments in 2-methylpropan-2-ol.

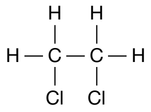


2-methylpropan-2-ol

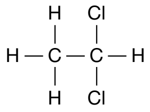
9.

Hydrogen set or atom	**Splitting pattern**	**Relative peak height**	**Chemical shift (ppm)**
$\mathbf{CH_3}CH_2COOH$	Triplet	3	0.8−1.0
$CH_3\mathbf{CH_2}COOH$	Quartet	2	2.1−2.7
$CH_3CH_2COO\mathbf{H}$	Singlet	1	9−13

10.



1,2-dichloroethane, CH_2ClCH_2Cl



1,1-dichloroethane, CH_3CHCl_2

CH_2ClCH_2Cl will only produce a single peak with no splitting. This peak will been seen at approximately 3.8 ppm.

CH_3CHCl_2 will produce two unique hydrogen environments. $R-CH_3$ will produce a doublet. The chemical shift will be further downfield at approximately 2.0 ppm. The other hydrogen environment will be split into a quartet of peaks. The chemical shift is approximately 5.9 ppm. The integration will show a ratio of 3:1 when comparing the doublet to the quartet. Sample responses can be found in your digital formats.

10.5 Combining spectroscopic techniques

Practice problem 4

a. $C_3H_6O_2$

b. A: $m/z = 29\ [C_2H_5]^+$

   B: $m/z = 45\ [COOH]^+$

   C: $m/z = 57\ [C_3H_5O]^+$

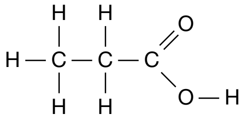
   D: $m/z = 74\ [C_3H_6O_2]^+$

c. i. 2500−3500 cm^{-1} ⇒ OH in a carboxylic acid

   ii. 1680−1740 cm^{-1} ⇒ a C=O (carboxylic acids) group

   iii. 1000−1300 cm^{-1} ⇒ a C−O bond

d. As there is an −OH bond, a C=O bond and a C−O bond, it is a carboxylic acid.



e. Propanoic acid

10.5 Exercise

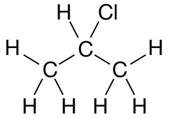
1. Ethanol, C_2H_5OH will produce a molecular ion on a mass spectrum of $m/z = 46$. Butan-1-ol, C_4H_9OH, will produce a molecular ion peak of $m/z = 74$. There will also be different fragments produced from the two molecular ions.

   The infrared spectra will show a broad absorption at both 3200−3600 cm^{-1} and 1050−1410 cm^{-1} that is characteristic of O−H(alcohols) and C−O(alcohols). Butan-1-ol will show a spectrum with more peaks in the 500−1500 region because it has more bonds to absorb the IR radiation.

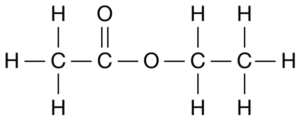
2. In the NMR spectrum the different functional groups produce different shifts. Ethanol will produce a RCH_2OH peak in the 50–90 ppm range. Ethanal will produce the RCHO peak in 190—200 ppm range characteristic of aldehyde functional groups.

   The ^1H NMR spectra will differ by the number of unique hydrogen environments. Ethanol will produce three sets of peaks whereas ethanal will only produce two. Ethanol will also produce a set of four peaks (quartet) and a set of three peaks (triplet) and a singlet due to the CH_3CH_2OH sequence. Ethanal will produce a quartet at 9.4−10.0 ppm due to the neighbouring CH_3 group. The other signal at approximately 2 ppm will be split into two peaks (doublet) due to the neighbouring CHO group from the CH_3.

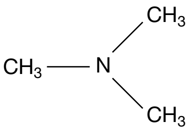
3. a. The Cl atom has two isotopes (^{35}Cl and ^{37}Cl) that produce molecular ion peaks at 78 and 80 *m*/*z*.
Sample responses can be found in your digital formats.
   b. C_3H_7Cl
   c. Two, because there are two sets of peaks with different chemical shifts.
   d. The septet is seen downfield due to the presence of the electronegative chlorine atom. This causes de-shielding of the hydrogen nuclei from the magnetic field so they achieve resonance at a higher frequency.
   e.

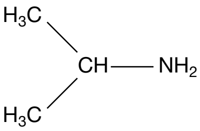


4. a. The IR spectrum indicates there are significant absorptions caused by the carbon to oxygen bonds.
$C{=}O$ (1780 cm^{-1})
$C{-}O$ (1200 cm^{-1})
   b. The ^{13}C NMR spectrum is in the ppm range for an ester, indicating the functional group $C{=}O$.
   c. Four, because there are four distinct peaks at different chemical shifts.
   d.



5.





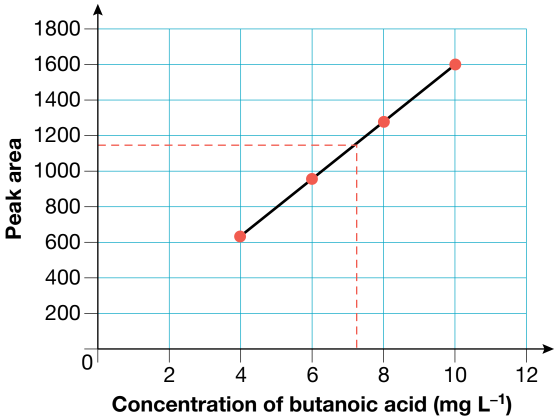
Sample responses can be found in your digital formats.

10.6 Chromatography

Practice problem 5

a. Methanol

b.



c. 7.2 mg L^{-1}

10.6 Exercise

1. Detailed sample responses can be found in your digital formats.
   a. The chemical(s) you are qualitatively or quantitatively investigating.
   b. The substance that the analyte adsorbs to and desorbs from as it is moved by the solvent.
   c. The solvent of which the analyte is carried through the stationary phase.
   d. Retention time (R_t) is the time it takes for a component of the analyte to be detected as it passes out of the column.
   e. A quantitative measure and is proportional to the amount or concentration of the component present in the analyte.
   f. The print out of peaks that have been detected due to the components in the analyte being detected.
   g. The instrument that performs the analysis and includes the column, pump, solvent reservoir and a detector.
2. a. Increasing the column will increase the time it takes for all components to be detected. This is one measure employed to separate many components in an analyte where peaks may overlap in shorter columns.
   b. Pumping the mobile phase through a column with increased pressure will be result in shorter retention times.
   c. Generally, increasing the temperature of the mobile phase will increase the solubility of the analyte in the mobile phase. Therefore, it will desorb from the stationary phase at a faster rate and result in a shorter retention time.
3. Adsorb and desorb are referring to the interaction between the surface of the stationary phase and the analyte. When an analyte is moved through a column, the components will adsorb to the surface of the stationary phase then desorb back into the mobile phase and continue to move through the column.
4. R_t of methanoic acid < ethanoic acid < propanoic acid < butanoic acid
Sample responses can be found in your digital formats.
5. RPLC uses a non-polar stationary phase and a polar mobile phase. Sample responses can be found in your digital formats.
6. R_t pentanoic acid < pentanol < pentane
Sample responses can be found in your digital formats.
7. a. Peak 4 Sample responses can be found in your digital formats.
   b. A pure standard would be run through the column under the same conditions to see if the times match.
   c. Peak 3 represents the highest concentration of amino acid.
   d. A series of serine standards would be run to produce peak areas above and below that of the area in the sample. A calibration graph of peak area versus serine concentration could be plotted and the peak area of the sample compared with those of the standards in order to determine the concentration.
8. a. Pure stanozolol would be run through the HPLC and its retention time recorded. A urine sample would be analysed and if a unique retention time of stanozolol is observed then its presence is detected.
   b. Provided a unique retention time of stanozolol is detected, a series of standard stanozolol solutions would be run to determine the peak area corresponding to various concentrations of stanozolol. Urine samples could then have the peak area of detected stanozolol compared with the area of the standards to determine the concentration.
   c. 2.5 mg L^{-1}. A calibration graph, can be found in the worked solutions in your digital formats.
   d. A concentration of 5.0 mg L^{-1} falls outside the range of the calibration graph.
   e. The sample could be diluted so that its concentration results in a peak area within the range of the standards.

Alternatively, standards of a higher concentration could be run to extend the range of the calibration graph.

10.7 Volumetric analysis by titration

Practice problem 6

$\%(m/v) = 70.0\%$ (accept 70.0 − 70.2)

Yes the contents of the bottle fall within the specifications shown on the label.

Practice problem 7

$[CH_3CHO]_{original} = 1.61\ M$

10.7 Exercise

1. a. Pipettes
   b. Burette
   c. Conical flask/beaker
2. a. The solution it will deliver
   b. The aliquot solution
   c. Distilled water
   d. Distilled water
3. Phenolphthalein/phenol red/thymol blue indicator.
4. The $Cr_2O_7^{2-}$ ion is orange because the oxidation state of the Cr ion is +6. When is it reduced to Cr^{3+} in a typical redox titration a green colour is observed.
5. $c(KH(C_8H_4O_4)) = 0.0999\ M$
6. a. $NaOH(aq) + HCl(aq) \rightarrow NaCl(aq) + H_2O(l)$
   or
   $H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$
   b. $c(NaOH) = 0.0860\ M$
   c. The reacting solutions are colourless. The indicator is needed to detect the end point.
   d. Yes. The concentration is now accurately known.
7. $c(HCl) = 0.124\ M$
8. $c(CH_3COOH) = 40.4\ g\ L^{-1}$
9. a. $m(C_2H_2O_4) = 0.900\ g$
   b. $[NaOH] = 2.11\ M$
   c. Burette rinsed with water: calculated [NaOH] lower
   Unsuitable indicator: end point falsely reached before true titre value therefore calulated [NaOH] higher than actual value.
   d. The reliability of the student's titres could be improved by increasing the number of titres/trials.

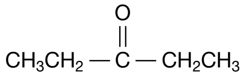
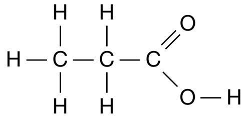
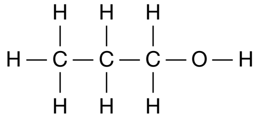
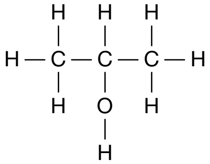
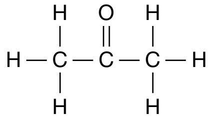
10.8 Review

10.8 Exercises

10.8 Exercise 1: Multiple choice questions

1. C.
2. C.
3. B.
4. C.
5. A.
6. D.
7. A.
8. B.
9. D.
10. B.

10.8 Exercise 2: Short answer questions

1. a. $m/z = 86$
   b. $m/z = 57$
   c. The peak at $m/z = 57$ corresponds to $[CH_3CH_2]\bullet$
   d.
   
   $CH_3CH_2-C(=O)-CH_2CH_3$
2. Ethanoic acid has a peak in the region 2500−3500 cm^{-1} due to the O−H(acid). Ethanoic anhydride has no peak in this region.
3. a. R_3-CH3 (1.0 ppm); R_2-CH_2 (1.3 ppm); R_1-COOH (10.5 ppm)
   b. There would be four peaks for the CH_2 group.
   c.
   
4. a.
   
   propan-1-ol
   
   propan-2-ol
   b. Sample responses can be found in your digital formats.
   Propanone
   
   c. $[CH_3CO]^+$
   d. $CH_3COCH_3^+ \rightarrow CH_3CO\bullet + CH_3^+$
   e. Two peaks in the ^{13}C NMR spectrum of compound B.
5. Separation occurs through the processes of adsorption and desorption on to and from the surface of the stationary phase. The larger the surface area, the greater the degree of adsorption and desorption, producing better separation.
6. The original mixture most likely contained substance X. Sample responses can be found in your digital formats.
7. a. The standards would allow the dichlorobenzyl alcohol peak from the original chromatogram to be identified because the peak would have the same retention time as the standards.
   b. A set of standards is used and then the area under their peaks is obtained to determine the relationship between concentration and peak area (a calibration curve), thus enabling the unknown concentration of other samples to be determined by interpolation.
   c. The manufacturer's claim is true. Sample responses can be found in your digital formats.
8. a. Compound E
   b. Compound A
9. a. $CH_3COOC_6H_4COOH(aq) + NaOH(aq) \rightarrow CH_3COOC_6H_4COONa(aq) + H_2O(l)$
   b. $m(\text{aspirin}) = 0.431\ g$
10. a. $c(C_6H_8O_6)$ of the diluted solution $= 0.00620\ M$
    b. $m(C_6H_8O_6) = 0.109\ g$
    c. 52.0 mg/100 g.

10.8 Exercise 3: Exam practice questions

1. D.
2. A.
3. B.
4. D.
5. **a.** $n(C_4H_6O_5) = 3.88 \times 10^{-4}$ mol
   b. %(m/m) = 5.19%
   c. **i.** 800 mg L^{-1}
      ii. %(m/m) = 0.400%
      iii. The MnO_4^- reacted with citric acid, tartaric acid and malic acid. The HPLC chromatogram shows three organic acids, which would have reacted with the oxidant in the titration leading to a false higher titre volume and therefore a false, higher concentration of malic acid.

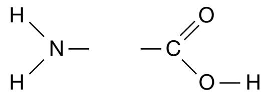
11 Key food molecules

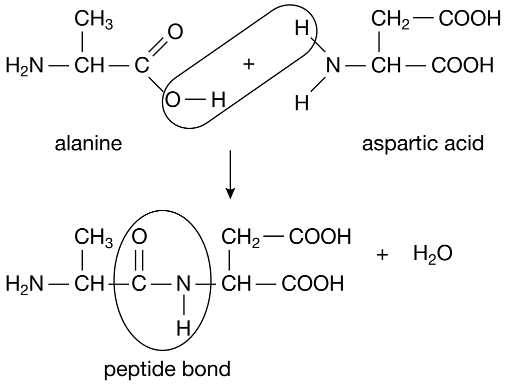
11.2 Proteins

Practice problem 1

See figure at foot of the page.*

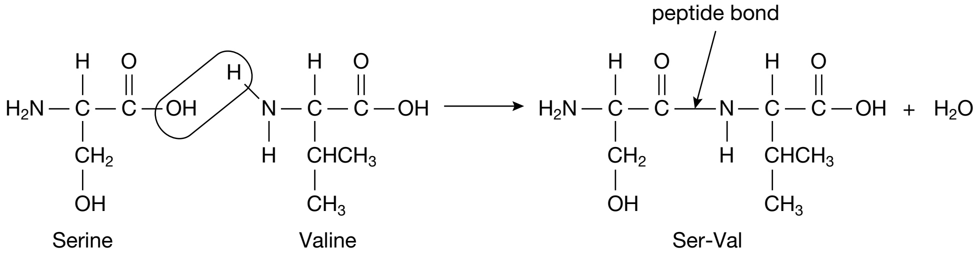
11.2 Exercise

1. **a.** Meat, eggs and cheese
   b. The body include the growth and repair of cells, acting as hormones, preventing infection as antibodies, forming muscle fibres, and carrying atoms and small molecules around the body.
2. The tertiary structure
3. 

amino carboxyl
4. Two examples are arginine and lysine.
5. **a** and **b**


   c. Enzyme-catalysed condensation
   d. Ala-Asp
   e. 204.0 g mol^{-1}
6. **a.** Phe-Val-Asn
   b. phenylalanine, valine and asparagine
   c. Covalent bonds called peptide bonds
   d. Covalent bond called a disulfide link
7. 6
8. Hydrogen bonding
9. In glutamic acid there is a carboxyl functional group in the side chain. This could result in hydrogen bonding between residues, where the hydrogen in the peptide links could bond with the oxygen atom in the carboxyl functional group.
10. **a.** Essential amino acids cannot be synthesised by animals from the other materials in their diets. Non-essential amino acids can be synthesised within the body.
    b. Essential: histidine; non-essential: alanine.

