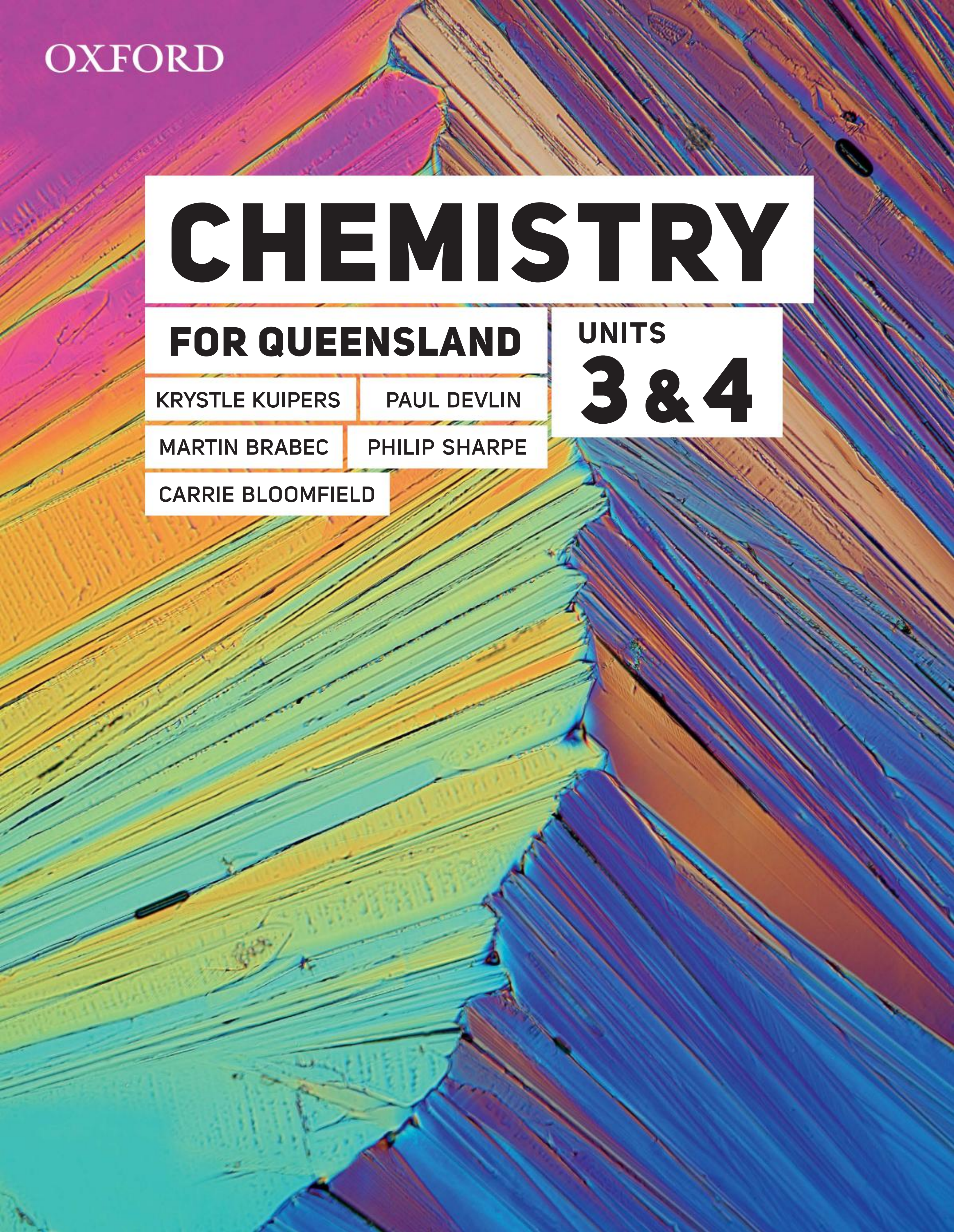

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CONTENTS


H_3PO_4

Chemistry for Queensland Units 3 & 4

Chemistry for Queensland Units 3 & 4 has been purpose-written to meet the requirements of the QCAA Chemistry General Senior Syllabus. The second of a two-volume series, *Chemistry for Queensland Units 3 & 4* offers complete support for teachers and students of Units 3 & 4 Chemistry, providing unparalleled depth and comprehensive syllabus coverage.


CHAPTER 9 Structure of organic compounds

OBJECTIVES

PRACTICALS

Chapter openers

Each chapter begins with a chapter opener that includes:

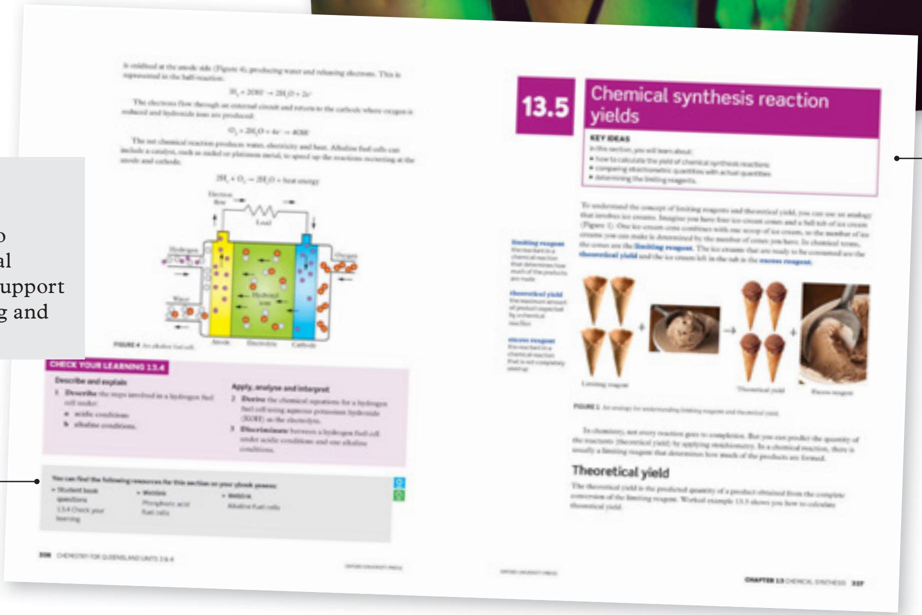
- subject matter from the **syllabus**
- a list of the **mandatory** and **suggested practicals** from the syllabus.


UNIT 4 STRUCTURE, SYNTHESIS AND DESIGN

Unit openers

Each unit begins with a unit opener that includes:

- an **overview of topics** in the unit
- **unit objectives** from the syllabus.


13.5 Chemical synthesis reaction yields

KEY IDEAS

CHECK YOUR LEARNING 13.4

Theoretical yield

obook assess

Every section includes links to a range of digital resources that support student learning and assessment.

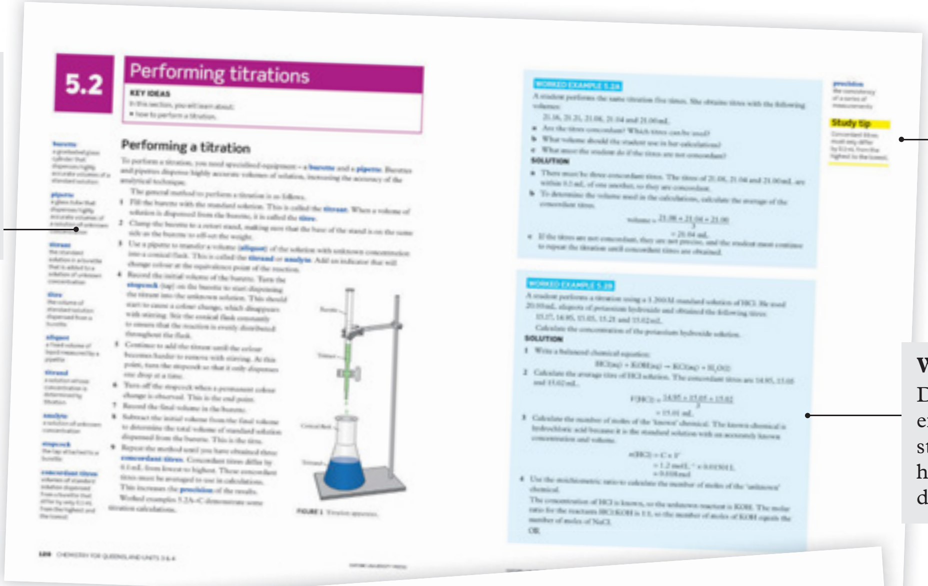
Section-based approach

Content is presented in clearly structured **sections**. Each section is clearly labelled and numbered to help navigation.

Margin glossary
Key terms and definitions are highlighted to help students recall important information.

Study tips
Practical assessment advice helps students improve their performance in assessment tasks.

Worked examples
Detailed worked examples take students through how to solve different problems.


5.2 Performing titrations

KEY IDEAS

Performing a titration

WORKED EXAMPLE 5.2A

WORKED EXAMPLE 5.2B

Study tip

Case studies
Real-life examples illustrate theoretical points being explained in the text.

Full-colour diagrams and photos
Rich visual material illustrates concepts and engages students.


CASE STUDY 3.4

pH values exceeding the common scale

CHECK YOUR LEARNING 3.4

3.5 The Brønsted-Lowry model

KEY IDEAS

CHALLENGE 3.5A

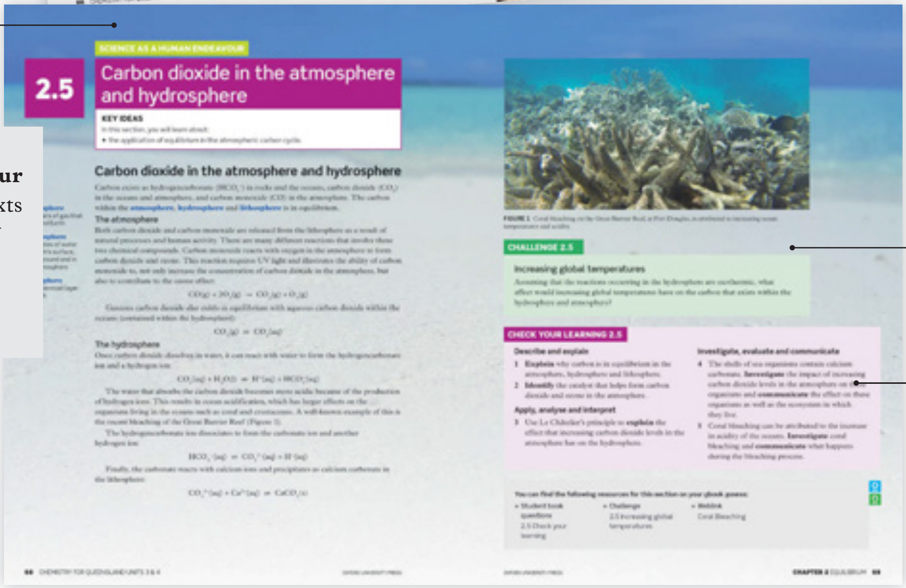
Battery acid reaction

Conjugate acid-base pairs

Science as a human endeavour
Real-world contexts promote curiosity and can be used as a starting point for research investigations.

Challenges
Scenarios and questions encourage critical thinking.

Check your learning
Each section ends with **Check your learning** questions that revise the content covered in the section and allow students to practise using cognitive verbs.


SCIENCE AS A HUMAN ENDEAVOUR

2.5 Carbon dioxide in the atmosphere and hydrosphere

KEY IDEAS

Carbon dioxide in the atmosphere and hydrosphere

CHALLENGE 2.5

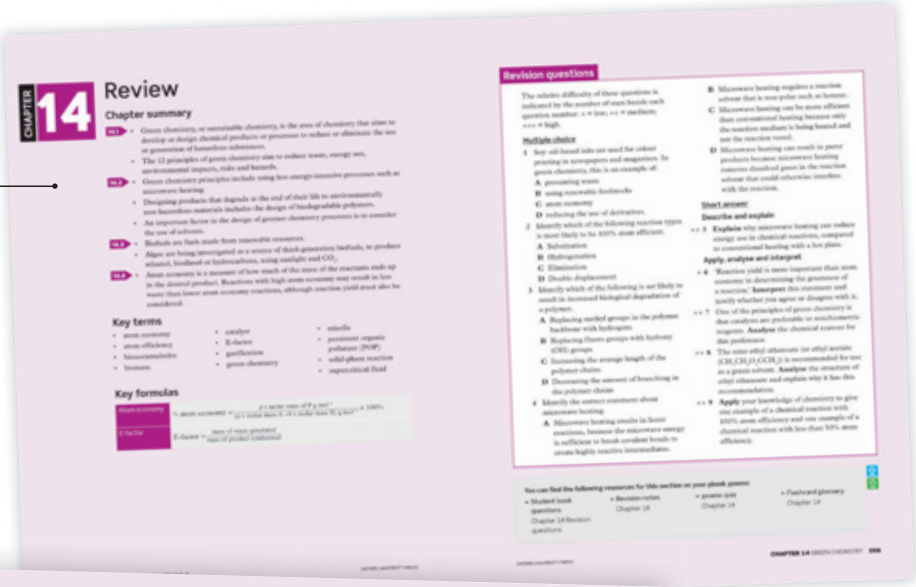
Increasing global temperatures

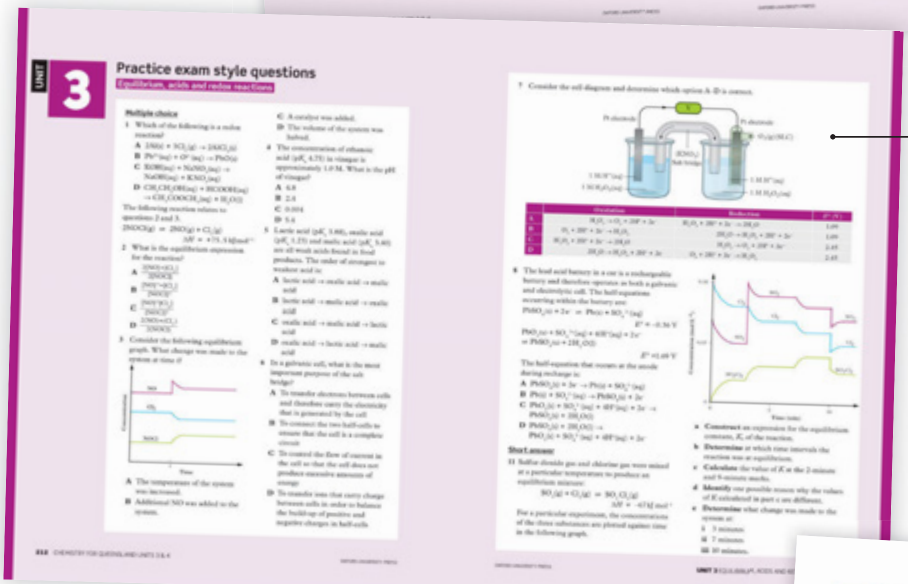
CHECK YOUR LEARNING 2.5

Chapter reviews

Each chapter review includes:

- a **summary of key learning** in each chapter
- **revision questions** written to target assessment through multiple-choice and short-answer questions
- **key terms** introduced throughout the chapter
- **key formulas** used in the chapter.





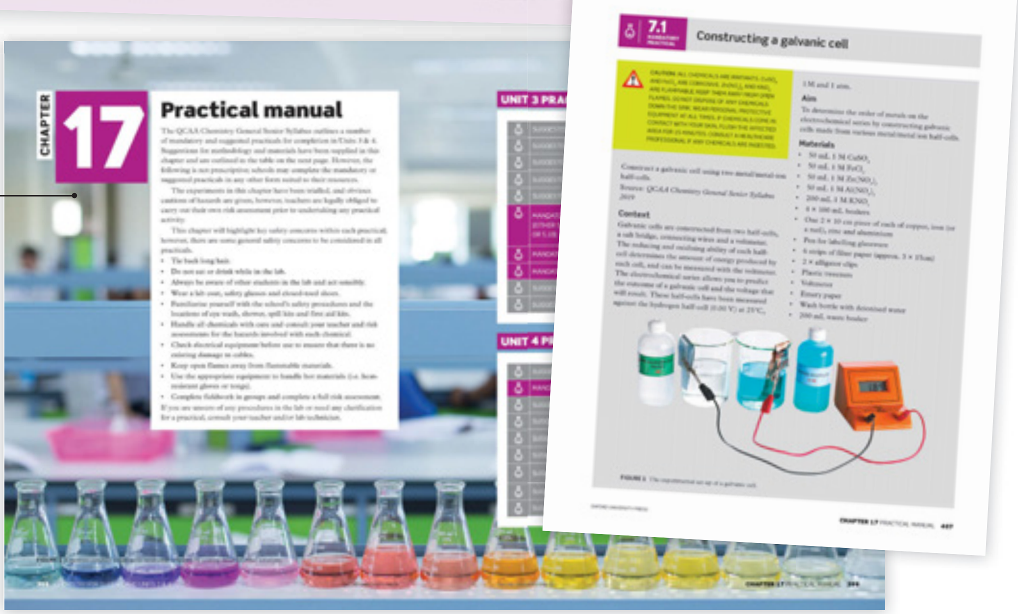
Practice exam questions

Each unit includes a set of practice questions to prepare students for their end-of-year external examination. Questions include:

- **multiple-choice questions** to consolidate learning
- **short-answer questions** with additional guidance on how long students should spend on each question.

Practical manual

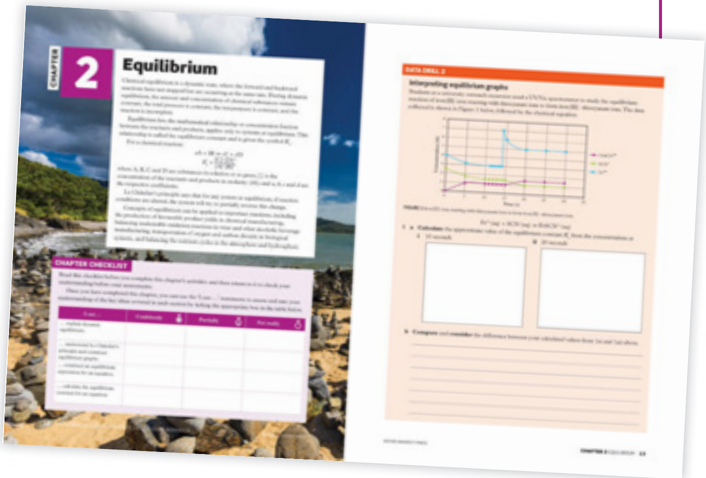
Each mandatory practical from the syllabus has **suggested methodologies and materials** included in the practical manual, and suggested practicals are included via obook assess. Each practical is flagged in the relevant section of the Student book.



Student workbooks

Chemistry for Queensland Units 3 & 4 and *Units 1 & 2* are supported by two Student workbooks that follow the same structure as the Student books, ensuring that students are consolidating relevant topic knowledge and developing key assessment skills. The workbooks include:

- a **toolkit** chapter that explains each key internal assessment
- **Data drill** activities that allow students to practise analysis and interpretation skills for the Data test
- **Experiment explorer** features to support the modification of a practical as required in the Student experiment
- **Research review** activities to help students develop skills in evaluating a claim and conducting research
- **Exam excellence** questions that include multiple-choice and short-answer questions to prepare students for the external assessment
- **practice internal assessments** (Data test, Student experiment and Research investigation)
- write-in worksheets for all **mandatory** and **suggested practicals**
- **answers** to all activities and practice assessments.

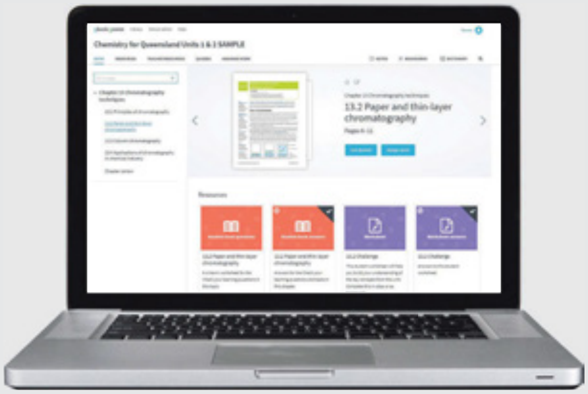


obook assess

Chemistry for Queensland Units 3 & 4 is supported by a range of engaging and relevant digital resources via obook assess.

Students receive:

- a complete digital version of the Student book with notetaking and bookmarking functionality
- video tutorials demonstrating key skills
- write-in worksheets to accompany all mandatory and suggested practicals
- interactive auto-correcting multiple-choice quizzes
- a range of engaging weblinks to support understanding
- access to work assigned by their teacher: reading, homework, tests, assignments.



In addition to the student resources, teachers also receive:

- detailed planning resources
- Student book answers
- printable (and editable) sample assessments, including data tests and exams with answers
- the ability to set up classes, set assignments, monitor progress and graph results, and to view all available content and resources in one place.

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Chapter 15: Shutterstock, 15.1.10, 15.1.12, 15.1.2, 15.1.3, 15.1.6, 15.1.8, 15.2.5, 15.2.7, 15.3.1, 15.3.2a, 15.3.2b, 15.3.3a, 15.3.3b, 15.3.5, 15.3.6, 15.4.1, 15.4.4, 15.5.2, 15.5.7, 15.5.8b, chapter opener.

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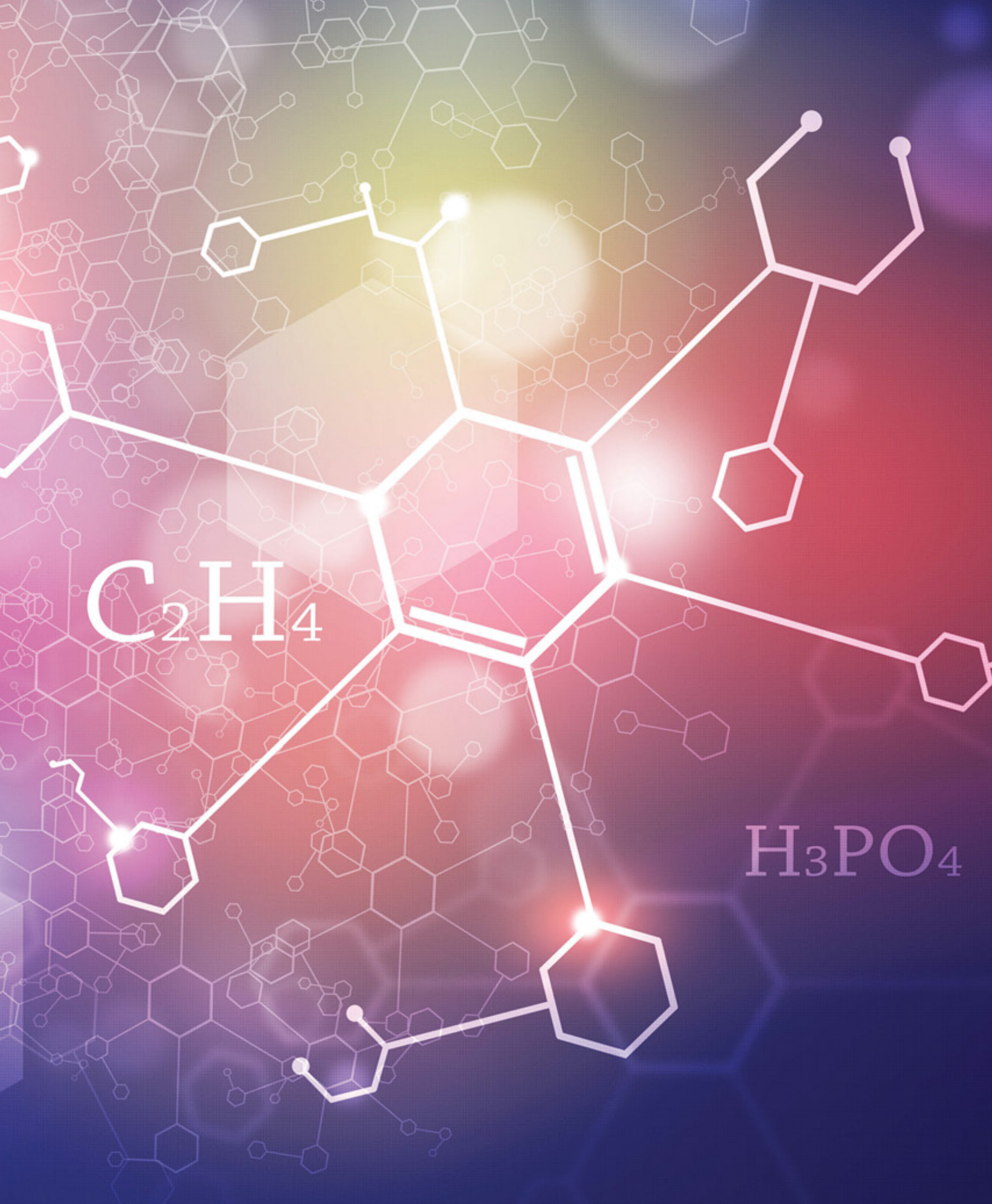

C_2H_4
H_3PO_4

CHAPTER 1

Chemistry toolkit

This chapter is intended as a toolkit to help you develop the skills you will need to successfully navigate the assessment tasks and requirements in Chemistry Units 3 and 4. You can refer to it any point through the year as a resource that provides guidance, including for the external examination to be held at the end of Unit 4.

There are hints and tips for dealing with the different types of questions and assessments that you will meet during Chemistry Units 3 and 4.

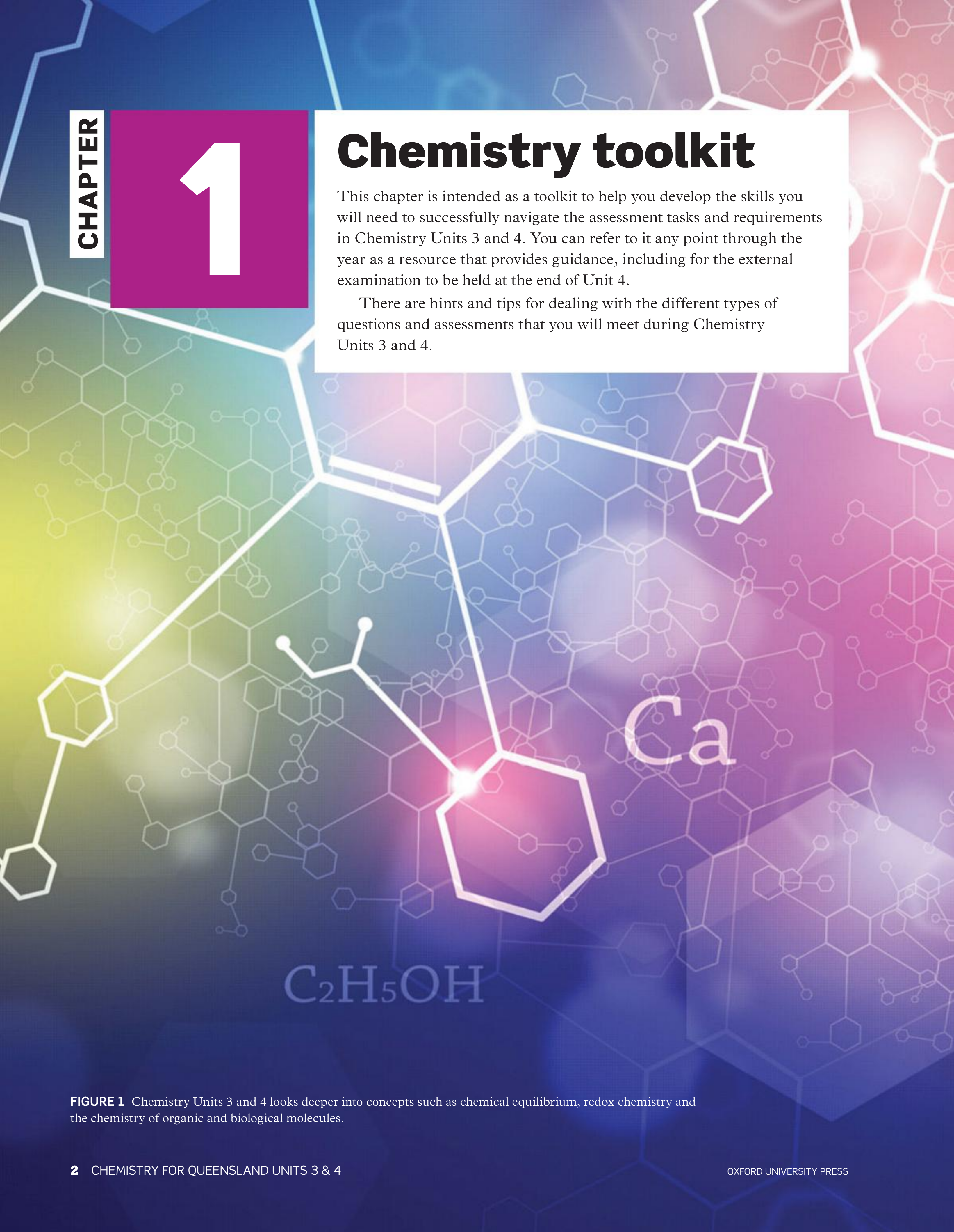


FIGURE 1 Chemistry Units 3 and 4 looks deeper into concepts such as chemical equilibrium, redox chemistry and the chemistry of organic and biological molecules.


C_2H_4
H_3PO_4

1.1

Year 12 assessment

KEY IDEAS

In this section, you will learn about:

- the Data test, Student experiment and Research investigation
- the external assessment.

Summative internal assessment

There are three internal assessment items in Units 3 and 4 that count towards your grade for Senior Chemistry. ('Internal' means set and marked by the teachers at your school.) These are the:

- Data test on chemical equilibrium or reduction and oxidation (worth 10%)
- Student experiment (20%)
- Research investigation (20%).

The last two items are longer tasks that require more planning, organisation and research to complete successfully.

Data test

The Data test consists of a 1-hour exam that includes 2–4 datasets (Figure 1). This data may be:

- **qualitative**, such as a statement of whether a reaction occurred or not

  or
- **quantitative**, such as the final concentrations of compounds in an equilibrium system at different temperatures.

qualitative
data that is descriptive and not numerical such as observations of chemical colours or the observable behaviour of gases

quantitative
data is numerical and allows for mathematical analysis to identify trends, patterns, relationships, limitations and uncertainty

The questions will include short-response items (with single words or sentence responses) up to short-paragraph responses (fewer than 50 words). There will also be calculation-type questions, and questions requiring you to interpret datasets. You will be allowed 10 minutes of reading time at the beginning and 60 minutes of writing time.

You will be allowed to use a graphics calculator. A chemical formula and data booklet is also permitted. Concentrate on how to use the formulas, constants and other information provided, rather than memorising this material.

Study tip

Practice Data tests can also be found for Units 1–3 in *Chemistry for Queensland Units 1 & 2 Student Workbook* and *Chemistry for Queensland Units 3 & 4 Student Workbook*.

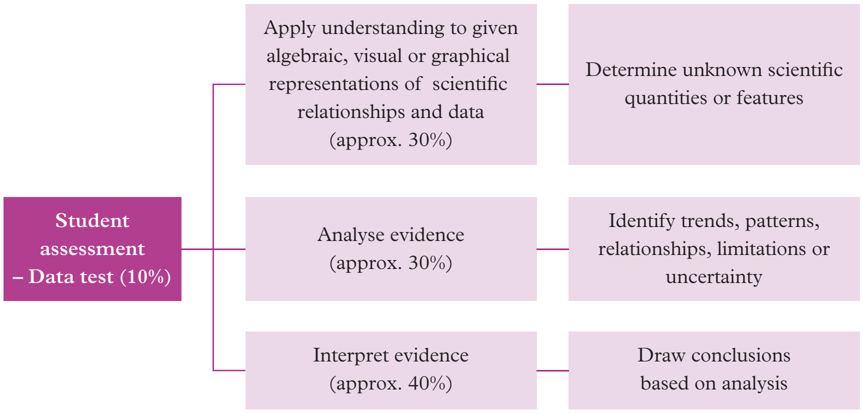


FIGURE 1 An outline of the components of the Data test, which is on chemical equilibrium or reduction and oxidation

Key tips

- Read the questions carefully. Be particularly wary of reading a question and assuming it is identical to something that you have seen before, only to realise the error when it is too late to fix.
- Do not state a conclusion without also outlining the evidence that you used to come to that conclusion. Watch out for giving evidence that is merely the conclusion stated in a different way; for example, 'The reaction was exothermic, because heat was given out', 'Acid A is a stronger acid than acid B because it has a lower pK_a'.
- Mention any limits on the degree of certainty with which you drew conclusions, if these exist. If you need to make certain assumptions to reach a conclusion, then state these assumptions; for example, 'It is assumed that the reaction solution was maintained at the same temperature throughout the reaction'.

Student experiment

The Student experiment is quite different from the other assessment items because it requires you to collect, analyse and synthesise primary data (Figure 2). You must plan and carry out experiments to generate the data that you will then use to answer a question or to confirm (or reject) a hypothesis related to chemical equilibrium systems or oxidation and reduction. You will do this over a period of 10 hours of class time, so it will be important to plan a timeline for the project. Remember to allow time for the things that won't go according to plan, or will take longer than expected.

To plan the experiment, you will need to research and think about how to conduct the experiment. You will need to be flexible to adapt the experiment as you identify challenges. Students can sometimes be frustrated when experiments do not work properly the first time or give unclear results. Part of the learning process required is to determine how to trouble-shoot, think clearly about what might be going wrong and adjust the experiment accordingly.

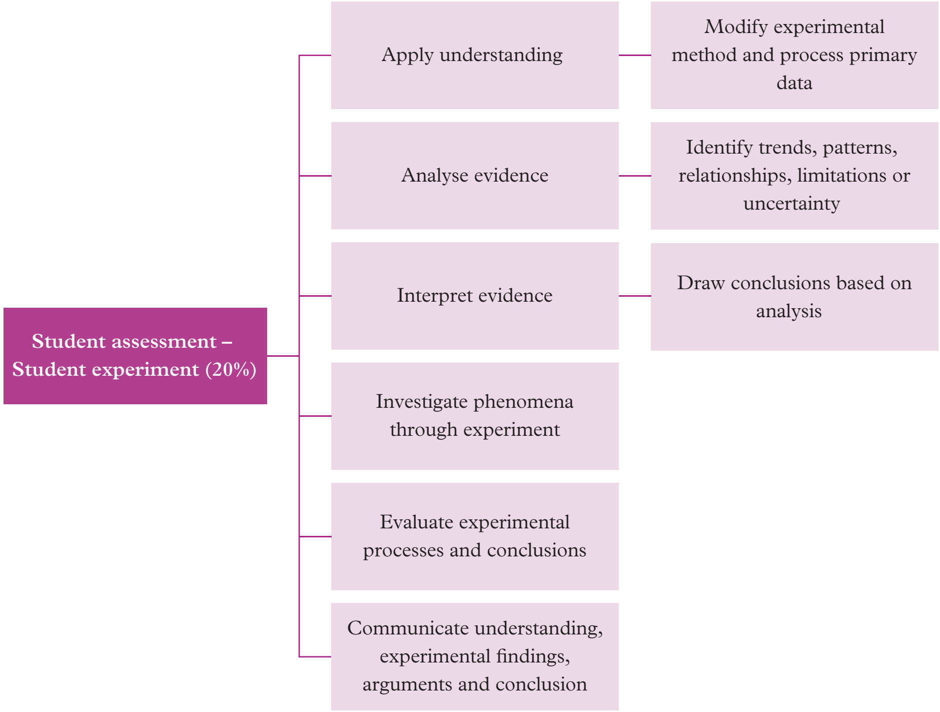


FIGURE 2 A summary of the Student experiment assessment

Study tip

In external examinations, you may be required to combine information from many different areas or be asked to extend your learning of known concepts in a new context.

You may need to go back and redo experiments. You can avoid some missteps by spending adequate time at the research and planning phase.

You then need to communicate the experimental data, results, findings and conclusion. You may present this in a written format such as a scientific report, of 1500–2000 words, or in a different format such as a scientific poster with an oral presentation of 9–11 minutes. Not all aspects of the report are weighted equally (Figure 3). You can find tips on how to write a high-quality scientific report on page 15.

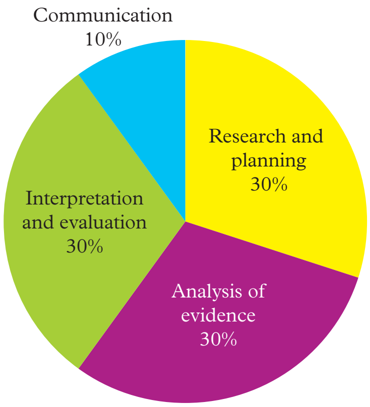


FIGURE 3 The breakdown of marks of the elements in the Student experiment

Research investigation

In the Research investigation task, you must evaluate a claim, by 'researching, analysing and interpreting **secondary evidence** from scientific texts' to justify a conclusion about your claim.

secondary evidence
evidence sourced from scientific works other than your own

In the Student experiment, you used primary evidence, i.e. data from your own experiments. In the Research investigation, you will use secondary evidence, which includes reports of findings and conclusions from other people such as scientific articles in journals (Figure 4). It will also be useful for you to review original research articles because they can provide an interpretation or summary of the current state of knowledge in a particular area. The authors of secondary evidence will have made judgements about what are the most important research findings to mention. Secondary evidence also includes textbooks and other specialist books in an area, as well as chemical encyclopedias, such as the *Kirk-Othmer Encyclopedia of Chemical Technology*.

Secondary sources of evidence for a Research investigation include:

- research articles – longer in-depth reports of experiments and research carried out by the authors
- communications – brief reports of 2–3 pages reporting new findings
- patents – legal documents that describe inventions such as new compounds or reaction methods
- research reviews – articles that summarise the current state of knowledge in a particular field and weigh up contributions from many researchers; they may give an overview of the history of a particular area
- news articles from scientific news sources – articles that report on particularly interesting new developments; for example, *Chemistry in Australia*, *ChemistryWorld*, *Chemical and Engineering News*
- textbooks – general chemistry textbooks or books on a specific topic such as organic chemistry or nanotechnology
- chemical dictionaries – useful for finding definitions of chemical terms; textbook glossaries may also be useful for this
- data compilations – collections of data such as tables of melting points, solubilities and spectroscopy data
- protocols and methods for experimental techniques – often found on the websites of large chemical or instrument suppliers
- multi-volume series on organic synthesis – for example, *Science of Synthesis* (Thieme), *Organic Syntheses*

- educational resources and guides – many chemistry organisations dedicate sections of their websites to helping high school students. The Royal Australian Chemical Institute, the Royal Society of Chemistry (UK) and the American Chemical Society all have information specifically for high-school students.

The evidence you use for this task must come from scientifically credible sources. These may be scientific journals, books written by experts in the area, websites of government bodies such as the CSIRO (Commonwealth Scientific and Industrial Research Organisation), or technical information provided by chemical supplier companies or instrument manufacturers.

To start the task, you must:

- select a claim to be evaluated. Your teacher will provide this for you
- develop a research strategy by identifying the relevant scientific concepts that connect with the claim. You could lose a lot of time by not having a plan for the research.

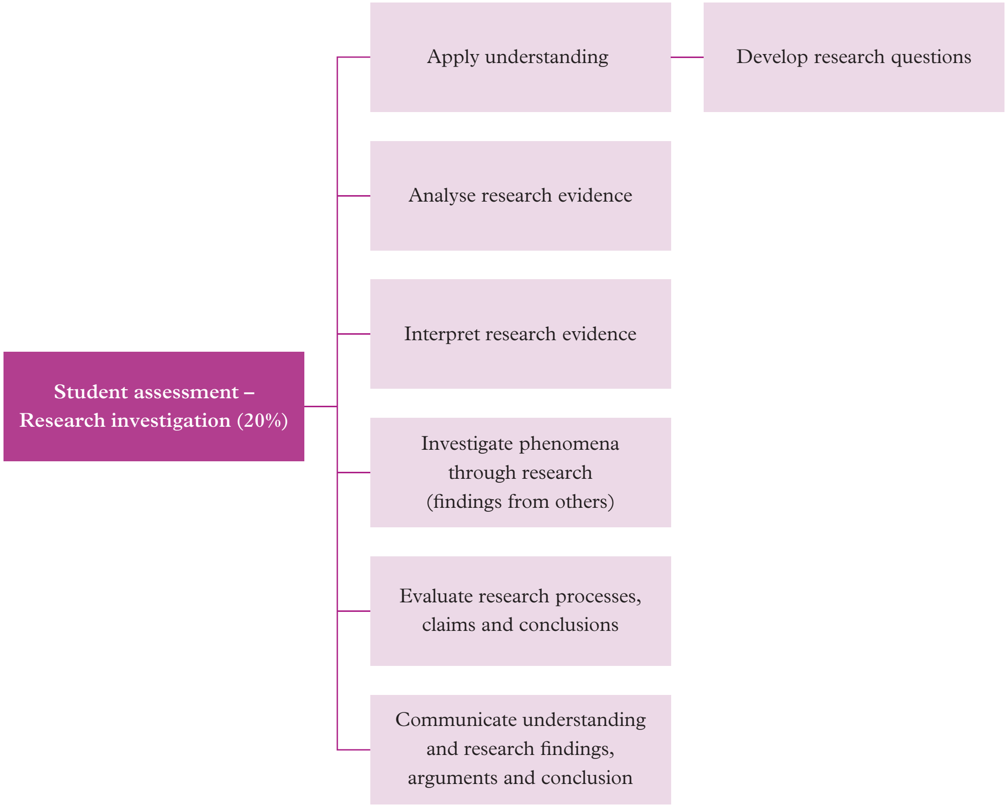


FIGURE 4 Key aspects of the Research investigation assessment

Section 1.3 contains some hints for researching and writing a Research investigation.

An example claim could be 'Solid-phase peptide synthesis is the most efficient chemical method for making peptides'. This would require background knowledge first about the different methods of making peptides (and what peptides are). The claim is broad enough to allow for research into different aspects of 'efficiency', such as yield and ease of purification, and green chemistry aspects such as use of solvents and energy inputs (see Chapter 14). There are restrictions in the claim, to make it achievable as well. It excludes biological methods of making peptides, such as expression in bacteria, as being outside the scope of the claim.

Study tip

Practice external examination questions can be found in the *Chemistry for Queensland Units 1 & 2 Student Workbook* and *Chemistry for Queensland Units 3 & 4 Student Workbook*.

Summative external assessment

Specifications

The summative external assessment is an external examination that will be held at the end of Unit 4, on the same day for all Year 12 students. The Chemistry external examination contributes to 50% to your overall Chemistry result and assesses both Units 3 and 4. (The content of Units 1 and 2 will not be specifically assessed, but Units 3 and 4 directly build on the material learnt in those units.) The exam papers will be collected and then marked by external markers.

Conditions

There will be two examination papers. They will both have 10 minutes of reading time and 90 minutes of writing time. You are allowed to bring in an approved graphics calculator and will be provided with the QCAA Chemistry formula and data book. It will be important to be familiar with how the calculator works and the layout of the tables of data in the data book, before the examination.

Paper 1 will be a mix of multiple choice and short answer questions and Paper 2 will be short answer questions only. Some questions may require you to interpret graphs, tables or other types of diagrams. Other questions may require you to respond to previously unseen data or a short passage of text.

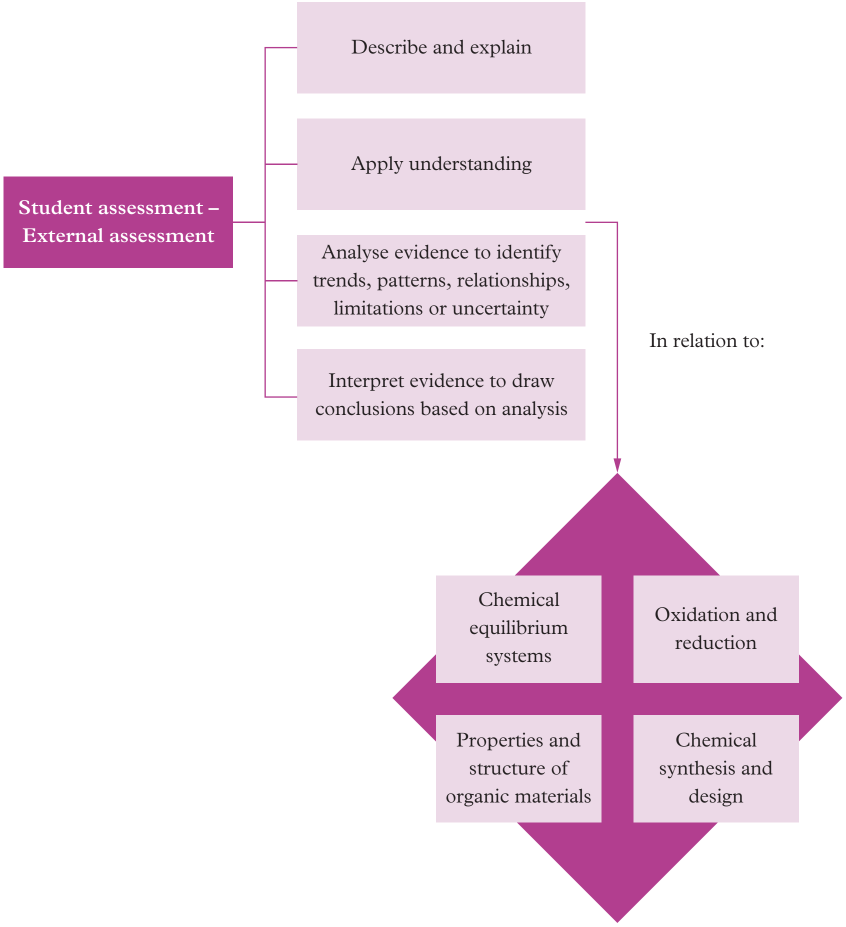


FIGURE 5 The objectives for the external assessment in Chemistry, used to determine student achievement

This textbook includes examples of all of these types of questions in the Check your learning problems and the chapter review problems. You will also find examples in online resources and the *Chemistry for Queensland Units 1 & 2* and *Units 3 & 4 Student workbooks*, so you should be confident that you have seen questions similar in format to those that may be asked. Practice exam style questions are also available for Unit 3 on page 212 and for Unit 4 on page 396. It would be a good idea to try practice examinations under conditions as close as possible to those of the actual examination.

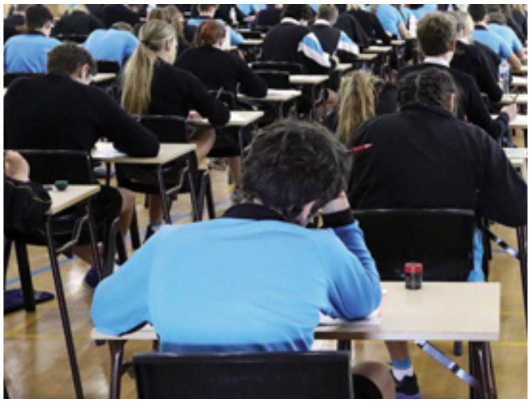


FIGURE 6 Completing your external exam can be stressful if you are underprepared.

Because the exam is marked externally, it is especially important that the meaning of your answers is clear and your writing is legible. Remember, marks can only be awarded for what is written on the examination paper, not what you may have intended to write. Rather than scribbling through part of an answer that you no longer want, simply rule a single line neatly through that section.

CHECK YOUR LEARNING 1.1

Describe and explain

1 **Describe** the required elements of the Research investigation task.

2 **Explain** the differences in the evidence that will be needed for the Student experiment and for the Research investigation.

Apply, analyse and interpret

3 **Analyse** the descriptions of each type of summative assessment in Units 3 and 4. **Predict** which aspect of each assessment will be most personally challenging and propose strategies to help meet these challenges.

Investigate, evaluate and communicate

4 **Investigate** what resources are available through your school library that relate to the properties or structure of organic materials or chemical synthesis and design. **Generate** a half-page summary of these resources.

5 Go to the online State Library of Queensland catalogue. Search for the most recent e-books in the digital library collection that relate to organic materials. **Evaluate** the titles and summaries provided to select three e-books that may be relevant to the Research investigation. Prepare an annotated bibliography that contains the basic citation information about the books (title, author or editor, publisher, place and date of publication) and a one- or two-sentence summary of what each book is about.

You can find the following resources for this section on your obook assess:

- Student book questions
  1.1 Check your learning
- Video
  The Data test
- Weblink
  QCAA syllabus

1.2 Student experiments

KEY IDEAS

In this section, you will learn about:

- the scientific method
- developing research questions
- drawing conclusions
- evaluating the validity of an experiment
- suggesting improvements for an experiment
- communicating your findings scientifically.

Study tip

Practice Student experiments can also be found for Units 1–3 in *Chemistry for Queensland Units 1 & 2 Student Workbook* and *Chemistry for Queensland Units 3 & 4 Student Workbook*.

In Chemistry Units 1–4, you are required to conduct your own experiment. This is an important part of the assessment, but it can also be a fun and interesting way to get more involved in chemistry. The goal of the Student experiment is to design an experiment in order to answer a research question. The methodology and research question of the experiment may be based on an existing practical, but it must be modified in some way.

Why might an experiment need modification?

- It may need to be *refined*, because the original technique or instrumentation was not precise enough. For example, instead of using colour-changing test strips to measure the amount of free chlorine in treated water, you could use a more precise titration method. The need for refinement may become clear after you look at the size of errors associated with measurements.
- It may need to be *extended* to allow for further investigations and to develop a greater understanding of the phenomena being studied. For example, if you observe a qualitative relationship between two variables, such as the relative humidity of air and the extent of corrosion of metal strips, then you may need to change the experimental method to find a quantitative relationship between the two variables.
- It may need to be *redirected*. For example, if you were investigating a hypothesis that higher nitrate levels in beetroot pickles increase metal leaching from metal tins, you may discover that the pH of the pickles and the concentration of citric acid have a much greater influence on the extent of metal leaching than the nitrate concentration. These would be examples of confounding variables that are only discovered after initial experiments.

Study tip

If you are having trouble finding an experiment to extend, redirect or refine, use a practical you have already completed in class and consider what could be improved.

The Student experiment involves the following steps.

1. Develop a research question.
2. Conduct background research for relevant scientific research that might help to modify the experiment.
3. Conduct a risk assessment for the modified experiment.
4. Conduct the experiment.
5. Collect qualitative and/or quantitative data.
6. Process and present the data.
7. Analyse the evidence.
8. Draw a conclusion.
9. Evaluate the validity of the experiment.

10 Suggest improvements to the experiment.
11 Communicate your findings scientifically (e.g. in a scientific report, poster or presentation).

You can do some of these steps in groups, such as developing a research question, conducting a risk assessment and conducting the experiment. However, it is important that you draw conclusions, evaluate the process and communicate your findings individually.

To conduct the Student experiment, you must have an understanding of the scientific method.

The scientific method

Scientists use the **scientific method** as an approach to problem-solving. It involves a series of steps that can be used to test hypotheses. The steps involved in the scientific method might not always be completed in order. For example, it might be necessary to repeat a test or to refine the experimental design to solve a problem or to correct a mistake.

The scientific method involves a series of steps to test a hypothesis (Figure 1).

scientific method the systematic exploration of a phenomenon or topic, using observation, measurement and experiment to support, disprove or modify hypotheses

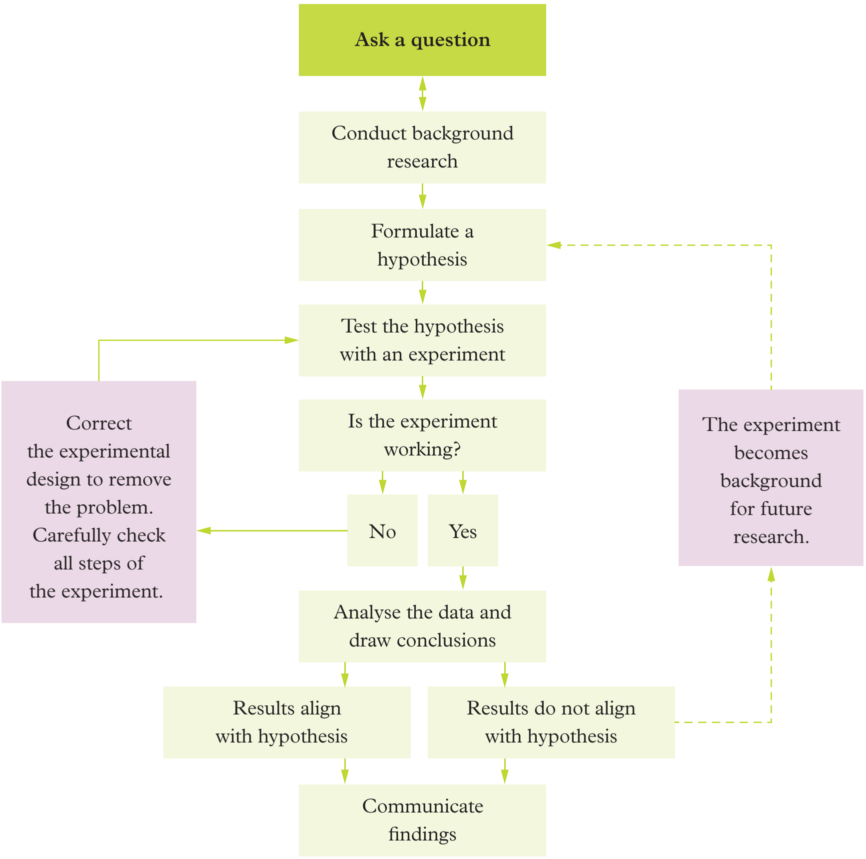


FIGURE 1 The scientific method

Developing a research question

The research question is the basis of the Student experiment and gives the research a focus, or clearer aim. Without a research question, it would be much harder to know what to test, and what data to collect.

research question a clear question that gives the research an aim or focus

Typically, a **research question** should contain a variable that can be changed in the experiment (such as temperature, time or volume) and a variable that can be measured.

For example, ‘How does temperature affect the rate of the chemical reaction between substance A and substance B?’.

In this example, the independent variable is temperature and the dependent variable is the rate of chemical reaction.

When developing a research question, remember the following.

- Is the question testable? You must be able to answer the question by using the scientific method to test the hypothesis.
- What is reasonably achievable? Time limits and resources can restrict what you can achieve. It is easy to underestimate how long experiments might take and to try looking at too many variables. It is important that you know what equipment is available in the school laboratory, because there is no point in planning experiments that rely on a piece of equipment that is not available. However, that doesn’t mean to give up! There is usually more than one way to conduct an experiment.

When planning an experiment, think about what type of measurements you will need to make. What equipment is available to make those measurements (Table 1)? Is your question sufficiently focused? If your research question can be answered with a simple ‘yes’ or ‘no’, then it is probably too narrow. If your question is too broad, you will not have enough time to answer it.

TABLE 1 Methods and equipment for making measurements

Quantity to be measured	Some suggested methods or equipment
Mass	Balance – pan balance or analytical balance? How many decimal places are required?
Temperature	Thermometer or digital temperature probe
Enthalpy change	Coffee can calorimeter, pan containing ice
Solution concentration	Titration with a suitable indicator, e.g. acid–base titration UV–visible spectrometer or colorimeter if light-absorbing Conductivity meter if solution of an ionic compound or electrolyte Gravimetry – selective formation of a precipitate and measurement of mass of filtered solid
pH	Indicator paper of pH test strips, or pH probe

FIGURE 2 High-precision laboratory scales measure small quantities of mass.

> The mere formulation of a problem is often far more essential than its solution, which may be merely a matter of mathematical or experimental skill. To raise new questions, new possibilities, to regard old problems from a new angle, requires creative imagination and marks real advances in science.
>
> Albert Einstein

Conducting a risk assessment

It is important to assess the risk involved in the planned experiment to ensure that everyone is safe and that no harm will come to anyone involved.

You must conduct a **risk assessment** before beginning the experiment. A risk assessment evaluates the materials, equipment and methods to be used in the experiment.

risk assessment a systematic evaluation of the potential risks and their likelihood when doing an experiment or activity

The aim is to identify any possible hazards and control or remove them from the experiment design if possible, or to reduce the risk to acceptable levels. Chemistry involves learning how to handle potentially dangerous materials safely, which means being aware and planning for what can go wrong.

All chemicals in Australia are supplied with a Material Safety Data sheet (MSDS). This contains information about the chemical, and guidance on how to use it and store it safely, and any known hazards to people or the environment.

When planning, think about what will happen to any chemicals after the experiment is finished. Some chemicals can safely be disposed of down the sink, dissolved in plenty of water. Other chemicals must be put in waste containers that are specially collected and disposed of.

A template to help conduct the risk assessment is available on the obook assess. Five key steps are involved in making a risk assessment.

1. Identify the potential hazards.
2. Determine who could be harmed and in what way.
3. Assess the risks and the action required. Decide how likely is it that a particular hazard could result in harm.
4. Record the risk assessment. This may be in your lab book or in a special folder or on a website.
5. Keep the risk assessment up to date if any changes are required. If the experiment is changed in any way or new information becomes available about a hazard, then you need to reconsider the risk assessment.

Collecting scientific evidence

Collecting evidence during the experimental process is a crucial part of the Student experiment. Presenting and analysing evidence, making conclusions and communicating findings all depend on keeping a detailed record.

Keeping a logbook

It is a good idea to keep a logbook to record key information throughout the experimental process, such as observations and measurements.

A bound book makes a good logbook, so that pages do not go missing. Another option is to keep an electronic version of a logbook; however, it is important that you back it up and that it can be authenticated.

Poor record-keeping can mean that you have to repeat experiments, which wastes time and materials. It could also result in distorted or incorrect findings and ultimately you may not be able to answer the research question accurately. Professional scientists keep a record of their experiments in a laboratory notebook. For a chemist, a record of an experiment should contain enough detail so that another chemist can understand what the experiment is about and repeat it if necessary.

Make your entries in the laboratory notebook as you carry out the experiment because it is too easy to forget things that may be important later.

In your logbook, you should record:

- the date
- equipment or instruments used
- the procedure that was followed
- amounts of any chemicals used (in grams or millilitres). Chemists also use the mole for amount, which is explained later in this textbook
- observations or results. You may enter these into a spreadsheet or data processing program for analysis, but printed copies of graphs and tables produced should also go into your logbook
- any other key points it may be important to remember while writing your report.

Make sure that you always write numbers followed by a space and then their associated units (with the exception of percentages).

For example, what do the following numbers refer to?

'Iron oxide (12.0) was added to the aluminium powder (4.0) and the mixture was ignited behind a safety screen.'

Does '12.0' refer to 12 g, 12 kg, 12 tonnes or something else? Without the units, it is impossible to be sure.

Drawing conclusions

Once you have conducted an experiment and collected and analysed the data, the final critical step is to draw conclusions about the meaning of the results. Students often neglect this step, perhaps because they have been thinking about the results so carefully that they may regard the conclusions as obvious. The success or failure of an experiment does not depend on whether a hypothesis was accepted or rejected, as long as the results are valid.

An experiment fails if there are flaws in the design or the reasoning that means it is not possible to draw definitive conclusions.

It is useful to break down this process into three components.

1. What is my conclusion?
2. What evidence am I relying on for this conclusion?
3. What is my argument or reasoning process to reach this conclusion?

Evaluating the validity of the experiment

The basic question to be asked here is 'What confidence can be placed in the result?'. An experiment always involves some compromise, because there are limits on the time or availability of materials, instruments or equipment. There may have been flaws in the research method because the effect being investigated was too small to be reliably measured or detected with the existing experimental design. There could also be other variables influencing the experiment that were not controlled. Was the experiment suitable to answer the questions proposed? Did the experiment test what it was meant to test?

This means evaluating the equipment, the experimental method, the adequacy of the results and the analysis of the results, including any calculations or statistical tests used.

For example, if you conducted an experiment to measure the rate of a reaction, as indicated by a colour change, the validity of the experiment could be affected by whether you use a clock or a stopwatch to measure time. A clock measures time to the nearest second and a stopwatch measures time to the nearest hundredth of a second. If you conducted an acid–base titration using an indicator that changed colour two pH units away from the pH at the equivalence point, how would this change your confidence in the results?

FIGURE 3 A stopwatch can be used to measure time to the nearest hundreth of a second.

Suggest improvements to the experiment

Sometimes an experiment does not go entirely to plan. Sometimes, during the experiment, a better way of testing might reveal itself. It is important that you note these ideas for improvement so that you can discuss them when it is time to communicate your findings and ideas. The conclusions that you draw may also form the basis for a new hypothesis or suggest a new research direction.

The experimental report

Experimental reports need to be both concise and precise. Table 2 lists the standard format of the report.

TABLE 2 Standard components of an experimental report

Title	A clear statement outlining the problem to be investigated. This is followed by the student's name and date of submission.
Abstract	A short summary of the findings.
Introduction	The introduction has several sections: • a short explanation of reason for and development of the research question • findings of previous studies (library research) • reasons for the method used • a hypothesis predicting the outcomes of the investigation (dependent variable) with change of the independent variable(s), the sample used, the conditions of the experiment, and the time frame.
Equipment list	A list of equipment used, including the brands and concentrations.
Safety audit	A list of all possible hazards and the measures taken to ensure safety. Ask your teacher for chemical Material Safety Data Sheets (MSDSs).
Method	An account of the activities that have been done in the investigation. It should be succinct, precise and with a logical order for apparatus set-up and activities performed in the experiment. Where appropriate, a diagram or photograph of the equipment set-up is included. The method is usually written as a concise list of instructions. It must be written in such a manner that another scientist could easily and exactly repeat the experiment.
Results	Qualitative or quantitative and presented clearly in a form or forms best suited to the results. The forms may be a verbal description, tables of data, graphs, photographs or any other suitable form. Any mathematical analyses of data should be included.
Discussion	A brief account that may answer the question posed by the hypothesis. It should not be a repeat of the results, but should be a genuine attempt to state and relate the theoretical aspects of knowledge with the experimental variables of the obtained results. It should include: • analysis of the data to support or reject the hypothesis, or show that it is inconclusive • a paragraph critiquing the methodology (the validity and reliability of the data, any possible variables that could not be controlled, and other relevant observations) • possible improvements, along with suggestions for future hypotheses or experimental ideas.
Conclusion	A short statement of the findings of the investigation that is related to the hypothesis.
Bibliography	An alphabetical list of all references used in the report.

CHECK YOUR LEARNING 1.2

Describe and explain

1 **Explain** the difference between refining and redirecting an experimental investigation.

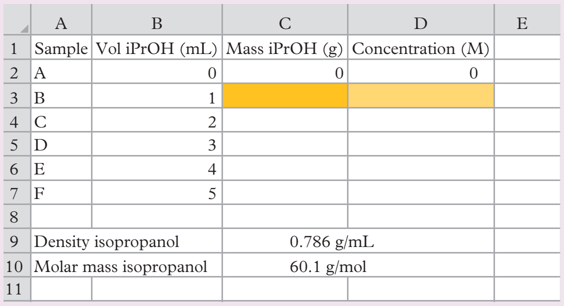
2 **Describe** the steps required in an experiment conducted according to the scientific method.

Apply, analyse and interpret

3 A student has collected data on the vapour pressure of an organic solvent at temperatures between 25°C and 50°C, in order to create a plot of natural log (vapour pressure) vs 1/temperature (in kelvin). The student decides that they need to have a greater spread of *x*-values for their graph, but only has time for one extra measurement. In their report, the student states: 'An extra measurement was made at 0°C, rather than 75°C because this increased the *x*-axis range to a greater extent'. **Analyse** the information given to come to a conclusion about whether this decision was correct.

4 A student prepares a series of aqueous isopropanol solutions by placing a set volume of isopropanol into a 10 mL volumetric flask and then adding water almost to the mark, mixing carefully, then adding water up to the mark. They start to fill in a spreadsheet to **calculate** the concentration of isopropanol in each of the solutions, as shown in Figure 4.

Analyse the spreadsheet. What formulas should be placed in C3 and D3 (highlighted) and then applied downwards to calculate the remainder of the concentrations?



	A	B	C	D	E
1	Sample	Vol iPrOH (mL)	Mass iPrOH (g)	Concentration (M)	
2	A	0	0	0	
3	B	1			
4	C	2			
5	D	3			
6	E	4			
7	F	5			
8					
9	Density isopropanol		0.786 g/mL		
10	Molar mass isopropanol		60.1 g/mol		
11					

FIGURE 4 The student's partially completed spreadsheet of experimental calculations

Investigate, evaluate and communicate

5 The reaction between sodium thiosulfate and sodium hypochlorite solutions is exothermic, resulting in an increase in the temperature of the reaction solution after mixing. **Investigate** an experimental method that could be used to determine the concentration of a sodium thiosulfate solution by reaction with a known amount of sodium hypochlorite. Make a list of equipment that would be required to complete the experiment.

6 **Investigate** how the calcium carbonate concentration of egg shells could be determined by a gravimetric method. **Communicate** the search strategy and steps used to find relevant information.

FIGURE 5 Calcium carbonate can be found in egg shells.

You can find the following resources for this section on your obook assess:

- » Student book questions
  1.2 Check your learning
- » Increase your knowledge
  Inserting formulas into MS Excel
- » Video
  Core experimental skills
- » Video
  The Student experiment

1.3

Research investigations

KEY IDEAS

In this section, you will learn about:

- clarifying the task
- beginning the task
- research techniques
- interpreting the data and evaluating the claim.

Study tip

Practice Research investigations can also be found for Units 1–4 in *Chemistry for Queensland Units 1 & 2 Student Workbook* and *Chemistry for Queensland Units 3 & 4 Student Workbook.*

In Chemistry Units 1–4, you are required to conduct your own Research investigation. This is an important part of the assessment, but it can also be a great way to learn more about chemistry in action. In the Research investigation, the goal is to modify or redesign an experiment in order to answer a hypothesis or question.

There are a number of steps involved in the Research investigation.

1. Select a claim to be evaluated.
2. Identify the relevant scientific concepts associated with the claim.
3. Pose a research question addressing an aspect of the claim.
4. Conduct research to gather scientific evidence that may be used to address the research question and subsequently evaluate the claim.
5. Analyse the data to identify sufficient and relevant evidence.
6. Identify the trends, patterns or relationships in the evidence.
7. Analyse the evidence to identify limitations.
8. Interpret the evidence to construct justified scientific arguments.
9. Interpret the evidence to form a justified conclusion to the research question.
10. Discuss the quality of the evidence.
11. Evaluate the claim by extrapolating the findings of the research question to the claim.
12. Suggest improvements and extensions to the investigation.
13. Communicate findings in an appropriate scientific genre (e.g. report, journal article, essay, conference presentation).

FIGURE 1 One method of presenting your Research investigation is a 9–11-minute presentation.

As with the Student experiment, it is important that you have an understanding of the scientific method. Developing research questions, analysing evidence, drawing conclusions and evaluating the validity of an experiment are all crucial skills for the Research investigation. These skills were explained in section 1.2.

Beginning the task

Your teacher should provide you with a number of claims, from which you can develop a possible research question.

Before you start your Research investigation, you may need to do a quick overview of the subject. Then you can draw up more detailed questions and a research plan.

Analyse the description of the task

Identify the key words in the claim you are evaluating. These can be the starting point to search for information.

Also relevant is how much time you have to answer the question. A one-paragraph answer required within 10 minutes has very different requirements from a 10-page report required within 6 weeks.

For example, suppose that you have been hired by the Brussels Sprouts Marketing Board to investigate claims made about the ideal level of glucosinolates in brussels sprouts. The research question might then become: 'What is the ideal level of glucosinolates in brussels sprouts?'

From the sound of the word 'glucosinolate', you might reasonably suspect that it is the name of a type of chemical. 'Glucose' is the name of a familiar chemical, so it is likely that glucosinolates are related in some way to glucose.

The words 'ideal level' suggest that the idea of amount or concentration will also come up in answering this question. The question also implies that the amount of this chemical can vary.

Start brainstorming and think about what background questions need to be answered. For example:

- What is a glucosinolate?
- What is the structure of these compounds (i.e. how are the atoms arranged and connected together)?
- Are these naturally occurring chemicals or synthetic (i.e. made in a laboratory)?
- How can these chemicals be detected and their amount measured?
- Is it possible to separate and purify them?
- Are they found in sources other than brussels sprouts?
- What effect do glucosinolates have? Are they toxic? If they are toxic, at what level? How stable are they? Are they water-soluble? What compounds are they made from in brussels sprouts?
- What is known about what affects the levels of these chemicals?
- Has anyone made these compounds in a laboratory?
- Can you buy these chemicals?

These are initial questions only, to act as a guide for further research. Some of them may not be relevant if you are only being asked to put together a written report. Some will only be relevant if you need to carry out laboratory research to discover new information to answer the questions.

Conducting research

Think about the sources of information to use to answer this question. There is a great deal of chemical information on the internet, and in libraries, textbooks, encyclopaedias and specialised chemistry books and databases. The problem becomes knowing where to look to find the most reliable information.

Search engines

If you type 'glucosinolate' into a search engine, you will quickly find information from Wikipedia about glucosinolates, including a chemical structure of the class of compounds.

This is only a starting point for further research. Wikipedia and other general sites can be very useful for getting a quick overview of a topic. But use them with caution – anyone can edit a Wikipedia page, whether they are an expert in the area or not. So, verify any information from sites such as this by checking a reputable source.

Books

Some scientific information is published in books and encyclopaedias. These can provide a good overview or summary about what is known, or you can look up a particular fact from a source known to be reputable. However, books are not usually as up to date as online sources.

Check that the information is still current and correct. How old is the source that you are using? Are there likely to have been recent developments?

Databases and collections

Chemical information is often collected into databases or collections of information, usually in the form of brief tables of data. There are several compilations of chemical data on different compounds and materials, which contain information such as melting and boiling points, densities and solubilities.

The *Merck Index* and the *CRC Handbook of Chemistry and Physics* are examples of these types of collections of data. Increasingly, this information can also be found in online versions of books or on scientific websites. For example, ChemSpider is a free resource put together by the Royal Society of Chemistry (UK) that covers about 71 million compounds (Figure 2).

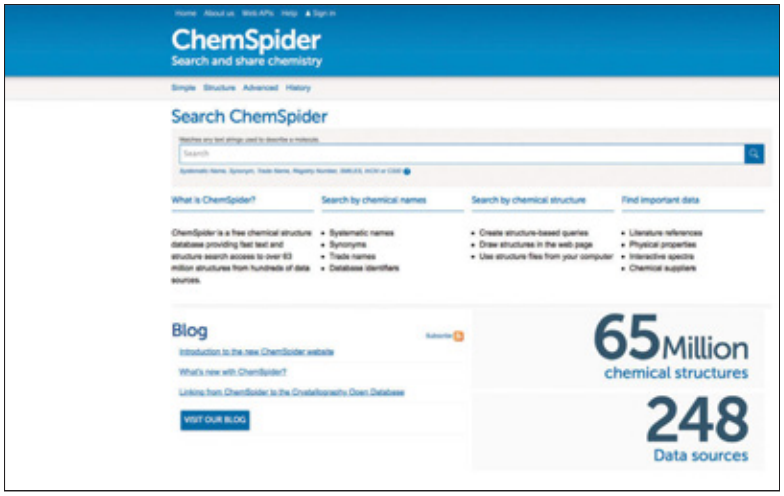


FIGURE 2 There is a link to the ChemSpider website on your obook assess.

Information about household chemicals and products can be found at a website put together by the US government, called the Household Products Database. Manufacturers who sell chemical products in Australia are required to supply a Material Safety Data Sheet (MSDS) with their product. Many suppliers of chemicals have online catalogues that contain basic information on the chemicals that they sell.

Journals

Most scientific knowledge is published in scientific journals. These are collections of articles written by researchers on particular topics, collected and published at regular intervals.

You will find the newest research reported in journals, and the best place to start is Google Scholar. Often journals will specialise in a particular area, such as the *Australian Journal of Chemistry*. Other scientific journals publish articles from all areas of science, including the very prestigious journals *Nature* and *Science*. One disadvantage of scientific articles is that they are written for an expert technical audience who usually already knows a great deal about the area being discussed. The articles may be written in very dense, technical language with many abbreviations. Students often make the mistake of using material from articles that they do not fully understand.

Open-source or open-access journals are accessible to the general public, but most journals require readers to pay a subscription or be a member of a library that subscribes. It can be frustrating to find a reference to an article that looks very relevant to your research question only to find that you need to pay to view the article.

The following points may help.

abstract
a summary of the most important findings of a research article

- Research articles often include a summary of the article at the start, called an **abstract**, which may contain all the information that you require. The abstract is usually free to view.
- Your school library may have an arrangement with a university library that gives school students access to more resources. Ask your teacher or school librarian about this; if you live close to a university, you may be able to visit the library on campus.
- When searching in an online research articles database such as Scopus or Science Direct, you can limit search results to those found only in open-access journals.
- The State Library of Queensland also has online resources for high-school students, as well as physical books and copies of journals.

When looking at a reference source, whether online or in print, be sure to ask whether it is a

FIGURE 3 Check that information obtained from a quick internet search is from a credible source.

trustworthy source of information. Who has written or gathered the information? How current is the information? Is it consistent with other sources of information? Are there references to other sources that the author has relied on? For what purpose was the article written?

Evaluating claims

When evaluating claims in a piece of scientific writing, the following points may be useful.

1. Identify the claim.
2. List the evidence being used to support the claim. This evidence must be a fact or measurement. Where the evidence being relied on is work of other scientists, is the work attributed to an identified scientific source, such as a particular book, an article in a scientific journal or a particular scientist or group? An opinion does not count as experimental evidence.
3. Evaluate the evidence. Is the evidence empirical; that is, is it based on observation and measurement? What is the source of the evidence? Are there any reasons why the evidence may be biased? For example, who funded the research? Is the evidence provided internally consistent or does it contain contradictions?
4. Evaluate the claim. Should the claim be accepted or should it be rejected? Is there a need for more evidence, better evidence or a better explanation of how the conclusions were reached?

In particular, do not confuse correlation with causation. Just because two variables are shown to be related does not necessarily mean that one causes the other.

Suppose that the relationship between amount of pocket money received per week and whether students at a secondary school study Chemistry was investigated and the results were graphed (Figure 4). From the graph, it could be concluded that giving secondary school students more pocket money causes them to be more interested in chemistry. (Perhaps they are spending the extra money on chemistry books!) A more likely explanation is that because Chemistry is studied in the later years of secondary school, Chemistry students are older and older children often receive more pocket money.

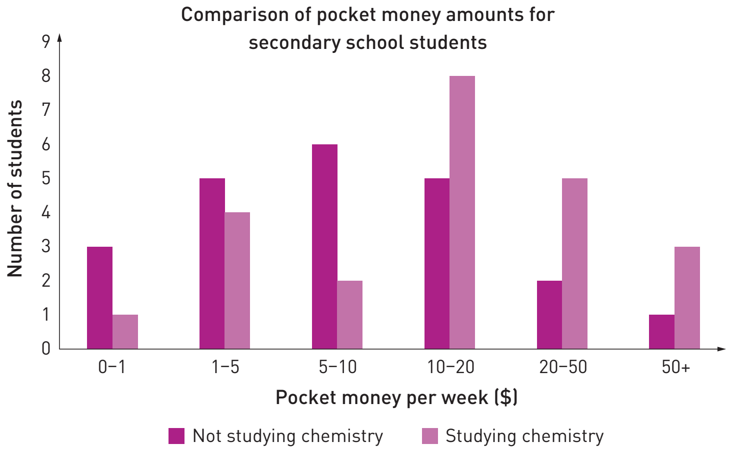


FIGURE 4 A comparison of the amounts of pocket money paid to secondary school students who do and do not study Chemistry

Writing the report

Write up the findings of the investigation scientifically at the end of the process.

A scientific report or essay should have:

- an introduction paragraph that explains what the report is about
- a background paragraph that gives the context to the essay and helps give the reader the necessary knowledge required to understand the rest of the essay
- a body of the essay covering the main arguments, with each main idea appearing in a separate paragraph.
- Possible paragraphs could be the:
  - claim being evaluated
  - statement of evidence that supports or disproves the claim
  - argument as to how the evidence supports the statement.
- a conclusion that summarises what has been said and stresses the most important points to the reader
- a bibliography or reference list so that the reader can follow up the sources that have been relied on in the essay.

Tips for writing scientifically

The following tips will help you write scientifically.

- Use shorter sentences and words where possible. This will make your meaning clearer and argument easier to follow. When there are many subordinate clauses, each winding around a meaning lost somewhere in a muddle of obscurantism and verbosity, included to make the author seem more clever and important, this often instead results in the reader becoming lost, in a maze of impenetrable text, when the sentence really needs to be split up into shorter, more digestible sentences in order to facilitate comprehension of the written text. How hard was the preceding sentence to read?

  Instead, keep it short, keep it simple.

  Poor: 'The aim of the present study by the author was to provide insight into …'

  Better: 'The aim of the experiment was to …'

FIGURE 5 You should write up the findings of your investigation.

- Use the first person 'I' or 'We' sparingly. This may be the opposite of the advice of many books on writing, but scientific writing, especially in chemistry, avoids the first person.
- If you are reporting experiments, then use the past tense because it is a report of work that you have already carried out. Often instructions to experiments are given in the present tense, but a lab report reports what was done; for example, 'The liquid was heated to 78°C, with the temperature measured using a thermometer'.
- When discussing analysis of data, use the present tense; for example, 'The mean of the results in Table 2 is 0.85 $mg\,L^{-1}$, which overestimates the actual concentration of Zn^{2+} by 23%'.
- It is never possible to prove a fact definitively. For this reason, chemists talk about evidence being consistent with a hypothesis, rather than proving the hypothesis. It is possible that results may show that a particular hypothesis should be rejected. If so, it is fine to say that.
- In referring to work done by others, there are a few verbs that are commonly used. These include 'claimed', 'suggested' and 'demonstrated' (in order of increasing confidence by the writer in what has been written).
- When using a key term or an unusual abbreviation for the first time, provide a definition. Some common abbreviations do not require an explanation, such as e.g., i.e., et al., ca. and etc. Use them correctly.
- Don't be vague. For example, do not use 'particle' when you mean 'atom'. If there is a specific chemical or scientific term, then use it.
- Always report numbers with their associated units. Consider using either scientific notation for very small or very large numbers or a unit with an appropriate prefix. For example, 0.000045 grams is better written as 4.5×10^{-5} g or 45 μg.
- Pictures, graphs, equations, chemical structures and reactions can all play an important part in communicating meaning in a scientific essay. These should be referred to in the main part of the text by their particular number; for example, 'Absorbance values levelled off after 5.8 ppm, as shown in Figure 1', 'The balanced reaction of calcium carbonate and sulfuric acid is shown in Reaction (8).'
- Use references to indicate in an essay where you are relying on the work of others. Your teacher will advise you on the precise format. One method is to put the surname of the authors and the year of the publication in brackets; for example (Smith and Jones, 2019). Another method is to include the reference as a superscript at the end of the relevant sentence or phrase. The full citation, including the authors and the details needed to find the reference, are included in a references section or bibliography at the end of the essay. There are various free online and downloadable tools to help you keep track of references and to create a properly formatted bibliography (e.g. Zotero, Citation Machine). However, even though these tools will do much of the work, you still need to check the end result and proofread it, particularly when it comes to consistency in references.

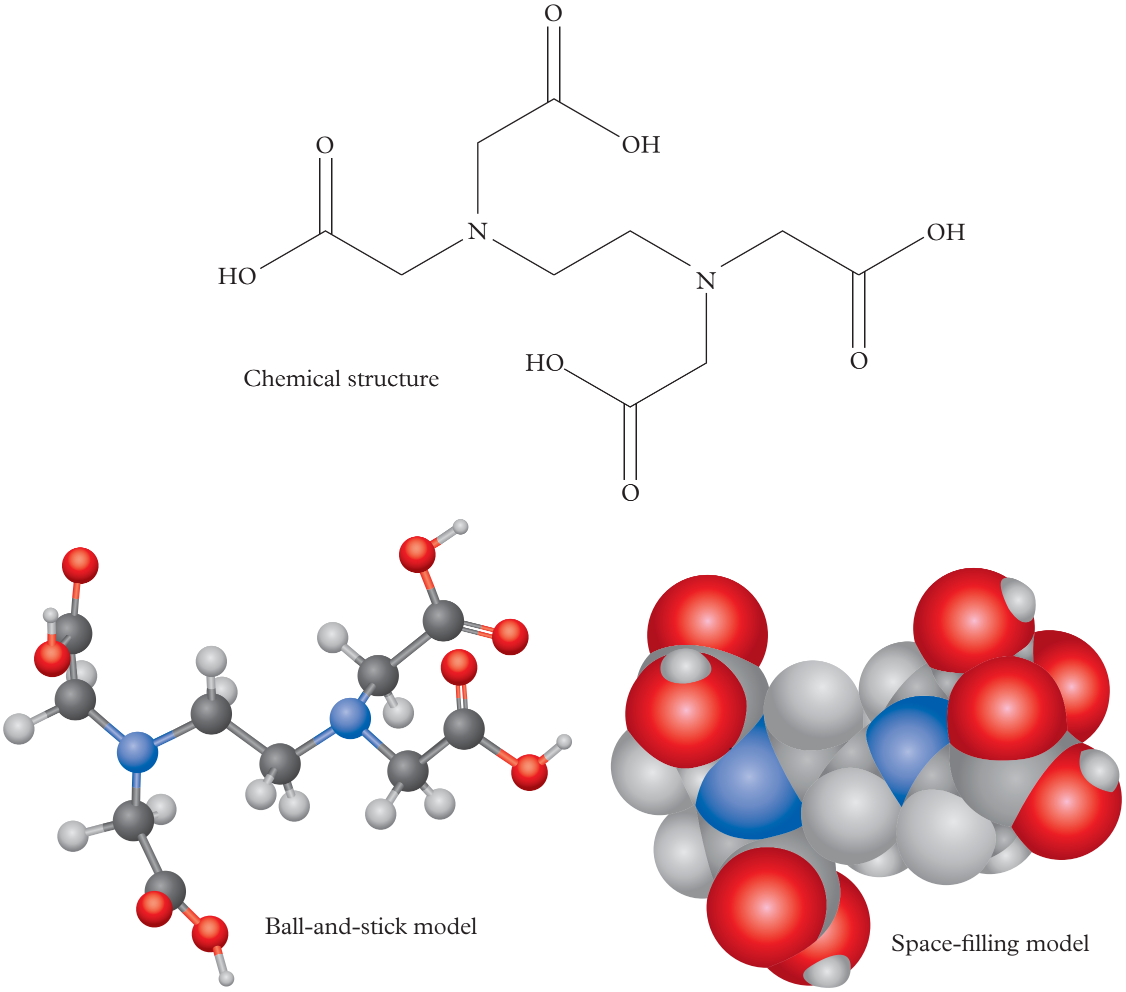
Drawing chemical structures

You are expected to communicate your findings in an appropriate scientific genre, such as a report, a journal article, an essay or a conference presentation. As part of that communication, you will need to present chemical structures. Sometimes it is tempting to use structures that are found by an image search on the internet. However, they may not stress the key features that need to be emphasised and can often appear fuzzy when reproduced. This will also be plagiarism, unless you acknowledge the source of the images. (It is possible to plagiarise images, as well as words and ideas.)

There are a number of free software tools for drawing chemical structures, which will make the presentation more professional. Part of the proofreading of the assignment is checking that any chemical structures you have drawn are correct. Make sure that you show the correct chemical structures and that they are chemically correct. Especially, watch out for carbon atoms with more than four bonds! Make sure that ionic charges are shown correctly if required. Think carefully about whether there are ways to highlight particular parts of structures that the reader should pay particular attention to, such as the use of colour or boxes around particular areas.

There may be a particular type of chemical representation that is more easily understood than another. For example, should you use a picture of a chemical structure, a ball and stick model, a space-filling model, or all of them (Figure 6)? The answer will depend on the particular aspect of the structure you want to emphasise.

You can enter equations and formulas into a document using an equation editor. For example, in Microsoft Word, choose the Insert tab, then Equation. There are also add-ons for programs, such as MathType, that make it easier to enter equations and give more control over the format of equations and calculations.



Chemical structure

Ball-and-stick model

Space-filling model

FIGURE 6 Representations of ethylenediaminetetraacetic acid, a chemical used to bind to metal ions and reduce water hardness. The chemical structure, ball-and-stick model and space-filling model can be used to emphasise different features.

If you are going to use a scientific poster to communicate your research findings, then you can create it in Microsoft PowerPoint or a similar program. In Microsoft PowerPoint, go to the Design tab and select Slide size and then Custom and enter the required dimensions of the poster. You can also find templates online to assist with the design and layout of a poster. Common mistakes with posters are to make the font too small to read from a reasonable distance (e.g. 1 metre) and to rely too much on text to explain the research, rather than a balanced mix of text and figures. Additional support on how to make a poster can be found in the *Chemistry for Queensland Units 1 & 2* and *Units 3 & 4 Student workbooks*.

CHECK YOUR LEARNING 1.3

Describe and explain

1 **Describe** how scientific writing differs in style from other kinds of writing.

2 **Explain** the purpose of a list of references at the end of a scientific report or essay.

Apply, analyse and interpret

3 **Compare** the advantages and disadvantages of books and websites as information sources in a chemistry Research investigation.

4 Using the ChemSpider website, **analyse** the experimental melting points reported for benzaldehyde and decide which is the correct value.

Investigate, evaluate and communicate

5 **Investigate** a free chemical structure drawing tool, such as MarvinSketch. Use it to draw the structure of retinol (vitamin A_1). Highlight the hydroxy group (OH) in a different colour from the rest of the molecule. Label other key features of the structure and create a document in a word processor that contains the image and a suitable figure caption.

6 Find two chemistry conference posters online. **Evaluate** and compare the two posters and conclude which is better presented.

FIGURE 7 Books can be a chemistry information source.

You can find the following resources for this section on your obook assess:

- » Student book questions
  1.3 Check your learning
- » Video
  The Research investigation
- » Weblink
  ChemSpider
- » Weblink
  Google Scholar

1.4

Exam preparation

KEY IDEAS

In this section, you will learn about:

- exam revision
- examination strategies.

Even though the external exam happens at the end of Unit 4, it is important to develop good study and revision techniques from the start of studying Chemistry. Cognitive psychology is an area of science that investigates learning and learning strategies. Research in this area suggests that some revision strategies work better than others. For example, a regular revision and testing program is better at helping students to learn new concepts than simply highlighting or rewriting notes. The goal is to adopt strategies that are proven to aid in both understanding and recall.

Be strategic about your learning. In class or while reading a textbook, think about what details are essential to know and which are added for purposes of explanation or interest.

Some things are worthwhile memorising because they make the rest of learning chemistry more efficient and easier. Psychologists have found that we can only keep a limited amount of information in our working memory – at the front of our awareness. When learning new information, the working memory can easily become overloaded and learning can become less efficient or even stop. For example, learning the symbol for sodium (Na) and its location in the periodic table is useful because you will use this information throughout high-school Chemistry and beyond. This means one less thing that you have to bring into active recall, and you can devote your attention to other parts of a question. It is not useful to memorise the average atomic mass of sodium to six decimal places (22.989 769 g mol^{-1}) because you will be provided with this information if needed. The process of internal thinking about learning is called metacognition and is a key characteristic of the best students, who self-assess whether they really understand something.

Time management

During the busy senior years of high school, you will have many competing demands on your time, not just from your other subjects, but also from family, personal, social and employment. Time management has the goal of using the time available most efficiently for the best outcomes. Average students should spend 3 hours of personal study time each week for each subject being studied.

A study timetable is useful for making sure that you spend sufficient time on your subjects across the week and have time for other activities. There are some key factors to guide the planning of a study timetable.

- Shorter, more frequent study sessions result in better learning and recall. Cramming for tests may be initially effective, but results in very poor long-term recall. External examinations in Chemistry at the end of Unit 4 will assume knowledge from throughout Senior Chemistry.
- Memory fades with time, so it is important to devote some time to refreshing earlier material. The more you bring particular information and knowledge into active recall, the easier it becomes to bring it into active recall at a later date.

TABLE 1 A sample study timetable

Time	Monday	Tuesday	Wednesday	Thursday	Friday	Saturday	Sunday
6.00–7.00 am	Check all set homework completed	Instrument practice		Instrument practice		Run	
Breakfast Travel Classes Travel	Study class 50 min – Physics		Study class 50 min – Biology	Study class 50 min – Maths	Study class 50 min – Chemistry	8.00–8.20 am Instrument practice 9.00–10.30 am Lawn mowing 11.00 am – 1.00 pm Assignments, lab reports and essays 2.00–2.30 pm German 3.00–3.30 pm Chemistry	
4.00–4.30 pm	German	Chemistry	Maths	Concert rehearsal	Work		Cook dinner
4.30–5.00 pm	Chemistry	Biology	English				
5:00 – 5.30 pm	Maths	Physics	Chemistry	Physics			
5.30–6.30 pm	Dinner	Dinner	Dinner	Dinner			
7.00–8.00 pm	English	German	Physics	English			
8.15–9.15 pm	Biology	Maths	German	Biology			

- Time you devote to self-testing and answering practice questions is more beneficial than time you spend highlighting or rewriting notes.
- Think when in the day you are most alert – morning, late afternoon or early evening. Make sure you get enough sleep: teenagers should get 8–10 hours per day, based on a review of over 300 studies. Too much screen time from phones, televisions or other devices in the evening can disrupt sleep patterns. Additionally, a 20-minute nap can help revive you if you are tired.
- The time you spend studying should be free from potential distractions such as social media, phones or a distracting environment.
- Break up study sessions with short breaks to stretch and refocus. Set a timer if you know you get easily distracted and will delay getting back to study.
- Try to review your classes the day after they are held. The break will give you a better indication of what you need to review.

An example of a weekly timetable is shown in Table 1. Include any study periods at school.

Table 2 lists six learning strategies that should be helpful for effective learning in Chemistry.

There is some evidence that certain popular study methods are not effective, such as highlighting and underlining and rereading materials. This may be because they don't require a lot of effort and are not effective in creating conditions that help long-term recall.

TABLE 2 Learning strategies

Strategy	Description	Application example	Why it is thought to help
Spaced practice	Spreading study schedule over time, rather than in one concentrated block	Choose times to study and restudy key concepts (such as Lewis structures) on multiple occasions before an exam, rather than cramming the night before. Create palm card sets on topics from earlier in the term or semester and revise them on a regular basis.	Allows consolidation of long-term memories and aids recall.
Interleaving	Switching between topics while studying	After doing problems on ionic bonding for a few minutes, switch to dipole–dipole interactions and hydrogen bonding.	Gives practice in identifying relevant information and selecting a solution strategy. Encourages greater use of long-term memory strategies.
Retrieval practice	Recalling previously learnt information from long-term memory on repeated occasions	Test yourself on what you can recall about solubility.	Testing by using long-term memory is thought to make accessing and recalling the information easier, by making the information more mentally organised. Also gives feedback on what areas need to be worked on.
Elaboration	Asking questions and explaining why or how things work that way	Ask and explain why ethanol is soluble in all proportions in water, but pentanol is much less soluble.	Being prompted to create an explanation for a stated fact supports the integration of new information with what is already known.
Concrete examples	Illustrating abstract concepts with specific examples	Compare the location of the nucleus and electrons in an atom to a pea in the middle of an oval.	Students can create memorable examples that are personally relevant.
Use of images (dual coding)	Combining words with pictures or diagrams	Draw structures of polyatomic ions given their formulas.	This can enhance mental organisation, improve understanding of information in a text form and help recall. Chemistry tests often involve diagrams and images.

Exam revision

Do not leave your exam revision to the last minute. Ideally, you should start revising when you first encounter a topic, revisiting the ideas and content being from time to time to keep them fresh. If you do this, then the immediate lead-up to an exam should not be stressful because you have already done the work and only need to revise the summaries that you have already been prepared.

Key factors to achieving this are organisation, planning and a commitment to your work over the whole of the year. By spreading the revision process over the whole of the year, you can break it down into smaller, more manageable units and the process of studying becomes less stressful. It is also more efficient because you do not need to relearn material in a rush at the end of the year.

You need to complete all your learning well before the examination period. You can do this by reviewing small sections of the material at regular intervals. There is a variety of study methods that aid learning. Study methods that do not work as well include rereading and highlighting notes.

In Chemistry, you are often assessed on what you are can do with your knowledge. So, it is important to attempt a variety of question styles and formats, not just your favourite type, such as multiple-choice or calculation questions. Also, don't mistake reading through the worked solution to a question with doing the question for yourself. If you do get stuck and need to refer to the worked solution, make a note to return to that question after a few days and work through it yourself. Or find similar questions, so that you can check that you have mastered that particular type of question.

For your study to be effective, avoid learning wrong information in the first place because this will be hard to unlearn. If you are unclear about any topic, clarify it with your teacher as soon as possible.

Be honest about the quality and the quantity of your study. A study session that is interrupted by bouts of social media or video gaming is not as productive as one focused entirely on the topic.

Be aware of getting into a loop of negative thinking. Some people convince themselves that they can't do Chemistry even before they have really tried. Persistence will pay off and it may

FIGURE 1 During the exam, read the questions and make a mental note of which questions to answer first.

be helpful to remind yourself of the eventual rewards from time to time. Learning Chemistry is a cumulative process that gets easier with time as you integrate new concepts into what you have already learnt.

Pay close attention to any feedback from your teachers and the results of formative quizzes and tests. The best students use this feedback to improve. Understanding where you may have gone wrong and how to fix it is potentially more valuable than knowing what you are doing right and don't need help with.

Exam techniques

Get a good night's sleep before the exam. Make sure that you arrive at the exam in plenty of time, with all the required equipment, including an adequate supply of pens, pencils and highlighters, an eraser and a ruler. A ruler is essential if you are asked to draw a graph and is also very useful for making sure that answers to multiple-choice questions are lined up properly on the answer sheet. Just before the examination, keep yourself calm and relaxed. Last-minute reading of notes is often not useful because there is usually only poor retention of the material. If you notice something at the last minute, it will probably only increase any stress you feel.

FIGURE 2 Make sure you bring all the required equipment to your exam.

During the exam

Examinations start with a perusal time. Use this time to read questions and make a mental note of which questions to answer first. Rules may vary about whether you can write during this time. If you are allowed to write on a rough piece of paper, make notes to yourself about the approach to use to solve problems.

Make sure that you have read and answered every part of each question. It is surprising how many times students answer a different question from the one actually asked on the examination paper. Plan your time according to the number of marks available for questions and sections of the paper, but remember to leave sufficient time to review and check your answers.

Multiple-choice questions

Many students prefer multiple-choice questions to written-response questions because they know that the correct answer must be included. Even if you are only partially familiar with an area, you might be able to recognise the correct answer. The major disadvantage is that no part marks are possible.

Multiple-choice questions are used to assess a variety of types of knowledge. Some questions rely on being able to recall basic content knowledge; for example, definitions of terms such as 'atom efficiency' or 'molecular ion'. Other questions ask you to apply knowledge, by analysing and interpreting some data. Such questions require that you have a detailed knowledge of the whole of a topic.

Multiple-choice questions are structured around the stem or body of the question. The answer is selected from four possibilities. The incorrect answers, or distractors, are often chosen from common misconceptions or mistakes that students make, so that they are likely to appear correct to at least some students. A useful technique when using multiple-choice questions for revision is to choose the correct answer and then also predict which would be the most common incorrect answer. This gives practice in avoiding common pitfalls and misconceptions.

Multiple-choice questions can vary in format. Often, an answer is selected to complete a given statement, but other types of questions may involve selecting the correct answer to a chemical calculation, or predicting the product formed from given reagents, or interpreting a graph or a chemical structure.

Sometimes a question may ask you to choose the incorrect answer (i.e. a statement that is wrong or false). Be careful here because students often do not read the question carefully, and incorrectly select a true statement rather than correctly selecting the false statement. Questions of this type have the word '**not**' bolded to help you recognise them.

Remember to check all of the answers and eliminate any answers that are obviously wrong. There is usually at least one answer that can be quickly eliminated, increasing your chances of choosing the correct answer.

Make sure you read all of the answer options. There is evidence to show that students are more likely to choose a wrong answer if the correct answer appears last or second last. This is because they have not read the question carefully enough. It is also sometimes possible to work backwards from the answers to double-check your answer.

Make sure that you answer every multiple-choice question.

External examinations are performed under a time limit, so it is important that you maximise the number of marks you obtain from the multiple-choice section, for the time available. That means that if you do not know the answers to any multiple-choice questions, it may be best to leave those questions and return to them later. Do not spend too much time on a multiple-choice question if there are more marks to be gained elsewhere in the examination.

Short-answer questions

Short-answer questions consist of an introduction and stimulus material. This may be a statement, a picture of a molecular structure, a reaction equation or a graph. The question follows, with cues about how it should be answered. The space provided for the answer indicates how much you should write. If you write significantly more than the space provided, then you are spending too much time on the question. A question with one line provided for an answer does not need an answer of many paragraphs.

Make sure that you fully answer every part of the question. For multi-part questions, it can be useful to underline the parts of the question that require an answer.

Devote time to questions in proportion to the number of marks available. Generally, each mark for a question indicates the number of things required to answer that question fully, so a five-mark question is likely to require five elements for full marks to be awarded.

As long as your answer is correct, the precise phrasing does not matter. But try and use the correct chemical terminology and know the key phrases related to a particular topic, so that a marker does not have to guess what you mean.

For example, consider the following example exam question on organic chemistry (studied in Unit 4):

> There are many industrially important compounds consisting of molecules with two carbon atoms and an additional functional group. A reaction equation to make one of these compounds is shown below:
>
> $$C_2H_4 + H_2O \rightarrow CH_3CH_2OH \text{ (acid catalysed)}$$
>
> **Describe** why the hydrocarbon reactant shown above is termed 'unsaturated'. (1 mark)

Note that the answer can only be awarded a maximum of one mark. This means that only a very short answer is required, possibly only one or two sentences.

There are several perfectly adequate, acceptable answers to this question.

- *C_2H_4 is the formula for ethene, which contains a double bond between the two carbon atoms. This means that there are fewer than the maximum possible number of hydrogen atoms for a two-carbon compound.*
- *Another two hydrogen atoms can be added to C_2H_4 to make the fully saturated C_2H_6, which has the maximum number of possible hydrogen atoms.*
- *C_2H_4 is an alkene and can undergo hydrogenation to form an alkane.*

Each of these answers shows clearly that the student understands that unsaturation refers to the number of hydrogens in a compound.

Poor answers would not make this clear.

- *C_2H_4 is an alkene.*

This statement is correct but hasn't shown an understanding of the concept of unsaturation, which is what the mark will be awarded for. This would likely receive only a half mark at most.

For questions involving calculations, there may be several correct methods to work out an answer. The reasoning process is important. Marks are often given to the working as well as the correct answer. Partial marks can often be given for working, even if a number has been written down incorrectly.

It is strongly recommended that you use dimensional analysis (e.g. Chapter 2 p. 63s) and include units in your working ('cancelling of units as you go') because this helps markers follow your reasoning process. You can still receive partial marks even if you make an error in working that is otherwise correct. It also makes it much easier for you to check the answer before the end of the exam. If your answer has incorrect units after cancelling, this indicates that there is an error in your working that needs to be fixed.

With calculations, you should always do a final check of your answer. Does the answer make sense? Has the answer been expressed in the units asked for in the question, or if no units were asked for, do they match the physical quantity? For example, an answer expressed in kPa, when the question asked for the volume of a gas must be incorrect.

Make sure that your final answer includes the correct number of significant figures. If you convert an answer to scientific notation, double check that you have used the correct exponent. A surprisingly common error is to miss a zero in a number when converting to scientific notation. Do not round intermediate answers in a multi-step calculation because this can introduce rounding errors. Only round the final answer.

For short-answer questions, you may be required to draw chemical structures or diagrams of experimental apparatus. If so, you should clearly show the required elements, with clear labels as appropriate.

In written responses, check that you have used the correct terms and that there are no contradictions in the answer. Check that you have answered all parts of the question.

FIGURE 3 Cross-checking your calculations is an important habit to get comfortable doing and something that all chemists practise.

Extended-response questions

Extended-response questions are often challenging because the precise scope of the answer is harder to define, and you could take a number of possible approaches. These types of questions test your ability to logically prepare and present an argument, supported by the use and weighing of relevant evidence and to come to a final judgement or conclusion.

Sketching out a brief plan of an essay response before starting to write your answer is a good use of time. Use your answer plan as a checklist so that you do not overlook key concepts and ideas in a rush to get your thoughts down on paper.

If you include diagrams, structures and reactions in your answer, put them underneath the writing on a separate line, instead of including them as part the main text. This makes them easier for a marker to locate.

Unless you don’t have enough time, structure your extended answer in paragraphs with a clear concluding paragraph.

Responding to cognitive verbs

In assessment tasks and examinations, you will encounter ‘cognitive verbs’. These verbs are ‘task words’ that indicate how to answer a question. A list of common cognitive verbs is included on your obook assess.

It is important to understand the difference between task words. For example, ‘compare’ is different from ‘contrast’. ‘Compare’ requires you to show similarities and differences, whereas ‘contrast’ only asks you to show the differences.

If you understand exactly what a cognitive verb is asking for, then you can provide exactly what the examiner is looking for. Examiners can only give students marks if they provide the correct information. For example, if a question asks you to analyse some data, you will not receive full marks if you only describe but do not analyse the data.

Table 3 is a list of cognitive verbs that you might encounter in your assessments.

TABLE 3 Cognitive verbs used in assessments

Cognitive verb	Definition	Sample question
Analyse	Dissect to ascertain and examine constituent parts and/or their relationships; break down or examine in order to identify the essential elements, features, components or structure; determine the logic and reasonableness of information Examine or consider something in order to explain and interpret it, for the purpose of finding meaning or relationships and identifying patterns, similarities and differences	**Analyse** the graph provided to identify the relationship between bond length and bond energy.
Apply	Use knowledge and understanding in response to a given situation or circumstance; carry out or use a procedure in a given or particular situation	**Apply** the Arrhenius definition of a base to show how $Ca(OH)_2$ qualifies as a base.
Calculate	Determine or find (e.g. a number, answer) by using mathematical processes; obtain a numerical answer showing the relevant stages in the working; ascertain/determine from given facts, figures or information	**Calculate** how many molecules are in 1 mole of hydrogen.
Consider	Think deliberately or carefully about something, typically before making a decision; take something into account when making a judgment; view attentively or scrutinise; reflect on	**Consider** how a plant's ability to absorb nutrients would be affected if lime (a base) was added to the soil.
Deduce	Reach a conclusion that is necessarily true, provided a given set of assumptions is true; arrive at, reach or draw a logical conclusion from reasoning and the information given	**Deduce** the relative stability of the reactant and product from the enthalpy level diagram.
Describe	Give an account (written or spoken) of a situation, event, pattern or process, or of the characteristics or features of something	**Describe** molar mass.
Determine	Establish, conclude or ascertain after consideration, observation, investigation or calculation; decide or come to a resolution	**Determine** the molar mass of a pure substance if 3.5 moles of the substance has a mass of 59.584 g.
Discuss	Examine by argument; sift the considerations for and against; debate; talk or write about a topic, including a range of arguments, factors or hypotheses; consider, taking into account different issues and ideas, points for and/or against, and supporting opinions or conclusions with evidence	The simple rules for solubility of salts in water state that some ionic compounds are 'slightly soluble'. **Discuss** this statement.
Evaluate	Make an appraisal by weighing up or assessing strengths, implications and limitations; make judgments about ideas, solutions or methods in relation to selected criteria; examine and determine the merit, value or significance of something, based on criteria	The optimum pH for water in a swimming pool is considered to be 7.4. A student claimed that this was a neutral pH. **Evaluate** this claim.
Explain	Make an idea or situation plain or clear by describing it in more detail or revealing relevant facts; give an account; provide additional information	**Explain** why it is impossible for the percentage yield to be 109%.
Identify	Distinguish; locate, recognise and name; establish or indicate who or what someone or something is; provide an answer from a number of possibilities; recognise and state a distinguishing factor or feature	**Identify** the range of values suggested by the measurement 10.3 ± 0.8 seconds.

Cognitive verb	Definition	Sample question
Justify	Give reasons or evidence to support an answer, response or conclusion; show or prove how an argument, statement or conclusion is right or reasonable	**Justify** why an absorption or emission spectrum is referred to as a fingerprint of an element.
Predict	Give an expected result of an upcoming action or event; suggest what may happen based on available information	An experiment found the density of nitrogen gas to be 1.2504 g L^{-1} at STP. **Predict** what would happen if the density of this gas was increased in a fixed volume container.
Propose	Put forward (e.g. a point of view, idea, argument, suggestion) for consideration or action	**Propose** a way to minimise the error caused by the vibrations of people walking past an electronic balance.

Source: *QCAA Chemistry General Senior Syllabus 2019*

CHECK YOUR LEARNING 1.4

Describe and explain

1 **Explain** why it is important to show clear working in the answers to calculation questions.

2 **Explain** why last-minute cramming is not an effective revision strategy for the external examination assessment in Chemistry.

Apply, analyse and interpret

3 The following examples of chemical equations contain mistakes often made by students in examinations (mostly due to nerves and lack of checking). **Analyse** each equation and explain the mistake that has been made.

a $2Fe(s) + O_2(g) + 4H_2O(l) \rightarrow 2Fe(OH)_2(s) + 2H_2O(l)$

b $C_9H_{20}(aq) + 14O_2(g) \rightarrow 9CO_2(g) + 10H_2O(aq)$

c $Br^- + 6OH^- + 2MnO_4^- + 8H^+ \rightarrow BrO_3^- + 2MnO_2 + 7H_2O$

d $2NO_2(g) \leftrightarrow N_2O_4(g)$

4 **Interpret** the data provided in the Chemistry data booklet to determine:

a the first row element that has the highest first ionisation enthalpy

b an estimate of the carbon–nitrogen bond enthalpy in acetonitrile (CH_3CN)

c a metal that is less reactive than gold

d how many of the common amino acids contain sulfur

e the colour of an aqueous solution at pH 5 containing bromothymol blue indicator

f the chemical formula of sodium thiosulfate.

Investigate, evaluate and communicate

5 **Consider** your strengths, weaknesses and preferences to come up with a flow chart that communicates in a concise way your preferred examination strategy for the Chemistry external examination papers.

6 Select three of the cognitive verbs that you find most difficult to understand or remember. Create a visually appealing poster that could be displayed on a classroom noticeboard to help **communicate** the meaning of these terms.

You can find the following resources for this section on your obook assess:

- » Student book questions
  1.4 Check your learning
- » Video
  How to prepare for your exam
- » Increase your knowledge
  Cognitive verbs
- » Increase your knowledge
  Study timetable template

CHAPTER 1

Review

Chapter summary

1.1
- There are three internal summative assessments in Units 3 and 4 – the Data test, Student experiment and Research investigation. There is also an external examination, made up of two 90-minute exam papers, consisting of a variety of question types.

1.2
- The scientific method is used as a basis for the Student experiment. This requires a research question and background research to modify or extend an experiment. A hypothesis should be written as a clear statement predicting how changes in the independent variable will affect the value of the dependent variable.

1.3
- Research investigations require students to develop a research question related to a particular claim. Students must then research the question, using credible sources to evaluate claims, draw conclusions and communicate findings scientifically.

1.4
- Preparation for the external examination requires planning, revision and commitment to study over an extended period. The examination will contain multiple-choice and short-answer questions, including calculations, and extended-response questions. A data booklet and graphics calculator are permitted.

Key terms

- abstract
- qualitative
- quantitative
- research question
- risk assessment
- scientific method
- secondary evidence

Revision questions

The relative difficulty of these questions is indicated by the number of starts beside each question number: ★ = low, ★★ = medium; ★★★ = high.

Multiple choice

1 Which of the following is **not** an internal assessment?

A Summative examination

B Research investigation

C Data test

D Student experiment

2 Which of the following is **not** a crucial part of a scientific report?

A References

B Method

C Research question

D Concept map

3 Which definition best describes the cognitive verb ‘**analyse**’?

A Dissect to ascertain and explain constituent parts and/or their relationships; break down or examine in order to identify the essential elements, features, components or structure; determine the logic and reasonableness of information

B Establish, conclude or ascertain after consideration, observation, investigation or calculation; decide or come to a resolution

C Reach a conclusion that is necessarily true, provided a given set of assumptions is true; arrive at, reach or draw a logical conclusion from reasoning and the information given

D Make an idea or situation plain or clear by describing it in more detail or revealing relevant facts; give an account; provide additional information

4 Which of the following best describes the cognitive verb ‘**discuss**’.

A Reach a conclusion that is necessarily true, provided a given set of assumptions is true; arrive at, reach or draw a logical conclusion from reasoning and the information given.

B Examine by argument; sift the considerations for and against; debate; talk or write about a topic, including a range of arguments, factors or hypotheses; consider, taking into account different issues and ideas, points for and/or against, and supporting opinions or conclusions with evidence.

C Put forward (e.g. a point of view, idea, argument, suggestion) for consideration or action.

D Give an expected result of an upcoming action or event; suggest what may happen based on available information.

5 Identify which of the following statements would be classified as an observation.

A Transition metal compounds are generally coloured due to incomplete filling of d-orbitals by electrons.

B Marble statues are prone to corrosion because industrial pollution creates chemicals that dissolve in rain and make it more acidic.

C Osmium is the element with the highest density.

D Production of biodegradable plastics will solve the problem of plastic pollution.

6 A very thin piece of gold foil has a thickness of 1.50 μm and a gold atom has a radius of 135 pm. ($1\ \mu m = 1 \times 10^{-6}$ m, $1\ pm = 1 \times 10^{-12}$ m).

Identify the answer that shows full and correct working to calculate the number of gold atoms across the thickness of the foil.

A

$$\text{Number of gold atoms} = \frac{1.5\ \mu\text{m}}{270\ \text{pm}} = 5556\ \text{atoms}$$

B

$$\text{Thickness of sheet} = 1.5\ \mu\text{m} \times \frac{1 \times 10^{-6}\ \text{m}}{1\ \mu\text{m}} = 1.50 \times 10^{-6}\ \text{m}$$

$$\text{Diameter Au atom} = 2 \times 135\ \text{pm} \times \frac{1 \times 10^{-12}\ \text{m}}{1\ \text{pm}} = 2.70 \times 10^{-10}\ \text{m}$$

$$\text{Number of gold atoms} = \frac{1.50 \times 10^{-6}\ \text{m}}{2.70 \times 10^{-10}\ \text{m}} = 5555.56\ \text{atoms} \approx 5600\ \text{atoms}$$

C

$$\text{Diameter Au atom} = 2 \times 135\ \text{pm} = 270 \times 10^{-12}\ \text{m}$$

$$\text{Thickness of foil} = 1.5\ \mu\text{m} = 1.5 \times 10^{-10}\ \text{m}$$

$$\text{Number of gold atoms} = \frac{1.5 \times 10^{-10}\ \text{m}}{2.70 \times 10^{-12}\ \text{m}} = 56\ \text{atoms}$$

D

$$\text{Radius Au atom} = 135\ \text{pm} \times \frac{1\ \text{m}}{1 \times 10^{12}\ \text{pm}} = 1.35 \times 10^{-10}\ \text{m}$$

$$\text{Thickness of foil} = 1.5\ \mu\text{m} \times \frac{1\ \text{m}}{1 \times 10^{6}\ \mu\text{m}} = 1.5 \times 10^{-6}\ \text{m}$$

$$\text{Number of Au atoms} = 2 \times \frac{1.5 \times 10^{-6}\ \text{m}}{1.35 \times 10^{-10}\ \text{m}} = 2.222 \times 10^{4}\ \text{atoms} \approx 2.2 \times 10^{4}\ \text{atoms}$$

7 Identify the statement about the summative assessment in Units 3 and 4 that is **not** correct.

A All steps of the Student experiment must be performed individually.

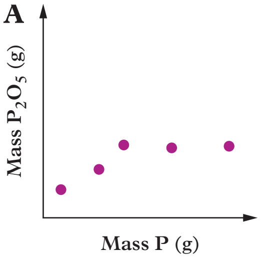
B Each external examination paper will have a time before the start of writing to read the exam questions.

C The Research investigation, if presented as a written report, should be no more than 2000 words long.

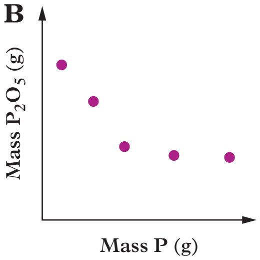
D The Data test will require the interpretation of up to four data sets.

8 Phosphorus reacts with oxygen to form phosphorus pentoxide (P_2O_5). A series of experiments was performed in which different amounts of phosphorus were reacted with a fixed mass of oxygen. Identify the graph that would best represent the masses of phosphorus pentoxide formed.

A



B



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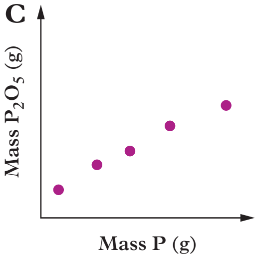

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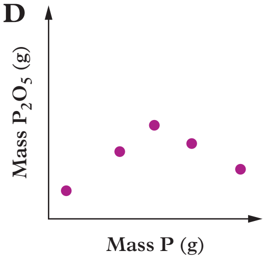


Short answer

Describe and explain

★★9 **Describe** how a 1 L volume of an aqueous magnesium nitrate solution of 1.00×10^{-5} mol L^{-1} concentration can be prepared, using a balance that can measure masses down to 0.01 g.

Apply, analyse and interpret

★10 **Consider** which topics you find interesting as these will be the best areas to investigate for your Research investigation.

★11 **Reflect** on which topics you find difficult prior to your examination so you can **derive** additional notes and a stronger understanding of these.

★12 **Consider** how managing your Chemistry workload affects your other subjects. **Construct** a study timetable that takes into account all your subjects for the year.

★★ **13** **Analyse** the following description of a process and identify each step as an observation, hypothesis, experiment or theory.

Oliver and Benjamin notice that the blueberry muffins that they have baked are not popular with the rest of their family. They undertake the following activities.

FIGURE 1 Blueberry muffins

a Benjamin notices that his family is concerned that the blueberries have turned an unappetising green colour.

b Oliver decides that something in the recipe is reacting with the blueberries to cause this colour change.

c Benjamin modifies the blueberry muffin recipe and makes four different batches – one without eggs, one without baking powder, one that adds a teaspoon of vinegar and one that uses fresh blueberries instead of frozen ones.

d The muffins are baked for equal amounts of time and a muffin from each batch is selected at random and cut in half.

e Benjamin compares the colour of the blueberries in each muffin and notes that the muffins made without baking powder or with added vinegar retain their purple-blue colour, whereas the blueberries in other muffin batches turn green.

f Oliver thinks that the sodium bicarbonate in the baking powder is reacting with the natural pigments in the blueberries to cause the colour change.

★★ **14** Graph the data in Table 1 for the amount of heat evolved during a reaction. **Analyse** the relationship between the amount of reactant and the heat evolved and state the nature of the relationship in words and in a mathematical relationship.

TABLE 1 Table of experimental data

Amount of reactant (mol)	Amount of heat evolved (kJ)
0.09536	26.32
0.07656	19.9
0.07256	18.46
0.06344	15.34
0.04736	9.82

★★ **15** A mixture of hexane (C_6H_{14}) and ethanal (CH_3CHO), with a mass of 8.50 g, is completely combusted in an excess of oxygen. The carbon dioxide formed is collected and found to have a mass of 21.46 g. **Calculate** the percentage by mass of ethanal in the mixture. Show all working.

Investigate, evaluate and communicate

★★★ **16** Acrolein is a starting material used in the manufacture of certain plastics. **Investigate** the resources available to find the following pieces of information. Look for both online and print resources where this information can be found.

a The structure of acrolein

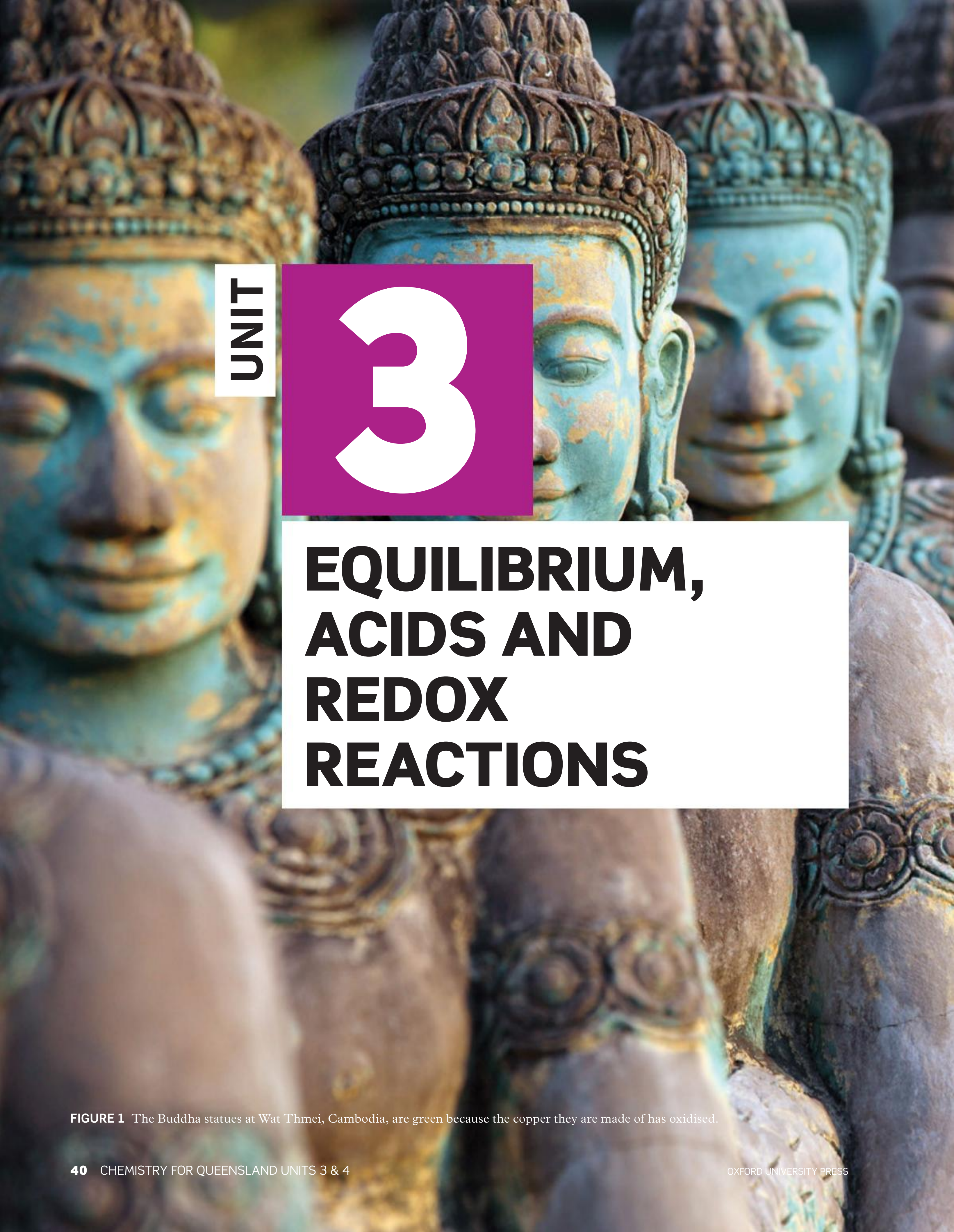
b The plastics made from acrolein

c A research article that looks at how acrolein can be synthesised

d Potential hazards of working with acrolein in the laboratory or in a factory.

You can find the following resources for this section on your obook assess:

- Student book questions
  Chapter 1 Revision questions
- Revision notes
  Chapter 1
- assess quiz
  Auto-correcting multiple-choice quiz
- Flashcard glossary
  Chapter 1



UNIT 3

EQUILIBRIUM, ACIDS AND REDOX REACTIONS

FIGURE 1 The Buddha statues at Wat Thmei, Cambodia, are green because the copper they are made of has oxidised.

Unit 3 Chemistry investigates the nature and processes involved in chemical reactions. These chemical reactions are typically based on the concept of equilibrium, which involves reversible reaction systems. Such reactions are the basis of acid and base reactions within the body, including the mechanism for maintaining a steady blood pH of 7.4. They are also involved in the generation of electricity in electrochemical cells or batteries. The process of electroplating (covering one material with more expensive and less corrosive metal), involves reversible reactions, which are non-spontaneous and require the input of electricity.

Various environmental processes also involve reversible reactions. Snow melts to water, which eventually evaporates into the air as water vapour. This water vapour condenses, forming rain and snow. Thus, the changing of states is also reversible.

Chapter guide

Topic 1	Chemical equilibrium systems	Chapters 2–7
Topic 2	Oxidation and reduction	Chapters 8–10

Unit objectives

- → Describe and explain chemical equilibrium systems and oxidation and reduction.
- → Apply understanding of chemical equilibrium systems and oxidation and reduction.
- → Analyse evidence about chemical equilibrium systems and oxidation and reduction.
- → Interpret evidence about chemical equilibrium systems and oxidation and reduction.
- → Investigate phenomena associated with chemical equilibrium systems and oxidation and reduction.
- → Evaluate processes, claims and conclusions about chemical equilibrium systems and oxidation and reduction.
- → Communicate understandings, findings, arguments and conclusions about chemical equilibrium systems and oxidation and reduction.

Source: *Chemistry 2019 v1.3 General Senior Syllabus*

CHAPTER 2

Equilibrium

Equilibrium reactions are some of the most important reactions that a chemist can use. These reactions occur in the human body, atmosphere and hydrosphere, and are used extensively in food chemistry and industrial chemistry.

Chemists must have a sound understanding of the factors affecting a chemical reaction and how to manipulate these factors to maximise the amount of desirable product from a reaction. The aim is to maximise the yield of a chemical reaction without losing or destroying any materials in the process.

A waste-water plant must utilise many chemical processes to remove the impurities from water and generate a cleaner product. The cleaner the water produced, the more money the water plant can make by selling it to consumers. Similarly, at a mining smelter, impurities in contaminated ore from the mine are removed by various chemical processes to maximise the yield of product (e.g. zinc or copper).

OBJECTIVES

→ Recognise that chemical systems may be open (allowing matter and energy to be exchanged with the surroundings) or closed (allow energy, but not matter, to be exchanged with the surroundings).

→ Understand that physical changes are usually reversible, whereas only some chemical reactions are reversible.

→ Appreciate that observable changes in chemical reactions and physical changes can be described and explained at an atomic and molecular level.

→ Symbolise equilibrium equations by using $\rightleftharpoons$ in balanced chemical equations.

→ Understand that, over time, physical changes and reversible chemical reactions reach a state of dynamic equilibrium in a closed system, with the relative concentrations of products and reactants defining the position of equilibrium.

→ Explain the reversibility of chemical reactions by considering the activation energies of the forward and reverse reactions.

→ Analyse experimental data, including constructing and using appropriate graphical representations of relative changes in the concentration of reactants and product against time, to identify the position of equilibrium.

→ Explain and predict the effect of temperature change on chemical systems at equilibrium by considering the enthalpy change for the forward and reverse reactions.

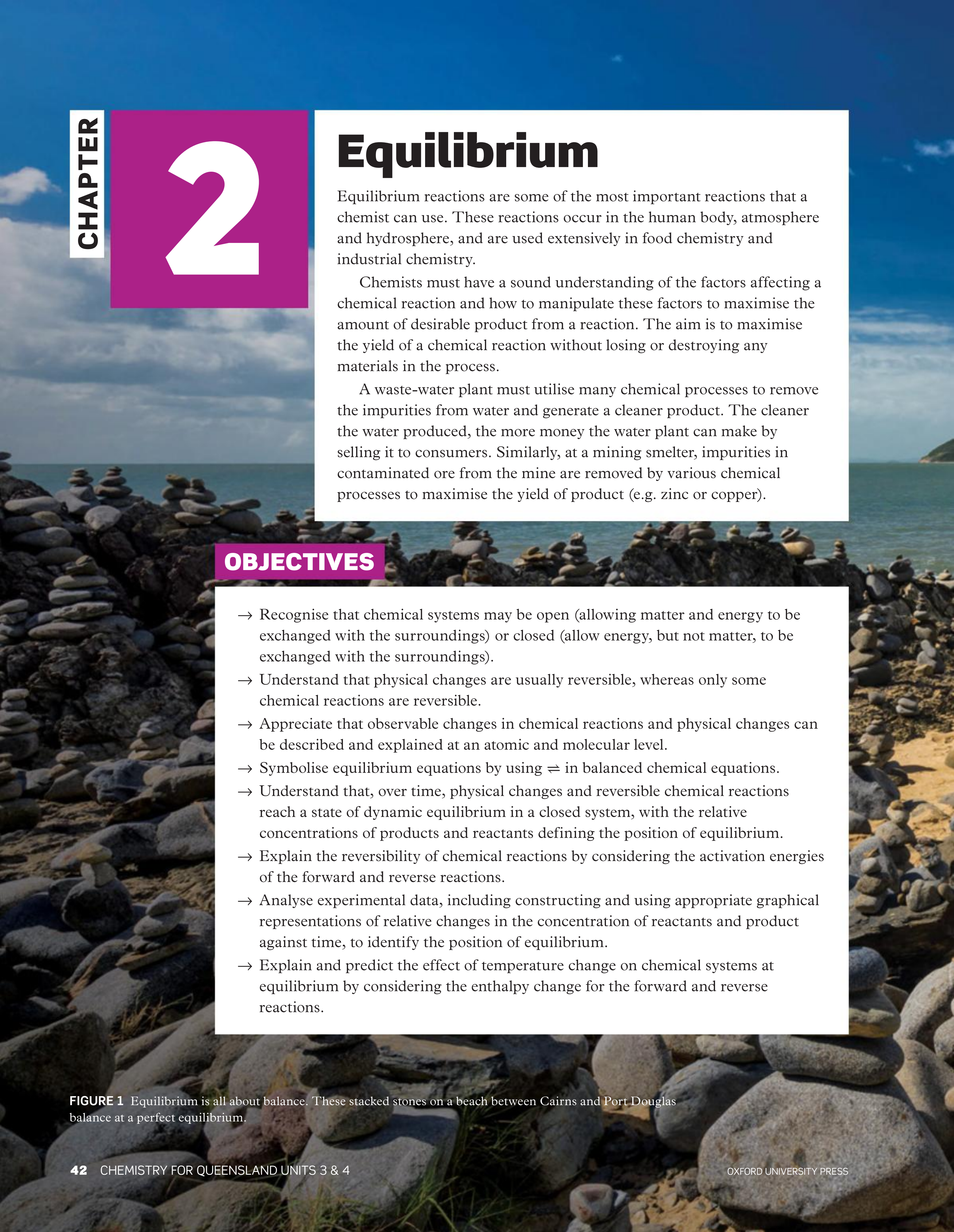
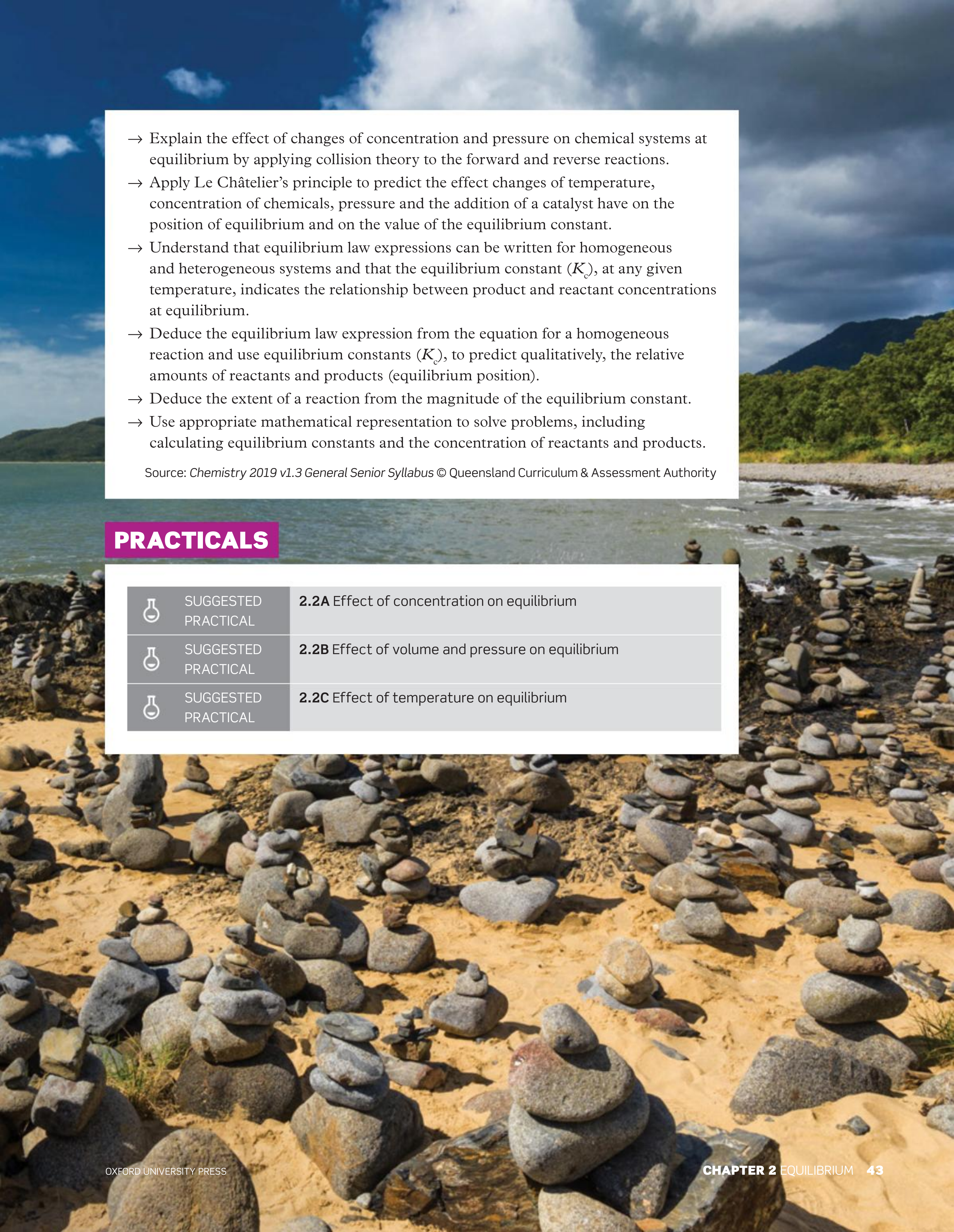


FIGURE 1 Equilibrium is all about balance. These stacked stones on a beach between Cairns and Port Douglas balance at a perfect equilibrium.



- → Explain the effect of changes of concentration and pressure on chemical systems at equilibrium by applying collision theory to the forward and reverse reactions.
- → Apply Le Châtelier's principle to predict the effect changes of temperature, concentration of chemicals, pressure and the addition of a catalyst have on the position of equilibrium and on the value of the equilibrium constant.
- → Understand that equilibrium law expressions can be written for homogeneous and heterogeneous systems and that the equilibrium constant (K_c), at any given temperature, indicates the relationship between product and reactant concentrations at equilibrium.
- → Deduce the equilibrium law expression from the equation for a homogeneous reaction and use equilibrium constants (K_c), to predict qualitatively, the relative amounts of reactants and products (equilibrium position).
- → Deduce the extent of a reaction from the magnitude of the equilibrium constant.
- → Use appropriate mathematical representation to solve problems, including calculating equilibrium constants and the concentration of reactants and products.

Source: *Chemistry 2019 v1.3 General Senior Syllabus* © Queensland Curriculum & Assessment Authority

PRACTICALS

SUGGESTED PRACTICAL	**2.2A** Effect of concentration on equilibrium
SUGGESTED PRACTICAL	**2.2B** Effect of volume and pressure on equilibrium
SUGGESTED PRACTICAL	**2.2C** Effect of temperature on equilibrium

2.1

Equilibrium systems

KEY IDEAS

In this section, you will learn about:

- how chemical reactions that can proceed both forwards and backwards become equilibrium reactions
- dynamic equilibrium
- energy profiles in equilibrium systems
- open and closed equilibrium systems.

Initially in a chemical reaction, there are only reactants. Energy is required to initiate the reaction. This energy is known as the activation energy. The smaller the activation energy, the more readily the reaction will form products. Over time, as the chemicals react, the concentrations of the reactants decrease and the concentrations of the products increase.

The products of some chemical reactions escape into the atmosphere. For example, a combustion reaction produces gaseous products that are often lost after they are formed. When ethanol reacts with oxygen, it combusts in a highly exothermic reaction to produce carbon dioxide and water vapour (a gas):

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

These gases are released into the atmosphere and are therefore no longer part of the reaction. The concentrations of ethanol and oxygen decrease as they react. However, the concentrations of the products do not increase because the products are being lost to the atmosphere. Therefore, the reaction continues in the forward direction to produce more products until there are no more reactants. This is an example of a complete chemical reaction, where no reactants are left.

However, some reaction systems do not lose products and can be contained within a reaction vessel. This means that they proceed both forwards and backwards, and at any one time there is a mixture of reactants and products.

FIGURE 1 Ethanol reacts with oxygen in a combustion reaction to produce carbon dioxide and water vapour.

Figure 2a shows the energy profile for an exothermic reaction. The activation energy for the reaction is 40 kJ. The enthalpy value is the difference between the energy of the products (20 kJ) and the energy of the reactants (40 kJ), and is –20 kJ. The change in enthalpy is negative because the total energy of the products is less than the reactants, and heat is released to the surroundings.

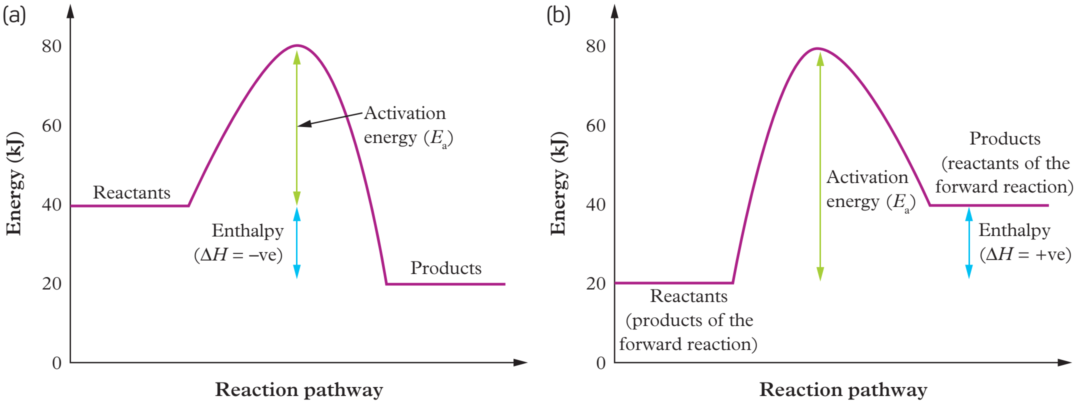


FIGURE 2 (a) An energy profile for an exothermic reaction. (b) The energy profile for the reverse endothermic reaction.

If this reaction were reversed, the products of the **forward reaction** now become the reactants of the **reverse reaction**. Therefore, the energy profile is reversed (Figure 2b). The reverse reaction has an **activation energy** of 60 kJ and an **enthalpy** of 20 kJ. The change in enthalpy is positive because the total energy of the products is greater than the reactants, and heat is absorbed from the surroundings.

Provided that the reaction has enough energy to overcome the activation energy for both the forward and reverse reactions, the reaction proceeds forwards and backwards, and equilibrium is maintained.

forward reaction
the reaction between reactants to form products

reverse reaction
the backwards reaction in which the products react to re-form the reactants

activation energy
the minimum amount of energy required in a collision for a reaction to occur

enthalpy
the energy stored within chemical substances, referred to as its chemical energy or heat content

Dynamic equilibrium

For systems at equilibrium, we represent the reactions proceeding both forwards and backwards with equilibrium arrows ⇌ rather than a forward reaction arrow →, which you would be more familiar with.

For example, weak acids only partially dissociate in water, and the reaction does not go to completion (where only products exist). Ethanoic (acetic) acid is an example of a weak acid that only partially dissociates in water:

$$CH_3COOH(aq) + H_2O(l) \rightleftharpoons CH_3COO^-(aq) + H_3O^+(aq)$$

At any given time, both reactants and products are present in the system. The reaction reaches a state of **dynamic equilibrium** when:

- the reaction is incomplete – it does not consist of only products
- bonds are being broken and re-formed constantly; particles never stop moving
- the rates of the forward and reverse reactions are equal (Figure 3).

dynamic equilibrium
the state a reaction reaches when the rates of the forward and reverse reactions are equal

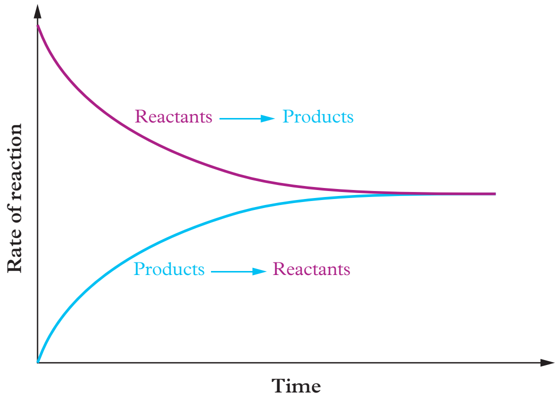


FIGURE 3 Dynamic equilibrium is reached when the rates of the forward and reverse reactions are equal.

Consider the synthesis reaction between nitrogen and hydrogen to form ammonia:

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

At dynamic equilibrium, nitrogen, hydrogen and ammonia are present in the reaction vessel, although not necessarily in equal concentrations. As the bonds in the nitrogen and hydrogen molecules are breaking, they are re-forming as ammonia. However, as ammonia is forming, its bonds are also breaking to re-form the nitrogen and hydrogen molecules. The rate of formation of ammonia at equilibrium is equal to the rate of formation of nitrogen and hydrogen.

Open and closed systems

open system
a reaction vessel that has no lid, meaning that reactants or products can be lost to the atmosphere

closed system
a reaction vessel that is closed off, or has a lid, meaning that no reactant or product particles can escape

Substances reach dynamic equilibrium when they undergo a physical change (i.e. they change state). Water in the open ocean is in an **open system** because the water that evaporates from the ocean surface is lost into the atmosphere. However, water in a sealed drink bottle is contained within a **closed system**.

Inside the water bottle, the energy of the molecules on the surface of the water is greater than the intermolecular hydrogen bonding attracting the molecules to one another. These surface molecules break free as a gas and reside in the air contained at the top of the bottle. Similarly, gaseous water molecules at the top of the bottle enter the liquid phase when they no longer have sufficient energy to overcome the hydrogen bonding in the liquid water. Alternatively, if the walls of the drink bottle are cooler than the liquid water, water droplets accumulate on the sides of the bottle, producing condensation (Figure 4).

On hot days, water evaporates more readily because the molecules have more energy and they can overcome the hydrogen bonding between water molecules in the liquid phase. This results in pressure building up in the bottle as more and more molecules enter the gas phase. This means that the gaseous side of the following equilibrium equation is favoured at higher temperatures because water enters the gas phase at high temperatures:

$$H_2O(l) \rightleftharpoons H_2O(g)$$

In an open system (i.e. a water bottle with the lid off), the gaseous water escapes into the atmosphere. Removing the product of the forward reaction means that less gaseous water is available to turn into liquid water within the bottle. Instead, the liquid water continues to form gaseous water, and the volume of water in the bottle gradually decreases.

FIGURE 4
Condensation accumulates on the sides of a closed water bottle.

Measurable and observable changes to reactions

It is very difficult to measure the concentration of a specific substance within a reaction unless you use volumetric analysis, chromatography or spectroscopy. Volumetric analysis and chromatography can only determine the concentration of a chemical at a specific moment in the reaction, not from the time it enters the system to the time it reaches equilibrium.

The two most common methods of measuring concentration in an equilibrium system rely on pH and observation.

pH

When an equilibrium reaction involves either an acid or a base, you can measure the change in **pH** to determine the concentration of the chemicals from the time they initially react until the time they reach equilibrium. Recall from *Chemistry for Queensland Units 1 & 2*, Chapter 17, that pH can be converted to the concentration of the hydronium ion in solution, using the following equations:

pH
a measure of hydrogen ion concentration in a solution and therefore a measure of the acidity or alkalinity of a solution

$$\mathrm{pH} = -\log_{10}[\mathrm{H}^+] \text{ and } [\mathrm{H}^+] = 10^{-\mathrm{pH}}$$

In the case of ethanoic acid (CH_3COOH), a weak acid:

$$CH_3COOH(aq) + H_2O(l) \rightleftharpoons CH_3COO^-(aq) + H_3O^+(aq)$$

you can measure the concentration of the H_3O^+ ion (also the H^+ ion) and then use simple stoichiometry to determine the concentration of all other chemicals in the reaction.

Observation

Colour can be used to indicate the extent of some reactions. Consider the reaction of iron(III) ions with thiocyanate ions to form the iron(III) thiocyanate ion. Initially, the iron(III) solution is yellow and the thiocyanate solution is clear. When the solutions are mixed, the iron(III) ions react with the thiocyanate ions producing iron(III) thiocyanate, which a deep blood-like red (Figure 5). The solution becomes darker red, indicating that the reaction has moved forward:

$$\underset{\text{yellow}}{Fe^{3+}(aq)} + SCN^-(aq) \rightleftharpoons \underset{\text{red}}{FeSCN^{2+}(aq)}$$

FIGURE 5 The addition of yellow iron(III) ions to thiocyanate ions produces the red iron(III) thiocyanate ions.

CASE STUDY 2.1

A discovery of equilibrium

The first scientist to propose that chemical reactions could proceed both forwards and backwards was French chemist Claude Berthollet in 1799–1800.

Berthollet assisted the French government during the French Revolution, developing a procedure for the production of gun powder and working to establish the metric system.

During this time, he gained the attention of Napoleon Bonaparte, who recruited him for an Egyptian campaign in 1798. There he observed that the concentration of the reactants in a system had a direct relationship with the concentration of the products formed, demonstrated by chemicals reacting in a molar ratio. This laid the foundation for the equilibrium law (see section 2.2).

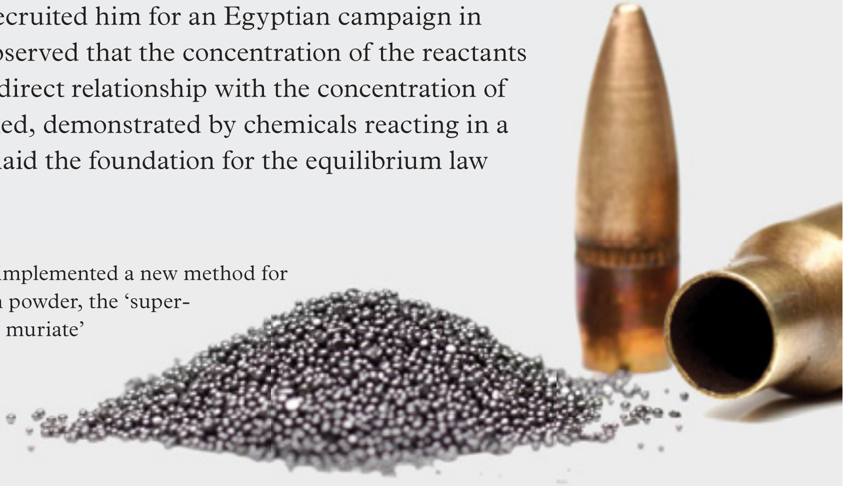


FIGURE 6 Berthollet implemented a new method for the preparation of gun powder, the 'super-oxygenated potassium muriate' method.

CHECK YOUR LEARNING 2.1

Describe and explain

1 **Define** 'dynamic equilibrium'.

2 **Explain** what is required for a reaction to reach dynamic equilibrium.

Apply, analyse and interpret

3 A container is built to allow nitrogen and hydrogen to react at 450°C in the presence of a catalyst. Unfortunately, the container has a defective seam and ruptures after 5 minutes. **Consider** how the number of molecules of ammonia, hydrogen and nitrogen compare to their original values.

4 With reference to dynamic equilibrium, **deduce** why wet clothes hanging on a clothes line on a hot day dry faster than wet clothes left in a washing basket on a cold day.

Investigate, evaluate and communicate

5 A student in your class claims that Earth is an open equilibrium system. **Evaluate** this claim and **communicate** whether you believe them to be correct. **Justify** your argument.

6 **Investigate** homogeneous and heterogeneous equilibria and **communicate** what these terms mean, giving an example of both.

You can find the following resources for this section on your obook assess:

- » Student book questions
  2.1 Check your learning
- » Weblink
  Open and closed systems
- » Weblink
  Claude Berthollet

SUGGESTED PRACTICAL

2.2A Effect of concentration on equilibrium
Go to your obook assess »

2.2

The effect of changes to equilibrium systems – Le Châtelier's principle

KEY IDEAS

In this section, you will learn about:

- Le Châtelier's principle, which can predict the effect of changes to an equilibrium system
- using graphs to represent changes to equilibrium systems.

Le Châtelier was a French chemist and engineer (Figure 1). He is best known for his work on equilibrium and the earliest (unsuccessful) attempts to synthesise ammonia from nitrogen and hydrogen before Haber met with success in the early 1900s. Le Châtelier laid the foundation for industrial chemistry because his theory explained how to optimise chemical yield. Chemical yield is the amount of desired product that is generated from a chemical reaction.

FIGURE 1 French chemist Henry Louis Le Châtelier (1850–1936) developed his principle, which predicts the effect of changes on a chemical equilibrium.

Le Châtelier's principle

Not all reactions reach completion. In equilibrium reactions, both reactants and products are present. An equilibrium reaction can be manipulated to push it forwards, increasing the concentrations of the products in a system, or backwards, increasing the concentrations of reactants.

Two factors that can change the equilibrium position of a reaction are **concentration** and **temperature**.

Le Châtelier developed a principle to predict the effect of these changes on a system at equilibrium. **Le Châtelier's principle** states: If an equilibrium system is subjected to a change, the system will adjust itself to partially oppose the effect of the change.

concentration
the amount of solute dissolved in a substance

temperature
a measure of the average kinetic energy of the particles within a system

Le Châtelier's principle
if an equilibrium system is subjected to a change, the system will adjust itself to partially oppose the effect of the change

pressure
the force exerted, per unit area, by one substance upon another substance

volume
a measure of the space occupied by a substance

Changes in concentration

Concentration is a measure of the number of particles in a given volume and can be changed by:

- adding or removing a reactant or product
- changing **pressure** and **volume**
- diluting aqueous solutions.

Adding or removing a reactant or product

When the concentration of a reactant or product is increased, the system *partially opposes* this change by moving to decrease this concentration. If the concentration of a reactant or product is decreased, the system *partially opposes* the change by moving to increase this concentration.

Short-answer questions about equilibrium and changes in concentration

When answering short-answer questions about equilibrium changes, you will have more success if you follow the structure outlined in Table 1. Start by stating what has happened, then how the system partially opposes the change and the effect of the equilibrium position. Note that the term 'partially opposes' is used in all answers. Also, when explaining the effect on the equilibrium position, it is only the 'net' effect because the system can never return to its original concentration.

TABLE 1 Structure for answering short-answer questions about equilibrium

Change (what has happened?)	Le Châtelier says (how does the system partially oppose the change?)	Effect (on equilibrium position)
When the reactant concentration is increased,	the system *partially opposes* the change by moving to the product side to decrease the reactant concentration,	resulting in a *net* forward reaction. →
When the product concentration is increased,	the system *partially opposes* the change by moving to the reactant side to decrease the product concentration,	resulting in a *net* backward reaction. ←
When the reactant concentration is decreased,	the system *partially opposes* the change by moving to the reactant side to increase the reactant concentration,	resulting in a *net* backward reaction. ←
When the product concentration is decreased,	the system *partially opposes* the change by moving to the product side to increase the product concentration,	resulting in a *net* forward reaction. →

Graphing

You can also represent changes to equilibrium systems graphically. Plot time on the x-axis and concentration on the y-axis. Worked examples 2.2A–F demonstrate this.

Study tip

When working through equilibrium questions, write the initial concentrations, change in concentrations and final equilibrium concentrations. This skill is discussed further on page 64 and can help you with complex equilibrium questions.

WORKED EXAMPLE 2.2A

A closed reaction vessel contains nitrogen (0.8 M), hydrogen (1.2 M) and ammonia (0.4 M) at equilibrium:

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

The concentration of hydrogen is increased by 0.5 M. At equilibrium, the concentration of hydrogen is 1.4 M. Determine and graph the effect of this increase in concentration on the equilibrium system.

SOLUTION

As the concentration of hydrogen is increased, the system will *partially oppose* this change by moving to the product side to decrease the concentration of hydrogen. Therefore, a net forward reaction results.

Notes on graphing

- At equilibrium, the lines are horizontal, indicating a constant concentration.
- After a certain amount of time, the concentration of hydrogen is increased by 0.5 M to 1.7 M and is represented as a vertical line, indicating it was increased suddenly.

- After the change, the concentration of hydrogen must decrease gradually (because there is a net forward reaction) until it reaches its concentration at equilibrium of 1.4 M. Note: 1.4 M is higher than the original concentration of 1.2 M. This is because, when the system opposes the change, it only partially opposes it. Therefore, the hydrogen concentration *cannot* decrease to 1.2 M or below it, because this would imply that the system had completely opposed the change.
- Because there is a net forward reaction, the concentration of nitrogen will also decrease, and the concentration of ammonia will increase.
- Because the chemicals react according to the molar ratio, the concentration changes must also follow the molar ratio. For example, any change that occurs to hydrogen is three times the change to nitrogen and 1.5 times the change to ammonia.
- When equilibrium is re-established, the lines on the graph must be horizontal again.

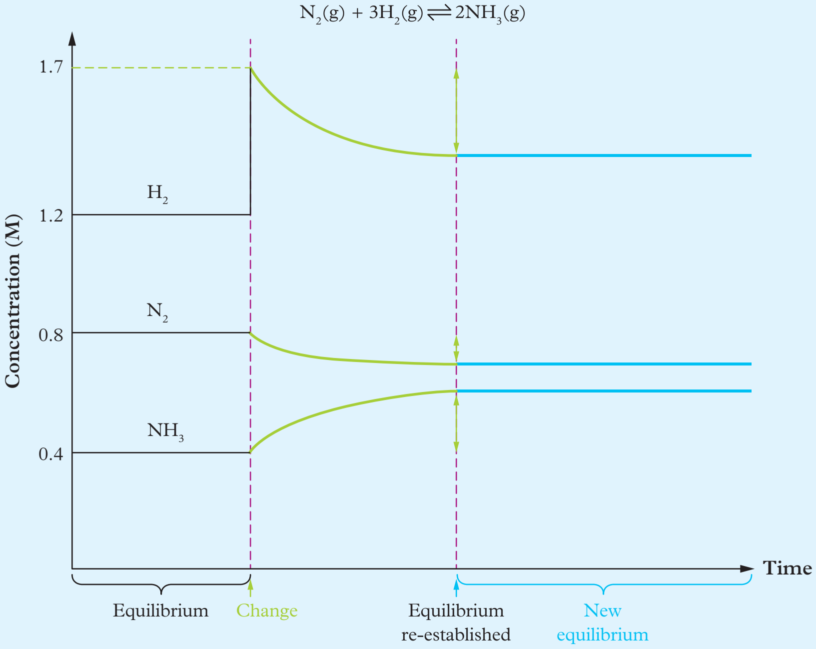


FIGURE 2 An equilibrium graph of the formation of ammonia

Pressure and volume in gaseous systems

Recall from *Chemistry for Queensland Units 1 & 2*, Chapter 14, that gases can exist in fixed-volume and variable-volume systems. According to Charles' law, in a variable-volume system, pressure and volume are inversely proportional. As the volume decreases, the pressure increases. This is because there are more collisions between the particles and the walls of the container because they are contained within a smaller space. Because the same number of particles are now contained within a smaller volume, the concentration of all particles, both reactant and product, increase.

In a fixed-volume system, volume cannot change and so any changes to pressure are not caused by changing the volume. Pressure in fixed-volume systems can be increased by adding a reactant or product, or by increasing temperature.

The addition of an inert (unreactive) gas, such as argon, can also increase the pressure of the system. However, this will have no effect on equilibrium because the inert gas does not cause any increase in the concentrations of reactants or products in the container. The same number of reactants and product molecules exist within the same volume of space, regardless of the increase in pressure caused by the inert gas. Therefore, the addition of an inert gas has no effect on a gaseous equilibrium system.

WORKED EXAMPLE 2.2B

At equilibrium, nitrogen dioxide has a concentration of 0.8 M and dinitrogen tetraoxide has a concentration of 0.3 M:

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

After some time, the volume of the system is doubled. When equilibrium is re-established, the concentration of nitrogen dioxide is 0.6 M. Determine and graph the effect of this decrease in volume on the equilibrium system.

SOLUTION

When the volume of the system is doubled, all concentrations decrease by half. The system partially opposes this change by moving to the side with more particles. Because there are two NO_2 molecules on the product side and only one N_2O_4 molecule on the reactant side, the product side has more molecules. This results in a net forward reaction.

Notes on graphing

- When the volume is doubled, the concentration of particles within the system is halved. At equilibrium, NO_2 has a concentration of 0.8 M, which is halved to 0.4 M, whereas N_2O_4 has a concentration of 0.3 M, which is halved to 0.15 M.
- All concentrations decrease sharply (halved), as indicated by the vertical lines, as the volume increases.
- After the change, $[NO_2]$ increases to 0.6 M. Because the chemicals are in a 2:1 ratio, $[N_2O_4]$ will decrease by half this amount.

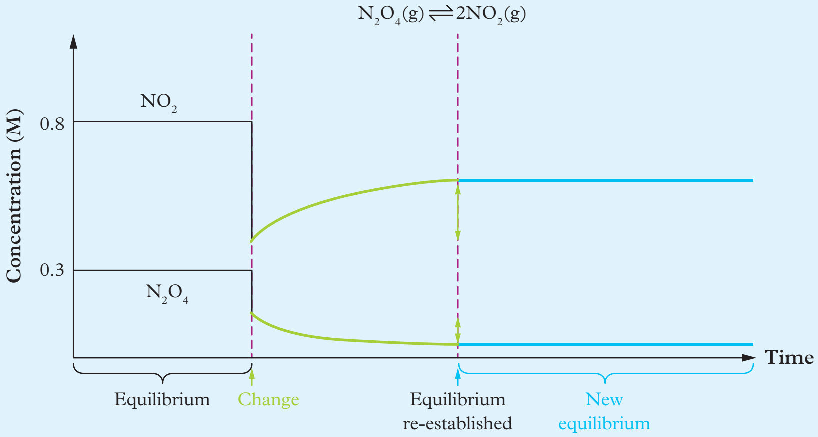


FIGURE 3 An equilibrium graph of the formation of nitrogen dioxide

Dilution in aqueous systems

The concentrations of particles in an aqueous system can be decreased by diluting the system with water. Increasing the concentration of all chemical species is far more challenging and is not covered here.

Graphing the dilution of an aqueous system follows the same method as for increasing the volume of a gaseous system. You can see this in Worked example 2.2C.

WORKED EXAMPLE 2.2C

A reaction between aqueous iron(III) ions and thiocyanate ions to form iron(III) thiocyanate ions is at equilibrium. Initially their concentrations are 1.4, 0.6 and 0.25 M, respectively. The volume of the reaction is doubled by adding water. When equilibrium is re-established, the concentration of thiocyanate is 0.4 M. Determine and graph the effect of diluting the following aqueous equilibrium system:

$$Fe^{3+}(aq) + SCN^{-}(aq) \rightleftharpoons FeSCN^{2+}(aq)$$

SOLUTION

Doubling the volume by adding water halves the concentration of all ions in the aqueous solution. The system will partially oppose this change by moving to the side with more particles. There are two particles on the reactant side and only one on the product side, so the reactant side has more particles. Therefore, a net backward reaction results.

Notes on graphing

- When the reaction is diluted by doubling it volume, all concentrations decrease by half because there are fewer particles per volume of water. This results in a steep decrease in all concentrations (halved), represented as vertical lines.
- Any change to the system to partially oppose the change will occur in a 1:1:1 ratio.

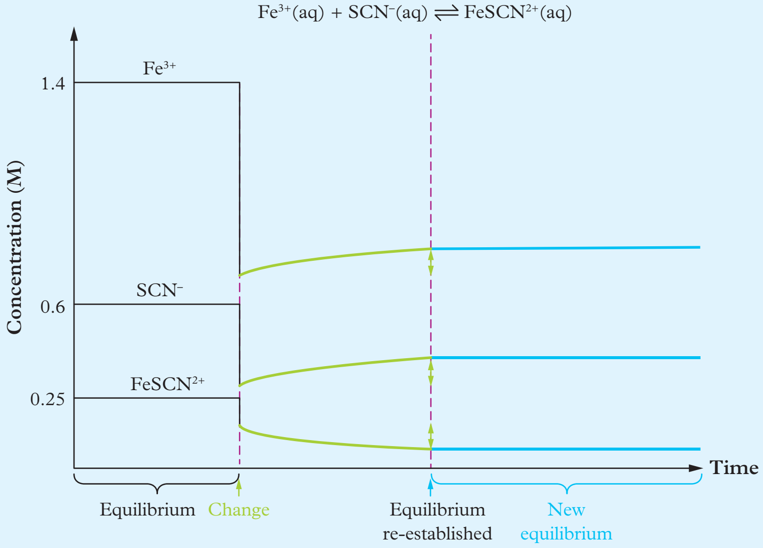


FIGURE 4 An equilibrium graph of the formation of iron(III) thiocyanate

SUGGESTED PRACTICAL

2.2C Effect of temperature on equilibrium
Go to your obook assess »

Changes in temperature

Temperature is a measure of energy. Therefore, increasing the temperature increases the energy in a reaction. All reactions require energy to overcome their activation energy. However, the amount of energy depends on the size of the activation energy and whether the reaction is exothermic or endothermic.

Endothermic reactions

In an endothermic reaction, products have more energy than reactants. This means that energy must be absorbed from the environment for the reaction to proceed because the enthalpy value is positive (Figure 5).

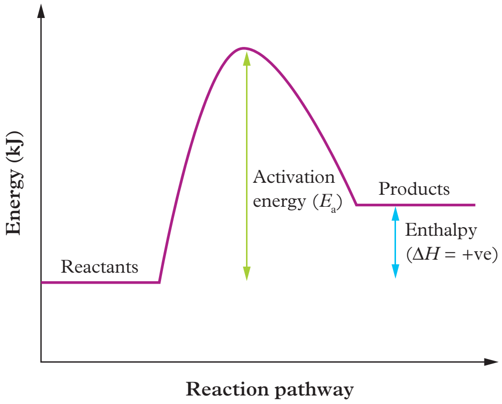


FIGURE 5 An endothermic reaction energy profile

The simplest method of determining the effect of temperature on a reaction is to consider the energy as a reactant or product. In an endothermic reaction, energy can be considered as a reactant:

$$\text{energy} + \text{reactants} \rightleftharpoons \text{products}$$

In an endothermic reaction, an increase in temperature results in the reaction working to remove the extra energy, according to Le Châtelier's principle. This means that it will move to the side where energy is absorbed and stored within the molecules. If the temperature is decreased, the reaction works to increase the energy of the system by moving to the side where energy is released from the molecules (Worked example 2.2D).

WORKED EXAMPLE 2.2D

Nitrogen and oxygen are in equilibrium with nitrogen monoxide. Initially, their concentrations are 0.2, 0.1 and 0.3 M, respectively. The temperature of the system is increased. When equilibrium is re-established, the concentration of oxygen is 0.075 M. Determine and graph the effect that an increase in temperature has on the following reaction:

$$N_2(g) + O_2(g) \rightleftharpoons 2NO(g) \qquad \Delta H = +180.5\,\text{kJ mol}^{-1}$$

SOLUTION

If temperature is increased in an endothermic system, the system will partially oppose an increase in energy by moving to the side where energy is stored within the molecules. This is the product side because the products have more energy that the reactants. Therefore, a net forward reaction results.

Notes on graphing

- When graphing changes caused by temperature, there is a gradual change in reactants and products over time. This is because the concentration does not immediately change. This is the only graph where all chemicals experience a gradual change, making a change in temperature easy to identify.
- The reaction changes by the molar ratio of 1:1:2.

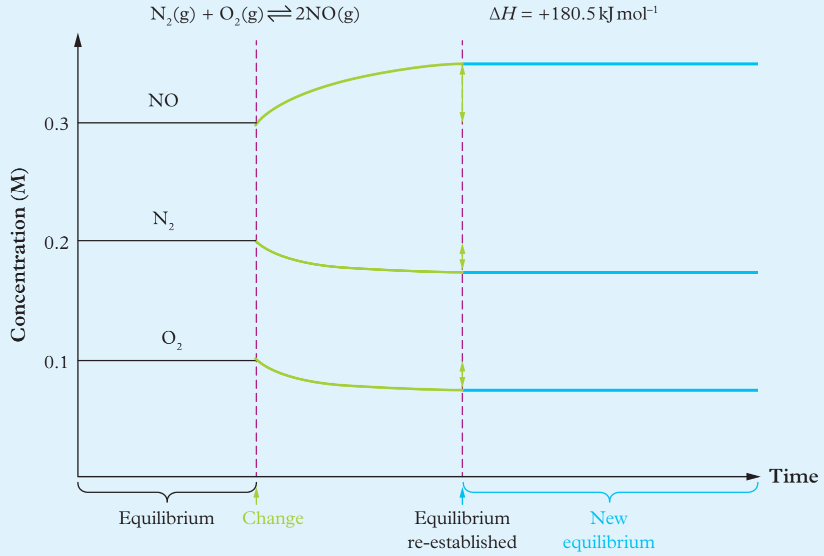


FIGURE 6 An equilibrium graph of the formation of nitrogen monoxide

For an additional worked example on how the equilibrium of the formation of nitrogen monoxide changes with a *decrease* in temperature, see Increase your knowledge on your obook assess.

Exothermic reactions

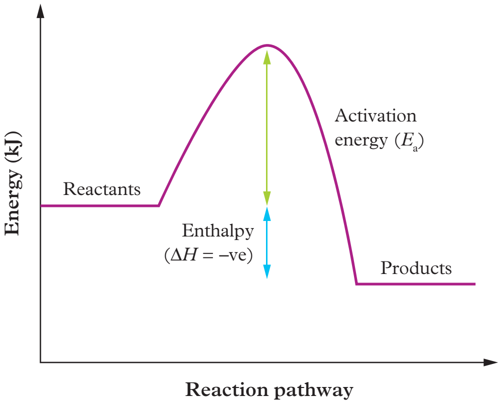


FIGURE 7 An exothermic reaction energy profile

In an exothermic reaction, reactants have more energy than products. This means that energy is released into the environment when products form and the enthalpy value is negative (Figure 7).