Practice problem 1*



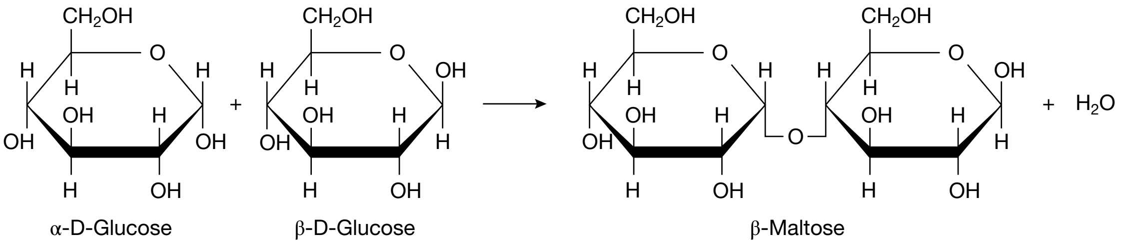
11.3 Carbohydrates

Practice problem 2

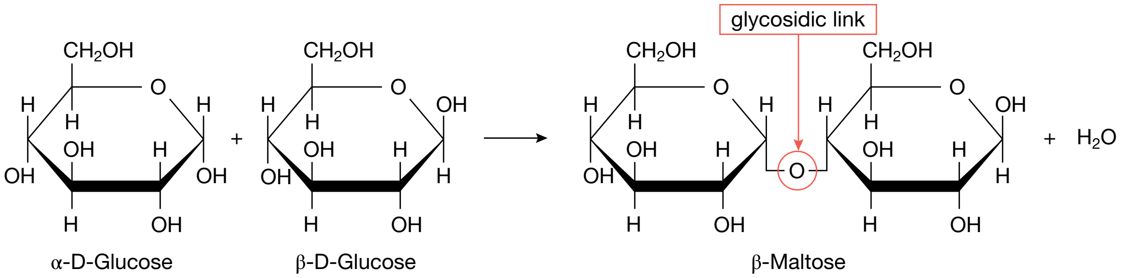
10.5×10^4 g mol^{-1}

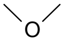
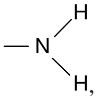
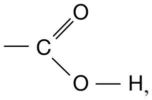
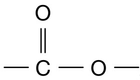
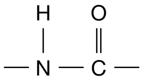
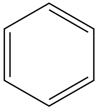
11.3 Exercise

1. $M(C_6H_{12}O_6) = 180$ g mol^{-1}
2. a. Dairy foods, fruit, grains, legumes, starchy vegetables and sugary foods
   b. To provide energy
3. a. Glucose + fructose → sucrose
   Glucose + glucose → maltose
   Galactose + glucose → lactose
   b.



   c. Enzyme-catalysed condensation reactions
   d. Glycosidic link (ether)

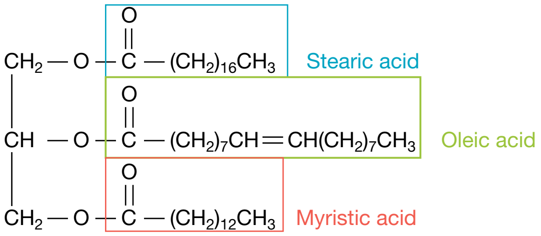


   e. Hydroxyl groups
4. Similarities: Both are simple carbohydrates consisting of carbon, hydrogen and oxygen. They are both polar and soluble in water. Differences: Galactose is a monosaccharide; lactose consists of galactose and glucose monomers combined in a condensation reaction to form a disaccharide.
5. 6.48×10^4 g mol^{-1}
6. The three polysaccharide polymers consist of glucose monomers. Glycogen and starch are formed from α-glucose and cellulose is formed from β-glucose. Starch is made up of two other polymers: amylose and amylopectin. Glycogen has many branches, amylopectin has less and amylose is a tight coil. Every second monomer in cellulose is inverted and the polymer strands are held together by extensive hydrogen bonding.
7. a. Starch
   b. Cellulose
   c. Glycogen
   d. Starch
   e. Cellulose
8. a. Glucose contains hydroxyl groups —O—H.
   b. Sucrose contains hydroxyl groups —O—H and a glycosidic  link.
   c. Aspartame contains amino, , carboxyl, , ester,  $-\overset{\overset{O}{\|}}{C}-O-$ amide  $-\overset{\overset{H}{|}}{N}-\overset{\overset{O}{\|}}{C}-$ and benzene  functional groups.
9. Aspartame is used in diet foods because only a small amount of it is needed to provide sweetness.
10. Aspartame is a methyl ester. It is used as a sweetener and combines well with different foods without adding extra kilojoules so it is beneficial when weight loss is desired.

11.4 Fats and oils

11.4 Exercise

1. a. Lauric, myristic, palmitic and stearic acid
   b. Palmitoleic and oleic acid
   c. Linoleic, linolenic and arachidonic acid
2. a. $C_3H_8O_3$
   b. $C_{18}H_{36}O_2$
3. Arachidonic
4. Ethanoic has only one methyl group and also a carboxyl group, which can hydrogen bond with water molecules. Myristic acid has a 13-carbon hydrocarbon chain, which is hydrophobic and so will not dissolve in water.
5. a. Trans-fatty acid
   b. Saturated fatty acids
   c. Longer fatty acids
6. Palmitic acid: $CH_3(CH_2)_{14}COOH$
   Oleic acid: $CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH$
   Linoleic acid:
   $CH_3(CH_2)_4CH{=}CHCH_2CH{=}CH(CH_2)_7COOH$
7. a. $C_{11}H_{23}COOH$.
   b. $CH_3(CH_2)_4CH{=}CHCH_2CH{=}CH(CH_2)_7COOH$.
8.



9. Essential fatty acids (EFAs) are fatty acids that must come from our diet because the body cannot produce them. Examples include alpha-linolenic acid (ALA) and linoleic acid (LA).
10. Linoleic acid. It is an omega-6 fatty acid.

Activity: A beriberi bad experiment

1. Dr. Eijkman's experiment showed good practice by having a control group and test group.
2. The flaw in experimental technique in Dr. Eijkman's second experiment was that the chickens were fed a different food from the initial experiment.
3. Vitamin B1
4. Hydrogen bonded to oxygen or nitrogen
5. Dr. Eijkman could have improved the experimental design of this experiment by having the same conditions for the two groups of infected chickens but fed one group brown rice and the other group white rice over the same period of time and observed the effects.

11.5 Vitamins

11.5 Exercise

1. Vitamins are organic compounds that are needed in very small quantities on a regular basis as part of a healthy diet.
2. Vitamins are essential for humans because they operate in cells to help catalyse cellular reactions.
3. Vitamin D
4. a. Vitamin C is found in citrus fruits, kiwi fruit and red capsicums.
   b. Vitamin D is found in fish like salmon and sardines, and egg yolks.
5. Water-soluble vitamins cannot be stored by the body. Fat-soluble vitamins remain stored in fatty deposits.
6. Fat-soluble vitamins tend to accumulate in the body
7. Vitamin C has four hydroxyl groups around the outside of the molecule whereas vitamin D_2 has mainly non-polar methyl groups and one hydroxyl group.
8. a. This molecule is fat-soluble because there are very few polar groups attached, mainly methyl groups.
   b. This molecule is water-soluble because there are a number of hydroxyl groups that can form hydrogen bonds with water.
9. $C_6H_8O_6$
10. Ascorbic acid

11.6 Review

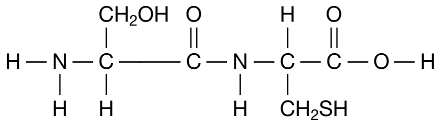
11.6 Exercises

11.6 Exercise 1: Multiple choice questions

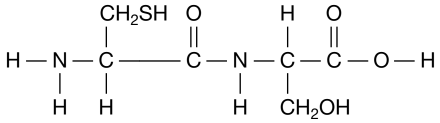
1. A.
2. D.
3. C.
4. C.
5. C.
6. C.
7. A.
8. C.
9. B.
10. B.
11. A.
12. A.
13. A.
14. D.
15. C.

11.6 Exercise 2: Short answer questions

1. They have bonded to a central carbon atom, an amino group, carboxyl group, a hydrogen atom and a R-group (side chain).
2. Glutamine has the R-group $-CH_2-CH_2-CONH_2$ (an amide group at the end). Glutamic acid has the R-group $-CH_2-CH_2-COOH$.
3. a. Amino acids react together in a condensation reaction to form a dipeptide and water.
   b.

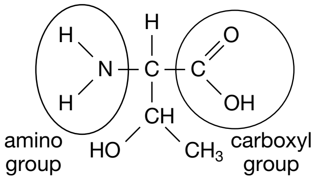


$$H-\underset{H}{N}-\overset{CH_2OH}{\underset{H}{C}}-\overset{O}{\overset{\|}{C}}-\underset{H}{N}-\overset{H}{\underset{CH_2SH}{C}}-\overset{O}{\overset{\|}{C}}-O-H$$



$$H-\underset{H}{N}-\overset{CH_2SH}{\underset{H}{C}}-\overset{O}{\overset{\|}{C}}-\underset{H}{N}-\overset{H}{\underset{CH_2OH}{C}}-\overset{O}{\overset{\|}{C}}-O-H$$

4. **a.** Theronine



b. See figure at foot of the page.*

5. **a.** Hydrogen bonding

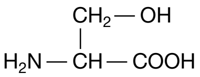
b. Dispersion forces, covalent bonds (disulfide bridge) and hydrogen bonds

6. **a.** 6

b. 27

c. See figure at foot of the page.*

7. Serine



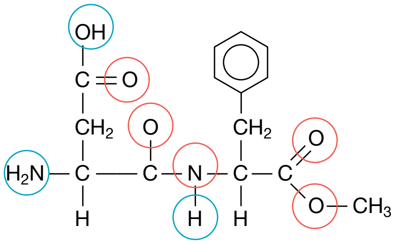
$$\begin{array}{l}\qquad\quad CH_2-OH\\ \qquad\quad\ |\\ H_2N-CH-COOH\end{array}$$

8. $C_{12}H_{22}O_{11}$

9. Starch comprises two different polymers: amylose and amylopectin. Amylose is made of tightly packed linear polymer chains of in a coil of α-glucose hydrogen bonded together. It is insoluble because most of the hydrogen bonds are involved in holding the coil together and unavailable to the water molecules. Amylopectin is made of open-branched polymer chains of α-glucose. The loose branched chains of glucose molecules allow access to water molecules for hydrogen bonding so amylopectin is soluble and more easily digested than amylose.

10. 1.04×10^5 g mol^{-1}

11.



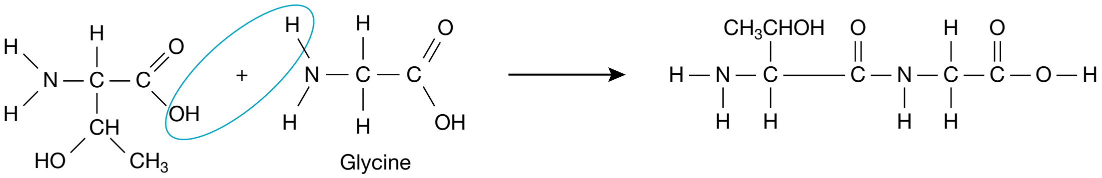
○ These hydrogen atoms can hydrogen bond to the oxygen atoms in water

○ These atoms can hydrogen bond with the hydrogen atoms in water

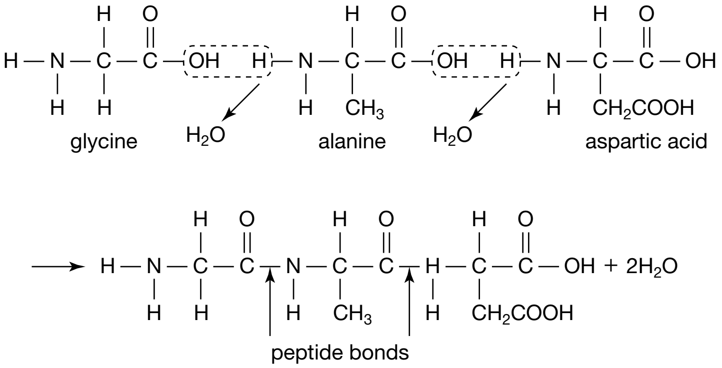
12. **a.** It has one double bond and is a long-chain carboxylic acid.

b. See figure at foot of the page.*

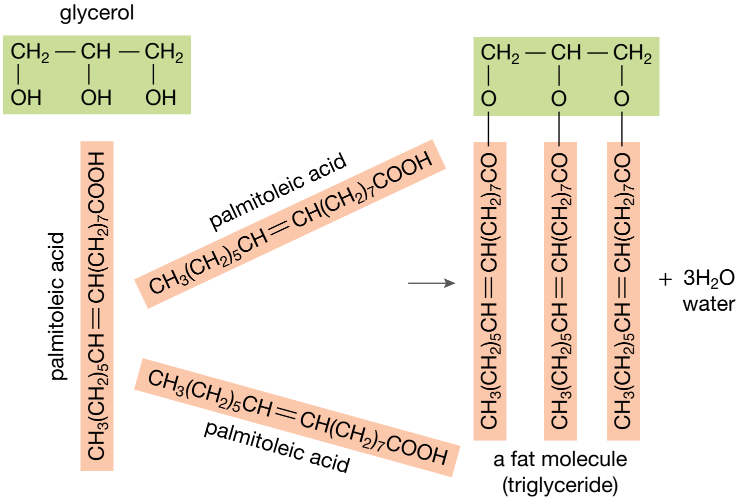
4b*



6c*



12b*



c. In an esterification reaction, the alcohol functional group of one molecule reacts in a condensation reaction with the carboxyl functional group of a carboxyl acid to form the ester functional group. When a triglyceride forms in a reaction between glycerol (a triol) and three fatty acid molecules, three ester groups form; it is an esterification reaction.

13. See figure at foot of the page.*

14. The polar −OH groups on carbohydrates form hydrogen bonds with water. The long hydrocarbon side chains in fats are non-polar and do not form bonds with water. Therefore carbohydrates are soluble in water and fats are not soluble in water.

15. See table at foot of the page.*

16. $n(H_2)\dfrac{16.8}{2.0} = 8.4$ moles

17. Normal functioning of the body requires some fatty acids not synthesised by the body. These fatty acids must come from the diet and are therefore known as essential fatty acids. They are described as omega-3 fatty acids because, in numbering from the methyl, or omega, end (instead of the usual functional group end), the first carbon double bond is located on carbon-3.