In an exothermic reaction, energy is a product:

reactants $\rightleftharpoons$ products + energy

In an exothermic reaction, a change in temperature is explained in the same way as an endothermic change is (Worked example 2.2E).

Table 2 will help you remember the effect of temperature on equilibrium:

TABLE 2 How changing temperature affects equilibrium reactions

Reaction	Increase temperature	Decrease temperature
Endothermic	Increase [products]	Decrease [products]
	Decrease [reactants]	Increase [reactants]
Exothermic	Increase [reactants]	Decrease [reactants]
	Decrease [products]	Increase [products]

WORKED EXAMPLE 2.2E

Phosphorus trichloride and chlorine gas are in equilibrium with phosphorus tetrachloride. Initially their concentrations are 1.2, 0.8 and 0.4 M, respectively. The temperature of the system is decreased. When equilibrium is re-established, the concentration of phosphorus tetrachloride is 0.6 M. Determine and graph the effect of a decrease in temperature on the following reaction:

$$PCl_3(g) + Cl_2(g) \rightleftharpoons PCl_5(g) \qquad \Delta H = -92.5\,kJ\,mol^{-1}$$

SOLUTION

If temperature is decreased in an exothermic system, the system partially opposes an increase in energy by moving to the side where energy is released from the molecules. This is the product side because the products have less energy than the reactants. Therefore, a net forward reaction results.

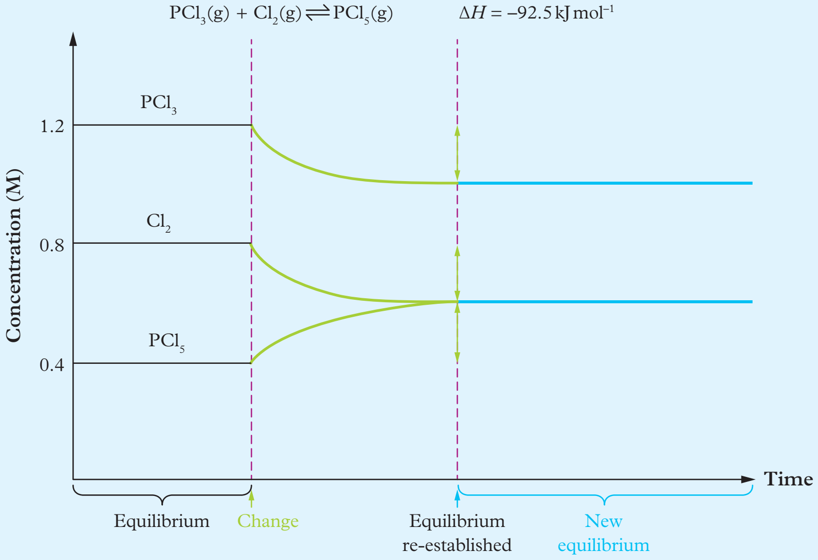


FIGURE 8 An equilibrium graph of the formation of phosphorus pentachloride

For an additional worked example on how the equilibrium of the formation of phosphorus tetrachloride changes with an *increase* in temperature see Increase your knowledge on your obook assess.

CHALLENGE 2.2A

Volume changes in equilibrium 1

Nitrogen and oxygen are in equilibrium with nitrogen monoxide. Initially, their concentrations are 0.8, 0.3 and 1.8 M respectively. The volume of the container is halved. Determine and graph the effect on the reaction. What are the final concentrations of the reactants and products at equilibrium?

Catalysts

When a **catalyst** is added, it lowers the activation energy of the system. It does not increase or decrease the concentration of any chemical within the system and therefore does not cause a 'change' as described by Le Châtelier's principle. It does not result in a net forward or backward reaction.

The effect of a catalyst on a system is to enable it to reach equilibrium faster. Therefore, any change that is made takes place in less time (Worked example 2.2F).

catalyst
a substance that increases the rate of a reaction without itself being consumed in the reaction

WORKED EXAMPLE 2.2F

A reaction between aqueous iron(III) ions and thiocyanate ions to form iron(III) thiocyanate ions is at equilibrium. Initially their concentrations are 1.4, 0.6 and 0.25 M, respectively. The volume of the reaction is doubled by adding water. When equilibrium is re-established, the concentration of thiocyanate is 0.4 M. Determine and graph the effect of diluting the following aqueous equilibrium system with and without using a catalyst:

$$Fe^{3+}(aq) + SCN^{-}(aq) \rightleftharpoons FeSCN^{2+}(aq)$$

SOLUTION

When the system is diluted by adding water to double its volume, all concentrations halve. The system partially opposes a decrease in all concentrations by moving to the side of the reaction with more particles, the reactant side. This results in a net backward reaction.

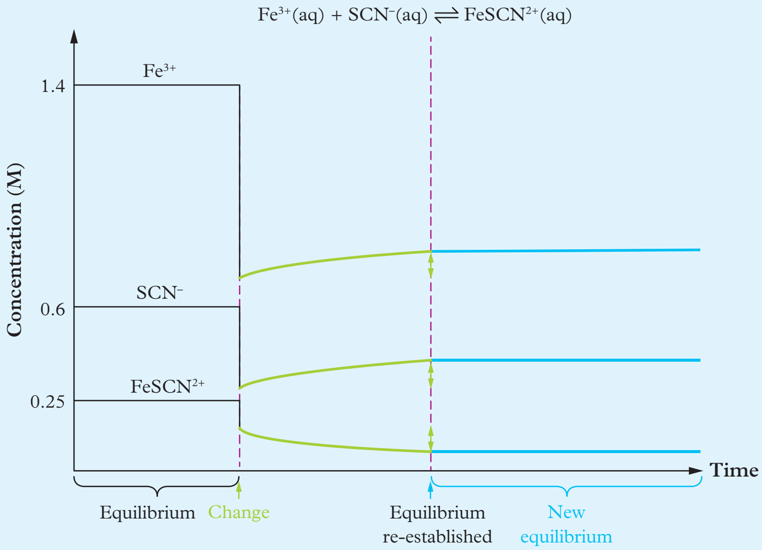


FIGURE 9 An equilibrium graph of the formation of iron(III) thiocyanate without a catalyst

When a catalyst is added to the solution, the exact same effect is seen but the amount of time between the change occurring and equilibrium being re-established is much shorter.

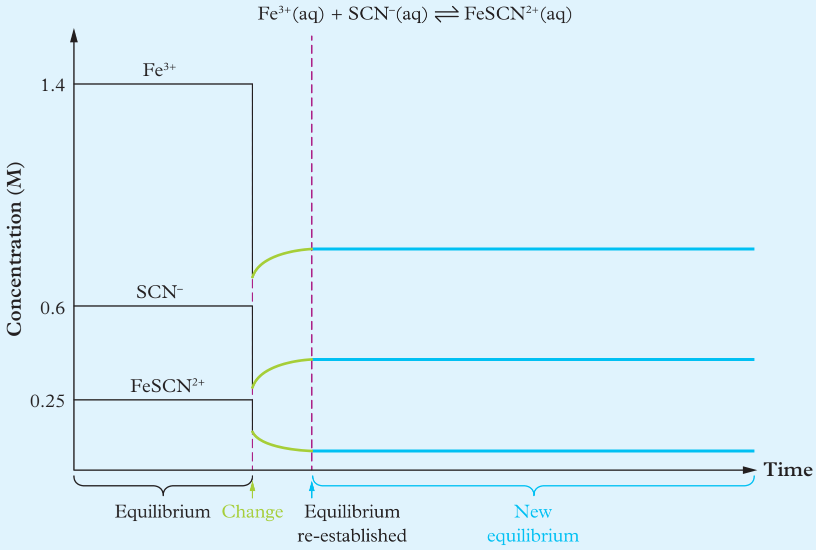


FIGURE 10 An equilibrium graph of the formation of iron(III) thiocyanate with the addition of a catalyst

CHALLENGE 2.2B

Volume changes in equilibrium 2

A fixed-volume container is filled with 1.0 mol of nitrogen monoxide gas and allowed to reach equilibrium at a temperature of 100°C. Nitrogen monoxide is a product in the reaction between nitrogen and oxygen, where its enthalpy value is $+180.8\,kJ\,mol^{-1}$.

Explain why the rate of the forward reaction will never be greater than the rate of the reverse reaction before the system reaches equilibrium and when it reaches equilibrium.

FIGURE 11 Nitrogen monoxide or nitric oxide is a colourless gas that is present in our bodies' blood vessels and used to signal when muscles need to relax to increase blood flow.

CHECK YOUR LEARNING 2.2

Describe and explain

1 **Describe** Le Châtelier's principle.

2 **Describe** the effect of an inert gas on a reaction. **Explain** why this effect occurs.

Apply, analyse and interpret

3 An equilibrium system contains 5.0 M of nitrogen, 2.0 M of hydrogen and 3.0 M of ammonia:

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \quad \Delta H = -91\,\text{kJ}\,\text{mol}^{-1}$$

Construct a graph for each of the following situations.

- **a** The mixture is at equilibrium for 10 seconds.
- **b** The volume of the system is halved. When equilibrium is re-established 20 seconds later, the concentration of nitrogen is 9.0 M.
- **c** At 20 seconds, the concentration of hydrogen is increased to 5.0 M. When equilibrium is re-established 15 seconds later, the concentration of ammonia is 11 M.
- **d** At 35 seconds, the temperature is increased. When equilibrium is re-established 30 seconds later, the concentration of nitrogen is 9.5 M.
- **e** At 65 seconds, an inert gas is added.

4 **Determine** the effect of the following changes on the equilibrium between sulfur dioxide, oxygen and sulfur trioxide:

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

- **a** The volume is increased.
- **b** The temperature is decreased.
- **c** The concentration of sulfur trioxide is increased.
- **d** The temperature is increased.

Investigate, evaluate and communicate

5 NO_2 (a dark brown gas) and N_2O_4 (a colourless and highly toxic gas) are placed in a large syringe and left to reach equilibrium. A student pushes the plunger in to determine the effect of decreasing the volume. Initially, the mixture becomes darker and then gradually becomes lighter. Using Le Châtelier's principle, **evaluate** this effect and **communicate** why this happens.

FIGURE 12 Changing the volume of a syringe with gas in it affects the equilibrium.

6 **Explain** how the rate and equilibrium trade-off applies to the production of ammonia:

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \quad \Delta H = -91\,\text{kJ}\,\text{mol}^{-1}$$

Investigate the Haber process and **communicate** how the trade-off is overcome. In your answer, include the temperature and pressure conditions and how these maximise the yield of ammonia.

You can find the following resources for this section on your obook assess:

- » Student book questions
  2.2 Check your learning
- » Suggested practicals
  2.2A, 2.2B, 2.2C
- » Increase your knowledge
  Extra worked examples of equilibrium reactions
- » Increase your knowledge
  Case study 2.2 The trade off between rate and equilibrium

SCIENCE AS A HUMAN ENDEAVOUR

2.3

Chemical balance in wine

KEY IDEAS

In this section, you will learn about:

- the application of chemical equilibrium in wine-making.

Chemical equilibrium has many different applications, not only in industrial chemistry and blood, but also in wine-making.

Chemical balance in wine

sulfite
a group of organic compounds with an SO_3^{2-} anion, which can also contain SO(g)

A typical bottle of wine contains about 81% water and 12% alcohol. The remaining 7% consists of all of the chemical compounds that give the wine its flavour – sugars, proteins, minerals, vitamins and various other compounds. These compounds include **sulfites**, which work as antioxidants, slowing the oxidation of ethanol to ethanoic acid (therefore preventing the alcohol from turning into vinegar), and inhibiting microbial activity.

Sulfites in wine

fermentation
the chemical breakdown of glucose, with a yeast catalyst, to form ethanol and carbon dioxide

oxidation
a reaction with oxygen

Glucose in the grape undergoes **fermentation** to form ethanol and carbon dioxide. The process requires a catalyst; yeasts are often used for this purpose:

$$C_6H_{12}O_6 \rightarrow 2CH_3CH_2OH + 2CO_2$$

The ethanol undergoes **oxidation** to form ethanoic acid (vinegar):

$$CH_3CH_2OH + O_2 \rightarrow CH_3COOH + H_2O$$

Molecular sulfur dioxide (SO_2) is a gas that readily dissolves in water. Once it dissolves, it reacts with the water molecules in an equilibrium reaction that forms bisulfite (HSO_3^-) and H^+. The bisulfite further dissociates to form the sulfite ion (SO_3^{2-}) and a second H^+. The whole process forms the multistep equilibrium reaction:

$$SO_2 + H_2O \rightleftharpoons HSO_3^- + H^+$$

$$HSO_3^- \rightleftharpoons SO_3^{2-} + H^+$$

Because this equilibrium involves H^+, the different forms of sulfite are pH dependent. To increase the amount of SO_2 in the wine, you must increase the concentration of H^+. This results in a net backwards reaction to remove the H^+ and increases the concentration of SO_2 in the process. Sulfites have an optimal pH range of pH 3–4.

The sulfite ion can act as a preservative. SO_3^{2-} reacts with dissolved oxygen within the wine, preventing it from reacting with the ethanol. The product of this reaction is sulfuric acid, which is not desirable in a bottle of wine, therefore sulfite concentration decreases as the pH of the wine decreases, and the wine becomes more acidic.

$$2SO_3^{2-} + O_2 + 4H^+ \rightarrow 2H_2SO_4$$

SO_2 prevents another oxidation process that causes the browning of wine. It does this by preventing some enzymes that catalyse oxidation reactions.

As an antimicrobial agent, SO_2 can pass through cell membranes, and bind with proteins and enzymes and stop enzymes from working properly. This kills the cell, preventing the microorganism from propagating.

CHECK YOUR LEARNING 2.3

Describe and explain

1 **Explain** why sulfur dioxide is an essential molecule in wine-making.

2 **Explain** the difference between fermentation and oxidation.

Apply, analyse and interpret

3 **Analyse** the impact of decreasing the pH of a wine on its ability to oxidise and limit microbial growth.

You can find the following resources for this section on your obook assess:

- » **Student book questions**
  2.3 Check your learning
- » **Weblink**
  Sulfites in wine
- » **Weblink**
  Chemical balance in wine

2.4

Measuring equilibrium

KEY IDEAS

In this section, you will learn about:

- equilibrium law and calculating K_c
- using the reactant quotient (Q) to determine the position of equilibrium.

As scientists developed the theory of equilibrium, they quickly realised that there was a relationship between the concentrations of reactants and the concentrations of products in a reaction system.

FIGURE 1 The balance between the reactants and products is crucial in equilibrium reactions.

Equilibrium law

equilibrium law
the law that states the concentration of products to the power of their coefficients, divided by the concentration of reactants to the power of their coefficients is equal to the equilibrium constant (K_c)

Equilibrium law is used to determine the mathematical relationship between the concentrations of reactants and products, called the **equilibrium constant (K_c)**. All concentrations are to the power of their coefficients. The concentrations of products are multiplied together and divided by the concentrations of the reactants.

A chemical reaction for the general equation is:

$$aA + bB \rightleftharpoons cC + dD$$

equilibrium constant (K_c)
the ratio of reactants to products in a reaction when it is at equilibrium

where A and B are the reactants, C and D are the products, and *a*, *b*, *c* and *d* are their respective coefficients. The concentrations of pure liquids and solids are not included in the equilibrium constant expression.

Equilibrium law can therefore be written as:

$$K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

If you apply the law to an equilibrium reaction, you generate an **equilibrium expression**. The expression must contain the reactants and products to the power of their coefficients and the equilibrium constant expressed as either K_c or a numerical value.

equilibrium expression
the non-numerical representation of the equilibrium law, which states the chemicals to the power of their coefficients

WORKED EXAMPLE 2.4A

Write the equilibrium expression for the following equilibrium equation:

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

SOLUTION

$$K_c = \frac{[CO_2]^2}{[CO]^2[O_2]}$$

Calculating K_c

Equilibrium is one of the few concepts in chemistry where the units change depending on the chemical reaction used in the calculation. Use dimensional analysis to determine the units for the equilibrium constant in each equation.

Consider the reaction:

$$CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g)$$

The equilibrium expression is:

$$K_c = \frac{[CO][H_2]^3}{[CH_4][H_2O]}$$

If the chemicals are removed so that only the ratios of concentration are considered, the equation becomes:

$$\begin{aligned} K_c &= \frac{\cancel{M} \times (\cancel{M} \times M \times M)}{\cancel{M} \times \cancel{M}} \\ &= \frac{M \times M}{1} \\ &= M^2 \end{aligned}$$

Study tip

Assumptions are made in equilibrium calculations. Be careful if a question says that the container was initially empty because, when chemicals are put into it, the initial concentration of the products in a reaction is 0.

WORKED EXAMPLE 2.4B

Calculate the equilibrium constant (K_c) for the following equilibrium equation, where the concentration of all reactants and products is 2 M:

$$2NO(g) + 2H_2(g) \rightleftharpoons N_2(g) + 2H_2O(g)$$

SOLUTION

$$K_c = \frac{[N_2][H_2O]^2}{[NO_2]^2[H_2]^2}$$

$$\begin{aligned} K_c &= \frac{2 \times 2^2}{2^2 \times 2^2} \\ &= \frac{2 \times 4}{4 \times 4} \\ &= \frac{8}{16} \\ &= 0.5 \end{aligned}$$

Study tip

Equilibrium constants have no units as they represent a ratio of each reaction's concentrations at equilibrium.

Magnitude of K_c

The larger the value of the numerator (concentration of products), the larger the value of K_c. The larger the value of the denominator (concentration of reactants), the smaller the value of K_c.

- If $K_c > 10^4$, which is a large number, it contains significantly more product than reactant.
- If $K_c < 10^{-4}$, which is a small number, it contains significantly more reactant than product.
- Anywhere between these values indicates that there is a significant amount of both reactants and products in the system.

Systems not at equilibrium

reaction quotient (Q_c)
the ratio of reactants to products in a reaction when it is not at equilibrium

If a system is not at equilibrium, you can still use the equilibrium law, but instead calculate the **reaction quotient (Q_c)**. The reaction quotient is calculated in the same way, using the same equation, and provides an understanding of the amounts of reactants and products in a reaction system before it reaches equilibrium. In this way, chemists can determine in which direction the reaction must proceed to reach equilibrium.

RICE table

For systems where you must calculate equilibrium, you can use a RICE table (Table 1). Worked example 2.4C demonstrates this process.

TABLE 1 RICE table

R	Ratio
I	Initial concentration (in M)
C	Change that occurs (in M)
E	Equilibrium concentration (in M)

WORKED EXAMPLE 2.4C

3 moles of SO_2 and 2 moles of O_2 are pumped into an empty 1 L container. At equilibrium, the concentration of the only product (SO_3) is 2 M. Calculate the value of K_c for the reaction system.

SOLUTION

1 Write a balanced chemical equation:

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

2 Convert all mole amounts to concentration. As $C = \frac{n}{V}$, and the volume of the container is 1 L, divide all mole amounts by 1 to convert to concentration.

$[SO_2] = 3\,M$

$[O_2] = 2\,M$

3 Recognise that when the SO_2 and O_2 are pumped into the container, it is empty. Therefore, initially, there is no product, only reactants.

4 Recognise that the concentration of SO_3 is measured at equilibrium and therefore $[SO_3]$ has increased from 0 M (initially) to 2 M at equilibrium.

5 Use the information to complete a RICE table.

	SO_2	O_2	SO_3
R (ratio from balanced equation)	2	1	2
I (initial concentration)	3	2	0
C (change in concentration)			
E (equilibrium concentration)			2

6 Determine the change in the product by finding the difference between the initial and equilibrium concentrations.

	SO_2	O_2	SO_3
R	2	1	2
I	3	2	0
C			(2 – 0) = 2 SO_3 increases by 2.
E			2

7 The concentration of the product has increased by 2 (Row C), so the concentrations of the reactants will decrease by the molar ratio of 2. To determine the equilibrium concentrations of the reactants (Row E), subtract these amounts from the initial concentrations.

	SO_2	O_2	SO_3
R	2	1	2
I	3	2	0
C	Ratio SO_2 to SO_3 is 2:2 $\frac{2}{2} \times 2 = 2$	Ratio O_2 to SO_3 is 1:2 $\frac{1}{2} \times 2 = 1$	+2
E	3 – 2 = 1	2 – 1 = 1	2

8 Determine the equilibrium expression and use the equilibrium values to find the value of K_c.

$$\begin{aligned} K_c &= \frac{[SO_3]^2}{[SO_2]^2[O_2]} \\ &= \frac{2^2}{1^2 \times 1} \\ &= \frac{4}{1} \\ &= 4 \end{aligned}$$

FIGURE 2
Temperature is the only parameter that affects the value of K_c of a system.

CHALLENGE 2.4

Calculating equilibrium constants

In the oxidation reaction of sulfur dioxide to form sulfur trioxide:

$$2SO_3(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

4.0 mol of SO_2 and 2.8 mol of O_2 are reacted in a 6.0 L vessel and allowed to reach equilibrium at 500°C. At this point, 25% has converted to product.

Calculate the equilibrium constant for the reaction.

Effects of changes on the value of K_c

Of all of the changes discussed in section 2.2, it is important to note that the only change that has an effect on the value of K_c is a change in temperature. Reversing a chemical equation will result in an inverse of the K_c value, doubling the coefficients will square the K_c value and halving the coefficients will result in the square root of the K_c value.

CASE STUDY 2.4

Carbon monoxide poisoning

Carbon monoxide is a colourless, odourless and tasteless gas. CO is a by-product of a combustion reaction when there is not enough oxygen to form carbon dioxide. It is formed in heating, food production, car exhaust fumes, lighting and various other processes.

Carbon monoxide is toxic for any animal that has the haemoglobin (Hb) protein in their blood to transport oxygen around their body. This is because carbon monoxide binds more readily to haemoglobin than oxygen does, preventing oxygen from entering the bloodstream and being used in various cellular processes such as energy production.

Haemoglobin binds to both oxygen and carbon monoxide to form compounds according to the following equations:

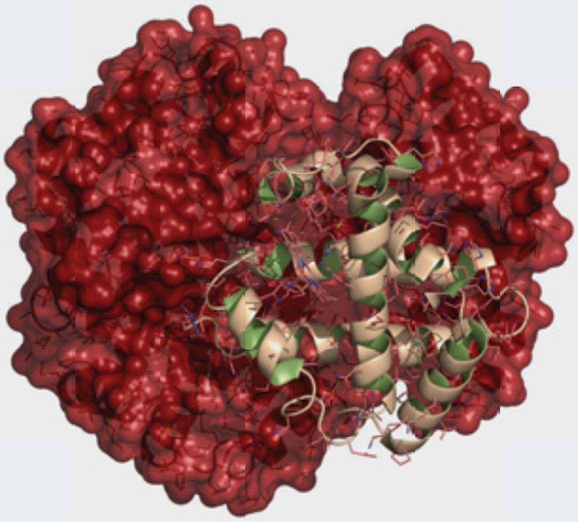


FIGURE 3 The haemoglobin protein within a red blood cell

$$\mathrm{Hb(aq) + CO(g) \rightleftharpoons HbCO(aq)} \qquad K = \text{large}$$

$$\mathrm{Hb(aq) + O_2(g) \rightleftharpoons HbO_2(aq)} \qquad K = \text{small}$$

Carbon monoxide binds to haemoglobin more tightly than oxygen does, so the first reaction forms more product and the second reaction will have high concentrations of reactants. This results in a large K_c value for the first equation and a small K_c value for the equation.

The recommended treatment for over-exposure to carbon monoxide is to breathe pure oxygen through an oxygen mask until bodily processes function normally again.

FIGURE 4 Carbon monoxide poisoning is treated by giving the patient oxygen.

WORKED EXAMPLE 2.4D

Consider the reaction between nitrogen and hydrogen to form ammonia:

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \qquad K_c = 95.6$$

Determine the effect on the equilibrium constant when the:

a reaction is reversed

b coefficients are tripled

c coefficients are halved.

SOLUTION

a $\frac{1}{95.6} = 0.01$

b $95.6^3 = 8.74 \times 10^5$

c $\sqrt{95.6} = 9.78$

CHECK YOUR LEARNING 2.4

Describe and explain

1 **Describe** the effect on K_c when the concentration of reactants in a chemical equation increases.

2 **Describe** the effect on K_c when the concentration of products in a chemical equation decreases.

3 1 mol of N_2 and 2 mol of H_2 are pumped into a 4 L vessel to form NH_3. At equilibrium, the concentration of N_2 is 0.1 M. **Calculate** the equilibrium constant.

4 2 mol of gaseous propane (C_3H_8) and 13 mol of oxygen are put into a sealed 20 L container. At equilibrium, there is 150 mol of water. **Calculate** the equilibrium constant.

Investigate, evaluate and communicate

5 10 mol of SO_2 and 6 mol of O_2 are added to a 2 L vessel. 30 seconds later, the concentration of SO_3 is measured as 4 M.

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

$$K_c = 2.0 \times 10^{-2}$$

Evaluate this information to:

a **calculate** Q_c

b **communicate** in which direction the reaction must proceed to reach equilibrium and **justify** your answer using the K_c and Q_c values.

6 A 1.5 L vessel contains 6 M NO and 8 M O_2. After 10 seconds the concentration of NO is found to have decreased by 6 M.

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

$$K_c = 2$$

Evaluate the above information to:

a **calculate** Q_c

b **communicate** in which direction the reaction must proceed to reach equilibrium and **justify** your answer using the K_c and Q_c values.

You can find the following resources for this section on your obook assess:

- Student book questions
  2.4 Check your learning
- Challenge
  2.4 Calculating equilibrium constants
- Increase your knowledge
  Extra worked example on calculating the equilibrium constant
- Video
  Balancing chemical equations

SCIENCE AS A HUMAN ENDEAVOUR

2.5

Carbon dioxide in the atmosphere and hydrosphere

KEY IDEAS

In this section, you will learn about:

- the application of equilibrium in the atmospheric carbon cycle.

Carbon dioxide in the atmosphere and hydrosphere

Carbon exists as hydrogencarbonate (HCO_3^-) in rocks and the oceans, carbon dioxide (CO_2) in the oceans and atmosphere, and carbon monoxide (CO) in the atmosphere. The carbon within the **atmosphere**, **hydrosphere** and **lithosphere** is in equilibrium.

atmosphere
the layers of gas that surround Earth

hydrosphere
the bodies of water on Earth's surface, underground and in the atmosphere

lithosphere
the outermost layer of Earth

The atmosphere

Both carbon dioxide and carbon monoxide are released from the lithosphere as a result of natural processes and human activity. There are many different reactions that involve these two chemical compounds. Carbon monoxide reacts with oxygen in the atmosphere to form carbon dioxide and ozone. This reaction requires UV light and illustrates the ability of carbon monoxide to, not only increase the concentration of carbon dioxide in the atmosphere, but also to contribute to the ozone effect:

$$CO(g) + 2O_2(g) \rightarrow CO_2(g) + O_3(g)$$

Gaseous carbon dioxide also exists in equilibrium with aqueous carbon dioxide within the oceans (contained within the hydrosphere):

$$CO_2(g) \rightleftharpoons CO_2(aq)$$

The hydrosphere

Once carbon dioxide dissolves in water, it can react with water to form the hydrogencarbonate ion and a hydrogen ion:

$$CO_2(aq) + H_2O(l) \rightleftharpoons H^+(aq) + HCO_3^-(aq)$$

The water that absorbs the carbon dioxide becomes more acidic because of the production of hydrogen ions. This results in ocean acidification, which has larger effects on the organisms living in the oceans such as coral and crustaceans. A well-known example of this is the recent bleaching of the Great Barrier Reef (Figure 1).

The hydrogencarbonate ion dissociates to form the carbonate ion and another hydrogen ion:

$$HCO_3^-(aq) \rightleftharpoons CO_3^{2-}(aq) + H^+(aq)$$

Finally, the carbonate reacts with calcium ions and precipitates as calcium carbonate in the lithosphere:

$$CO_3^{2-}(aq) + Ca^{2+}(aq) \rightleftharpoons CaCO_3(s)$$

FIGURE 1 Coral bleaching on the Great Barrier Reef, at Port Douglas, is attributed to increasing ocean temperatures and acidity.

CHALLENGE 2.5

Increasing global temperatures

Assuming that the reactions occurring in the hydrosphere are exothermic, what effect would increasing global temperatures have on the carbon that exists within the hydrosphere and atmosphere?

CHECK YOUR LEARNING 2.5

Describe and explain

1 **Explain** why carbon is in equilibrium in the atmosphere, hydrosphere and lithosphere.

2 **Identify** the catalyst that helps form carbon dioxide and ozone in the atmosphere.

Apply, analyse and interpret

3 Use Le Châtelier's principle to **explain** the effect that increasing carbon dioxide levels in the atmosphere has on the hydrosphere.

Investigate, evaluate and communicate

4 The shells of sea organisms contain calcium carbonate. **Investigate** the impact of increasing carbon dioxide levels in the atmosphere on these organisms and **communicate** the effect on these organisms as well as the ecosystem in which they live.

5 Coral bleaching can be attributed to the increase in acidity of the oceans. **Investigate** coral bleaching and **communicate** what happens during the bleaching process.

You can find the following resources for this section on your obook assess:

- » Student book questions
  2.5 Check your learning
- » Challenge
  2.5 Increasing global temperatures
- » Weblink
  Coral bleaching

CHAPTER 2

Review

Chapter summary

2.1
- Equilibrium reactions are reversible reactions.
- Dynamic equilibrium is reached when the rate of the forward and reverse reactions are equal.
- Equilibrium can occur in open or closed systems and include changes in state.

2.2
- Le Châtelier's principle states that equilibrium systems will partially oppose any change made to them. It explains the effect that changes in concentration, volume, pressure, temperature and a catalyst have on the position of a reaction and can be summarised as resulting in a net forward reaction, a net reverse reaction or no effect on the reaction system.

2.3
- The concept of equilibrium can be applied to wine-making. The balance of sulfites in wine stops the alcohol from converting to vinegar.

2.4
- The equilibrium law outlines a mathematical relationship between the concentration of reactants and products in an equilibrium reaction. It results in the calculation of an equilibrium constant (K_c), which represents this ratio at equilibrium.
- For reactions not at equilibrium, the equilibrium law calculates a reaction quotient (Q_c).
- The equilibrium constant and reaction quotient can be calculated using a RICE table. The values can be compared to determine in which direction a reaction must proceed in order to reach equilibrium.

2.5
- The concept of equilibrium can be applied to nutrient cycles in the atmosphere and hydrosphere. The acidity balance in the oceans is important for all marine life.

Key terms

- activation energy
- atmosphere
- catalyst
- closed system
- concentration
- dynamic equilibrium
- enthalpy
- equilibrium constant (K_c)
- equilibrium expression
- equilibrium law
- fermentation
- forward reaction
- hydrosphere
- Le Châtelier's principle
- lithosphere
- open system
- oxidation
- pH
- pressure
- reaction quotient (Q_c)
- reverse reaction
- sulfite
- temperature
- volume

Key formulas

Concentration	$C = \frac{n}{V}$
Equilibrium constant	$K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}$

Revision questions

The relative difficulty of these questions is indicated by the number of stars beside each question number: ★ = low; ★★ = medium; ★★★ = high.

Multiple choice

1 In an equilibrium reaction, when a reactant concentration is increased:

A there is a net forward reaction
B there is a net backward reaction
C there is no reaction
D the reaction remains at equilibrium.

2 An increase in temperature in an equilibrium reaction:

A increases the energy in a reaction
B decreases the energy in a reaction
C causes no change to a reaction
D always drives a forward reaction.

3 The equilibrium law states that the concentration of:

A products to the power of their coefficients divided by the concentration of reactants to the power of their coefficients is equal to the equilibrium constant
B products to the power of their coefficients multiplied by the concentration of reactants to the power of their coefficients is equal to the equilibrium constant
C reactants to the power of their coefficients divided by the concentration of products to the power of their coefficients is equal to the equilibrium constant
D reactants to the power of their coefficients added to the concentration of products to the power of their coefficients is equal to the equilibrium constant.

4 The RICE table stands for:

A ratio, initial concentration, change that occurs, equilibrium constant
B reaction, initial concentration, complete reaction, equilibrium constant
C ratio, inert gas, complete reaction, equilibrium constant
D reactant, initial concentration, change that occurs, equilibrium constant.

5 For the following reaction:

$$CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g) \qquad \Delta H = +206\,kJ\,mol^{-1}$$

which changes would maximise the yield of hydrogen?

A Decrease volume and decrease temperature.
B Decrease volume and increase temperature.
C Increase volume and decrease temperature.
D Increase volume and increase temperature.

6 Which of the following statements about dynamic equilibrium is false?

A Reactants and products are breaking down and re-forming in the molar ratio.
B Both reactants and products are present in the reaction.
C Molar amounts of reactants and products are equal.
D The rates of the forward and reverse reactions are equal.

The following equation relates to questions 7–10.

Butane combusts in oxygen in a sealed container according to the following equation:

$$2C_4H_{10}(g) + 13O_2(g) \rightleftharpoons 8CO_2(g) + 10H_2O(g) \qquad \Delta H = \text{exothermic}$$

7 The equilibrium expression used to represent the equation is:

A $K_c = \frac{[C_4H_{10}]^2[O_2]^{12}}{[CO_2]^8[H_2O]^{10}}$

B $K_c = \frac{8[CO_2]^{10}[H_2O]}{2[C_4H_{10}]^{13}[O_2]}$

C $K_c = \frac{2[C_4H_{10}]^{13}[O_2]}{8[CO_2]^{10}[H_2O]}$

D $K_c = \frac{[CO_2]^8[H_2O]^{10}}{[C_4H_{10}]^2[O_2]^{13}}$

8 To maximise the yield of carbon dioxide, a chemist should:

- **A** increase the concentration of products
- **B** add an inert gas
- **C** double the volume
- **D** increase the pressure.

9 To maximise the concentration of butane:

- **A** increase the temperature and increase the volume
- **B** increase the temperature and decrease the volume
- **C** decrease the temperature and decrease the volume
- **D** decrease the temperature and increase the volume.

10 The effect on K_c when the reaction is reversed and the coefficients are doubled is:

- **A** $\frac{1}{K_c^{2}}$
- **B** $\frac{1}{2 \times K_c}$
- **C** K_c^{2}
- **D** $\sqrt{K_c^{2}}$

Short answer

Describe and explain

★ 11 **Define** 'activation energy'.

★ 12 **Describe** how the energy profile of an exothermic reaction differs from that of an endothermic reaction.

★ 13 **Construct** balanced chemical equations for the following reactions.

- **a** $NaHCO_3 \rightarrow Na_2CO_3 + CO_2 + H_2O$
- **b** $MnS + HCl \rightarrow H_2S + MnCl_2$
- **c** $CaO + C \rightarrow CaC_2 + CO$

★ 14 **Explain** the difference between an observed change and measured change in a reaction.

★ 15 **Define** Le Châtelier's principle.

★ 16 **Construct** the equilibrium expression for:

- **a** $N_2O_4(g) \rightleftharpoons 2NO_2(g)$
- **b** $CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$

★ 17 **Explain** the effect a catalyst has on an equilibrium system.

★18 **Explain** the effect of adding an inert gas into an equilibrium system.

★★19 Nitrosyl chloride (NOCl) decomposes according to the equation:

$$2NOCl(g) \rightleftharpoons 2NO(g) + Cl_2(g)$$

Initially, 3.6 mol of NOCl(g) is placed in an empty 2.5 L flask and allowed to reach equilibrium. If the concentration of Cl_2 is 0.50 M at equilibrium, **calculate** the equilibrium constant for the reaction.

Apply, analyse and interpret

★★★20 Methanol can be formed in the following reaction:

$$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$$

$$\Delta H = +128\ \text{kJ mol}^{-1}$$

At 25°C, the equilibrium constant for the reaction is measured as $3.9 \times 10^{-2}\ \text{M}^{-2}$.

- **a** **Determine** what can be concluded about the concentrations of reactants and products.
- **b** Use Le Châtelier's principle to **determine** the effect of:
  - **i** adding methanol to the reaction vessel at a constant temperature
  - **ii** decreasing the temperature of the system
  - **iii** doubling the volume of the system.

★★★21 Hydrogen iodide is formed according to the following equilibrium reaction:

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

Initially, 0.9 mol of H_2 and 0.5 mol of I_2 are added to a 2 L vessel. Two minutes into the reaction, the concentration of HI is measured at 0.4 M.

- **a** **Calculate** Q_c.
- **b** At equilibrium, $K_c = 0.5$. Using Q_c and K_c, **determine** the direction that the reaction must move in to reach equilibrium.
- **c** **Deduce** the units of the equilibrium constant.

Investigate, evaluate and communicate

★★22 **Investigate** the concept of a buffer and **communicate** how it is able to maintain the pH of equilibrium systems. Use human blood as an example to **justify** your answer.

FIGURE 1 Woman donating blood

★★★23 **Consider** the following equilibrium system:

$$Fe^{3+}(aq) + SCN^{-}(aq) \rightleftharpoons FeSCN^{2+}(aq)$$

Investigate the effect of the following changes and use Le Châtelier's principle to **justify** the effect on the position of equilibrium. You may need to consider the precipitation reactions of the ions and refer to solubility rules table or *Chemistry for Queensland Units 1 & 2*, page 379.

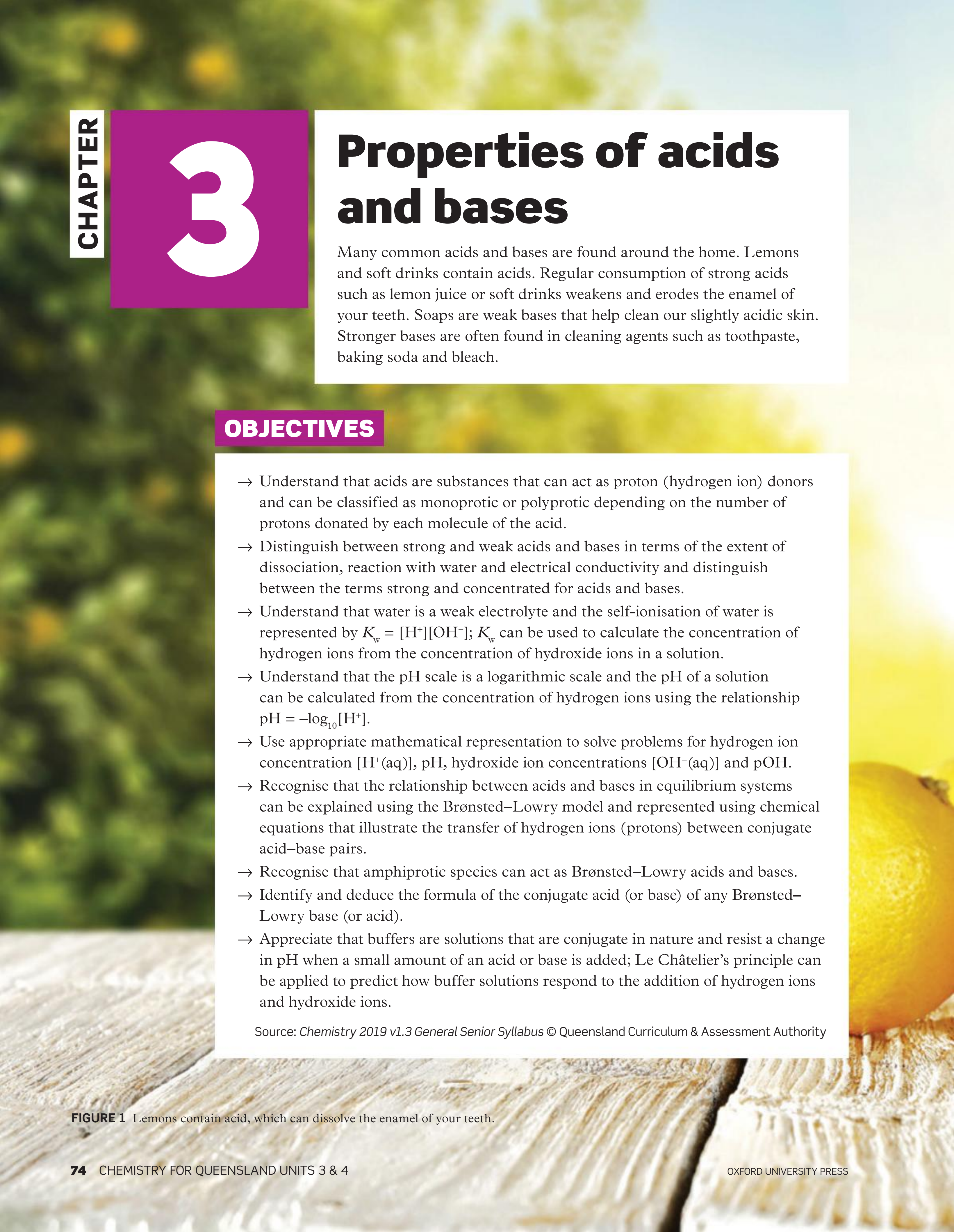
- **a** $AgNO_3(aq)$ is added to the reaction.
- **b** NaF(aq) is added to the reaction.
- **c** The reaction is diluted.
- **d** NaOH is added to the reaction.

★★★24 Nitric acid is produced in a similar manner to sulfuric acid – in a multistep process containing equilibrium reactions. **Investigate** the production of nitric acid.

- **a** **Construct** the three equilibrium reaction equations and **clarify** whether they are endothermic or exothermic.
- **b** **Define** the optimal conditions for the production of nitric acid for each equation (i.e. temperature, pressure, concentration, catalyst).
- **c** **Discuss** where the 'trade-off' exists in the production of nitric acid. **Explain** the concept of a 'trade-off' and **communicate** how it is overcome in this process.

You can find the following resources for this section on your obook assess:

- » Student book questions
  Chapter 2 Revision questions
- » Revision notes
  Chapter 2
- » assess quiz
  Auto-correcting multiple-choice quiz
- » Flashcard glossary
  Chapter 2



CHAPTER 3

Properties of acids and bases

Many common acids and bases are found around the home. Lemons and soft drinks contain acids. Regular consumption of strong acids such as lemon juice or soft drinks weakens and erodes the enamel of your teeth. Soaps are weak bases that help clean our slightly acidic skin. Stronger bases are often found in cleaning agents such as toothpaste, baking soda and bleach.

OBJECTIVES

- → Understand that acids are substances that can act as proton (hydrogen ion) donors and can be classified as monoprotic or polyprotic depending on the number of protons donated by each molecule of the acid.
- → Distinguish between strong and weak acids and bases in terms of the extent of dissociation, reaction with water and electrical conductivity and distinguish between the terms strong and concentrated for acids and bases.
- → Understand that water is a weak electrolyte and the self-ionisation of water is represented by $K_w = [H^+][OH^-]$; K_w can be used to calculate the concentration of hydrogen ions from the concentration of hydroxide ions in a solution.
- → Understand that the pH scale is a logarithmic scale and the pH of a solution can be calculated from the concentration of hydrogen ions using the relationship $pH = -\log_{10}[H^+]$.
- → Use appropriate mathematical representation to solve problems for hydrogen ion concentration $[H^+(aq)]$, pH, hydroxide ion concentrations $[OH^-(aq)]$ and pOH.
- → Recognise that the relationship between acids and bases in equilibrium systems can be explained using the Brønsted–Lowry model and represented using chemical equations that illustrate the transfer of hydrogen ions (protons) between conjugate acid–base pairs.
- → Recognise that amphiprotic species can act as Brønsted–Lowry acids and bases.
- → Identify and deduce the formula of the conjugate acid (or base) of any Brønsted–Lowry base (or acid).
- → Appreciate that buffers are solutions that are conjugate in nature and resist a change in pH when a small amount of an acid or base is added; Le Châtelier's principle can be applied to predict how buffer solutions respond to the addition of hydrogen ions and hydroxide ions.

Source: *Chemistry 2019 v1.3 General Senior Syllabus* © Queensland Curriculum & Assessment Authority

FIGURE 1 Lemons contain acid, which can dissolve the enamel of your teeth.

PRACTICALS

SUGGESTED PRACTICAL	**3.7** Measuring pH

3.1

Acids

KEY IDEAS

In this section, you will learn about:

- acids acting as proton donors
- monoprotic and polyprotic acids.

Acids are all around you. Lemons, energy drinks, milk and many other common foods and substances contain acids. In the 17th century, British scientist Robert Boyle found that when acids or bases were added to substances such as vegetable juice, they changed colour.

What makes an acid acidic? All acids contain hydrogen. When acids dissolve in water, they donate hydrogen ions (H^+). Therefore, an acid is a substance that can act as a **proton donor**.

proton donor
a substance that can donate H^+ (hydrogen ions)

Proton donors

If an acid such as hydrochloric acid (HCl) is added to water, the hydrogen atom in HCl bonds to one of the two lone pairs of the oxygen of a water molecule. The H–Cl bond breaks and a hydronium ion and a chloride ion form:

$$HCl(aq) + H_2O(l) \rightarrow H_3O^+(aq) + Cl^-(aq)$$

A solvent containing labile (reactive) hydrogen cations is called a protic solvent. Different acids can donate different amounts of hydrogen depending on their chemical composition. A **monoprotic acid**, such as hydrochloric acid, can donate one (*mono* = 'one') proton per molecule on dissociation, forming a hydronium ion (H_3O^+). Other common monoprotic acids are hydrogen bromide (HBr), nitric acid (HNO_3) and ethanoic acid (CH_3COOH), commonly known as acetic acid or vinegar.

monoprotic acid
an acid that can donate one hydrogen ion per molecule

Polyprotic acids can donate more than one proton per molecule (*poly* = 'many'). Common polyprotic acids include diprotic (donate two H^+ per molecule) and triprotic acids (donate three H^+ per molecule).

polyprotic acid
an acid that can donate more than one hydrogen ion per molecule

Diprotic acids such as sulfuric acid dissociate in water in two dissociation steps:

$$H_2SO_4(aq) \rightleftharpoons H^+(aq) + HSO_4^-(aq)$$

$$HSO_4^-(aq) \rightleftharpoons H^+(aq) + SO_4^{2-}(aq)$$

The first step takes place to a greater extent than the second step because $H_2SO_4(aq)$ is a strong acid but $HSO_4^-(aq)$ is only weakly acidic.

Triprotic acids such as phosphoric acid (H_3PO_4) dissociate in three steps:

$$H_3PO_4(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + H_2PO_4^-(aq)$$

$$H_2PO_4^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HPO_4^{2-}(aq)$$

$$HPO_4^{2-}(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + PO_4^{3-}(aq)$$

Phosphoric acid is not a strong acid.

CASE STUDY 3.1

Ocean acidity and the Great Barrier Reef

As more carbon dioxide is released into the atmosphere, the oceans absorb larger amounts of carbon dioxide. Carbon dioxide reacts with water to form carbonic acid (H_2CO_3), which makes the water more acidic. Ocean acidification can reduce coral growth and weaken the reef structure, ultimately destroying the reef's ecosystem.

In 2016, the Commonwealth Scientific and Industrial Research Organisation (CSIRO) started a landmark monitoring program. The program was called Future Reef 2.0 and its aim was to monitor changes in water chemistry by taking water samples along the length of the Great Barrier Reef for 3 years. The program is the first large-scale research investigation of ocean acidification.

FIGURE 1 CSIRO investigates water chemistry of healthy corals (left) and dying bleached corals (right) to attempt to understand the destructive processes involved.

Study tip

An extended Case study on ocean acidification, and a practice Research investigation can be found in the *Chemistry Units 3 & 4 Student workbook*.

CHECK YOUR LEARNING 3.1

Describe and explain

1 **Explain** the following terms and give examples.
  - **a** Proton donor
  - **b** Monoprotic acid
  - **c** Polyprotic acid

2 **Identify** five acidic substances in your home.

Apply, analyse and interpret

3 **Determine** the chemical equation of the dissociation of:
  - **a** nitric acid (HNO_3)
  - **b** carbonic acid (H_2CO_3)
  - **c** arsenic acid (H_3AsO_4).

Investigate, evaluate and communicate

4 Lemons are strongly acidic (pH 2–3). **Investigate** why the juice of a lemon is not dangerous for humans.

5 **Investigate** three monoprotic and three polyprotic acids and classify them as strong or weak.

6 **Discuss** how the ocean's acidity is increasing and **research** how this affects the Great Barrier Reef.

You can find the following resources for this section on your obook assess:

- » Student book questions
  3.1 Check your learning
- » Weblink
  Ocean acidity
- » Weblink
  Acids

3.2

Strong and weak acids and bases

KEY IDEAS

In this section, you will learn about:

- the properties of strong and weak acids and bases
- electrical conductivity properties of acids and bases.

Which is more acidic, an apple or an energy drink? What makes it more acidic? This section discusses the properties that makes an acid or a base strong or weak. Remember that acid and base **strength** is not the same as concentration. **Strong acids** and **bases** completely ionise in water. **Weak acids** and **bases** do not completely ionise (Figure 1).

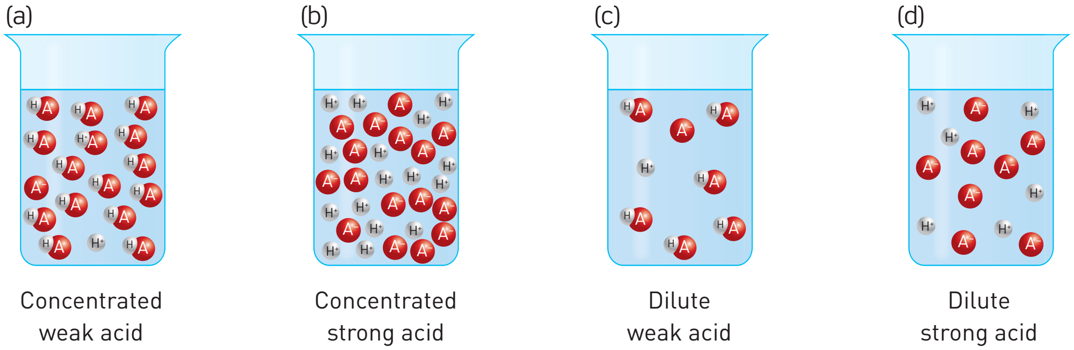
strength
the level of dissociation of an acid or a base

strong acid
an acid that completely ionises in water

strong base
a base that completely ionises in water

weak acid
an acid that does not completely ionise in water

weak base
a base that does not completely ionise in water



Concentrated weak acid

Concentrated strong acid

Dilute weak acid

Dilute strong acid

FIGURE 1 (a) A concentrated weak acid contains many acid molecules but only a few ionise and release hydrogen ions. (b) A concentrated strong acid has many ionised acid molecules. (c) A dilute weak acid has few acid molecules with a low number of ionised acid molecules. (d) A dilute strong acid contains a few ionised acid molecules in a solution.

Weak acids

Weak acids only partially ionise (Figure 1a,c). A common weak acid is ethanoic acid (or acetic acid) (CH_3COOH), which is found in vinegar (Figure 2). When ethanoic acid dissolves in water, it donates protons, forming hydronium ions (H_3O^+). Eventually, an equilibrium is established with a significant amount of non-ionised ethanoic acid molecules. Only about 5% of the ethanoic acid molecules will ionise.

$$CH_3COOH(aq) + H_2O(l) \rightleftharpoons CH_3COO^-(aq) + H_3O^+(aq)$$

FIGURE 2 Vinegar is made up of ethanoic (acetic) acid, water and trace amounts of other chemicals.

To work out the hydronium ion concentration of weak acid solutions, you need to apply an acid dissociation constant, K_a (also known as acidity constant or acid ionisation constant) (see Chapter 4).

Strong acids

Strong acids ionise completely (Figure 1b,d). When hydrogen chloride gas dissolves in water, the gaseous HCl reacts with the polar water molecules and donates a proton (H^+):

$$HCl(g) + H_2O(l) \rightarrow Cl^-(aq) + H_3O^+(aq)$$

The reaction keeps producing products until there is no more HCl left.

Some common strong acids are listed in Table 1.

TABLE 1 Some common strong acids

Name	Formula	Examples of uses
Hydrochloric acid	HCl	Maintaining the pH of swimming pools Household cleaning
Hydrobromic acid	HBr	In industrial processes such as polymerisation (HBr is one of the strongest inorganic acids)
Nitric acid	HNO_3	Producing fertilisers and explosives Extracting gold
Sulfuric acid (diprotic acid: only first ionisation is strong)	H_2SO_4	In car batteries and fertilisers

Weak bases

Weak bases react with water to establish an equilibrium and only partially ionise. A common weak base is ammonia, which reacts with water to form ammonium ions and hydroxide ions:

$$NH_3(g) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

To work out the hydroxide ion concentration for weak bases, you need to use the equilibrium constant K_b (see Chapter 4).

Strong bases

Strong bases such as sodium hydroxide completely dissociate in water. Each mole of sodium hydroxide dissolves to produce one mole of hydroxide ions in solution:

$$NaOH(s) \rightarrow Na^+(aq) + OH^-(aq)$$

CHALLENGE 3.2

Strong bases and the periodic table

Superbases, or Lewis bases, are strong bases that are impossible to keep in aqueous solution as they completely react with water. Identify which area of the periodic table host cations that produce superbases. Write a balanced chemical equation for a superbase reacting with water.

Some common strong bases are listed in Table 2.

TABLE 2 Some common strong bases

Name	Formula	Examples of uses
Sodium hydroxide	NaOH	Manufacturing paper, textiles, soaps and detergents Treating drinking water
Potassium hydroxide	KOH	Producing potassium carbonate, potassium phosphates, liquid fertilisers, potassium soaps and detergents
Lithium hydroxide	LiOH	In breathing gas purification systems for spacecraft and submarines

Electrical conductivity

A common way of determining the strength of an acid or base is to use an indicator. Another method is to test for **electrical conductivity**. Acids and bases are **electrolytes** because they dissociate into positive and negative ions (cations and anions). This means they can conduct an electric current. The cations and anions migrate towards the oppositely charged terminals (cathode and anode) of an electric circuit (see Chapter 7).

It is possible to make a battery from a lemon. The lemon battery can't produce electricity itself, but it allows two different metals to react with each other and therefore acts as an electrolyte. These kinds of reactions are called redox reactions and are explained in Chapter 6. One metal is reduced (gains electrons), whereas the other is oxidised (loses electrons).

electrical conductivity
the degree to which a material conducts an electric current

electrolyte
a substance that conducts electricity when melted or dissolved in a solution

CHECK YOUR LEARNING 3.2

Describe and explain

1 **Describe** the difference between weak and strong acids.

2 **Describe** the difference between concentrated and strong acids.

Apply analyse and interpret

3 **Determine** whether the following acids are strong or weak.

  a Sulfuric acid

  b Ethanoic acid

4 **Construct** a chemical equation for the dissociation of ammonia (NH_3) when it reacts with water (H_2O).

You can find the following resources for this section on your obook assess:

- » Student book questions
  3.2 Check your learning
- » Challenge
  3.2 Strong bases and the periodic table
- » Weblink
  Strong and weak acids
- » Weblink
  Electrical conductivity

3.3

Water as a weak electrolyte

KEY IDEAS

In this section, you will learn about:

- water as a weak electrolyte that can self-ionise
- the ionic product constant of water (K_w)
- the relationship between temperature, K_w and pH.

Advertisements for sport drinks often say that the drinks can carry electrical charges that stimulate muscles and nerves owing to electrolytes such as sodium, calcium and magnesium. Generally, solutions conduct a current when positive and negative ions are dissolved. Tap water is also a weak electrolyte because it can self-ionise and contains minerals and other elements.

FIGURE 1 Water is a weak electrolyte because it can self-ionise.

Self-ionisation of water

In water, a small fraction of H_2O molecules react to form H_3O^+ and OH^- ions:

$$2H_2O \rightleftharpoons H_3O^+ + OH^-$$

The whole process is called **self-ionisation of water** and can be written as an equilibrium expression (Figure 2).

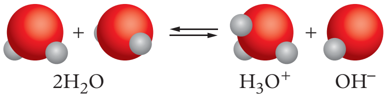


FIGURE 2 The self-ionisation of water

self-ionisation of water
the reaction in which a water molecule loses a hydrogen ion to become a hydroxide ion (OH^-) and the hydrogen ion immediately reacts with another water molecule to form a hydronium (H_3O^+)

Calculating concentration with ionic product constant of water, K_w

The concentration of water can be considered as constant because only a small fraction ionises. The self-ionisation reaction of water shown in Figure 2 can be expressed as an equilibrium constant called the **ionic product constant of water (K_w)**:

$$K_w = [H_3O^+][OH^-]$$

or simplified to:

$$K_w = [H^+][OH^-]$$

In pure water, for every hydrogen ion, there is an equal number of hydroxide ions:

$$[H^+]=[OH^-]$$

so

$$[H^+] = \sqrt{K_w}$$

ionic product constant of water (K_w)
the equilibrium constant for the self-ionisation of water

K_w has fixed values at different temperatures (Table 1). At room temperature (25°C or 298 K), $K_w = 1.00 \times 10^{-14}$, so:

$$\begin{aligned} K_w &= [H^+][OH^-] = [H^+]^2 \text{ when } [H^+] = [OH^-] \\ [H^+] &= \sqrt{K_w} \\ &= \sqrt{1 \times 10^{-14}} \\ &= 1 \times 10^{-7}\,\text{mol}\,\text{L}^{-1} \end{aligned}$$

To convert to pH:

$$\begin{aligned} \text{pH} &= -\log_{10}[H^+] \\ &= -\log_{10}(1.00 \times 10^{-7}) \\ &= 7 \end{aligned}$$

Pure water is a poor electrical conductor because it contains low levels of ions.

The reason that K_w has different values at different temperatures is because of Le Châtelier's principle. If the temperature of the water is increased, the equilibrium moves to lower the temperature. It does this by absorbing the extra heat. This means that the forward reaction is favoured and therefore more hydrogen and hydroxide ions are formed.

$$H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq)$$

The effect of this is an increased K_w value.

TABLE 1 The relationship between temperature, K_w and pH

T (°C)	T (K)	K_w	pH
0	273	0.11×10^{-14}	7.48
10	283	0.29×10^{-14}	7.27
20	293	0.68×10^{-14}	7.08
25	298	1.00×10^{-14}	7.00
30	303	1.47×10^{-14}	6.92

CHECK YOUR LEARNING 3.3

Describe and explain

1 **Explain** what K_w represents.

2 **Describe** the process of self-ionisation of water.

Investigate, evaluate and communicate

3 **Justify** the K_w value for water at 30°C. Show all your working.

4 **Evaluate** Table 1 and continue the table up to 100°C (in 10°C increments).

You can find the following resources for this section on your obook assess:

- » Student book questions
  3.3 Check your learning
- » Weblink
  Self-ionisation of water
- » Weblink
  K_w

3.4 The logarithmic pH scale and concentration equations

KEY IDEAS

In this section, you will learn about:

- the pH scale and what it means to be logarithmic
- how to calculate the concentration of hydrogen ions using the relationship $pH = -\log_{10}[H^+]$
- mathematical representations for solving problems for hydrogen ion concentrations, pH, hydroxide ion concentrations and pOH.

Acidity can be described by the hydrogen ion activity, or concentration. A solution is acidic if the H^+ concentration is between 1×10^0 and 1×10^{-7} mol L^{-1}. The hydrogen concentrations range over a large order of magnitude and include inconveniently small numbers, as listed in Table 1. This inconvenience motivated Søren Sørensen (1868–1939) to developed the pH scale, which is defined as the negative logarithm of the concentration of H^+ (or H_3O^+):

$$pH = -\log_{10}[H^+]$$

The term 'pH' comes from Latin and means 'potentia hydrogenii' – the power of hydrogen or the potential of hydrogen. pH values are generally between 0 and 14. It is important to understand that $\log_{10}$ stands for the logarithm with base 10. This means a solution of pH 3 (H^+ concentration of 1×10^{-3} mol L^{-1}) is 10 times more acidic than a solution of pH 4 (H^+ concentration of 1×10^{-4} mol L^{-1}).

FIGURE 1 Søren Sørensen developed the pH scale.

TABLE 1 The relationship between pH, H^+ and OH^-

pH	H^+ concentration (mol L^{-1})	OH^- concentration (mol L^{-1})
0	1×10^{0}	1×10^{-14}
1	1×10^{-1}	1×10^{-13}
2	1×10^{-2}	1×10^{-12}
3	1×10^{-3}	1×10^{-11}
4	1×10^{-4}	1×10^{-10}
5	1×10^{-5}	1×10^{-9}
6	1×10^{-6}	1×10^{-8}
7	1×10^{-7}	1×10^{-7}
8	1×10^{-8}	1×10^{-6}
9	1×10^{-9}	1×10^{-5}
10	1×10^{-10}	1×10^{-4}
11	1×10^{-11}	1×10^{-3}
12	1×10^{-12}	1×10^{-2}
13	1×10^{-13}	1×10^{-1}
14	1×10^{-14}	1×10^{0}

Calculating $[H^+]$

If you know the pH of a solution, you can calculate the concentration of hydrogen ions by applying the inverse of the equation $pH = -\log_{10}[H^+]$:

$$[H^+] = 10^{-pH}$$

Use the inverse log on your calculator:

$$[H^+] = \log^{-1}(-pH)$$

So, for a solution of pH 6.5, the hydrogen ion concentration is $[H^+] = 10^{-6.5}$, which equals 3×10^{-7} mol L^{-1}.

Calculating pH

To find the pH of an aqueous solution, you need to know the concentration of the hydrogen ions (or hydroniums). You can then calculate the pH from the expression:

$$pH = -\log_{10}[H^+]$$

WORKED EXAMPLE 3.4A

Find the pH of a 0.0123 M hydrochloric acid (HCl) solution.

SOLUTION

HCl is a strong acid and is completely ionised. Therefore, the hydrogen or hydronium concentration is also 0.0123 M.

$$\begin{aligned} pH &= -\log_{10}(0.0123) \\ &= 1.910 \end{aligned}$$

Therefore, the pH is 1.91.

Calculating pOH

pOH
a measure of hydroxide ion concentration in a solution and consequently a measure of basicity

pOH is a measure of hydroxide ion (OH^-) concentration. So, pOH is a measure of the alkalinity of a solution. To calculate the pOH of a solution, you need to know the concentration of the hydroxide ions in moles per litre (molarity). Then calculate pOH as follows:

$$pOH = -\log_{10}[OH^-]$$

WORKED EXAMPLE 3.4B

Find the pOH of a solution with a hydroxide ion concentration of 4.2×10^{-5} M.

SOLUTION

$$\begin{aligned} pOH &= -\log_{10}(4.2 \times 10^{-5}) \\ &= 4.4 \end{aligned}$$

Therefore, the pOH is 4.4.

At 25°C, for an aqueous solution, the relationship between pH and pOH is:

$$pH + pOH = 14$$

Calculating $[OH^-]$

Hydroxide ion (OH^-) concentration can be obtained by using the pH or pOH value. If the pH value is given, convert the value into pOH by rearranging the previous equation:

$$\text{pH} + \text{pOH} = 14$$

$$\text{pOH} = 14 - \text{pH}$$

and rearranging

$$\text{pOH} = -\log_{10}[OH^-]$$

$$[OH^-] = 10^{-\text{pOH}}$$

to gain the hydroxide ion concentration.

Worked example 3.4C demonstrates how to determine $[OH^-]$ if you know the pH.

WORKED EXAMPLE 3.4C

Find the hydroxide ion concentration of a solution of NaOH with a pH of 13.0.

SOLUTION

1 Convert pH to pOH:

$$\begin{aligned} \text{pH} + \text{pOH} &= 14 \\ \text{pOH} &= 14 - \text{pH} \\ \text{pOH} &= 14 - 13.0 \\ &= 1.0 \end{aligned}$$

2 Apply $[OH^-] = 10^{-\text{pOH}}$

$$\begin{aligned} [OH^-] &= 10^{-1.0} \\ &= 0.1\,\text{M} \end{aligned}$$

Therefore, the hydroxide ion concentration is 0.1 M.

WORKED EXAMPLE 3.4D

The optimal pH level of a backyard swimming pool is 7.4, which is the same pH level as the human eye and mucous membranes. Convert a pH of 7.4 into:

a pOH

b hydrogen ion concentration.

SOLUTION

a

$$\begin{aligned} \text{pH} + \text{pOH} &= 14 \\ \text{pOH} &= 14 - \text{pH} \\ \text{pOH} &= 14 - 7.4 \\ &= 6.6 \end{aligned}$$

b

$$\begin{aligned} \text{pH} &= -\log_{10}[H^+] \\ [H^+] &= 10^{-\text{pH}} \\ &= 10^{-7.4} \\ &= 3.98 \times 10^{-8}\,\text{M} \end{aligned}$$

CASE STUDY 3.4

pH values exceeding the common scale

Some of the most acidic water ever measured is water at mine sites. The water can have a pH value as low as –3.6. These extremely low values can result from pyrite oxidation and high concentrations due to evaporation.

Common pH measurement methods do not work under these conditions, so glass membrane electrodes are used. The glass membrane electrodes must be calibrated for low pH values. This can be challenging because below pH 0.5, a graph of pH values becomes non-linear.

FIGURE 2 The water run-off from some mines has a very low pH, which is outside the common pH scales of 1–14.

CHECK YOUR LEARNING 3.4

Describe and explain

1 **Identify** the relationship between pH value and H^+ concentration.

2 **Contrast** acidic solutions of pH 3 and pH 5.

3 **Calculate** the pH of a sodium hydroxide solution at 25°C (hydroxide ion concentration is 0.0077 M).

4 **Calculate** the pOH of a solution with a hydroxide ion concentration of 3.8×10^{-4} M.

5 **Calculate** the hydroxide ion concentration of a solution of NaOH with pH 11.5.

Apply, analyse and interpret

6 The hydrogen ion concentration in human blood is 4.0×10^{-8} M. **Determine** the pH and pOH of human blood.

You can find the following resources for this section on your obook assess:

- » Student book questions
  3.4 Check your learning
- » Weblink
  Calculating pH and pOH
- » Weblink
  Søren Sørensen

3.5

The Brønsted–Lowry model

KEY IDEAS

In this section, you will learn about:

- using the Brønsted–Lowry model to explain the relationship between acids and bases in equilibrium systems
- using chemical equations to illustrate the transfer of hydrogen ions between conjugate acid–base pairs
- amphiprotic species acting as Brønsted–Lowry acids and bases
- how to identify and deduce the formula of the conjugate acid (base) of any Brønsted–Lowry bases (or acids).

Arrhenius acids are species that can increase the concentration of H^+ in aqueous solutions. Arrhenius bases are species that can increase the concentration of OH^-. A limitation of the Arrhenius theory is that it only describes acid–base reactions in water.

In 1923, chemists Johannes Nicolaus Brønsted and Thomas Martin Lowry independently developed definitions of acids and bases and their ability to donate or accept protons (H^+). The Brønsted–Lowry model is more general and applies to a broader range of chemical reactions than the Arrhenius theory. The Brønsted–Lowry model defines:

- acids as any species that can donate protons (H^+)
- bases as any species that accept protons.

CHALLENGE 3.5A

Battery acid reaction

Research the chemical reactions for a functioning battery consisting of lead plates and sulfuric acid. Why are there two reactions?

Conjugate acid–base pairs

conjugate acid
an acid formed when a base accepts an H^+

conjugate base
a based formed by removing an H^+ from an acid

According to the Brønsted–Lowry acid–base theory, a **conjugate acid** is a base that accepts H^+ protons and a **conjugate base** is an acid that donates protons. The equation in an equilibrium can be represented as:

$$\text{acid} + \text{base} \rightleftharpoons \text{conjugate base} + \text{conjugate acid}$$

An example of an acid–base reaction is ammonium (NH_4^+), as the acid, reacting with hydroxide (OH^-), as the base:

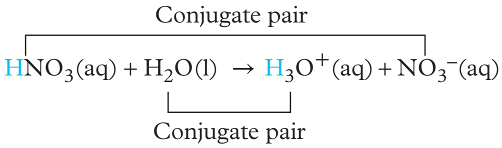
$$NH_4^+ + OH^- \rightleftharpoons NH_3 + H_2O$$

FIGURE 1 Sulfuric acid dissolves lead plates in a standard battery.

Ammonium donates a hydrogen ion to the hydroxide ion to produce a water molecule and the conjugate base ammonia (NH_3). The water molecule is the conjugate acid of the hydroxide ion. The reverse reaction can also occur, in which NH_4^+ is then referred to as the conjugate acid of ammonia and OH^- as the conjugate base of water. For this reason, it is important to recognise the terms ‘acid’, ‘base’, ‘conjugate acid’ and ‘conjugate base’ are not fixed for a certain chemical compound, but are interchangeable depending on the direction of the reaction taking place.

Identifying conjugate acids and bases

You need to be able to determine the formulas of the conjugate acid/base of a Brønsted–Lowry base/acid. Consider the chemical equation for the reaction of nitric acid and water:



$$HNO_3(aq) + H_2O(l) \rightarrow H_3O^+(aq) + NO_3^-(aq)$$

Nitric acid donates a hydrogen ion (in blue), so is acting as a Brønsted–Lowry acid. Water accepts this proton to form H_3O^+ and acts as a Brønsted–Lowry base. Consequently, H_3O^+ is the conjugate acid of water and NO_3^- is the conjugate base of HNO_3. The conjugate pairs are indicated above and are compounds that differ by the presence of one proton (H^+).

Some common Brønsted–Lowry acids and bases are listed in Table 1.

TABLE 1 Some common Brønsted–Lowry acids and bases and their conjugates

Acid	Conjugate base	Base	Conjugate acid
HCl	Cl^-	OH^-	H_2O
HNO_3	NO_3^-	NH_3	NH_4^+
H_2SO_4	HSO_4^-	C_5H_5N	$C_5H_5NH^+$
H_2O	OH^-	S^{2-}	HS^-

Amphiprotic species

amphiprotic
a molecule or ion that can either donate or accept a proton and so therefore can act as an acid or base

Some molecules (or ions) can donate or accept a proton depending on the other reactants. These substances are called **amphiprotic** substances and can act as either an acid or a base (*amphi* is Greek for ‘both’). Common examples are water, amino acids and hydrogencarbonate ions (HCO_3^-).

Hydrogencarbonate ions

In aqueous solution, HCO_3^- reacts with water in two different ways:

$$HCO_3^-(aq) + H_2O(l) \rightarrow CO_3^{2-}(aq) + H_3O^+(aq)$$

$$HCO_3^-(aq) + H_2O(l) \rightarrow H_2CO_3(aq) + OH^-(aq)$$

In the first equation, HCO_3^- acts as a proton donor (acid).

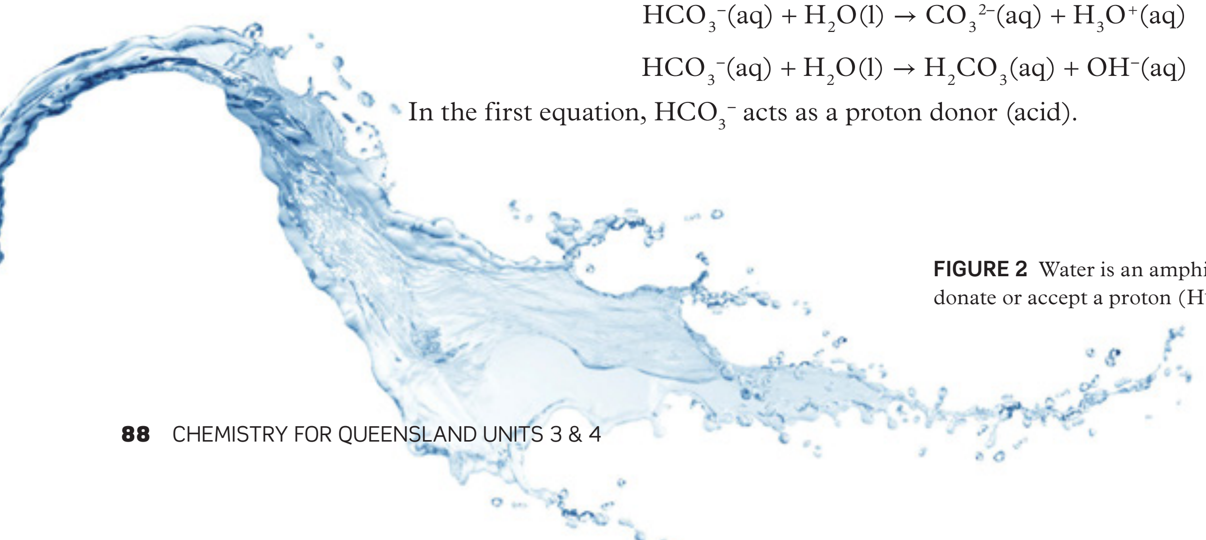


FIGURE 2 Water is an amphiprotic species. It can donate or accept a proton (H^+ ion).

In the second equation, HCO_3^- acts as a proton acceptor (base).

In alkaline (basic) solution, HCO_3^- acts as an acid:

$$\underset{\text{acid}}{HCO_3^-(aq)} + OH^-(aq) \rightarrow H_2O(l) + \underset{\text{conjugate base}}{CO_3^{2-}(aq)}$$

However, when HCO_3^- is placed in an acid solution, it acts as a base:

$$\underset{\text{base}}{HCO_3^-(aq)} + H^+(aq) \rightarrow \underset{\text{conjugate acid}}{H_2CO_3(aq)}$$

Note that these two reactions go to completion and therefore have one-directional arrows.

CHALLENGE 3.5B

Amphiprotic vs amphoteric

The two different terms, amphiprotic and amphoteric, commonly get confused in acid base chemistry. Explain the key difference between the two terms and provide an example of both to highlight this difference.

CHECK YOUR LEARNING 3.5

Describe and explain

1 **Deduce** the conjugate bases of nitric acid (HNO_3) and ammonium (NH_4^+).

2 **Identify** the two conjugate acid–base pairs of the following reaction:

$$HSO_4^-(aq) + PO_4^{3-}(aq) \rightarrow SO_4^{2-}(aq) + HPO_4^{2-}(aq)$$

hydrogen sulfate + phosphate ion →
sulfate + hydrogen phosphate

3 **Explain** what amphiprotic species are.

Apply, analyse and interpret

4 **Determine** the amphiprotic species from the following list and write chemical equations illustrating the amphiprotic character:

a HSO_3^-
b S^{2-}
c CO_3^{2-}
d $H_2PO_4^-$
e H_2O

5 Perchloric acid ($HClO_4$) reacts with water as follows:

$$HClO_4(aq) + H_2O \rightleftharpoons H_3O^+(aq) + ClO_4^-(aq)$$

Determine the two conjugate acid–base pairs.

You can find the following resources for this section on your obook assess:

- Student book questions 3.5 Check your learning
- Challenge 3.5A Battery acid reactions
- Challenge 3.5B Amphiprotic vs amphoteric
- Weblink Brønsted–Lowry model

SCIENCE AS A HUMAN ENDEAVOUR

3.6 The history of acids and bases

KEY IDEAS

In this section, you will learn about:

- the history of acids and bases.

Today, we know a lot about acids and bases and use them every day, so it can be easy to forget that it took centuries for them to be thoroughly understood.

Acids and bases in ancient science

Ancient Greek philosophers and scientists, such as Aristotle, had only a vague understanding of the properties and applications of acids and bases. During this time, humans first attempted to categorise substances. One of the properties used to categorise substances was taste, and so scientists divided substances into sour, bitter, salty and sweet. This ancient Greek knowledge was passed on to the Romans, who referred to vinegar or lemon juice as 'acid', derived from the Latin meaning 'sour tasting'.

Although the ancient Greeks couldn't describe acids and bases in our modern scientific language, they knew that bases neutralised acids and used this principle to benefit their lives. For example, they produced soap (a base) with ash from fire and animal fat. The basic soap neutralised and cleaned the acidic skin.

Alchemy

In medieval Europe, alchemists began to understand more about acids and bases. Their experiments revealed that stronger acid solutions could increase the rate of corrosion of metals and dissolve specific rocks. Medieval and Islamic alchemists made use of acids and bases such as:

- sodium carbonate (Na_2CO_3)
- potassium carbonate (K_2CO_3)
- ammonia (NH_3)
- hydrochloric acid (HCl)
- sulfuric acid (H_2SO_4).

After the 13th century, acid–base indicators such as litmus were used. Robert Boyle (1627–91) found that some plants changed colour when immersed in acids or bases.

FIGURE 1 The ancient Greek philosopher and scientist Aristotle (born 384 BCE) made preliminary investigations into acids and bases.

Classifying acids and bases

The first known systematic attempt to classify and chemically characterise acids and bases was made by French chemist Antoine Lavoisier (1743–94). He believed that acidity was caused by the presence of oxygen in a compound. Lavoisier came up with the word ‘oxygen’, which stems from the Greek words *oxys*, meaning ‘sour’, and *genes*, meaning ‘born’. His theory turned out to be wrong.

In the 18th century, chemists discovered neutralisation reactions between acids and bases, possibly in laboratories like the one in Figure 2.

FIGURE 2 Medieval alchemists experimented with acids and bases.

CHECK YOUR LEARNING 3.6

Describe and explain

1 **Describe** the involvement of the following people in the discovery of acid and bases.
  a Aristotle
  b Robert Boyle
  c Antoine Lavoisier

Investigate, evaluate and communicate

2 **Research** the history of acids and bases and **construct** a timeline of the main events.

You can find the following resources for this section on your obook assess:

- » **Student book questions**
  3.6 Check your learning
- » **Weblink**
  Medieval alchemy
- » **Weblink**
  Antoine Lavoisier

3.7

Buffer solutions

KEY IDEAS

In this section, you will learn about:

- how buffer solutions conjugate and resist a change in pH
- predicting a buffer solution's response to the addition of hydrogen ions and hydroxide ions.

It is crucial that many chemical and biological systems maintain their pH within a certain range. The general equilibrium equation is:

$$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$

where HA is a weak acid and A^- is its conjugate base.

For example, the pH range of the blood of a healthy person is typically 7.35–7.45, which is a bit more basic than tap water and a bit more acidic than seawater. If the pH is too low, the body suffers from acidosis; if it is too high, alkalosis occurs. In extreme cases, either of these conditions can lead to death.

buffer solution
a solution that resists changes in pH when small quantities of acids or alkalis are added

The body maintains a safe pH level through **buffer solutions**. A buffer solution contains appreciable amounts of a weak acid and its conjugate base, or a weak base and its conjugate acid. Consequently, a buffer solution resists change in pH when small amounts of acid or base are added. Table 1 lists some examples of buffer solutions made from weak acids and their conjugate bases.

TABLE 1 Examples of some buffer solutions

Buffer	Weak acid	Conjugate base
Ethanoic acid/ethanoate	Ethanoic acid	Sodium ethanoate
Ammonium chloride/ammonia	Ammonium chloride	Ammonia
Bicarbonate/carbon dioxide	Bicarbonate	Carbon dioxide
Citric acid/citrate	Citric acid	Citrate

How buffer solutions resist a change in pH

Human blood is maintained within the vital limits of pH 7.35–7.45 by an important buffer system. This buffer system consists of the weak acid carbonic acid (H_2CO_3) and its conjugate base bicarbonate (HCO_3^-).

If a small amount of acid is added to the blood, the acid reacts with the bicarbonate anions:

$$H_3O^+ + HCO_3^- \rightleftharpoons H_2CO_3 + H_2O$$

If a small amount of base is added to the blood, the base reacts with the carbonic acid:

$$OH^- + H_2CO_3 \rightleftharpoons HCO_3^- + H_2O$$

These two reactions control the pH of the blood by removing excess hydronium and hydroxide ions.

SUGGESTED PRACTICAL

3.7 Measuring pH
Go to your obook assess »

Le Châtelier's principle and buffer solutions

Le Châtelier's principle can be used to predict the response of a buffer solution to the addition of acids or bases. In general, when stress is applied to a system in equilibrium, the reaction shifts in the direction that reduces stress. For example, the chemical reaction describing the equilibrium between carbonic acid and bicarbonate is as follows:

$$CO_2(g) + H_2O(l) \rightleftharpoons H_2CO_3(aq) \rightleftharpoons HCO_3^-(aq) + H^+(aq)$$

If a process releases acid (H^+) into the blood, then the reaction shifts to the left and absorbs the excess H^+ ions. Because H_2CO_3 is unstable, it decomposes to form carbon dioxide and water.

If a process releases base (OH^-) into the blood, then the equilibrium shifts to the right, and produces H^+, which react with the excess OH^- ions.

Study tip

For the exam, you will not need to perform any buffer calculations.

CASE STUDY 3.7

Controlling the pH of shampoo

The pH of many household and cosmetic products needs to be controlled to prevent skin irritation. Most shampoos are slightly acidic and contain citric acid. Shampoos also contain a conjugate base such as sodium citrate, which acts as a buffer and prevents skin irritation.

Studies also show that a lower pH flattens the scales on a hair follicle, making the hair feel smooth. If you wash your hair with soap (alkaline), your hair feels coarse because the scales on your hair follicles are not flat, making your hair frizzy.

CHECK YOUR LEARNING 3.7

Describe and explain

1 **Explain** what a buffer solution is and give an example.

2 **Describe** the buffer response when a small amount of acid is added to human blood.

Investigate, evaluate and communicate

3 **Consider** the following equilibrium equation:

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

  a **Determine** which molecule/ion is an acid, conjugate base, base or conjugate acid.

  b **Apply** Le Châtelier's principle and **predict** what would happen if a small amount of acid were added.

  c **Discuss** what would happen if a small amount of base were added.

You can find the following resources for this section on your obook assess:

- » Student book questions
  3.7 Check your learning
- » Suggested practical
  3.7 Measuring pH
- » Weblink
  Buffer solutions

CHAPTER 3

Review

Chapter summary

- **3.1** Acids are proton (H^+) donors. Monoprotic acids can donate one H^+; polyprotic acids can donate more than one H^+.
- **3.2** A strong acid completely ionises, whereas a weak acid only partially ionises. Strong bases such as sodium hydroxide fully dissociate in water.
- **3.3** Water can self-ionise and is therefore slightly conductive. The self-ionisation reaction of water can be expressed with the ionic product constant of water (K_w), which is temperature dependent.
- **3.4** The pH scale is logarithmic. This means a solution of pH 3 is ten times more acidic than a solution of pH 4. Hydrogen and hydroxide ion concentrations can be determined from the equation $pH = -\log_{10}[H^+]$.
- **3.5** The relationship between acids and bases in an equilibrium system can be explained by using the Brønsted–Lowry model. The transfer of hydrogen ions between conjugate acid–base pairs can be illustrated by using chemical equations.
- Amphiprotic species (proton donor and acceptor) can act as both acids and bases.
- **3.6** The interest in acids and bases dates back to the ancient Greeks and has been continually developed and refined to produce the model we use today.
- **3.7** Buffer solutions conjugate and resist a change in pH.
- Many systems in the human body involve buffers.
- It is possible to predict a buffer solution's response to addition of hydrogen ions or hydroxide ions.

Key terms

- amphiprotic
- buffer solution
- concentration
- conjugate acid
- conjugate base
- electrical conductivity
- electrolyte
- ionic product constant of water (K_w)
- monoprotic acid
- pH
- pOH
- polyprotic acid
- proton donor
- self-ionisation of water
- strength
- strong acid
- strong base
- weak acid
- weak base

Key formulas

Ionic product constant of water	$K_w = [H^+][OH^-]$
pH	$pH = -\log_{10}[H^+]$
pOH	$pOH = -\log_{10}[OH^-]$
At 25°C for an aqueous solution	$pH + pOH = 14$

Revision questions

The relative difficulty of these questions is indicated by the number of stars beside each question number: ★ = low; ★★ = medium; ★★★ = high.

Multiple choice

1 Monoprotic acids are:
- **A** acids that are only used once
- **B** acids that can donate one hydrogen ion per molecule
- **C** antacids
- **D** conjugate bases (used as a synonym).

2 Identify the three acids from:
- **A** milk
- **B** vinegar
- **C** egg white
- **D** rain water.

3 pH 6 is less acidic than pH 2 by:
- **A** 1000 times
- **B** three times
- **C** 10 000 times
- **D** 3000 times.

Short answer

Describe and explain

★**4** **Explain** the difference between strong and weak acids and bases.

★**5** **Define** 'pH' and 'pOH'.

★**6** **Define** 'amphiprotic'.

★**7** **Explain** how a buffer solution maintains a steady pH.

★**8** **Identify** three examples of solutions that need to be maintained at a stable pH.

★**9** **Calculate** the pOH and hydrogen ion concentration of a solution at pH:
- **a** 8.5
- **b** 3.6
- **c** 10.2.

★★**10** **Calculate** the hydroxide ion concentration of a solution of NaOH with pH 12.0.

Apply, analyse and interpret

★★**11** **Determine** the pH of a 0.0321 M hydrochloric acid (HCl) solution.

★★**12** **Determine** the conjugate bases of hydrogen sulfate ion (HSO_4^-) and phosphoric acid (H_3PO_4).

Investigate, evaluate and communicate

★★**13** **Investigate** different buffer solutions in your body using an appropriate resource and **evaluate** their role and their importance.

★★★**14** **Investigate** why pH + pOH = 14 for an aqueous solution at 25°C. **Consider** how this equation may differ with a change in temperature.

You can find the following resources for this section on your obook assess:

- Student book questions
  Chapter 3 Revision questions
- Revision notes
  Chapter 3
- assess quiz
  Auto-correcting multiple-choice quiz
- Flashcard glossary
  Chapter 3

CHAPTER 4

Dissociation constants and acid-base indicators

pH is not the only way to describe the acidity or basicity of a solution. This chapter discusses ionisation constants, another quantitative way of describing acids and bases, and their relative strengths. In the second part of the chapter, you will learn about acid–base indicators and how to determine which indicator to choose for a titration. Red cabbage juice can be used as a pH indicator. In strong acids the indicator turns red, at pH 7 the indicator is purple and in strong alkaline solutions the indicator is yellow.

OBJECTIVES

- → Recognise that the strength of an acid is explained by the degree of ionisation at equilibrium in aqueous solution, which can be represented with chemical equations and equilibrium constants (K_a).
- → Determine the expression for the dissociation constant for weak acids (K_a) and weak bases (K_b) from balanced chemical equations.
- → Analyse experimental data to determine and compare the relative strengths of acids and bases.
- → Use appropriate mathematical representation to solve problems, including calculating dissociation constants (K_a and K_b) and the concentration of reactants and products.
- → Understand that an acid–base indicator is a weak acid or a weak base where the components of the conjugate acid–base pair have different colours; the acidic form is of a different colour to the basic form.
- → Explain the relationship between the pH range of an acid–base indicator and its pK_a value.
- → Recognise that indicators change colour when the pH = pK_a and identify an appropriate indicator for a titration, given equivalence point of the titration and pH range of the indicator.

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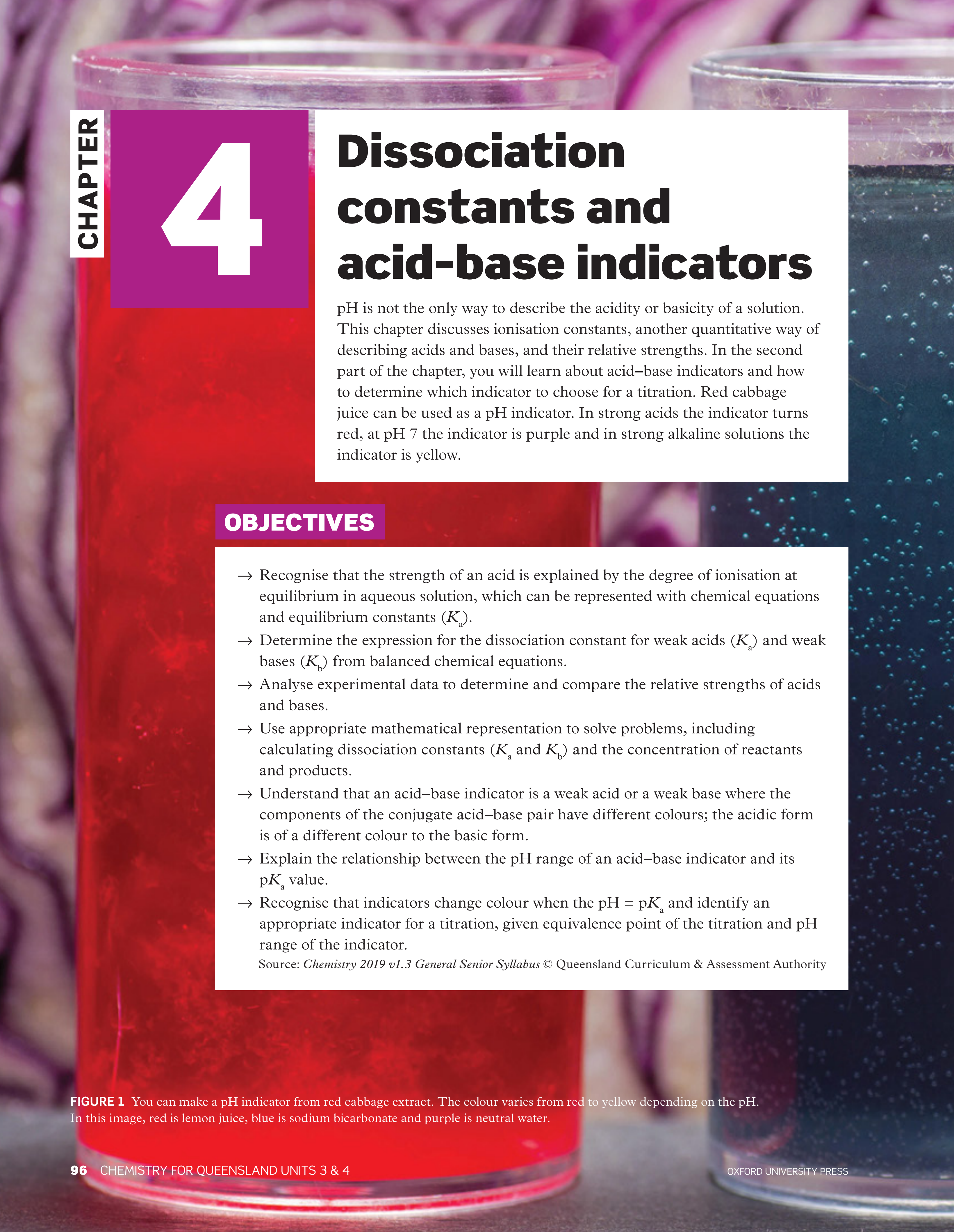
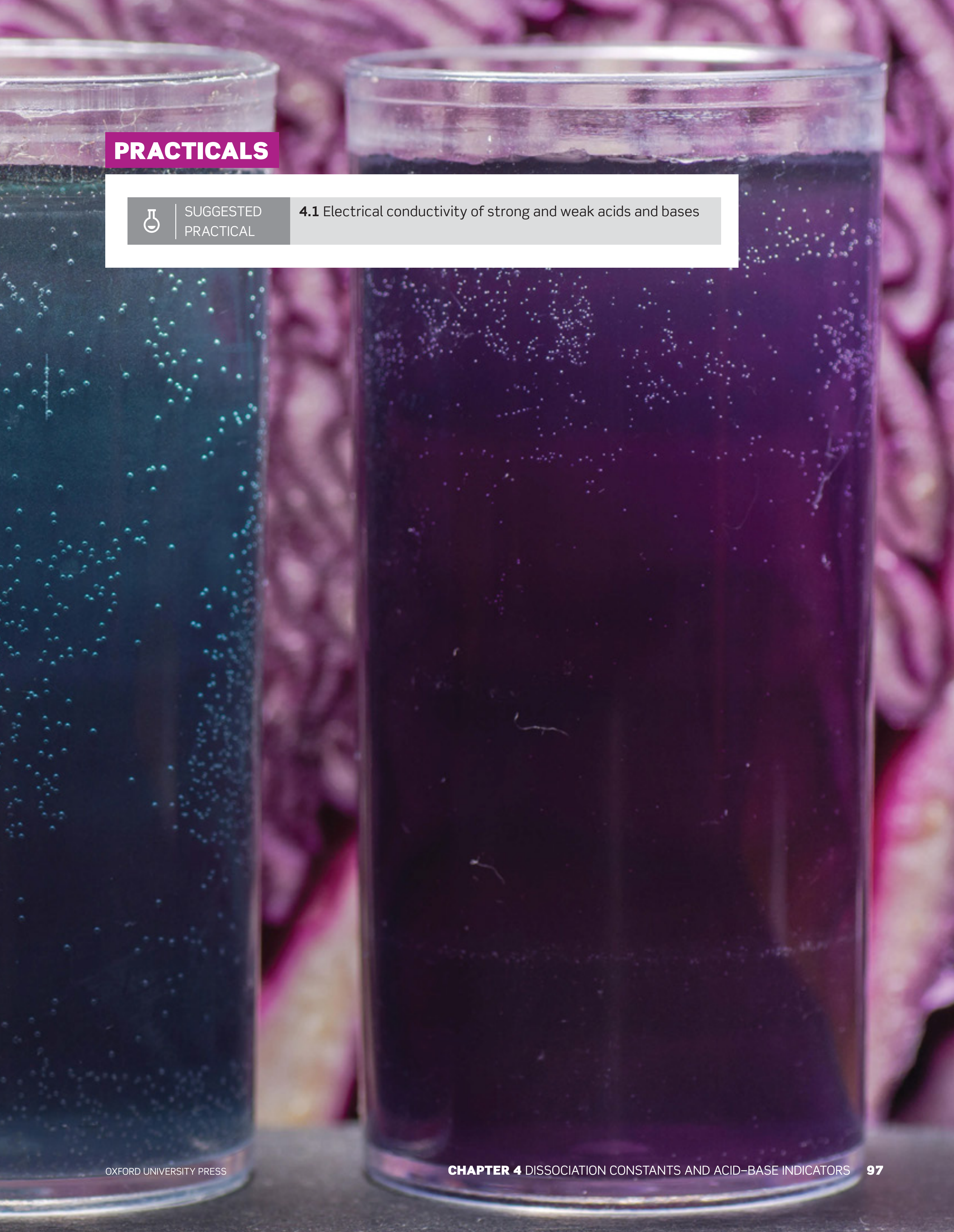


FIGURE 1 You can make a pH indicator from red cabbage extract. The colour varies from red to yellow depending on the pH. In this image, red is lemon juice, blue is sodium bicarbonate and purple is neutral water.



PRACTICALS

SUGGESTED PRACTICAL **4.1** Electrical conductivity of strong and weak acids and bases

4.1

Strength of acids and bases

KEY IDEAS

In this section, you will learn about:

- how the strength of acids can be explained by the degree of ionisation
- the degree of ionisation, which can be expressed with chemical equations and equilibrium constants (K_a)
- how to determine the dissociation constant for weak acids and bases
- comparing the relative strengths of acids and bases.

The proverb 'What you don't know cannot hurt you' might not be applicable to chemistry. If you handle acids or bases, you want to know how strong they are and what personal protective equipment you should wear. Strong acids and bases can cause severe burns like the one in Figure 1.

FIGURE 1 Both acids and bases can cause severe burns to the skin.

Dissociation constants for acids

As explained in Chapter 3, the strength of an acid is given by its degree of ionisation in an aqueous solution. If the ionisation process is at equilibrium, a general chemical equation can be written as:

$$HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)$$

where HA represents an acid that dissociates into the conjugate base A^- and a hydronium ion (H_3O^+).

acid dissociation constant (K_a) the equilibrium constant for the dissociation of an acid in aqueous solution

The chemical species are considered to be in equilibrium when their concentrations do not change over time. When the concentration of an acid does not change over time, the reaction is at equilibrium. The equilibrium constant (also known as acid ionisation constant or **acid dissociation constant (K_a)**) can be written as:

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

You can see that K_a is a ratio of the products to the reactants. The more an acid dissociates into H_3O^+ and conjugate base (A^-), the stronger the acid is and consequently the greater the value of K_a. In other words, if K_a is large, the products are favoured; if K_a is small, the undissociated acid is favoured.

So, the larger the K_a value, the stronger the acid.

- Weak acids are defined as having $K_a < 1$.
- Strong acids are defined as having $K_a > 1$.

SUGGESTED PRACTICAL

4.1 Electrical conductivity of strong and weak acids and bases
Go to your obook assess »

Carboxylic acids (RCOOH), such as ethanoic acid and methanoic acid, are weak acids. Carbonic acid is also a weak acid – it is found in soft drinks (Figure 2) and acid rain (Figure 3).

Because pH is related to the concentration of H_3O^+ ions, pH is a function of K_a. It is important to realise that as pH decreases, K_a increases.

FIGURE 2 Carbon dioxide is added to soft drinks. When it dissolves in water, it forms carbonic acid.

Dissociation constant for bases

As explained in Chapter 3, weak acids and weak bases only partially ionise and therefore do not fully dissociate. To quantify the relative strengths of weak acids and bases, you can look at their dissociation constants.

Similar to acids, the general equilibrium equation for bases is as follows:

$$B(aq) + H_2O(l) \rightleftharpoons BH^+(aq) + OH^-(aq)$$

where B represents a base, and BH^+ and OH^- are the products.

The **base dissociation constant (K_b)** for a Brønsted–Lowry base is:

$$K_b = \frac{[BH^+][OH^-]}{[B]}$$

K_b indicates the equilibrium position. If K_b is large, the product side of the reaction is favoured. If K_b is small, the base is favoured.

So, the larger the K_b value, the stronger the base.

- Weak bases are defined as having a low K_b.
- Strong bases are defined as having a high K_b.

Study tip

The conjugate base of a weak acid is a strong base. The conjugate acid of a weak base is a strong acid.

base dissociation constant (K_b) the equilibrium constant for the dissociation of a base in aqueous solution

Relationship between K_a and K_b

Hydrochloric acid is a relatively strong acid. Its reaction with water is:

$$HCl(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + Cl^-(aq)$$

The equilibrium constant expression for the ionisation of HCl is:

$$K_a = \frac{[H_3O^+][Cl^-]}{[HCl]}$$

The chloride ion (Cl^-) is a base. The reaction for Cl^- reacting with water is:

$$Cl^-(aq) + H_2O(l) \rightleftharpoons HCl(aq) + OH^-(aq)$$

and the corresponding equilibrium constant expression for the reaction of Cl^- with water is:

$$K_b = \frac{[OH^-][HCl]}{[Cl^-]}$$

Although the reactions appear similar, they produce different products. An acid reacting with water produces H_3O^+ and a base reacting with water produces OH^-.

If you multiply K_a of an acid by K_b of its conjugate base, the product is the dissociation constant of water (K_w).

$$\begin{aligned} K_a \times K_b &= \left(\frac{[H_3O^+][Cl^-]}{[HCl]}\right)\left(\frac{[OH^-][HCl]}{[Cl^-]}\right) \\ &= \left(\frac{[H_3O^+][Cl^-]}{[HCl]}\right)\left(\frac{[OH^-][HCl]}{[Cl^-]}\right) \\ &= [H_3O^+] \times [OH^-] \\ &= K_w \end{aligned}$$

The water dissociation constant has a value of 1.0×10^{-14} at 25°C. K_w represents the equilibrium constant for the reaction of H_3O^+ and OH^- to produce two water molecules.

$$H_3O^+ (aq) + OH^- (aq) \rightleftharpoons 2H_2O(l)$$

Worked example 4.1 demonstrates how to express equilibrium constants, given a chemical reaction.

WORKED EXAMPLE 4.1

Write the equilibrium constants for the following reactions.

a $CH_3CO_2H(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3CO_2^-(aq)$

b $NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$

SOLUTION

a Use the acid equilibrium constant equation:

$$\begin{aligned} K_a &= \frac{[H_3O^+][A^-]}{[HA]} \\ &= \frac{[H_3O^+][CH_3CO_2^-]}{[CH_3CO_2H]} \end{aligned}$$

b Use the base equilibrium constant equation:

$$\begin{aligned} K_b &= \frac{[BH^+][OH^-]}{[B]} \\ &= \frac{[NH_4^+][OH^-]}{[NH_3]} \end{aligned}$$

CHALLENGE 4.1

The danger of acids

What happens chemically when a strong acid such as the acid of a car battery comes in contact with your skin? Why does it burn you?

FIGURE 3 This statue has been eroded by acid rain (H_2CO_3) to become almost unrecognisable.

Introducing pK_a and pK_b

Values for K_a and K_b span a wide range. So, the acid dissociation constant is often expressed as **pK_a**, where:

$$pK_a = -\log_{10} K_a$$

The lower the value of pK_a, the higher the value of K_a and the greater the ionisation of the acid in water.

Similarly, the base dissociation constant can be expressed as **pK_b**:

$$pK_b = -\log_{10} K_b$$

The lower the value of pK_b, the higher the value of K_b and the greater the ionisation of the base in water.

Tables 1 and 2, on the following pages, show some selected acids and bases and their strength.

pK_a
a measure of acid strength; the negative logarithm (to base 10) of the acid dissociation constant

pK_b
a measure of base strength; the negative logarithm (to base 10) of the base dissociation constant

TABLE 1 Selected acids and their conjugate base with their K_a, pK_a, K_b and pK_b values

Acid	Formula	K_a	pK_a	Relative acid strength increasing ↓	Conjugate base	K_b	pK_b	Relative base strength increasing ↑
Carbonic acid (2)*	HCO_3^-	4.7×10^{-11}	10.3		CO_3^{2-}	4.7×10^{3}	3.7	
Carbonic acid (1)	H_2CO_3	4.4×10^{-7}	6.35		HCO_3^-	4.4×10^{7}	7.65	
Acetic acid	CH_3COOH	1.8×10^{-5}	4.74		$CH_3CO_2^-$	5.8×10^{-10}	9.24	
Formic acid	HCO_2H	1.8×10^{-4}	3.75		HCO_2^-	5.6×10^{-11}	10.25	
Sulfuric acid (2)	HSO_4^-	1.0×10^{-2}	1.99		SO_4^{2-}	9.8×10^{-13}	12.01	
Hydronium ion	H_3O^+	1.0	0.0		H_2O	1.0×10^{-14}	14.0	
Nitric acid	HNO_3	2.3×10^{1}	–1.37		NO_3^-	4.3×10^{-16}	15.37	
Sulfuric acid (1)	H_2SO_4	1.0×10^{2}	–2		HSO_4^-	1.0×10^{-16}	16.0	
Hydrochloric acid	HCl	1.0×10^{6}	–5.9		Cl^-	1.0×10^{13}	19.9	
Hydroiodic acid	HI	2.0×10^{9}	–9.3		I^-	5.0×10^{-24}	23.3	

*The numbers in the brackets refer to the ionisation step of the polyprotic acids.

TABLE 2 Selected bases and their K_b and pK_b values at 25°C

Name	Formula	K_b	pK_b	
Ammonia	NH_3	1.8×10^{-5}	4.75	Relative base strength increasing ⟶
Methylamine*	CH_3NH_2	4.6×10^{-4}	3.34	
Ethylamine	$C_2H_5NH_2N$	4.5×10^{-4}	3.35	
Barium hydroxide (first OH^-)	$Ba(OH)_2$	7.1×10^{-1}	0.15	
Barium hydroxide (second OH^-)		2.3×10^{-1}	0.64	
Lithium hydroxide†	LiOH	1.1×10^{0}	−0.04	
Sodium hydroxide	NaOH	3.6×10^{0}	−0.56	
Potassium hydroxide	KOH	5.0×10^{0}	−0.7	
Rubidium hydroxide	RbOH	2.5×10^{1}	−1.4	
Caesium hydroxide	CsOH	5.8×10^{1}	−1.76	

*All amines are weak bases.

†All group 1 hydroxides are strong bases.

CHECK YOUR LEARNING 4.1

Describe and explain

1 **Describe** what a dissociation constant is.

2 **Construct** the general chemical equation of an ionisation process at equilibrium for an acid and **explain** the process.

Apply, analyse and interpret

3 **Determine** the expression for K_a for the following reactions.

a $H_3PO_4(aq) + H_2O(l) \rightleftharpoons H_2PO_4^-(aq) + H_3O^+(aq)$

b $HCO_2H(aq) + H_2O(l) \rightleftharpoons H_2CO_2^-(aq) + H_3O^+(aq)$

4 **Determine** the expression for K_b for the following reactions.

a $NH_2^-(aq) + H_2O(l) \rightleftharpoons NH_3(aq) + OH^-(aq)$

b $HS^-(aq) + H_2O(l) \rightleftharpoons H_2S(aq) + OH^-(aq)$

You can find the following resources for this section on your obook assess:

» Student book questions
4.1 Check your learning

» Suggested practical
4.1 Electrical conductivity of strong and weak acids and bases

» Challenge
4.1 The danger of acids

4.2

Calculating dissociation constants and concentrations

KEY IDEAS

In this section, you will learn about:

- how to calculate dissociation constants (K_a and K_b)
- how to calculate the concentration of reactants and products
- using K_a and K_b to calculate pH.

Calculating K_a of a weak acid

You can calculate the acid dissociation constant (K_a) of a weak acid if you know the pH and concentration of a solution of the acid.

Consider 0.029 mole of ethanoic (or acetic) acid (CH_3COOH) dissolved in 1 litre of water. The solution has a pH of 3.15 at 25°C. The chemical equation for the equilibrium is:

$$CH_3COOH(aq) + H_2O(l) \rightleftharpoons CH_3COO^-(aq) + H_3O^+(aq)$$

The expression for K_a is:

$$K_a = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]}$$

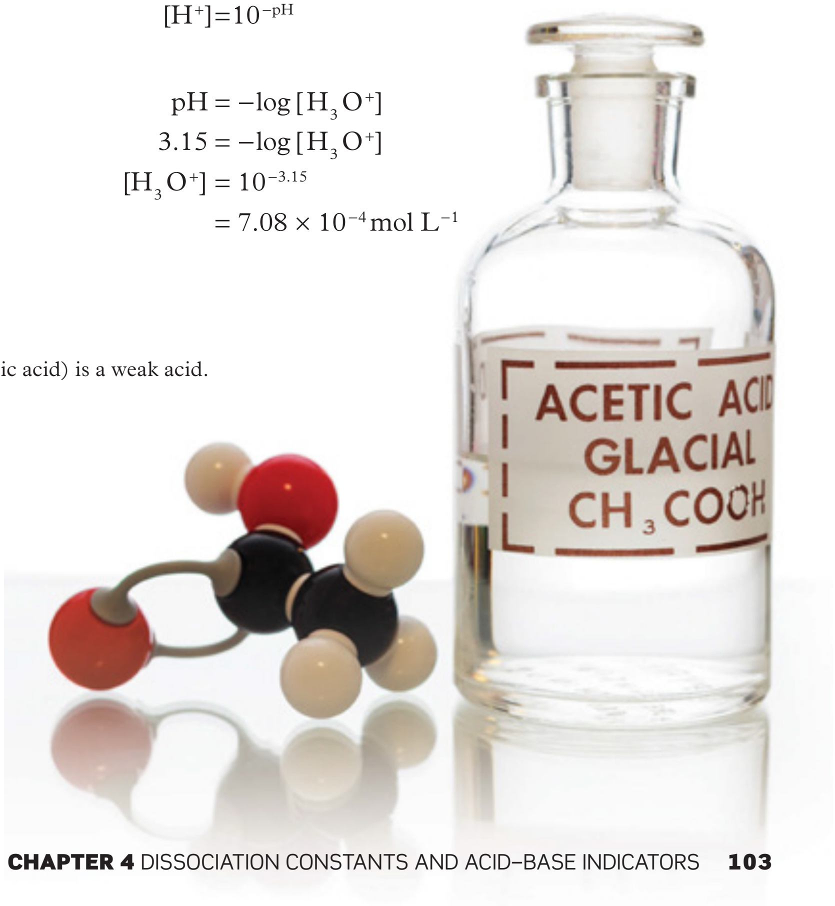
You already know the initial concentration [CH_3COOH], so you need to determine the concentration of [H_3O^+] and [CH_3COO^-]. Use the equation for pH to find [H_3O^+] (i.e. [H^+]):

$$pH = -\log[H^+]$$
$$[H^+]=10^{-pH}$$

Therefore:

$$\begin{aligned} pH &= -\log[H_3O^+] \\ 3.15 &= -\log[H_3O^+] \\ [H_3O^+] &= 10^{-3.15} \\ &= 7.08 \times 10^{-4}\,mol\,L^{-1} \end{aligned}$$

FIGURE 1 Ethanoic acid (acetic acid) is a weak acid.



To determine the concentration of ethanoate (CH_3COO^-), you can apply the ICE method (Table 1), which uses the initial concentration, change in concentration and final concentration of ethanoic acid.

Study tip

RICE and ICE tables are used interchangeably in chemistry to determine concentrations. The ratio (R) is only required when there are different coefficients on either side of a reaction.

TABLE 1 Using ICE to determine $[CH_3COO^-]$

	CH_3COOH	H_2O	H_3O^+	CH_3COO^-
Initial concentration ($mol\ L^{-1}$)	0.029	H_2O is a liquid, so has an initial concentration of 1	0	0
Change in concentration ($mol\ L^{-1}$)	$-x$		$+x$	$+x$
Equilibrium concentration ($mol\ L^{-1}$)	$0.029 - x$		x	x

From Table 1, you can see that:

$$[CH_3COO^-] = [H_3O^+]$$
$$= 7.08 \times 10^{-4}\ mol\ L^{-1}$$

and therefore:

$$[CH_3COOH] = 0.029\ mol\ L^{-1} - 7.08 \times 10^{-4}\ mol\ L^{-1}$$
$$= 0.028\ mol\ L^{-1}$$

Now you can substitute the values into the equilibrium equation below:

$$K_a = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]}$$
$$= \frac{(7.08 \times 10^{-4})^2}{0.028}$$
$$= 1.8 \times 10^{-5}$$

So, K_a of acetic acid is calculated to a value of 1.8×10^{-5} (which you can confirm is correct in Table 1, section 4.1).

Calculating the pH of a weak base

You can calculate the pH of a solution of a weak base if you know the base dissociation constant (K_b). Firstly, find the concentration of $[OH^-]$ from the expression for K_b and then you can calculate the pOH and pH.

Consider a 0.15 $mol\ L^{-1}$ solution of ammonia (NH_3); ($K_b = 1.8 \times 10^{-5}$). The chemical equation for the equilibrium is:

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

The expression for K_b is therefore:

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]}$$

Ammonia is a weak base, so it only slightly ionises in water. Therefore, its concentration is equal to the original concentration of the solution, 0.15 $mol\ L^{-1}$. Also, the chemical equation indicates that the concentration of ammonium ion and hydroxide ion are equal, $[NH_4^+] = [OH^-]$ (you can also use the ICE method shown in Table 1 on the previous page to work this out). Use the expression for K_b to find $[OH^-]$:

$$
\begin{aligned}
K_b &= 1.8 \times 10^{-5}\ \text{mol}\,\text{L}^{-1} \\
1.8 \times 10^{-5}\ \text{mol}\,\text{L}^{-1} &= \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} \\
&= \frac{[\text{OH}^-]^2}{0.15\ \text{mol}\,\text{L}^{-1}} \\
[\text{OH}^-]^2 &= (0.15\ \text{mol}\,\text{L}^{-1}) \times (1.8 \times 10^{-5}\ \text{mol}\,\text{L}^{-1}) \\
&= 2.7 \times 10^{-5}\ \text{mol}^2\,\text{L}^{-2} \\
[\text{OH}^-] &= \sqrt{2.7 \times 10^{-6}\ \text{mol}^2\,\text{L}^{-2}} \\
&= 5.2 \times 10^{-3}\ \text{mol}\,\text{L}^{-1}
\end{aligned}
$$

You can now use the concentration of [OH⁻] to calculate pOH according to the following equation (Chapter 3).

$$
\begin{aligned}
\text{pOH} &= -\log[\text{OH}^-] \\
[\text{OH}^+] &= 10^{-\text{pOH}}
\end{aligned}
$$

Therefore:

$$
\begin{aligned}
\text{pOH} &= -\log[\text{OH}^-] \\
&= -\log(5.2 \times 10^{-3}) \\
&= 2.3
\end{aligned}
$$

And we know that at 25°C for any aqueous solution:

$$\text{pH} + \text{pOH} = 14$$

Therefore:

$$
\begin{aligned}
\text{pH} + \text{pOH} &= 14 \\
\text{pH} &= 14 - \text{pOH} \\
&= 14 - 2.3 \\
&= 11.7
\end{aligned}
$$

So, the solution of ammonia has a pH of 11.7.

CHECK YOUR LEARNING 4.2

Describe and explain

1 **Explain** the steps involved in determining the acid dissociation constant K_a from pH.

2 **Describe** how to calculate pOH, given pH.

Apply, analyse and interpret

3 **Deduce** the equation for the reaction of the weak base aniline ($C_6H_5NH_2$) with water.

4 A 0.1 M solution of an acid has pH 4.0. **Determine** its K_a value.

5 A 0.01 M solution of a base has pH 8.0. **Determine** its K_b value.

Investigate, evaluate and communicate

6 **Calculate** the pH of 0.1 mol L^{-1} sodium hydroxide (NaOH) ($K_b = 3.6 \times 10^0$). Start by writing the equilibrium equation. **Discuss** your results.

You can find the following resources for this section on your obook assess:

- Student book questions
  4.2 Check your learning
- Weblink
  K_a and K_b
- Weblink
  pK_a and pK_b

4.3

Acid–base indicators

KEY IDEAS

In this section, you will learn about:

- acid–base indicators being weak acids or weak bases and the components of the conjugate acid–base pair having different colours
- the relationship between the pH range of an acid–base indicator and its pK_a
- indicators changing colour when $pH = pK_a$
- how to identify an appropriate indicator for a titration.

indicator
a chemical substance that changes colour at different pH values

You have already learnt about acid–base indicators and how they change colour as pH changes. There are many different **indicators**, which work in different ways. This section discusses some of the most common indicators, their properties and applications.

Indicators as weak acids or weak bases

Acid–base indicators are usually weak acids or bases, which dissociate slightly in water and form ions. Indicators change colour in acidic and basic solutions, so they can provide information about the pH of a solution.

Weak acids

Most indicators are weak acids (HIn). In solution, the acid is in equilibrium with its conjugate base (In^-):

$$\underset{\text{colour A}}{HIn(aq)} + H_2O(l) \rightleftharpoons \underset{\text{colour B}}{In^-(aq)} + H_3O^+(aq)$$

The acid and its conjugate base are different colours. At low pH, the concentration of H^+ is high, so the equilibrium position is on the left, and the solution shows colour A (the colour of HIn). At high pH, $[H^+]$ is low and the equilibrium position is on the right, indicating colour B.

For example, phenolphthalein is a colourless weak acid (HPhph) that dissociates in water to form pink anions ($Phph^-$). In acid, the equilibrium shifts to the left and the solution is colourless because the concentration of the anions is too low for the pink indicator to be seen. Under alkaline conditions, the equilibrium shifts to the right and the solution becomes pink because of the higher concentration of the anions.

$$\underset{\text{colourless}}{HPhph(aq)} + H_2O(l) \rightleftharpoons \underset{\text{pink}}{Phph^-(aq)} + H_3O^+(aq)$$

Weak bases

Weak bases (BOH) can also be used as indicators. If the weak base indicator is added to an alkaline solution, the indicator is in its BOH form and therefore displays colour A. If the weak base indicator is added to an acidic solution, the indicator dissociates to B^+, and colour B is displayed:

$$\underset{\text{colour A}}{BOH(aq)} \rightleftharpoons \underset{\text{colour B}}{B^+(aq)} + OH^-(aq)$$

pH range and pK_a

Indicators change colour when the solution contains equal amounts of both forms. Consider the equilibrium equation:

$$HIn(aq) \rightleftharpoons In^-(aq) + H^+(aq)$$

When you apply the equilibrium law to the equation, the following is true:

$$K_a = \frac{[H^+][In^-]}{[HIn]}$$

At equilibrium, $[In^-] = [HIn]$. Therefore, you can cancel them from the above equation:

$$\begin{aligned} K_a &= \frac{[H^+]\cancel{[In^-]}}{\cancel{[HIn]}} \\ &= [H^+] \end{aligned}$$

which leads to:

$$\begin{aligned} K_a &= [H^+] \\ pK_a &= pH \end{aligned}$$

This means that the colour of the indicator changes when $pK_a = pH$.

Different indicators change colour over different pH ranges. Most indicators change colour over a range of $pK_a \pm 1$ (Table 1).

TABLE 1 Selected indicators and their pH ranges

Indicator	pH range	Colour of acidic form	Colour of basic form
Methyl orange	3.1–4.4	Red	Yellow
Bremophenol blue	3.0-4.6	Yellow	Blue
Bromocresol green	4–5.6	Yellow	Blue
Methyl red	4.4–6.2	Pink	Yellow
Bromothymol blue	6.0–7.6	Yellow	Blue
Phenol red	6.8–8.4	Yellow	Red
Phenolphthalein	8.3–10.0	Colourless	Pink

titration
the addition of a solution of known concentration to a known volume of a solution of unknown concentration until reaction reaches neutralisation

equivalence point
the point in a titration when the reactants have reacted in the molar ratio of the balanced chemical equation

end point
the point in a titration when the indicator changes colour

Indicators for titration

Indicators are used in titrations (see Chapter 5). **Titration** is a method for determining the concentration of an unknown acid or base by neutralising it with a known base or acid. The **equivalence point** in a titration is when just enough titrant (known solution) has been added to completely neutralise the analyte (unknown solution) solution for an acid–base pair. The number of moles of base is equal to the number of moles of acid and the solution only contains salt and water (neutralisation reaction).

pH indicators are important for finding the **end point**, which is close to the equivalence point. The end point is the point when the indicator actually changes colour. For a titration to be accurate, it is important to choose an indicator that changes colour close to the equivalence point.

FIGURE 1 pH indicators can be used to detect the end point of titrations.

titration curve
a graph of pH against volume of reactant added

Titration of a strong acid with a strong base

Figure 2 shows the **titration curve** of a strong acid and a strong base. It shows how pH changes during the course of the titration. On neutralisation, the pH rapidly increases from pH 3 to 11. The equivalence point is at pH 7. In this case, it is an easy task to choose an indicator because all common indicators change colour within this range (see Table 1). In this instance, the end point also coincides with the equivalence point.

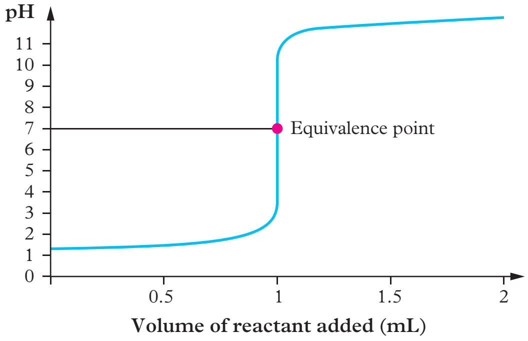


FIGURE 2 The titration curve for a strong acid with a strong base. On neutralisation, the pH rapidly changes from 3 to 11.

Titration of a weak acid with a strong base

Figure 3 shows the titration curve of a weak acid and a strong base. You can see that the equivalence point is greater than pH 7. The change in pH on neutralisation is less than that for a strong acid–strong base and occurs at pH 7–11. The only suitable indicator from Table 1 is phenolphthalein.

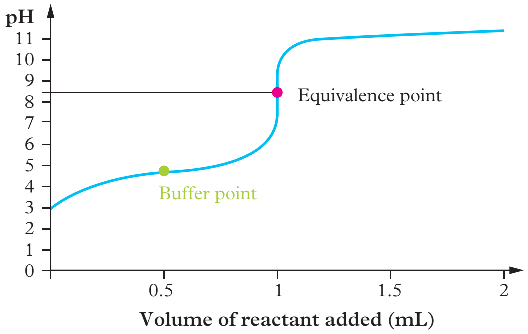


FIGURE 3 The titration curve for a weak acid with a strong base

Titration of a weak base with a strong acid

Figure 4 shows the titration curve for a weak base–strong acid. The equivalence point is less than pH 7. The change in pH on neutralisation is less than that for a strong acid–strong base and occurs at pH 3–7. Suitable indicators are methyl orange, bromocresol green and methyl red.

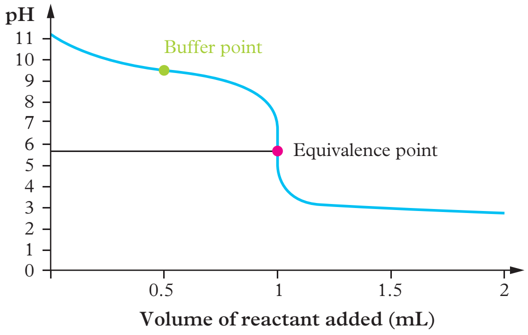


FIGURE 4 The titration curve for a weak base with a strong acid

Titration of a weak acid with a weak base

The pH change during the titration of a weak acid with a weak base is gradual and does not show a steep increase. This behaviour makes it impossible to use an indicator to find the equivalence point. In this case, a different type of titration is used – a conductometric titration in which the electrolytic conductivity of the reaction mixture is monitored while adding titrant. The equivalence point is the point when the conductivity changes suddenly due to the presence of water and salt.

CASE STUDY 4.3

Testing soil pH

You might have overheard a neighbour or someone in your family complaining about the vegetables in their garden – they are too small, not ripe, or just not how they are supposed to be. Different vegetables grow best at different soil pH values so that they can absorb nutrients from the soil and grow well. Many vegetables grow best in neutral soils. However, carrots, pumpkins, and tomatoes grow best in acidic soil, whereas asparagus, cauliflower and broccoli grow best in a slightly basic soil.

Gardeners can test the pH of soil by using an indicator that is in the form of a white powder (Figure 5). Once sprinkled directly onto the soil, the powder changes colour depending on the pH of the soil. Gardeners then compare the colour with a colour chart to determine the pH. If the soil is too basic, they can add lime and chicken manure to decrease the pH. If the soil is too acidic, adding compost or sulfur will increase the pH, making the soil more favourable for crops that require basic soils.

FIGURE 5 Gardeners can use powder indicators to test the pH of their soil.

CHECK YOUR LEARNING 4.3

Describe and explain

1 **Explain** the relationship between pH and pK_a.

2 **Explain** how to choose an appropriate pH indicator for a titration.

3 **Explain** what the end point represents in a titration.

4 **Explain** what the equivalence point represents in a titration.

Apply, analyse and interpret

5 **Determine** the types of titration (e.g. strong acid–strong base) for which the following indicators are suitable.

  a Crystal violet, pH range 0.8–2.6, colour change from yellow to blue-violet

  b Thymolphthalein, pH range 9.4–10.6, colour change from red to yellow

  c Alizarin yellow, pH range 10.1–12.0, colour change from yellow to red

You can find the following resources for this section on your obook assess:

- » Student book questions
  4.3 Check your learning
- » Weblink
  pH indicators
- » Weblink
  Testing pH of soils

CHAPTER 4

Review

Chapter summary

4.1
- The strength of an acid or base is given by its degree of ionisation in an aqueous solution, which can be expressed as a dissociation constant K_a for acids and K_b for bases.
- K_a and K_b can have a wide range of values so they are commonly expressed pK_a and pK_b, where $pK_a = -\log_{10}K_a$ and $pK_b = -\log_{10}K_b$.

4.2
- Dissociation constants (K_a and K_b) and concentrations of reactants and products can be calculated. K_a and K_b can be used to calculate pH.

4.3
- Acid–base indicators are weak acids or bases, which dissociate slightly in water and form ions. Indicators can be used in titrations. It is important to select an appropriate indicator that suits the class of titration.

Key terms

- acid dissociation constant (K_a)
- base dissociation constant (K_b)
- end point
- equivalence point
- indicator
- pK_a
- pK_b
- titration
- titration curve

Key formulas

Acid dissociation constant	$K_a = \frac{[H^+][A^-]}{[HA]}$
Base dissociation constant	$K_b = \frac{[BH^+][OH^-]}{[B]}$
Dissociation constant of water	$K_w = K_a \times K_b$
pK_a	$pK_a = -\log_{10}K_a$
pK_b	$pK_b = -\log_{10}K_b$
At 25°C for an aqueous solution	pH + pOH = 14

Revision questions

The relative difficulty of these questions is indicated by the number of stars beside each question number: ★ = low; ★ ★ = medium; ★ ★ ★ = high.

Multiple choice

1 K_a stands for:

- **A** correlation constant for acids
- **B** acid dissociation constant
- **C** potassium acid
- **D** none of the above.

2 The relationship between K_a, K_b and K_w is:

- **A** $K_w = \frac{K_a}{K_b}$
- **B** $K_a = K_w \times K_b$
- **C** $K_w = K_a \times K_b$
- **D** $K_w = -\log_{10} K_a + -\log_{10} K_b$

3 The relationship between pK_b and K_b is:

- **A** $K_b = -\log_{10} pK_b$
- **B** $pK_b = -\log_{10} K_b$
- **C** $K_b = \log_{10} pK_b$
- **D** $pK_b = \log_{10} K_b$

4 When a strong base is mixed with a strong acid, the equivalence point is:

- **A** at pH 7
- **B** below pH 7
- **C** above pH 7
- **D** the same as the end point.

Short answer

Describe and explain

★★ 5 **Explain** how to find an appropriate acid–base indicator for a titration of a:

- **a** strong acid with a strong base
- **b** weak acid with a strong base
- **c** weak base with a strong acid.

Apply, analyse and interpret

★★ 6 A 0.2 M solution of an acid has a pH of 3.0. **Determine** its K_a value.

★★ 7 Methyl orange has a pH range of 3.1–4.4. **Determine** the types of titration that methyl orange is suitable for.

Investigate, evaluate and communicate

★★ 8 **Investigate** Figure 1 and justify what type of titration it represents.

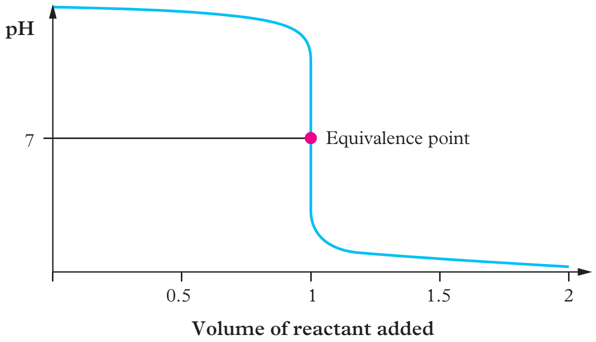


FIGURE 1 Titration curve

★★★ 9 Table 1 lists the colours of three unknown solutions (A, B and C) with various indicators. **Predict** the pH of each solution. If a result is not conclusive, **describe** another test that could be performed to determine the result.

TABLE 1 The results table of the three unknown solutions

Indicator	A	B	C
Methyl orange	Yellow		Yellow
Bromothymol blue		Green	
Phenolphthalein	Colourless	Colourless	
Litmus			Blue

You can find the following resources for this section on your obook assess:

- » Student book questions
  Chapter 4 Revision questions
- » Revision notes
  Chapter 4
- » assess quiz
  Auto-correcting multiple-choice quiz
- » Flashcard glossary
  Chapter 4

CHAPTER 5

Volumetric analysis

Volumetric analysis is an essential wet chemical technique that chemists use to determine the concentration or amount of a solute in a larger volume of solvent. It is a very reliable quantitative technique and produces highly accurate and reliable results.

Volumetric analysis was first developed in the late 1700s, and has been highly effective and useful ever since. It is typically used in food chemistry to determine the amounts of nutrients in a food sample, in the development of biodiesel as a fuel, in mining to analyse minerals, and in environmental chemistry to analyse nutrients in seawater (Figure 1).

OBJECTIVES

- Distinguish between the terms end point and equivalence point.
- Recognise that acid–base titrations rely on the identification of an equivalence point by measuring the associated change in pH, using chemical indicators or pH meters, to reveal an observable end point.
- Sketch the general shapes of graphs of pH against volume (titration curves) involving strong and weak acids and bases. Identify and explain their important features, including the intercept with pH axis, equivalence point, buffer region and points where pK_a = pH or pK_b = pOH.
- Use appropriate mathematical representations and analyse experimental data and titration curves to solve problems and make predictions, including using the mole concept to calculate moles, mass, volume and concentration from volumetric analysis data.

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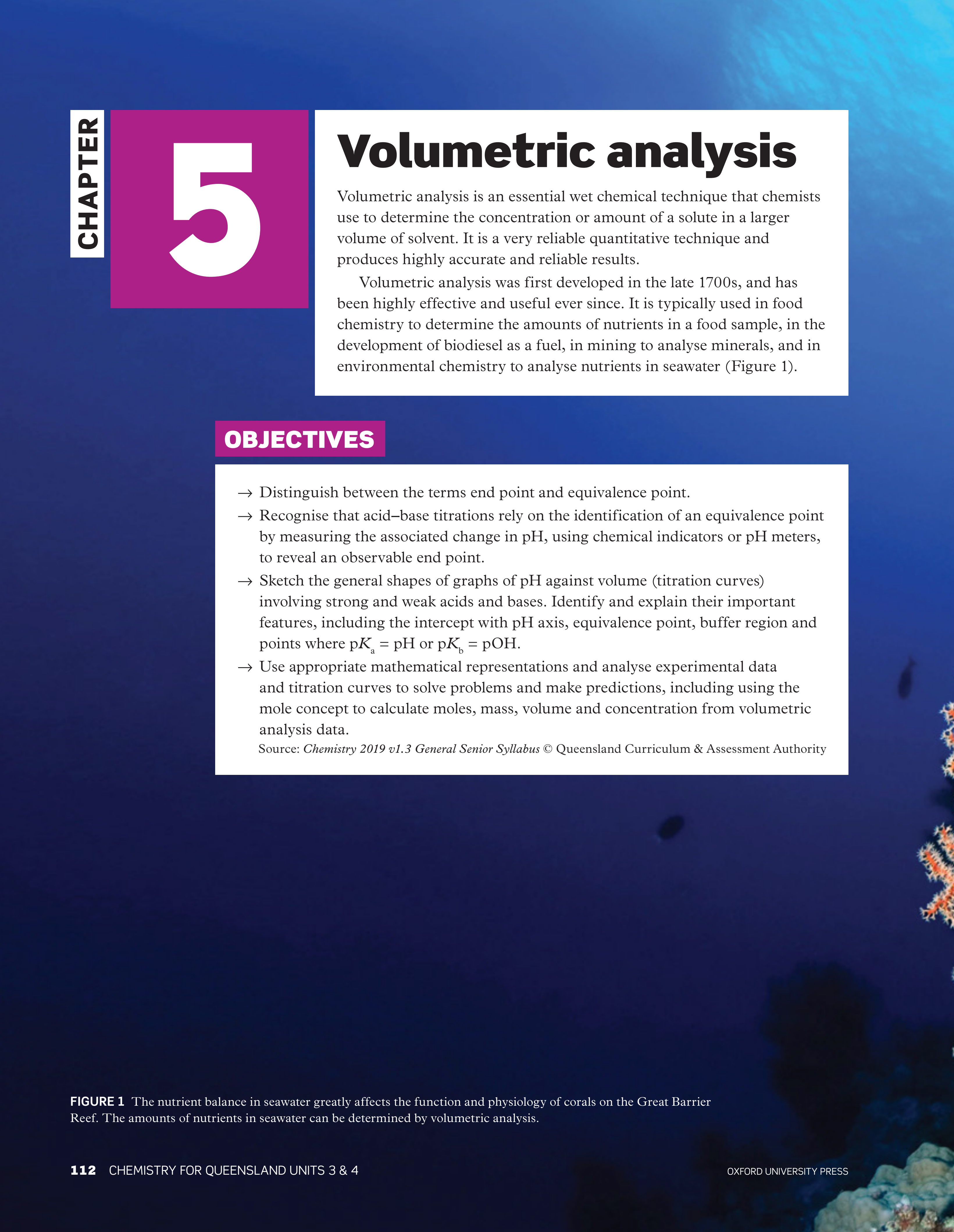
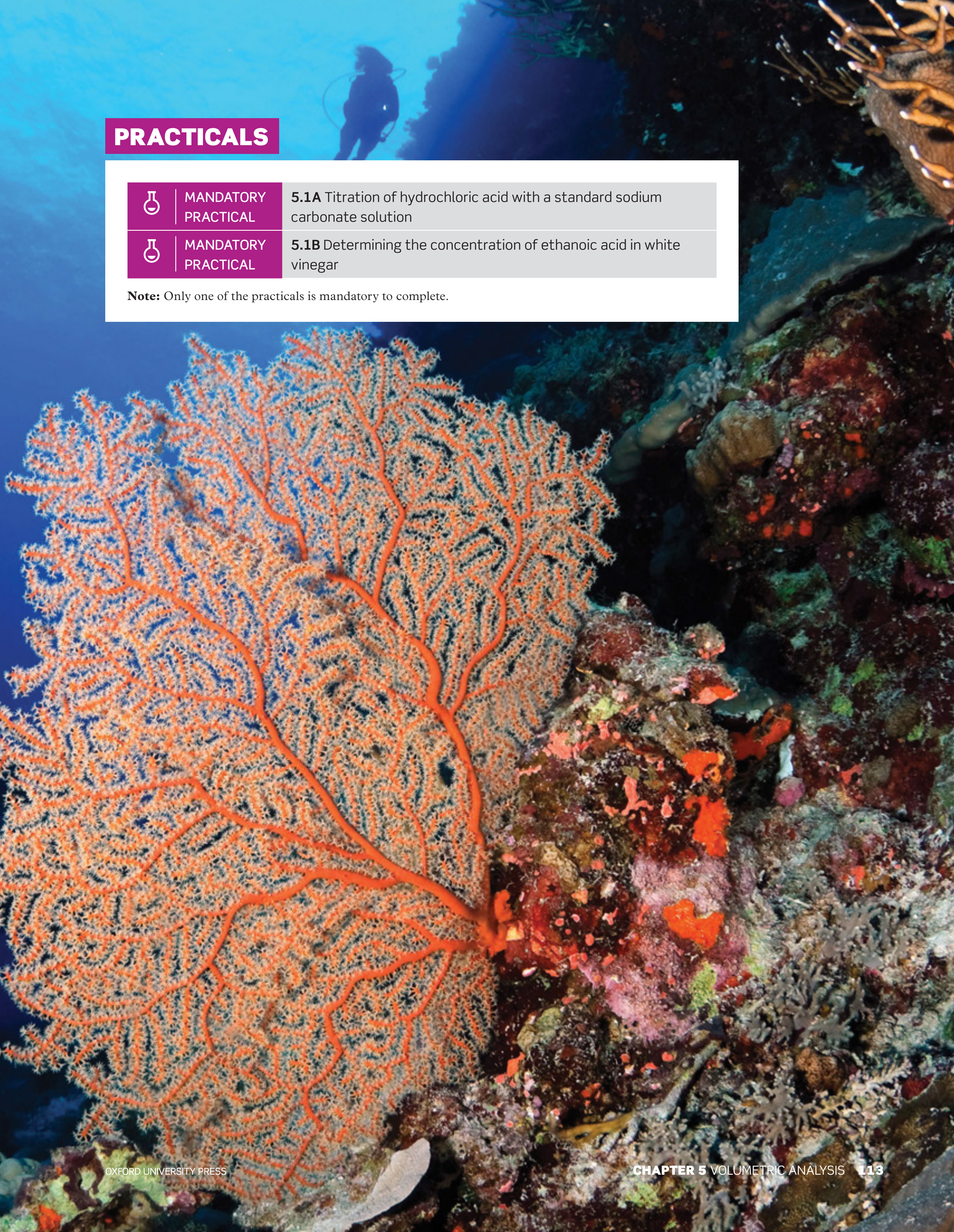


FIGURE 1 The nutrient balance in seawater greatly affects the function and physiology of corals on the Great Barrier Reef. The amounts of nutrients in seawater can be determined by volumetric analysis.



PRACTICALS

MANDATORY PRACTICAL	**5.1A** Titration of hydrochloric acid with a standard sodium carbonate solution
MANDATORY PRACTICAL	**5.1B** Determining the concentration of ethanoic acid in white vinegar

Note: Only one of the practicals is mandatory to complete.

5.1

An introduction to titrations

KEY IDEAS

In this section, you will learn about:

- the difference between end point and equivalence point
- indicators as a measure of an end point.

volumetric analysis
a quantitative analytical technique for determining the concentration of a solution by titrating it against a solution of known concentration

solution
a mixture of a solute dissolved in a solvent

stoichiometry
the calculation of reactants and products in chemical reactions by using a balanced equation

stoichiometric ratio
the coefficient ratio in a chemical equation

Volumetric analysis uses stoichiometry to determine the concentration of a **solution** of accurately known volume, by titrating it against another solution of known concentration. **Stoichiometry** is covered in detail in *Chemistry for Queensland Units 1 & 2*, Chapter 8.

Titration

Titration is a technique in which a solution of known concentration is added to a solution of unknown concentration until they have reacted in equal mole amounts (see Chapter 4). Titration uses equipment that dispenses highly accurate volumes of solutions. If the volumes of both reactants are known accurately, and one of their concentrations is also known, you can calculate the concentration of the second reactant. Titration is the process by which the volumes are accurately measured.

Consider the titration of a solution of phosphoric acid (H_3PO_4) with a solution of sodium hydroxide (NaOH). Phosphoric acid and sodium hydroxide react according to the equation:

$$H_3PO_4(aq) + 3NaOH(aq) \rightarrow Na_3PO_4(aq) + 3H_2O(l)$$

If you know the volume and concentration of phosphoric acid, you can calculate the number of moles of phosphoric acid from the formula:

$$n = C \times V$$

Then you can use the **stoichiometric ratio** in the balanced chemical equation to calculate the number of moles of sodium hydroxide. If the volume of the sodium hydroxide is also accurately known, you can determine the concentration of this solution. Worked example 5.1A demonstrates this process.

WORKED EXAMPLE 5.1A

In a titration, 10 mL of 2.0 M phosphoric acid reacts with 15 mL of sodium hydroxide of unknown concentration. Determine the concentration of the sodium hydroxide solution.

SOLUTION

1 Write a balanced chemical equation for the reaction:

$$H_3PO_4(aq) + 3NaOH(aq) \rightarrow Na_3PO_4(aq) + 3H_2O(l)$$

2 Calculate the moles of the ‘known’ chemical phosphoric acid.

$$\begin{aligned} n(H_3PO_4) &= C \times V \\ &= 2\,\text{mol L}^{-1} \times 0.010\,\text{L} \\ &= 0.02\,\text{mol} \end{aligned}$$

3 Use the stoichiometric ratio (H_3PO_4 : NaOH is 1:3) to calculate the number of moles of the 'unknown' chemical sodium hydroxide.

$$\begin{aligned} n(\text{NaOH}) &= n(\text{H}_3\text{PO}_4) \times 3 \\ &= 0.2\,\text{mol} \times 3 \\ &= 0.06\,\text{mol} \end{aligned}$$

4 Use the number of moles of the 'unknown' to solve the problem

The problem asks for the concentration of sodium hydroxide. Use the volume and the number of moles to calculate its concentration.

$$\begin{aligned} C(\text{NaOH}) &= \frac{n}{V} \\ &= \frac{0.06\,\text{mol}}{0.015\,\text{L}} \\ &= 4\,\text{mol L}^{-1} \\ &= 4.0\ \text{M} \end{aligned}$$

Study tip

When completing stoichiometry problems, always calculate the number of moles of the chemical with known values first.

Standard solutions

In order to perform a titration, you need to prepare a **standard solution**. For this, you require a piece of specialised equipment, called a **volumetric flask** (Figure 1), which results in a solution of highly accurate volume.

To prepare a standard solution, first select a **primary standard** as the **solute**. A primary standard is a very pure chemical that is weighed and dissolved in a **solvent**, using a volumetric flask, to create the standard solution with a highly accurate concentration.

A primary standard must have several important qualities. It must:

- be a solid that is soluble in water, in order to dissolve and make a standard solution
- be highly pure
- have a known chemical formula
- have a high molar mass in order to minimise errors during weighing
- be stable or unreactive so as not to absorb water, carbon dioxide or other chemicals from the atmosphere or surrounding environment
- be anhydrous. For example, $MgSO_4.7H_2O$ (hydrated magnesium sulfate or epsom salt) is not an appropriate standard because the seven water molecules can evaporate, changing the chemical formula and molar mass
- be reasonably priced.

Common primary standards include:

- oxalic acid ($H_2C_2O_4$)
- potassium hydrogen phthalate ($KH(C_8H_4O_4)$)
- anhydrous sodium carbonate (Na_2CO_3)
- sodium borate ($Na_2B_4O_7$)
- potassium hydrogen iodate (HI_2KO_6).

standard solution
a solution of accurately known concentration

volumetric flask
a piece of laboratory glassware that can measure highly accurate volumes

primary standard
a substance that is dissolved in a solvent to create a standard solution

solute
the minor component of a solution; the substance dissolved in the solvent

solvent
the major component of a solution; what the solute is dissolved in

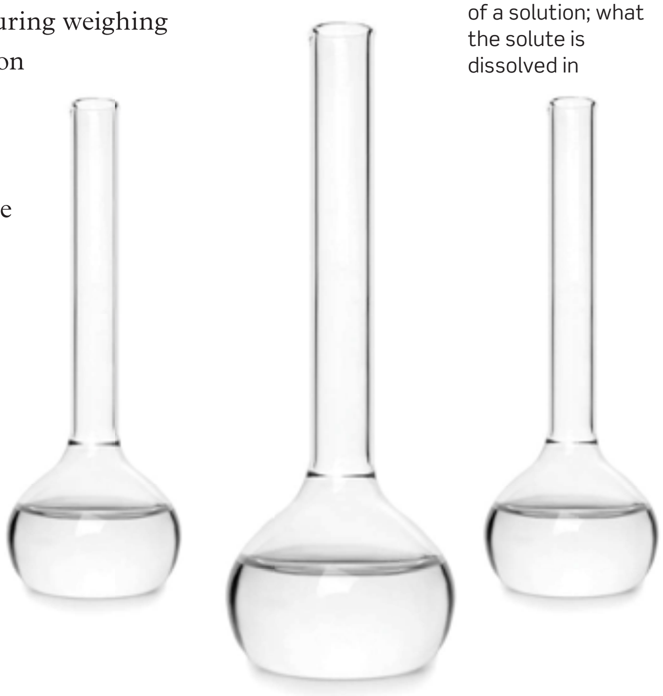


FIGURE 1 A volumetric flask is calibrated to measure highly accurate volumes.

Preparing a standard solution

A common method for preparing a standard solution is as follows.

1 Rinse the volumetric flask with water and then with the desired solvent, if it is not water. While rinsing, hold the lid on the flask and tip the flask upside down to check that the lid seals without any leaks.

2 Weigh the primary standard on an electronic balance and record its mass (Figure 2a).

3 Add the primary standard to a volumetric flask, using a funnel.

Add the standard slowly to the funnel, ensuring that the funnel does not become blocked. If it does become blocked, tap it gently to get the solid moving. Do not use the solvent to wash it down because the powdered standard might clump and clog the funnel. Only use the solvent to wash the remaining debris off the funnel after the solid has passed through (Figure 2b).

4 Half-fill the volumetric flask with solvent, put the lid on the flask and swirl the flask until the standard is completely dissolved (Figure 2c).

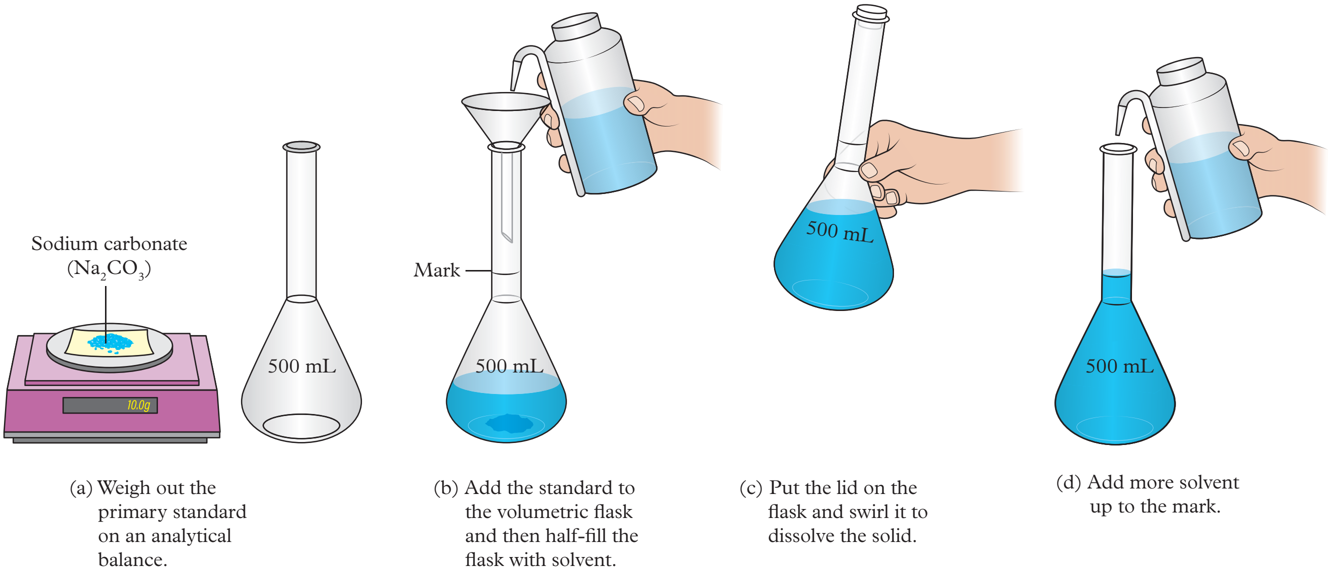
If the standard does not dissolve easily, do not be tempted to shake the flask. This will introduce errors because some of the solution will come into contact with the lid and may leak out. If you do need to shake the flask, wash any solution that remains on the lid into the flask by using a wash bottle containing solvent.

5 Use a wash bottle to make the solution up to the mark on the flask. The bottom of the **meniscus** must sit on this line (Figure 2d). Place the volumetric flask on the bench and crouch down so that the meniscus is at eye level to minimise errors.

meniscus
the curved upper surface of a liquid in a piece of measurement glassware

6 Place the lid back on the flask and hold it firmly in place while you tip the flask upside down and then upright again at least five times. This will ensure that the solution has an evenly distributed concentration.

Worked examples 5.1B and 5.1C demonstrate the calculations required for preparing standard solutions.



(a) Weigh out the primary standard on an analytical balance.

(b) Add the standard to the volumetric flask and then half-fill the flask with solvent.

(c) Put the lid on the flask and swirl it to dissolve the solid.

(d) Add more solvent up to the mark.

FIGURE 2 The procedure for preparing a standard solution

WORKED EXAMPLE 5.1B

Students make 0.20 M standard solution of aqueous sodium carbonate (Na_2CO_3) in a 250 mL volumetric flask. What mass of sodium carbonate should they use?

SOLUTION

1 Using concentration and volume, calculate the number moles of sodium carbonate.

$$\begin{aligned} n(\mathrm{Na_2CO_3}) &= C \times V \\ &= 0.2\,\mathrm{mol\,L^{-1}} \times 0.250\,\mathrm{L} \\ &= 0.05\,\mathrm{mol} \end{aligned}$$

2 Using moles and molar mass, calculate the mass of sodium carbonate.

$$\begin{aligned} m(\mathrm{Na_2CO_3}) &= n \times M \\ &= 0.05\,\mathrm{mol} \times 106\,\mathrm{g\,mol^{-1}} \\ &= 0.53\ \mathrm{g} \end{aligned}$$

Therefore, the student must use 0.53 g of sodium carbonate.

WORKED EXAMPLE 5.1C

A standard solution is made from 1.25 g of sodium hydroxide (NaOH) in water in a 20.00 mL volumetric flask. What is the concentration of the solution?

SOLUTION

1 Calculate the number of moles of sodium hydroxide, using mass and molar mass.

$$\begin{aligned} n(\mathrm{NaOH}) &= \frac{m}{M} \\ &= \frac{1.25\ \mathrm{g}}{40\,\mathrm{g\,mol^{-1}}} \\ &= 0.031\mathrm{mol} \end{aligned}$$

2 Use the number of moles and volume to calculate the concentration of sodium hydroxide. Avoid rounding the number of moles from step 1 to get a precise value.

$$\begin{aligned} C(\mathrm{NaOH}) &= \frac{n}{V} \\ &= \frac{0.031\,\mathrm{mol}}{0.020\,\mathrm{L}} \\ &= 1.56\,\mathrm{mol\,L^{-1}} \\ &= 1.56\ \mathrm{M} \end{aligned}$$

Therefore, the concentration of sodium hydroxide is 1.56 M.

Study tip

Never round off your answers at any point in a calculation. Always keep values in your calculator, or your final answers will be incorrect.

Study tip

In stoichiometry problems, volumes must be expressed in litres.

Study tip

Refer to Section 8.2 of the *Chemistry for Queensland Units 1 & 2 Student book* for information how to calculate molar mass.

Study tip

Concentration is usually expressed in $\mathrm{mol\,L^{-1}}$ (M), $\mathrm{g\,L^{-1}}$ and ppm, but other units include ppb ($\mathrm{\mu g\,L^{-1}}$), %w/v (g in 100 mL), %w/w (g in 100 g) and %w/v (g in 100 mL).

Errors and misconceptions with standard solutions

Students often make two common errors and misconceptions when preparing and discussing standard solutions.

1 Not washing the volumetric flask before adding the solute. It is essential to wash the flask because it may contain impurities that will contaminate the solution and may result in a reaction within the flask. First, rinse the flask with water to dissolve any water-soluble impurities. Then wash it with the solvent. If the solvent is water, wash the volumetric flask a second time.

A common misconception is that washing the flask with water will dilute the solution within the flask. But if the flask is first washed with water and then the solute is added, more water must be added to finish making the solution. Having water in the volumetric flask before adding the solute will not affect the concentration of the standard solution.

2 Adding the solvent to the volumetric flask first. The solute must be added to the volumetric flask before the solvent.

A common misconception is that, to make a 250 mL solution, you need 250 mL of solvent. But, as shown in Figure 3, this is incorrect because the solute has volume too. Ammonium dichromate is added to the volumetric flask and water is added to make up to 250 mL. The solute and solvent have a combined volume of 250 mL. Thus, the solute must be added before the solvent.

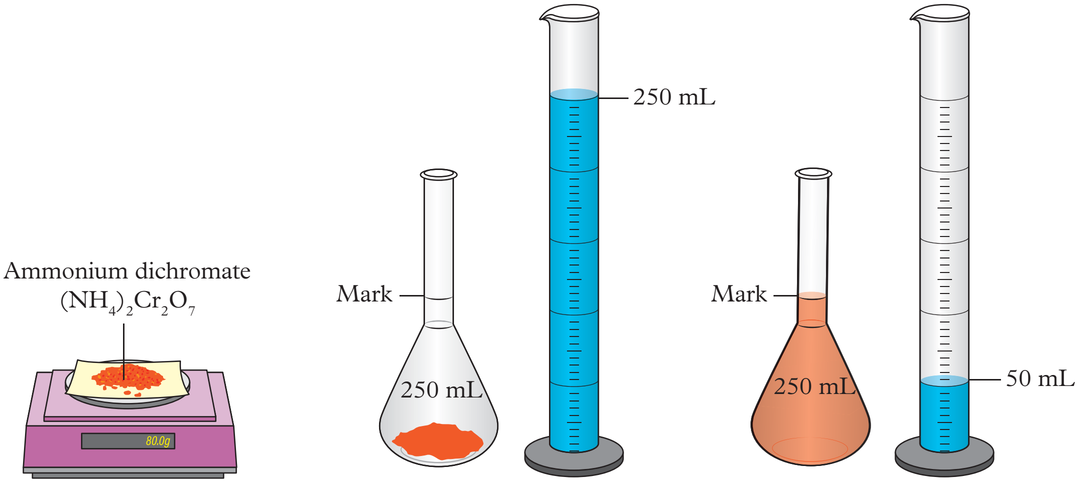


FIGURE 3 A 250 mL solution does not mean that 250 mL of solvent has been added to the solute.

CHALLENGE 5.1A

Not enough primary standard?

A student wishes to synthesise a standard solution of 0.3 M sodium chloride (NaCl). In the chemical storeroom, there is only 0.2 g of NaCl. Calculate the volume of solution that could be prepared using this mass.

Outline a procedure for the preparation of this solution, including the volume of the volumetric flask, if volumetric flasks carry volumes that must be a multiple of 5 mL.

Equivalence point is a measure of a stoichiometric ratio

The equivalence point of a titration is reached when chemicals have reacted according to their molar ratio and no reactant is in excess (see Chapter 4). At the equivalence point, there are no reactants remaining, only products. Consider the reaction between sodium hydroxide and hydrochloric acid:

$$NaOH(aq) + HCl(aq) \rightarrow NaCl(aq) + H_2O(l)$$

One mole of NaOH will react with 1 mole of HCl to produce 1 mole of NaCl and 1 mole of H_2O. At the equivalence point, no NaOH or HCl remain; there is only NaCl and H_2O.

MANDATORY PRACTICAL

5.1A Titration of hydrochloric acid with a standard sodium carbonate solution
Go to page 400 »

MANDATORY PRACTICAL

5.1B Determining the concentration of ethanoic acid in white vinegar
Go to page 403 »

End point is a change in indicator colour

In order to determine when the equivalence point has been reached in a chemical reaction, an indicator is used. The point at which the indicator changes colour is called the end point (see Chapter 4). It is important that the indicator changes colour as close as possible to the equivalence point.

CHALLENGE 5.1B

Titration involving dilution

Some students were set the task of determining the concentration of ethanoic (acetic) acid in a particular brand of vinegar. A 10 mL sample of vinegar was diluted by a factor of 10 in a 100 mL volumetric flask and a pipette was used to transfer 20.00 mL of diluted vinegar to a 100 mL conical flask. The vinegar was titrated with a 0.1 M NaOH standard solution and the following titres were obtained 15.31, 15.35 and 15.39 mL.

The equation for the reaction is:

$$NaOH(aq) + CH_3COOH(aq) \rightarrow CH_3COONa(aq) + H_2O(l)$$

Calculate the concentration of ethanoic acid (in $mol\,L^{-1}$) in the original vinegar sample to the correct number of significant figures.

CHECK YOUR LEARNING 5.1

Describe and explain

1 **Describe** the difference between a primary standard and a standard solution.

2 **Describe** the difference between an end point and an equivalence point.

Investigate, evaluate and communicate

3 A student performs a titration and forgets to rinse the burette with standard solution before filling it. **Evaluate** the effect on the concentration determined for the unknown solution, using a calculation to support your answer.

You can find the following resources for this section on your obook assess:

- Student book questions
  5.1 Check your learning
- Mandatory practical
  5.1A Titration of hydrochloric acid with a standard sodium carbonate solution
- Mandatory practical
  5.1B Determining the concentration of ethanoic acid in white vinegar
- Challenge
  5.1A Not enough primary standard?

5.2

Performing titrations

KEY IDEAS

In this section, you will learn about:

- how to perform a titration.

Performing a titration

To perform a titration, you need specialised equipment – a **burette** and a **pipette**. Burettes and pipettes dispense highly accurate volumes of solution, increasing the accuracy of the analytical technique.

The general method to perform a titration is as follows.

1 Fill the burette with the standard solution. This is called the **titrant**. When a volume of solution is dispensed from the burette, it is called the **titre**.

2 Clamp the burette to a retort stand, making sure that the base of the stand is on the same side as the burette to off-set the weight.

3 Use a pipette to transfer a volume (**aliquot**) of the solution with unknown concentration into a conical flask. This is called the **titrand** or **analyte**. Add an indicator that will change colour at the equivalence point of the reaction.

4 Record the initial volume of the burette. Turn the **stopcock** (tap) on the burette to start dispensing the titrant into the unknown solution. This should start to cause a colour change, which disappears with stirring. Stir the conical flask constantly to ensure that the reaction is evenly distributed throughout the flask.

5 Continue to add the titrant until the colour becomes harder to remove with stirring. At this point, turn the stopcock so that it only dispenses one drop at a time.

6 Turn off the stopcock when a permanent colour change is observed. This is the end point.

7 Record the final volume in the burette.

8 Subtract the initial volume from the final volume to determine the total volume of standard solution dispensed from the burette. This is the titre.

9 Repeat the method until you have obtained three **concordant titres**. Concordant titres differ by 0.1 mL from lowest to highest. These concordant titres must be averaged to use in calculations. This increases the **precision** of the results.

Worked examples 5.2A–C demonstrate some titration calculations.

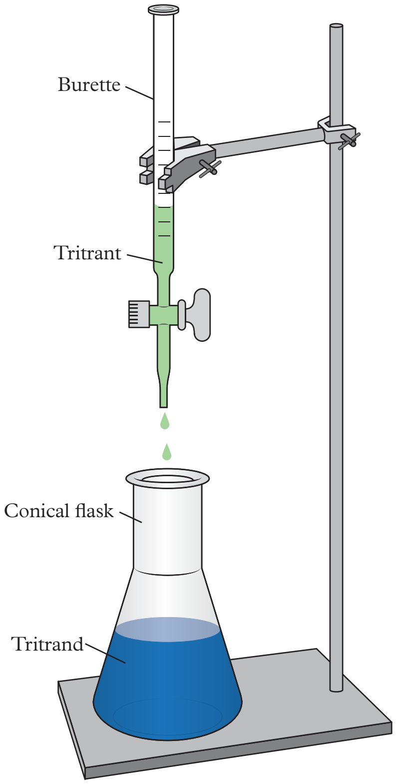


FIGURE 1 Titration apparatus

burette	a graduated glass cylinder that dispenses highly accurate volumes of a standard solution
pipette	a glass tube that dispenses highly accurate volumes of a solution of unknown concentration
titrant	the standard solution in a burette that is added to a solution of unknown concentration
titre	the volume of standard solution dispensed from a burette
aliquot	a fixed volume of liquid measured by a pipette
titrand	a solution whose concentration is determined by titration
analyte	a solution of unknown concentration
stopcock	the tap attached to a burette
concordant titres	volumes of standard solution dispensed from a burette that differ by only 0.1 mL from the highest and the lowest

precision
the consistency of a series of measurements

Study tip

Concordant titres must only differ by 0.1 mL from the highest to the lowest.

WORKED EXAMPLE 5.2A

A student performs the same titration five times. She obtains titres with the following volumes: 21.16, 21.21, 21.08, 21.04 and 21.00 mL

a Are the titres concordant? Which titres can be used?

b What volume should the student use in her calculations?

c What must the student do if the titres are not concordant?

SOLUTION

a There must be three concordant titres. The titres of 21.08, 21.04 and 21.00 mL are within 0.1 mL of one another, so they are concordant.

b To determine the volume used in the calculations, calculate the average of the concordant titres.

$$\begin{aligned}\text{volume} &= \frac{21.08 + 21.04 + 21.00}{3}\\ &= 21.04\text{ mL}\end{aligned}$$

c If the titres are not concordant, they are not precise, and the student must continue to repeat the titration until concordant titres are obtained.

WORKED EXAMPLE 5.2B

A student performs a titration using a 1.200 M standard solution of HCl. He used 20.00 mL aliquots of potassium hydroxide and obtained the following titres: 15.17, 14.95, 15.05, 15.21 and 15.02 mL

Calculate the concentration of the potassium hydroxide solution.

SOLUTION

1 Write a balanced chemical equation:

$$HCl(aq) + KOH(aq) \rightarrow KCl(aq) + H_2O(l)$$

2 Calculate the average titre of HCl solution. The concordant titres are 14.95, 15.05 and 15.02 mL.

$$\begin{aligned}V(\text{HCl}) &= \frac{14.95 + 15.05 + 15.02}{3}\\ &= 15.01\text{ mL}\end{aligned}$$

3 Calculate the number of moles of the 'known' chemical. The known chemical is hydrochloric acid because it is the standard solution with an accurately known concentration and volume.

$$\begin{aligned}n(\text{HCl}) &= C \times V\\ &= 1.2\text{ mol L}^{-1} \times 0.01501\text{ L}\\ &= 0.018\text{ mol}\end{aligned}$$

4 Use the stoichiometric ratio to calculate the number of moles of the 'unknown' chemical.

The concentration of HCl is known, so the unknown reactant is KOH. The molar ratio for the reactants HCl:KOH is 1:1, so the number of moles of KOH equals the number of moles of NaCl.

OR

$$n(\text{KOH}) = n(\text{NaCl})$$
$$n(\text{KOH}) = n(\text{HCl})$$
$$= 0.018\,\text{mol}$$

5 Use the number of moles of the 'unknown' to solve the problem.

The problem asks for the concentration of potassium hydroxide. Use the volume and number of moles to calculate concentration.

$$C(\text{KOH}) = \frac{n}{V}$$
$$= \frac{0.018\,\text{mol}}{0.020\,\text{L}}$$
$$= 0.90\,\text{mol}\,\text{L}^{-1}$$
$$= 0.90\,\text{M}$$

WORKED EXAMPLE 5.2C

1.32 g of lithium hydroxide (LiOH) is dissolved in water in a 200.0 mL volumetric flask. An average titre of 12.13 mL of this solution was obtained when titrating with 15.00 mL aliquots of a nitric acid (HNO_3) solution.

a What is the concentration of the LiOH solution?

b What is the concentration of the nitric acid?

SOLUTION

a Write a balanced chemical equation for the reaction.

$$\text{LiOH(aq)} + \text{HNO}_3\text{(aq)} \rightarrow \text{LiNO}_3\text{(aq)} + \text{H}_2\text{O(l)}$$

Calculate the concentration of the standard solution.

$$n(\text{LiOH}) = \frac{m}{M}$$
$$= \frac{1.32\text{ g}}{23.9\text{ g}\,\text{mol}^{-1}}$$
$$= 0.0552\,\text{mol}$$
$$C(\text{LiOH}) = \frac{n}{V}$$
$$= \frac{0.055\,\text{mol}}{0.200\,\text{L}}$$
$$= 0.276\,\text{M}$$

b Calculate the number of moles of the standard solution in the average titre.

$$n(\text{LiOH}) = C \times V$$
$$= 0.276\,\text{mol}\,\text{L}^{-1} \times 0.01213\,\text{L}$$
$$= 0.00335\,\text{mol}$$

- Use the mole ratio from the balanced chemical equation to determine the number of moles of the aliquot.

$$n(\text{HNO}_3) = n(\text{LiOH})$$
$$= 0.00335\,\text{mol}$$

- Use the aliquot volume to determine the concentration of HNO_3.

$$C(\text{HNO}_3) = \frac{n}{V}$$
$$= \frac{0.00335\,\text{mol}}{0.015\,\text{L}}$$
$$= 0.223\,\text{M}$$

Burette

A burette dispenses an accurate volume of standard solution (titrant) into the conical flask. The solution is dispensed gradually by using the stopcock.

The following points will help you to use a burette effectively.

1 Wash the burette.

Rinse the burette with water and then with the titrant. When rinsing with water, hold the burette over the sink with the stopcock open. Use a wash bottle to wash down the sides of the burette with water. The water should wash through the burette and down the sink.

When rinsing with the titrant, attach the burette to a retort stand and place a waste beaker underneath to catch any waste titrant. Most chemicals have hazards associated with them, so never assume that a chemical can be washed down the sink.