18. Eicosapentaenoic acid and docosahexaenoic acid are omega-3 fatty acids, and arachidonic is an omega-6 fatty acid because if we count from the methyl end the first double bond is on the third carbon for the first two compounds and on the sixth carbon for the third compound.

19. It is possible to have a deficiency of vitamin C because it is water soluble (due to the presence of several −OH groups) so is not retained by the body. By comparison, vitamin D is a fat-soluble vitamin (long hydrocarbon chain and only one −OH group present) so it can accumulate in the body.

20. This molecule would be soluble in water due to the presence of the hydroxyl functional groups and N and O atoms that can form H bonds with water.

11.6 Exercise 3: Exam practice questions

1. B.

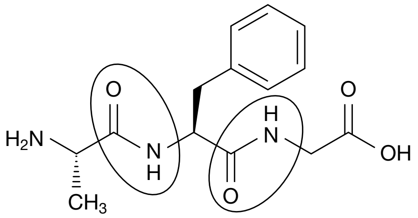
2. C.

3. A.

4. D.

5. A.

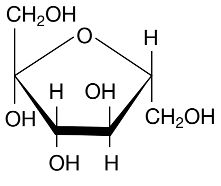
6.



The amino acids are (from left to right): alanine, phenylanaline and glycine.

7. a. Glucose and fructose

b.



fructose

c. Enzyme-catalysed condensation reaction

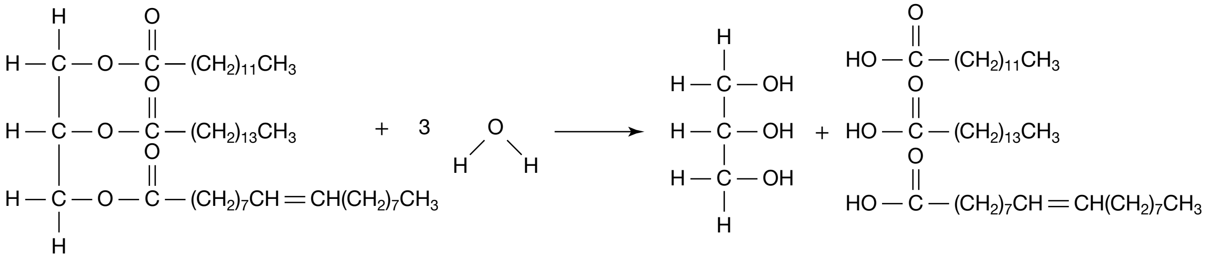
d. Hydroxyl and glycosidic

e. In increasing order of sweetness: glucose, sucrose, fructose

f. $C_{12}H_{22}O_{11}$

8. 1.70×10^3

13*



15*

	Saturated fatty acids	**Unsaturated fatty acids**
Structures	Only contain single C−C bonds	Monounsaturated fatty acids contain one C=C bond. Polyunsaturated contain more than one C=C bond
Properties	Occur as straight chain molecules that can be packed tightly, which increases the dispersion forces between molecules, increasing melting and boiling points.	Occur as bent molecules, which prevents tight packing of molecules. The effect of dispersion forces is lower than in straight chain molecules resulting in lower melting and boiling points.
Susceptibility to oxidation	Single C−C bonds are not susceptible to oxidation.	Double bonds increase susceptibility to oxidation as oxygen reacts across double bond (more likely to become rancid)

12 Metabolism of food in the human body

12.2 Metabolism of food

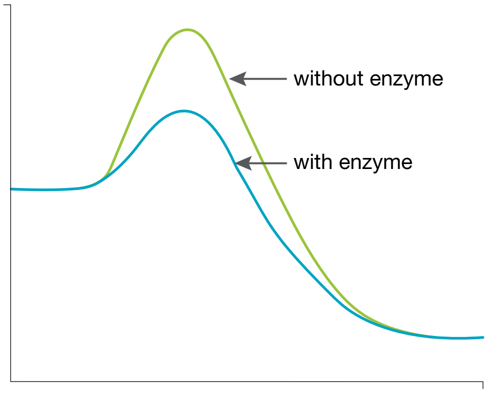
12.2 Exercise

1. So that they can be easily absorbed into the bloodstream.
2. a. Carbohydrates → (hydrolysis) → disaccharides → (hydrolysis) → monosaccharides → glucose → (condensation polymerisation/respiration) → glycogen/energy
   b. Fats and oils → (hydrolysis) → glycerol and fatty acids → (condensation reaction) → triglycerides → stored energy
   c. Proteins → (hydrolysis) → amino acids → (condensation reaction) → proteins → growth and repair
3. a. Hydrolysis reactions are the chemical breakdown of a compound due to reaction with water. For example, maltose is hydrolysed to two molecules of glucose.
   b. Condensation reactions occur when two molecules combine to form a larger molecule with the elimination of a small molecule, such as water. For example, two amino acids combining to form a dipeptide and water.
4. a. Condensation
   b. Condensation
   c. Hydrolysis
   d. Condensation
   e. Hydrolysis
   f. Hydrolysis
   g. Hydrolysis
5. a. Glycerol and saturated fatty acids
   b. Glucose
   c. Amino acids
   d. Glucose
   e. Glycerol and unsaturated fatty acids
   f. Glucose

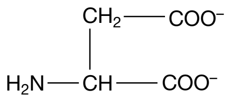
12.3 Enzymes as protein catalysts

12.3 Exercise

1.



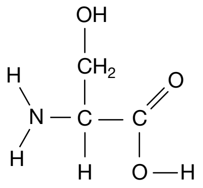
2. See figure at foot of the page.*
3. Dispersion forces with another non-polar group.
4. Glycine is the only amino acid to have two hydrogen atoms attached to the central carbon because the R-group in glycine is just a hydrogen atom.
5. In the **lock-and-key model** the substrate fits perfectly into the shape of the active site. In the **induced fit model** active site changes shape to firmly bond to the substrate.
6. a. Denaturation is a change in the structure or function of a protein due to disruptions of interactions in the secondary, tertiary and quaternary structures, where the α-helix and β-sheets uncoil and change their shape. The primary structure is not affected.
   b. Denaturation can occur by the action of heat, pH changes, radiation, presence of particular organic compounds, or heavy metal ions.
7.



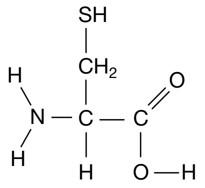
$H_2N-CH(CH_2-COO^-)-COO^-$

8. The conditions in the stomach are acidic but in the small intestine they are alkaline.
9. a. The optimum temperature is the temperature at which an enzyme is most effective.
   b. Optimum temperature is 37 °C and optimum pH is 8.
10. a. This minimizes random error and increases the accuracy of the results.
    b. The control experiment was the one carried out with water.
    c. Amylose
    d. pH, type of enzyme, concentration of enzyme, volume of solution and amount of iodine used.
    e. Optimum temperature: 37 °C, (pH 6.7−7.0)

Practice problem 1



serine



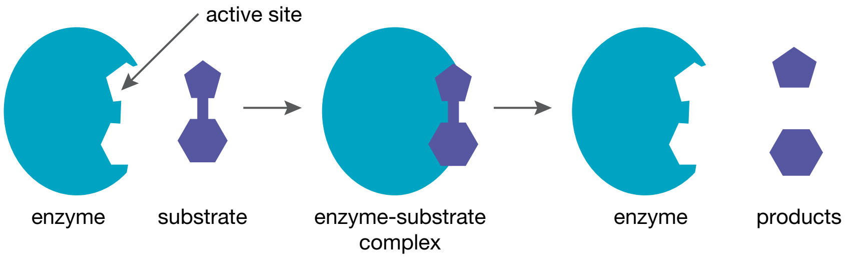
cysteine

12.4 Denaturation and hydrolysis of proteins

12.4 Exercise

1. a. The secondary, tertiary and quaternary structure of proteins
   b. The primary structure of proteins

2*



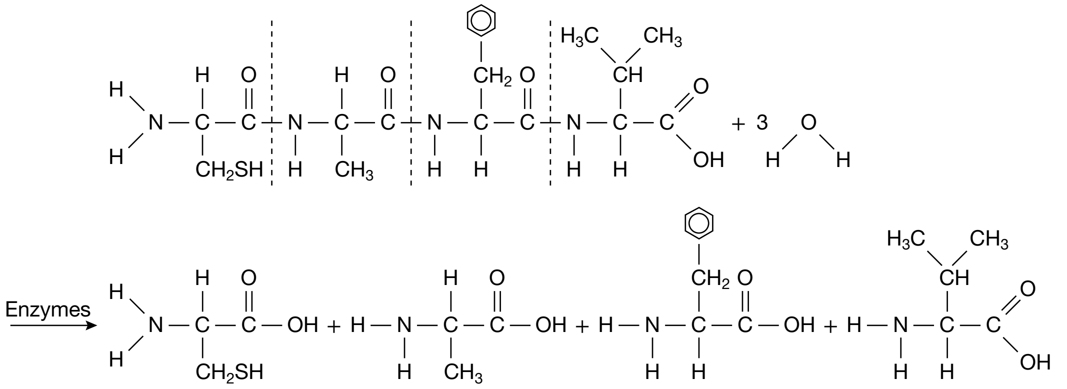
2. a. See figure at foot of the page.*
   b. Cysteine, alanine, phenylalanine and valine
3. The primary structure consisting of chains of amino acids is covalently bonded, and therefore is not disrupted when denaturation occurs.
4. A peptide link is lost
5. A carboxyl group and amino group are formed
6. Amino acids
7. a. 4, Cys-Ala, Ala-Gly, Gly-Gly, Gly-Ala
   b. 3, Cys, Ala, Gly
   c. 3, Cys-Ala, Ala-Gly, Gly-Gly
   d. 3, Cys-Ala-Gly, Ala-Gly-Gly, Gly-Gly-Ala
   e. Zero
8. When an egg is cooked the proteins in the 'white' part of the egg are denatured by the heat. Different bonds are formed between the peptide chains and this is visible by the 'white' going from transparent to opaque.

12.5 Carbohydrates

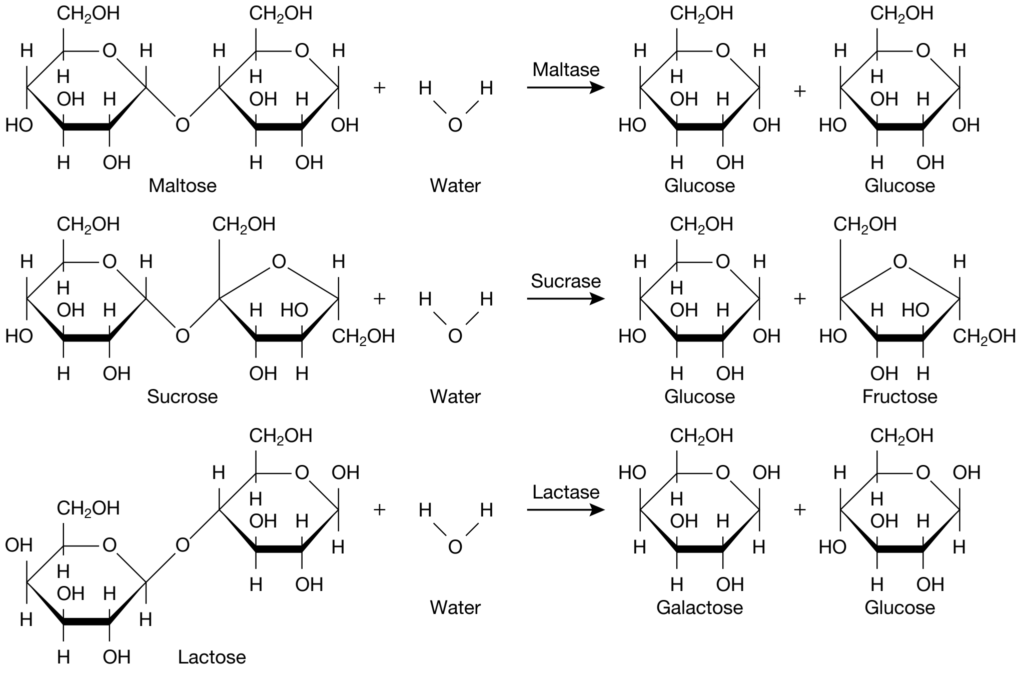
12.5 Exercise

1. a. Starch and cellulose are carbohydrates that have been formed by condensation polymerisation of glucose.
   b. Starch is a condensation polymer of α-glucose, while cellulose is a condensation polymer of β-glucose. In starch, the α-glucose monomers link up regularly when they polymerise, but in cellulose, alternate β-glucose monomers are inverted when they link up. Starch comprises two different polymers: amylose (linear polymer chains) and amylopectin (branched polymer chains). Cellulose comprises only one type of unbranched polymer chain that forms extensive hydrogen bonds to other unbranched polymer chains.
2. Humans do not have the enzymes to digest cellulose whereas animals like cows have bacteria that do have the enzyme to digest cellulose.
3. See figure at foot of the page.*
4. a. Lactose is soluble in milk because milk has a high water content and the lactose can readily form hydrogen bonds with water molecules. Butter and cheese have a lower water content and a higher fat content which make the polar lactose molecule less soluble.
   b. $C_{12}H_{22}O_{11}$.
5. a. A hydrolysis reaction.
   b. Glucose and galactose.

2a*



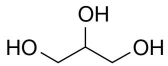
3*



6. Some people do not have the enzyme lactase to breakdown milk so the lactose passes into the large intestine where bacteria breakdown the lactose into small carboxylic acids and gases, which cause the unpleasant symptoms.
7. The glycaemic index (GI) is used to indicate how quickly carbohydrates influence glucose levels in the blood. The GI is determined by giving a group of people a particular mass of carbohydrate (usually 50 g) and measuring their glucose levels over three hours. These readings are then compared with eating pure glucose. The highest value is 100 for glucose.
8. Low GI foods help to prevent diabetes and also make people feel full for longer, which assists in limiting weight gain.
9. Glucose is readily and directly broken down in respiration to provide energy; it does not need to be converted into other substances.
10. 90 mg in 100 mL (1 dL)

12.5 Fats and oils

12.5 Exercise

1. a. $C_3H_8O_3$
   $CH_2(OH)CH(OH)CH_2OH$
   

   b. It is a triol.
2. a. See figure at foot of the page.*
   b. Ester (−COO−), hydroxyl (−OH) and carboxyl (−COOH).
3. Oxidative rancidity is the deterioration of lipids by reaction with atmospheric oxygen.
4. Oxygen from the air readily reacts across the reactive double bonds present in unsaturated fats, making them more susceptible to rancidity.
5. Aldehydes −CHO, ketones −CO− and carboxylic acids (carboxyl group) −COOH
6. Antioxidants are reducing agents and are therefore preferentially oxidised. A natural antioxidant is vitamin C (ascorbic acid); synthetic antioxidants include butylated hydroxytoluene (BHT), butylated hydroxyanisole (BHA) and propyl gallate.
7. a. $C_6H_8O_6(aq) \rightarrow C_6H_6O_6(aq) + 2H^+(aq) + 2e^-$
   b. This is an oxidation reaction because there is a loss of electrons and increase in oxidation number.
   c. Two hydroxyl groups are oxidised to two carbonyl groups.
8. The presence of light and heat will increase the likelihood that the oil will become rancid.
9. Sample responses can be found in your digital formats.