With the stopcock open, use a funnel to tip some of the titrant into the burette, washing down the sides and any water droplets that remain from the previous wash. If there is water in the burette, it will lower the concentration of the standard solution.

2 Fill the burette after washing.

Leave the waste beaker underneath the burette and ensure that the stopcock remains open. Use the same funnel to start filling the burette. The titrant will start washing through the burette into the waste beaker. This is deliberate to avoid any bubbles forming in the tip of the burette (Figure 2). If bubbles do form, remove them before you start the experiment. If the bubble washes into the conical flask during the titration, you will record the volume as being higher than it actually is.

3 Avoid parallax error.

Always read the burette at eye level. Figure 3 show how the volume reads differently when you look at the meniscus from three different angles from above, at eye level and from below.

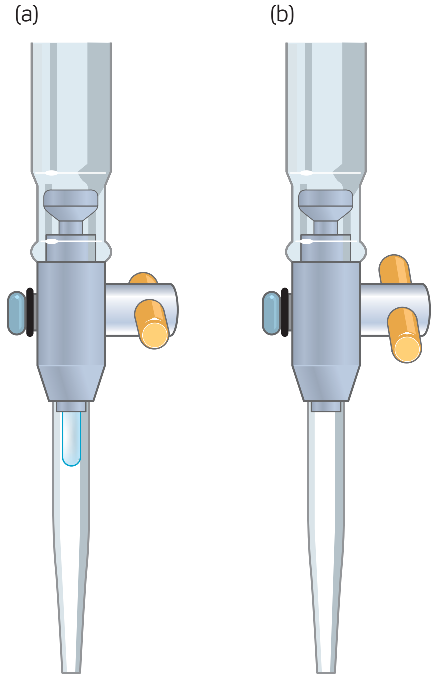


FIGURE 2 (a) A bubble formed in the tip of the burette introduces errors in the titre volume. (b) A burettle without a bubble.

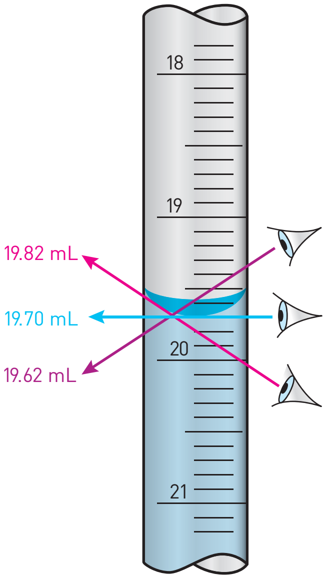


FIGURE 3 The changes in measurement when not viewed at eye level. From above to below: a measurement of 19.62 mL, the correct measurement of 19.70 mL and a measurement of 19.82 mL.

Pipette

A pipette also dispenses highly accurate volumes. In a titration, a pipette is used to measure and dispense the solution of unknown concentration into a volumetric flask.

The following points will help you to use a pipette effectively.

bulb
a piece of equipment responsible for drawing solutions into the pipette

1 Wash the pipette.

As with the burette, you must wash the pipette with water and then with the titrant, before measuring a sample. Place the **bulb** on the top of the pipette and draw water into the pipette from a beaker of water. When the pipette is filled to the marked line, dispense the water into a sink or waste beaker. Place some of the titrant in a clean beaker and fill the pipette. Never put the pipette in the flask holding the solution of unknown concentration because if the pipette is unclean, this will contaminate the solution. Dispose of the chemical into a waste beaker. Fill the burette with titrant for a second time and dispense it into the conical flask. This is the analyte or sample.

2 Leave the drop of solution that remains in the pipette tip.

When you have dispensed the solution into the conical flask, there will be a drop left in the tip of the pipette. The pipette's volume has been calibrated to account for this drop. Do not force the drop through or the aliquot volume will be higher than intended.

3 Avoid parallax error.

View the meniscus at eye level. If you view it from too high or too low, the meniscus won't be on the line.

CASE STUDY 5.2

Vitamin C in Ribena juice

In May 2007, two 14-year-old New Zealand school girls conducted an experiment involving a titration. Their aim was to determine the content of vitamin C in juice drinks. They hypothesised that more expensive drinks would contain more vitamin C than cheaper brands.

Vitamin C, or ascorbic acid (Figure 5), is a weak acid that is oxidised (see Chapter 8) by iodine solution ($I_2(aq)$). As the iodine solution reacts with ascorbic acid, it produces the iodide ion ($I^-(aq)$). A starch indicator is used to monitor the reaction. The solution turns dark blue in excess iodine, when no more ascorbic acid is available to react, indicating the equivalence point.

When the students performed their titration, they found that the indicator turned blue much faster than they were expecting. They determined that there was 7 mg of vitamin C per 100 mL of Ribena juice, a concentration that was so low it was concluded that there were 'no detectable levels' in the drink.

The label claimed that Ribena contained four times the vitamin C of oranges, so the students initially thought that their findings were incorrect or that they had performed the titration incorrectly. However, they

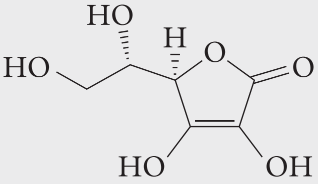


FIGURE 4 The structure of ascorbic acid (vitamin C)

double checked their solutions and methodology and discussed it with their teacher, and they concluded that the error was in the company's claim, not their technique.

After writing to and calling the company, the students received no response, so they contacted a consumer affairs TV program, which passed on their concerns to the New Zealand Commerce Commission, a government watchdog.

The company was fined $217 000 (NZD), ordered to run corrective advertisements and made to place a message on their website.

FIGURE 5 Ribena fruit drink

CHECK YOUR LEARNING 5.2

Describe and explain

1 **Calculate** to the correct number of significant figures the:
   a concentration of a standard solution of sodium hydroxide (NaOH) when 0.8 g is dissolved in water in a 100 mL volumetric flask
   b mass required to produce an aqueous 0.50 M standard solution of sodium carbonate (Na_2CO_3) in a 250 mL volumetric flask.

2 0.96 g of potassium hydroxide (KOH) is dissolved in water in a 200.0 mL volumetric flask. 10.00 mL aliquots of this solution are titrated with sulfuric acid. An average titre of 31.36 mL is found. **Identify** the concentration of the KOH solution. **Identify** the concentration of the sulfuric acid. Express your answer to the correct number of significant figures.

Apply, analyse and interpret

3 When weighing a primary standard on an electronic balance, a student neglects to tare the balance. Before adding the solid to the weigh boat, the balance reads –0.50 g. **Determine** the effect of this error on the:
   a concentration of the standard
   b number of moles of the standard that reacts with the analyte
   c concentration of the analyte.

You can find the following resources for this section on your obook assess:

- » Student book questions
  5.2 Check your learning
- » Increase your knowledge
  Challenge 5.2 Back titrations
- » Weblink
  Ribena titration

5.3 Acid–base titrations

KEY IDEAS

In this section, you will learn about:

- identifying an equivalence point by measuring a change in pH
- titration curves and the information that can be deduced from them.

Acid–base titration is a technique that is widely used in the food industry. It is often used to determine the amount of salt, sugar or vitamins in a food product and compare this to the manufacturer's claims. It is also used to determine the amount of sulfuric acid in acid rain (Figure 1) and the amount of various nutrients in water samples.

Acid–base titrations rely on identifying the equivalence point by measuring the change in pH of the reaction. This can be done by using indicators or pH meters to reveal an observable end point.

The principles of acid–base titration

In an acid–base titration, an acid is reacted with a base to form products that have a different pH from the reactants. The pH of the reactants depends upon the strength of the acid and the base. There are four different types of acid–base reactions (see also Chapter 4):

- strong acid and strong base
- strong acid and weak base
- weak acid and strong base
- weak acid and weak base.

When a strong acid reacts with a strong base, salt and water are formed. The salt water solution is neutral (pH 7). The pH of the reaction is measured in the conical flask. If the conical flask contains a strong acid, the initial pH is very low (approximately 1 or lower). As a strong base is added from the burette, the pH gradually increases. When the pH of the conical flask reaches 7, the equivalence point has been reached. If an indicator is selected that changes colour at a pH of 7, the indicator will change colour at the equivalence point.

Titration curves

To determine the end point and therefore the indicator required in a titration, a titration curve is developed. The titration is set up and a pH meter is placed in the conical flask. The initial pH of the analyte is recorded when no titrant has been added. The titrant is then added, approximately 1 mL at a time. For every millilitre of titrant added, the pH of the solution is recorded in a results table. The pH initially changes very gradually and increases as more titrant is added. When the pH starts to change more rapidly, the titrant is added in smaller volumes – ideally, one drop at a time. The pH should change drastically and then start to become constant again.

The resulting data is plotted as a titration curve – a graph that has the volume of titrant (from the burette) on the x-axis and the pH of the analyte solution in the conical flask on the y-axis. Titration curves change shape depending on whether strong or weak acids or bases are used, because they have different pH values.

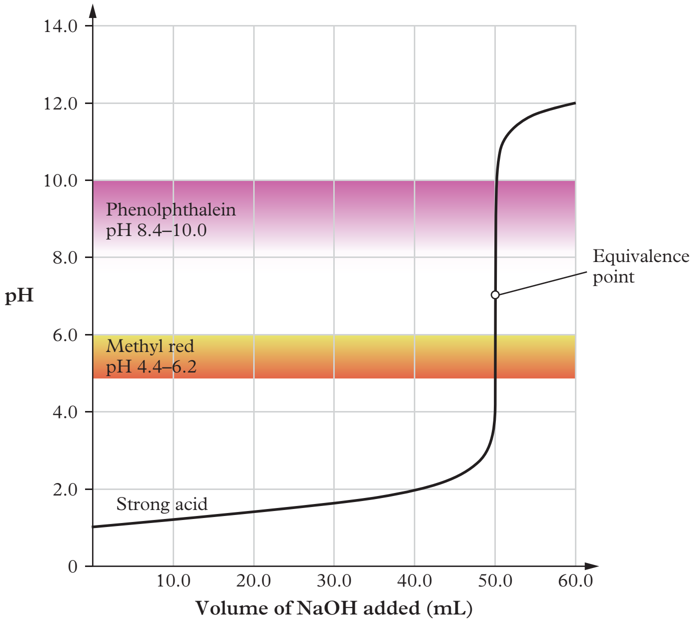


FIGURE 1 The titration curve generated when a sodium hydroxide (NaOH) titrant is added to a hydrochloric acid (HCl) analyte. Both methyl red and phenolphthalein are suitable indicators for this titration.

Strong acid and strong base

The graph observed when a strong acid reacts with a strong base is shown in Figure 1.

The following conclusions can be drawn from the graph in Figure 1.

1 The pH curve starts at a very low pH. Therefore, the solution in the conical flask is an acid.
2 The titration curve begins at a pH of 1 and finishes at a pH greater than 12, so a strong acid is being titrated with a strong base.
3 The steepest section of the graph represents a large change in pH (between pH 3 and 11) caused by the addition of one drop of titrant. The middle of this steep line is the equivalence point.
4 The equivalence point occurs on a section of the graph where pH changes between 3 and 11 with the addition of one drop of titrant, so a pH indicator can be selected that changes colour between these pH values. Table 1, on the next page lists some relevant acid–base indicators and Figure 2 shows the colours of various indicators.

TABLE 1 Acid–base indicator pH ranges and colour changes

Name	pH range	Colour change from lower pH to higher pH in range
Thymol blue (1st change)	1.2–2.8	Red to yellow
Methyl orange	3.1–4.4	Red to yellow
Bromophenol blue	3.0–4.6	Yellow to blue
Bromocresol green	3.8–5.4	Yellow to blue
Methyl red	4.4–6.2	Pink to yellow
Bromothymol blue	6.0–7.6	Yellow to blue
Phenol red	6.8–8.4	Yellow to red
Thymol blue (2nd change)	8.0–9.6	Yellow to blue
Phenolphthalein	8.3–10.0	Colourless to pink

Study tip

The QCAA formula and data book has seven different pH indicators that you will need for your external examination. These can be found in Section 4.3. Figure 2 shows many more pH indicators.

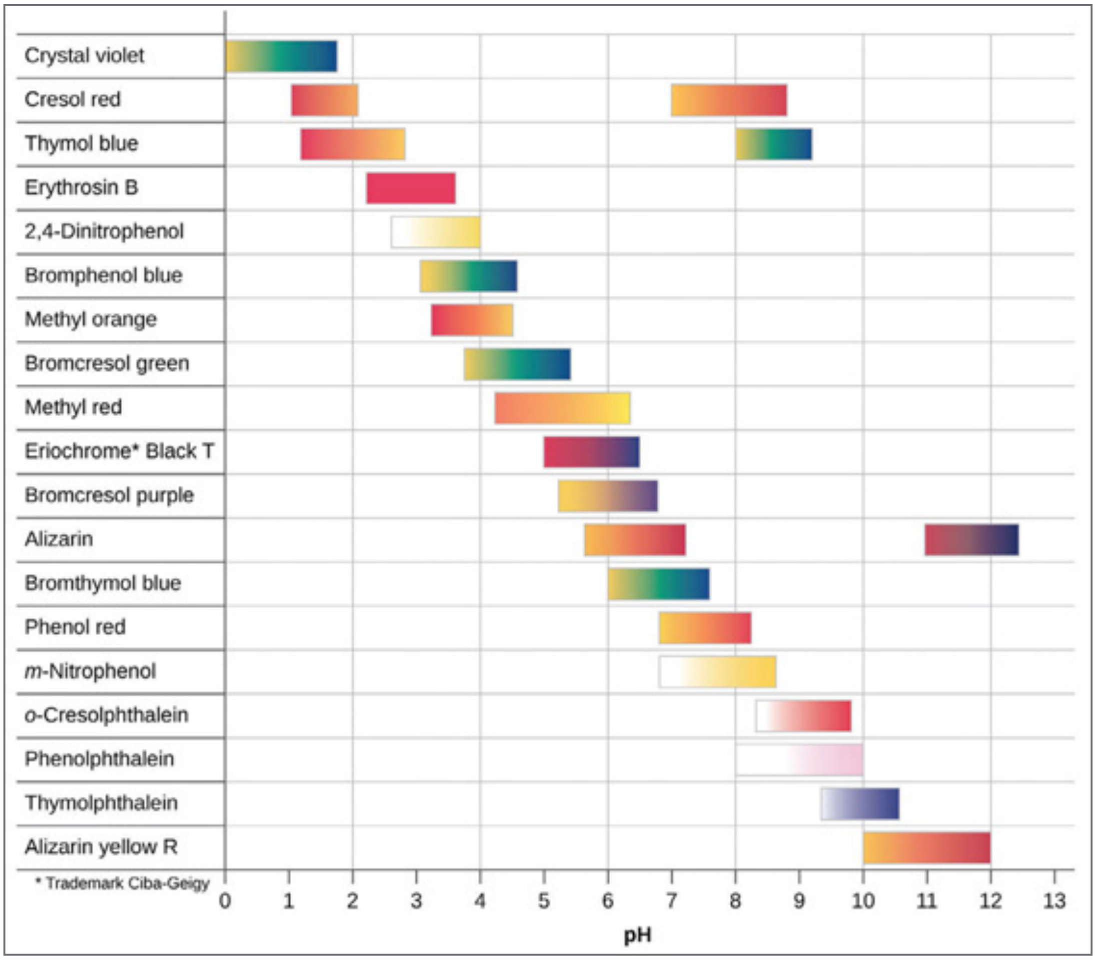


FIGURE 2 The colour changes of some acid–base indicators and the pH at which these changes occur

Weak acid and strong base

Weak acids have a pH range of approximately 3–7.

When a weak acid is titrated with a strong base, it generates a titration curve like that shown in Figure 3.

1 The initial pH is about 3, so there must have been a weak acid in the conical flask at the start of the titration.

2 The pH remains relatively unchanged until the equivalence point is reached. This is called the **buffer region**.

3 The equivalence point is in the middle of the steepest part of the gradient, pH 8.73.

4 The **half-equivalence point** is the point in the buffer region at which the concentration of the titre is equal to half of the original concentration of the analyte. In other words, the concentration of the standard is half of the concentration of the unknown. It is also called the midpoint.

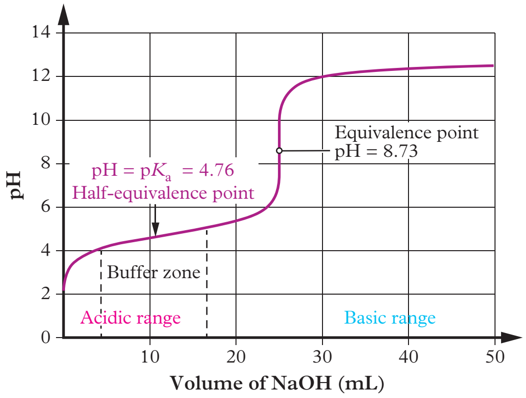


FIGURE 3 The titration of a 0.1 M solution of a weak acid (e.g. ethanoic acid (CH_3COOH)) with a strong base (0.1 M NaOH)

buffer region
the section of a titration curve that is relatively flat because adding more acid or base does not drastically affect the pH

half-equivalence point
a point in a titration curve where the concentration of the titre is equal to half the original concentration of the analyte; also called the midpoint

5 At the half-equivalence point, pH = pK_a (see Chapter 4).
(Note: At the half-equivalence point, pH = pK_a or pOH = pK_b. This allows you to identify a pK_a or pOH value from a titration curve.)

Strong acid and weak base

Weak bases have a pH range of approximately 7–11.

When a strong acid is titrated with a weak base, it generates a titration curve like that in Figure 4. The equivalence point is in the middle of the steepest gradient of the graph at pH 5. The indicator must be one that changes colour between pH 3 and 8.

1 The initial pH is about 12, so there must have been a weak base in the conical flask at the start of the titration.
2 The pH remains relatively unchanged until the equivalence point is reached. This is the buffer region (pH 8–10).
3 The equivalence point is in the middle of the steepest part of the gradient, pH 5.27.
4 The half-equivalence point is the point in the buffer region that is halfway to the equivalence point volume.
5 At the half-equivalence point, pH = pK_a. If pOH was plotted on the *y*-axis instead of pH, the titration curve would flip horizontally and the half-equivalence point would be pOH = pK_b.

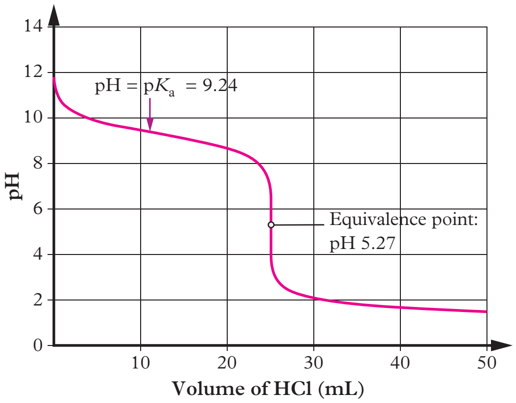


FIGURE 4 The titration of a strong acid (0.1 M HCl) and weak base (25 mL of 0.1 M NH_3)

Weak acid and weak base

The titration of a weak acid with a weak base is more difficult to analyse. The titration curve for this reaction (Figure 5) has no steep gradient at the equivalence point, which makes it very challenging to determine. For this reason, very little information can be interpreted from this graph. You are not required to know this type of titration.

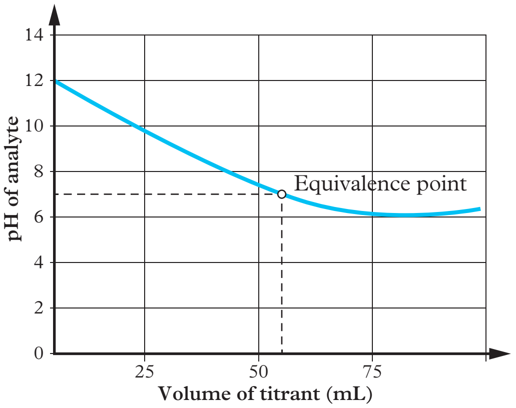


FIGURE 5 The titration curve of a weak acid and a weak base. Because there is no steep section of the curve, it is too difficult to determine the equivalence point from the graph.

The relationship between pK_a and K_a

You can use the pK_a value from a titration curve to determine the equilibrium acidity constant of a weak acid. The following equations can be used to calculate pK_a.

$$pK_a = -\log K_a$$

$$K_a = 10^{-pK_a}$$

$$K_a(\text{monoprotic acid}) = \frac{[H_3O^+][A^-]}{[HA]}$$

$$= \frac{[H^+]^2}{[HA]}$$

Taking logs of both sides and simplifying:

$$pH = pK_a + \log\left(\frac{[A^-]}{[HA]}\right)$$

CASE STUDY 5.3

Titrating waste vegetable oil to make biodiesel

Around the world, vegetable oil (a triglyceride) is used for cooking food. The oil is heated to high temperatures, breaking down some of the triglyceride into free fatty acids. Vegetable oil is recycled after use by reacting the triglyceride with methanol, using a NaOH or KOH catalyst, to form a mixture of fatty esters (methyl esters, called biodiesel) and propane-1,2,3-triol (also known as glycerol or glycerin) (see Figure 6).

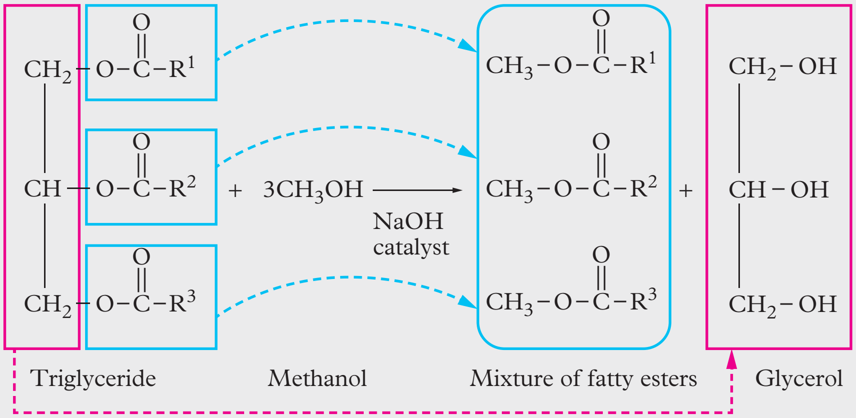


FIGURE 6 The chemical reaction of a triglyceride with methanol to form glycerol and a mixture of fatty esters (biodiesel)

However, the presence of free fatty acids results in an unintended reaction – the weak fatty acid reacts with the reaction catalyst, a strong base (NaOH) to form soap. The more the oil (triglyceride) has been used and heated in cooking, the more unwanted free fatty acid is formed, and more catalyst ends up becoming a reactant in the formation of soap. Thus, more NaOH must be added to the reaction so that there is enough to neutralise the free fatty acid and to act as a catalyst in the formation of biodiesel.

When making biodiesel, it is important to use the correct amount of NaOH for a given oil. Too much NaOH results in the formation of soap, whereas too little results in an incomplete reaction in which not all of the reactants form products, and a poor-quality fuel results.

To determine how much NaOH catalyst to add to a sample of vegetable oil, a titration is conducted. The triglyceride produces fatty acids, so the oil is acidic and is neutralised by the NaOH base. This reaction involves a strong base and weak acid, so the end point occurs at about pH 9, and phenolphthalein is used as an indicator. The end point indicates the point where there is no more free fatty acid and the NaOH can start to act as a catalyst.

FIGURE 7 Vegetable oil that has been used for cooking can be recycled to produce biodiesel.

CHALLENGE 5.3

Diprotic and triprotic acids

Diprotic acids, such as sulfuric acid (H_2SO_4), have two protons that dissociate in water. Triprotic acids, such as phosphoric acid (H_3PO_4), have three protons that dissociate in water.

Use your knowledge of acids and bases and equilibrium constants to predict the shape of diprotic and triprotic titration curves. Explain why they are shaped in this way.

CHECK YOUR LEARNING 5.3

Describe and explain

1 **Explain** the purpose of a titration curve.

Apply, analyse and interpret

2 A student standardises a solution of sodium hydroxide using 20.00 mL aliquots. 0.11 M of standardised hydrochloric acid is used with methyl orange as indicator. Titres of 17.68, 17.73 and 17.69 mL are obtained.

- **a** **Construct** the equation for the reaction occurring during this titration.
- **b** **Calculate** the molarity of the sodium hydroxide solution.
- **c** **Determine** why methyl orange was chosen as the indicator.
- **d** Once its concentration is determined, can the sodium hydroxide solution be called a standard solution? **Explain**.

3 'Cloudy ammonia' is often used as a household cleaner. A student adopts the following procedure to determine the concentration of ammonia in a solution of cloudy ammonia.

The student prepares a bucket of the solution by following the directions on the packaging. He then pipettes 20.00 mL aliquots of the cloudy ammonia into conical flasks and titrates them against a standard solution of 0.0214 mol L^{-1} hydrochloric acid. Using phenolphthalein as the indicator, an average titre of 19.65 mL is obtained.

Determine the concentration of ammonia in the bucket (in g L^{-1}).

Investigate, evaluate and communicate

4 In an acid–base titration, an acid is titrated against a basic standard solution. The indicator used in the titration has not been chosen appropriately and changes colour too soon. **Investigate** the impact on the:

- **a** titre
- **b** moles in the aliquot
- **c** concentration of the aliquot.

You can find the following resources for this section on your obook assess:

» Student book questions
5.3 Check your learning

» Challenge
5.3 Diprotic and triprotic acids

» Weblink
Titration curves

CHAPTER 5

Review

Chapter summary

5.1
- Volumetric analysis uses the technique of titration to determine the volume of chemicals when they react in their molar ratio. This occurs at the equivalence point. An indicator can be selected that changes colour when the reaction reaches this point. The colour change is referred to as the end point.

5.2
- A standard solution is one of a highly accurate volume, concentration and number of moles. It is reacted in a titration to determine the concentration of the second reactant.

5.3
- The equivalence point of an acid–base reaction can be determined from a titration curve. The equivalence point is in the middle of the steepest part of the curve. An indicator can be used to indicate the equivalence point if its colour change also occurs in this steep section.
- Weak acids and bases, when titrated against a strong acid or base, can demonstrate a buffer region where there is a significant amount of both acid and base. The midpoint (pK_a) of the buffer region is the point where the concentration of the titre is half the concentration of the analyte. This pK_a value can be used to accurately determine the concentration of a weak acid.

Key terms

- aliquot
- analyte
- buffer region
- bulb
- burette
- concordant titres
- half-equivalence point
- meniscus
- pH
- pipette
- precision
- primary standard
- solute
- solution
- solvent
- standard solution
- stoichiometric ratio
- stoichiometry
- stopcock
- titrand
- titrant
- titration curve
- titre
- volumetric analysis
- volumetric flask

Key formulas

Number of moles	$n = C \times V$
Number of moles	$n = \frac{m}{M}$
pK_a	$pK_a = -\log K_a$ $K_a = 10^{-pK_a}$
Acid dissociation constant	$K_a = \frac{[H_3O^+][A-]}{[HA]}$

Revision questions

The relative difficulty of these questions is indicated by the number of stars beside each question number: ★ = low; ★★ = medium; ★★★ = high.

Multiple choice

The titration curve in Figure 1 relates to questions 1 and 2.

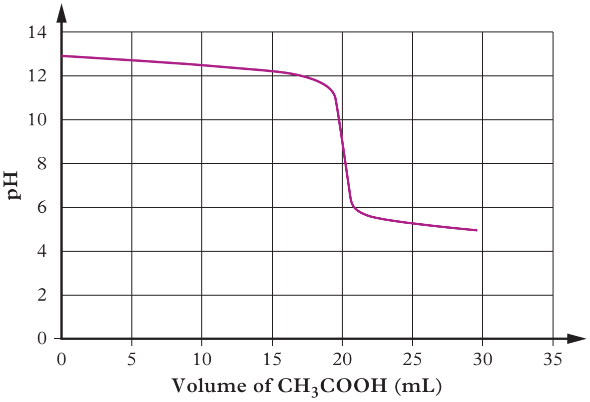


FIGURE 1 The titration of 10.00 mL of 0.10 M NaOH with CH_3COOH

1 A suitable indicator for the titration and the colour change observed is:

A methyl red, from yellow to red

B methyl red, from red to yellow

C phenolphthalein, from colourless to pink

D phenolphthalein, from pink to colourless.

2 Assuming that the average titre is 20.00 mL, and chemicals react in a 1:1 ratio, the concentration of CH_3COOH is:

A 0.5 M

B 5 M

C 50 M

D 0.05 M.

3 The volume of 0.35 M HCl required to react completely with 18 mL of 0.6 M Na_2CO_3 solution is:

A 61.7 mL

B 30.8 mL

C 15.4 mL

D 7.71 mL.

4 Identify the equation that best represents the reaction from the titration curve in Figure 2.

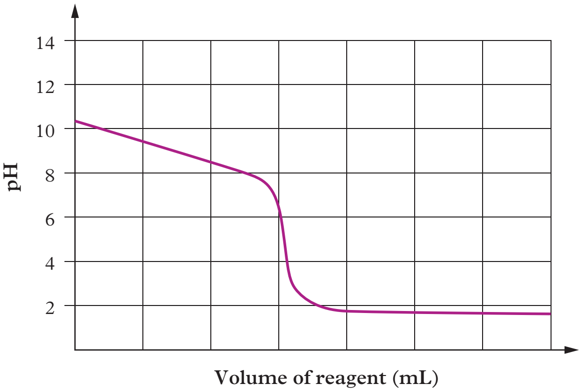


FIGURE 2 A titration curve

A $HCl(aq) + NH_3(aq) \rightarrow NH_4Cl(aq)$

B $HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l)$

C $CH_3COOH(aq) + NH_3(aq) \rightarrow CH_3COONH_4(aq)$

D $CH_3COOH(aq) + NaOH(aq) \rightarrow CH_3COONa(aq) + H_2O(l)$

5 Which of the following is an indicator of the end point of a titration?

A Temperature increase

B Emperature decrease

C Colour change

D Bubbling of solution

6 What is the correct definition of a titre?

A A graduated glass cylinder that dispenses highly accurate volumes of a standard solution

B The standard solution in the burette that is added to the solution of unknown concentration

C The volume of standard solution dispensed from the burette

D A glass tube that dispenses highly accurate volumes of a solution of unknown concentration

7 Which piece of equipment is not required for a titration experiment?

A Hotplate
B Retort stand
C Conical flask
D Stopcock

8 To correctly read the volume of liquid in a piece of measurement glassware, you need to read at:

A eye level above the meniscus
B an angle looking down to the meniscus
C eye level to the meniscus
D an angle looking up to the meniscus.

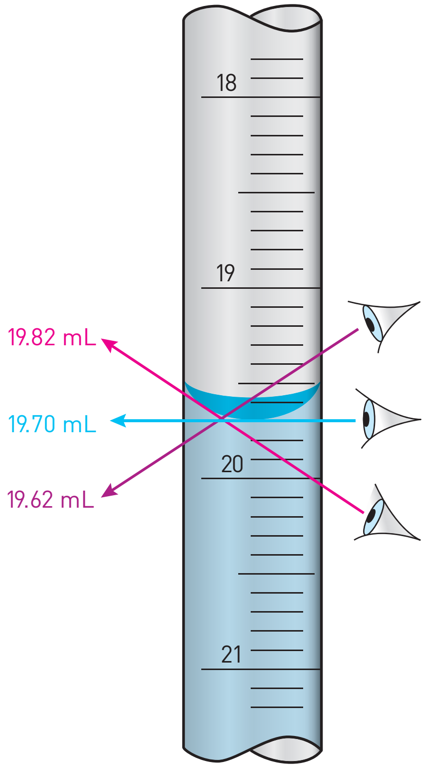


FIGURE 3 Correctly reading volume in glassware

9 To determine the titre, you have to:

A subtract the initial volume from the final volume to determine the total volume of standard solution dispensed from the burette
B subtract the final volume from the initial volume to determine the total volume of standard solution dispensed from the burette
C add the initial volume to the final volume to determine the total volume of standard solution dispensed from the burette
D divide the initial volume by the final volume to determine the total volume of standard solution dispensed from the burette.

Short answer

Describe and explain

★ **10 Define** ‘buffer region’. How does it relate to pK_a and half-equivalence point?

★ **11 Define** ‘parallax error’. Why must it be avoided when measuring?

★ **12 Explain** the relationship between an end point and an equivalence point. **Sketch** a titration curve to support your answer.

★ **13 Identify** five ways of introducing error into the titre volume.

★ **14 Explain** why there are so many different ways of introducing errors in a titration experiment.

Apply, analyse and interpret

★ **15 Construct** a research question for Case study 5.3 ‘Titrating waste vegetable oil to make biodiesel’.

★★ **16 Determine** the final volume when 0.250 M hydrobromic acid (HBr) reacts completely with 20.0 mL of 0.100 M calcium hydroxide ($Ca(OH)_2$) solution. The molar ratio of HBr to $Ca(OH)_2$ is 2:1.

★★ **17** An aliquot of strong base (pH 13) is titrated against a weak acid (pH 4). A titre of 14 mL is obtained. **Sketch** a fully labelled titration curve for the reaction. From the graph, **identify** the equivalence point, half-equivalence point and pK_a.

★★ **18** An aliquot of weak base (pH 10) is titrated against a strong acid (pH 1). A titre of 26.4 mL is obtained. **Sketch** a fully labelled titration curve for the reaction. From the graph, **identify** the equivalence point, half-equivalence point and pK_a.

★★ **19** 12.29 g of potassium hydrogen phthalate ($KHC_8H_4O_4$) is dissolved in a 250.00 mL volumetric flask to create a standard solution. This solution is titrated against 10.00 mL aliquots of a NaOH solution according to the following chemical equation:

$NaOH(aq) + KHC_8H_4O_4(aq) \rightarrow KNaC_8H_4O_4(aq) + H_2O(l)$

Deduce the concentration of the NaOH solution.

★★★ **20** Use your knowledge of acid–base titration equilibrium constants for weak acids to answer the following question. To determine the concentration of a solution of HA (a weak acid), a student titrates a 20.0 mL aliquot of HA with a standard 0.100 M sodium hydroxide solution (NaOH(aq)). The titration curve in Figure 4 is produced.

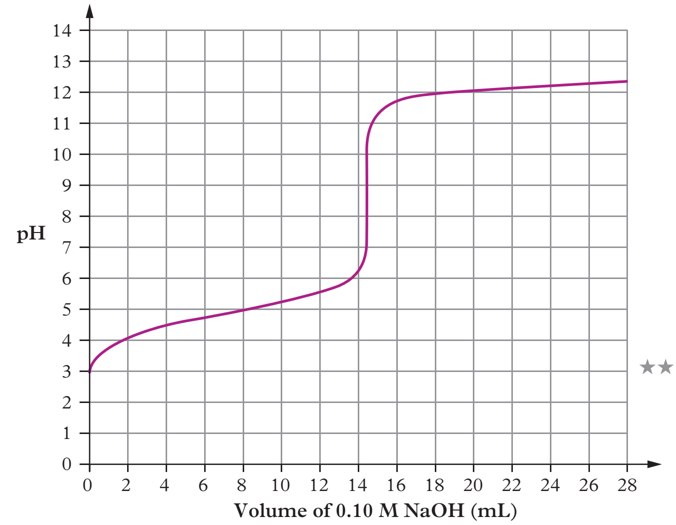


FIGURE 4 A titration curve

Use the information on the graph to **determine**:

a the volume of NaOH used to neutralise the solution of HA

b [HA]

c the concentration of hydronium ions (H_3O^+) in the solution of HA before it is reacted with NaOH.

d K_a for the weak acid HA.

e whether your answer for part d correlates with the titration curve.

Investigate, evaluate and communicate

★★ **21** **Create** a mind map of the different ways of introducing errors into titration.

★★★ **22** In a titration, a student prepares a standard solution of NaOH to titrate an unknown concentration of HCl. 1.00 g of NaOH is dissolved in a 250.00 mL volumetric flask. A 20.00 mL aliquot of the HCl results in an average titre of 25.00 mL.

A second student prepares a standard solution in the same way but leaves the solution on the bench over the school holidays. Upon returning, the student uses a 20.00 mL aliquot of HCl and obtains a titre of 27.78 mL.

Evaluate what happens to cause the difference in titre volumes. **Justify** your answer using calculations.

★★★ **23** Two students perform an aqueous titration. One student accidentally spills water from the wash bottle into the conical flask. The second student insists that they must obtain a new aliquot in a fresh conical flask. **Evaluate** the student's claim and provide a justification.

You can find the following resources for this section on your obook assess:

- Student book questions
  Chapter 5 Revision questions
- Revision notes
  Chapter 5
- assess quiz
  Auto-correcting multiple-choice quiz
- Flashcard glossary
  Chapter 5

CHAPTER 6

Redox reactions

Redox reactions involve the transfer of electrons, and therefore the movement of electrons, from one atom to another. The movement of electrons generates an electrical current, making redox reactions one of the most important types of chemical reaction. Redox reactions convert chemical potential energy into electrical energy, so are used to generate a major source of energy in the world.

Redox reactions can also be highly destructive. Some are responsible for killing bacteria and make excellent household cleaners. They can also sterilise unsanitary environments or hospitals and destroy certain metal structures and biomolecules. For example, the rusting of metals (especially cars) and the browning (or oxidation) of fruit are the result of redox reactions.

OBJECTIVES

→ Recognise that a range of reactions, including displacement reactions of metals, combustion, corrosion and electrochemical processes, can be modelled as redox reactions involving oxidation of one substance and reduction of another substance.

→ Understand that the ability of an atom to gain or lose electrons can be predicted from the atom's position in the periodic table, and explained with reference to valence electrons, consideration of energy and the overall stability of the atom.

→ Identify the species oxidised and reduced, and the oxidising agent and reducing agent, in redox reactions.

→ Understand that oxidation can be modelled as the loss of electrons from a chemical species, and reduction can be modelled as the gain of electrons by a chemical species; these processes can be represented using balanced half-equations and redox equations (acidic conditions only).

→ Deduce the oxidation state of an atom in an ion or compound and name transition metal compounds from a given formula by applying oxidation numbers represented as roman numerals.

→ Use appropriate representations, including half-equations and oxidation numbers, to communicate conceptual understanding, solve problems and make predictions.

Source: *Chemistry 2019 v1.3 General Senior Syllabus* © Queensland Curriculum & Assessment Authority

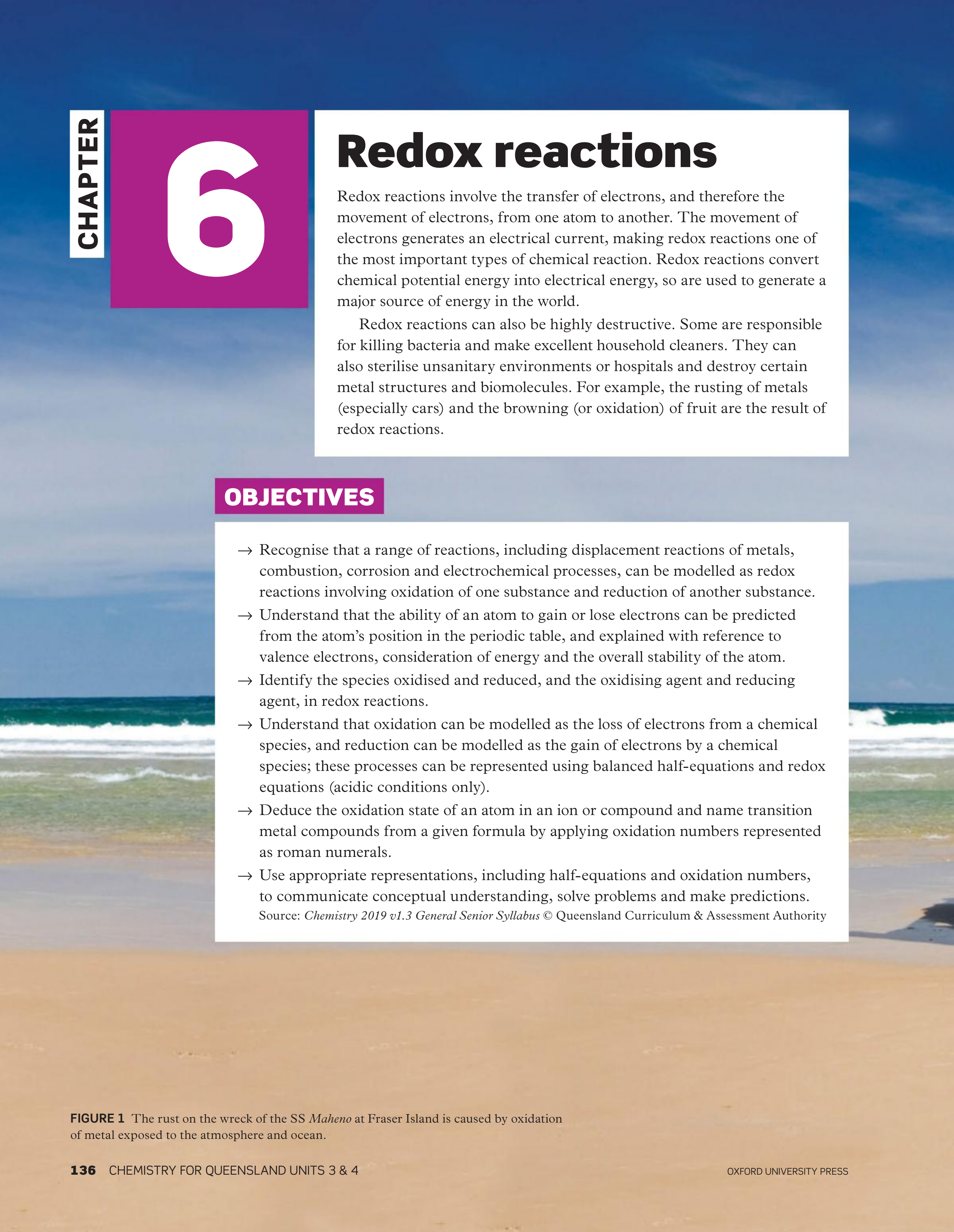
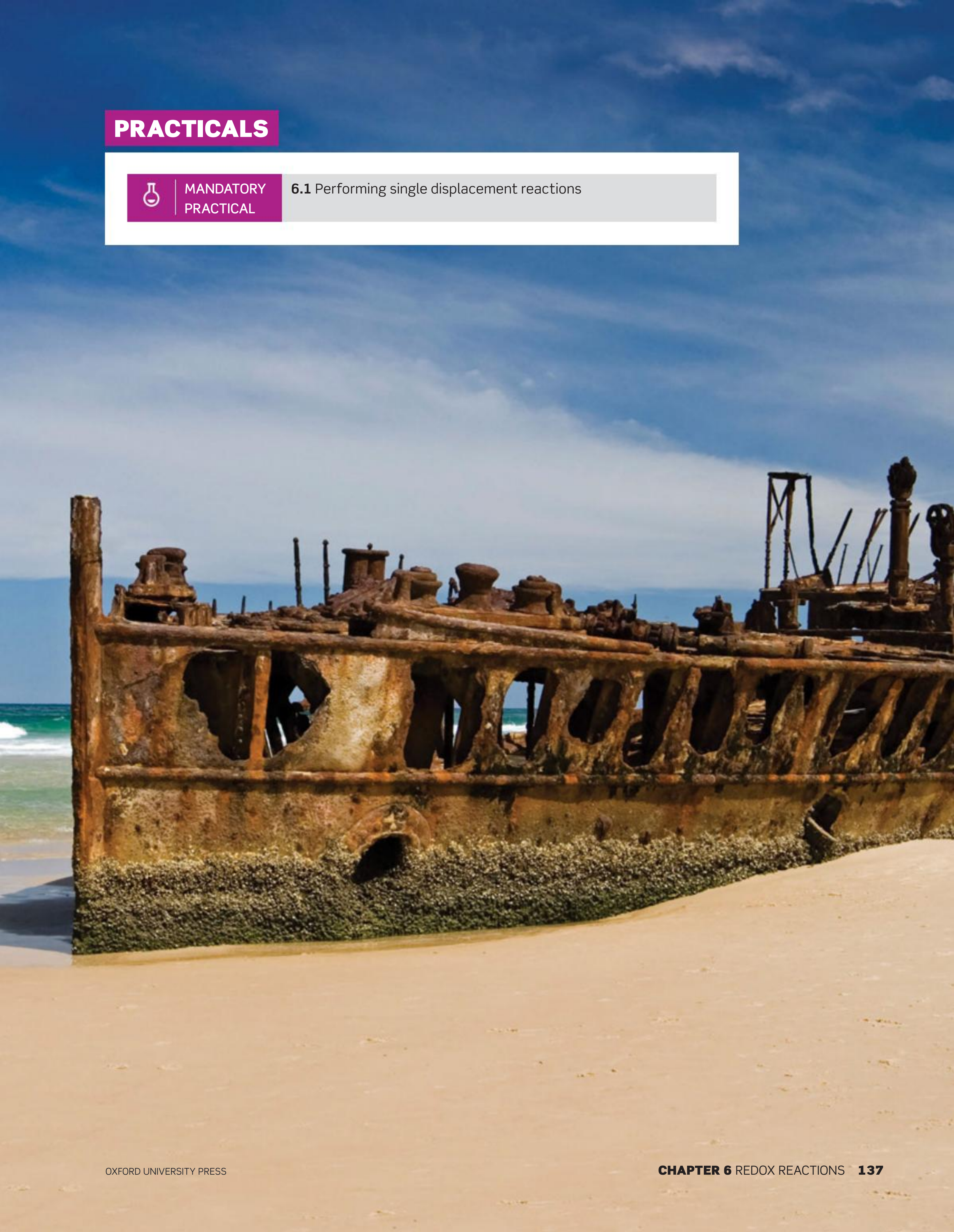


FIGURE 1 The rust on the wreck of the SS *Maheno* at Fraser Island is caused by oxidation of metal exposed to the atmosphere and ocean.



PRACTICALS

MANDATORY PRACTICAL	**6.1** Performing single displacement reactions

6.1 Reduction and oxidation reactions

KEY IDEAS

In this section, you will learn about:

- how reduction is a gain of electrons, whereas oxidation is a loss of electrons
- valence electrons and their involvement in the transfer of electrons and energy
- terminology such as 'reduction', 'oxidation', 'reducing agent' and 'oxidising agent'.

Negatively charged electrons move between chemical species. When they move, energy is exchanged. This exchange of electrons between chemicals is like a financial transaction. When a substance loses one or more electrons, another substance accepts them.

Redox is an abbreviation for a pair of reactions in which electrons are exchanged between reactants. The reactions occur simultaneously. These reactions are called **oxidation** and **reduction** reactions, and one cannot occur without the other.

redox
a chemical reaction involving the transfer of electrons from one reactant to another

oxidation
a loss of electrons

reduction
a gain of electrons

A transfer of electrons

Reduction and oxidation reactions are characterised by the transfer of electrons. As one reactant loses one or more electrons, the second reactant gains them to form new products.

- Oxidation occurs when a chemical species loses one or more electrons.
- Reduction occurs when a chemical species gains one or more electrons.

Study tip

A useful method of remembering oxidation and reduction is OIL RIG. This stands for 'Oxidation is Loss' and 'Reduction is Gain'.

Valence electrons

The reaction between sodium and oxygen to form sodium oxide is an example of a redox reaction:

$$4Na(s) + O_2(g) \rightarrow 2Na_2O(s)$$

The Bohr model of electron configuration of the sodium and oxygen atoms (Figure 1) demonstrates that sodium has one **valence electron**, which it must lose in order to become stable. Oxygen has six valence electrons and must gain two to complete its octet, have a complete valence shell and be stable. This means that two sodium atoms are required for every oxygen atom because sodium loses one electron and oxygen gains two.

valence electron
an electron in the outermost shell of an atom, according to the Bohr model of electron configuration

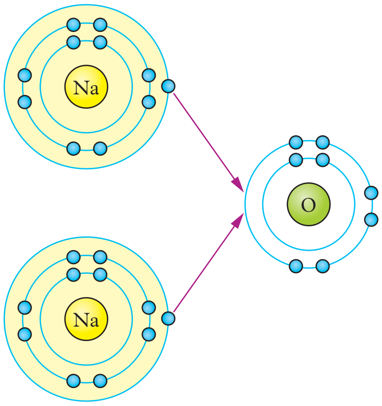


FIGURE 1 Sodium has one valence electron. Oxygen has six valence electrons. Two sodium atoms each transfer an electron to an oxygen atom to form sodium oxide.

This example demonstrates the transfer of electrons between reactants. Sodium loses an electron and oxygen gains two electrons. The transfer of electrons results in Na becoming the ion Na^+ and O becoming the ion O^{2-}. Sodium loses an electron and develops a positive charge. Oxygen gains electrons and develops a negative charge. Therefore, sodium has undergone oxidation and oxygen has undergone reduction. Sodium has been **oxidised** and oxygen has been **reduced**. The general process is summarised in Figure 2.

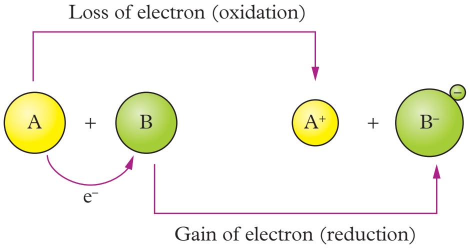


FIGURE 2 The transfer of an electron from A to B results in a positive cation (A^+) and negative anion (B^-), forming an ionic compound (AB).

oxidise
to lose electrons

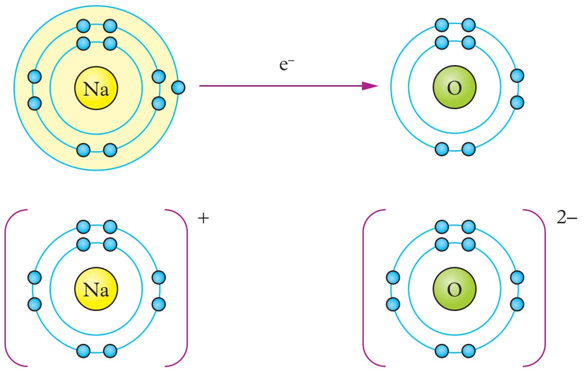
reduce
to gain electrons

Terminology

In the example between sodium and oxygen to form sodium oxide, sodium is oxidised, and oxygen is reduced. However, sodium will not lose this electron unless oxygen is able to accept it. For this reason, the oxygen causes the sodium to lose an electron and, similarly, the sodium causes the oxygen to gain an electron. The chemical species responsible for causing oxidation and reduction are called **oxidising agents** and **reducing agents** (Figure 3).

oxidising agent
a reactant that causes another reactant to lose electrons and be oxidised and is itself reduced

reducing agent
a reactant that causes another reactant to gain electrons and be reduced and is itself oxidised



The Na atom loses an electron.
Na is oxidised.
Na is the reducing agent.

The O atom gains two electrons from two Na atoms.
O is reduced.
O is the oxidising agent.

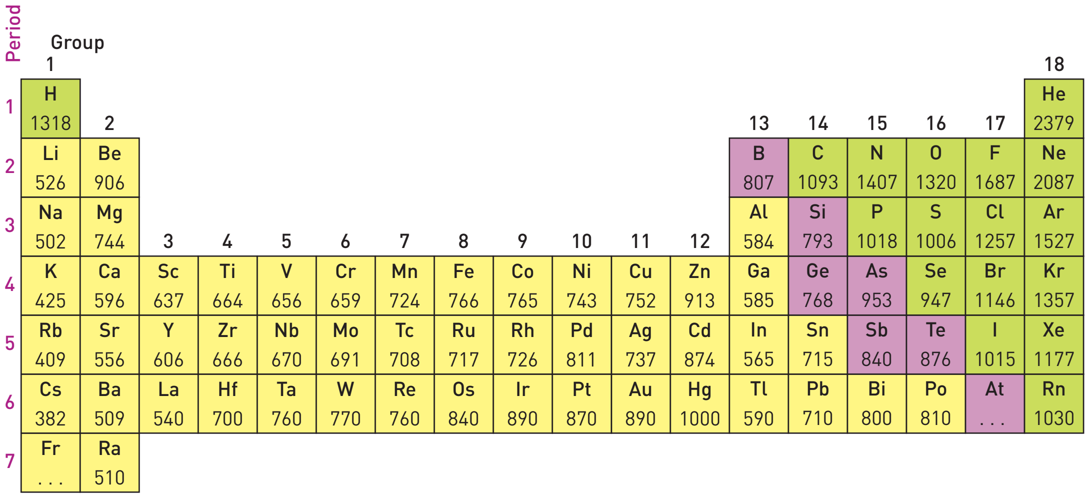
FIGURE 3 A summary of the redox process and the terminology used to describe this process

Predicting redox reactions from the periodic table

Elements in groups 1 and 2 of the periodic table readily lose their valence electrons to form more stable positive cations. By losing these electrons, they are oxidised and act as reducing agents. Metals that donate their valence electrons more readily are stronger reducing agents.

Figure 4 lists the first ionisation energies for elements. The first ionisation energy is the energy required to remove one electron from an element. Elements in the bottom left of the table have the lowest **ionisation energies**, and lose their valence electrons more readily.

ionisation energy
the energy (in kJ mol^{-1}) required by a gaseous atom to remove an electron from its valence shell



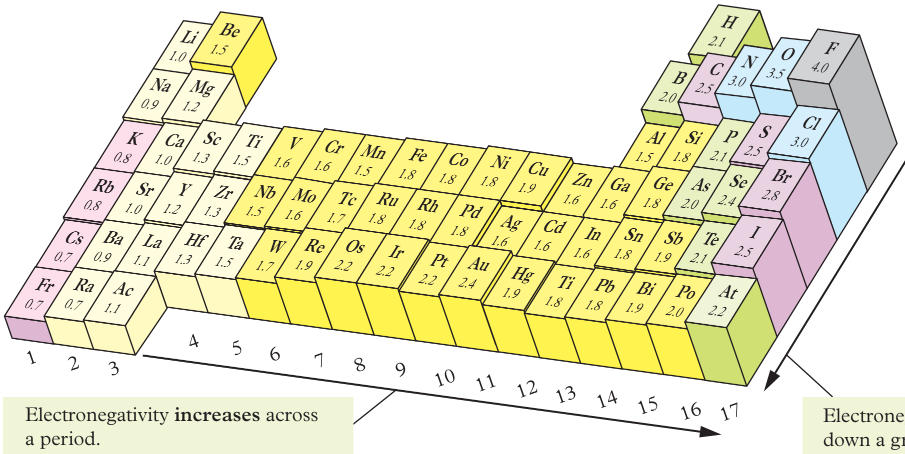
Period \ Group	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	H 1318																	He 2379
2	Li 526	Be 906											B 807	C 1093	N 1407	O 1320	F 1687	Ne 2087
3	Na 502	Mg 744											Al 584	Si 793	P 1018	S 1006	Cl 1257	Ar 1527
4	K 425	Ca 596	Sc 637	Ti 664	V 656	Cr 659	Mn 724	Fe 766	Co 765	Ni 743	Cu 752	Zn 913	Ga 585	Ge 768	As 953	Se 947	Br 1146	Kr 1357
5	Rb 409	Sr 556	Y 606	Zr 666	Nb 670	Mo 691	Tc 708	Ru 717	Rh 726	Pd 811	Ag 737	Cd 874	In 565	Sn 715	Sb 840	Te 876	I 1015	Xe 1177
6	Cs 382	Ba 509	La 540	Hf 700	Ta 760	W 770	Re 760	Os 840	Ir 890	Pt 870	Au 890	Hg 1000	Tl 590	Pb 710	Bi 800	Po 810	At . . .	Rn 1030
7	Fr . . .	Ra 510																

FIGURE 4 The first ionisation energies (kJ mol^{-1}) of elements on the periodic table

Group 17 elements readily gain valence electrons to form more stable negative anions. In gaining electrons, they are reduced and act as oxidising agents. Non-metals that accept electrons more readily are stronger oxidising agents.

electronegativity the attraction between a positively charged nucleus and the negatively charged electrons of a neighbouring atom

Figure 5 lists the **electronegativities** of elements. You can see that the elements in the top right-hand side of the periodic table (except the noble gases) have the strongest electronegativities – they more readily accept electrons.



Electronegativity **increases** across a period.

Electronegativity **decreases** down a group.

FIGURE 5 The electronegativities of elements on the periodic table

WORKED EXAMPLE 6.1

Consider the chemical reaction between fluorine and lithium to form lithium fluoride:

$$F_2(g) + 2Li(s) \rightarrow 2LiF(s)$$

1 Draw the Bohr electron configurations of lithium and fluorine and show the electron transfer.
2 Identify the chemicals that gain and lose electrons.
3 Identify the chemicals oxidised and reduced.
4 Identify the oxidising agent and the reducing agent.

SOLUTION

1

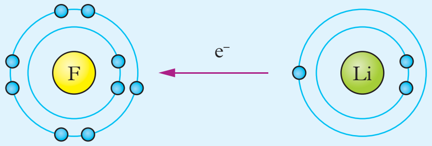


FIGURE 6 The reaction of fluorine with lithium to form lithium fluoride

2 Fluorine gains an electron. Lithium loses an electron.
3 Lithium is oxidised. Fluorine is reduced.
4 Fluorine is the oxidising agent. Lithium is the reducing agent.

MANDATORY PRACTICAL
6.1 Performing single displacement reactions
Go to page 406 »

Redox can be modelled using a range of reactions

Several different types of chemical reactions can be regarded as redox reactions. Because redox reactions involve a transfer of electrons, they can often be identified by reactions involving elements, ions and metals, but not always. Reactions that involve a transfer of electrons include:

- displacement reactions
- **combustion** reactions
- **corrosion** reactions.

combustion
a chemical reaction with oxygen to form a metal oxide, a covalent compound or carbon dioxide and water

corrosion
the degradation of a metal to form a more stable metal oxide when exposed to gases and liquids

single displacement
a chemical reaction in which a more reactive metal ion replaces a less reactive metal ion in a molecule

Displacement reactions of metals

Displacement reactions of metals are often called **single displacement** reactions. This type of reaction is covered in detail in Chapter 9 of *Chemistry for Queensland Units 1 & 2*. Single displacement reactions occur when a stronger reducing agent replaces a weaker reducing agent. Figure 7 shows the reactivity series of the metals.

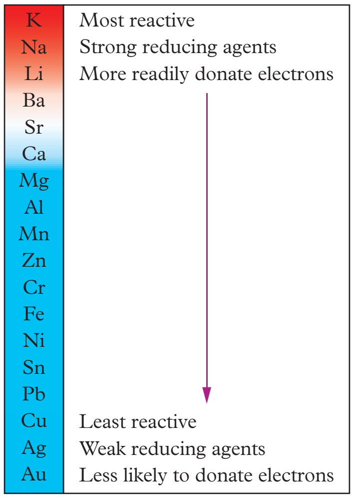


FIGURE 7 The metal reactivity series

Consider the reaction of magnesium with zinc nitrate:

$$Zn(NO_3)_2(aq) + Mg(s) \rightarrow Mg(NO_3)_2(aq) + Zn(s)$$

Magnesium is a stronger reducing agent – it gives away its electrons more readily than zinc does. Therefore, magnesium displaces the zinc atom (knocks it off the nitrate ion) to form magnesium nitrate and zinc metal.

Zinc is the cation in an ionic compound. It gains electrons to form zinc metal. Therefore, zinc undergoes reduction.

Magnesium metal loses electrons to form a positive metal cation in the ionic compound. Therefore, magnesium undergoes oxidation.

Combustion

A combustion reaction is a reaction with oxygen. Metals and non-metals react in very different ways to form an ionic or a covalent compound.

A metal combusts to form a metal oxide, according to the equation:

$$\text{metal} + \text{oxygen} \rightarrow \text{metal oxide}$$

Consider the reaction between copper and oxygen:

$$2Cu(s) + O_2(g) \rightarrow 2CuO(s)$$

Copper metal loses electrons to form a positive metal cation. Therefore, copper undergoes oxidation. Oxygen gas gains electrons to form a negative non-metal anion. Therefore, oxygen undergoes reduction.

Corrosion

Corrosion is a process in which metals react with chemicals in the atmosphere (including rain and atmospheric gases such as oxygen and carbon dioxide) to form a more stable chemical compound. For the reaction to occur, the metal must be more stable as an ion than as a solid metal. Thus, the metal readily donates an electron according to the general equation (where M represents the metal):

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

For example, iron is a highly corrosive metal. When water interacts with the surface of the iron metal (Figure 8), iron loses two electrons to form aqueous iron ions and is therefore oxidised according to the equation:

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

Oxidation cannot occur without reduction, so the reduction occurs at the surface of the water droplet where water reacts with oxygen to form hydroxide ions:

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

The iron ions and hydroxide ions react with each other to form iron(II) hydroxide:

$$Fe^{2+}(aq) + 2OH^{-}(aq) \rightarrow Fe(OH)_2(aq)$$

The iron hydroxide, which is now a part of the water droplet solution, also reacts with oxygen at the surface to form iron(III) hydroxide:

$$4Fe(OH)_2(aq) + O_2(g) + 2H_2O(l) \rightarrow 4Fe(OH)_3(aq)$$

The iron(III) hydroxide decomposes because of the presence of oxygen to form a brown hydrated iron oxide complex:

$$4Fe(OH)_3(aq) \rightarrow 2Fe_2O_3{\cdot}H_2O(aq)$$

Iron oxide is the chemical that gives rust its characteristic brown colour (Figure 8).

FIGURE 8 The corrosion of iron metal forms rust, seen here as red-brown patches.

CASE STUDY 6.1

Why is it called 'reduction' if it is a gain in electrons?

The earliest chemists realised that they could extract pure metals in metal ore from the ground by melting (or smelting) the ore. The metal obtained at the end of the process had less mass than the original ore, so these chemists called the process 'reduction'.

The French chemist Antoine Lavoisier (1743–1794) was the first to determine that this loss of mass was due to the ore losing oxygen. At the time, scientists did not know what electrons were and they were only developing an understanding of atoms. Therefore, it is understandable that the process was named without any true understanding of the electrons that are transferred from one atom to another.

Today, students struggle with the idea of a gain in electrons being called reduction. It is only when a deeper level of understanding is obtained, and oxidation numbers are investigated, that a link between the term 'reduction' and a decrease in oxidation number can be made (see section 6.2).

FIGURE 9 Smelting of copper ore to make copper plates

CHALLENGE 6.1

Ionisation energy, electronegativity and redox

How does the ionisation energies of atoms and their electronegativities relate to the ability of an atom to gain or lose electrons and therefore their strength as an oxidant or reductant? Use francium and fluorine as examples to support your answer.

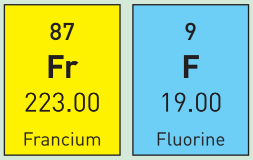


FIGURE 10 Francium and fluorine are both chemical elements.

CHECK YOUR LEARNING 6.1

Describe and explain

1 **Explain** the processes of reduction and oxidation. How are they related?

2 **Describe** what happens to the valence shell electrons during redox reactions.

Apply, analyse and interpret

3 **Use** your knowledge of valence shell diagrams to demonstrate the transfer of electrons between the following pairs of atoms.

- **a** Lithium metal (Li) and sulfur (S)
- **b** Magnesium metal (Mg) and fluorine (F_2)
- **c** Aluminium metal (Al) and oxygen (O_2)

Determine:

- **i** which atom is oxidised and which atom is reduced
- **ii** the reducing and oxidising agent
- **iii** the product of the reaction.

4 **Determine** the oxidised and reduced species in the following reactions.

- **a** $H_2(g) + Cl_2(g) \rightarrow 2HCl(aq)$
- **b** $Cu(NO_3)_2(aq) + Fe(s) \rightarrow Fe(NO_3)_2(aq) + Cu(s)$
- **c** $2AgNO_3(aq) + Pb \rightarrow Pb(NO_3)_2(aq) + 2Ag(s)$

Investigate, evaluate and communicate

5 Oxidation is a name given to many chemical reactions. It can also be defined as a gain in oxygen or a loss of hydrogen. **Evaluate** these definitions and provide examples of these types of reactions.

Using this information, **devise** a more accurate definition for oxidation and reduction.

6 Your teacher claimed that the corrosion of a metal can sometimes be beneficial, but does not explain why. Your friend was absent from this chemistry lesson and asks you to explain it to them. **Investigate** a circumstance where this is true and **devise** the answer that you would give to your friend.

You can find the following resources for this section on your obook assess:

- » **Student book questions**
  6.1 Check your learning
- » **Mandatory practical**
  6.1 Performing single displacement reactions
- » **Challenge**
  6.1 Ionisation energy, electronegativity and redox
- » **Weblink**
  Redox

6.2 Oxidation numbers

KEY IDEAS

In this section, you will learn about:

- the rules for assigning oxidation numbers
- the use of oxidation numbers to determine which chemical species is oxidised and which is reduced.

overall equation a reaction that combines the two half-equations after electrons have been balanced and cancelled out

oxidation state oxidation number

Often, redox reactions are complex, and the **overall equation** involves more than two chemical species. For this reason, it can be difficult to identify which species have gained or lost electrons without identifying their **oxidation states** (or oxidation numbers) before and after reacting.

Assigning oxidation numbers

The oxidation number (often called oxidation state) of an element can help you to determine whether electrons have been gained or lost. Oxidation numbers do not always represent the charge of individual chemical elements but are used to keep track of how many electrons an atom has. Oxidation numbers can be calculated for elements, ions or covalent molecules. Table 1 outlines the rules for assigning oxidation numbers to atoms.

TABLE 1 Rules for assigning oxidation numbers

Rule	Examples
Elements have an oxidation number of 0.	O_2, F_2, He, Fe, Zn, Li
Certain elements when present in compounds have common oxidation numbers.	Group 1 metals are always +1 (Li^+, Na^+, K^+). Group 2 metals are always +2 (Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}). Hydrogen is +1 (except in metal hydrides, where it is –1, e.g. LiH). Oxygen is –2 (except in peroxide (H_2O_2), where it is –1).
For monatomic ions, the oxidation number is given by the charge on the ion.	Cu^{2+} has an oxidation number of +2. Na^+ has an oxidation number of +1.
In polyatomic ions, the sum of oxidation numbers is equal to the charge of the ion.	In PO_4^{3-}, the sum of the oxidation numbers is –3. $P + (4 \times O) = -3$. Oxygen is –2 and $4 \times -2 = -8$. $P + -8 = -3$, so phosphorus has an oxidation number of +5.
In a neutral compound, the sum of oxidation numbers is equal to 0.	HCl is a neutral compound and has an oxidation number of 0. As hydrogen is +1, chlorine must be –1.
The most electronegative element has a negative oxidation number.	NO_2 is a neutral compound. Oxygen is more electronegative and therefore has a negative oxidation number. Oxygen is –2 and $2 \times -2 = -2$. The sum of the oxidation numbers is 0, so nitrogen has an oxidation numbers of +4.

Oxidation and reduction using oxidation numbers

oxidation number the number of electrons gained or lost by an atom

When an atom gains one or more electrons, it gains some negative charge and its oxidation state decreases. Therefore, reduction, a gain in electrons, causes a decrease in the **oxidation number**. In reduction, the oxidation number reduces.

When an atom loses one or more electrons, it loses some negative charge and consequently becomes more positive. Therefore, oxidation, a loss of electrons, causes an increase in oxidation number. In oxidation, the oxidation number increases.

Worked examples 6.2A, 6.2B and 6.2C show you how to work out oxidation states.

WORKED EXAMPLE 6.2A

Determine the oxidation state of a magnesium ion.

SOLUTION

1. Magnesium is in group 2 of the periodic table.
2. When Mg becomes an ion, it loses 2 valence electrons, resulting in a charge of 2+ (Mg^{2+}).
3. Therefore, the oxidation state of a magnesium ion is +2.

WORKED EXAMPLE 6.2B

Determine the oxidation state of chlorine gas (Cl_2).

SOLUTION

1. $Cl_2(g)$ is an uncharged molecule, because it is in its elemental form.
2. Therefore, the oxidation state of a chlorine molecule is 0.

WORKED EXAMPLE 6.2C

Determine the oxidation state of all the elements in a water molecule (H_2O) and confirm the oxidation state of water.

SOLUTION

1. H_2O is an uncharged compound; therefore, the sum of all oxidation numbers must be 0.

$$\text{Oxidation state } H_2O = 0$$

2. Use Table 1 Rules for assigning oxidation numbers:
The oxidation state of oxygen is always –2 (unless in hydrogen peroxide).
The oxidation state of hydrogen is +1 (unless in a metal hydride).
There are 2 hydrogens and one oxygen in the water molecule:

$$\text{Oxidation state } (H^+) = +1$$
$$\text{Oxidation state } (O2^-) = -2:$$
$$(2 \times +1) + (1 \times -2) = 0$$

3. Therefore, hydrogen has an oxidation state of +1, oxygen has an oxidation state of –2 and combined in a water molecule, the oxidation state is 0, as expected.

Oxidation states of transition metals

Transition metals have multiple oxidation states. This is true of several non-transition metals as well. When determining oxidation numbers, if there is no rule for an atom then its oxidation number must be determined using other atoms in the chemical species.

For example, permanganate exists as MnO_4^-. To determine the oxidation state of the manganese atom, you must determine all other pieces of information.

- The molecular ion has a charge of 1–. Therefore, its oxidation state is –1.
- The oxidation state of oxygen is –2, unless in peroxide.

Study tip

The terms ‘oxidation number’ and ‘oxidation state’ are interchangeable. They mean the same thing.

$$
\begin{aligned}
\text{Oxidation state } (\mathrm{MnO_4}) &= -1 \\
\mathrm{Mn} + (4 \times -2) &= -1 \\
\mathrm{Mn} + (-8) &= -1 \\
\mathrm{Mn} + (-8) + 8 &= -1 + 8 \\
\mathrm{Mn} &= +7
\end{aligned}
$$

Therefore, the oxidation state of manganese is +7.

Oxidation states of transition metals are indicated by roman numerals in brackets after the atom. For example, manganese +7 is written manganese(VII) (or $\mathrm{Mn^{VII}}$). Roman numerals are also used in the name of a molecule to identify the oxidation state of the metal.

Study tip

Molecules with a charge of 1– or 1+ are just written as – or + (e.g. $\mathrm{Cl^-}$ or $\mathrm{K^+}$).

For example:

- copper has an oxidation state of +1 or +2 (rarely +3). Therefore, it is $\mathrm{Cu^{I}}$ or $\mathrm{Cu^{II}}$. When naming copper in copper sulfate, it is either copper(I) sulfate ($\mathrm{Cu_2SO_4}$) or copper(II) sulfate ($\mathrm{CuSO_4}$)
- iron has an oxidation state of +2 or +3. Therefore, it is $\mathrm{Fe^{II}}$ or $\mathrm{Fe^{III}}$. When naming iron in iron nitrate, it is either iron(II) nitrate ($\mathrm{Fe(NO_3)_2}$) or iron(III) nitrate ($\mathrm{Fe(NO_3)_3}$).

Worked example 6.2D shows to determine the oxidation state of a transition metal.

WORKED EXAMPLE 6.2D

Determine the oxidation states of all the elements in dichromate ($\mathrm{Cr_2O_7^{2-}}$).

SOLUTION

1 $\mathrm{Cr_2O_7^{2-}}$ is a charged compound; therefore, the sum of all the oxidation numbers must be equal to its charge (–2).

$$
\begin{aligned}
\text{Oxidation state } (\mathrm{Cr_2O_7^{2-}}) &= -2 \\
(2 \times \mathrm{Cr}) + (7 \times \mathrm{O}) &= -2
\end{aligned}
$$

2 The oxidation state of oxygen is always –2 (unless in hydrogen peroxide); chromium is a transition metal and has multiple oxidation states. Therefore, determine the oxidation state of chromium.

$$
\begin{aligned}
(2 \times \mathrm{Cr}) + (7 \times -2) &= -2 \\
(2 \times \mathrm{Cr}) + (-14) &= -2 \\
(2 \times \mathrm{Cr}) + (-14) + 14 &= -2 + 14 \\
2 \times \mathrm{Cr} &= +12
\end{aligned}
$$

3 Therefore, chromium has an oxidation state of +6.

Because chromium is a transition metal, it can be identified as $\mathrm{Cr^{VI}}$.

CHALLENGE 6.2

Oxidation of alcohol

The alcohol ethanol undergoes oxidation by the permanganate ion in an acidic environment according to the equation:

$$
\begin{gathered}
\mathrm{3CH_3CH_2OH(aq) + 2MnO_4^-(aq) + 4H^+(aq) \rightarrow} \\
\mathrm{3CH_3COOH(aq) + 2Mn^{2+}(aq) + 5H_2O(l)}
\end{gathered}
$$

Identify the species that is oxidised and the species that is reduced as well as the oxidising and reducing agent.

CASE STUDY 6.2

What happened to the Statue of Liberty?

The Statue of Liberty was given to the American people by the French people and was erected in New York Harbour on 19 June 1885. The statue has an outer coating of copper, about twice the thickness of an Australian 20-cent coin. The internal metals are cast iron and stainless steel. When it was first erected, the statue was brown because of the external copper coating.

Over time, the copper reacted with oxygen in the air, corroding to form copper oxide. Copper loses electrons to oxygen, forming Cu^+ and O^{2-}. Therefore, copper is oxidised and oxygen is reduced, forming the red solid Cu_2O.

$$4Cu(s) + O_2(g) \rightarrow 2Cu_2O(s)$$

The Cu^+ in the Cu_2O is further oxidised, forming Cu^{2+} in CuO, a black solid.

$$2Cu_2O(s) + O_2(g) \rightarrow 4CuO(s)$$

In the late 1800s, the large amount of coal that was burnt released sulfur dioxide and carbon dioxide into the atmosphere. This caused further reactions such as the precipitation of the copper-based minerals malachite (green), azurite (blue) and brochantite (green).

$$2CuO(s) + CO_2(g) + H_2O(l) \rightarrow \underset{\text{malachite}}{Cu_2CO_3(OH)_2(s)}$$

$$3CuO(s) + 2CO_2(g) + H_2O(l) \rightarrow \underset{\text{azurite}}{Cu_3(CO_3)_2(OH)_2(s)}$$

$$4CuO(s) + SO_3(g) + 3H_2O(l) \rightarrow \underset{\text{brochantite}}{Cu_4SO_4(OH)_6(s)}$$

The corroded layer formed a protective coat on the surface of the statue, not unlike a coat of paint, protecting it from further damage.

It took 30 years to form the outer patina (green coating) and it is now a part of the iconic appearance of the Statue of Liberty.

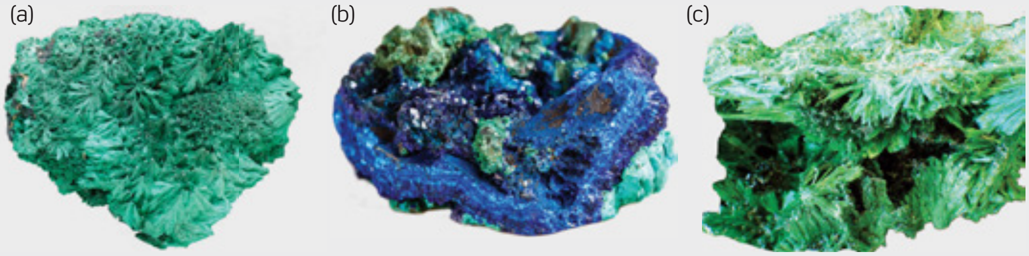


FIGURE 1 (a) Malachite is a green mineral with formula $Cu_2CO_3(OH)_2$. (b) Azurite is a blue mineral with formula $Cu_3(CO_3)_2(OH)_2$. (c) Brochantite is a green mineral with formula $Cu_4SO_4(OH)_6$.

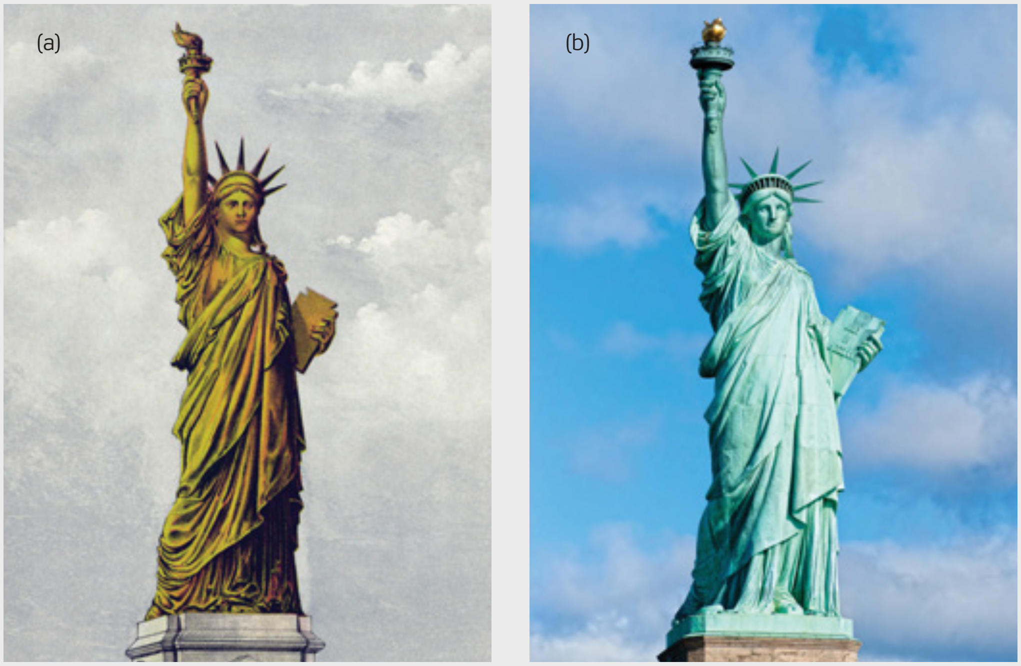


FIGURE 2 The Statue of Liberty (a) as it was originally in 1885 and (b) as it is today.

CHECK YOUR LEARNING 6.2

Describe and explain

1 **Define** 'oxidation state'.

2 **Explain** what happens to oxidation numbers in reduction reactions.

Apply, analyse and interpret

3 **Determine** the oxidation numbers of the atoms in the following chemical substances.

a	O_2	**e**	NaOH
b	NO_2	**f**	H_2O_2
c	SO_4^{2-}	**g**	NaH
d	CH_3COO^-	**h**	PO_4^{3-}

4 **Determine** the oxidised and reduced atoms in the following equations. Use their oxidation numbers to **justify** your answers.

a $2Fe(OH)_3(aq) + 3OCl^-(aq) \rightarrow 2FeO_4^{2-}(aq) + 3Cl^-(aq) + H_2O(l) + 4H^+(aq)$

b $Fe^{2+}(aq) + 6H^+(aq) + VO_4^{3-} \rightarrow Fe^{3+}(aq) + VO^{2+}(aq) + 3H_2O(l)$

c $2Cr_2O_7^{2-}(aq) + 16H^+(aq) + C_2H_5OH(l) \rightarrow 4Cr^{3+}(aq) + 2CO_2(g) + 11H_2O(l)$

Investigate, evaluate and communicate

5 **Investigate** steel and stainless steel.

- **a** What are both materials made of?
- **b** What are they used for?
- **c** Do they corrode? **Justify** your answer with a chemical equation or an explanation.
- **d** What are the advantages and disadvantages of using both materials?

6 In an experiment, copper metal was placed in a solution of silver nitrate. A silver metal and a blue solution of copper(II) nitrate formed. **Evaluate** these results and determine the oxidation and reduction equations as well as a balanced overall equation.

You can find the following resources for this section on your obook assess:

- » Student book questions
  6.2 Check your learning
- » Challenge
  6.2 Oxidation of alcohol
- » Weblink
  Corrosion of steel
- » Weblink
  Corrosion of stainless steel

6.3

Half-equations and overall redox equations

KEY IDEAS

In this section, you will learn about:

- oxidation and reduction half-equations
- combining oxidation and reduction half-equations to develop an overall redox equation.

half-equation
an equation that represents either an oxidation or a reduction half of a chemical equation; it includes electrons to demonstrate electron transfer

Redox chemical equations can become quite complicated because of the number of chemical species involved. For this reason, redox equations are balanced in two **half-equations** – the oxidation half-equation and the reduction half-equation. These equations are then combined to form an overall chemical redox equation.

Identifying and writing half-equations

The oxidation half-equation demonstrates an atom losing electrons, whereas the reduction half-equation demonstrates an atom gaining electrons.

The following reaction between copper(II) sulfate and zinc metal shows you how to identify the chemical species being oxidised and reduced, and how to write the oxidation and reduction half-equations from an overall equation.

$$CuSO_4(aq) + Zn(s) \rightarrow Cu(s) + ZnSO_4(aq)$$

Assign oxidation states to identify chemicals being oxidised and reduced. In this case, it is easier to deal with sulfate because its oxidation state is equal to its charge of –2.

$$\overset{+2\ -2}{CuSO_4}(aq) + \overset{0}{Zn}(s) \rightarrow \overset{0}{Cu}(s) + \overset{+2\ -2}{ZnSO_4}(aq)$$

spectator ion
an ion that exists in the same form on the reactant side and product side of a redox reaction. There is no change in its oxidation state

Both copper and zinc are participating in the chemical equation because they are changing oxidation states. Sulfate exists in the same form on both sides of the equation. There is no change in its oxidation state. It is regarded as a **spectator ion** and so it is not included in the half-equations.

The oxidation state of copper decreases from +2 to 0. Therefore, copper undergoes reduction. To represent the reduction half-equation, rewrite the copper species:

$$\overset{+2}{Cu^{2+}}(aq) \rightarrow \overset{0}{Cu}(s)$$

Although copper is balanced in the equation, the charge is not. To balance charge, add electrons to one side of the equation. Electrons are negative, so they will decrease the charge on whichever side they are added. In the copper half-equation, the reactant has a charge of +2 and the product has a charge of 0. Therefore, add a charge of –2 to the reactant side to balance the reduction half-equation.

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

The oxidation state of zinc increases from 0 to +2. Therefore, it undergoes oxidation.

$$\overset{0}{Zn}(s) \rightarrow \overset{+2}{Zn^{2+}}(aq)$$

Balance the +2 charge on the product side by adding two electrons to produce the oxidation half-equation.

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

Overall redox equations

When you have identified the oxidation and reduction half-equations, combine them to form an overall redox equation. To do this, both half-equations must have the same number of electrons so that they can cancel out in the final equation.

The zinc and copper half-equations combine easily because they both have two electrons. When you combine the half-equations, the electrons can be cancelled out to give the following balanced equation:

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

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

An additional example using aluminium ions and magnesium metals can be found on your obook assess.

WORKED EXAMPLE 6.3

Identify the oxidation and reduction half-equations and the overall redox equation in the following reaction:

$$\mathrm{Fe(s) + 2HCl(aq) \rightarrow FeCl_2(aq) + H_2(g)}$$

SOLUTION

1 Assign oxidation states to identify the atoms that have been oxidised and reduced.

$$\overset{0}{\mathrm{Fe}}\mathrm{(s)} + 2\overset{+1}{\mathrm{H}}\overset{-1}{\mathrm{Cl}}\mathrm{(aq)} \rightarrow \overset{+2}{\mathrm{Fe}}\overset{-1}{\mathrm{Cl_2}}\mathrm{(aq)} + \overset{0}{\mathrm{H_2}}\mathrm{(g)}$$

Chlorine has no change in oxidation state so it is a spectator in the reaction.

2 The oxidation state of iron increases from 0 to +2, so iron is oxidised. The oxidation half-equation is:

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

3 The oxidation state of hydrogen decreases from +1 to 0, so hydrogen is reduced. H_2 is formed, so balance the hydrogens before adding electrons. The reduction half-equation is:

$$\mathrm{2H^+(aq) + 2e^- \rightarrow H_2(g)}$$

4 Combine the reduction and oxidation half-equations to get the overall equation (you do not need to multiply these equations because they have the same number of electrons):

$$\text{Overall: } \mathrm{Fe(s) + 2H^+(aq) \rightarrow Fe^{2+}(aq) + H_2(g)}$$

Study tip

When combining half-equations, they must have the same number of electrons. Multiply the coefficients of the electrons in both equations if the charges are not balanced. Examples are provided in Section 6.4.

CHALLENGE 6.3A

Oxidation of butanol

Butanol is oxidised to butanoic acid by a solution of acidified sodium dichromate according to the following half-equations:

$$\mathrm{Cr_2O_7^{\,2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)}$$

$$\mathrm{CH_3CH_2CH_2CH_2OH(aq) + H_2O(l) \rightarrow CH_3CH_2CH_2COOH(aq) + 4H^+(aq) + 4e^-}$$

Combine the half-equations and write the balanced overall equation for the reaction.

CASE STUDY 6.3

Photography

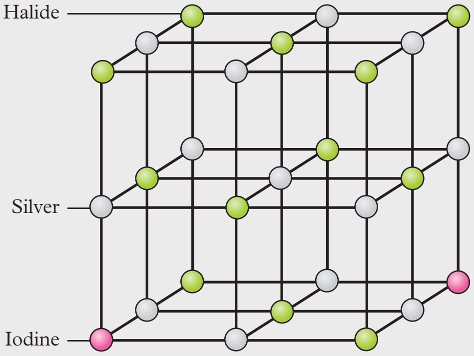


FIGURE 1 The structure of silver halide crystals

Today, taking a photo is as simple as using your smartphone or digital camera. However, 100 years ago, photography relied on cameras that contained photographic film. When exposed to light, a chemical reaction would occur on the film, resulting in an image. This film was refined and improved until the invention of digital cameras, which became commercially available in the late 1980s.

Photographic film is covered with an emulsion that contains light-sensitive silver halide crystals. The crystal is formed from a 3D structure containing silver, bromide, chloride and iodide ions (Figure 1).

Photographic film works when photons of light strike the silver bromide on the film and initiate a redox reaction. The photon causes an electron to dissociate from the bromide ion. The silver ions migrate towards the free electron (where the light has struck the film), forming solid silver (Ag). Where the solid silver forms, a latent (hidden) image is located. An increase in light in an area of the film means that more silver will precipitate in that location.

The overall redox equation for this process is:

$$AgBr(s) \rightarrow Ag(s) + Br_2(g)$$

The film is kept in a darkened casing until it is developed. If it is exposed to light before it is developed, the film will be completely black when it is developed because all of the silver ions will have precipitated as silver metal.

Once the film has been developed (Figure 2) and the chemicals have been fixed, no more reaction occurs, and the film can be viewed in the light. Photographers sometimes manipulate the images on the film by scratching the darkened silver metal from the film for artistic effect.

FIGURE 2 A developed film roll: the darkened areas represent where the silver has precipitated

CHALLENGE 6.3B

Oxidation of olivine

Olivine, a heavy metal silicate, has two different forms: fayalite (Fe_2SiO_4) and fosterite (Mg_2SiO_4). Construct the two different redox reactions for the oxidation of olivine.

FIGURE 3 Olivine crystals show two different colours depending on whether they are oxidised or not. Yellow crystals are oxidised and green are not.

CHECK YOUR LEARNING 6.3

Describe and explain

1 **Describe** what all oxidation half-equations have in common.

2 **Describe** what all reduction half-equations have in common.

3 **Explain** why overall redox equations must have the same number of electrons on the reactant and product sides.

4 **Construct** the half-equations and overall equations for the following reactions. Identify the half-equations as reduction or oxidation.

  a $Fe(s) + Cl_2(g) \rightarrow FeCl_3(s)$

  b $S(s) + F_2(g) \rightarrow SF_6(g)$

  c $N_2(g) + Cl_2(g) \rightarrow N_2Cl_4(g)$

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

5 **Identify** the oxidants and reductants in the reaction equations developed in question 4.

Investigate, evaluate and communicate

6 Copper has been found in ancient burial sites that date back to as early as 9000 BCE. **Investigate** how copper was smelted in ancient times compared to today. **Discuss** the key differences in the processes.

7 **Investigate** tarnished silverware and **create** a procedure for cleaning the silverware by using redox chemistry. Include chemical equations in your method.

You can find the following resources for this section on your obook assess:

- » Student book questions
  6.3 Check your learning
- » Challenge
  6.3A Oxidation of butanol
- » Challenge
  6.3B Oxidation of olivine
- » Increase your knowledge
  Extra overall redox equation

SCIENCE AS A HUMAN ENDEAVOUR

6.4 Redox reactions in breathalysers

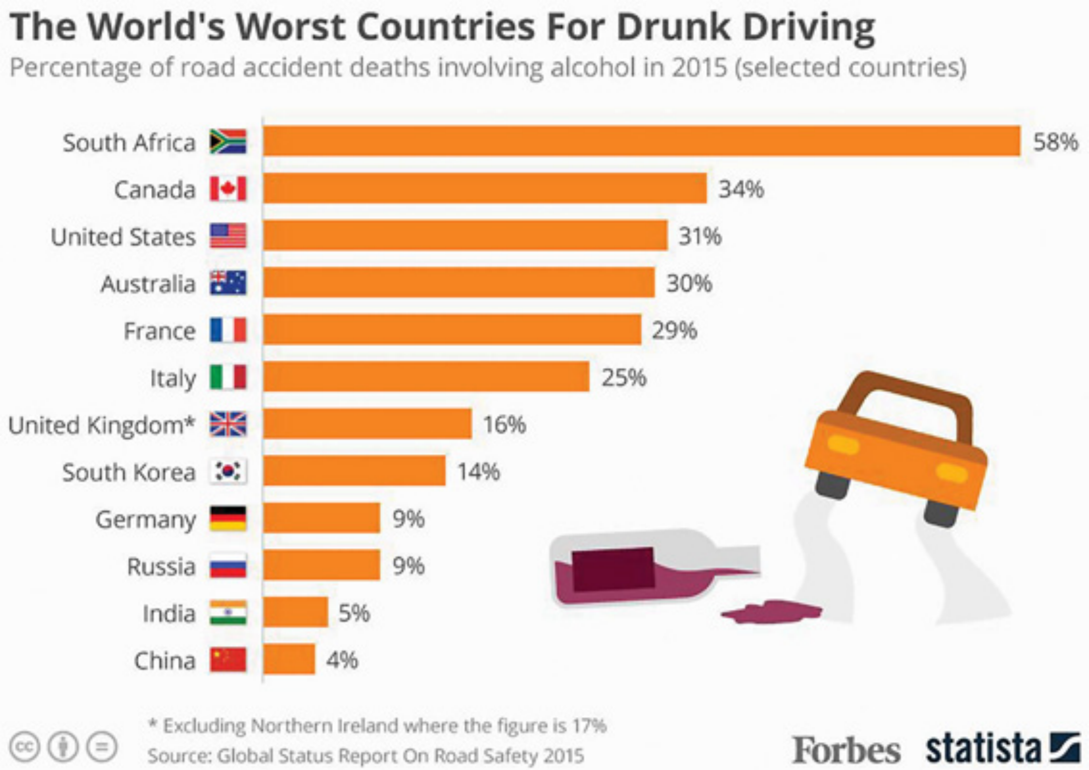
KEY IDEAS

In this section, you will learn about:

- the incidence of drink driving in Queensland and Australia
- the chemistry involved with breathalysers.

BAC
blood alcohol concentration

Drink driving has always been a problem on Australian roads. In 2015, Australia was ranked fourth for the percentage of road incident deaths involving alcohol, with 30% (Figure 1) of road fatalities connected to alcohol consumption and blood alcohol concentration (**BAC**).


The World's Worst Countries For Drunk Driving

Percentage of road accident deaths involving alcohol in 2015 (selected countries)

* Excluding Northern Ireland where the figure is 17%

Source: Global Status Report On Road Safety 2015

FIGURE 1 The percentage of road deaths caused by drink driving around the world

Incidence of drink driving in Queensland

breathalyser
a device for determining the blood alcohol concentration of a motorist

In Queensland, the incidence of drink driving has decreased since the introduction of **breathalysers** in 1982 and their formal commencement in 1988. The 2016–2017 Annual Statistical Review, published by the State of Queensland (Queensland Police Service), reported statistics for drink-driving offences since 1980 (Figure 2).

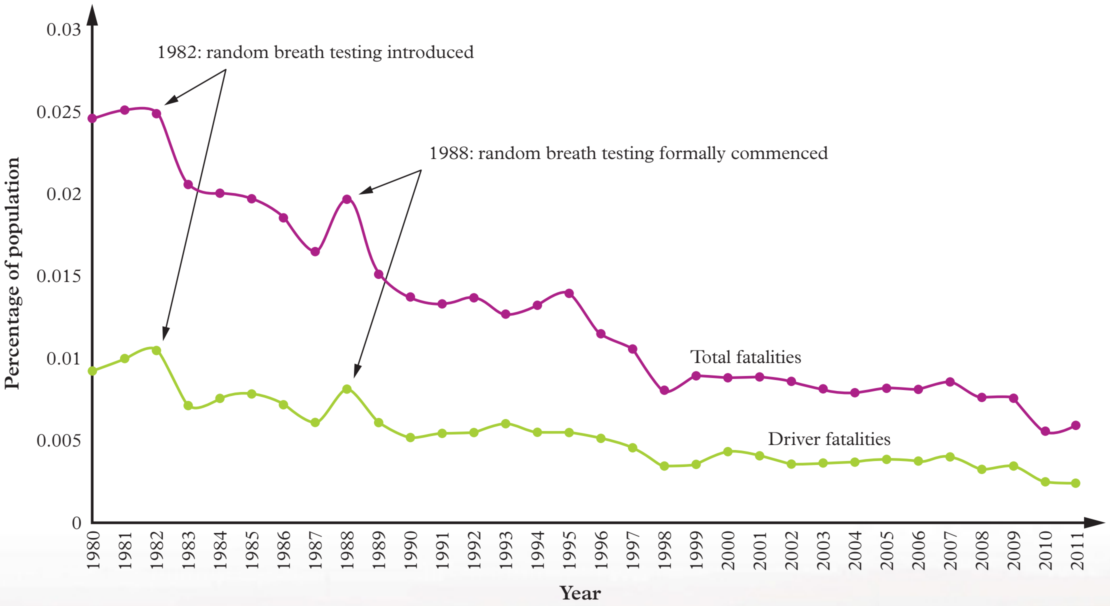


FIGURE 2 Incidence of fatalities due to drink driving in Queensland between 1980 and 2011

Blood alcohol concentration and breathalysers

According to Henry's law, the amount of dissolved gas is proportional to its partial pressure in the gas phase. In terms of BAC, this means that the amount of alcohol that is present in the blood is proportional to the amount of alcohol in a motorist's breath. Therefore, if you measure the alcohol concentration on the breath, you can determine the blood alcohol concentration. This will tell you whether it is safe to operate heavy machinery such as cars, motorbikes and trucks. Instruments that measure the amount of alcohol in a motorist's breath are called breathalysers.

Drunkometer and Intoximeter – using permanganate

The first breathalysers, called the Drunkometer and Intoximeter, were developed in the US in the 1930s by scientists Rolla Harger and Glen Forrester. The motorist blew into a balloon located within the device, which was then pumped through a solution of acidified potassium permanganate. Potassium permanganate is a dark purple colour but becomes colourless when the permanganate ion (MnO_4^-) is reduced to the manganese ion (Mn^{2+}). The half-equation for this is:

$$\underset{\text{purple}}{MnO_4^-(aq)} + 8H^+(aq) + 5e^- \rightarrow \underset{\text{colourless}}{Mn^{2+}(aq)} + 4H_2O(l)$$

Any alcohol (ethanol) present in the breath sample is oxidised to ethanoic acid. This reaction uses some of the permanganate and the solution loses colour and becomes paler:

$$\underset{\text{ethanol}}{CH_3CH_2OH(aq)} + H_2O(l) \rightarrow \underset{\text{ethanoic acid}}{CH_3COOH(aq)} + 4H^+(aq) + 4e^-$$

The greater the colour change from purple to pale purple and eventually to colourless, the more alcohol is present in the breath sample. The overall redox equation for this process is:

$$4MnO_4^-(aq) + 5CH_3CH_2OH(aq) + 6H^+(aq) \rightarrow 5CH_3COOH(aq) + 4Mn^{2+}(aq) + 11H_2O(l)$$

Alcometer – using starch

The Alcometer was an improvement on the permanganate method. In this instrument, a solution of iodine was reduced to iodide. In the presence of a starch indicator, the iodine solution is colourless or white, but becomes blue in the presence of iodide:

$$\underset{\text{colourless–white}}{I_2(s) + 2e^-} \rightarrow \underset{\text{blue}}{2I^-(aq)}$$

The ethanol is oxidised according to the half-equation shown above, and the overall redox reaction for the process is:

$$CH_3CH_2OH(aq) + H_2O(l) + 2I_2(s) \rightarrow CH_3COOH(aq) + 4H^+(aq) + 4I^-(aq)$$

This method to determine BAC proved less stable and less reliable than the original instruments. So it was quickly discarded in favour of better alternatives.

Photocells – using dichromate

After the 1940s, photocells were used to detect the colour change more accurately. In this instrument, acidified dichromate was used instead of permanganate. The dichromate ion ($Cr_2O_7^{2-}$) appears yellow–orange and undergoes reduction in an acidified solution to form the chromium ion (Cr^{3+}), which is green:

FIGURE 3 A photocell is a sensor that detects light.

$$\underset{\text{yellow–orange}}{Cr_2O_7^{2-}(aq)} + 14H^+(aq) + 6e^- \rightarrow \underset{\text{green}}{2Cr^{3+}(aq)} + 7H_2O(l)$$

The ethanol is oxidised to form ethanoic acid:

$$\underset{\text{ethanol}}{CH_3CH_2OH(aq)} + H_2O(l) \rightarrow \underset{\text{ethanoic acid}}{CH_3COOH(aq)} + 4H^+(aq) + 4e^-$$

The overall chemical reaction for the process is:

$$3CH_3CH_2OH(g) + 2Cr_2O_7^{2-}(aq) + 16H^+(aq) \rightarrow 3CH_3COOH(aq) + 4Cr^{3+}(aq) + 11H_2O(l)$$

Once the dichromate has reacted with the ethanol in the breath sample, the resultant solution is compared to a separate sample of unreacted dichromate. The colours are compared by using a photocell. The photocell creates an electric current that is proportional to the amount of colour change.

However, organic substances similar to ethanol that are consumed as a part of a balanced diet often gave false readings in permanganate and dichromate tests. All alcohols and aldehydes can be oxidised by the same chemical methods.

Electrochemical cells – measuring the flow of electrons

To avoid using colour-based indicators, a fuel cell was developed as an alternative. The half-equations involve the transfer of electrons, so an electric current is produced. This current can be measured and used to determine the concentration of ethanol in the breath and therefore the blood.

Atmospheric oxygen is reduced in acidic conditions to form water:

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

The ethanol is oxidised to ethanoic acid:

$$CH_3CH_2OH(aq) + H_2O(l) \rightarrow CH_3COOH(aq) + 4H^+(aq) + 4e^-$$

The overall chemical reaction is:

$$CH_3CH_2OH(aq) + O_2(g) \rightarrow CH_3COOH(aq) + H_2O(l)$$

CHALLENGE 6.4

False positive BAC readings

What products that are available in supermarkets may interfere with a BAC reading? How do they effect the BAC and which ingredients are responsible for this effect?

CHECK YOUR LEARNING 6.4

Describe and explain

1 **Explain** what a breathalyser measures.

2 **Define** the limit for blood alcohol concentration in Queensland.

Apply, analyse and interpret

3 **Apply** your understanding of spectroscopy to **determine** why a permanganate and dichromate breathalyser must be frequently calibrated.

4 There have been many myths about how to cheat a breathalyser. **Determine** if any of these be accurate from your knowledge of BAC.

Investigate, evaluate and communicate

5 **Research** the factors that influence a person's BAC. **Describe** what these factors are and **determine** how they affect an individual's BAC.

You can find the following resources for this section on your obook assess:

- » Student book questions
  6.4 Check your learning
- » Challenge
  6.4 False positive BAC readings
- » Weblink
  Blood alcohol levels

CHAPTER 6

Review

Chapter summary

6.1
- Redox reactions occur when electrons are transferred from one reactant to another. A reactant undergoes oxidation if it loses electrons (OIL) or undergoes reduction if it gains electrons (RIG).
- Electrons move between the valence shells of the reactants. The reactant that loses one or more electrons causes reduction in the other reactant and so is called the reductant. The other reactant takes one or more electrons, causing oxidation in the other reactant and so is called the oxidant.
- Displacement, oxidation and corrosion are examples of redox reactions.

6.2
- Oxidation numbers are used to determine if oxidation or reduction has occurred. There are rules to follow to determine the oxidation number of an atom. If the oxidation number decreases or reduces, then reduction has occurred. If the oxidation number increases, then oxidation has occurred.
- The oxidation states of transition metals are represented by roman numerals after the element's name or symbol, e.g. chromium(III), Cr(III).

6.3
- A half-equation represents one half of a redox equation, either the oxidation or the reduction reaction. Half-equations show electrons being gained or lost. Half-equations do not include spectator ions and can be combined to form overall redox reactions.
- When combining the reactions, the number of electrons must balance. The whole half-equation must be multiplied to ensure that both half-equations have the same number of electrons before combining them.

6.4
- Redox reactions are used in breathalysers to determine blood alcohol content, which is proportional to the amount of gaseous alcohol on the breath.

Key terms

- BAC
- breathalyser
- combustion
- corrosion
- electronegativity
- half-equation
- ionisation energy
- overall equation
- oxidation
- oxidation number
- oxidation state
- oxidise
- oxidising agent
- redox
- reduce
- reducing agent
- reduction
- single displacement
- spectator ion
- valence electron

Key formulas

Combustion of metal to form a metal oxide	metal + oxygen → metal oxide

Revision questions

The relative difficulty of these questions is indicated by the number of stars beside each question number: ★ = low; ★★ = medium; ★★★ = high.

Multiple choice

The following equation relates to questions 1 and 2.

$$2Au^{3+}(l) + 6Br^{-}(l) \rightarrow 2Au(s) + 3Br_2(l)$$

1 In this reaction:

A Au is oxidised; Br_2 is reduced
B Br_2 is oxidised; Au is reduced
C Au^{3+} is oxidised; Br^{-} is reduced
D Br^{-} is oxidised; Au^{3+} is reduced.

2 In this reaction:

A Au is the oxidant; Br_2 is the reductant
B Br_2 is the oxidant; Au is the reductant
C Au^{3+} is the oxidant; Br^{-} is the reductant
D Br^{-} is the oxidant; Au^{3+} is the reductant.

FIGURE 1 Gold is an atom.

The following equation relates to questions 3 and 4.

$$H_2Te(g) + S(s) \rightarrow Te(s) + H_2S(g)$$

3 In this reaction:

A H_2Te is oxidised; S is reduced
B S is oxidised; H_2Te is reduced
C Te is oxidised; H_2S is reduced
D H_2S is oxidised; Te is reduced.

4 In this reaction:

A H_2Te is the oxidant; Se is the reductant
B Se is the oxidant; H_2Te is the reductant
C Te is the oxidant; H_2S is the reductant
D H_2S is the oxidant; Te is the reductant.

5 Identify the oxidation state of copper in $Cu_3(CO_3)_2(OH)_2$.

A +3
B +2
C +1
D –1

6 Identify the oxidation state of phosphorus in $P_2O_7^{2-}$.

A +10
B +6
C +5
D +3.5

7 Identify the oxidation half-equation.

A $NO_3^{-}(aq) + 4H^{+}(aq) + 3e^{-} \rightarrow NO(g) + 2H_2O(l)$
B $O_2(g) + 4H^{+}(aq) + 2e^{-} \rightarrow 2H_2O(l)$
C $AuCl_4^{-}(aq) + 3e^{-} \rightarrow Au(s) + 4Cl^{-}(aq)$
D $2Ag(s) + S^{2-}(aq) \rightarrow Ag_2S(s) + 2e^{-}$

8 Identify the reduction half-equation.

A $Zn^{2+}(aq) + 2e^{-} \rightarrow Zn(s)$
B $Mn^{2+}(aq) + 4H_2O(l) \rightarrow MnO_4^{-}(aq) + 8H^{+}(aq) + 5e^{-}$
C $Cu(s) \rightarrow Cu^{2+}(aq) + 2e^{-}$
D $H_2(g) \rightarrow 2H^{+}(aq) + 2e^{-}$

9 Reduction means there is:

A a loss of electrons
B a gain of electrons
C an electron in the outermost shell of an atom
D a negative charge.

10 For monatomic ions, the oxidation number is:

A the same as the charge on the ion
B always +1
C always neutral
D always negative.

Short answer

Describe and explain

★ 11 **Describe** why a reducing agent is different from reduction.

★ 12 **Describe** the difference between charge of an ion and an oxidation state.

★ 13 **Explain** why corrosion is an example of oxidation.

★ 14 **Construct** the Bohr electron configuration of $Ca(s) + Cl_2(g) \rightarrow CaCl_2(s)$ and show the electron configuration.

★ 15 **Identify** the missing word in the statement: 'The attraction between a positively charged nucleus and the negatively charged electrons of a neighbouring atom is called ______________'.

★ 16 **Explain** why the term 'reduction' is a gain of electrons.

★ 17 **Define** 'ionisation energy'.

★ 18 **Describe** how the location of elements on the periodic table affects their ability to gain or lose electrons.

★ 19 **Explain** the terms 'oxidising agent' and 'reducing agent'. How would you use them to **describe** redox reactions?

★ 20 **Describe** what is common to breathalyser redox reactions. Why does this commonality exist?

FIGURE 2 A breathalyser can be used to estimate BAC from a breath sample.

★★ 21 A student placed a piece of iron metal into a solution of lead(II) nitrate. **Construct** two half-equations to demonstrate the oxidation and reduction processes. **Construct** a balanced overall equation to represent the chemical reaction.

★★ 22 A piece of solid nickel was placed in a solution of blue copper(II) sulfate. Over time, the solution became paler in colour and an orange coloured precipitate formed. **Construct** two half-equations to demonstrate the oxidation and reduction processes. **Construct** a balanced overall equation to represent the chemical reaction.

Apply, analyse and interpret

★ 23 **Determine** the oxidation number of:

- **a** nitrogen in NH_3
- **b** silicon in $CaSiO_3$
- **c** chromium in $BaCrO_4$
- **d** vanadium in VO_2^+.

★ 24 **Determine** the oxidation number of:

- **a** cadmium in Br_2CdO_6
- **b** thorium in ThO_2
- **c** manganese in $MnCO_3$
- **d** zinc in $Zn(OH)_2$.

★ 25 **Determine** the oxidation number of iron in:

- **a** Fe_2O_3
- **b** FeO
- **c** Fe_2SiO_4
- **d** Fe(s).

★★ 26 **Deduce** why iron can have many different oxidation numbers.

★★★ 27 **Consider** the following unbalanced chemical equation.

$$CO_2(g) + H_2(g) \rightarrow CO(g) + H_2O(g)$$

- **a** **Identify** oxidation numbers of all atoms.
- **b** **Determine** which atom has been oxidised and which has been reduced.
- **c** **Determine** which atoms are the oxidising and reducing agents.
- **d** **Construct** the oxidation and reduction half-equations.
- **e** **Construct** the balanced overall redox reaction.

★★★ 28 **Consider** the following unbalanced chemical equation.

$$Zn(s) + H_2SO_4(aq) \rightarrow ZnSO_4(aq) + H_2(g)$$

a **Identify** oxidation numbers for all atoms.

b **Determine** which atom has been oxidised and which has been reduced.

c **Determine** which atoms are the oxidising and reducing agents.

d **Construct** the oxidation and reduction half-equations.

e **Construct** the balanced overall redox reaction.

★★★ 29 **Consider** the following unbalanced chemical equation.

$$Ag(s) + H_2S \rightarrow Ag_2S(g) + H_2(g)$$

a **Identify** oxidation numbers of all atoms.

b **Determine** which atom has been oxidised and which has been reduced.

c **Determine** which atoms are the oxidising and reducing agents.

d **Construct** the oxidation and reduction half-equations.

e **Construct** the balanced overall redox reaction.

Investigate, evaluate and communicate

★★ 30 A student claimed that the best method to produce sodium hydroxide is the redox reactions between sodium metal and water to form sodium hydroxide and hydrogen gas. The half-equation for the water reaction is:

$$2H_2O(l) + 2e^- \rightarrow 2OH^-(aq) + H_2(g)$$

a **Construct** the two half-equations to demonstrate the oxidation and reduction processes.

b **Construct** a balanced overall equation to represent the chemical reaction.

c **Evaluate** the student's claim and **discuss** the strengths and weaknesses of this reaction.

FIGURE 3 Hydrogen gas

★★★ 31 A claim was made that the oxidation numbers of all atoms in an yttrium barium copper oxide ($YBa_2Cu_3O_7$) cannot be determined. **Evaluate** this claim and **discuss** your opinion, using the theory learnt in this chapter.

★★★ 32 A student placed a piece of silver metal in a blue solution of copper(II) sulfate. After 10 minutes, the student observed that the solution had not changed colour. **Evaluate** the student's results and **discuss** a reason for this observation, using the terminology learnt in this chapter.

FIGURE 4 A piece of silver metal and a copper(II) sulfate solution.

You can find the following resources for this section on your obook assess:

- Student book questions
  Chapter 6 Revision questions
- Revision notes
  Chapter 6
- assess quiz
  Auto-correcting multiple-choice quiz
- Flashcard glossary
  Chapter 6

CHAPTER

7

Electrochemical cells and electrode potential

Electrochemical cells (galvanic cells) are essential to modern life. They convert potential energy stored in chemicals, even in foods and drinks, into electrical energy. This technology has many applications but is mainly used in batteries.

The invention of the battery has been credited to Alessandro Volta in 1800. However, his invention would not have been possible without the work of his predecessors (including Benjamin Franklin) in static electricity. Volta's creation was so popular that, in 1801, Napoleon Bonaparte (Emperor of France 1804–1814) volunteered to act as his laboratory assistant.

Since its discovery, the battery has continued to improve. New technology and devices require a power source, and different batteries come in a range of sizes and produce a range of voltages to power almost any device.

OBJECTIVES

- → Understand that electrochemical cells, including galvanic and electrolytic cells, consist of oxidation and reduction half-reactions connected via an external circuit that allows electrons to move from the anode (oxidation reaction) to the cathode (reduction reaction).
- → Understand that galvanic cells, including fuel cells, generate an electrical potential difference from a spontaneous redox reaction which can be represented as cell diagrams including anode and cathode half-equations.
- → Recognise that oxidation occurs at the negative electrode (anode) and reduction occurs at the positive electrode (cathode) and explain how two half-cells can be connected by a salt bridge to create a galvanic cell (examples of half-cells are Mg, Zn, Fe and Cu and their solutions of ions).
- → Describe, using a diagram, the essential components of a galvanic cell; including the oxidation and reduction half-cells, the positive and negative electrodes and their solutions of their ions, the flow of electrons and the movement of ions, and the salt bridge.
- → Determine the relative strength of oxidising and reducing agents by comparing standard electrode potentials.

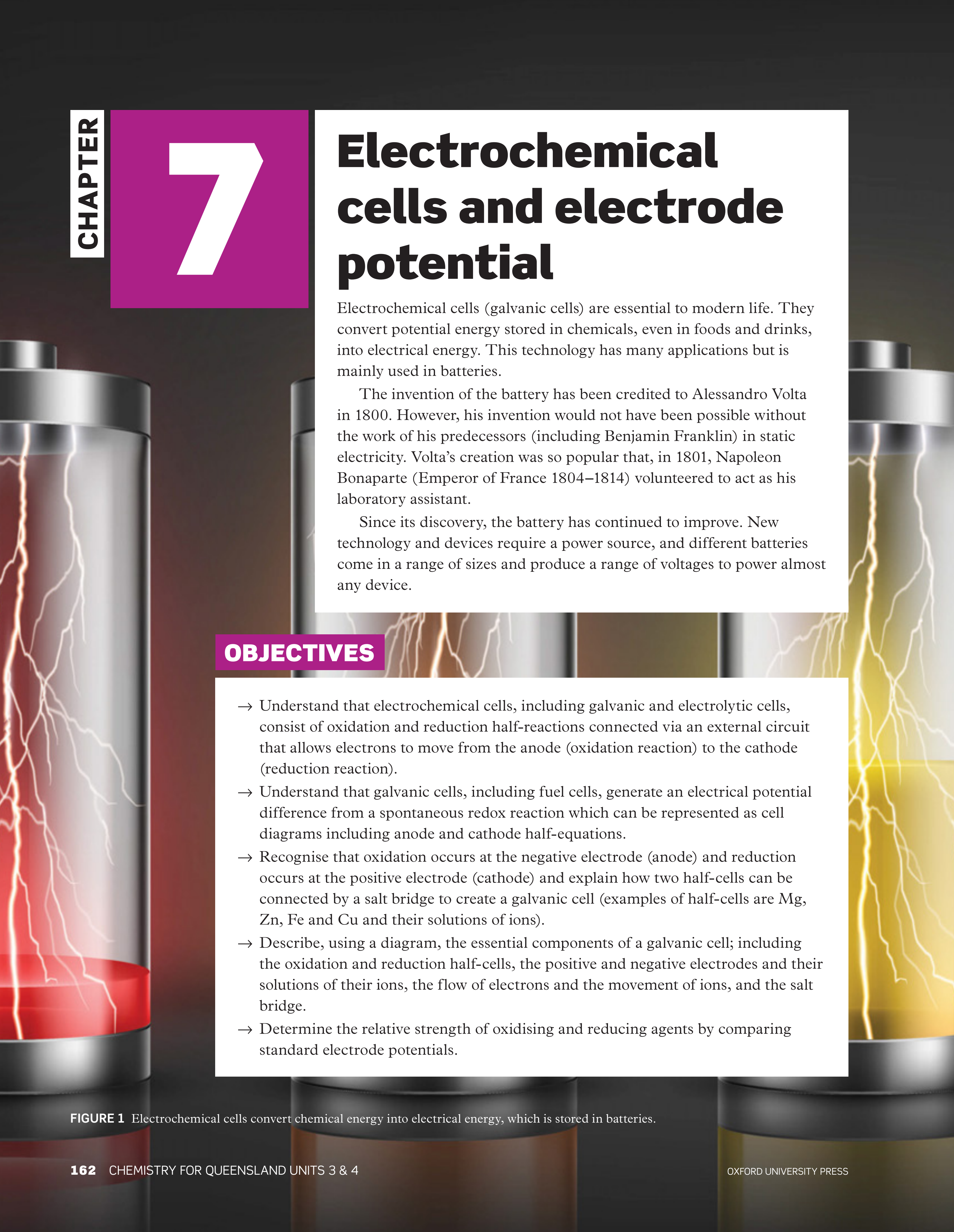


FIGURE 1 Electrochemical cells convert chemical energy into electrical energy, which is stored in batteries.

- → Recognise that cell potentials at standard conditions can be calculated from standard electrode potentials; these values can be used to compare cells constructed from different materials.
- → Recognise the limitation associated with standard reduction potentials.
- → Use appropriate mathematical representation to solve problems and make predictions about spontaneous reactions, including calculating cell potentials under standard condition.

Source: *Chemistry 2019 v 1.3 General Senior Syllabus* © Queensland Curriculum & Assessment Authority

PRACTICALS

MANDATORY PRACTICAL	**7.1** Constructing a galvanic cell

7.1

Galvanic cells

KEY IDEAS

In this section, you will learn about:

- using the electrochemical series to determine the strength of oxidising and reducing agents
- using of redox reactions to generate electricity in a galvanic cell.

redox reaction
a reaction involving oxidation of one reactant and reduction of the other reactant

electrochemical series
a table of the strongest oxidants and reductants written as reversible reduction half-equations; the strongest oxidant is at the top left of the table and the strongest reductant is at the bottom right

Redox reactions convert chemical potential energy to electrical energy. In redox reactions, reactants lose and gain electrons. One reactant is oxidised and the other is reduced. The ability of elements, ions or molecules to gain or lose electrons can be determined from the **electrochemical series**.

The electrochemical series

Some chemicals gain or lose electrons more readily than others. You can use the periodic table to determine the strength of oxidants or reductants. However, this won't tell you about the strengths of molecules or complex ions that contain more than one atom. A more accurate way of determining the strengths of oxidants and reductants is to use the electrochemical series (Table 1).

The electrochemical series lists all half-equations as reduction half-equations, arranged from the strongest reduction half-equation (i.e. the half-equation with the strongest oxidant) to the weakest reduction half-equation. All oxidants are on the left-side of the half-equations. The weakest reduction half-equation can be reversed to become the strongest oxidation half-equation containing the strongest reductant.

The strongest reduction half-equation is:

$$F_2(g) + 2e^- \rightarrow 2F^-$$

$F_2(g)$ is the strongest oxidant because it accepts electrons more readily than any other molecule or ion, causing oxidation in another chemical species.

The weakest reduction half-equation is:

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

Therefore, the strongest oxidation half-equation is:

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

Li(s) is the strongest reductant because it donates electrons more readily than any other molecule or ion, causing reduction in another chemical species.

RED SOX
a method for determining whether two chemicals will react spontaneously in a redox reaction; it looks at the positions of the half-equations on the electrochemical series; 'RED' stands for reduction, the 'S' denotes the reactants and products and 'OX' stands for oxidation

Predicting redox reactions from the electrochemical series

The half-equations on the electrochemical series are reversible. They are equilibrium reactions written as reduction half-equations. This is why electrons are always on the left-hand side of the equation as shown in Table 1. $E°$ is the standard reduction potential, measured under standard conditions.

To determine whether two chemicals will react spontaneously in a redox reaction, you can use the **RED SOX** method.

1 Find the appropriate half-equations on the electrochemical series.
2 Identify the chemical species that are reacting.

3 The strongest oxidant (top left) will react with the strongest reductant (bottom right) spontaneously. This is summarised in the ‘S’ configuration of Figure 1.

4 Reduction is on the top of the S and oxidation is on the bottom (hence, RED SOX).

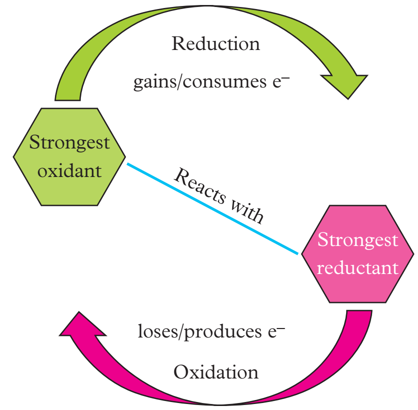


FIGURE 1 The ‘S’ configuration is used to determine whether chemical substances will react spontaneously.

TABLE 1 The electrochemical series: standard reduction potentials (*E*°) for half-reactions of 1 M solutions at 25°C

	Half-reaction	*E*° (V)	
Strongest oxidising agents	$F_2(g) + 2e^- \rightleftharpoons 2F^-(aq)$	+2.89	Weakest reducing agents
	$H_2O_2(aq) + 2H^+(aq) + 2e^- \rightleftharpoons 2H_2O(l)$	+1.77	
	$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightleftharpoons Mn^{2+}(aq) + 4H_2O(l)$	+1.52	
↓	$Au^{3+}(aq) + 3e^- \rightleftharpoons Au(s)$	+1.50	↑
	$Cl_2(g) + 2e^- \rightleftharpoons 2Cl^-(aq)$	+1.36	
	$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightleftharpoons 2Cr^{3+}(aq) + 7H_2O(l)$	+1.36	
	$\frac{1}{2}O_2(g) + 2H^+(aq) + 2e^- \rightleftharpoons H_2O(l)$	+1.23	
	$Br_2(l) + 2e^- \rightleftharpoons 2Br^-(aq)$	+1.08	
	$AuCl_4^-(aq) + 3e^- \rightleftharpoons Au(s) + 4Cl^-(aq)$	+1.00	
	$NO_3^-(aq) + 4H^+(aq) + 3e^- \rightleftharpoons NO(g) + 2H_2O(l)$	+0.96	
	$Ag^+(aq) + e^- \rightleftharpoons Ag(s)$	+0.80	
	$\frac{1}{2}\ Hg^{2+} + 2e^- \rightleftharpoons Hg(l)$	+0.79	
	$NO_3^-(aq) + 2H^+(aq) + e^- \rightleftharpoons NO_2(g) + H_2O(l)$	+0.78	
	$Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+}(aq)$	+0.77	
	$O_2(g) + 2H^+(aq) + 2e^- \rightleftharpoons H_2O_2(aq)$	+0.68	
	$I_2(s) + 2e^- \rightleftharpoons 2I^-(aq)$	+0.54	
	$Cu^+(aq) + e^- \rightleftharpoons Cu(s)$	+0.52	
	$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$	+0.34	
	$Cu^{2+}(aq) + e^- \rightleftharpoons Cu^+(aq)$	+0.16	
	$Sn^{4+}(aq) + 2e^- \rightleftharpoons Sn^{2+}(aq)$	+0.15	
	$S(s) + 2H^+(aq) + 2e^- \rightleftharpoons H_2S(aq)$	+0.14	
	$2H^+(aq) + 2e^- \rightleftharpoons H_2(g)$	0.00	
	$Pb^{2+}(aq) + 2e^- \rightleftharpoons Pb(s)$	–0.13	
	$Sn^{2+}(aq) + 2e^- \rightleftharpoons Sn(s)$	–0.14	
	$Ni^{2+}(aq) + 2e^- \rightleftharpoons Ni(s)$	–0.24	
	$Co^{2+}(aq) + 2e^- \rightleftharpoons Co(s)$	–0.28	
	$Cd^{2+}(aq) + 2e^- \rightleftharpoons Cd(s)$	–0.40	
	$Se(s) + 2H^+ + 2e^- \rightleftharpoons H_2Se(g)$	–0.40	
	$Cr^{3+}(aq) + e^- \rightleftharpoons Cr^{2+}(aq)$	–0.41	
	$Fe^{2+}(aq) + 2e^- \rightleftharpoons Fe(s)$	–0.44	
	$Cr^{3+}(aq) + 3e^- \rightleftharpoons Cr(s)$	–0.74	
	$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s)$	–0.76	
	$2H_2O(l) + 2e^- \rightleftharpoons H_2(g) + 2OH^-(aq)$	–0.83	
	$Mn^{2+}(aq) + 2e^- \rightleftharpoons Mn(s)$	–1.18	
	$Al^{3+}(aq) + 3e^- \rightleftharpoons Al(s)$	–1.68	
	$Mg^{2+}(aq) + 2e^- \rightleftharpoons Mg(s)$	–2.36	
	$Na^+(aq) + e^- \rightleftharpoons Na(s)$	–2.71	
	$Ca^{2+}(aq) + 2e^- \rightleftharpoons Ca(s)$	–2.87	
	$Sr^{2+}(aq) + 2e^- \rightleftharpoons Sr(s)$	–2.90	
	$Ba^{2+}(aq) + 2e^- \rightleftharpoons Ba(s)$	–2.91	
Weakest oxidising agents	$K^+(aq) + e^- \rightleftharpoons K(s)$	–2.94	Strongest reducing agents
	$Rb^+(aq) + e^- \rightleftharpoons Rb(s)$	–2.92	
	$Li^+(aq) + e^- \rightleftharpoons Li(s)$	–3.04	

Study tip

A copy of the electrochemical series can be found in the QCAA Formula and data book but note that the reactions are presented in reverse sequence and the RED SOX technique needs to be modified to suit. Your teacher will show you how to do this.

Study tip

A copy of the periodic table can be found in the appendix.

For example:

A solution of copper(II) sulfate and zinc metal are placed in a beaker. Follow these steps to determine whether a reaction will occur.

1 Find the appropriate half-equations on the electrochemical series.

$$Cu^{2+} + 2e^- \rightarrow Cu \qquad E^\circ = +0.34\,V$$

$$Zn^{2+} + 2e^- \rightarrow Zn \qquad E^\circ = -0.76\,V$$

Study tip

There are often multiple half-equations for one element, covering different ions and states (i.e. Cu^{2+}, Cu^+ or Cu(aq) and Cu(s)). Make sure you have the correct $E°$ value for your reaction before beginning.

2 Identify the chemical species that are reacting.

$$Cu^{2+} + 2e^- \rightarrow Cu \qquad E° = +0.34\,V$$
$$Zn^{2+} + 2e^- \rightarrow Zn \qquad E° = -0.76\,V$$

3 The copper(II) ions are the strongest oxidant (top left), and react with solid zinc, the strongest reductant (bottom right) spontaneously. Assign the 'S' configuration (Figure 2).

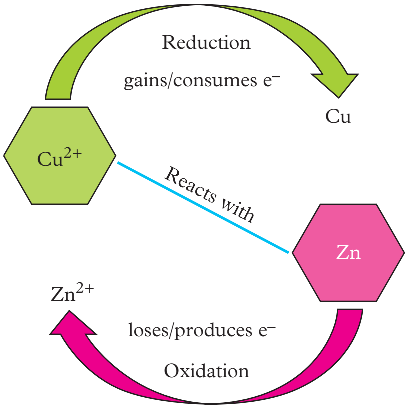


FIGURE 2 The 'S' configuration for the reaction between Zn and Cu^{2+}

Zinc metal loses electrons to form zinc(II) ions. The electrons lost are gained by the copper(II) ions to form copper metal.

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

If a strip of zinc is placed in a solution of copper(II) sulfate, copper metal precipitates out of solution onto the zinc metal (Figure 3). This is the site of the reaction where electrons are produced. The copper(II) sulfate solution starts to become colourless as the concentration of copper(II) ions in solution decreases.

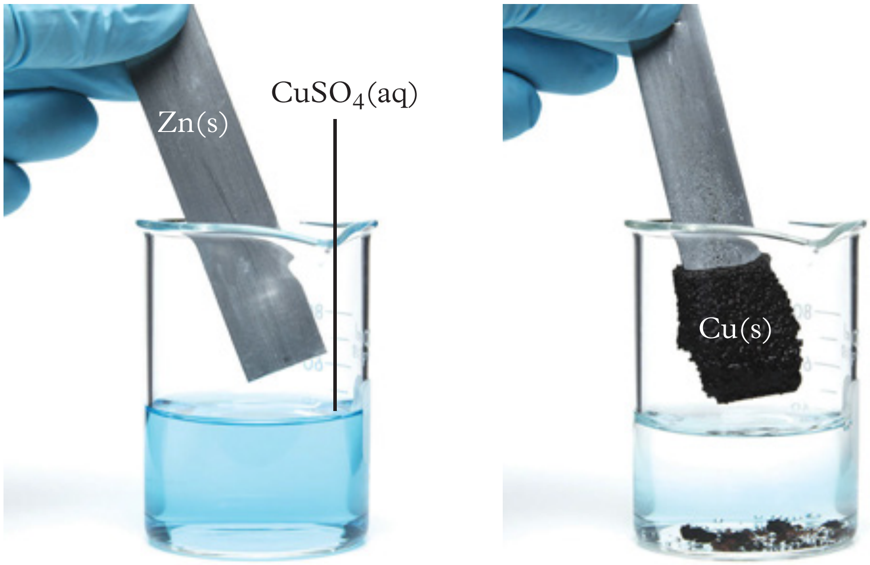


FIGURE 3 A solution of copper(II) sulfate and zinc metal. Copper metal precipitates out of solution.

Non-spontaneous redox reactions

If copper metal were placed in a solution of zinc(II) sulfate, instead of zinc metal in a solution of copper(II) sulfate, no reaction would occur.

Copper metal is on the right of the equation, so it must undergo oxidation to form copper(II). This would make copper the reductant. However, zinc metal is a stronger reducing agent than copper metal. Also, copper(II) ions are a stronger oxidising agent than zinc(II) ions. This means that the copper metal and zinc ions will not react because they are the weaker reducing and oxidising agents.

$$Cu^{2+} + 2e^- \rightarrow Cu \qquad E° = +0.34\,V$$
$$Zn^{2+} + 2e^- \rightarrow Zn \qquad E° = -0.76\,V$$

Worked example 7.1A demonstrates the process of predicting whether a redox reaction occurs.

WORKED EXAMPLE 7.1A

Predict whether a reaction will occur between iron(II) nitrate ($Fe(NO_3)_2$) and:

a magnesium metal (Mg)

b lead(II) nitrate ($Pb(NO_3)_2$).

SOLUTION

a Iron(II) ions are the strongest oxidant and magnesium solid is the strongest reductant:

$$Fe^{2+}(aq) + 2e^- \rightarrow Fe(s) \qquad E° = -0.44\,V$$

$$Mg^{+}(aq) + e^- \rightarrow Mg(s) \qquad E° = -2.36\,V$$

Therefore, you can draw the 'S' configuration (Figure 4).

Fe^{2+} and Mg will react spontaneously.

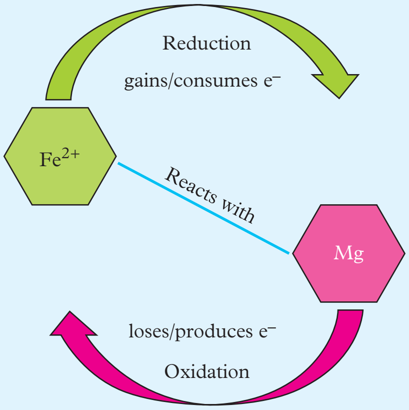


FIGURE 4 The 'S' configuration for the reaction between Fe^{2+} and Mg

b Iron(II) ions are involved in two half-equations. Therefore, there are two possible sets of half-equations:

$$Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq) \qquad E° = +0.77\,V$$

$$Pb^{2+}(aq) + 2e^- \rightarrow Pb(s) \qquad E° = -0.13\,V$$

or

$$Pb^{2+}(aq) + 2e^- \rightarrow Pb(s) \qquad E° = -0.13\,V$$

$$Fe^{2+}(aq) + 2e^- \rightarrow Fe(s) \qquad E° = -0.44\,V$$

In the first option, neither iron(II) nor lead(II) is the strongest oxidant or reductant, so they will not react.

In the second option, lead(II) is the strongest oxidant, but iron(II) is also an oxidant. Neither ion will donate electrons and so no reaction will occur.

Study tip

After identifying the two redox half-equations on the electrochemical series, the top left and bottom right species will react. If the reactants are not in this configuration, they will not react.

Generating electricity from redox reactions

Electrochemical cells convert chemical energy into electrical energy. **Galvanic cells** contain a spontaneous redox reaction that produces electrical energy. The half-equations are separated in different electrochemical cells. One cell produces electrons and the other consumes them. By separating the cells, the reaction occurring in each cell cannot take place unless electrons are transferred between the two parts, similar to an electric circuit.

galvanic cell
an electrochemical cell in which the reduction and oxidation half-equations are separated and connected through a circuit to generate electricity

half-cell
half of an electrochemical cell, where either oxidation or reduction occurs

electrode
a solid conductor of electricity either into or out of a half-cell

Galvanic cell components

Half-cells

Galvanic cells typically incorporate two redox half-equations, which are contained within separate **half-cells**. In laboratory-based galvanic cells, the half-cells consist of a beaker that contains an ionic solution and an **electrode** made of a metal. The electrode can be an inert (unreactive) substance, such as platinum or carbon, or the metal of the solution (e.g. a copper electrode in a copper(II) sulfate solution) (Figure 5).

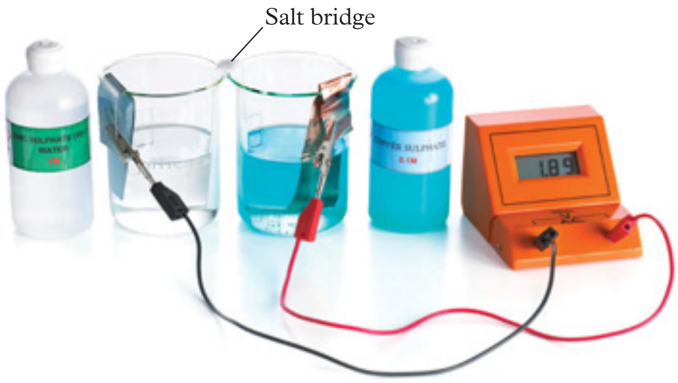


FIGURE 5 The experimental set-up of a galvanic cell

Study tip

Electrolytic cells are another example of electrochemical cells and discussed in detail in Chapter 8.

inert electrode
an electrode that conducts electricity in the half-cell, but does not participate in the reaction, i.e. it is neither a reactant nor a product

Half-cells are represented as the metal and the metal ion (Figure 6). A copper half-cell containing a solution of copper(II) sulfate and copper metal is represented as $Cu(s)/Cu^{2+}(aq)$. A half-cell may contain an inert electrode, which does not take part in the reaction but only serves as a conductor of electrons. Inert electrodes are typically made of platinum, mercury or carbon. If a solution of copper(II) sulfate contains an **inert electrode**, the half-cell is represented as $C(s)/Cu^{2+}(aq)$ or $Pt(s)/Cu^{2+}(aq)$. The spectator ions (SO_4^{2-}) do not react and so are not represented.

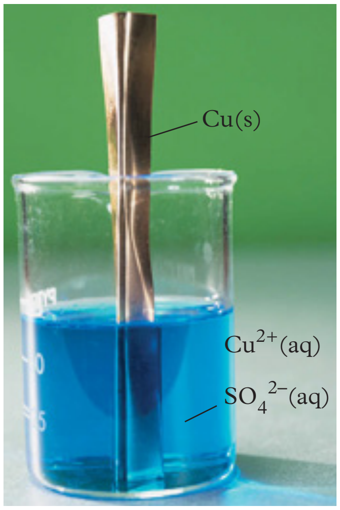


FIGURE 6 A copper half-cell containing copper metal (Cu(s)) and a solution of copper(II) sulfate ($Cu^{2+}(aq)$ and $SO_4^{2-}(aq)$). The $SO_4^{2-}(aq)$ acts as a spectator ion.

When a galvanic cell is in operation, one of two reactions occurs in the half-cell.

- One reaction produces electrons when the metal is converted into a solution of the metal. This is the oxidation half-cell. The metal (M) electrode breaks down into the solution and therefore cannot be made of an inert substance:

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

  You do not always need to use a reactive metal electrode. Some cells convert solids, gases or aqueous ions. For example, chlorine gas is converted into chloride ions. This does not require an electrode made of chlorine gas, but an inert electrode:

  $$Cl_2(g) + 2e^{-} \rightarrow 2\,Cl^{-}(aq)$$

  Another example is the conversion of iron(III) to iron(II). Using an electrode made of solid iron will cause a reaction between iron(II) and Fe(s), so the electrode must be inert:

  $$Fe^{3+}(aq) + e^{-} \rightarrow Fe^{2+}(aq)$$

- The other reaction consumes electrons when the ions in solution gain electrons to form a metal. This is the reduction half-cell. This metal will plate (cover) the electrode because the electrode is the site of the reaction. Because the electrode will not break down in this half-cell, it can be made of an inert substance.

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

Anode and cathode

anode
the electrode where oxidation occurs

cathode
the electrode where reduction occurs

The electrodes that are used in the half-cells are called the **anode** and the **cathode**.

Oxidation occurs at the anode. Oxidation is the loss of electrons (OIL) from a reactant. So, electrons are generated at the anode, which results in the anode having a negative charge. In an oxidation reaction, electrons are lost from a metal to form a positive ion. Therefore, the metal electrode breaks down into the solution. Over time, the solution becomes more concentrated. The anode breaks down over time as the metal goes into solution.

Reduction occurs at the cathode. Reduction is the gain of electrons (RIG) by a reactant. So, electrons are consumed at the cathode and the cathode is positively charged.

polarity
the charge of an electrode, either positive or negative

Charges at the anode and cathode are often referred to as the **polarity** of the electrodes.

External circuit

external circuit
the electric circuit (wires) that allow for electron movement from anode to cathode

Electrons are produced at the negative anode, and then move through the **external circuit**, made of wires and a voltmeter (or multimeter), to the positive cathode where they are consumed. The voltmeter measures the voltage generated by the galvanic cell when current flows from the anode to the cathode.

MANDATORY PRACTICAL
7.1 Constructing a galvanic cell
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Salt bridge

The **salt bridge** is the **internal circuit** that connects the two half-cells. Its purpose is to allow the movement of ions between the half-cells.

- As electrons are produced at the anode, positive ions are formed as the metal electrode beaks down into the solution. This causes a build-up of positive charge in the oxidation half-cell. Negative ions in the salt bridge migrate towards this half-cell to balance the charge (Figure 7).
- As electrons are consumed at the cathode, positive ions are removed from the solution to either plate onto the electrode or be converted to an uncharged molecule. This causes a build-up of the negative spectator ions that are left over in the solution. Positive ions in the salt bridge migrate towards this half-cell to balance the charge (Figure 7).

salt bridge
an electrical connection between the two half-cells of an electrochemical cell; it allows for the flow of charge by moving ions – cations to the cathode and anions to the anode

internal circuit
the part of an electrochemical cell that allows for ion flow, e.g. the salt bridge

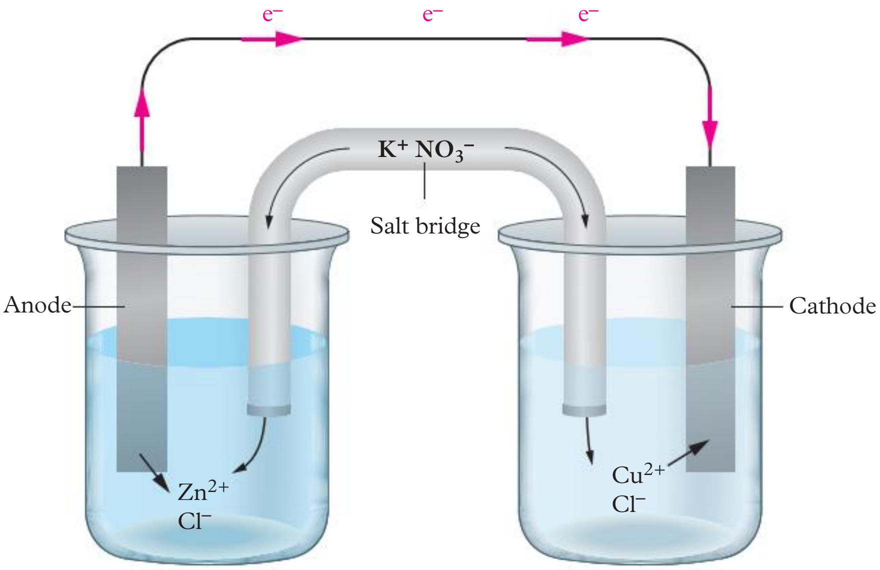

FIGURE 7 The flow of ions through the salt bridge in a galvanic cell. The potassium cations in the salt bridge migrate to the cathode to balance the charge lost when copper cations plate onto the cathode. The nitrate anions in the salt bridge migrate to the anode to balance the charge gained when the anode breaks down to form zinc cations.

Study tip

An easy way to remember that reduction occurs at the cathode and oxidation occurs at the anode is to say galvanic cells involve AN OX and a RED CAT.

AN OX
a mnemonic to remember that oxidation occurs at the anode

RED CAT
a mnemonic to remember that reduction occurs at the cathode

Cell diagrams

Cell diagrams are used to demonstrate the two redox half-equations, overall redox equation and therefore the flow of electrons through a galvanic cell. Cell diagrams must include:

- two half-cells (including half-equations, spectator ions and ion movement)
- an anode and a cathode (labelled with polarity)
- an external circuit: consisting of wires and a voltmeter
- an internal circuit: consisting of a salt bridge (demonstrating ion movement).

cell diagram
a diagram of a galvanic cell that has all key components, reaction mechanisms and electron/ion movement labelled

Drawing cell diagrams

When drawing a galvanic cell, you must include all aspects of the cell. Consider the example of a $Cu(s)/Cu^{2+}(aq)$ half-cell and a $Zn(s)/Zn^{2+}(aq)$ half-cell.

Before labelling the diagram, find the half-equations in the electrochemical series (Table 1). Use the order of the half-equations and position of reactants to determine whether a spontaneous reaction will occur, and which chemical undergoes oxidation and reduction:

$$Cu^{2+} + 2e^- \rightarrow Cu \qquad E° = +0.34\,V$$
$$Zn^{2+} + 2e^- \rightarrow Zn \qquad E° = -0.76\,V$$

Study tip

Chemistry and physics handle the polarity of electrodes differently. Don't get confused.

Study tip

Negative anions move to the negative anode. Positive cations move to the positive cathode.

You can use the RED SOX method to show that copper(II) ions are the strongest oxidant (top left), and react with solid zinc, the strongest reductant (bottom right) spontaneously (Figure 8).

You can draw several conclusions from this information.

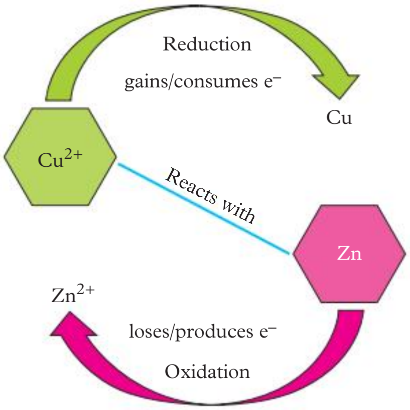

FIGURE 8 The 'S' configuration for the reaction between Zn and Cu^{2+}

1 The $Zn(s)/Zn^{2+}(aq)$ half-cell is the oxidation half-cell. The half-equation is:

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

Oxidation occurs at the negative anode, where electrons are produced. These electrons move through the external circuit from the anode to the cathode.

The anions in the salt bridge move into this half-cell to balance the build-up of positive charge as the zinc metal forms zinc cations.

2 The $Cu(s)/Cu^{2+}(aq)$ half-cell is the reduction half-cell. The half-equation is:

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

Reduction occurs at the positive cathode, where electrons are consumed. These electrons come from the external circuit (the wire). The cations in the salt bridge move into this half-cell to replace the Cu^{2+} ions, which form copper metal.

3 The overall equation is shown in the cell diagram in Figure 9.

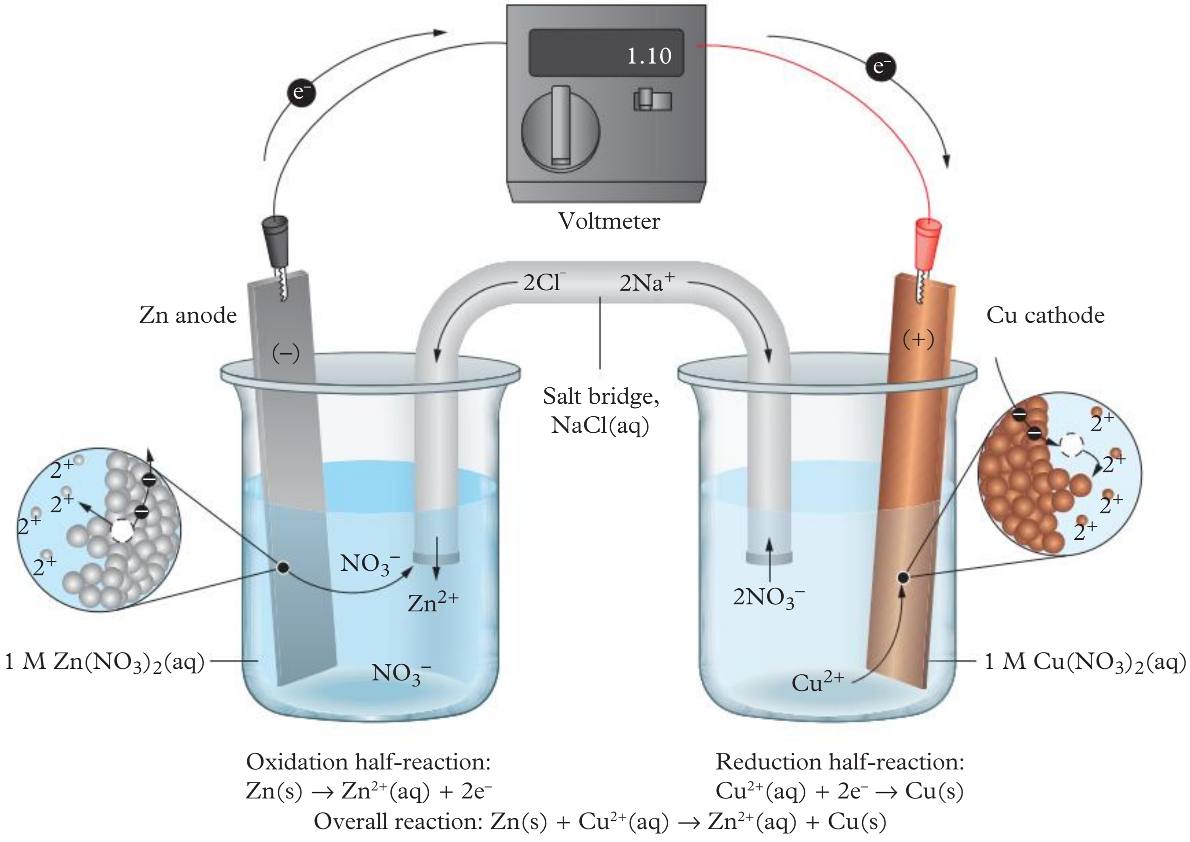

FIGURE 9 The cell diagram for the Cu^{2+} and Zn galvanic cell

Worked example 7.1B shows you the steps involved in drawing a cell diagram.

WORKED EXAMPLE 7.1B

Draw a fully labelled galvanic cell that has Fe^{3+}/Fe^{2+} and Sn^{2+}/Sn half-cells. Your cell diagram must show:

- reduction and oxidation half-equations
- anode and cathode
- polarity of electrodes
- the material that each electrode is made of
- electron movement
- a suitable salt bridge solution
- the direction of ion movement in the salt bridge
- the direction of ion movement in each half-cell
- the overall redox equation.

SOLUTION

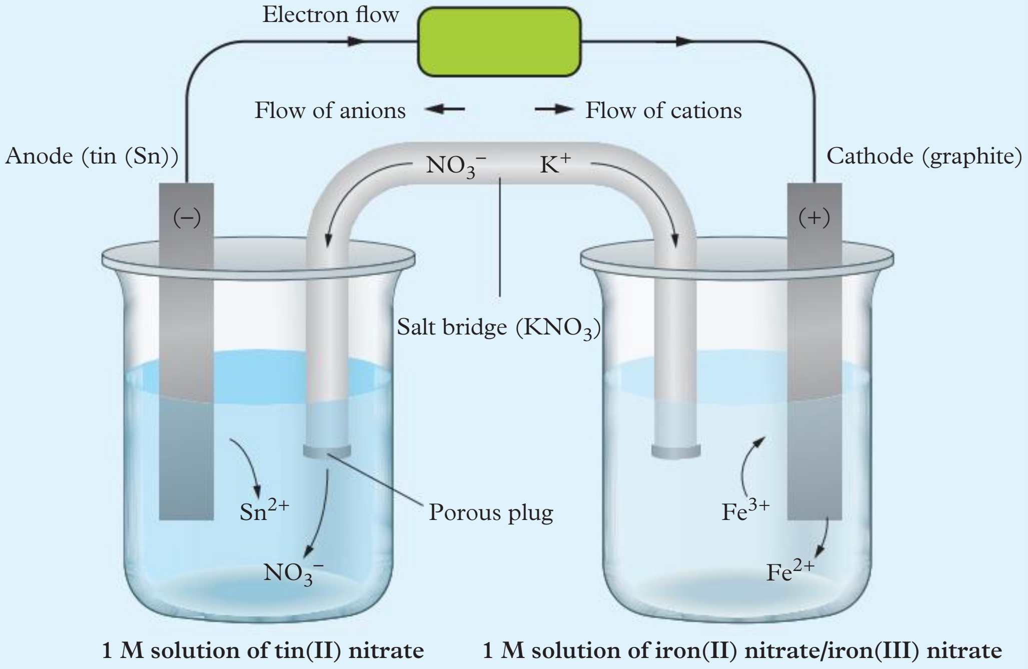

FIGURE 10 The cell diagram for the Fe^{3+} and Sn galvanic cell

Oxidation half-reaction:	Reduction half-reaction:
$Sn(s) \rightarrow Sn^{2+}(aq) + 2e^-$	$Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq)$

Overall reaction:

$$Sn(s) + 2Fe^{3+}(aq) \rightarrow Sn^{2+}(aq) + 2Fe^{2+}(aq)$$

CASE STUDY 7.1

The first electrochemical batteries

FIGURE 11 Alessandro Volta developed one of the first batteries in 1800.

Invented by Alessandro Volta (Figure 10) in 1800, the voltaic pile (Figure 12) was one of the first batteries (galvanic cells) to be developed for the purpose of producing electrical energy. The pile was made up of a series of alternating copper and zinc disks. Between the disks was salt water, which acted as an electrolyte and salt bridge, connecting the half-cells with one another.

Subsequent inventions that built upon Volta's model include the Daniell cell. This cell consisted of a copper pot filled with copper(II) sulfate. Inside the pot was a porous container containing sulfuric acid and a zinc electrode. This meant that there were three half-equations involved in the cell:

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

$$H^+(aq) + 2e^- \rightarrow H_2(g) \qquad E^\circ = 0.00\,V$$

$$Zn^{2+}(aq) + 2e^- \rightarrow Zn(s) \qquad E^\circ = -0.76\,V$$

Zinc is the strongest reductant and copper(II) ions are the strongest oxidant. However, the zinc electrode was in contact with the acid solution. Because the hydrogen ions are also an oxidant, they reacted spontaneously with the zinc metal to produce hydrogen gas. Once a hydrogen bubble formed, it meant that the two half-cells were no longer in contact. So, the Daniell cell would only operate for a limited time before the bubble short-circuited the system.

To overcome this problem, the sulfuric acid was replaced with a zinc(II) sulfate solution. This avoided the formation of a gas bubble, and the zinc solution was much safer than the highly reactive acid.

FIGURE 12 The voltaic pile was invented by Alessandro Volta.

CHALLENGE 7.1

Changing electrodes

Refer to Worked example 7.1B to indicate why it would not be a good idea to use an iron metal electrode in the iron half-cell. Use half-equations and the electrochemical series to justify your answer.

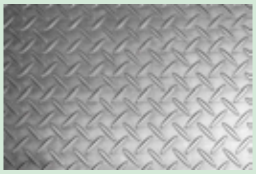

FIGURE 13 Iron metal is not an effective electrode in an iron-half equation.

CHECK YOUR LEARNING 7.1

Describe and explain

1 **Describe** how a galvanic cell can generate electricity. Refer to ion and electron movement in your answer.

2 **Explain** the purpose of a salt bridge in a galvanic cell.

3 **Construct** a fully labelled galvanic cell with half-cells of:

- a zinc and magnesium
- b iron(II) and copper.

Apply, analyse and interpret

4 **Determine** what material each electrode can be made of in a:

- a zinc half-cell, where the electrode is the anode
- b copper half-cell, where the electrode is the cathode
- c half-cell containing a solution of HNO_3 in which the hydrogen ion undergoes reduction
- d half-cell in which hydrogen telluride (H_2Te) is bubbled through water to create an acidified solution.

Investigate, evaluate and communicate

5 A student constructed a copper/silver galvanic cell, using a sodium chloride salt bridge. After setting up the cell, the student noticed that it did not generate any electricity. **Investigate** why the cell produced no current. **Evaluate** the method and provide an alternative that would work.

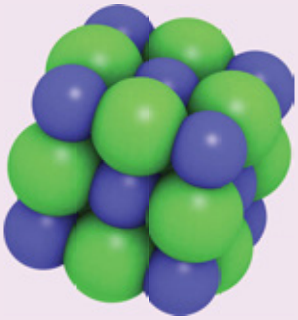

FIGURE 14 Sodium chloride was used as the salt bridge.

6 **Investigate** and **communicate** why it is essential to separate a lithium/fluorine galvanic cell into two half-cells. **Determine** the consequences if the reactants were kept in the same beaker.

You can find the following resources for this section on your obook assess:

- » Student book questions
  7.1 Check your learning
- » Mandatory practical
  7.1 Constructing a galvanic cell
- » Challenge
  7.1 Changing electrodes
- » Weblink
  The first battery

7.2

Standard electrode potentials

KEY IDEAS

In this section, you will learn about:

- the voltage generated by galvanic cells
- the effect of running cells under non-standard conditions.

Measuring the strength of electrochemical cells

The position of all the half-equations in the electrochemical series and their strengths as oxidising and reducing agents are measured by connecting them to a hydrogen half-cell ($H^+(aq)/H_2(g)$). This determines whether a half-equation contains a stronger oxidant or reductant than the hydrogen cell.

- If the hydrogen half-cell converts hydrogen ions into hydrogen gas, then it is the reduction half-equation:

  $$2H^+(aq) + 2e^- \rightarrow H_2(g)$$

  So, the hydrogen ion is the strongest oxidant and hydrogen is higher up on the electrochemical series.

  Bubbles of hydrogen will be produced at one electrode. Also, $[H^+]$ will decrease as H^+ ions are consumed in the reaction. The cell will become less acidic, which you can observe by an increase in its pH.

- If the hydrogen half-cell converts hydrogen gas into hydrogen ions, then it is the oxidation half-equation:

  $$H_2(g) \rightarrow 2H^+(aq) + 2e^-$$

  So, hydrogen gas is the strongest reductant and hydrogen is lower down on the electrochemical series.

  Hydrogen gas will be consumed by one electrode, meaning that the gas must be in contact with the electrode. Also, $[H^+]$ will increase as H^+ ions are produced. The cell will become more acidic, which you can observe by a decrease in its pH.

standard electrode potential ($E°$) the electrical potential that an electrode generates under standard conditions

Standard electrode potentials

As well as observing the formation of hydrogen gas and measuring pH, you can measure the voltage that is generated by the galvanic cell. **Standard electrode potentials ($E°$)** are the voltages generated by redox half-equations under standard conditions and are used to order the half-equations in the electrochemical series. This is an essential concept in the development of new battery technologies. Materials are selected according to how much current they can generate when they react in a galvanic cell.

The standard hydrogen half-cell is used as a reference cell to measure the voltages of all half-cells, which are listed as an $E°$ value on the electrochemical series.

The hydrogen half-cell (Figure 1) is given an arbitrary value of 0.00 V. Where a galvanic cell is constructed with a hydrogen half-cell, the voltage generated by the cell must be equal to the $E°$ of the second half-cell. This is how the $E°$ values on the electrochemical series have been measured.

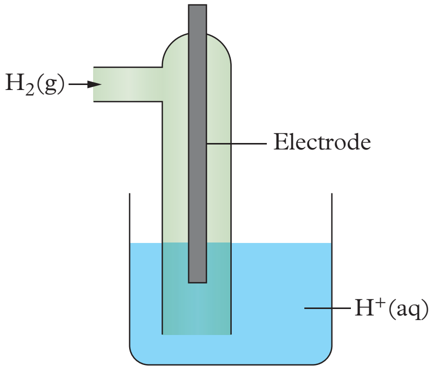

FIGURE 1 The standard hydrogen half-cell has an $E°$ of 0.0 V.

Calculating cell potential difference

When any two half-cells from the electrochemical series are connected in a galvanic cell, you can calculate the voltage generated by the cell as the difference in the amount of electricity consumed at the cathode and generated at the anode – the **cell potential difference**. This is called the **electromotive force (EMF)** and is the difference in potential that generates electricity.

cell potential difference the electrical potential difference (V) between two electrodes; the voltage that the galvanic cell can generate under standard conditions

electromotive force (EMF) the difference in potential across a cell that generates electricity

$$\text{EMF} = E^\circ_{\text{reduction half-cell}} - E^\circ_{\text{oxidation half-cell}}$$

To determine the EMF of a zinc–hydrogen galvanic cell, use the RED SOX method (Figure 2).

$$2H^+ + 2e^- \rightarrow H_2 \qquad E^\circ = 0.00\,V$$
$$Zn^{2+} + 2e^- \rightarrow Zn \qquad E^\circ = -0.76\,V$$

The acidic hydrogen ions undergo reduction at the cathode, gaining electrons to form hydrogen gas.

When calculating the voltage generated by the galvanic cell, the EMF calculation is used:

$$\begin{aligned}\text{EMF} &= E^\circ_{\text{reduction half-cell}} - E^\circ_{\text{oxidation half-cell}}\\ &= 0.00\,V - (-0.76\,V)\\ &= 0.00\,V + 0.76\,V\\ &= 0.76\,V\end{aligned}$$

Therefore, the cell produces 0.76 volts (Figure 3).

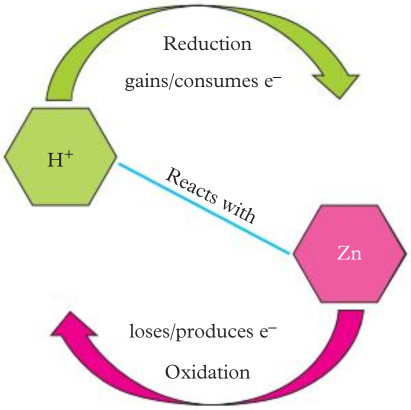

FIGURE 2 The 'S' diagram of H⁺ reacting with Zn

Study tip

In galvanic cells, the reduction half-equation is higher on the electrochemical series. Therefore, to calculate EMF, subtract the bottom E° from the top E°.

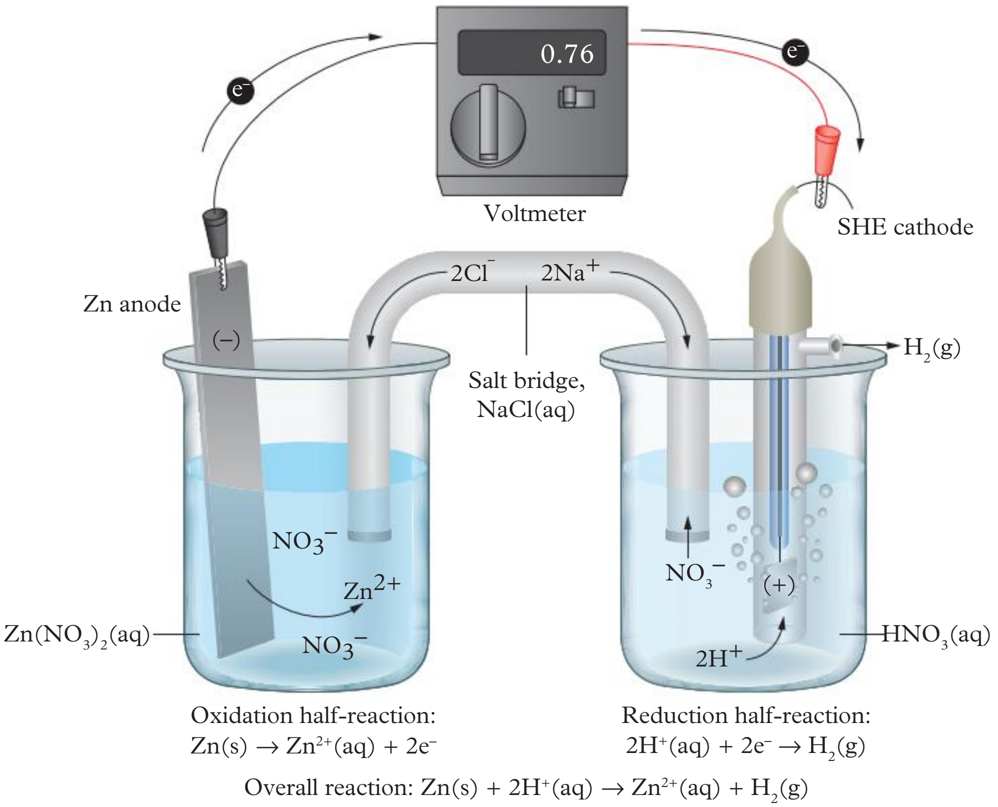

FIGURE 3 The zinc–hydrogen galvanic cell generates 0.76 V.

Worked example 7.2 demonstrates how to calculate the voltage from a galvanic cell.

WORKED EXAMPLE 7.2

Calculate the voltage produced when a Pb^{2+}/Pb half-cell is connected to an Al^{3+}/Al half-cell.

$$Pb^{2+}(aq) + 2e^- \rightarrow Pb(s) \qquad E^\circ = -0.13\,V$$
$$Al^{3+}(aq) + 3e^- \rightarrow Al(s) \qquad E^\circ = -1.68\,V$$

SOLUTION

$$\begin{aligned} \text{EMF} &= E^\circ_{\text{reduction half-cell}} - E^\circ_{\text{oxidation half-cell}} \\ &= -0.13\,V - (-1.68\,V) \\ &= -0.13\,V + 1.68\,V \\ &= 1.55\,V \end{aligned}$$

Standard conditions

standard conditions
the conditions under which all E° values are measured: 25°C, 1 atm and 1 M

It is essential to understand that standard electrode potentials are measured under **standard conditions** of 25°C, 1 atm and 1 M.

When galvanic cells operate under non-standard conditions (i.e. a different temperature, pressure or concentration) the E° values change. Therefore, the order of the half-equations can change. When the conditions under which the galvanic cells operate change, the corresponding change in E° value is not usually very large. Half-equations that have quite close E° values may swap positions on the electrochemical series.

CHALLENGE 7.2

Photochemical galvanic cells

A galvanic cell is set up with an aqueous solution of zinc nitrate and graphite electrode at the cathode and an aqueous solution of aluminium nitrate and aluminium electrode at the anode.

A student observed gas bubbles forming on one of the electrodes rather than metal plating onto the electrode.

a Provide a reason for this observation.
b Provide the half-equations and the overall reaction occurring in the cell.
c State a safety consideration for this galvanic cell, referring to your answer in part b.

CASE STUDY 7.2

Pacemakers

The heart contains an electrical system. It is responsible for regulating both heart rate (beats per minute) and sinus rhythm (synchronised pumping of the four chambers of the heart). An electrical signal travels through the cells of the body and forces the heart muscles to expand or contract to regulate this motion.

People who suffer from an irregular heartbeat (arrhythmia) may have a pacemaker inserted into their chest. A pacemaker is a small device that helps to control an irregular heartbeat. There are two parts to this device:

- a pulse generator, which contains the battery (a galvanic cell) and regulates the heartbeat
- a set of small wires that send an electrical signal to the heart. The electrical signal can force the heart muscles to expand or contract and therefore regulates the rhythm when the body cells fail to do so.

The first batteries used in pacemakers were NiCd (nickel–cadmium) batteries. They operated under the principles of a galvanic cell:

$$\mathrm{Cd(s) + 2NiOOH(s) + 2H_2O(l) \rightarrow Cd(OH)_2(s) + 2Ni(OH)_2(s)}$$

Although NiCd batteries could be recharged hundreds of times, the battery was heavy, which was a problem for the people who had to carry them around all day every day. Recharging the battery was also problematic because it needed to be connected to an external power source.