12.7 Coenzymes

12.7 Exercise

1. Coenzymes are small, organic, non-protein molecules that are required to temporarily and loosely bind with the active site in the enzyme to accommodate the substrate so that it fits into the site.
2. Coenzymes can make the active site a better fit for a particular substrate. They can also act as carriers of electrons, atoms or small groups of atoms from one substrate to another.
3. Coenzymes are changed in particular reactions but regenerated in other reactions.
4. Vitamins
5. NAD^+ (nicotinamide adenine nucleotide) and coenzyme A.
6. Enzymes are large complex protein molecules; coenzymes are smaller organic compounds that are not proteins.
7. NADH is a reducing agent because it is oxidised and loses electrons.
8. Coenzymes can transfer electrons, alkyl groups and acetyl groups.

12.8 Review

12.8 Exercises

12.8 Exercise 1: Multiple choice questions

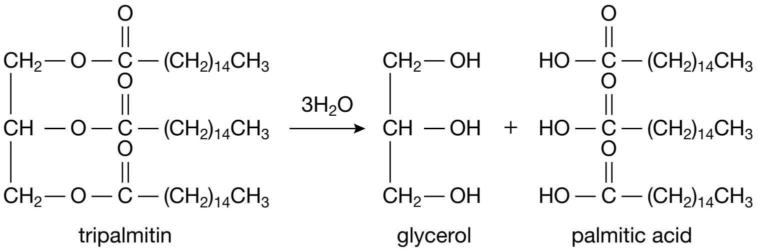
1. D.
2. C.
3. B.
4. D.
5. D.
6. C.
7. B.
8. A.
9. B.
10. A.
11. C.
12. D.
13. B.
14. D.
15. C.
16. C.
17. B.
18. B.
19. D.
20. A.

12.8 Exercise 2: Short answer questions

1. Enzymes and inorganic catalysts both increase the rate of a reaction. However, enzymes can speed reactions to a much greater degree than inorganic catalysts. Enzymes operate

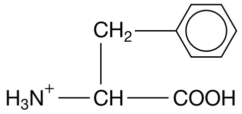
---

2a*

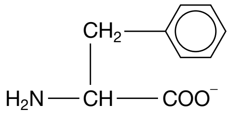


under much milder conditions. Enzymes operate within narrower temperature and pH ranges. Enzymes are much more selective than inorganic catalysts as each enzyme catalyses a particular type of reaction, so there are many different enyzmes within our bodies. Inorganic catalysts can increase the rate of many different reactions.

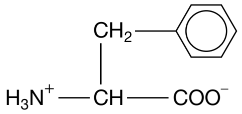
2. a.



b.



c.



3. a. An enzyme is a biological catalyst. It is a complex protein that increases the rate of a chemical reaction without being changed.

b. Each enzyme is specific and catalyses a particular reaction. It interacts with a substance called the substrate.

c. Enzymes each have a unique three-dimensional shape that is determined by the nature of the bonding and side chains in the protein. The reactant molecule (substrate) fits into a region in this shape that is called the active site.

d. A coenzyme is a non-protein compound that may be necessary for the effective functioning of an enzyme.

4. a. An enzyme is said to fit together with a substrate like a lock and key. The substrate fits perfectly into the shape produced by the relevant enzyme.

b. See figure at foot of the page.*

5. Denaturation is an alteration of a protein's shape that makes the protein unable to carry out its usual function.

6. By heat, a change in pH, a change in salt concentration or the presence of heavy metals.

7. a. The acid build-up via the production of lactic acid causes disruptions in the hydrogen bonding due to the increase in H^+ ions in the milk from the acid. These disruptions cause the milk protein caseinogen to denature. The proteins denature by unfolding and interacting with each other, clumping together. The presence of these lumps is called curdling.

b. The acid disrupts the bonds in the secondary and tertiary structures but not the strong covalent peptide bonds in the primary structure. New bonds form between the unwound chains of the protein. This formation of a new structure is called coagulation.

8. a. Digestive enzymes are proteins. It is important to wash at normal room temperatures so the proteins are not denatured.

b. Digestive enzymes are used to remove biological stains containing starches, lipids or proteins from clothes.

c. The specific shape of the enzyme allows the bonding of the substrate (biological molecule) to the active site and decreases the activation energy by providing an alternative pathway for the hydrolysis of starches, lipids and proteins. The resulting sugars, fatty acids, glycerol and amino acids are removed during the rest of the washing process.

9. If hot water is used to remove the blood, it can cause the blood protein to denature and coagulate. In this process, the protein molecules bind to the fibres of the material, making them harder to remove.

10. a. Pineapple contains an enzyme called bromelain. Enzymes and acids from fruits such as pineapples can denature muscle and connective proteins in meat so that it is more tender.

b. The enzyme is denatured when the can is heated during the canning process.

11. pH, temperature, volume of solutions, concentration of enzyme, concentration of substrate.

12. $C_8H_{15}O_5N_3(s) + 2H_2O(l) \rightarrow C_2H_5O_2N(s) + C_3H_7O_2N(s) + C_3H_7O_3N(s)$

13. Amylose and amylopectin both consist of chains of α-glucose monomers. Amylose has a linear structure with tightly wound coils bound by hydrogen bonding and is insoluble. Amylopectin is a branched, loosely-arranged polymer and is soluble. Amylose changes the colour of iodine to blue-black but amylopectin produces a reddish colour.

14. GI is a measure of how a carbohydrate affects blood glucose levels. The more amylose that is present, the slower the rate of digestion and the lower the GI. Food B would have the higher GI value because it has more amylopectin, which is more easily digested.

15. Lactose intolerance arises because an individual does not have enough of the lactase enzyme to break down the

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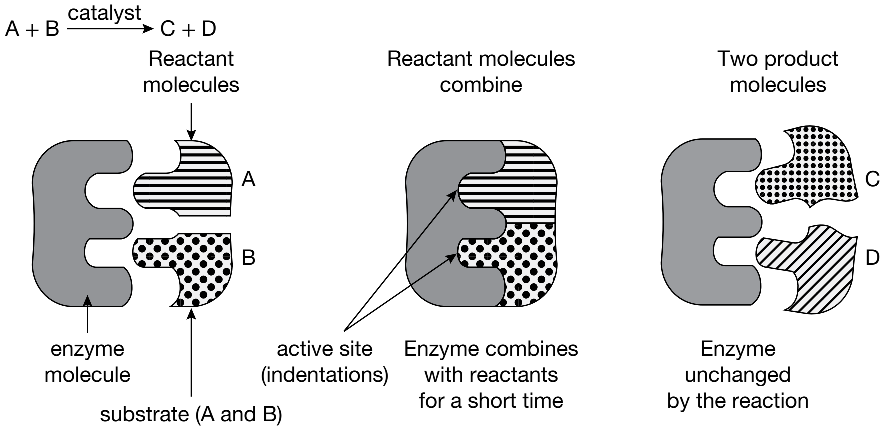
4b*



lactose in milk. This means that the lactose continues into the large intestine where bacteria breaks it down into small carboxylic acids and gases, which can cause the symptoms described. Lactose intolerance increases from childhood. People of Asian, African, South American, southern European and Australian Aboriginal heritage are more likely to become lactose intolerant than people of northern European descent.

16. Cellulose is a polymer of β-glucose with alternate molecules inverted. Extensive hydrogen bonding holds the chains together, making cellulose insoluble. It is indigestible by humans because humans lack the necessary enzyme to break the structure down. It is described as fibre and is necessary to the human diet because it contributes to digestion by helping to push food through the digestive system.

17. See figure at foot of the page.*

18. Fatty acids can be saturated (have only C—C bonds), monounsaturated (have one C=C bond) or polyunsaturated (have more than one C=C bonds). The double bond in unsaturated fats make these fats more susceptible to oxidation than saturated fats because oxygen in the air reacts across the double bond.

19. a. Rancidity is the natural process of decomposition of fats or oils by either hydrolysis or oxidation or both. This process of degradation often gives rise to an unpleasant odour and taste in foods, making them either unpalatable or unhealthy to ingest.

- **b.** Compounds that limit oxidative rancidity in foods are called antioxidants.
- **c.** Antioxidants limit rancidity in foods because they slow down oxidation and prevent (or limit) food from spoiling. They can do this because they are relatively strong reducing agents that are preferentially oxidised. Vitamin E is an antioxidant, so it prevents canola oil from becoming rancid.
- **d.** Other methods of limiting oxidation in foods include vacuum packaging, storage in a nitrogen atmosphere, cold storage, storage in opaque/dark containers or storage in a dark cupboard.

20. Enzymes are organic protein molecules while coenzymes are organic non-protein molecules. Enzymes act as catalysts while coenzymes assist some enzymes to act as catalysts.

12.8 Exercise 3: Exam practice questions

1. B.

2. A.

3. a. $CH_3CH_2OH \rightarrow CH_3CHO + 2H^+ + 2e^-$

- **b.** $NAD^+ + H^+ + 2e^- \rightarrow NADH$
- **c.** $CH_3CHO + H_2O \rightarrow CH_3COOH + 2H^+ + 2e^-$
- **d.** This is a different reaction with a different substrate so another enzyme, with an active site specific to the new substrate, is used to accommodate this new substrate.

4. a. Fats and oils are insoluble in water so they must be emulsified by bile. Bile breaks up the fat globules into smaller droplets with greater surface area. The lipase can react with the small droplets to break down the fat.

- **b.** Glycerol, fatty acids and monoglycerides
- **c.** Lipase increases the rate of hydrolysis of the oils and fats.
- **d.** At high temperatures, the lipase is denatured and becomes ineffective because its structure is destroyed.
- **e.** The tertiary structure of a protein gives the shape of its active site.
- **f.** Co-lipase acts as a coenzyme. It binds with the active site of the enzyme to ensure the correct conformation of the enzyme to accept the substrate.

5. The central carbon atom in alanine is chiral. It has four different atoms or groups of atoms bonded to it. This allows it to have non-superimposable mirror images and it is therefore an enantiomer.

13 Energy content of food

13.2 Energy values of carbohydrates, proteins and fats and oils

13.2 Exercise

1. Digestion, maintaining the heartbeat, breathing, nervous system, movement, heat generation and maintaining constant body conditions

2. 82.2 kJ

3. 1.9×10^3 kJ

4. Saturated fats are mostly made up of saturated fatty acids, which have single carbon to carbon bonds, for example: lauric, myristic or palmitic acids.

5. Cellulose

6. Monosaccharides (e.g. glucose) and disaccharides (e.g. maltose)

7. a. Yes

b. Protein : 409.7 kJ
Fat : 1102.6 kJ
Carbohydrate : 457.6 kJ
Total energy : 2.0×10^3 kJ

The berry bar has slightly more energy than the nut bar.

8. a. Butter or margarine

- **b.** Water

9. a. Monounsaturated refers to the fact that it has one carbon to carbon double bond.

- **b.** The oleic acid in olive oil contains a double bond which causes a bend in the fatty acid chains. This

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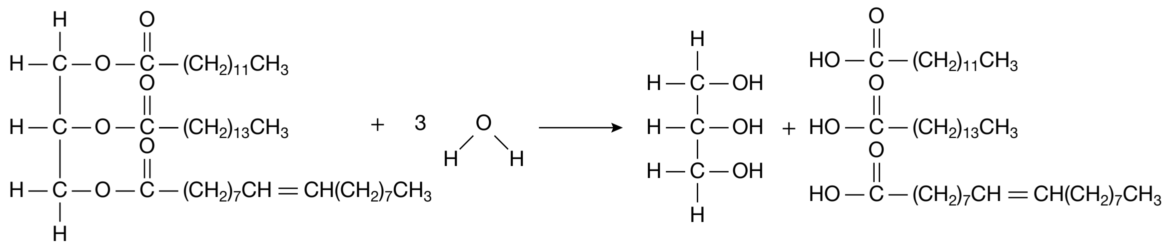
17*



prevents the molecules getting very close together, resulting in weaker intermolecular dispersion forces allowing more movement of molecules and forming a liquid.

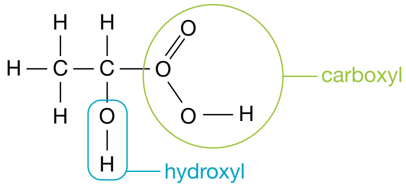
c. $2C_{18}H_{34}O_2(l) + 51O_2(g) \rightarrow 36CO_2(g) + 34H_2O(l)$

10. 63 minutes

13.3 Energy values of carbohydrates, proteins and fats and oils

13.3 Exercise

1. **a.** Glucose, $C_6H_{12}O_6$
   b. In the liver and muscles
   c. Glycogen
2. Brain
3. 15.9 kJ
4. Glucose is broken down to carbon dioxide via an oxidation reaction, which is exothermic.
5. Monosaccharides contain hydroxyl (−OH) and glycosidic (−O−) functional groups.
6.



7. The cramps could be due to the build-up of lactic acid because there is a limited supply of oxygen resulting in anaerobic respiration. The reaction for the breakdown of glucose in the absence of oxygen produces lactic acid.
   $C_6H_{12}O_6(aq) \rightarrow 2CH_3CH(OH)COOH(aq)$
8. **a.** $C_6H_{12}O_6(aq) \rightarrow 2CH_3CH_2OH(aq) + 2CO_2(g)$
   b. Fermentation
   c. The carbon dioxide produced causes bubbles in dough, which helps the bread to rise.

Practice problem 1

Energy going into the water:
$q = 8.15$ kJ
Energy per gram:
7.54 kJ g^{-1}

Practice problem 2

Calibration factor $= 332$ J °C^{-1}

Practice problem 3

$\Delta H = +2.80$ kJ mol^{-1}

Practice problem 4

$\Delta H = -37.9$ kJ mol^{-1}

Practice problem 5

Energy per gram $= 8.93$ kJ g^{-1}

Practice problem 6

CF $= 7.40$ kJ °C^{-1}

13.4 Principles of calorimetry

13.4 Exercise

1. 3.13×10^2 kJ
2. **a.** 21 kJ g^{-1}
   b. To prevent heat escape and improve the accuracy of the experiment, use a metal shield to help contain the heat and direct it to the water.
   c. A biscuit is a mixture and so will not have molar mass. The appropriate units are grams.
3. **a.** Calorimetry is a method used to determine the changes in energy of a system by measuring heat exchanges with the surroundings.
   b. When carrying out a reaction in a calorimeter not all of the heat produced goes into the water due to imperfect insulation or absorbance by parts of the calorimeter. By calibrating the instrument these factors are taken into account and allows the relationship of temperature to heat to be more accurately calculated.
   c. There would be no difference to the calculations because 1 °C is the same as 1K and it is the difference of two temperatures being used.
   d. If 50.0 mL was used in a calibration instead of 100.0 mL the change in temperature of the water would be greater. The calibration factor would be lower (this can be determined by using the equation:
   $$\text{calibration factor} = \frac{VIt}{\Delta T_c}.$$
4. $\Delta T_r = 0.492$ °C
5. **a.** Sample answer: The student would use an electric heater, connected into an electric circuit, to pass a known quantity of energy through 100.0 mL of water in the same calorimeter used for the experiment. Then, by calculating the change in temperature of the water in the calorimeter, the calibration factor (CF) can be calculated from the relationship CF $= \dfrac{VIt}{\Delta T}$ where $\Delta T =$ change in temperature of the 100 mL of water.
   b. $\Delta H = -54.9$ kJ mol^{-1}
   c. A higher concentration of base than acid was used to ensure that all of the acid had reacted.
   d. There would be no change because the amount in moles of the limiting reactant did not change.
   e. Random errors might involve measurement of the solution volume and temperature, and not stirring the reaction mixture during the reaction. Random errors can be minimised by repeating experiments. Another error is heat losses due to insufficient insulation.
6. **a.** Bomb calorimeters are used for reactions involving combustion reactions (which produce gases); solution calorimeters are used for reactions that take place in solution, such as dissolution or neutralisation.
   b. Bomb calorimeters have a pressurised container for the reaction to take place, an oxygen supply and an ignition source. The bomb calorimeter is designed for reactions involving gases and requires a tightly sealed container.
7. **a.** 1.18×10^3 J °C^{-1}
   b. 3.0×10^3 J g^{-1}.

- **c.** The reaction involves gases as reactants and/or products. All reactants and products must be contained to determine the overall energy transfers in the reaction. Therefore, a bomb calorimeter is required.
- **d.** Cereal is a mixture and consequently does not have a molar mass, so grams are the appropriate unit to use.

13.5 Review

13.5 Exercises

13.5 Exercise 1: Multiple choice questions

1. D.
2. A.
3. D.
4. A.
5. D.
6. D.
7. C.
8. D.
9. C.
10. B.

13.5 Exercise 2: Short answer questions

1. Carbohydrate = 272 kJ
   Protein = 119 kJ
   Fat = 333 kJ

   Total = 7.24×10^2 kJ
2. $9.4 \times 10_2$ kJ.
3. Oxidation reactions
4. Both produce energy from oxidation reactions and produce CO_2 and H_2O. Both can be stored. Carbohydrates produce energy more quickly and use less oxygen; fats take longer and use more oxygen.
5. $\Delta H = -140\,\text{kJ}$
6. $CH_3(CH_2)_{10}COOH + 17O_2 \rightarrow 12CO_2 + 12H_2O$
7. Slightly less than $2 \times 2816 = 5632\ \text{kJ mol}^{-1}$
   $\approx 5600\ \text{kJ mol}^{-1}$.
8. From 10 minutes the lactic acid starts to increase as the lungs and heart are not delivering enough oxygen to the muscles. From 18 minutes the lactic acid concentration starts to decrease as the athlete replaces the oxygen so that aerobic respiration can begin to take place. It takes about 27 minutes to get back to the starting level of lactic acid.
9. $587\ \text{J}\ ^\circ\text{C}^{-1}$
10. $306\ \text{kJ}\ ^\circ\text{C}^{-1}$
11. **a.** $176\ \text{J}\ ^\circ\ \text{C}^{-1}$
    b. $-7.26\ \text{kJ mol}^{-1}$
    c. The calorimeter was poorly insulated resulting in considerable heat loss in both the calibration stage and the actual reaction.
    d. The assumption in this experiment is that the reaction has gone to completion.
12. **a.** $17.3\ \text{kJ g}^{-1}$
    b. The biscuit is a mixture (not a pure substance) and consequently does not have a molar mass. Grams is the appropriate unit.
    c. The energy obtained is less than the experimentally determined value because not all of the food that is ingested is completely digested and so not all of the energy will be absorbed.

13.5 Exercise 3: Exam practice questions

1. **a.** 15 g fat
   b. Energy in 15 g of fat = 5.6×10^2 kJ
   c. Mass of protein = 40.9 g
   d. Remaining mass = 44 g
   which is probably mainly water.
2. **a.** $CH_3(CH_2)_{14}COOH + 23O_2 \rightarrow 16CO_2 + 16H_2O$
   b. Palmitic acid is saturated because all of the carbon to carbon bonds are single.
   c. 7.80×10^2 kJ
   d. 2.39 g
3. $10\ \text{kJ g}^{-1}$
4. $39.9\ \text{kJ g}^{-1}$
5. **a.** $5.4 \times 10^3\ \text{J g}^{-1}$
   b. There would be random errors associated with uncertainty in the measurement of the current, voltage, time and temperature for the calibration. There would also be random errors with the measurement of the mass and temperature in the combustion process. The consequence of random error is to obtain a result that can vary either above or below the expected result. The effects of random error can be minimised by repeating measurements. Other factors are incomplete reaction and insulation issues.

14 Practical investigation

14.2 Key science skills in chemistry

Practice problem 1

To write a research question, the IV and DV first should be determined. The IV is the type of clothing and the DV is the speed in which Jill rolls down the hill.

Research question: A research question needs to be testable and clearly outlines what is occurring in the investigation.

Aim: An aim must clearly link the relationship between the IV and DV.

Hypothesis: A hypothesis predicts the relationship between the IV and DV. It is often written in the form 'If [statement involving independent variable], then [statement involving dependent variable].'

Sample responses can be found in your digital formats.

14.2 Exercise

1. In order to be a testable question, it must link the independent and dependent variable and be able to investigate through scientific method and be practicable.
2. A logbook is important because it shows evidence of each step of an investigation, allowing work to be validated as your own.
3. The dependent variable is measured by the investigator and is influenced by the independent variable. The independent variable is manipulated and changed by the investigator.
4. To make sure that the dependent variables measured are only influenced by the independent variable and not unfairly influenced by other factors.

5. a. The independent variable is the changing temperature. The dependent variable is the rate of combustion.
   b. Controlled variables included the type of fuel used and likely included factors such as the measuring equipment used.
   c. The investigation is not controlling the concentration of the fuel at different temperatures, so it would be impossible to tell if results were from increasing the temperature or the concentration. Concentration should be controlled and kept consistent across all three tests.
6. a. Type of bread
   b. Change of temperature
   c. Some examples of controlled variables the size of bread, the mass of the bread, the age of the bread, the amount of water in the test tube, and the thermometer used to record the temperature.
7. B.
8. B, A, E, F, C, D
9. a. Sample answer: If alkanes have a higher boiling point than alkenes then heating an alkane and alkene with the same number of carbons would show that the alkene became a gas at a lower temperature.
   b. B.

14.3 Concepts specific to an investigation

Practice problem 2

a. 1.496×10^8
b. 2.8×10^{-8}
c. 9.0×10^8 or 9×10^8

14.3 Exercise

1. Key terms can be defined either within a report or in a glossary. Sample responses can be found in your digital formats.
2. Representations are useful in scientific reporting because they allow us to show complex and abstract concepts in an easy-to-understand form, enhancing the clarity in scientific communication.
3. a. 6.67×10^{-4}
   b. 1.5×10^{-14}
   c. 9.0×10^5 or 9×10^5
4. a. 0.0006524
   b. 512 340
   c. 15.4
   d. 0.01201
   e. 450
   f. 0.000002457
   g. 0.00009024

14.4 Scientific research methodologies

Practice problem 3

a. Student 1
b. Student 1
c. The student with the most precise data was student 2, and the student with the most accurate data was also student 2. Sample responses can be found in your digital formats.

14.4 Exercise

1. Reliability is linked with the repeatability of an investigation and whether or not someone could follow your protocol and get similar results. However, validity is more about the credibility of data and if it shows what it was intended to.
2. Yes, an experiment needs to be replicated in order to be seen as reliable.
3. Results would not be considered reliable if repetitions of an investigation lead to vastly different answers.
4. Findings are said to be valid when variables have been controlled, the results address the hypothesis and the purpose of the investigation and bias has not been used to manipulate or alter results.
5. Some examples of procedures that could have an impact of the internal validity of results include:
   - Not correctly testing the variable outlined in the hypothesis
   - Misinterpreting measurements
6. Reliability can be affected by the validity of an experiment. An experiment might be invalid because the technique used did not control variables properly. It would also not be considered reliable if others achieved a very different set of results due to other factors influencing the dependent variable.
7. Precision is a measure of how close various measurements are to each other. Accuracy is how close to the expected and known quantity a result is. Sample responses can be found in your digital formats.
8. A strength of quantitative data is it provides a clearer understanding of trends and patterns in results. A weakness is that it can be harder and more time-consuming to collect.
   A strength of qualitative data is that it is often easy and quick to collect. A weakness is that it can be subjective (i.e. one person might class a colour as blue, and another might state it is purple).

14.5 Ethics, health and safety

14.5 Exercise

1. a. Sample answer: 0.5 mol L^{-1} of sodium hydroxide can cause serious eye and skin irritation. Appropriate safety precautions would be wearing gloves, glasses and lab coats during use, and immediately rinsing off with running water if it comes into contact with eyes or skin.
   b. Sample answer: Beakers, being made of glass, can break or chip, leading to possible cuts or lacerations. Appropriate precautions include immediately reporting and sweeping up broken glass (do not pick it up with your hands), and discarding any damaged beakers because these are more prone to breaking.
   c. Sample answer: Methane is extremely flammable. Appropriate safety precautions would be not using ignition sources near methane and only producing methane in small quantities.
   d. Sample answer: Bunsen burners are sources of ignition. The blue roaring flame is extremely hot and difficult to see, and can lead to burns. Damage to the bases, jet and tubes can cause flames and increased

temperatures, which may also lead to burns. Safety precautions including avoiding touching the bunsen burner while hot, especially while on the roaring flame, and tying back any loose clothing or long hair before use.

2. Sample answer: Ethics may be important when confidentiality or personal beliefs are involved. Sample responses can be found in your digital formats.
3. Sample answer:
   - Identifying hazards with equipment or chemicals
   - Suggesting standard handling procedures
   - Outlining the correct disposal of chemicals
   - Outlining any first aid that might be required
   - Providing information for the practical, including the location, time and date.
4. Sample answer: chemicals produced in an experiment (not just those used), further information about allergies, contacts to emergency hotlines, and clear information about how many students will be in each group and at each bench.
5. Answers will vary between schools and different laboratories.
   Sample responses can be found in your digital formats.
6. Students should wear safety glasses to prevent the chemical from reaching their eyes, and gloves and lab coats to avoid exposure to skin. It should be kept away from any ignition sources and used in either a fume hood or a well-ventilated area.

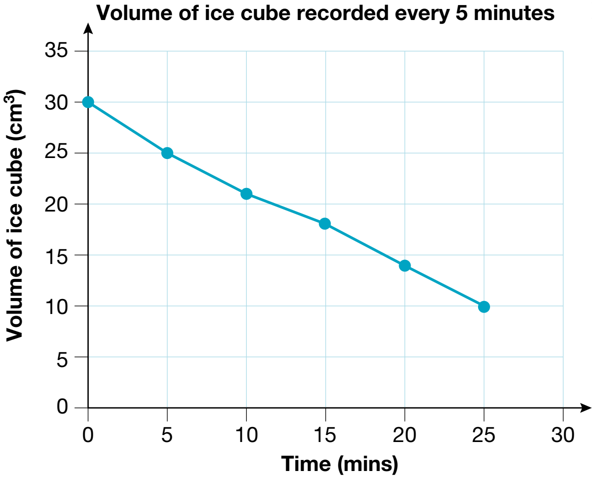
14.6 Methods of organising, analysing and evaluating primary data

Practice problem 4

a. 0.12 ± 0.005 g
b. 0.195 ± 0.0005 g

14.6 Exercise

1. A random error is chance variation in measurements and usually affects the precision of data. They can be improved by repeating an experiment. A systematic error usually affects the accuracy of an experiment, and is often due to equipment errors. This means they cannot be improved by repeating the experiment using the same equipment.
   Sample responses can be found in your digital formats
2. Taking multiple results and averaging them out or by using more precise equipment (i.e. if measuring 3 mL, use a measuring cylinder with marks every 1 mL, not a beaker with marks every 10 mL).
3. a. A bar graph would be most appropriate, because one variable is qualitative (household liquid) and the other is quantitative (pH).
   b. A line graph would be most appropriate because both variables (pH and temperature) are quantitative and a line graph would allow for trends to be seen. However, a scatterplot with a line of best fit might also be appropriate.
   c. A line graph would be most appropriate because a variable (temperature) is being observed over time.
   d. A histogram would be most appropriate because frequency and intervals are being used.
4. The following line graph would be an appropriate choice.



   It can be seen that as time passes, the volume of the ice cube decreases. On average, it decreases by approximately 4 cm^3 per minute, except between 10 and 15 minutes, when the rate of size reduction is slower, and between 0 to 5 minutes, when the rate of size reduction is slightly faster. This may be due to minor changes in room temperature, a different surface temperature or the surface area of the ice cube.
5. An outlier should be mentioned and discussed, with an outline of possible reasons for its occurrence. However, it is usually excluded when calculating averages or trying to add a line of best fit.
6. 11.42 mL or 11.43 mL
7. A burette reading is taken from the top down. This reading should be 7.32 mL.
8. a. 9.6 ± 0.25 cm
   b. 8.5 ± 0.125 cm
   c. 11.9 ± 0.05 cm
9. a. Measuring cylinder
   b. Volumetric flask
   c. Conical flask

14.7 Models and theories to understand observed phenomena

14.7 Exercise

1. Models can be useful because they:
   - Allow us to visualise objects and concepts we can't see (i.e. atoms)
   - Make abstract concepts tangible
   - Provide explanatory frameworks for a variety of chemical concepts, allowing for more in-depth concepts to be explored.
2. Some limitations of models include:
   - An oversimplification of complex situations, because models cannot show every detail
   - A misrepresentation of the concept in the real world when conditions are not as carefully controlled
   - The ever-changing nature of models and research means that models aren't definite.
3. A model is a representation of a phenomena, whereas a theory is a well-supported explanation of a phenomena. Often, we can use a model to represent a theory.

4. Theories allow us to understand phenomena because they are based on investigations and observations, and provide us with a structured idea that can be applied to different concepts. Sample responses can be found in your digital formats.

14.8 Nature of evidence and key findings of investigations

14.8 Exercise

1. A hypothesis is supported based on the evidence we have at the time and how this is interpreted. However, the nature of evidence is that as new knowledge becomes available, the evidence we obtain can change. Therefore, we cannot definitively prove a hypothesis, but rather support it with what we have at that point in time.
2. Three examples of strong evidence include quantitative data that was obtained when investigating a single variable, data that was not influenced by bias, and data that has been obtained through a reliable method and repeated and obtained by other investigators.
3. Key findings communicated in your discussion should include information about trends and patterns in your data, the relationship to chemical concepts and theory, and a clear answer to the question of your investigation.
4. It is important to link your results to chemical concepts to demonstrate how it is being used to show and support theory and phenomena. It gives an investigation more validity.