A new battery was developed that was lighter and could maintain charge for tens of years. The LiI (lithium–iodine) battery operates according to the overall reaction equation:

$$\mathrm{2Li(s) + I_2(s) \rightarrow 2LiI(s)}$$

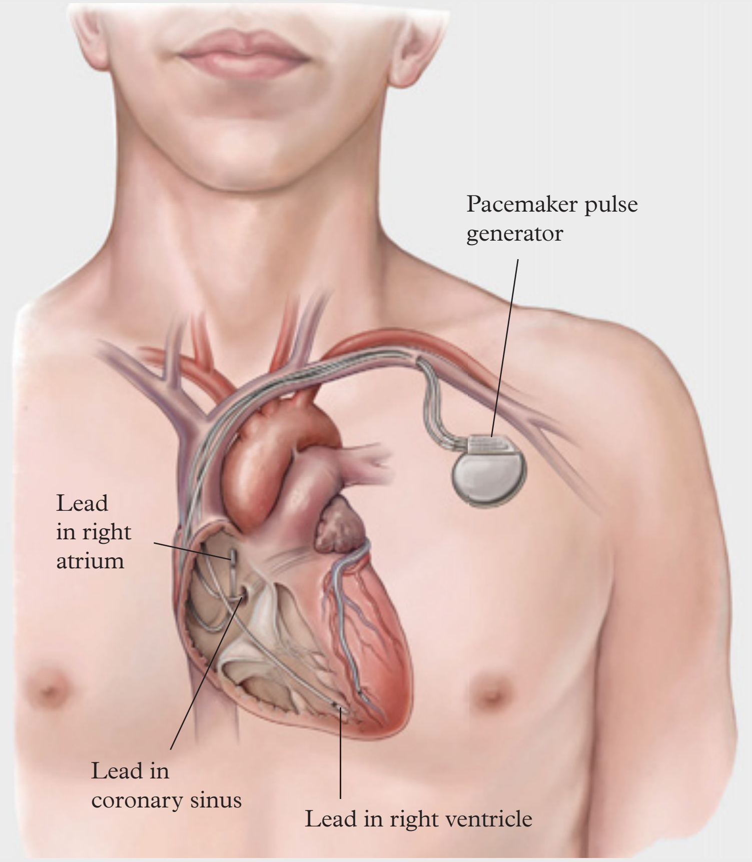

FIGURE 4 A pacemaker connected to an irregularly beating heart by three current-carrying leads

CHECK YOUR LEARNING 7.2

Describe and explain

1 **Explain** the purpose of the hydrogen half-cell in the electrochemical series.

2 **Describe** standard conditions. **Explain** what happens if a galvanic cell is not run under standard conditions.

3 **Calculate** the $E°$ values of the following galvanic cells.

- **a** Cu^{2+}/Cu and Zn^{2+}/Zn
- **b** Mg^{2+}/Mg and Cu^{2+}/Cu
- **c** Fe^{2+}/Fe and Mg^{2+}/Mg
- **d** Cu^{2+}/Cu and Fe^{2+}/Fe
- **e** Mg^{2+}/Mg and Zn^{2+}/Zn
- **f** Zn^{2+}/Zn and Fe^{2+}/Fe

Apply, analyse and interpret

4 **Consider** the following half-equations:

$$Sn^{4+}(aq) + 2e^- \rightleftharpoons Sn^{2+}(aq)$$

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

$$Cl_2(g) + 2e^- \rightleftharpoons 2Cl^-(aq)$$

- **a** **Identify** the electrode required in each cell if it underwent reduction.
- **b** **Identify** the electrode required in each cell if it underwent oxidation.
- **c** **Calculate** the $E°$ values for each combination of half-cell (there should be three combinations).
- **d** **Sketch** the three galvanic cells from part c.
- **e** **Determine** which chemical is the strongest oxidant and which is the strongest reductant.
- **f** **Determine** which combination of half-cell produces the highest voltage.

Investigate, evaluate and communicate

5 **Evaluate** and **communicate** the impact of using a copper half-cell as the reference cell, rather than hydrogen. What effect would this have on the voltage produced by the cell, the voltage calculated on the electrochemical series and the $E°$ values of the electrochemical series?

6 Pieces of magnesium and zinc are often used to prevent solid iron from undergoing oxidation to form iron(II). **Investigate** why this occurs and **communicate** your findings, making sure to reference oxidants, reductants and the electrochemical series.

FIGURE 5 99.95% fine magnesium

You can find the following resources for this section on your obook assess:

- » Student book questions 7.2 Check your learning
- » Challenge 7.2 Photochemical galvanic cells
- » Weblink Pacemakers

7.3 Applications of spontaneous reactions

KEY IDEAS

In this section, you will learn about:

- the application of redox reactions in batteries
- the application of redox reactions in fuel cells.

alkaline
basic

Car batteries can produce voltages of 12 V or more, whereas an **alkaline** AA battery can only produce 1.1 V. These batteries are designed for specific purposes and functions. More than half of all batteries sold are alkaline AA batteries, so producing higher voltages is not always advantageous, especially if it is unnecessary.

Non-rechargeable batteries – primary cells

primary cell
a non-rechargeable battery; a galvanic cell that produces an electrical current

A galvanic cell is often called a **primary cell** or battery. If the battery is rechargeable, it is called a secondary cell, but primary cells can only be discharged. This means that, once the chemical reaction within the battery has used all the reactants, the battery dies and must be thrown out. Therefore, this reaction is not reversible. As the solid anode is oxidised to form ions in solution, it breaks down and this is usually what causes the battery to die because the anode no longer completes the circuit.

Batteries do not have a salt bridge; instead they contain an electrolyte. The electrolyte is an ionic solution that carries charge between the electrodes. The electrodes are both submerged in the electrolyte, which contains an acidic (H^+) or an alkaline (OH^-) solution.

Primary cells do not produce high voltages. They are mostly used for low current devices.

Alkaline batteries

Alkaline batteries are named for the basic electrolyte they contain. Some of the most common batteries are the AA and AAA batteries, which are also called zinc–carbon galvanic cells.

An alkaline cell (Figure 2) has a powdered zinc ($Zn(s)$) anode in a potassium hydroxide (basic KOH) electrolyte. The cathode is made of a mixture of manganese dioxide ($MnO_2(s)$) and graphite. The separator ensures that the reactants do not react spontaneously with one another. These types of batteries produce approximately 1.5 V, which decreases with time as the reactants contained within the cell are consumed in the reaction.

At the anode, solid zinc reacts with the hydroxide ions in the electrolyte to form zinc hydroxide and two electrons:

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

At the cathode, manganese dioxide reacts with water in the aqueous electrolyte, using two electrons, to form manganese oxide–hydroxide and hydroxide:

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

The overall reaction equation for an alkaline battery is:

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

FIGURE 1 AA and AAA batteries

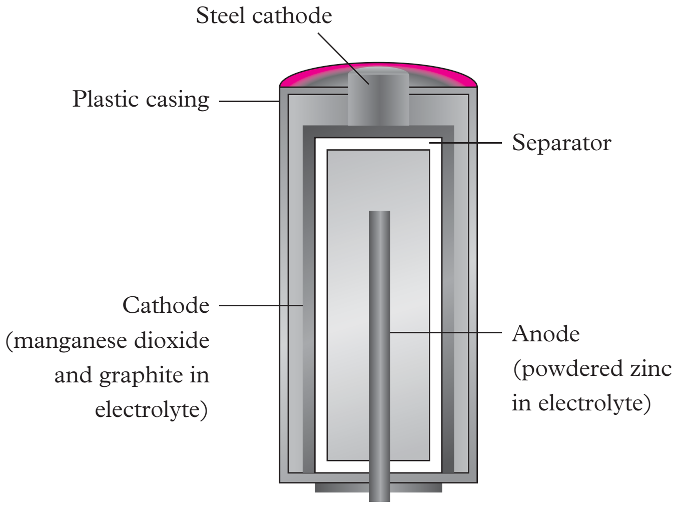

FIGURE 2 An alkaline cell

Button cells

Button cells are much smaller than alkaline cells and can be used in very small electrical devices such as watches, hearing aids, calculators and cameras. However, they can produce similar voltages to alkaline cells – approximately 1.5 V or sometimes higher.

One of the more efficient types of button cell, the silver oxide cell, consists of a powdered zinc anode with an alkaline potassium hydroxide (KOH) electrolyte. The cathode is made of a mixture of silver oxide and graphite (Figure 3).

At the anode, zinc reacts with the hydroxide ions from the electrolyte to form zinc oxide, water and two electrons:

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

At the cathode, silver oxide reacts with water, requiring two electrons, to form silver and hydroxide:

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

The overall reaction equation for this type of button cell is:

$$Zn(s) + Ag_2O(s) \rightarrow 2Ag(s) + ZnO(s)$$

A button cell is more expensive than an alkaline battery, but it can produce a stable voltage over long periods of time.

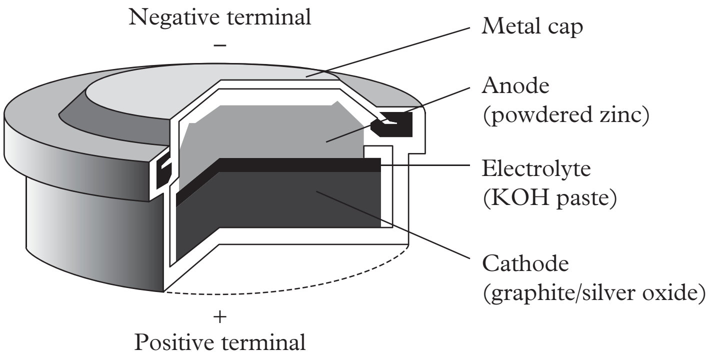

FIGURE 3 A silver oxide button cell

Fuel cells

The main problem with any primary cell is that, eventually, the voltage that it produces decreases and the cell terminates as the reactants are consumed and cannot produce a flow of electrons.

Fuel cells are an alternative way of producing an electrical current. A fuel cell has a constant supply of reactants and inert electrodes that cannot break down. The reactants and products are gaseous, liquid or aqueous so there is no build-up of solid products, which might block the flow of charge through the cell. A fuel cell can produce a current for as long as it has reactants.

fuel cell
a galvanic cell that produces electricity by using a constant supply of reactants (often hydrogen and oxygen) and inert electrodes that do not break down

Fuel cells are considered to be galvanic cells because they operate to produce electrical energy from chemical potential energy and therefore function as a discharge cell.

Alkaline fuel cell

One of the most common fuel cells is the alkaline fuel cell, or hydrogen–oxygen fuel cell (Figure 4). Its reactants are hydrogen and oxygen gas and it contains a basic electrolyte, often potassium hydroxide (KOH). The electrodes are constructed from porous carbon. The pores increase the surface area of the electrodes and therefore increase the amount of reactant coming into contact with the electrodes. As the hydrogen and oxygen enter their own separate compartments, they come into contact with the electrodes.

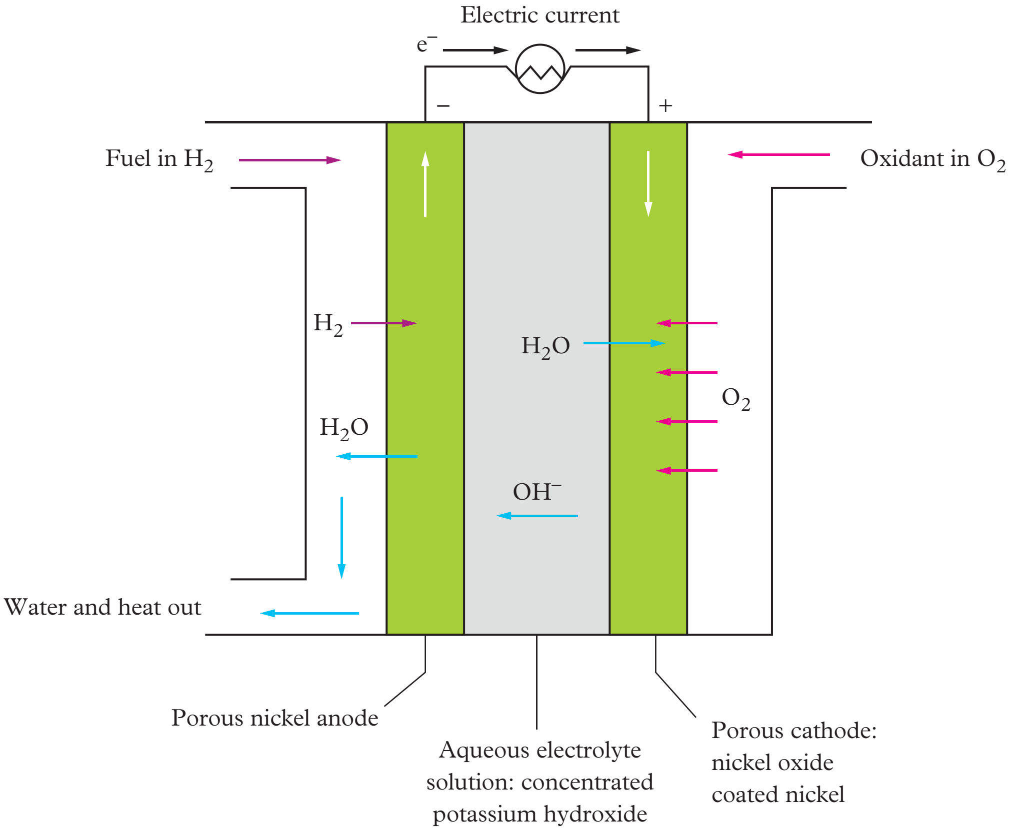

FIGURE 4 The set-up of an alkaline hydrogen oxygen fuel cell

At the anode, hydrogen reacts with the hydroxide in the electrolyte to form water and two electrons:

$$H_2(g) + 2OH^-(aq) \rightarrow 2H_2O(l) + 2e^-$$

At the cathode, oxygen reacts with water in the aqueous electrolyte and consumes four electrons to form hydroxide.

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

Overall, the hydroxide that reacts at the anode is replaced into the electrolyte when it is formed at the cathode and so its concentration remains relatively constant. The product of the fuel cell is liquid or gaseous water, depending on the temperature of the fuel cell.

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

Hydrogen–oxygen fuel cells are carbon neutral and less polluting than fossil-fuel based sources of power. Before they can be used on a larger scale, some technological problems need to be solved, such as the safe production and storage of hydrogen, which is an explosive gas.

Case study 7.3

Launching a space shuttle

Alkaline fuel cells were most commonly used on space shuttles as part of the electrical power system. Each space shuttle contains three fuel cell power plants, which are supplied with hydrogen and oxygen gases. The water produced is stored and used for other purposes. Any heat produced by the fuel cell is transferred to freon coolant loops. The electricity generated is directed toward the shuttle's power systems.

The external tanks that launch a space shuttle into orbit around Earth are filled with liquid hydrogen and liquid oxygen to keep the reactants separated in different half-cells or compartments (Figure 5). The hydrogen and oxgyen react spontaneously, producing large quantities of heat energy in an exothermic reaction. A direct reaction results in the conversion of chemical potential energy to heat, light and sound energy. When separated in a galvanic cell (fuel cell), they produce electrical energy.

FIGURE 5 The space shuttle attached to external fuel tanks

Approximately 8.5 minutes into launch, the fuel has been reacted and the external tanks are rendered useless. They are now essentially dead weight. The tanks detach from the space shuttle and fall back to Earth.

CHALLENGE 7.3

Hydrogen–oxygen fuel cells

Write the oxidation, reduction and overall balanced equations for a hydrogen–oxygen fuel cell that operates with an acidic electrolyte.

CHECK YOUR LEARNING 7.3

Describe and explain

1 **Describe** the difference between a primary and a secondary cell. Give examples of both.

2 **Identify** the two differences between primary cells and galvanic cells. Provide examples.

Apply, analyse and interpret

3 a **Determine** the difference between a battery that can only be discharged and one that can also be recharged.

  b **Identify** the feature of a cell that means it can only discharge.

  c **Describe** the design feature required for a battery to be able to recharge.

FIGURE 6 Some batteries can be recharged.

4 Use the electrochemical series to answer the following questions. See Table 1, page 165.

  a **Determine** the lowest voltage battery that you can construct.

  b **Determine** is the highest voltage battery that you can construct. **Explain** the type of electrolyte you would use. **Explain** some of the hazards involved with designing, making and running this cell.

Investigate, evaluate and communicate

5 **Investigate** fuel cells and galvanic cells and **compare** and **contrast** them in terms of:

- their set-up
- how they work
- what they are used for
- specific design features
- energy transformations
- energy efficiency
- applications.

You can find the following resources for this section on your obook assess:

» Student book questions
7.3 Check your learning

» Challenge
7.3 Hydrogen-oxygen fuel cells

» Weblink
Space shuttle fuel tanks

CHAPTER 7

Review

Chapter summary

7.1
- A galvanic cell connects the reduction and oxidation half-equations through a circuit to generate a flow of electrical energy. Reduction occurs at the positive electrode, called the cathode. Oxidation occurs at the negative electrode, called the anode. The internal circuit consists of a salt bridge, which is made of an unreactive salt solution. Negative ions move towards the negative electrode to balance the positive ions that move into the solution when the metal undergoes oxidation. Positive ions move towards the positive electrode to replace the positive ions that plate as a metal onto the cathode when they undergo reduction.

7.2
- The voltage generated by a galvanic cell can be determined by using the electrochemical series. The oxidation $E°$ is subtracted from the reduction $E°$ to calculate the cell potential difference (also called the EMF or voltage).

7.3
- Galvanic cells have many applications but are most commonly used in batteries.
- A non-rechargeable battery is called a primary cell. There are many different types of primary cells; for example, alkaline batteries and button cells.
- Fuel cells are galvanic cells that produce electrical energy by using a constant supply of reactants; for example, hydrogen and oxygen.

Key terms

- alkaline
- AN OX
- anode
- cathode
- cell diagram
- cell potential difference
- electrochemical series
- electrode
- electromotive force (EMF)
- external circuit
- fuel cell
- galvanic cell
- half-cell
- inert electrode
- internal circuit
- oxidation
- polarity
- primary cell
- RED CAT
- RED SOX
- redox reaction
- reduction
- salt bridge
- standard conditions
- standard electrode potential ($E°$)

Key formulas

Voltage generated by a galvanic cell	$\text{EMF} = E°_{\text{reduction half-cell}} - E°_{\text{oxidation half-cell}}$

Revision questions

The relative difficulty of these questions is indicated by the number of stars beside each question number: ★ = low; ★★ = medium; ★★★ = high.

Multiple choice

1 A standard galvanic cell is set up with $Mg(s)/Mg^{2+}(aq)$ and $Cl_2(g)/Cl^-(aq)$ half-cells. In this cell:

A Cl^- is the strongest oxidant and Mg^{2+} is the strongest reductant

B Cl_2 is the strongest oxidant and Mg is the strongest reductant

C Mg^{2+} is the strongest oxidant and Cl^- is the strongest reductant

D Mg is the strongest oxidant and Cl_2 is the strongest reductant.

2 A student sets up a galvanic cell consisting of two half-cells: (1) $Cr^{3+}(aq)/Cr^{2+}(aq)$ and (2) $Cr^{3+}(aq)/Cr(s)$. Suitable materials for the electrodes are:

A (1) platinum and (2) platinum

B (1) platinum and (2) chromium

C (1) chromium and (2) platinum

D (1) chromium and (2) chromium.

3 A methane–oxygen fuel cell operates with the following half-equation at the anode:

$$CH_4(g) + 2H_2O(l) \rightarrow CO_2(g) + 8H^+(aq) + 8e^-$$

The reaction occurring at the cathode is:

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

B $4H^+(aq) + O_2(g) \rightarrow 2H_2O(l)$

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

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

4 The electrode where the metal is reduced is called the:

A cathode and has a positive charge

B anode and has a positive charge

C cathode and has a negative charge

D anode and has a negative charge.

5 The electrons in a galvanic cell flow from the:

A positive anode to negative cathode

B positive cathode to negative anode

C negative cathode to positive anode

D negative anode to positive cathode.

The following information relates to questions 6 and 7.

A galvanic cell is constructed using the following half-cells:

Half-cell 1: silver electrode and a colourless solution of $AgNO_3$

Half-cell 2: copper electrode in a blue solution of $CuCl_2$

6 Identify which of the following is likely to occur.

A Chlorine gas forms at the anode.

B The silver electrode decreases in mass.

C The blue solution becomes darker.

D The clear solution becomes cloudy.

7 A suitable salt bridge solution would contain:

A NaCl

B $NaNO_3$

C NaOH

D NaBr

8 Three half-cells A, B and C were constructed from unknown solutions according to the diagrams in Figure 1.

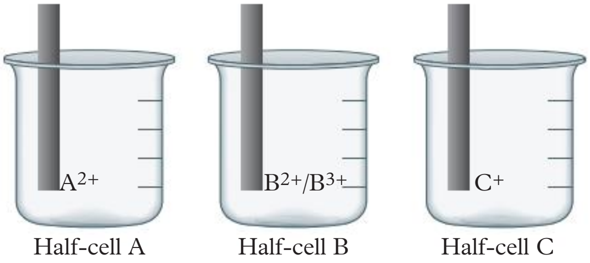

FIGURE 1 Three half-cells

The following information was determined experimentally when the half-cells were combined:

- The electrode in half-cell B is negative when combined with half-cell A.
- The electrode in half-cell C is negative when combined with half-cell B.

The strongest reductant is:

A A

B C^+

C B^{2+}

D C

9 Which of the following metals will not be oxidised by an aqueous 1.0 M acid solution?

A Copper

B Magnesium

C Zinc

D Iron

10 When aluminium metal is welded to the hull of a steel ship, it helps protect the steel from corrosion. This is achieved because a galvanic cell is produced between two metals. In this galvanic cell the:

A aluminium acts as the anode

B steel hull acts as the anode

C aluminium acts as the cathode

D aluminium gains electrons and acts as an oxidant or oxidising agent.

FIGURE 2 Aluminium protects steel from corrosion on this cruise ship.

Short answer

Describe and explain

★ **11** **Describe** the main purposes of separating the half-cells in a galvanic cell.

★★ **12** **Explain** why most galvanic cells are operated at standard conditions.

★★ **13** **Describe** the purpose of an electrolyte, and how is it different from a salt bridge. **Explain** when an electrolyte is used.

★★★ **14** **Construct** fully labelled galvanic cells for the following half-cells.

a Ag/Ag^+ and Cu^{2+}/Cu

b $Cr_2O_7^{2-}/Cr^{3+}$ and Fe^{2+}/Fe

c H_2O_2/H_2O and O_2/H_2O_2

You must include:

- labelled anode, cathode, polarity of electrodes and the material the anode and cathode are made from
- fully balanced half-equations, including states, and labelled as oxidation or reduction
- a labelled salt bridge (propose a suitable chemical and demonstrate ion movement)
- the direction of electron flow
- all reactants and products in the two half-cells
- full calculations showing the $E°$ of the cell
- the overall balanced chemical equation, including states.

★★★ **15** **Calculate** the $E°$ values for the galvanic cells in question 14.

★★★ **16** A nickel–cadmium galvanic cell is constructed (Figure 3), where:

$$Cd^{2+}(aq) + 2e^- \rightleftharpoons Cd(s) \qquad E° = -0.40\,V$$

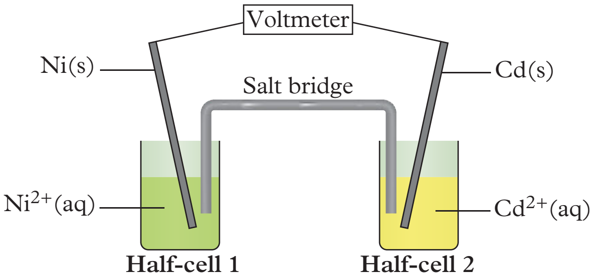

FIGURE 3 A NiCd galvanic cell

Copy Figure 2 into your book and:

a **identify** the oxidation and reduction half-cells

b **identify** the anode and cathode and polarity of each

c **construct** the half-equations and overall equations

d **identify** a suitable salt bridge substance and justify your choice

e **clarify** the direction of ion and electron movement

f **calculate** the $E°$ of the cell.

Apply, analyse and interpret

★★ **17** Consider the following pairs of half-cells.

- **a** (Mg^{2+}/Mg) and (Fe^{2+}/Fe)
- **b** (Cu^{2+}/Cu) and (Ag^{+}/Ag)
- **c** (Al^{3+}/Al) and (H^{+}/H_2)
- **d** (Fe^{3+}/Fe^{2+}) and $(H_2O/H_2 + OH^{-})$

For each pair of half-cells, state the:

- **i** strongest reductant
- **ii** strongest oxidant
- **iii** oxidising agent
- **iv** reducing agent
- **v** two half-equations
- **vi** overall equation.

★★★ **18** An iron nail is placed in aqueous solutions of:

- **i** $AgNO_3$
- **ii** $Mg(NO_3)_2$
- **iii** $CuSO_4$
- **iv** $Pb(NO_3)_2$
- **v** $Zn(NO_3)_2$

- **a** In which solution(s) would you expect a coating of another metal on the iron nail?
- **b** Use the electrochemical series to **explain** why some solutions would not result in the coating of another metal on the nail.
- **c** **Explain** the purpose of the SO_4^{2-} and NO_3^{-} ions in the solutions.

Investigate, evaluate and communicate

★★ **19** **Communicate** the difference between galvanic cells, primary cells and fuel cells. Your answer must include:

- structural differences
- advantages
- disadvantages
- applications.

★★★ **20** **Investigate** why blocks of zinc are attached to the steel supports on oil rigs in Bass Strait.

★★★ **21** A student wished to identify an unknown metal (X). The metal is cleaned, cut into 1 cm × 1 cm pieces and placed in separate solutions of:

- $Mg(NO_3)_2$
- $AgNO_3$
- $Al(NO_3)_3$
- $AuNO_3$

The student observed that a layer of metal formed on metal X when placed in the silver and gold solutions, but no reaction was observed when it was placed in the magnesium and aluminium solutions.

- **a** **Evaluate** the results of the experiment and **communicate** what is happening to cause these results.
- **b** **Determine** a possible identity for the metal and justify your choice, using the electrochemical series.

You can find the following resources for this section on your obook assess:

» Student book questions
Chapter 7 Revision questions

» Revision notes
Chapter 7

» assess quiz
Auto-correcting mutiple-choice quiz

» Flashcard glossary
Chapter 7

CHAPTER 8

Electrolytic cells

Electrolytic cells operate in the opposite way to galvanic cells. Instead of converting chemical energy to electrical energy in a redox reaction, they convert electrical energy to chemical energy.

Electrolytic cells put electrical energy into the cell to reverse the reactions and convert the electrical energy to chemical energy. These reactions are essential to modern society because they are the basis of rechargeable batteries, which power devices such as cars, laptops and phones. Batteries provide a portable power supply and can be recharged by plugging them in to a power point that uses mains power.

A common misconception is that batteries provide cleaner energy because they are rechargeable, and they do not produce any waste or generate harmful atmospheric gases such as carbon dioxide. However, when they are recharged, they use mains power, which in Australia is mostly generated by burning coal. Burning coal produces harmful greenhouse gases that contribute to the ever-increasing issue of climate change.

Batteries that are charged by solar panels, wind turbines or hydroelectricity (as in Tasmania) are more sustainable because the electricity used to recharge them is generated from renewable energy sources.

New technologies in electrochemistry are focusing on making solar cells more efficient and generating batteries that can be easily and efficiently recharged from renewable energy sources.

OBJECTIVES

→ Understand that electrolytic cells use an external electrical potential difference to provide the energy to allow a non-spontaneous redox reaction to occur, and appreciate that these can be used in small-scale and industrial situations, including metal plating and the purification of copper.

→ Predict and explain the products of the electrolysis of a molten salt and aqueous solutions of sodium chloride and copper sulfate. Explanations should refer to $E°$ values, the nature of the electrolyte and the concentration of the electrolyte.

→ Describe, using a diagram, the essential components of an electrolytic cell; including source of electric current and conductors, positive and negative electrodes, and the electrolyte.

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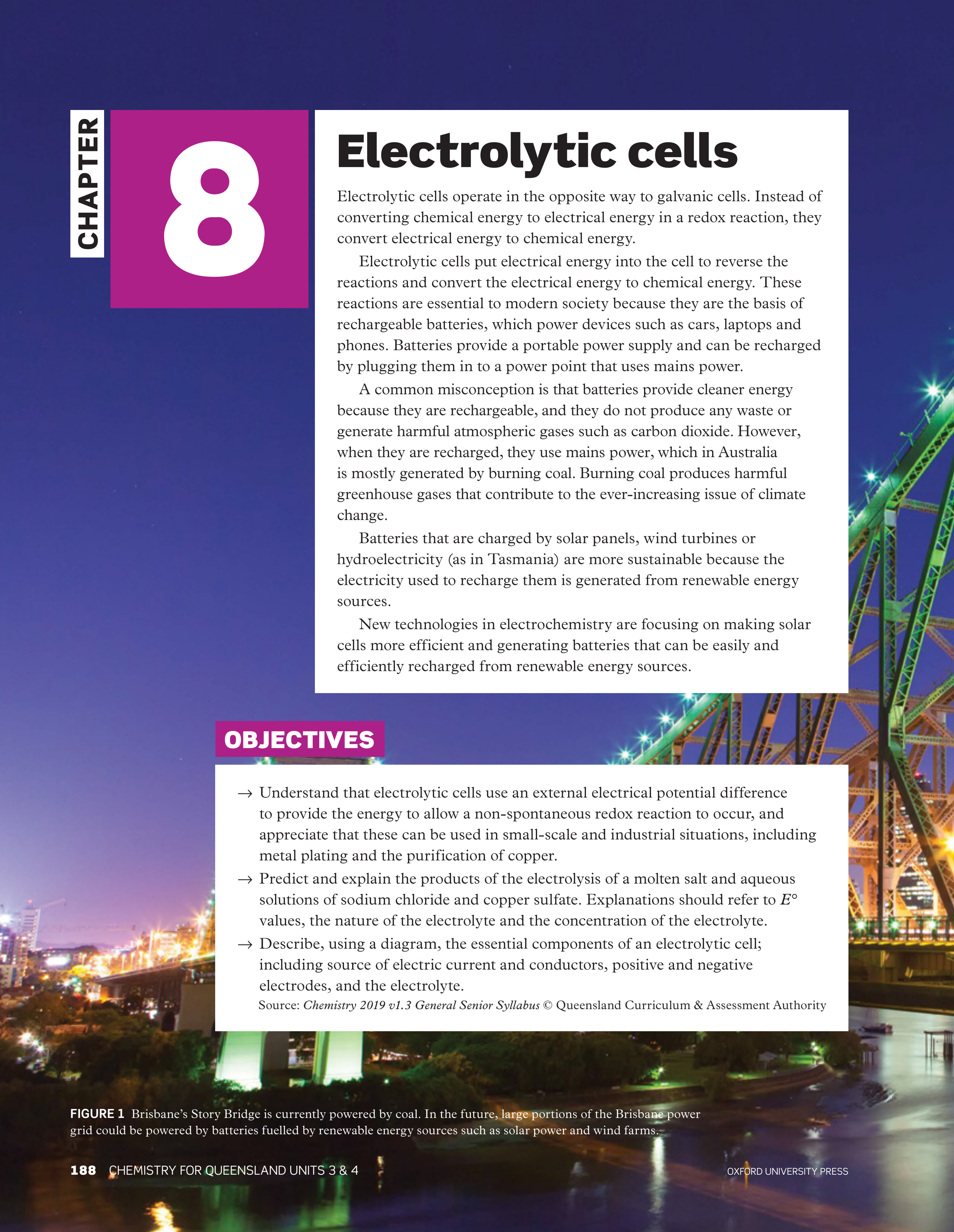


FIGURE 1 Brisbane's Story Bridge is currently powered by coal. In the future, large portions of the Brisbane power grid could be powered by batteries fuelled by renewable energy sources such as solar power and wind farms.

PRACTICALS

SUGGESTED PRACTICAL	**8.1A** Electrolysis of water
SUGGESTED PRACTICAL	**8.1B** Electroplating of copper

8.1

Electrolytic cells

KEY IDEAS

In this section, you will learn about:

- the process of electrolysis
- the electrolysis of molten liquids and aqueous solutions.

electrolysis
the process by which electrical energy is passed into a cell, using a power source, resulting in the reversal of spontaneous redox reactions

Electrolytic cells use an external electrical potential difference to provide the energy for non-spontaneous redox reactions to occur. **Electrolysis** is the process by which electrical energy is passed into a cell, rather than electricity being produced by the cell. The reactions that occur in a galvanic cell (Chapter 7) are reversed. In reversing these equations, it allows the cell to recharge so that it can then be used again in discharge. An example of this process is a rechargeable battery, otherwise known as a secondary cell – it can both discharge and recharge.

Electrolysis

In a galvanic cell, chemical energy is converted to electrical energy in a redox reaction. Electrolysis is the opposite of this process. It converts the products of a galvanic cell back into reactants so that they can react again to produce more electricity. In order to do this, the electrical energy must be converted back into chemical energy.

There are several key differences between an electrolytic cell (Figure 1) and a galvanic cell.

- In an electrolytic cell, the reaction takes place in a single container that typically has a porous divider down the middle. The purpose of the divider is to separate the products of an electrochemical reaction because they are the reactants in a galvanic cell. In a galvanic cell, the reactants must be kept separated because they react spontaneously.
- An electrolytic cell uses an electrolyte, whereas a galvanic cell has a salt bridge. An electrolyte is a conducting solution made of an ionic compound (a salt). This solution conducts electricity – negative anions move towards the positive electrode and positive cations move towards the negative electrode.
- An electrolytic cell uses a power source to push electrons onto one of the electrodes. This is the negative electrode because it has a negative charge due to the electrons being pushed onto it.
- Positive ions move towards the negative electrode to gain electrons:

$$M^+ + e^- \rightarrow M$$

The oxidation number of the ion decreases from a positive number to zero, so it undergoes reduction. Reduction always occurs at the cathode. Therefore, reduction occurs at the negative cathode. (In a galvanic cell, the cathode is positive.)

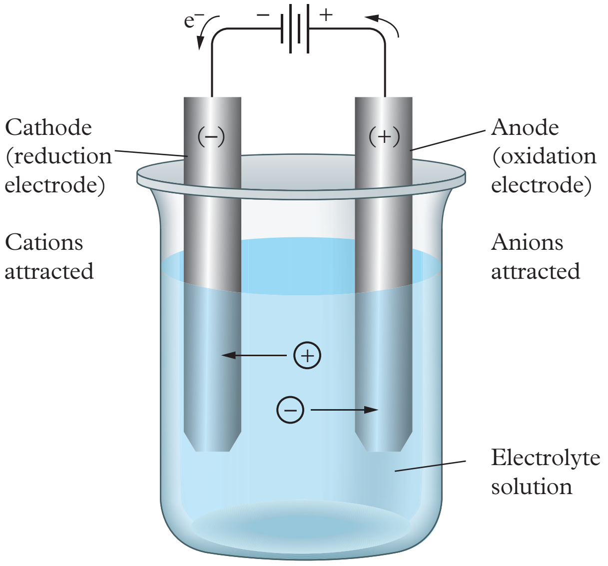


FIGURE 1 A basic diagram of an electrolytic cell

- Negative ions move towards the positive electrode where they lose electrons:

$$X^- \rightarrow X^+ + e^-$$

  As the oxidation number of the ion increases from zero to a positive charge, it undergoes oxidation. Oxidation always occurs at the anode. Therefore, oxidation occurs at the positive anode. (In a galvanic cell, the anode is negative.)
- The voltage required by an electrolytic cell must be greater than the EMF that the galvanic cell would generate on discharge. For example, a copper–zinc galvanic cell that produces a voltage of 1.1 V when discharging, requires more than 1.1 V to recharge.

Reversing a galvanic cell

Consider a galvanic cell with Cd^{2+}/Cd and Cu^{2+}/Cu half-cells (Figure 2).

$$E°_{Cd} = -0.40 V, \ E°_{Cu} = +0.34 V.$$

- Copper(II) is the strongest oxidant. Therefore, copper(II) ions are reduced at the cathode, which is positive because electrons are consumed by the Cu^{2+} ions to form copper metal.
- Cadmium is the strongest reductant. Therefore, cadmium is oxidised at the anode, which is negative because electrons are produced when Cd^{2+} is formed.
- Electrons move from the anode (where electrons are produced) to the cathode (where electrons are consumed).
- You can predict the reactants and products by using the RED SOX method (Figure 2):

$$\begin{aligned} \text{EMF} &= E°_{\text{reduction half-cell}} - E°_{\text{oxidation half-cell}} \\ &= 0.34\,V - (-0.40\,V) \\ &= 0.34\,V + 0.40\,V \\ &= 0.74\,V \end{aligned}$$

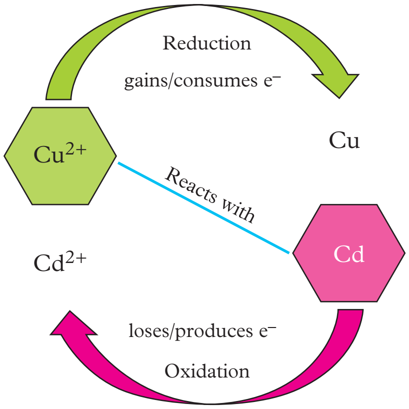


FIGURE 2 The RED SOX method for determining reactants and products in a copper/cadmium galvanic cell

  Consider the corresponding electrolytic cell.

- The power supply must be set up so that electrons are pushed onto the negative electrode to reverse the reaction that produced electrons to now consume them. A voltage greater than 0.74 V is required to do this.
  The negative electrode in a galvanic cell remains negative in an electrolytic cell.
- Positive cadmium ions are attracted to the negative electrode, forming cadmium metal and thus undergoing reduction. Reduction occurs at the cathode, so the negative electrode is now the cathode.
- Copper metal from the negative electrode oxidises to form copper(II) ions and electrons, and thus undergoes oxidation. Oxidation occurs at the anode, but the anode is now positive.
- The reactants and products are determined by using a Z, and not an S. Oxidation is now the top equation and reduction is the bottom one. Therefore, RED SOX in galvanic, becomes OX Z RED in electrolytic cells (Figure 3).
- Cd^{2+} is the strongest oxidant because it causes the copper to undergo oxidation.
- Copper metal is the strongest reductant because it causes Cd^{2+} to undergo reduction.

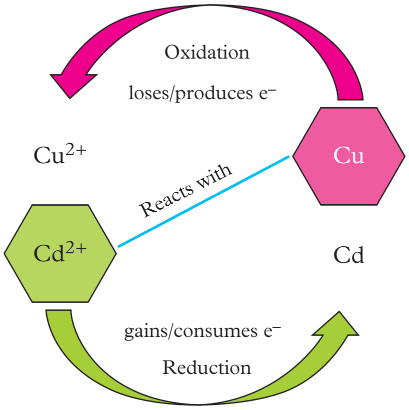
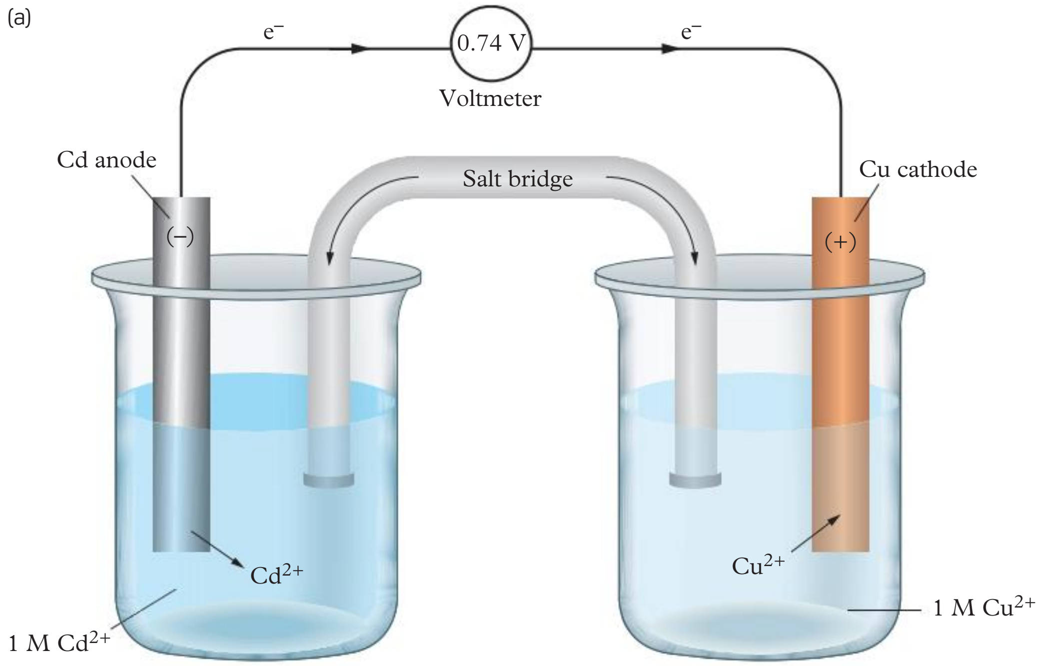


FIGURE 3 The OX Z RED method for determining reactants and products in a copper/cadmium electrolytic cell

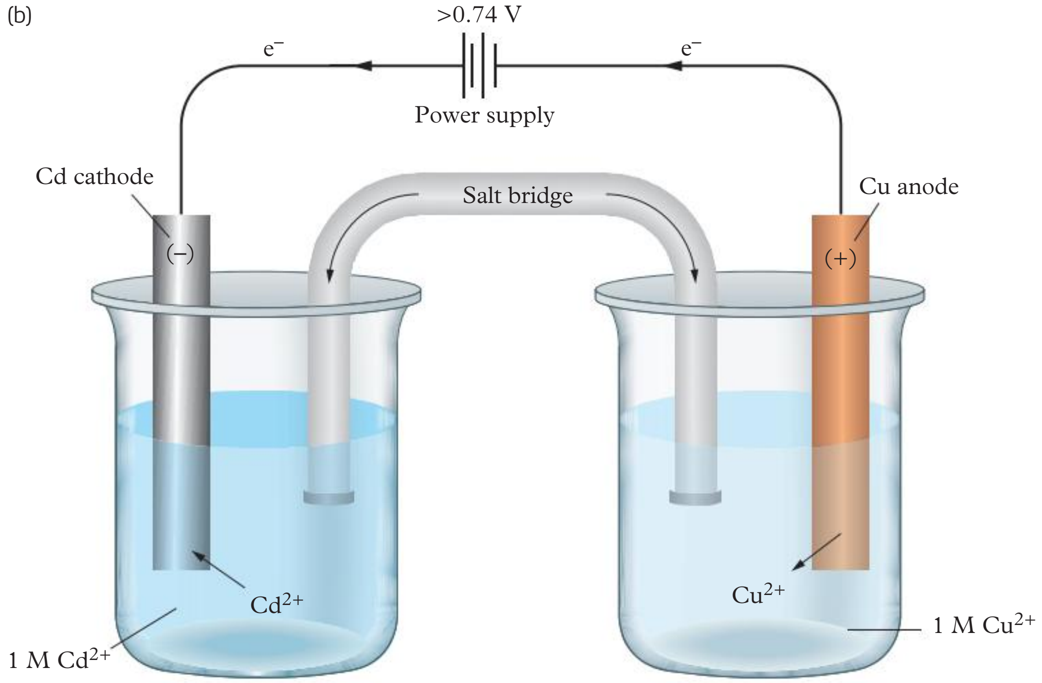
Figure 4 (page 192) shows how the redox reactions are reversed in the galvanic and electrolytic cells for the copper/cadmium system.



Anode:
$Cd(s) \rightarrow Cd^{2+}(aq) + 2e^-$

Cathode:
$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$

Overall reaction: $Cd(s) + Cu^{2+}(aq) \rightarrow Cd^{2+}(aq) + Cu(s)$



Cathode:
$Cd^{2+}(aq) + 2e^- \rightarrow Cd(s)$

Anode:
$Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$

Overall reaction: $Cd^{2+}(aq) + Cu(s) \rightarrow Cd(s) + Cu^{2+}(aq)$

FIGURE 4 The reaction in the (a) copper/cadmium galvanic cell can be reversed by (b) using the power supply to push electrons onto the negative electrode.

Study tip

Reduction always occurs at the cathode. RED CAT always applies.

Molten electrolysis

The electrolysis of **molten** salts occurs at very high temperatures because the salt must be a liquid. The melting point of sodium chloride is 801°C. Therefore, a significant amount of energy must be used to run the cell, not only to provide electrons to the negative cathode, but also to maintain the very high temperature to keep the salt molten.

molten
a substance that has been melted to form a liquid

Consider a molten sodium chloride electrolytic cell (Figure 5).

- The power source pushes electrons onto the negative electrode (the cathode). The sodium/chlorine galvanic cell produces 4.07 V, so a voltage greater than this is required.
- Positive ions in the liquid (Na^+) are attracted to the negative electrode, where they undergo reduction. As the melting temperature of sodium metal is 97.79°C, and the cell is maintained at over 801°C, sodium metal is formed as a liquid.

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

- The negative Cl^- ions in the liquid are attracted to the positive electrode (the anode) where they lose an electron to become chlorine gas (Cl_2).

$$2\,Cl^-(l) \rightarrow Cl_2(g) + 2\,e^-$$

- Because all the reactants and products are contained within the same cell, a porous screen is used to separate the sodium metal from the chlorine gas to prevent them reacting spontaneously to form sodium chloride. The pores in the screen allow ions to pass from one side of the cell to the other, but do not allow the products to pass through.
- The overall reaction equation for this process is:

$$2\,Na^+(l) + 2\,Cl^-(l) \rightarrow 2Na(l) + Cl_2(g)$$

Figure 6 illustrates the molten sodium chloride electrolytic cell.

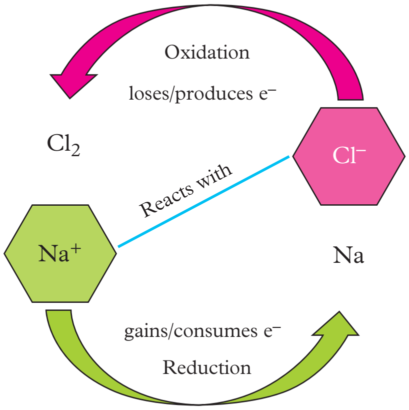


FIGURE 5 The OX Z RED method to determine reactants and products in a sodium/chlorine electrolytic cell

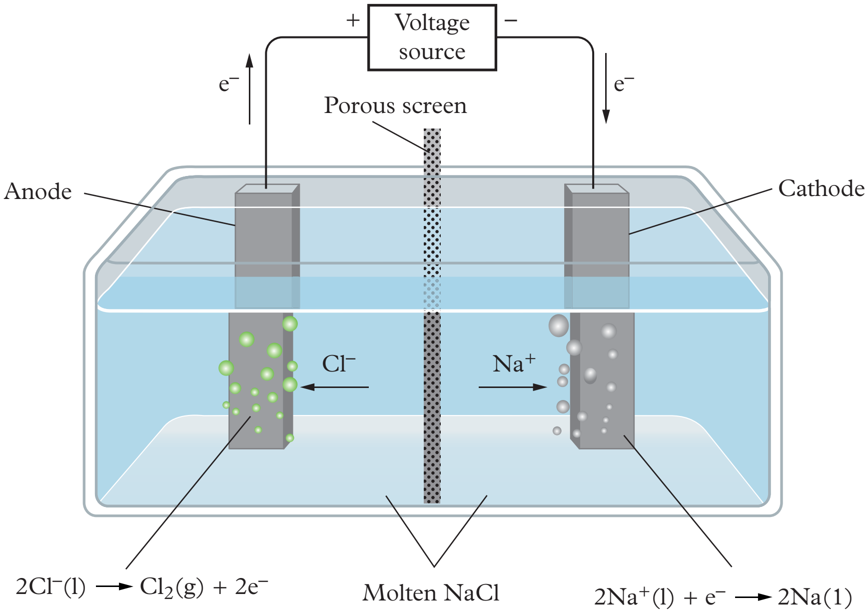


FIGURE 6 The electrolysis of molten sodium chloride

SUGGESTED PRACTICAL

8.1A Electrolysis of water
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WORKED EXAMPLE 8.1A

Draw an electrolytic cell for molten potassium iodide, which has a melting point of 681°C. Label all components, including electron flow and ion flow. Identify the oxidation and reduction half-equations and write the overall equation for the process.

SOLUTION

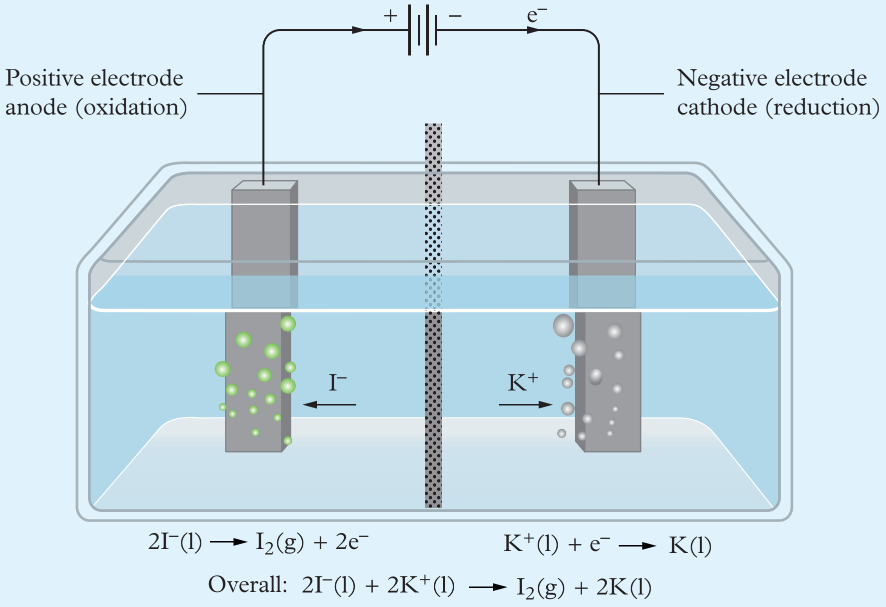


FIGURE 7 The electrolytic cell for molten potassium iodide

Aqueous electrolysis

Often, it is impractical to produce the high temperatures that are required for the electrolysis of molten salts, so aqueous solution can be used instead. In the electrolysis of aqueous solution, water can also be a reactant. The water half-equations that are used in electrolysis are:

$\frac{1}{2}O_2(g) + 2H^+(aq) + 2e^- \rightarrow H_2O(l)$ $E^\circ = +1.23\,V$

$2H_2O(l) + 2e^- \rightarrow 2OH^-(aq) + H_2(g)$ $E^\circ = -0.83\,V$

This results in a competition between reactants. In an aqueous sodium chloride electrolytic cell, there are four possible half-equations. When determining which chemicals react, highlight the species that are in the reaction vessel. In the case of NaCl(aq), these are:

$Cl_2(g) + 2e^- \rightarrow 2Cl^-(aq)$ $E^\circ = +1.36\,V$
$\frac{1}{2}O_2(g) + 2H^+(aq) + 2e^- \rightarrow H_2O(l)$ $E^\circ = +1.23\,V$
$2H_2O(l) + 2e^- \rightarrow 2OH^-(aq) + H_2(g)$ $E^\circ = -0.83\,V$
$Na^+(aq) + e^- \rightarrow Na(s)$ $E^\circ = -2.71\,V$

Chloride and water can both undergo oxidation, but only the strongest reductant will react. Because the strongest reductant on the electrochemical series is on the bottom right, water is more reactive than chloride and will undergo electrolysis.

$Cl_2(g) + 2e^- \rightarrow 2Cl^-(aq)$ $E^\circ = +1.36\,V$
$\frac{1}{2}O_2(g) + 2H^+(aq) + 2e^- \rightarrow H_2O(l)$ $E^\circ = +1.23\,V$

Sodium ions and water can undergo reduction, but only the strongest oxidant will react. Because the strongest oxidant on the electrochemical series is on the top left, water is more reactive than sodium ions and will undergo electrolysis.

$2H_2O(l) + 2e^- \rightarrow 2OH^-(aq) + H_2(g)$ $\qquad E° = -0.83\,V$

$Na^+(aq) + e^- \rightarrow Na(s)$ $\qquad E° = -2.71\,V$

Therefore:

- at the cathode, the reduction half-equation is: $2H_2O(l) + 2e^- \rightarrow 2OH^-(aq) + H_2(g)$
- at the anode, the oxidation half-equation is: $H_2O(l) \rightarrow \frac{1}{2}O_2(g) + 2H^+(aq) + 2e^-$
- the overall reaction equation is:

$$3H_2O(l) \rightarrow 2OH^-(aq) + H_2(g) + \frac{1}{2}O_2(g) + 2H^+(aq)$$

The $2OH^-(aq)$ and $2H^+(aq)$ form $2H_2O(l)$, so the equation can be further simplified to:

$$H_2O(l) \rightarrow H_2(g) + \frac{1}{2}O_2(g)$$

or

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

Figure 8 illustrates the components of an aqueous sodium chloride electrolytic cell.

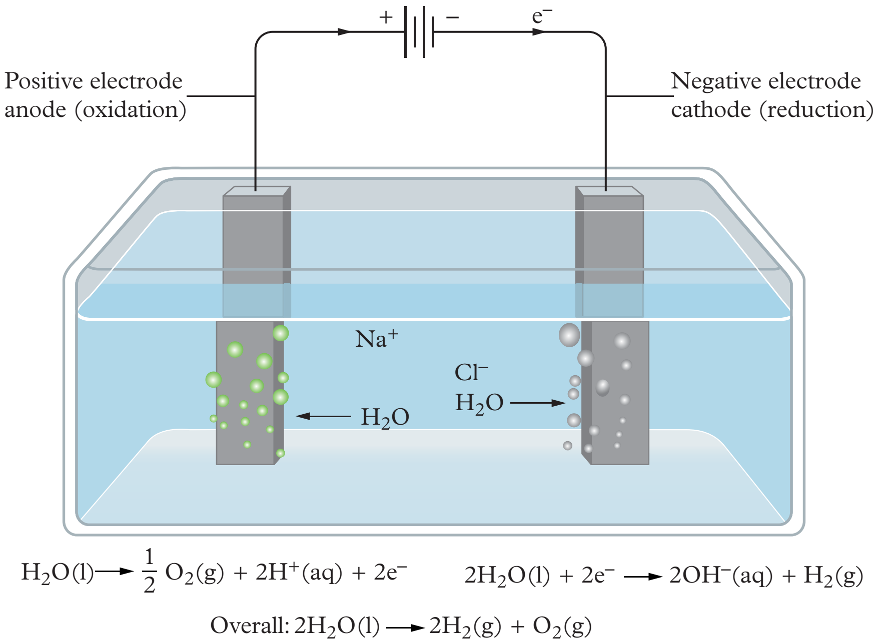


FIGURE 8 The aqueous sodium chloride electrolytic cell under standard conditions produces oxygen gas

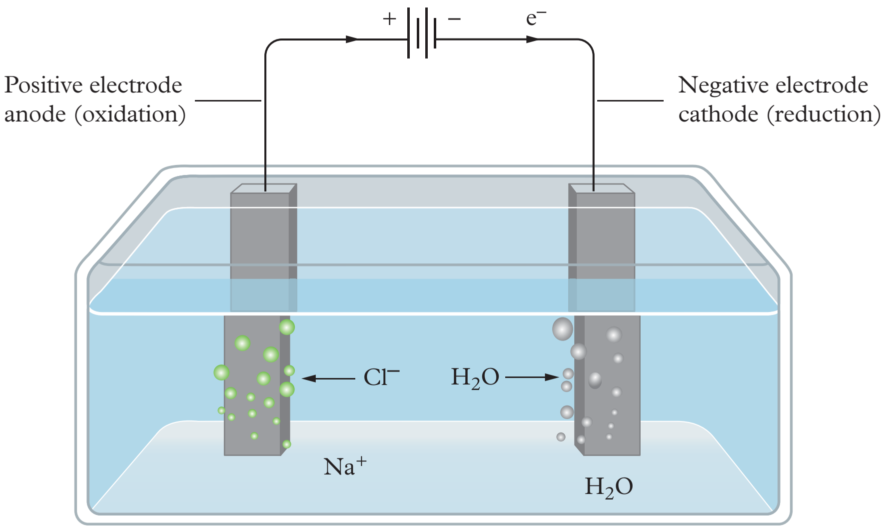
Effect of non-standard conditions

In the aqueous sodium chloride electrolytic cell, the standard electrode potentials of the chloride and water half-equations are very similar. See Figure 9 on the following page.

$Cl_2(g) + 2e^- \rightarrow 2Cl^-(aq)$ $\qquad E° = +1.36\,V$

$\frac{1}{2}O_2(g) + 2H^+(aq) + e^- \rightarrow H_2O(l)$ $\qquad E° = +1.23\,V$

Under non-standard conditions (conditions other than 1 M, 1 atm and 25°C), the electrode potentials of each half-equation changes. Under non-standard conditions, the half-equation for chlorine has a lower electrode potential than the oxygen half-equation, so the electrolytic cell produces chlorine gas, rather than oxygen. The chloride ion becomes the strongest reductant and reacts before water does.



$2Cl^-(aq) \longrightarrow Cl_2(g) + 2e^-$ $2H_2O(l) + 2e^- \longrightarrow 2OH^-(aq) + H_2(g)$

Overall: $2H_2O(l) + 2Cl^-(aq) \longrightarrow 2OH^-(aq) + H_2(g) + Cl_2(g)$

FIGURE 9 The aqueous sodium chloride electrolytic cell under non-standard conditions produces chlorine gas rather than oxygen

Purification of blister copper

Blister copper is impure (approximately 98–99.5%) copper that is contaminated with bubbles of sulfur dioxide and other metals. Blister copper can be purified by electrolysis.

The impure copper is the anode and pure copper is the cathode. The electrodes are placed in a solution of aqueous copper sulfate. Because copper is present as both a metal and an ion, it has two forms in which it can react. It is the strongest oxidant as Cu^{2+} and the strongest reductant as Cu. So, any copper that plates onto the pure copper cathode from the solution will be replaced as the copper in the blister breaks down. The concentration of copper ions in solution does not change.

$\frac{1}{2}O_2(g) + 2H^+(aq) + 2e^- \rightarrow H_2O(l) \qquad E° = +1.23\,V$

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

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

$2H_2O(l) + 2e^- \rightarrow 2OH^-(aq) + H_2(g) \qquad E° = -0.83\,V$

The impurities in the blister copper are also affected by the electrolysis process. Silver and gold are above copper on the electrochemical series (see Chapter 7). Therefore, they will remain as solids and gather at the base of the container (Figure 10). Any metal that is below copper on the electrochemical series, will become an ion and move into the solution.

If the copper(II) sulfate solution contains sulfuric acid (H_2SO_4), two extra half-equations apply:

$SO_4^{2-}(aq) + 2H^+(aq) + 2e^- \rightarrow SO_2(g) + 2H_2O(l) \qquad E° = +0.17\,V$

$2H^+(aq) + 2e^- \rightarrow H_2(g) \qquad E° = 0.00\,V$

Without the acidic environment, the sulfate acts as a spectator ion. In an acidic environment, rich in H^+, the sulfate and hydrogen ions react to form sulfur dioxide gas and water. However, even in an acidic environment, neither the sulfate ion nor the hydrogen ion is the strongest oxidant, so the same outcome is achieved where copper ions are the strongest oxidant and copper metal is the strongest reductant.

$\frac{1}{2}O_2(g) + 2H^+(aq) + 2e^- \rightarrow H_2O(l)$ $E° = +1.23\,V$

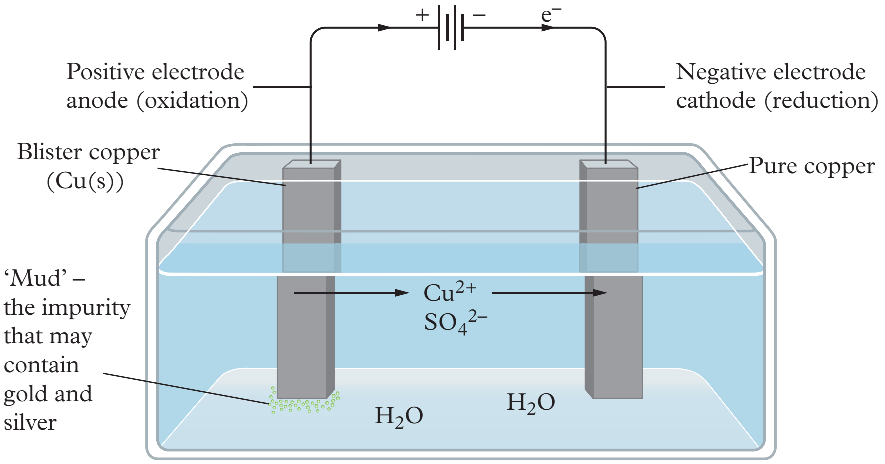
$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$ $E° = +0.34\,V$

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

$SO_4^{2-}(aq) + 2H^+(aq) + 2e^- \rightarrow SO_2(g) + 2H_2O(l)$ $E° = +0.17\,V$

$2H^+(aq) + 2e^- \rightarrow H_2(g)$ $E° = 0.00\,V$

$2H_2O(l) + 2e^- \rightarrow 2OH^-(aq) + H_2(g)$ $E° = -0.83\,V$



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

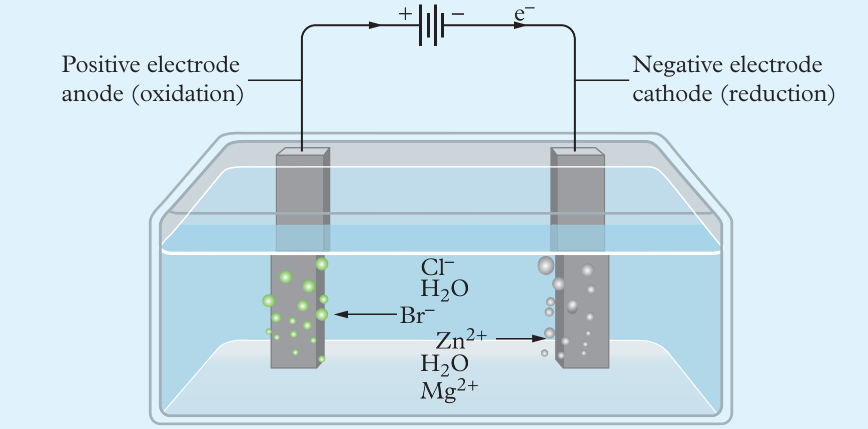
Overall: $Cu(s) + Cu^{2+}(aq) \rightarrow Cu^{2+}(aq) + Cu(s)$

FIGURE 10 The electrolytic cell for purifying blister copper

WORKED EXAMPLE 8.1B

Draw an electrolytic cell that is made from an aqueous solution of both magnesium bromide and zinc chloride. Label all components, including electron and ion flow. Identify the oxidation and reduction half-equations and write the overall equation for the process.

SOLUTION



$2Br^-(aq) \rightarrow Br_2(l) + 2e^-$ $Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$

Overall: $2Br^-(aq) + Zn^{2+}(aq) \rightarrow Br_2(l) + Zn(s)$

FIGURE 11 The electrolytic cell for aqueous magnesium bromide and zinc chloride

Study tip

Don't forget that spectator ions are not included in the half-reaction and overall redox reactions.

SUGGESTED PRACTICAL **8.1B** Electroplating of copper
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Electroplating

FIGURE 12 Electroplating iron spoons with silver prevents the iron rusting

Electroplating is the process of covering a metal with another. Typically, the metal that is covered is highly reactive, susceptible to corrosion or cheap. These metals are coated with a thin layer of a corrosion-resistant metal, which is often more expensive. By plating one metal onto the other, the product is cheaper to produce but looks the same as the solid corrosion-resistant metal.

Iron is a cheap metal that can be easily smelted into various objects. However, iron is easily corroded and reacts to form iron oxide (rust). To prevent iron objects from rusting, they are electroplated with unreactive metals such as tin and silver. For example, iron cans are electroplated with tin, and iron cutlery is electroplated with silver (Figure 12).

Testing electrolytic cells

FIGURE 13 A U-tube used in the electrolysis of potassium iodide with a phenolphthalein indicator

In a laboratory, a U-tube is used to test an electrolytic cell (Figure 13). The tube is filled with an aqueous solution, and often with universal indicator or another indicator such as phenolphthalein. The electrodes are placed in the openings of the tube and a current is run through the cell. The products are separated as they form at the electrodes and are used to verify the half-equations of the reactions. For example, a gas is indicated by the formation of bubbles (especially if it has an odour, like chlorine), acids and bases are indicated by colour changes of the indicator, and metals are indicated by the plating of another metal.

Study tip

The positive electrode attracts anions (negative ions). The negative electrode attracts cations (positive ions).

Comparing galvanic and electrolytic cells

Table 1 summarises the differences between galvanic cells and electrolytic cells.

TABLE 1 Summary table comparing galvanic and electrolytic cells

	Galvanic	Electrolytic
Energy transformation	Chemical to electrical	Electrical to chemical
Structural features	Two half-cells separate reactants Cells connected by a salt bridge (internal circuit)	One cell: products are separated, and an electrolyte is used
Anode	Negative Oxidation	Positive Oxidation
Cathode	Positive Reduction	Negative (electrons are pushed onto the electrode from the power source) Reduction
Electron transfer	Anode to cathode (in the external circuit)	Power source to the cathode and anode to power source
Terminology	The strongest oxidant is reduced The strongest reductant is oxidised	The strongest oxidant is reduced The strongest reductant is oxidised

CHECK YOUR LEARNING 8.1

Describe and explain

1 **Describe** the structural differences between a galvanic cell and an electrolytic cell.

2 **Describe** the differences between the electrodes of galvanic and electrolytic cells.

3 **Construct** an electrolytic cell for:
  a molten potassium bromide
  b a molten mixture of lithium fluoride and magnesium chloride
  c molten aluminium fluoride.

4 **Construct** an electrolytic cell for:
  a aqueous magnesium chloride
  b aqueous cobalt iodide
  c aqueous acidified potassium permanganate.

On the diagrams, label:
- the anode and cathode
- electrode polarity
- oxidation and reduction half-equations
- the strongest oxidant and strongest reductant
- the overall equation
- the movement of ions in the cell
- the movement of electrons.

Investigate, evaluate and communicate

5 A scientist needed to use chlorine gas in a reaction and decided to use electrolysis to generate the gas. **Communicate** a methodology to produce chlorine gas under:
  a standard conditions
  b non-standard conditions.

6 The experiment in Figure 12 was set up to plate silver metal onto a zinc fork.

First, the fork and the silver metal electrode were cleaned with emery paper to remove any products of oxidation. A 1 M solution of silver nitrate was placed in the beaker. The positive terminal of the battery was connected to the fork and the negative terminal to the silver electrode. The battery was turned to 4 V and run for 10 minutes.

  a **Predict** the outcome of the experiment based on the method.
  b **Evaluate** the method and communicate anything that may affect the ability to plate silver onto the fork.
  c **Communicate** an improved method.

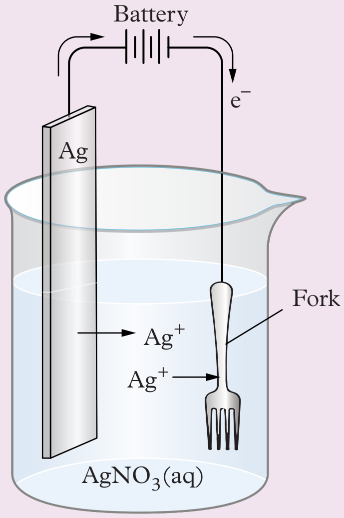


FIGURE 14 Electroplating of silver onto a fork

You can find the following resources for this section on your obook assess:

- » Student book questions
  8.1 Check your learning
- » Suggested practical
  8.1A Electrolysis of water
- » Suggested practical
  8.1B Electroplating of copper
- » Increase your knowledge
  Challenge 8.1 Electrolysis of water with basic and acidic electrolytes

8.2

Applications of electrolysis

KEY IDEAS

In this section, you will learn about:

- the application of electrochemistry to rechargeable batteries and beauty therapies.

Electrolysis is used in many industries; for example, for electroplating, for purifying metals, in batteries and in beauty treatments.

Secondary cells – rechargeable batteries

Unlike primary cells that can no longer produce electricity once the reactants have been consumed, **secondary cells** are rechargeable. By applying a current back into the cell, the redox reactions are reversed and the battery is returned to almost its original state. Over time, rechargeable batteries degrade and can store less and less charge. This is because recharging the battery does not convert all of the chemicals to their original state.

secondary cell
a rechargeable battery; an electrochemical cell that operates as a galvanic cell, discharging energy, and an electrolytic cell, recharging to return chemicals to their original state in order to undergo a spontaneous reaction again

Batteries degrade faster when kept at extreme temperatures, outside the range of 10–30°C. Typically, a smartphone temporarily shuts down when it is very cold or very hot. This is because the battery is operating outside of its optimal temperature range and is prone to damage with continued use.

Car batteries – the lead–acid accumulator

A typical car battery is called a lead–acid accumulator because of the lead electrodes and the sulfuric acid (H_2SO_4) electrolyte. The two half-equations occurring in this type of secondary cell are:

$$PbO_2(s) + 4H^+(aq) + SO_4{}^{2-}(aq) + 2\,e^- \rightleftharpoons PbSO_4(s) + 2H_2O(l) \qquad E^\circ = 1.69\,V$$

$$PbSO_4(s) + 2e^- \rightleftharpoons Pb(s) + SO_4{}^{2-}(aq) \qquad E^\circ = -0.36\,V$$

On discharge, the top reaction is the reduction half-equation and the bottom reaction, when reversed, is the oxidation reaction:

Cathode (reduction):

$$PbO_2(s) + 4H^+(aq) + SO_4{}^{2-}(aq) + 2e^- \rightarrow PbSO_4(s) + 2H_2O(l) \qquad E^\circ = 1.69\,V$$

Anode (oxidation):

$$Pb(s) + SO_4{}^{2-}(aq) \rightarrow PbSO_4(s) + 2e^- \qquad E^\circ = +0.36\,V$$

Overall:

$$PbO_2(s) + Pb(s) + 2SO_4{}^{2-}(aq) + 4H^+(aq) \rightarrow 2PbSO_4(s) + 2H_2O(l)$$

FIGURE 1 Most smartphone batteries have an optimum temperature limit

On the reactant side, four hydrogen ions ($4H^+$) and two sulfate ions ($2SO_4^{2-}$) are formed. When combined, these form two sulfuric acid molecules ($2H_2SO_4$). Therefore, the overall reaction equation can be simplified to:

$$PbO_2(s) + Pb(s) + 2H_2SO_4(aq) \rightarrow 2PbSO_4(s) + 2H_2O(l)$$

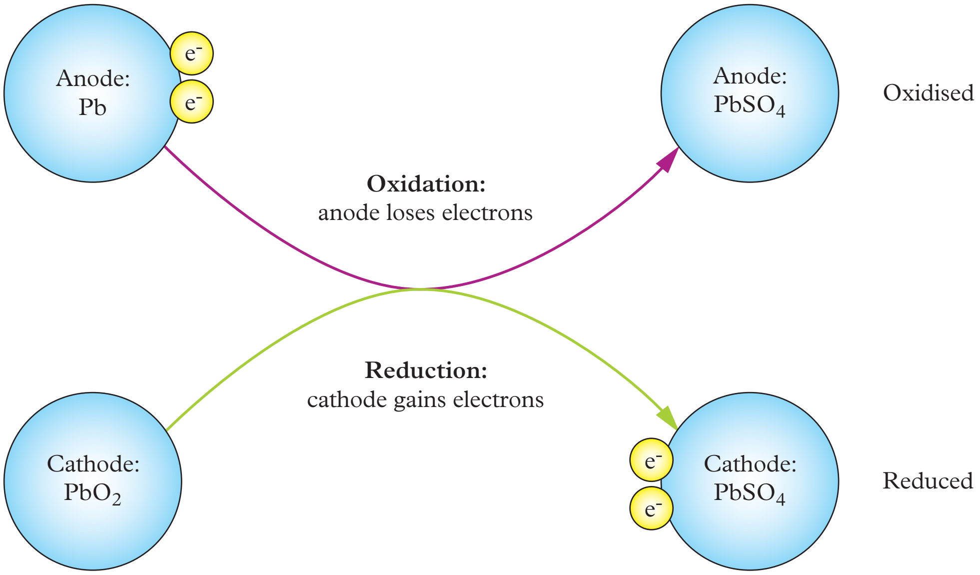


FIGURE 2 The oxidation and reduction process occurring in a lead–acid car battery

When fully charged, the battery has a high level of chemical potential energy. The electrodes are made of lead(II) oxide and lead, and there is an aqueous solution of sulfuric acid as an electrolyte. As the battery discharges, sulfate ions are removed from the electrolyte, decreasing the concentration of the acid, and lead sulfate forms on the electrodes, coating them and stopping the spontaneous reaction (Figure 3).

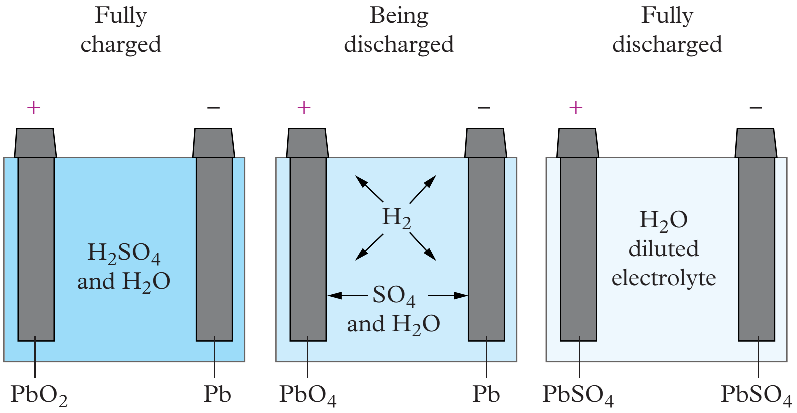


FIGURE 3 The nature of the electrodes and the electrolyte in a lead–acid battery

Each lead–acid cell can produce a voltage of 2.05 V. When multiple cells are connected in series, the voltage of the battery is the sum of the cells. A car battery is required to be 12 V. Therefore, six lead-acid cells are connected, at 2 V each, to produce a 12 V battery (Figure 4).

FIGURE 4 Six 2 V lead–acid cells in series produce a car battery of 12 V

To recharge the battery, you need to use more than 12 V. The reactions are reversed and the following reaction results:

Cathode (reduction):

$$PbSO_4(s) + 2e^- \rightarrow Pb(s) + SO_4{}^{2-}(aq)$$

Anode (oxidation):

$$PbSO_4(s) + 2H_2O(l) \rightarrow PbO_2(s) + 4H^+(aq) + SO_4{}^{2-}(aq) + 2e^-$$

Overall:

$$2PbSO_4(s) + 2H_2O(l) \rightarrow PbO_2(s) + Pb(s) + 2H_2SO_4(aq)$$

Lithium ion batteries

Lithium ion batteries are named for the lithium ions that move from the negative to the positive electrodes when the cell is in discharge. The cell contains a graphite electrode, doped (covered) with lithium, which acts as the anode when the cell is discharging, and a metal oxide (such as cobalt oxide (CoO_2)) cathode, also doped with lithium (Figure 5). As the cell undergoes discharge the following half-equations occur:

$$\text{Anode }(-)\text{: } LiC_6 \rightleftharpoons 6C + Li^+ + e^-$$

$$\text{Cathode }(+)\text{: } CoO_2 + Li^+ + e^- \rightleftharpoons LiCoO_2$$

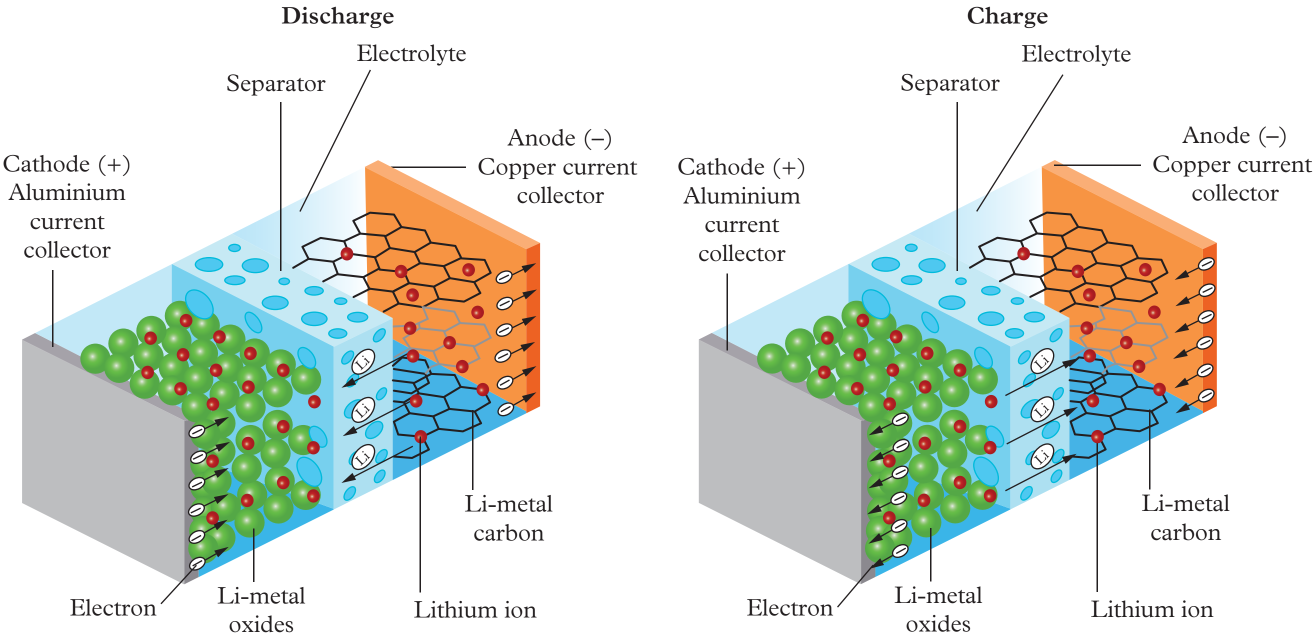


FIGURE 5 The lithium ion battery

As the cell discharges, the lithium ions in the electrodes pass through the electrolyte to the metal oxide electrode, which they dope. When the battery is recharged, the reactions reverse and the lithium at the metal oxide electrode moves back to the graphite electrode (Figure 6).

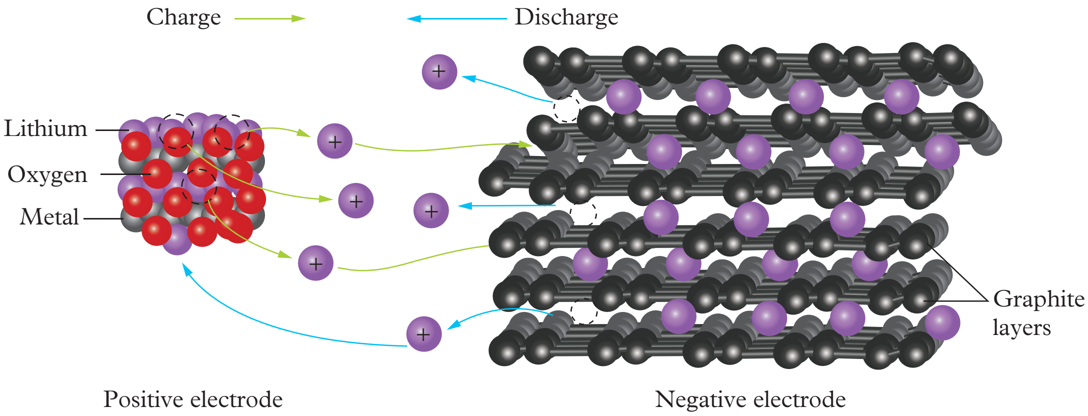


FIGURE 6 The electrodes of a lithium ion battery, doped with lithium ions (purple)

The half-equations for the lithium ion cell in recharge are:

$$\text{Anode } (+)\text{: } 6C + Li^+ + e^- \rightleftharpoons LiC_6$$

$$\text{Cathode } (-)\text{: } LiCoO_2 \rightleftharpoons CoO_2 + Li^+ + e^-$$

A typical lithium ion battery can produce approximately 4 V and can withstand up to 1200 recharges before it dies. These types of batteries are also some of the most efficient and have a wide variety of uses in portable devices, power tools and even electric cars.

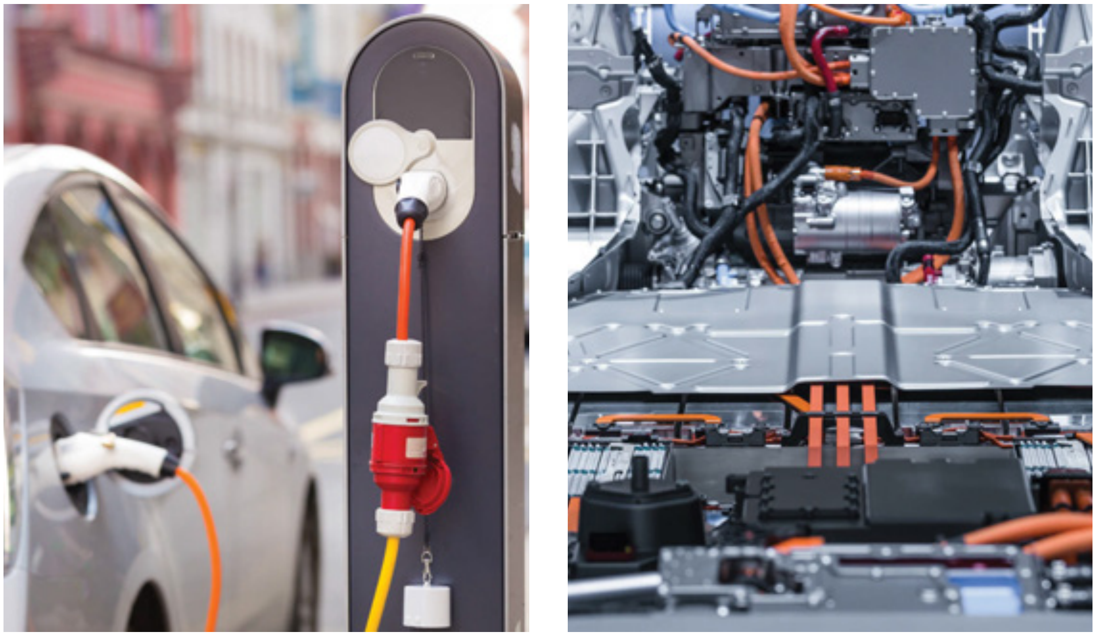


FIGURE 7 Lithium ion battery packs are used to power electric cars

CASE STUDY 8.2

Galvanic electrolysis for hair removal

Galvanic electrolysis was first used in 1869 by Charles Michel, an American ophthalmologist. Michel used an electrified needle to treat ingrown eyelashes.