14.9 Conventions of scientific report writing and scientific poster presentation

Practice problem 5

a. 738300 nmol
b. 0.08233 km

Practice problem 6

0.28943 mol

14.9 Exercise

1. a. 0.14 L
   b. 670 g
   c. 0.762 184 m
2. a. 1670 000
   b. 0.198 mmol
3. a. The introduction is used to summarise key background concepts, explain any other research that has been done in this field, outline key terms, explain the purpose of your investigation and why you choose the question, and outline the hypothesis being explored.
   b. The discussion is used to outline any trends and patterns in your data, describe any outliers and how they were treated, evaluate your results and link them to theory, discuss any errors, uncertainties and limitations, describe the precision, accuracy, reliability and validity of your investigation, and suggest improvements and future investigations.
   c. The conclusion acts to sum up your investigation, provide a clear answer to your question and link back to your aim and your hypothesis.
4. *In-text:* (Taylor, Stubbs and Stokes, 2020)
   Reference list: Taylor, N, Stubbs A., Stokes, R. (2020) *Jacaranda Chemistry 2 VCE Units 3 & 4.* 2nd edition. Milton: John Wiley & Sons.
5. a. 4 significant figures.
   b. 3 significant figures.
   c. 4 significant figures.
   d. 3 significant figures.
6. a. 13
   b. 3.7
   c. 76.3
   d. 0.6
   e. 227
   f. 68.82
7. a. 53 g/mL.
   b. 34.8 g.
   c. 2.9 mol.
   d. 110 g

14.10 Review

14.10 Exercises

14.10 Exercise 1: Multiple choice questions

1. B.
2. B.
3. C.
4. A.
5. D.
6. B.
7. D.
8. A.
9. D.
10. C.

14.10 Exercise 2: Short answer questions

1. a. Quantitative data includes the energy content and the temperature change of water when burning the food type
   b. You could measure this using a thermometer or a calorimeter (solution or bomb)
   c. Qualitative data includes qualities around the food — for example colour. You could observe if burning the food lead to water boiling and the extent of this (rather than recording the temperature)
   d. You could use visual observations to record this qualitative data.
2. a. Independent variables are manipulated by the investigator. Dependent variables are measured and are the result of changes to the independent variable
   b. Models are representations of ideas, phenomena and processes, whereas a theory is an explanation of a phenomena. Often models can be used to represent theories.
   c. Systematic errors are those that affect the accuracy of a measurement, that cannot be improved by repeating an experiment. They are usually due to equipment or system errors. Random errors are chance variations in measurements that affect the precision of results, but can be improved by repeated experiments.

d. Primary sources of data are from the initial source of data collection, often through direct investigation. Secondary data is a summary of analysed primary data.

e. Uncertainty is around the limit to the precision of a piece of equipment (i.e. is a measurement on a ruler 0.011, 0.012 cm). Error is factors affecting the accuracy of the experiment and how close results are to their true value.

3. a. 6 significant figures

b. 8.12010×10^2 °C

4. a. 12.5%;interpolation

b. 14.1%:extrapolation

c. It would be difficult to give a reliable estimate of the ethanol level.

d. Sample answer: As the ethanol concentration increases, the peak area increases in a linear pattern when using gas chromatography. A calibration curve allows for the ethanol concentration of an alcoholic beverage to be determined based on the peak area measured in the readings.

5. a. The graph should have a clear heading, scale and labelled axis Sample responses can be found in your digital formats.

b. There is an initial steady increase of the temperature over the first 180 seconds. This levels off between 180 and 210 seconds, in which it then begins to slowly decrease.

c. The conclusion would be that temperature increases over a period of time before it decreases.

14.10 Exercise 3: Exam practice questions

1. a. Vicki has not taken enough safety precautions — she only was only wearing gloves. She should be wearing suitable protective clothing including a lab coat and safety glasses, and ensure long hair is tied back.

b. The mass of the balloon and flask

c. Sample answer:
- Amount of calcium carbonate powder
- Type of balloon
- Amount of hydrochloric acid
- Same batch of calcium carbonate
- Same scales used for measurements

d. Measuring cylinder and scales
Factors that may affect accuracy include, calibration, tolerance and student capability.

e. Responses will vary. Sample responses can be found in your digital formats.

2. a. Sample answer: To examine how the volume of a gas is impacted by changing pressure.

b. The hypothesis must clearly link the IV and DV, and must be tentative and testable.

c. Sample answer:
Qualitative data: seeing if the pressure causes the volume to increase or decrease.
Quantitative data may include recorded volume of the gas.

d. Sample response: Factors that may lead to different results by students include:
- Different interpretation of the volume
- Different conditions under which the experiment is conducted — some might be looking at the practical in warmer conditions compared to others
- Different methods of changing the pressure applied to the volume
- Different types of gases (or purity of gases) being used.

e. Sample response available in your digital formats.

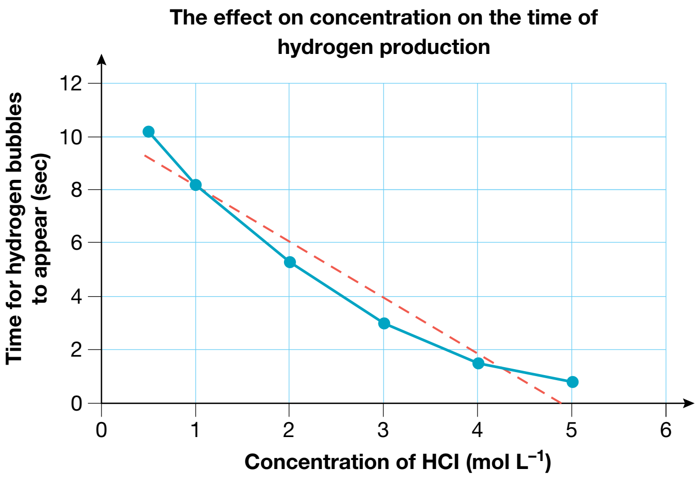
3. a. See figure at foot of the page.*

b. Some trends shown in the data include:
- A negative correlation/downwards trend, the time for hydrogen bubbles to appear decreases as the concentration of HCl increases
- As the concentration of HCl increases, the graph levels off, and the time drop for bubbles to appear is not as prominent
- On average, the time for bubbles to appear drops around 2 seconds for every 1 mol L^{-1} increase in the concentration

c. The smooth line joining the points is a much more accurate representation of the data, as it shows that the relationship is not quite linear, as the rate of the time drop decreases as concentration increases — there is not a perfect correlation between the two

---

3a*



4. a. An error that may have occurred includes:
    - Faulty thermometer and scales— (systematic error): make sure all thermometers and scales have been calibrated or test the temperature and mass using three different thermometers and get an average.
    - Incorrectly recorded measurements (random error): Repeat the experiment multiple times and take an average or get another student to check the measurement

    Sample response available in your digital formats.

    b. $10.7\,\text{kJ g}^{-1}$

    c. The known energy content of carbohydrates in 16 kJ g^{-1}. Accuracy requires data to be closest to the known value. Joe's data had a maximum deviation of 5.9 kJ g^{-1} from the actual value, whereas Robert had a maximum deviation of 6.1 kJ g^{-1}. Therefore Joe is more accurate than Robert.

    d. $14\ 000\ \text{J g}^{-1}$ (or 1.4×10^4 J)

5. a. The student provided a tentative explanation in their hypothesis.

    Sample response available in your digital formats.

    b. It does not provide accurate results in regards to the liquids that boil above 100 °C such as propanoic acid. This means that the results for this cannot be determined, as it may be 100.1 °C or 150.1 °C.

    c. 0.25 °C. This means that there is a level of uncertainty with the data and the results obtained by each individual) are not as accurate as they could be

    d. Sample answers:
    - The inability to exactly interpret boiling point (as it is a subjective)
    - The inability to completely control room temperature
    - The lack of accuracy in the recorded results (due to the thermometer used)
    - The lack of repetition in the method
    - The starting temperature were not consistent

    e. Bar graph with the type of molecule on the horizontal axis and the boiling point on the vertical axis. This is the best choice as one variable is qualitative and the other is quantitative.

    f. Sample conclusion:

    It was found that propanoic acid had the highest recorded boiling point, however the exact value for this could not be determined as it was above 100 °C. The highest boiling points that followed were that of propan-1-ol, propan-2-ol, propanone and lastly propanal. The hypothesis was supported, as propanoic acid did have the highest boiling point.

GLOSSARY

absolute zero the lowest temperature that is theoretically possible; 0 K

absorbed taken into another substance

aquifer underground rock layers that contain water; this groundwater can be extracted using a well

abundance the relative amount of a substance

accuracy how close an experimental measurement is to a known value

acid rain rain that has a pH lower than 5

activation energy the minimum energy required by reactants in order to react

active site a region on an enzyme that binds to a reactant molecule (substrate) during a reaction

addition reactions reactions in which one molecule bonds covalently with another molecule without losing any other atoms

adipose a form of fatty tissue used to store energy

adsorption the adhesion of atoms, ions or molecules from a gas, liquid or dissolved solid to a surface

aim a statement outlining the purpose of an investigation, linking the dependent and independent variables

alcohols organic hydroxyl compounds containing the $-\mathrm{OH}$ group

aliphatic describes organic compounds in which carbon atoms form open chains

aliquot the liquid from a pipette

alkaline fuel cell (AFC) fuel cell that converts oxygen (from the air) and hydrogen (from a supply) into electrical energy and heat

alkanols alcohols containing only carbon, hydrogen and oxygen

alkenes the family of hydrocarbons that contain one carbon–carbon double bond

alkyl groups hydrocarbon branches joined to the parent hydrocarbon chain (e.g. CH_3 (methyl) CH_2CH_3 (ethyl))

alkynes the family of hydrocarbons with one carbon–carbon triple bond

allotropes different physical forms in which an element can exist

amide link formed when a carboxyl group reacts with an amino group in a polymerisation reaction

amino acids molecules that contain an amine and a carboxyl group

amphoteric describes amino acids that can behave as both acids and bases

amylopectin consists of 300–5000 α-glucose units; combines with amylose to form starch

amylose consists of 50–300 α-glucose units in a continuous chain formed from C1–C4 linkages only; combines with amylopectin to form starch

anaerobic respiration breakdown of glucose in the absence of oxygen

analytes the components of a sample

anode the electrode at which oxidation occurs. In a galvanic cell, it is the negative electrode, because it is the source of negative electrons for the circuit. If the reducing agent is a metal, it is used as the electrode material.

antioxidants a substance that slows oxidation

arenes aromatic, benzene-based hydrocarbons

aromatic describes a compound that contains at least one benzene ring and is characterised by the presence of alternating double bonds within the ring

aspartame a common artificial sweetener

atom economy measurement of the efficiency of a reaction that considers the amount of waste produced by calculating the percentage of the molar mass of the desired product compared to the molar mass of all reactants

α-helices hydrogen bonds are formed between an oxygen atom of a $\mathrm{C{=}O}$ bond and a hydrogen atom of a $\mathrm{N{-}H}$ bond that is four amino acids away on the same chain

β-pleated sheets two sections of the peptide chain line up and are held together in a sheet-like structure by hydrogen bonds between one oxygen atom of a C=O bond and a hydrogen atom of a N−H bond in the parallel or anti-parallel sheet

backbone a peptide chain of covalently bonded nitrogen and carbon atoms

bar graphs graphs in which data is represented by a series of bars. They are usually used when one variable is quantitative and the other is qualitative.

base peak the most abundant ion in a mass spectrum

benzene an aromatic hydrocarbon with the formula C_6H_6

bias the intentional or unintentional influence on a research investigation

bile a liquid produced by the liver to aid digestion through emulsification

biodiesel a fuel produced from vegetable oil or animal fats and combined with an alcohol, usually methanol

bioethanol ethanol produced from plants, such as sugarcane, and used as an alternative to petrol

biofuel renewable, carbon-based energy source formed in short period of time from from living matter

biogas fuel produced from the fermentation of organic matter

Boyle's law describes the relationship between pressure and volume of a gas, such that for a fixed amount of gas at constant temperature, pressure is inversely proportional to volume. $p_1V_1 = p_2V_2$

bomb calorimeter an insulated steel container enclosed in water used to perform measurements of heat of combustion

bond length the distance between two nuclei involved in covalent bonding

burette a graduated glass tube for delivering known volumes of a liquid, especially in titrations

button cell a small, long-life cell used in devices such as calculators, hearing aids, pacemakers, cameras and watches

C-terminal the end of a peptide chain with a free carboxyl group

calibrated ensure an instrument's accuracy

calibrating finding a relationship between two quantities

calibration curves a graph of reading versus concentration

calorie a measurement of heat energy needed to raise 1 g of water. 1 °C = 4.18 joule

calorimeter apparatus used to measure heat changes during a chemical reaction or change of state

calorimetry a method used to determine the changes in energy of a system by measuring heat exchanges with the surroundings

carbohydrates general name for a class of carbon compounds that include sugars, starch and cellulose. Carbohydrates contain the elements carbon, hydrogen and oxygen.

carbon neutral no net release of carbon dioxide into the atmosphere

catalyst a substance that alters the rate of a reaction without a change in its own concentration

categorical data also known as qualitative data, this is when data has labels or names rather than a range of numerical quantities

cathode the electrode at which reduction occurs. In a galvanic cell, it is the positive electrode, because the negative electrons are drawn towards it and then consumed by the oxidising agent, which is present in the electrolyte.

cell potential difference the difference between the reduction potentials of two half-cells

cellular respiration process that occurs in cells to oxidise glucose in the presence of oxygen to carbon dioxide, water and energy

cellulose the most common carbohydrate and a condensation polymer of D-glucose. Humans cannot hydrolyse cellulose, so it is not a source of energy.

chain isomers a type of structural isomer that involves more branching

change in enthalpy the amount of energy released or absorbed in a chemical reaction

Charles' law describes the relationship between temperature and volume of a gas, such that for a given amount of gas at constant pressure, volume is directly proportional to the absolute temperature. $\frac{V_1}{T_1} = \frac{V_2}{T_2}$

chemical calibration calibration of a calorimeter using a combustion reaction with a known ΔH

chemical energetics a branch of science that deals with the properties of energy and the way it is transformed in chemical reactions

chemical shift the horizontal scale on a NMR spectra

chiral describes compounds containing an asymmetric carbon atom or chiral centre. The molecule cannot be superimposed upon its mirror image.

chiral centres asymmetric carbon atoms

chromatogram a chart that results from analysis by chromatography

cis–trans isomers types of stereoisomers that are formed when the same two different groups are bonded to each of the carbon atoms in a carbon–carbon double bond. A cis isomer has identical groups on the same side of the double bond; a trans isomer has the groups on opposite sides.

climate change changes in various measures of climate over a long period of time

closed system a system in which all the reactants and products are contained in some manner with no escape to the surrounding environment

coagulation the process of turning a liquid into a solid

coal the world's most plentiful fossil fuel; formed from the combined effects of pressure, temperature, moisture and bacterial decay on vegetable matter over several hundred million years

coenzyme an organic non-protein molecule required to temporarily and loosely bind with the protein molecule to form an active enzyme

column graphs see **bar graphs**

combustion rapid reaction of a compound with oxygen

concentration fraction essentially, the concentrations of the products divided by the concentrations of the reactants, including the coefficients of each component in the reaction

conclusion a section at the end of a report that relates back to the question, sums up key findings and states whether the hypothesis was supported or rejected

concordant describes titres that are within a defined volume of each other, such as 0.10 mL

condensation polymerisation step-growth polymerisation in which two monomers combine and a smaller molecule is eliminated

condensation reaction a reaction in which molecules react and link together by covalent bonding with the elimination of a small molecule, such as water or hydrogen chloride, from the bond that is formed

control group a group that is not affected by the independent variables, and is used as a baseline for comparison

controlled variables variables that are kept constant across different experimental groups

covalent bonds bonds involving the sharing of electron pairs between atoms

D-glucose an isomer that occurs in nature

Daniell cell one of the first electrochemical cells to produce a reliable source of electricity; it uses the redox reactions between zinc metal and copper ions to produce electricity

denaturation change in the structure or function of a large molecule, such as a protein

dependent variable the variable that is influenced by the independent variable. It is the variable that is measured.

desorption the removal of a substance from or through a surface; the opposite of adsorption

dipeptide formed when two amino acids combine

dipolar ion an ion containing equal positive and negative charges

direct methanol fuel cell (DMFC) a new technology that is powered by pure methanol

disaccharides two sugar molecules (monosaccharides) bonded together

discussion a detailed area of a report in which results are discussed, analysed and evaluated, relationships to concepts are made, errors, limitations and uncertainties are assessed, and suggestions for future improvements are made

dry cell an electrochemical cell in which the electrolyte is a paste, rather than a liquid; also called a Leclanché cell

dynamic nature of equilibrium refers to the fact that at equilibrium forward and backward reactions are occurring at the same rate

efficiency efficiency (of energy conversion) the ratio between useful energy output and the energy input

electric calibration calibration of a calorimeter by supplying a known quantity of electricity

electrical potential the ability of a galvanic cell to produce an electric current

electrochemical cell cell that generates electrical energy from chemical reactions

electrochemical series a series of chemical elements arranged in order of their standard electrode potentials

electrodes a solid used to conduct electricity in a galvanic half-cell

electrolysis the decomposition of a chemical substance (in solution or the molten state) by the application of electrical energy

electrolytes liquids that can conduct electricity

electrolytic cell an electric cell in which a non-spontaneous redox reaction is made to occur by the application of an external potential difference across the electrodes

electron configuration the number of electrons and shells they occupy (e.g. 2,4 or $1s^2 2s^2 2p^2$)

electroplating adding a thin metal coating by electrolysis

eluent a substance used as a solvent in separating materials

emulsifier a substance that increases the surface area of fat by breaking it into smaller droplets

enantiomers chiral molecules that are non-superimposable mirror images of one another

end point the experimentally determined equivalence point at which the indicator just changes colour or the pH curve becomes vertical

endothermic describes a chemical reaction in which energy is absorbed from the surroundings

energy profile diagram a graph or diagram that shows the energy changes involved in a reaction from the reactants through the intermediate stages to the products

enhanced greenhouse effect the effect of increasing concentrations of greenhouse gases in the atmosphere as the result of human activity

enthalpy a thermodynamic quantity equivalent to the total heat content of a system; the total energy in a substance

enzymes proteins that catalyse chemical reactions

equilibrium constant the value of the concentration fraction at equilibrium; also called the equilibrium constant, *K*c

equilibrium law the relationship between the concentrations of the products and the reactants, taking into account their stoichiometric values

equilibrium reaction a reaction in which both forward and reverse reactions are significant

equivalence point where two reactants have reacted in their correct mole proportions in a titration

error differences between a measurement taken and the true value that is expected; they lead to a reduction in the accuracy of the investigation

essential amino acids amino acids that cannot be synthesised by animals from materials in their diets and therefore must be supplied directly in the diet

essential fatty acids fatty acids that must come from our diet because the body cannot produce them; often called omega fatty acids

esterification the process of ester formation

ethanol an alcohol with two carbons produced from fermentation of glucose by yeast

ethics acceptable and moral conduct determining what 'right' and what is 'wrong'

excited state when electrons moved to higher energy orbitals when energy is applied

exothermic describes a chemical reaction or process in which energy is released to the surroundings

experimental group test groups that are exposed to the independent variable

external circuit circuit composed of all the connected components within an electrolytic or a galvanic cell to achieve desired conditions

falsifiable there has to be a way to be prove the hypothesis wrong

Faraday constant a constant that represents the amount of electric charge carried by 1 mole of electrons

Faradays first law of electrolysis The amount of current passed through an electrode is directly proportional to the amount of material released from it.

Faradays second law of electrolysis When the same quantity of electricity is passed through several electrolytes, the mass of the substances deposited are proportional to their respective chemical equivalent or equivalent weight.

fat a triglyceride formed from glycerol and three fatty acids

fatty acids long-chain carboxylic acids usually containing an even number of 12–20 carbon atoms

fibrous describes long fibres in proteins that serve a structural role in the body; insoluble in water

fingerprint region the lower end of the infrared spectrum

flashpoint the temperature at which a particular organic compound gives off sufficient vapour to ignite in air

fossil fuels fuels formed from once-living organisms

fracking the process of pumping a large amount of mainly water under high pressure into a drilled hole, in order to break rock so that it will release gas or oil

fractional distillation the process of separating component fuels based on their different boiling points

fuel a substance that burns in air or oxygen to release useful energy

fuel cell an eletrochemical cell that produces electrical energy directly from a fuel

functional group elements in Group 17 (7) of the periodic table: F, Cl, Br, I and At

functional isomerism isomers containing different functional groups

global warming a gradual increase in the overall temperature of the Earth's atmosphere

globular describes proteins with a compact rounded shape and are usually soluble

glucose a simple carbohydrate stored in the liver or muscles

glycaemic index (GI) a figure representing the relative ability of a carbohydrate food to increase the level of glucose in the blood

glycerol an alcohol; it is a non-toxic, colourless, clear, odorless and viscous liquid that is sweet-tasting and has the semi-structural formula $CH_2OHCH(OH)CH_2OH$

glycogen the storage form of glucose in animals. It has a similar structure to amylopectin but is even more highly branched.

glycosidic link a particular type of ether bond

green chemistry a relatively new branch of chemistry that emphasises reducing the amounts of wastes produced, the more efficient use of energy and the use of renewable and recyclable resources

greenhouse effect a natural process that warms the Earth's surface. When the Sun's energy reaches the Earth's atmosphere, some of it is reflected back to space and the rest is absorbed and re-radiated by greenhouse gases.

greenhouse gases gases that contribute to the greenhouse effect by absorbing infrared radiation

haemoglobin the oxygen-carrying pigment and predominant protein in red blood cells

half-cell one half of a galvanic cell containing an electrode immersed in an electrolyte that may be the oxidising agent or the reducing agent depending on the oxidising strength of the other cell to which it is connected

Hall–Héroult the method of aluminium production used in primary aluminium smelters throughout the world

halogens elements in Group 17 of the periodic table: F, Cl, Br, I and At

heat content a thermodynamic quantity equivalent to the total heat content of a system

heat of reaction the heat evolved or absorbed during a chemical reaction taking place under conditions of constant temperature and of either constant volume or, more often, constant pressure

heterogeneous reaction a reaction in which some of the substances involved are in different phases

histograms a graph in which data is sorted in intervals and frequency is examined. This is used when both pieces of data are quantitative. Columns are not separated in a histogram.

homogeneous reaction a reaction in which all of the substances involved are in the same phase

homologous series a series of organic compounds that have the same structure but in which the formula of each molecule differs from the next by a CH_2 group

HPLC high-performance liquid chromatography; method used to separate the components of a mixture

hydrogenation the addition of hydrogen to unsaturated compounds, such as fatty acids

hydrolysis a hydrolytic reaction; the chemical breakdown of a compound due to reaction with water

hydrophilic describes a molecule more likely to interact with water and other polar substances

hydrophobic describes non-polar molecules that repel water molecules

hygroscopic a tendency to absorb water vapour from the atmosphere

hypothesis a tentative, testable and falsifiable statement for an observed phenomenon that acts as a prediction for the investigation

immiscible does not form a homogeneous mixture when mixed with another liquid

independent variable the variable that is changed or manipulated by an investigator

indicator a chemical compound that changes color and structure when exposed to certain conditions and is therefore useful for chemical tests

induced fit model a model of enzyme action where, in the presence of a substrate, the active site may change in order to fit the substrate's shape

infrared (IR) describes spectroscopy that deals with the infrared region of the electromagnetic spectrum

internal circuit a circuit within a conductor. Anions flow to the anode and cations flow to the cathode.

iodine number used to measure the degree of unsaturation. The iodine number is the mass of iodine that reacts with 100 g of a fat or oil.

irreversible reaction a reaction which, to all practical purposes, occurs only on the forward direction

kelvin the SI base unit of thermodynamic temperature, equal in magnitude to the degree Celsius

kinetic energy energy associated with movement, in doing work

kinetic molecular theory of gases Gas particles are in continuous, random motion. Collisions between gas particles are completely elastic.

kilojoule (kJ) a unit of energy

Law of Conservation of Energy Energy cannot be created or destroyed but only changed from one form into another or transferred from one object to another.

L-amino acids the stereoisomer of amino acids that is found in proteins in organisms. Enzyme-catalysed reactions occur only between molecules with this particular stereoisomerism.

lactic acid organic acid, $C_3H_6O_3$, present in muscle tissue as a by-product of anaerobic respiration

lactose milk sugar

Le Châtelier's principle When a change is made to an equilibrium system, the system moves to counteract the imposed change and restore the system to equilibrium.

lead–acid accumulator a battery with lead electrodes using dilute sulfuric acid as the electrolyte; each cell generates about 2 volts

Leclanché cell see **dry cell**

limitations factors that have impacted the interpretation and/or collection of findings in a practical investigation

line graphs graphs in which points of data are joined by a connecting line. These are used when both pieces of data are quantitative (numerical).

line of best fit a trend line that is added to a scatterplot to best express the data shown. These are straight lines, and are not required to pass through all points.

lipids substances such as a fat, oil or wax that dissolve in alcohol but not in water

lithium cells cells that use lithium anodes and can produce a high voltage

lock-and-key model model of enzyme action where only molecules with complementary shapes can react with the enzyme

liquefied petroleum gas (LPG) a hydrocarbon fuel that consists mainly of air propane and butane; non-toxic, non-corrosive, lead-free and denser than air

molar gas constant R, the constant of the universal gas equation; $R = 8.31 \text{ J mol}^{-1} \text{ K}^{-1}$ when pressure is measured in kPa, volume is measured in L, temperature is measured in K and the quantity of the gas is measured in moles (n).

molar gas volume the volume occupied by a mole of a substance at a given temperature and pressure. At SLC, 1 mole of gas occupies 24.8 litres.

mass spectrometry the investigation and measurement of the masses of isotopes, molecules and molecular fragments by ionising them and determining their trajectories in electric and magnetic fields

Maxwell–Boltzmann distribution curve a graph that plots the number of particles with a particular energy (vertical axis) against energy (horizontal axis)

membrane cell used for the electrolysis of brine

metabolism the chemical processes that occur within a living organism in order to maintain life

micelle a group of surfactant molecules surrounding a fat droplet with the hydrophobic ends dissolved in the fat and polar ends dissolve in the water

mobile phase the liquid or gas that flows through a chromatography system, moving the materials to be separated at different rates over the stationary phase

models representations of ideas, phenomena or scientific processes; they can be physical models, mathematical models or conceptual models

molecular ion whole molecules that produce ions with a peak at the relative molecular mass of the compound

monosaccharides the simplest form of carbohydrate, consisting of one sugar molecule

monounsaturated describes fatty acids containing only one double carbon to carbon bond

N-terminal the end of the peptide that has a free amino group

n+1 rule for simple molecules; the number of peaks is one more than the number of hydrogen atoms on the carbon atom next to that hydrogen atom and chemically different from that hydrogen atom

natural gas a source of alkanes (mainly methane) of low molecular mass

non-essential amino acid the 11 of the 20 amino acids necessary to make proteins that humans can produce

non-essential fatty acid fatty acids that humans can synthesise from food

numerical data also known as quantitative data, this is when data involves numbers and can be measured or counted

nutrients food molecules that organisms need to make energy, grow, reproduce and maintain a healthy life. These are: proteins, vitamins, minerals, fats and carbohydrates.

non-renewable (with reference to energy sources) energy sources are consumed faster than they are being formed

oligosaccharides three to ten monosaccharides bonded together

omega-3 fatty acid polyunsaturated fatty acids with a carbon to carbon double bond on the third carbon from the methyl end

omega-6 fatty acid polyunsaturated fatty acids with a carbon to carbon double bond on the sixth carbon from the methyl end

open system a system in which some or all the reactants or products can escape to the surrounding environment

optical isomers see **enantiomers**

optimum pH the pH at which enzymes function best

optimum temperature the temperature at which enzymes function best

outlier results that are a long way from other results and seen as unusual

oxidants see **oxidising agents**

oxidation an increase in the oxidation number; a loss of electrons

oxidation numbers a set of rules that assist in the identification of redox reactions

oxidative rancidity the deterioration of lipids by atmospheric oxygen

oxidising agents electron acceptors

pascal (Pa) unit of pressure

petroleum viscous, oily liquid composed of crude oil and natural gas that was formed by geological processes acting on marine organisms over millions of years; a mixture of hydrocarbons used to manufacture other fuels and many other chemicals

peptide formed when amino acids react

peptide link formed when a carboxyl group reacts with an amino group in a polymerisation reaction

percentage atom economy given by the formula

$$\%\ \text{atom economy} = \frac{\text{molar mass of desired product}}{\text{molar mass of all reactants}} \times \frac{100}{1}$$

percentage yield measurement of the efficiency of a reaction by calculating the percentage of the actual yield compared to the theoretical yield

pipette a slender tube for transferring or measuring small quantities of liquid

potential energy energy that is stored, ready to do work

polypeptides many amino acid residues bonded together

polysaccharides more than 10 monosaccharides bonded together

polyunsaturated describes fatty acids containing more than one double carbon to carbon bond

positional isomers isomers where the position of the functional group differentiates the compounds

precision how close multiple measurements of the same investigation are to each other

pressure the force per unit area that one region of a gas, liquid or solid exerts on another

primary alcohols alcohols in which the carbon atom that carries the $-OH$ group is attached to only one alkyl group

primary cells an electrolytic cell in which the cell reaction is not reversible

primary source direct or firsthand evidence about some phenomenon

primary standard a substance used in volumetric analysis that is of such high purity and stability that it can be used to prepare a solution of accurately known concentration

primary structure the order of amino acids in a protein molecule

proteins large molecules composed of one or more long chains of amino acids

proton exchange membrane fuel cell (PEMFC) a fuel cell being developed for transport applications as well as for stationary fuel cell applications and portable fuel cell applications

qualitative analysis an investigation used to identify the presence or absence of elements, ions or molecules in a sample

qualitative data categorical data that examines the quality of something (i.e. colour, gender), rather than numerical values

quantitative analysis an investigation used to determine the amount of a given element or compound in a known weight or volume of material

quantitative data numerical data that examines the quantity of something (i.e. length, time)

quaternary structure structure formed when individual protein molecules link together in a particular spatial arrangement

racemate a 50:50 mixture of two enantiomers; often occurs when optically active substances are synthesised in the laboratory

racemic mixture see **racemate**

random errors chance variations in measurements

reaction quotient essentially, the concentrations of the products divided by the concentrations of the reactants, including the coefficients of each component in the reaction

rechargeable describes a battery that is an energy storage device; it can be charged again after being discharged by applying DC current to its terminals

recharging forcing electrons to travel in the reverse direction and, because the discharge products are still in contact with the electrodes, the original reactions are reversed

redox reactions reactions that involve the transfer of one or more electrons between chemical species

reducing agents electron donors

reductants see **reducing agents**

reduction a decrease in the oxidation number; a gain of electrons

reduction potential a measure of the tendency of an oxidising agent to accept electrons and so undergo reduction

reliability whether or not another researcher could repeat your investigation by following your method and obtain similar results

renewable (with reference to energy sources) energy sources that can be produced faster than they are used

residue what remains when two or more amino acids combine to form a peptide

respiration when monosaccharides are converted to glucose, which is used as an energy source to power body cells including the brain, muscles and red blood cells

results a section in a report in which all data obtained is recorded, usually in the form of tables and graphs

retention time the time taken for each component of a sample to travel from the injection port to the end of the column

reversible reaction a reaction in which the reformation of products into reactants occurs to a significant extent

risk assessment a document that examines the different hazards in an investigation and suggests safety precautions

salt bridge a component that provides a supply of mobile ions that balance the charges built up in the half-cells of a galvanic cell during reaction

sample a substance to be analysed

saturated describes fatty acids containing only single carbon to carbon bonds

scatterplots graphs in which two quantitative variables are plotted as a series of dots

scientific method sometimes referred to as scientific process, this is the procedure that must be followed in scientific investigations that consists of questioning, researching, predicting, observing, experimenting and analysing

scientific research methodology the principles of research based on the scientific method

secondary alcohols alcohols in which the carbon atom that carries the $-\text{OH}$ group attached is joined directly to two alkyl groups, which may be the same or different

secondary cells electrolytic cells in which the cell reaction is reversible and which can be recharged once their production of electric current drops; often called rechargeable batteries

secondary fuel a fuel that is produced from another energy source

secondary source comments on or summaries and interpretations of primary data

secondary structure structure formed from hydrogen bonding between carboxyl and amino groups in a protein molecule

serving size recommended amount of food on nutrition label for one serving

side chain R group attached to an amino acid

solution calorimetry an insulated device used to measure heat changes in a solution, for example, heat of dissolution and neutralisation reactions

percentage yield given by the formula

$$\%\ \text{yield} = \frac{\text{actual yield}}{\text{theoretical yield}} \times \frac{100}{1}$$

specific heat capacity (*c*) energy needed to change the temperature of 1 g of a substance by 1 °C

spectroscopy the investigation and measurement of spectra produced when matter interacts with or emits electromagnetic radiation

standard cell potential difference the measured cell potential difference, under standard conditions, when the concentration of each species in solution is 1 M, the pressure of a gas, where applicable, is 100 kPa and the temperature is 25 °C (298 K)

standard hydrogen half-cell a standard reference electrode; assigned 0.00 volts

standard laboratory conditions (SLC) 100 kPa and 25°C

stoichiometry calculating amounts of reactants and products using a balanced chemical equation

standard solution a solution that has a precisely known concentration

starch a condensation polymer of α-D-glucose that is made up of two polymers: amylose and amylopectin

stationary phase a solid with a high surface area, or a finely divided solid coated with liquid. It shows different affinities for various components of a sample mixture when separating them by chromatography.

stereoisomerism where two or more compounds differ only in the spatial arrangements of their atoms

stereoisomers two or more compounds differing only in the spatial arrangements of their atoms

structural isomers molecules that have the same molecular formula but different structural formulas

substitution reactions reactions in which one or more atoms of a molecule are replaced by different atoms

substrate the substance on which an enzyme acts

surfactant molecule a molecule that has a polar (hydrophilic) and a non-polar (hydrophobic) end, for example, a detergent molecule

sustainable energy energy that meets present needs without compromising the ability of future generations to meet their own needs

systematic errors errors that affect the accuracy of a measurement, that cannot be improved by repeating an experiment. They are usually due to equipment or system errors.

tertiary structure structure formed from side-group interaction, including hydrogen bonding, ionic bonding, dipole–dipole interactions and disulfide bridges, in a protein molecule

testable a hypothesis can be easily tested by observations and/or experiments

theory a well-supported explanation of a phenomena, based on facts that have been obtained through investigations, research and observations

thermochemistry the branch of chemistry concerned with the quantities of heat evolved or absorbed during chemical reactions

thermochemical equations balanced stoichiometric chemical equations that include the enthalpy change

thermochemical equations chemical equations that include the ΔH value

titrant a solution of known concentration

titration process used to determine the concentration of a substance by using a pipette to deliver one substance and a burette to deliver another substance until they have reacted exactly in their mole ratios

titration curve curve used to measure the volume of a titrant against pH

titre the volume delivered by a burette

triglycerides fats and oils formed by a condensation reaction between glycerol and three fatty acids

transesterification the reaction between an ester of one alcohol and a second alcohol to form an ester of the second alcohol and an alcohol from the original ester

uncertainty a limit to the precision of equipment, it is a range within which a measurement lies

universal gas equation $PV = nRT$, where pressure is in kilopascals, volume is in litres and temperature is in kelvin

unsaturated describes hydrocarbons containing at least one double carbon–carbon bond

valence number the number of electrons occupying the orbitals in the outermost electron shell

validity credibility of the research results from experiments or from observations. Validity shows how much results measure what they intend to and how well they show the claims they make.

viscosity a measure of a fluid's resistance to flow

vitamins organic compounds that are needed in minute quantities on a regular basis as part of a healthy diet

volumetric analysis determination of the concentration, by volume, of a substance in a solution, such as by titration

yield amount of product

zinc–air cell cell that uses oxygen from the air as a reactant

zwitterion a dipolar ion containing equal positive and negative charges

INDEX

Note: Figures and tables are indicated by italic *f* and *t*, respectively, following the page reference.

PERIODIC TABLE OF THE ELEMENTS

Alkali metals ↓ Group 1

Alkaline earth metals ↓ Group 2

			Key
Period 1	1	2	← Atomic number
	Hydrogen	Helium	← Name
	H	**He**	← Symbol
	1.0	**4.0**	← Relative atomic mass

Transition metals (Group 3 – Group 9)

	Group 1	Group 2	Group 3	Group 4	Group 5	Group 6	Group 7	Group 8	Group 9
Period 1	1 Hydrogen **H** **1.0**								
Period 2	3 Lithium **Li** **6.9**	4 Beryllium **Be** **9.0**							
Period 3	11 Sodium **Na** **23.0**	12 Magnesium **Mg** **24.3**							
Period 4	19 Potassium **K** **39.1**	20 Calcium **Ca** **40.1**	21 Scandium **Sc** **45.0**	22 Titanium **Ti** **47.9**	23 Vanadium **V** **50.9**	24 Chromium **Cr** **52.0**	25 Manganese **Mn** **54.9**	26 Iron **Fe** **55.8**	27 Cobalt **Co** **58.9**
Period 5	37 Rubidium **Rb** **85.5**	38 Strontium **Sr** **87.6**	39 Yttrium **Y** **88.9**	40 Zirconium **Zr** **91.2**	41 Niobium **Nb** **92.9**	42 Molybdenum **Mo** **96.0**	43 Technetium **Tc** **(98)**	44 Ruthenium **Ru** **101.1**	45 Rhodium **Rh** **102.9**
Period 6	55 Caesium **Cs** **132.9**	56 Barium **Ba** **137.3**	57–71 Lanthanoids	72 Hafnium **Hf** **178.5**	73 Tantalum **Ta** **180.9**	74 Tungsten **W** **183.8**	75 Rhenium **Re** **186.2**	76 Osmium **Os** **190.2**	77 Iridium **Ir** **192.2**
Period 7	87 Francium **Fr** **(223)**	88 Radium **Ra** **(226)**	89–103 Actinoids	104 Rutherfordium **Rf** **(261)**	105 Dubnium **Db** **(262)**	106 Seaborgium **Sg** **(266)**	107 Bohrium **Bh** **(264)**	108 Hassium **Hs** **(267)**	109 Meitnerium **Mt** **(268)**

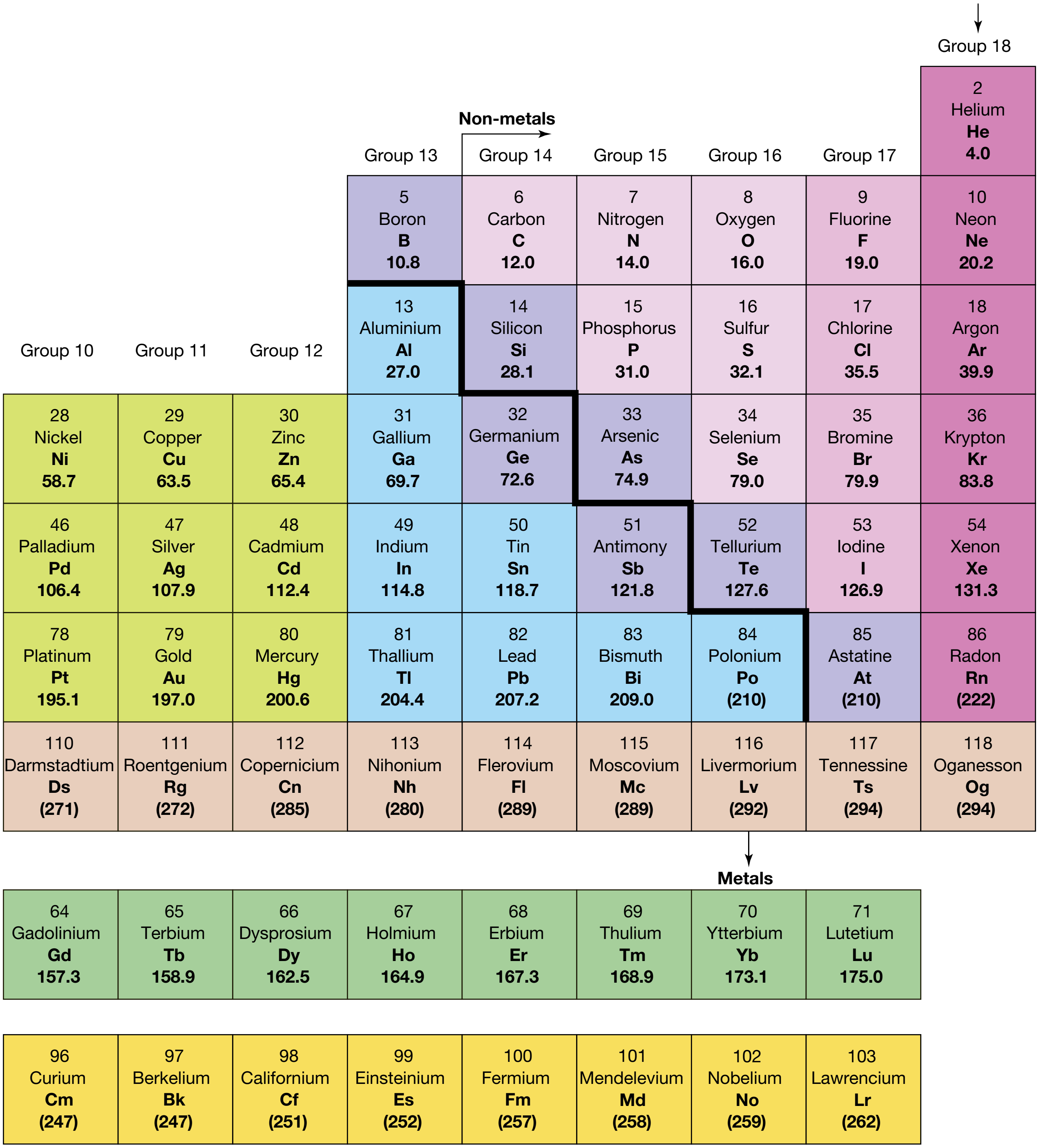
- 🟧 Alkali metal
- 🟨 Alkaline earth metal
- 🟩 Transition metal
- 🟩 Lathanoids
- 🟨 Actinoids
- 🟫 Unknown chemical properties
- 🟦 Post-transition metal
- 🟪 Metalloid
- ⬜ Reactive non-metal
- 🟪 Halide
- 🟪 Noble gas

Lanthanoids

57 Lanthanum **La** **138.9**	58 Cerium **Ce** **140.1**	59 Praseodymium **Pr** **140.9**	60 Neodymium **Nd** **144.2**	61 Promethium **Pm** **(145)**	62 Samarium **Sm** **150.4**	63 Europium **Eu** **152.0**

Actinoids

89 Actinium **Ac** **(227)**	90 Thorium **Th** **232.0**	91 Protactinium **Pa** **231.0**	92 Uranium **U** **238.0**	93 Neptunium **Np** **(237)**	94 Plutonium **Pu** **(244)**	95 Americium **Am** **(243)**



Group 10	Group 11	Group 12	Group 13	Group 14	Group 15	Group 16	Group 17	Group 18
								2 Helium **He** **4.0**
			5 Boron **B** **10.8**	6 Carbon **C** **12.0**	7 Nitrogen **N** **14.0**	8 Oxygen **O** **16.0**	9 Fluorine **F** **19.0**	10 Neon **Ne** **20.2**
			13 Aluminium **Al** **27.0**	14 Silicon **Si** **28.1**	15 Phosphorus **P** **31.0**	16 Sulfur **S** **32.1**	17 Chlorine **Cl** **35.5**	18 Argon **Ar** **39.9**
28 Nickel **Ni** **58.7**	29 Copper **Cu** **63.5**	30 Zinc **Zn** **65.4**	31 Gallium **Ga** **69.7**	32 Germanium **Ge** **72.6**	33 Arsenic **As** **74.9**	34 Selenium **Se** **79.0**	35 Bromine **Br** **79.9**	36 Krypton **Kr** **83.8**
46 Palladium **Pd** **106.4**	47 Silver **Ag** **107.9**	48 Cadmium **Cd** **112.4**	49 Indium **In** **114.8**	50 Tin **Sn** **118.7**	51 Antimony **Sb** **121.8**	52 Tellurium **Te** **127.6**	53 Iodine **I** **126.9**	54 Xenon **Xe** **131.3**
78 Platinum **Pt** **195.1**	79 Gold **Au** **197.0**	80 Mercury **Hg** **200.6**	81 Thallium **Tl** **204.4**	82 Lead **Pb** **207.2**	83 Bismuth **Bi** **209.0**	84 Polonium **Po** **(210)**	85 Astatine **At** **(210)**	86 Radon **Rn** **(222)**
110 Darmstadtium **Ds** **(271)**	111 Roentgenium **Rg** **(272)**	112 Copernicium **Cn** **(285)**	113 Nihonium **Nh** **(280)**	114 Flerovium **Fl** **(289)**	115 Moscovium **Mc** **(289)**	116 Livermorium **Lv** **(292)**	117 Tennessine **Ts** **(294)**	118 Oganesson **Og** **(294)**

64 Gadolinium **Gd** **157.3**	65 Terbium **Tb** **158.9**	66 Dysprosium **Dy** **162.5**	67 Holmium **Ho** **164.9**	68 Erbium **Er** **167.3**	69 Thulium **Tm** **168.9**	70 Ytterbium **Yb** **173.1**	71 Lutetium **Lu** **175.0**
96 Curium **Cm** **(247)**	97 Berkelium **Bk** **(247)**	98 Californium **Cf** **(251)**	99 Einsteinium **Es** **(252)**	100 Fermium **Fm** **(257)**	101 Mendelevium **Md** **(258)**	102 Nobelium **No** **(259)**	103 Lawrencium **Lr** **(262)**