In this treatment, an electric current is applied with a very fine needle-shaped electrode, or metal probe, into each hair follicle to destroy the root (Figure 8). Water and sodium chloride salt in the skin act as the reactants:

$$\text{Anode (+): } Cl^-(aq) \rightarrow Cl_2(g) + 2e^-$$

$$\text{Cathode (–): } H_2O(l) + 2e^- \rightarrow 2OH^-(aq) + H_2(g)$$

If enough hydroxide is produced, it can damage the cells that cause hair growth and prevent it from growing in the future.

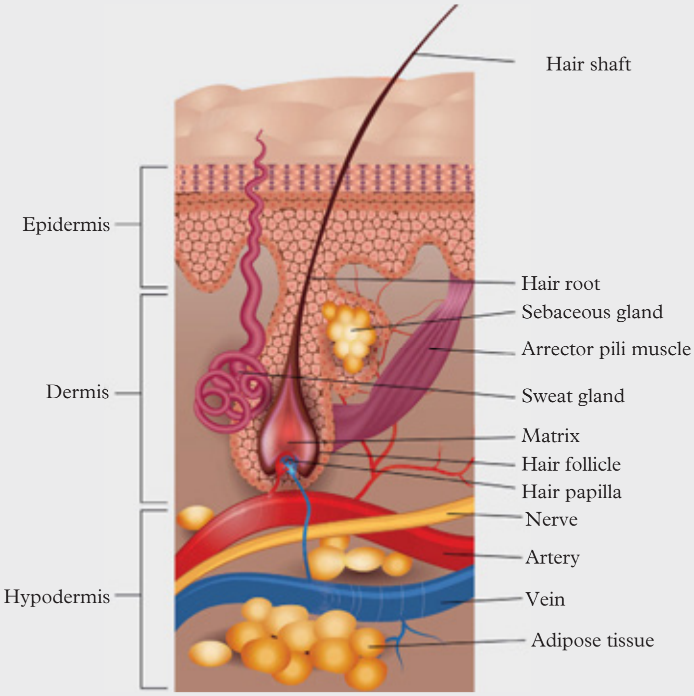


FIGURE 8 The anatomy of a hair follicle – electrolysis destroys the root.

CHALLENGE 8.2

Electrolysis to remove rust

Electrolysis is used for the conversion of rust (iron(II) oxide) back to its original iron form. After the process is complete, the metal contains scars where the rust has been removed.

a Outline the half- and overall equations involved in the rusting of iron to form iron(II) oxide.

b How is electrolysis conducted to convert the iron(II) oxide back to iron?

c Outline relevant half- and overall equations involved in converting the iron(II) oxide back to iron as well as the voltage required and a suitable electrolyte.

CHECK YOUR LEARNING 8.2

Describe and explain

1 **Describe** the difference between a primary and secondary cell.

Apply, analyse and interpret

2 The following half-equations occur in a nickel–cadmium alkaline battery:

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

$$NiO(OH)(s) + H_2O(l) + e^- \rightarrow Ni(OH)_2(s) + OH^-(aq)$$

- **a** Use your knowledge of oxidation numbers to **identify** the species that undergo oxidation and reduction. **Determine** which reaction occurs at the anode and which reaction occurs at the cathode.
- **b** **Construct** the overall chemical equation.
- **c** **Construct** the half-equations occurring at the anode and cathode in recharge and **identify** them as oxidation or reduction.

3 In a vanadium redox flow battery, the following half-equations are used to produce electricity.

$$VO_2^+(aq) + 2H^+(aq) \rightarrow VO^{2+}(aq) + H_2O(l) + e^- \quad E° = +0.99\,V$$

$$V^{3+}(aq) + e^- \rightarrow V^{2+}(aq) \quad E° = -0.26\,V$$

- **a** **Construct** the half-equation occurring at the anode and cathode in recharge.
- **b** **Construct** the overall electrolytic reaction equation.
- **c** **Determine** the voltage required to recharge the cell.
- **d** **Deduce** a suitable electrolyte for the cell.

Investigate, evaluate and communicate

4 The temperature of the human body is slightly higher than 37°C. **Investigate** the impact of running galvanic electrolysis, to kill hair follicles, at this temperature. **Evaluate** the chemical half-equations that would result under these non-standard conditions and make a conclusion about the viability of this method at body temperature.

5 You may have constructed a battery from lemons when you were younger. **Investigate** a lemon battery and use your knowledge of galvanic and electrolytic cells to answer the following questions:

- **a** **Construct** the half-equations and overall chemical equation occurring in the lemon battery.
- **b** **Determine** what voltage may be gained from a lemon battery. What types of appliances or devices could it provide power for?
- **c** **Discuss** what happens to the battery over time. How does this compare to commercial batteries?
- **d** **Evaluate** the term ‘battery’ in a lemon battery.

You can find the following resources for this section on your obook assess:

- » Student book questions
  8.2 Check your learning
- » Challenge
  8.2 Electrolysis to remove rust
- » Weblink
  Hair removal using galvanic electrolysis

SCIENCE AS A HUMAN ENDEAVOUR

8.3 Electrochemistry for clean water

KEY IDEAS

In this section you will learn about:

- the production of clean water from electrolysis.

Water purification

Electrochlorination

Water is an essential resource for all living organisms on our planet. Water quality is important for human health. In Australia, we can drink clean water straight from the tap. But before the 1900s, drinking water was not as clean or reliable. Sand and gravel filtration were used to remove particles from the water and provide some purification. However, this did not remove bacteria and disease-causing microorganisms.

Water is now purified by electrochlorination. In countries where electrochlorination was introduced to treat water in the early 1900s, deaths due to waterborne diseases have decreased significantly. Electrochlorination kills bacteria and microorganisms.

electro-chlorination the passage of electricity into salty water to generate hypochlorite, an antibacterial agent

In **electrochlorination**, an electric current is passed through a solution of aqueous sodium chloride ($NaCl(aq)$). The process produces hypochlorite (ClO^-), which acts as a bleach and disinfects the water to kill bacteria, control algae and arrest biological growth. It prevents the spread of waterborne diseases such as dysentery, typhoid and cholera.

FIGURE 1 Many highly populated locations still don't have access to safe drinking water. Delhi, India, has a population of 29 million and tap water there is not safe to drink.

In the electrolytic process, chloride is oxidised to chlorine gas, and water is oxidised to produce hydroxide:

Anode: $2Cl^-(aq) \rightarrow Cl_2(g) + 2e^-$ $\quad E° = +1.36\,V$

Cathode: $2H_2O(l) + 2e^- \rightarrow 2OH^-(aq) + H_2(g)$ $\quad E° = -0.83\,V$

The chlorine gas then reacts with the hydroxide ion to form hypochlorite (ClO^-).

$$Cl_2(g) + 2OH^-(aq) \rightarrow ClO^-(aq) + Cl^-(aq) + H_2O(l)$$

FIGURE 2 Most tap water is cleaned by electrochlorination.

The chloride and water products of this reaction can undergo electrolysis again to produce more chlorine and hydroxide:

Hypochlorite reacts with water to form an equilibrium with hypochlorous acid:

$$\mathrm{ClO^-(aq) + H_2O(l) \rightleftharpoons HClO(aq) + OH^-(aq)}$$

The chlorine is then removed from the water by adding a chemical that reacts with it. Alternatively, the water can be aerated by bubbling oxygen through it, but this is time consuming and costly and is not the preferred method.

CHECK YOUR LEARNING 8.3

Describe and explain

1 **Explain** why humans need clean drinking water.

2 **Identify** what decreased deaths due to waterborne disease.

Apply, analyse and interpret

3 **Distinguish** what the term ‘electrochlorination’ means.

You can find the following resources for this section on your obook assess:

- Student book questions
  8.3 Check your learning
- Weblink
  Clean drinking water
- Weblink
  Electrochlorination

CHAPTER 8

Review

Chapter summary

8.1
- Electrolytic cells operate by passing an electrical current into a galvanic cell to reverse the spontaneous chemical reactions. The polarity of electrodes is reversed as electrons are pushed onto one electrode, making it negative and the site of reduction as electrons are consumed at this electrode. To reverse the chemical reactions, a higher voltage must be used than was produced by the cell when it was discharging.

8.2
- Electrolysis has applications in many industries, mainly the production of batteries.

8.3
- Clean drinking water is now possible through electrochlorination. This is the process of generating the antibacterial agent hypochlorite through electricity.

Key terms

- electrochlorination
- electrolysis
- molten
- secondary cell

Key formulas

Reduction half-equation	$M^+ + e^- \rightarrow M$
Oxidation half-equation	$M \rightarrow M^+ + e^-$
Net voltage of oxidation and reduction half-equations	$\text{EMF} = E°_{\text{reduction half-cell}} - E°_{\text{oxidation half-cell}}$

Revision questions

The relative difficulty of these questions is indicated by the number of stars beside each question number: ★ = low; ★★ = medium; ★★★ = high.

Multiple choice

1 In an electrolytic cell:
- **A** oxidation occurs at the negative electrode, which is connected to the negative terminal of the battery
- **B** reduction occurs at the negative electrode, which is connected to the negative terminal of the battery
- **C** oxidation occurs at the positive electrode, which is connected to the negative terminal of the battery
- **D** reduction occurs at the positive electrode, which is connected to the negative terminal of the battery.

2 In an electrolytic cell, the:
- **A** salt bridge allows for the movement of ions in the internal circuit
- **B** electrolyte allows for the movement of electrons in the internal circuit
- **C** salt bridge allows for the movement of electrons in the internal circuit
- **D** electrolyte allows for the movement of ions in the internal circuit.

3 The voltage used to recharge a cell in electrolysis is:
- **A** less than the voltage produced in the galvanic process
- **B** equal to the voltage produced in the galvanic process
- **C** greater than the voltage produced in the galvanic process
- **D** always a minimum 1 V higher than the voltage produced in the galvanic process.

4 A secondary cell is an electrochemical cell that can produce:
- **A** chemical energy from electrical energy by applying an external current
- **B** electrical energy from chemical energy when in use (discharge)
- **C** electrical energy from chemical energy when an external current is applied
- **D** a constant supply of electrical energy because there are unlimited reactants.

5 Identify the half-equation that would be occurring at the anode of a cell in recharge.
- **A** $O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$
- **B** $H_2O_2(aq) \rightarrow O_2(g) + 2H^+(aq) + 2e^-$
- **C** $S(s) + 2H^+(aq) + 2e^- \rightarrow H_2S(g)$
- **D** $2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$

6 Identify the half-equation that would be occurring at the cathode of a cell in recharge.
- **A** $Au(s) + 4Cl^-(aq) \rightarrow AuCl_4^-(aq) + 3e^-$
- **B** $NO_2(g) + H_2O(l) \rightarrow NO_3^-(aq) + 2H^+(aq) + e^-$
- **C** $MnO_2(s) + 4H^+(aq) + 2e^- \rightarrow Mn^{2+}(aq) + 2H_2O(l)$
- **D** $2OH^-(aq) + H_2(g) \rightarrow 2H_2O(l) + 2e^-$

The following information relates to questions 7 and 8.

A molten electrolytic cell was set up using inert electrodes and a solution of sodium chloride and barium bromide.

7 Which half-equation occurs at the anode?
- **A** $Cl_2(g) + 2e^- \rightarrow 2Cl^-(l)$
- **B** $2Br^-(l) \rightarrow Br_2(l) + 2e^-$
- **C** $Br_2(l) + 2e^- \rightarrow 2Br^-(l)$
- **D** $2Cl^-(l) \rightarrow Cl_2(g) + 2e^-$

8 Which half-equation occurs at the cathode?
- **A** $Na(l) \rightarrow Na^+(l) + e^-$
- **B** $Ba^{2+}(l) + 2e^- \rightarrow Ba(l)$
- **C** $Na^+(l) + e^- \rightarrow Na(l)$
- **D** $Ba(l) \rightarrow Ba^{2+}(l) + 2e^-$

9 Which of the following occurs during the electrolysis of a dilute copper(II) nitrate solution using platinum electrodes?
- **A** The negative electrode decreases in mass.
- **B** A colourless and odourless gas is produced at the negative electrode.
- **C** A colourless and odourless gas is produced at the positive electrode.
- **D** The electrolyte solution becomes darker in colour.

10 During the electrolysis of a tin nitrate solution, nitrate ions are:

A attracted to the cathode, where they undergo reduction

B attracted to the anode, where they undergo oxidation

C not attracted to either electrode because they are spectator ions only

D attracted to one electrode but are neither oxidised nor reduced.

Short answer

Describe and explain

★ **11** **Explain** whether electrons can move through solution.

★ **12** **Explain** why the polarity of electrodes is reversed in an electrolytic cell, compared to a galvanic cell.

★ **13** **Explain** why reactants are kept in the same vessel in an electrolytic cell but must be separated in a galvanic cell.

★★ **14** Nickel metal is plated onto an iron cup using an aqueous electrolyte of nickel(II) nitrate. **Construct** the electrolytic cell for this process, labelling the:

- anode and cathode
- electrode polarity
- oxidation and reduction half-equations
- strongest oxidant and strongest reductant
- overall equation
- movement of ions in the cell
- movement of electrons.

★★★ **15** For each of the following, **construct** an experiment that would result in these outcomes. You must include:

- half-equations, labelled as oxidation and reduction
- the strongest oxidant and reductant
- the oxidising and reducing agent
- a balanced overall equation.

a $H_2(g)$ forms at a negative cathode.

b $Cl_2(g)$ forms at a positive anode.

c Ag is plated onto a positive cathode.

d The pH of the electrolyte in the cell decreases.

★★★ **16** Sketch the following electrolytic cells.

a A mixture of molten lithium chloride and molten calcium iodide

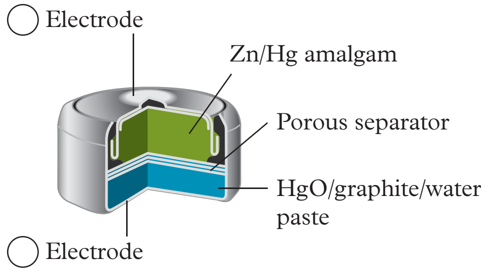
b A mixture of aqueous calcium nitrate, aqueous cadmium bromide and aqueous potassium chloride

c An aqueous solution of hydrogen peroxide (H_2O_2)

Identify the:

- anode and cathode
- electrode polarity and the material the electrodes are made from
- oxidation and reduction half-equations, including states, and labelled as oxidation or reduction
- electrolyte (demonstrating ion movement within the cell)
- direction of electron flow
- the minimum voltage required for the cell to recharge
- overall balanced chemical equation including states.

★★★ **17** A diagram of a zinc–mercury button cell battery is provided in Figure 1.



Cell reaction:
$Zn(s) + HgO(s) \rightarrow Hg(l) + ZnO(s)$

FIGURE 1 A button cell battery

a **Identify** the positive and negative electrodes of the cell.

b **Construct** the half-equation for the reaction that occurs at the anode in discharge.

c Assume that this button cell is rechargeable. **Construct** the half-equation for the reaction that occurs at the cathode in recharge.

Apply, analyse and interpret

★★★ **18** A secondary battery uses the following half-equations.

$$\mathrm{Fe(s) + 2OH^-(aq) \rightarrow Fe(OH)_2(s) + 2e^-}$$

$E°$ is positive

$$\mathrm{Ni(OH)_2(s) + OH^-(aq) \rightarrow Ni(OH)_3(s) + e^-}$$

$E°$ is negative

- **a** **Identify** the anode and cathode half-equations in both discharge and recharge and **identify** the polarity of electrodes that would result.
- **b** **Identify** the overall equations in discharge and recharge.
- **c** **Determine** what you know about the nature of the electrolyte in this cell.

Investigate, evaluate and communicate

★★ **19** **Evaluate** the products, in terms of half-equations and overall equation, that would result from electrolytic cells where the electrolyte is:

- **a** molten NaCl
- **b** concentrated NaCl(aq)
- **c** dilute NaCl(aq).

★★ **20** **Use** a mind map to **communicate** the links and ideas between the following concepts: redox, oxidation, reduction, oxidant, reductant, oxidising agent, reducing agent, galvanic cell, primary cell, electrolytic cell, secondary cell, fuel cell, salt bridge, electrolyte, anode, cathode, polarity, $E°$ and power source.

★★ **21** **Summarise** a summary of Chapters 7 and 8, outlining the similarities and differences between galvanic cells, primary cells, secondary cells and fuel cells.

Your summary must include:

- structural and chemical differences
- structural and chemical similarities
- advantages
- disadvantages
- applications.

★★★ **22** The mercury(II) oxide battery was in common use until it was banned in 1991. The HgO battery could supply a constant voltage of 1.35 V and had many applications. Investigate the mercuric oxide battery and:

- **a** **construct** the cathode and anode half-equations in discharge, labelling them as oxidation or reduction
- **b** **construct** the overall reaction equation in discharge
- **c** use these equations to **evaluate** the battery, specifically communicating why it was banned in 1991
- **d** **investigate** the health effects of this type of battery
- **e** **determine** what battery was introduced as a substitute for the HgO battery
- **f** **construct** the cathode and anode half-equations in discharge for the substitute battery, labelling them as oxidation or reduction
- **g** **construct** the overall reaction equation for the substitute battery in discharge
- **h** use these equations to **evaluate** the substitute battery, specifically why it is safer than the HgO battery.

You can find the following resources for this section on your obook assess:

- » Student book questions
  Chapter 8 Revision questions
- » Revision notes
  Chapter 8
- » assess quiz
  Auto-correcting mutiple-choice quiz
- » Flashcard glossary
  Chapter 8

UNIT 3

Practice exam-style questions

Equilibrium, acids and redox reactions

Multiple choice

1 Which of the following is a redox reaction?

A $2Al(s) + 3Cl_2(g) \rightarrow 2AlCl_3(s)$

B $Pb^{2+}(aq) + O^{2-}(aq) \rightarrow PbO(s)$

C $KOH(aq) + NaNO_3(aq) \rightarrow NaOH(aq) + KNO_3(aq)$

D $CH_3CH_2OH(aq) + HCOOH(aq) \rightarrow CH_3COOCH_3(aq) + H_2O(l)$

The following reaction relates to questions 2 and 3.

$$2NOCl(g) \rightleftharpoons 2NO(g) + Cl_2(g) \qquad \Delta H = +75.5\ kJ\,mol^{-1}$$

2 What is the equilibrium expression for the reaction?

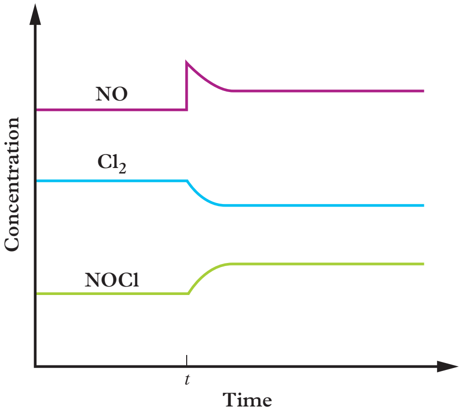
A $\frac{2[NO]+[Cl_2]}{2[NOCl]}$

B $\frac{[NO]^2+[Cl_2]}{[NOCl]^2}$

C $\frac{[NO]^2[Cl_2]}{[NOCl]^2}$

D $\frac{2(NO)+(Cl_2)}{2(NOCl)}$

3 Consider the following equilibrium graph. What change was made to the system at time *t*?



A The temperature of the system was increased.

B Additional NO was added to the system.

C A catalyst was added.

D The volume of the system was halved.

4 The concentration of ethanoic acid (pK_a 4.75) in vinegar is approximately 1.0 M. What is the pH of vinegar?

A 4.8

B 2.4

C 0.004

D 5.4

5 Lactic acid (pK_a 3.88), oxalic acid (pK_a 1.23) and malic acid (pK_a 3.40) are all weak acids found in food products. The order of strongest to weakest acid is:

A lactic acid → oxalic acid → malic acid

B lactic acid → malic acid → oxalic acid

C oxalic acid → malic acid → lactic acid

D oxalic acid → lactic acid → malic acid

6 In a galvanic cell, what is the most important purpose of the salt bridge?

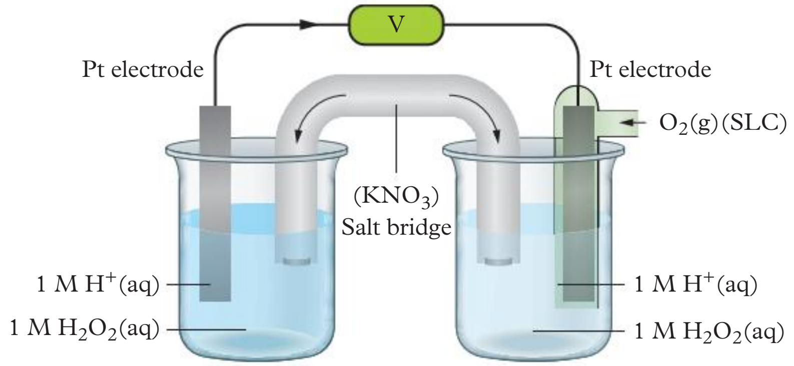
A To transfer electrons between cells and therefore carry the electricity that is generated by the cell

B To connect the two half-cells to ensure that the cell is a complete circuit

C To control the flow of current in the cell so that the cell does not produce excessive amounts of energy

D To transfer ions that carry charge between cells in order to balance the build-up of positive and negative charges in half-cells

7 Consider the cell diagram and determine which option A–D is correct.



	Oxidation	Reduction	$E°$ (V)
A	$H_2O_2 \rightarrow O_2 + 2H^+ + 2e^-$	$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$	1.09
B	$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$	$2H_2O \rightarrow H_2O_2 + 2H^+ + 2e^-$	1.09
C	$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$	$H_2O_2 \rightarrow O_2 + 2H^+ + 2e^-$	2.45
D	$2H_2O \rightarrow H_2O_2 + 2H^+ + 2e^-$	$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$	2.45

8 The lead acid battery in a car is a rechargeable battery and therefore operates as both a galvanic and electrolytic cell. The half-equations occurring within the battery are:

$$PbSO_4(s) + 2e^- \rightleftharpoons Pb(s) + SO_4^{2-}(aq) \quad E° = -0.36\text{ V}$$

$$PbO_2(s) + SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \rightleftharpoons PbSO_4(s) + 2H_2O(l) \quad E° = 1.69\text{ V}$$

The half-equation that occurs at the anode during recharge is:

A $PbSO_4(s) + 2e^- \rightarrow Pb(s) + SO_4^{2-}(aq)$

B $Pb(s) + SO_4^{2-}(aq) \rightarrow PbSO_4(s) + 2e^-$

C $PbO_2(s) + SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \rightarrow PbSO_4(s) + 2H_2O(l)$

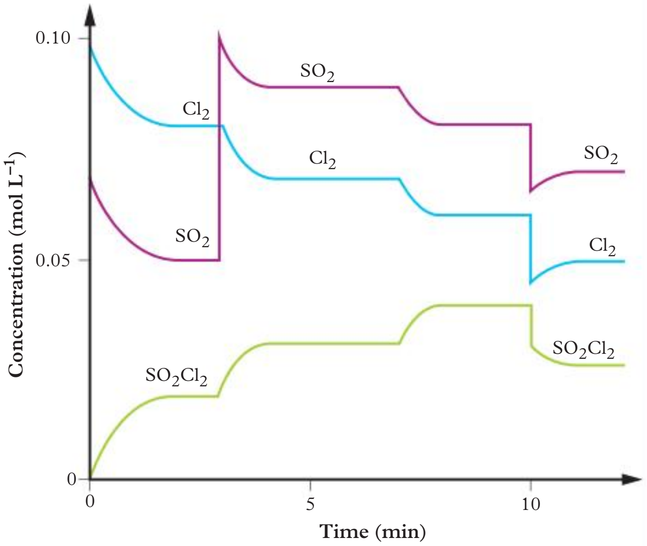
D $PbSO_4(s) + 2H_2O(l) \rightarrow PbO_2(s) + SO_4^{2-}(aq) + 4H^+(aq) + 2e^-$

Short answer

9 Sulfur dioxide gas and chlorine gas were mixed at a particular temperature to produce an equilibrium mixture:

$$SO_2(g) + Cl_2(g) \rightleftharpoons SO_2Cl_2(g) \quad \Delta H = -67\text{ kJ mol}^{-1}$$

For a particular experiment, the concentrations of the three substances are plotted against time in the following graph.



a **Construct** an expression for the equilibrium constant, K, of the reaction.

b **Determine** at which time intervals the reaction was at equilibrium.

c **Calculate** the value of K at the 2-minute and 9-minute marks.

d **Identify** one possible reason why the values of K calculated in part c are different.

e **Determine** what change was made to the system at:

i 3 minutes

ii 7 minutes

iii 10 minutes.

10 Chlorine gas is generated in an equilibrium reaction between hydrochloric acid and oxygen:

$$4HCl(g) + O_2(g) \rightleftharpoons 2H_2O(g) + 2Cl_2(g)$$

$$\Delta H = -128\,kJ\,mol^{-1}$$

- **a** **Construct** an equilibrium expression for the reaction if its equilibrium constant has a value of 2.46.
- **b** Initially, 20 moles of HCl and 6 moles of O_2 are injected into a 2 L vessel. At equilibrium, the concentration of O_2 was measured to be 1 M. **Calculate** Q_c of the reaction at 30 seconds.
- **c** **Determine** what you can conclude about the equilibrium position of the reaction mixture based on the Q_c value that you have calculated.
- **d** Use your answer to part b to **infer** the direction the reaction would need to move in order to reach equilibrium. **Explain** your answer.
- **e** Using Le Châtelier's principle, **explain** the effect of increasing the temperature of the system.
- **f** Using Le Châtelier's principle, **explain** the effect of decreasing the volume of the system.

11 Blood contains a natural carbonic acid/bicarbonate buffer. Carbon dioxide is absorbed into the blood. A simplified representation of this process is provided in the equilibrium equation:

$$CO_2(g) + 2H_2O(l) \rightleftharpoons H_3O^+(aq) + HCO_3^-(aq)$$

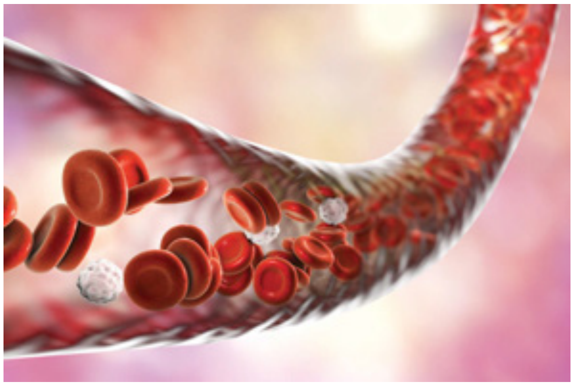


FIGURE 1 Carbon dioxide gets absorbed in the blood.

- **a** **Explain** how a buffer can stabilise the pH of a solution.
- **b** When blood is oxygenated, the concentration of CO_2 is approximately 1.3×10^{-5} M and pH is 7.4.
  - **i** **Calculate** the concentration of H_3O^+.
  - **ii** **Calculate** K_a for the equation.
- **c** Muscles metabolise fats and sugars and produce energy, both CO_2 and H^+ produced as by-products. **Explain** what would happen to a person who regularly exercises excessively.

12 At 0°C, the concentration of hydroxide ions in water is 2.95×10^{-7} M.

- **a** **Construct** the ionisation equation for water.
- **b** **Calculate** the pOH of the water and therefore the pH.
- **c** **Calculate** the concentration of H^+.
- **d** **Calculate** K_w.
- **e** **Calculate** the pH.
- **f** The self-ionisation of water is an endothermic process. **Explain** what happens to the pH of the water as temperature increases.

13 A household cleaner containing hydrochloric acid is analysed in a laboratory to determine whether the concentration of the acid is stated correctly on the packaging. The label claims that it contains 30% w/w HCl. The concentration of hydrochloric acid is determined by an acid–base titration using a standard solution of sodium carbonate.

- **a** **Deduce** why sodium carbonate is considered to be a good standard solution.
- **b** To analyse the cleaner, 10.0 g is dissolved in a 250.00 mL volumetric flask. 10.00 mL aliquots of this solution are pipetted into conical flasks and titrated against 0.115 M sodium carbonate. The data in the table outlines the titres of sodium carbonate obtained from the titration.

	Initial volume (mL)	Final volume (mL)	Titre volume (mL)
Flask 1	0.00	21.43	21.43
Flask 2	21.43	41.35	19.92
Flask 3	10.56	30.58	20.02
Flask 4	15.21	35.27	20.06

i **Construct** the balanced chemical equation for the reaction.

ii **Calculate** the amount of HCl, in mol, in the 10.00 mL aliquots.

iii **Calculate** the amount of HCl, in mol, in the 250.00 mL volumetric flask.

iv **Calculate** the mass of the HCl in the cleaner.

v **Calculate** the concentration of HCl in % m/m.

vi **Compare** the experimental concentration to the one stated on the cleaner. **Determine** what conclusions you can make.

c **Explain** the colour change that would be observed with a methyl orange indicator.

d After the experiment, a student realises that their partner had rinsed the burette with water and then filled it with standard solution before beginning the titration. **Justify** the effect of this error on the final concentration of HCl calculated in the experiment.

14 **Construct** a galvanic cell that can be used to plate silver onto a cheaper metal. Your choice of materials must be safe enough to use in a high school laboratory.

a **Determine** and label the:

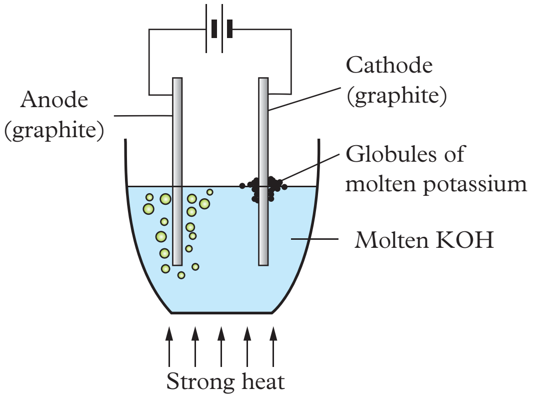
- solutions used in the two half-cells and whether they undergo oxidation or reduction
- two half-equations and the balanced overall equation, all must include appropriate states
- materials used as the anode and cathode and the polarity of each electrode
- salt bridge and a suitable chemical, identifying the movement of ions in the bridge
- direction of electron flow.

b **Justify** your choice of material for each electrode, using the electrochemical series and your knowledge of oxidants and reductants.

c **Justify** your choice of chemical for the salt bridge.

The following diagram relates to questions 7 and 8.

Potassium was discovered in 1807 by English scientist Sir Humphrey Davy. Davy passed a current through a molten solution of potassium hydroxide and observed the production of a gas at one electrode and beads of a shiny metal at the other. The metal was identified as potassium.



15 **a** **Identify** the missing components below.

	Polarity of electrode	Half-equation
Anode		
Cathode		

b **Construct** the overall reaction equation.

c **Determine** what voltage is required to run the cell.

d **Deduce** what issue is involved with not including a porous membrane between the electrodes.

16 The cell was recreated using a 1 M aqueous solution of KOH at 25°C and 1 atm.

a **Identify** the missing components below.

	Polarity of electrode	Half-equation
Anode		
Cathode		

b **Construct** the overall reaction equation.

c **Determine** what voltage is required to run the cell.

d **Determine** the effect of running the same aqueous cell at 2 M concentrations. **Justify** your answer using the electrochemical series.

e A student suggests that it is not possible to produce solid potassium using aqueous electrolysis. **Critique** their statement.

UNIT 4

STRUCTURE, SYNTHESIS AND DESIGN

The term ‘organic’ is usually associated with a product that has been generated without the use of artificial chemicals such as fertilisers and pesticides. However, in chemistry ‘organic’ is used to describe carbon-based chemicals. These chemicals have a skeleton made of carbon and hydrogen. Different organic chemicals have different bonding arrangements and may include other elements such as oxygen, nitrogen and halogens.

Fruits and vegetables are made of organic compounds, whether they were grown with the use of fertilisers and pesticides or not. Organic compounds also include complex structures such as proteins, carbohydrates, fats and synthetic polymers. The structure of organic compounds affects their chemical properties and, in turn, their reactivity.

The synthetic design of compounds involves knowing the link between a compound’s structure and its reactivity, as well as optimising the synthetic methodologies intended to produce the compound.

Analytical techniques provide information about the bonding in a compound, and can separate the components of mixtures by properties such as their size, shape or overall charge. Analytical techniques are initially used to confirm that the desired product has been formed. However, analytical techniques are also used to determine how successful a synthetic pathway is, or its yield.

Synthetic chemistry is focusing more on sustainability as the industry recognises the need for more environmentally friendly techniques that use optimised products to reduce or eliminate the consumption of precious resources and the production of harmful products.

Chapter guide

Topic 1	Properties and structure of organic materials	Chapters 9–12
Topic 2	Chemical synthesis and design	Chapters 13–16

Unit objectives

- Describe and explain the properties and structure of organic materials and chemical synthesis and design.
- Apply understanding of the properties and structure of organic materials and chemical synthesis and design.
- Analyse evidence about the properties and structure of organic materials and chemical synthesis and design.
- Interpret evidence about the properties and structure of organic materials and chemical synthesis and design.
- Investigate phenomena associated with the properties and structure of organic materials and chemical synthesis and design.
- Evaluate processes, claims and conclusions about the properties and structure of organic materials and chemical synthesis and design.
- Communicate understandings, findings, arguments and conclusions about the properties and structure of organic materials and chemical synthesis and design.

Source: *Chemistry 2019 v 1.3 General Senior Syllabus*

CHAPTER

9

Structure of organic compounds

Organic chemistry is based on the carbon-containing compounds that make up all living organisms and play a major role in the universe. Carbon is an element with four electrons in its valence energy level. It covalently bonds with other atoms such as hydrogen, nitrogen, oxygen, sulfur, halogens and itself. Organic compounds include fossil fuels (methane gas, butane gas and petroleum), medications (paracetamol, penicillin and amphetamine), harmful compounds (mustard gas and cyanide poison), the fragrant components of perfumes, natural and synthetic clothing, and many components in cosmetics. The carbohydrates, lipids, proteins and nucleic acids in living organisms are also organic compounds.

OBJECTIVES

- → Recognise that organic molecules have a hydrocarbon skeleton and can contain functional groups, including alkenes, alcohols, aldehydes, ketones, carboxylic acids, haloalkanes, esters, nitriles, amines, amides and that structural formulas (condensed and extended) can be used to show the arrangement of atoms and bonding in organic molecules.
- → Deduce the structural formulas and apply IUPAC rules in the nomenclature of organic compounds (parent chain up to 10 carbon atoms) with simple branching for alkanes, alkenes, alkynes, alcohols, aldehydes, ketones, carboxylic acids, haloalkanes, esters, nitriles, amines and amides.
- → Identify structural isomers as compounds with the same molecular formula but different arrangement of atoms; deduce the structural formulas and apply IUPAC rules in the nomenclature for isomers of the non-cyclic alkanes up to C_6.
- → Identify stereoisomers as compounds with the same structural formula but with different arrangement of atoms in space; describe and explain geometrical (*cis* and *trans*) isomerism in non-cyclic alkenes.
- → Recognise that organic compounds display characteristic physical properties, including melting point, boiling point and solubility in water and organic solvents that can be explained in terms of intermolecular forces (dispersion forces, dipole-dipole interactions and hydrogen bonds), which are influenced by the nature of the functional groups.

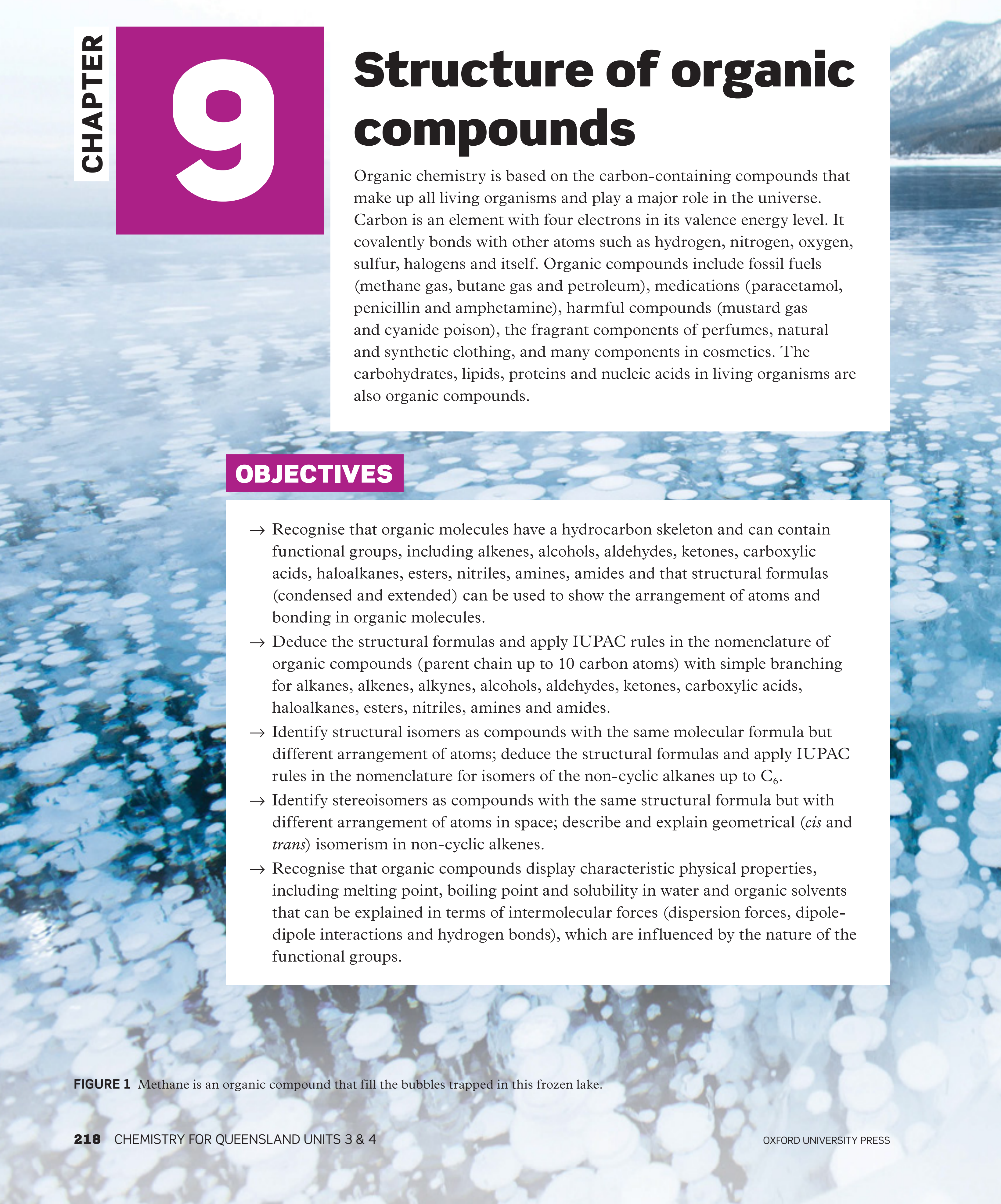


FIGURE 1 Methane is an organic compound that fill the bubbles trapped in this frozen lake.

→ Predict and explain the trends in melting and boiling point for members of a homologous series.

→ Discuss the volatility and solubility in water of alcohols, aldehydes, ketones, carboxylic acids and halides.

Source: *Chemistry 2019 v1.3 General Senior Syllabus* © Queensland Curriculum & Assessment Authority

PRACTICALS

SUGGESTED PRACTICAL	**9.3** Interpreting 2D and 3D functional groups
MANDATORY PRACTICAL	**9.4** Modelling isomers of organic molecules

9.1 Hydrocarbons

KEY IDEAS

In this section, you will learn about:

- the nomenclature of simple hydrocarbons
- types of bonding present in hydrocarbons
- how the level of branching affects hydrocarbon nomenclature.

Hydrocarbons are the simplest form of organic compound, consisting only of the elements carbon and hydrogen. Hydrocarbons consist of a **main chain** of carbon atoms bonded together. Each carbon is also bonded to hydrogen atoms and so reaches a stable octet of electrons. The **nomenclature** of hydrocarbons is mainly determined by the number of carbon atoms present in the main chain, and the bonding that exists between the carbon atoms.

hydrocarbon
an organic compound consisting of only carbon and hydrogen atoms

main chain
the longest chain of carbon atoms in a hydrocarbon molecule

nomenclature
a set of rules by IUPAC used to name organic compounds

prefix
a group of letters added to the beginning of a word; the first part of an organic compound's name

FIGURE 1 Oil and gas (sourced from below the seafloor) are examples of simple hydrocarbons.

Study tip

For a refresher on the octet rule, which refers to the tendency of carbon atoms to share electrons in order to achieve 8 electrons in the valence energy level, refer to *Chemistry for Queensland Units 1 & 2, Section 3.1.*

Study tip

The prefixes for 5–10 carbons are the same as those used for naming polygons in mathematics. If you know this, then all you need to memorise are the terms for the first four carbons.

Number of carbons in the main chain

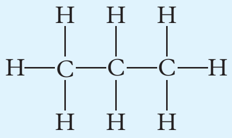
The main chain of an organic compound is derived from the longest continuous chain of carbon atoms that exists within the molecule. In the International Union of Pure and Applied Chemistry (IUPAC) system of organic chemistry nomenclature, the name of a hydrocarbon includes the number of carbons in the main chain. This number is represented in the name by a **prefix**. The prefixes for the hydrocarbons with 1–10 carbons are listed in Table 1.

TABLE 1 Main chain nomenclature

Number of carbons	Prefix for main chain
1	Meth
2	Eth
3	Prop
4	But
5	Pent
6	Hex
7	Hept
8	Oct
9	Non
10	Dec

WORKED EXAMPLE 9.1A

Apply nomenclature rules to name the following hydrocarbon.



$$\begin{array}{ccccccc} & & H & & H & & H & & \\ & & | & & | & & | & & \\ H & - & C & - & C & - & C & - & H \\ & & | & & | & & | & & \\ & & H & & H & & H & & \end{array}$$

SOLUTION

There are three carbon atoms in the molecule's main chain, so the prefix is 'prop'.

The bonds between each carbon atom are single (as represented by a single line), so the suffix is 'ane'.

The name of the molecule is propane.

Bonding between carbons in the main chain

The name of a hydrocarbon also indicates the type of bonding between carbons. If the molecule contains only single covalent bonds (involving two electrons), the name of the hydrocarbon ends with the **suffix** 'ane' and the hydrocarbon is an alkane; for example, hexane. Worked example 9.1A shows you how to name an **alkane**.

If the hydrocarbon contains a double bond, then the name includes the suffix 'ene' and the hydrocarbon is an **alkene**; for example, hexene. The double bond is represented by two lines in the structural formula.

If the hydrocarbon contains a triple bond, then the name includes the suffix 'yne' and the hydrocarbon is an **alkyne**; for example, hexyne. The triple bond is represented by three lines in the structural formula.

CHALLENGE 9.1A

Levels of saturation

A 'saturated' hydrocarbon only has single carbon–carbon bonds. Hence, it contains a maximum number of hydrogen atoms.

Deduce the definition of an unsaturated hydrocarbon. Draw three examples each of saturated and unsaturated hydrocarbons.

Locants

Locants are used to pinpoint the location of double and triple bonds in organic compounds. Each carbon atom in the molecule is assigned a number, beginning with 1 for the first carbon on the end of the main chain. The location of the **multiple bond** is indicated by the lower number of the two carbon atoms in the bond. The number is included in the compound's name with hyphens either side; for example, hex-1-ene. Worked example 9.1B shows you how to name an alkene.

suffix
a group of letters added to the end of a word; the last part of an organic compound's name

alkane
a class of organic compound that contains single bonds between the carbon atoms

alkene
a class of organic compound that contains one or more double bonds between the carbon atoms

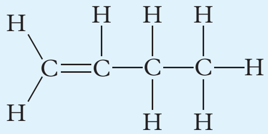
alkyne
a class of organic compound that contains one or more triple bonds between the carbon atoms

locant
a number or letter that indicates the position of a substituent or functional group within an organic compound

multiple bond
a double or triple bond in an organic compound

WORKED EXAMPLE 9.1B

Apply nomenclature rules to name the following hydrocarbon.



SOLUTION

There are four carbon atoms in the molecule's main chain, so the prefix 'but' is used.

There is one double bond, so the suffix is 'ene'. The double bond is between the first and second carbon atoms, so the locant is 1.

The name of the molecule is but-1-ene.

Study tip

'But' is pronounced 'b-you-t'. Butane gas is a common four-carbon hydrocarbon.

In the name of a hydrocarbon, the locant must immediately precede the component of the molecule that it relates to. This avoids confusion and ambiguity when naming larger, complex organic compounds.

Hydrocarbon substituents

Hydrocarbon molecules can contain carbon (and hydrogen) atoms that branch off the main chain. These **substituents** are bonded to the main chain at one point (not on the end of the main chain). To name such compounds, number the carbons in the main chain and indicate the position of the substituent as a prefix in the molecule's name. The prefix will end with 'yl'. Indicate the position of the substituent by using a locant; for example, 3-methylhexane.

Worked example 9.1C demonstrates how to name a hydrocarbon with a substituent.

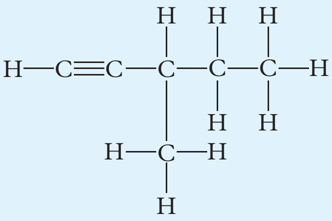
substituent
an atom or group of atoms bonded to a carbon atom in the main chain

Study tip

Older textbooks and internet resources can sometimes refer to the former IUPAC nomenclature for the position of locants. For example, 2-hexene, while technically correct and unambiguous, has been updated to hex-2-ene.

WORKED EXAMPLE 9.1C

Apply nomenclature rules to name the following hydrocarbon.



SOLUTION

There are five carbon atoms in the molecule's main chain, so the prefix 'pent' is used.

There is a triple bond between carbons 1 and 2, so the name includes the suffix '1-yne'.

There is a one-carbon substituent on carbon 3, so the name includes '3-methyl'.

The name of the molecule is 3-methylpent-1-yne.

Multiple substituents

When there is more than one substituent in a molecule, then name the substituents in alphabetical order. For example, ethyl appears before methyl.

If there are more than one substituent of the same type, then use a **multiplier** alongside the substituent to communicate how many there are. For example, 'di' means 2 and 'tetra' means 4 (Table 2).

multiplier
a term used to indicate the number of substituents of the same type

Study tip

You do not need to list multipliers in alphabetical order. For example, 'dimethyl' does not come before 'ethyl' in the prefix section of a name.

TABLE 2 Multipliers used in organic nomenclature

Number of substituents	Multiplier
2	Di
3	Tri
4	Tetra
5	Penta

Assigning locants

There are strict IUPAC guidelines for numbering carbon atoms in the name of a molecule.

- Assign the suffix the lowest possible locant. For example, the triple bond in 3-methylpent-1-yne is at carbon 1 (numbering left to right) rather than carbon 4 (right to left).
- When there are multiple substituents, number the positions from left to right or right to left so that they have the lowest value.

  For example, you can name the hydrocarbon in Figure 2 as follows.
  - There are five carbons in the main chain, so the name includes 'pentane'.
  - There are three methyl substituents. So, the name includes 'trimethyl'.
  - Numbering from left to right, the methyl groups are at 2,4,4; numbering from right to left, the methyl groups are at 2,2,4. The first point of difference is the second value, and numbering from right to left gives the lower value.

  The name of the molecule is 2,2,4-trimethylpentane.

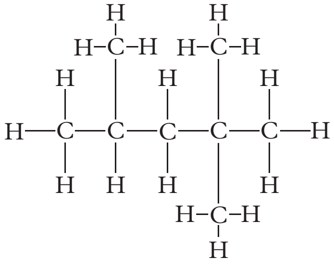


FIGURE 2 An eight-carbon hydrocarbon

- When there are multiple branches and there are no points of difference, list the substituents in alphabetical order. For example, you can name the hydrocarbon in Figure 3 as follows.
  - The main chain has six carbons so is hexane.
  - There are two hydrocarbon substituents – a methyl and an ethyl.
  - Since 'e' appears before 'm' in the alphabet, list ethyl before methyl in the name and assign the ethyl group the lowest possible number. Numbering from left to right, ethyl is on carbon 3; from right to left, ethyl is on carbon 4.
  - The name of the molecule is 3-ethyl-4-methylhexane.

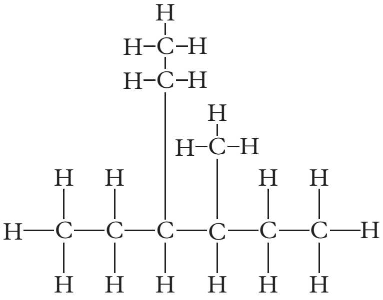


FIGURE 3 A nine-carbon hydrocarbon

non-cyclic
an organic compound that has a straight main chain with two ends

cyclic
an organic compound that consists of a ring of carbons

Cyclic hydrocarbons

The main chain of a hydrocarbon is the longest continuous chain of carbon atoms, and can be either straight (**non-cyclic**) or **cyclic**. So far, the hydrocarbons discussed have all been non-cyclic hydrocarbons, which have two ends of the main chain.

A cyclic hydrocarbon consists of a ring of carbons and its name includes 'cyclo' as a prefix. For example, cyclohexane is a ring of six carbons. Assigning carbon 1 depends on the positions of any multiple bonds and substituents, which are given the lowest number according to the rules already discussed.

For example, you can name the cyclic hydrocarbon in Figure 4 as follows.

- The molecule contains a six-membered carbon ring, which also has one double bond. The double bond must be between carbon atoms 1 and 2 because it is the suffix and has greatest priority. Therefore, it is a cyclohex-1-ene.
- There are three hydrocarbon substituents – two methyl groups and an ethyl group. In the anticlockwise direction, the numbering of the substituents would be 2-ethyl-3,3-dimethyl. In the clockwise direction, the substituents would be 1-ethyl-6,6-dimethyl. The first point of difference for the substituents is the value of the ethyl, so the clockwise direction is used.

The name of the molecule is 1-ethyl-6,6-dimethylcyclohex-1-ene.

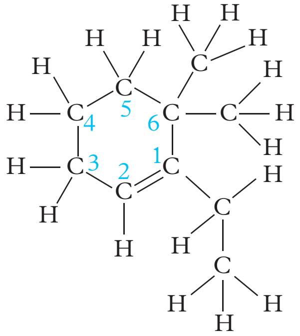


FIGURE 4 1-Ethyl-6,6-dimethylcyclohex-1-ene

CHALLENGE 9.1B

Aromaticity

Aromatic compounds are cyclic compounds that have specific bonding qualities that make them very stable. This is achieved through delocalisation of electrons.

The most common example of an aromatic is benzene. Benzene consists of a six-carbon ring with alternating double and single bonds. Electron delocalisation causes the placement of these bonds to shift constantly and have resonance structures. For this reason, benzene can be drawn three ways (Figure 5).

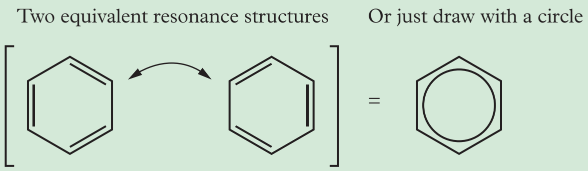


FIGURE 5 The different ways to draw benzene: alternating double bonds or a circle to indicate delocalised electrons

Research other common aromatic compounds, and their everyday applications.

CHECK YOUR LEARNING 9.1

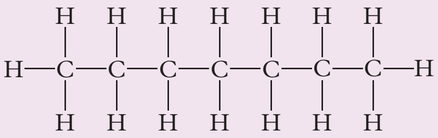
Describe and explain

1 **Describe** the term ‘hydrocarbon’.

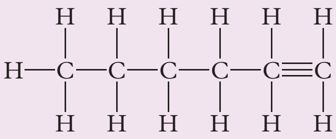
2 **Explain** the structure of a hydrocarbon name, including all components and punctuation.

3 **Identify** the functional groups in the following hydrocarbons.

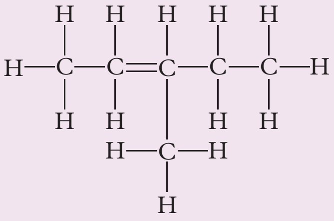
a



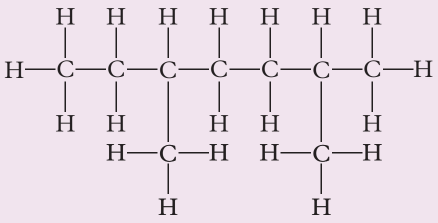
b



c



d



Apply, analyse and interpret

4 **Apply** IUPAC rules to name the hydrocarbons in question 3.

Investigate, evaluate and communicate

5 **Evaluate** the significance of IUPAC rules in the scientific community.

6 **Construct** the first three alkenes as diagrams – ethene, propene and butene.

You can find the following resources for this section on your obook assess:

- Student book questions
  9.1 Check your learning
- Challenge
  9.1A Levels of saturation
- Challenge
  9.1B Aromaticity

9.2 Functional groups

KEY IDEAS

In this section, you will learn about:

- structures and names of functional groups containing oxygen, nitrogen and various halogens
- how to apply IUPAC nomenclature to name classes of organic compounds such as alcohols, ketones, esters and amides
- structures and names of alcohols and amines
- how to apply IUPAC nomenclature to name complex organic compounds that contain more than one functional group.

Organic compounds containing oxygen

Oxygen is an element often found in organic compounds (except hydrocarbons). The most common **functional groups** that contain oxygen are **hydroxyl**, **carbonyl** and **carboxyl** (Figure 1).

Alcohols

Alcohols are a class of organic compound that contains the hydroxyl functional group. The hydroxyl group can be located on any carbon in the main chain. To name an alcohol, identify the main chain and omit the final letter 'e'. Then add 'ol' as a suffix, which is immediately preceded by the locant; for example, hexan-2-ol.

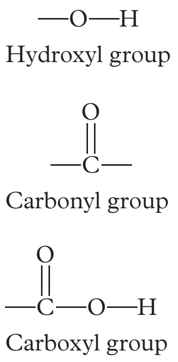


FIGURE 1 Common functional groups that contain oxygen

functional group
an atom or a group of atoms in an organic compound that determines the reactivity of that compound

hydroxyl
a functional group consisting of an –OH group, which is an oxygen atom and a hydrogen atom joined by a single bond

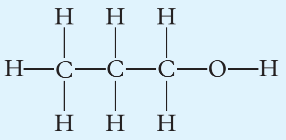
carbonyl
a functional group consisting of an oxygen atom double bonded to a carbon atom in the main chain (–CO–)

carboxyl
a functional group consisting of a hydroxyl group attached to the carbon of a carbonyl group (–COOH)

alcohol
a class of organic compound that contains a hydroxyl functional group (–OH)

WORKED EXAMPLE 9.2A

Apply nomenclature rules to name the following molecule.



$$\mathrm{CH_3CH_2CH_2OH}$$

SOLUTION

The main chain is three carbon atoms long, so the prefix 'prop' is used.

There is a hydroxyl functional group on a terminal carbon (numbered 1 as a result), so it is an alcohol.

The name of the molecule is propan-1-ol.

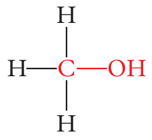
Types of alcohols

Primary alcohols are alcohols in which the carbon that is bonded to the hydroxyl group is only bonded to one other carbon (the hydroxyl group is located on the end of a carbon chain). Methanol, CH_3OH in Figure 2, is called a primary alcohol even though there are no alkyl groups attached to the carbon with the –OH group.

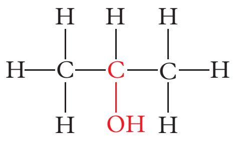
Secondary alcohols are alcohols in which the carbon that is bonded to the hydroxyl group is bonded to two other carbons (the hydroxyl group is located in the middle of the main chain).

Tertiary alcohols are alcohols in which the carbon that is bonded to the hydroxyl group is bonded to three other carbons (the hydroxyl is located in the middle of the main chain that also has hydrocarbon substituents).

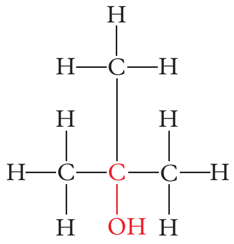
The three types of alcohol are illustrated in Figure 2.



Primary



Secondary



Tertiary

FIGURE 2 Primary, secondary and tertiary alcohols

Aldehydes and ketones

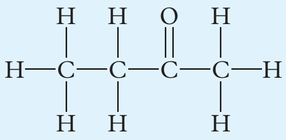
Aldehydes and **ketones** are two classes of organic compounds that contain the carbonyl functional group, but in different locations on the main chain. Aldehydes have a carbonyl group on the end of the main chain (carbon 1). Ketones have a carbonyl group within the main chain.

To name an aldehyde, identify the main chain and omit the final letter ‘e’. Then add ‘al’ as a suffix; for example, hexanal. You do not need to indicate the position of the carbonyl functional group with a number because the carbonyl group is always on carbon 1.

To name a ketone, identify the main chain and omit the final letter ‘e’. Then add ‘one’ as a suffix, which is immediately preceded by the locant; for example, hexan-2-one.

WORKED EXAMPLE 9.2B

Apply nomenclature rules to name the following molecule.



SOLUTION

The main chain contains four carbon atoms, so the prefix ‘but’ is used.

There is a carbonyl functional group in the middle of the main chain, so the compound is a ketone.

The lowest number the carbonyl group can take is 2 (counting from right to left).

The name of the molecule is butan-2-one.

primary alcohol an alcohol in which the carbon that is bonded to the OH group is bonded to one other carbon

secondary alcohol an alcohol in which the carbon that is bonded to the OH group is bonded to two other carbons

tertiary alcohol an alcohol in which the carbon that is bonded to the OH group is bonded to three other carbons

aldehyde a class of organic compound that has a carbonyl group on the end of the main chain

ketone a class of organic compound that has a carbonyl group on a carbon within the main chain

Study tip

The suffix for ketones is pronounced ‘own’.

carboxylic acid
a class of organic compound that contains a carboxyl functional group

Carboxylic acids

Carboxylic acids are a class of organic compound that have a carboxyl functional group. The chain containing the COOH group becomes the main chain and the carboxyl carbon is carbon 1).

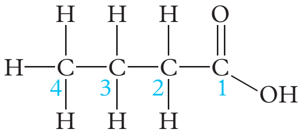


FIGURE 3 In carboxylic acids the COOH group is assigned as carbon 1. This is butanoic acid.

To name a carboxylic acid, count the carbons in the chain containing the carboxylic acid. Omit the final 'e' of the parent hydrocarbon name and add 'oic acid'. The carboxyl carbon is numbered 1 but do not include the locant for the COOH group in the name. For example, hexanoic acid is a carboxylic acid that has six carbons and methanoic acid is a single-carbon carboxylic acid.

ester
a class of organic compound that contains a carbonyl attached to an oxygen, which is bonded to another carbon

Esters

Esters are a class of organic compound that are derived from a carboxylic acid and an alcohol. The ester functional group contains a carbonyl group attached to an oxygen linked to another carbon.

The name of an ester consists of two parts – the first part from the alcohol and the second part from the carboxylic acid. For example, the ester ethyl propanoate was formed from ethanol and propanoic acid.

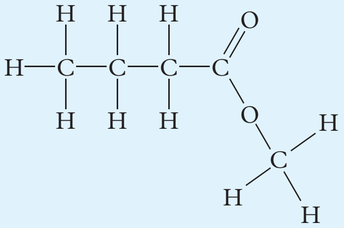
To name an ester:

- assign the carbon in the carbonyl functional group as carbon 1
- count the number of carbons in the chain attached to the carbonyl group, name the chain and add the suffix 'oate'
- count the number of carbons in the chain attached to the oxygen, name the chain and add the suffix 'yl'.

Neither part of the name requires locants. However, any other substituent would need a locant.

WORKED EXAMPLE 9.2C

Apply nomenclature rules to name the following molecule.



SOLUTION

There is a carbonyl on a four-carbon chain, so this part of the name includes the prefix 'but'.

The carbonyl group is carbon 1.

The chain attached to the oxygen contains only one carbon, so the ester substituent is methyl.

The name of the molecule is methyl butanoate.

Organic compounds containing nitrogen

Nitrogen is another element often found in organic compounds. Nitrogen-containing compounds play major roles in biological systems. **Amines** and **amides** are derived from the molecule ammonia (NH_3). Whereby one or more of the hydrogen atoms is replaced by an **alkyl group** (symbolised as R).

amine
a class of organic compound that contains a nitrogen atom bonded to three other groups, either hydrogen atoms or alkyl groups

amide
a class of organic compound that contains amine and carbonyl functional groups adjacent to each other

alkyl group
a group formed by removing a hydrogen from an alkane and can be present as a substituent in an organic compound

Amines

Amines are a class of organic compound that contains the amino functional group, and their names include the suffix 'amine'. Amines are classified as primary, secondary or tertiary depending on the number of alkyl groups bonded to the nitrogen atom (Figure 4).

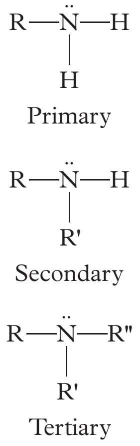


FIGURE 4 Primary, secondary and tertiary amines

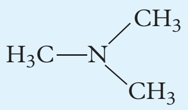
When naming simple amines, you do not need to include locants for the alkyl groups because they all stem from the central nitrogen atom.

To name an amine:

- identify and name each alkyl group
- place each alkyl group in alphabetical order, and use multipliers if necessary
- add the suffix 'amine' to the end of the name.

WORKED EXAMPLE 9.2D

Apply nomenclature rules to name the following molecule.



SOLUTION

The molecule contains three alkyl groups attached to a nitrogen, so it is a tertiary amine.

The alkyl groups are all methyl groups.

The name of the molecule is trimethylamine.

Amides

Amides are another class of organic compound derived from carboxylic acids. The amide functional group contains a carbonyl group attached to an amine group. Amides are also classified as primary, secondary or tertiary depending on the number of alkyl groups attached to the carbonyl and amine of the amide functional group (Figure 5).

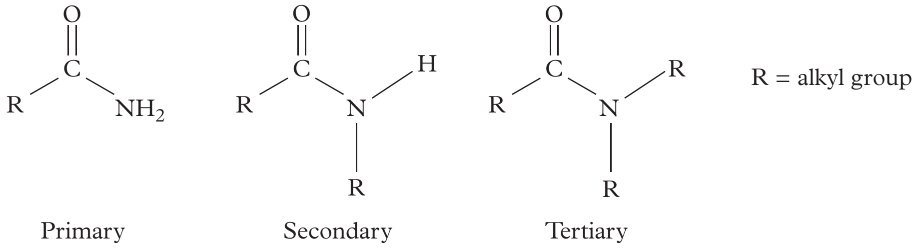


FIGURE 5 Primary, secondary and tertiary amides

To name an amide:

- identify the main chain
- number the carbonyl carbon as carbon 1
- add the suffix ‘amide’
- use *N* to represent bonds to the nitrogen atom in complex amine molecules.

Figure 6 shows two amides. Butanamide is a very simple amide with four carbons in the main chain. *N*-Methylpropanamide is a more complex amide. The locant *N* indicates that there is an alkyl group attached to the nitrogen atom. Worked example 9.2F shows you how to name another amide.

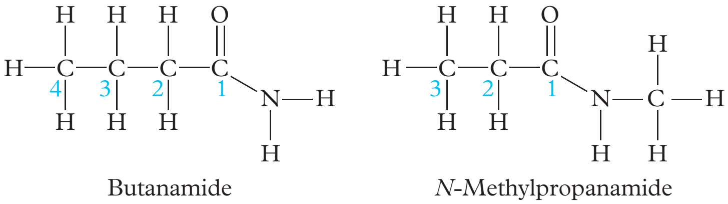
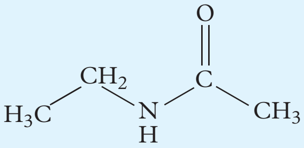


FIGURE 6 Butanamide and *N*-methylpropanamide

WORKED EXAMPLE 9.2E

Apply nomenclature rules to name the following molecule.



SOLUTION

The molecule contains an amide functional group.

The carboxylic acid component is ethanoic acid, which will become ethanamide.

The alkyl group attached on the other side of the nitrogen also has two carbon atoms, and will have the locant ‘*N*’. The name of the molecule is *N*-ethylethanamide.

Nitrile

nitrile
a class of organic compound that contains a nitrogen atom with a triple bond to a carbon atom

Nitriles are a class of organic compound that contain a functional group consisting of a carbon triple-bonded to a nitrogen. In simple nitriles, the carbon atom in the functional group is carbon 1, and the name includes the suffix ‘nitrile’. For example, a five-carbon nitrile with a one carbon substituent coming off the fourth carbon atom is named 4-methylpentanenitrile.

Organic compounds containing halogens

haloalkane
a class of organic compound that contains a halogen substituent

Many organic compounds contain halogens such as chlorine. These compounds are called **haloalkanes** (represented as R–X). The halogen is always represented in the prefix component of a molecule’s name. When naming a haloalkane, the halogen’s name is shortened and ends with ‘o’. For example, a methane molecule bonded to two chlorine atoms is given the name dichloromethane. The other halogens often found in haloalkanes are fluorine R–F (fluoro), bromine R–Br (bromo) and iodine R–I (iodo).

Polyfunctional compounds

Complex organic compounds can often have more than one functional group present. These are known as polyfunctional compounds. Only one functional group is represented in the molecule's suffix. This is known as the principal functional group. You can determine which group is the principal functional group by referring to Table 1, which lists functional groups in order highest priority to lowest priority. If a functional group becomes subordinate, then the prefix name in the table is used, with a locant.

TABLE 1 The order of priority functional groups in polyfunctional compounds

Class of compound	Prefix	Suffix
Carboxylic acid	Carboxy	-oic acid
Ester	Alkoxycarbonyl	-oate
Amide	Carbamoyl	-amide
Nitrile	Cyano	-nitrile
Aldehyde	Formyl	-al
Ketone	Oxo	-one
Alcohol	Hydroxy	-ol
Amine	Amino	-amine
Alkene	Alkenyl (e.g. propenyl)	-ene
Alkyne	Alkynyl (e.g. propynyl)	-yne
Alkane	Alkyl (e.g. ethyl)	-ane

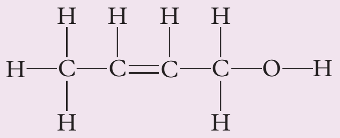
CHECK YOUR LEARNING 9.2

Describe and explain

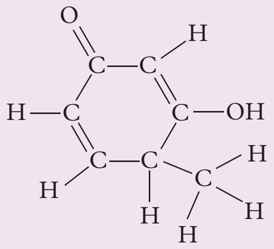
1 **Describe** the structure of hydroxyl and carbonyl functional groups.

2 **Identify** the functional groups in the following organic compounds.

a



b



Apply, analyse and interpret

3 **Apply** IUPAC rules to name the organic compounds in question 2.

Investigate, evaluate and communicate

4 **Evaluate** the importance of the order of priority in terms of principal and subordinate groups.

You can find the following resources for this section on your obook assess:

- » Student book questions
  9.2 Check your learning
- » Weblink
  Organic and inorganic compounds
- » Weblink
  Organic compounds containing nitrogen

9.3

Structural formulas

KEY IDEAS

In this section, you will learn about:

- how condensed and line structural formulas provide limited information about the organic compound when compared with extended structural formulas
- translating between types of structural formulas
- deducing structural formulas when given the name of the organic compound.

structural formula
a representation of an organic compound used to inform the arrangement and bonding of atoms

Organic compounds can be represented in a variety of ways, including empirical and molecular formulas as well as several types of structural formulas. **Structural formulas** are used to show the arrangement of atoms in the molecule and/or the bonding between them.

Extended structural formulas

Extended structural formulas provide information about both the arrangement and bonding in an organic molecule without any room for ambiguity. The molecules represented so far throughout this chapter have been extended structural formulas. Single bonds are represented using a single line, and double and triple bonds are represented with two and three lines. Bonds are drawn with 90°, 120° and 180° angles to reflect electron repulsion. For example, ethene has a double bond between the carbon atoms, and then each carbon atom has two bonds to hydrogen atoms. The bonds around each carbon are at angles of 120° (Figure 1).

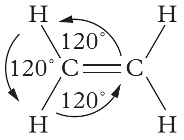


FIGURE 1 In ethene, the bonds around each carbon are drawn at angles of 120°.

Condensed structural formulas

Condensed structural formulas (e.g. $CH_3CH_2CH_3$) provide information about the carbon arrangements in an organic molecule, but they don't show the bonding that takes place between each of the atoms. To determine the bonding, you need to consider how many bonds each atom should have. If the formula does not include enough atoms to account for all the octets, it is probably because the compound contains double or single bonds.

For example, the condensed structural formula of ethene is CH_2CH_2. Each carbon atom bonds four times, and each hydrogen atom bonds once. In the condensed structural formula, each carbon atom is shown to bond to two hydrogens as well as the other carbon atom. To achieve an octet for the carbon atoms, the bond between them needs to be a double bond.

Condensed structural formulas also use brackets to represent a repeating pattern within the organic molecule, or to represent a substituent that branches above or below the main chain. For example, $CH_3(CH_2)_3CH_3$ is the structural formula of pentane, and $(CH_3)_2CHCH_2CH_3$ is the structural formula of 2-methylbutane.

Study tip

For a refresher on empirical and molecular formulas refer to *Chemistry for Queensland Units 1 & 2*, Section 8.3.

Study tip

Place a dot on each 'end' and 'bend' of the line structural formulas, to help count the carbon atoms.

Line structural formulas

Line structural formulas provide information about the bonding within an organic molecule, as well as information about some of the atoms present. Line structural formulas are drawn as a zigzag line (Figure 2). Carbon atoms are not written in but are represented by the ends and corners of the diagonal lines. Hydrogen atoms are not written in (except in the case of hydroxyl and amine functional groups) but are assumed to be present to complete the octets of the other atoms in the molecule. Other elements are written in, using their elemental symbol.

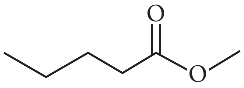


FIGURE 2 The line structural formula of methyl pentanoate

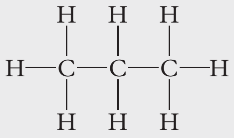
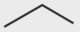
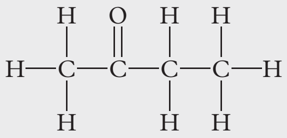
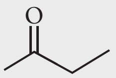
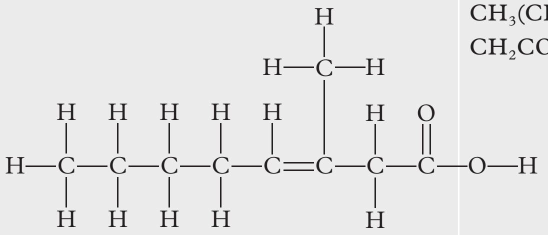
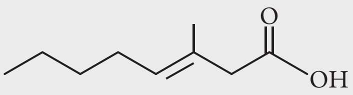
SUGGESTED PRACTICAL

9.3 Interpreting 2D and 3D functional groups
Go to your obook assess »

WORKED EXAMPLE 9.3

Deduce the extended, condensed and line structural formulas for propane, butan-2-one and 3-methyloct-3-enoic acid.

SOLUTION

	Extended	Condensed	Line
Propane		$CH_3CH_2CH_3$	
Butan-2-one		$CH_3C(O)CH_2CH_3$	
3-Methyloct-3-enoic acid		$CH_3(CH_2)_3CHC(CH_3)CH_2CO_2H$	

CHECK YOUR LEARNING 9.3

Describe and explain

1 **Describe** the term ‘structural formula’.

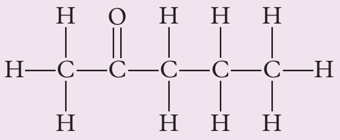
2 **Explain** the steps involved in interpreting a condensed structural formula.

Apply, analyse and interpret

3 **Deduce** the extended and condensed structural formulas of:
  - **a** diethylamine
  - **b** 3-methylbut-1-yne
  - **c** 4-oxo propyl hexanoate
  - **d** *N*-methyloctanamide

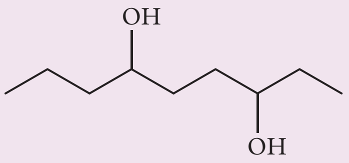
4 **Apply** IUPAC rules to name the following organic compounds.

a



b $CH_3(CH_2)_5CN$

c



Investigate, evaluate and communicate

5 **Construct** the line structural formula of 2-methylhexane.

6 **Investigate** the other condensed structural formulas that exist, and **evaluate** their usefulness in terms of representing the atom arrangement and bonding within molecules.

You can find the following resources for this section on your obook assess:

- » Student book questions
  9.3 Check your learning
- » Suggested practical
  9.3 Interpreting 2D and 3D functional groups
- » Weblink
  Structural formulas

9.4 Isomers

KEY IDEAS

In this section, you will learn about:

- comparing structural and stereoisomers
- identifying all possible structural formulas of an organic compound, when given the molecular formula
- how to apply IUPAC nomenclature to name structural and stereoisomers.

Structural isomers

structural isomers two or more organic compounds that have the same atoms but a different arrangement and bonding

Structural isomers are compounds that have the same molecular formula but a different structural formula. For example, C_4H_{10} has two structural isomers – butane and 2-methylpropane (also known as isobutane). The two isomers both have four carbon atoms and 10 hydrogen atoms, but have different arrangements of atoms (bonding) and different names.

Structural isomers have different physical and chemical properties because of the different atom arrangements. Butane, the straight-chain isomer of C_4H_{10}, has a boiling point of –1°C and a melting point of –138°C. 2-Methylpropane, the branched-chain isomer of C_4H_{10}, has a boiling point of –12°C and a melting point of –159°C (Figure 1).

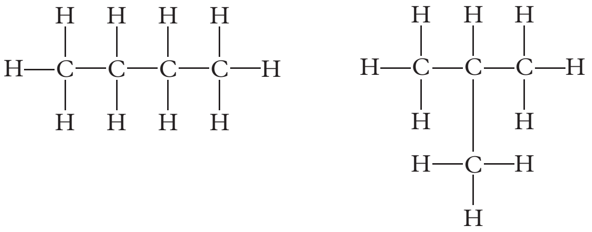


FIGURE 1 Structural isomers of C_4H_{10}: butane and 2-methylpropane

Stereoisomers

stereoisomers two or more organic compounds that have the same atoms and bonding but a different spatial arrangement

Stereoisomers are compounds that have the same molecular formula and structural formula but a different arrangement of atoms in space. Stereoisomers have different physical and chemical properties.

Geometrical isomers

geometrical isomers two organic compounds that have different arrangements of atoms around a rigid double bond

Geometrical isomers are stereoisomers that have different arrangements of atoms around a rigid double bond. This is due to a lack of rotational ability in the double bond, causing fixed arrangements of the substituents attached to those carbon atoms. The geometry of these substituents can be one of two isomeric forms: *cis* or *trans*.

cis geometrical isomers have similar substituents on the same side of the double bond, whether geometrically above or below the double bond. *trans* geometrical isomers have similar substituents on the opposite sides of the double bond, where one substituent is geometrically above the double bond and the other substituent is geometrically below.

But-2-ene has *cis* and *trans* geometrical isomers, in which the substituents are the end carbon atoms (CH_3). *cis*-But-2-ene is represented by drawing both methyl groups on the same

MANDATORY PRACTICAL

9.4 Modelling isomers of organic molecules
Go to page 409 »

side of the double bond and *trans*-but-2-ene is represented by drawing the methyl groups on opposite sides of the double bond (Figure 2). The different geometries mean that the melting point of *cis*-but-2-ene is –139°C, whereas the melting point of *trans*-but-2-ene is –106°C.

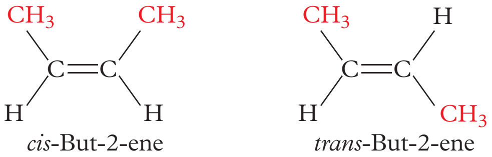


FIGURE 2 The geometrical isomers of C_4H_8: *cis*-but-2-ene and *trans*-but-2-ene

The substituents on geometrical isomers do not need to be identical, but they do need to have at least two substituents other than hydrogen attached to the double bond. This means that geometrical isomers cannot generally form on the end of the main chain, because one of the carbon atoms will only have hydrogen atoms rather than substituents.

Enantiomers

Enantiomers are a type of stereoisomer that have an asymmetrical (chiral) carbon atom with four different substituents covalently bonded in a tetrahedral arrangement. Enantiomers are mirror images of each other, and are non-superimposable.

We represent enantiomers as a tetrahedral arrangement and use solid and dashed wedge-shaped bonds to show the three-dimensional nature of the substituent arrangements in space. The solid wedge represents a bond coming out of the page. The dashed wedge represents a bond going into the page. CHFClBr and $CH_3CH(OH)CH_2CH_3$ are examples of enantiomers (Figure 3).

enantiomers
two organic compounds that have the same atoms and bonding but a different arrangement of four substituents around a chiral carbon atom

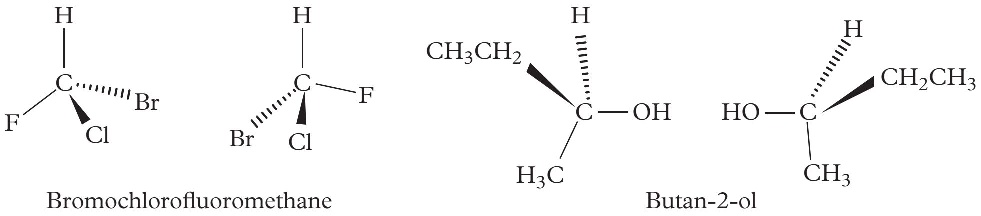


FIGURE 3 The enantiomers of bromochlorofluoromethane and butan-2-ol

Left and right hands are enantiomers because they are mirror images of each other and cannot be superimposed. Ears, feet, and bird and butterfly wings (Figure 4) are also enantiomers.

FIGURE 4 These butterfly wings are mirror images of each other.

CASE STUDY 9.4

Thalidomide isomer tragedy

Thalidomide was a pharmaceutical drug that was first synthesised in 1954 by German chemical manufacturer Chemie Grünenthal. Preliminary laboratory and animal testing in 1956 showed promise as a sedative due to its low toxicity and lack of harmful side effects. Human trials showed that healthy adults and children, as well as people suffering from insomnia and mental illnesses, found the sedative useful and experienced minimal side effects.

Thalidomide entered the pharmaceutical market in late 1956 as a treatment for the common flu, and this quickly expanded to include treatments for stress and anxiety, and nausea during pregnancy. Thalidomide was widely used to treat first trimester morning sickness in Australia, Europe and Japan, but was never approved in the US because of their Food and Drug Administration.

In early 1959, the first reports of patients suffering numbness in their hands and feet appeared. By 1960, there were growing reports of deformities in newborn babies. The diverse physical abnormalities affected the children's arms, hands, legs, feet and internal organs. By late 1961, thalidomide had been removed from the market. However, approximately 10 000 children worldwide had been born with phocomelia (malformed limbs). The effects of thalidomide in embryos and foetuses are thought to be due to the inhibition of new blood vessel development.

FIGURE 5 Thalidomide causes babies to be born with malformed limbs.

Thalidomide exists as a mixture of two enantiomers (Figure 6). One isomer (with the dashed wedge-shape bonds) has sedative effects and the other isomer (with the solid wedge-shaped bond has teratogenic effects (causes birth defects). Even if a pure sample of the non-toxic enantiomer is administered, the body can convert it into the opposite, toxic, enantiomer.

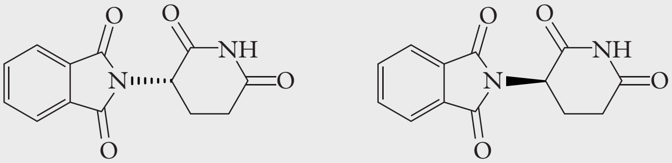


FIGURE 6 The enantiomers of thalidomide

Thalidomide is now used to treat rare conditions such as leprosy and blood cancer multiple myeloma. However, the renewed use of thalidomide is controversial.

CHALLENGE 9.4

Alkane structural isomers

There is no limit for the number of carbon atoms present in alkane molecular formulas. This means, there can be a large number of structural isomers for alkanes with a high number of carbon atoms. Identify the three alkanes that have only one structural isomer. Identify two alkanes that have over 1000 different structural isomers.

CHECK YOUR LEARNING 9.4

Describe and explain

1 **Describe** the term ‘geometrical isomer’.

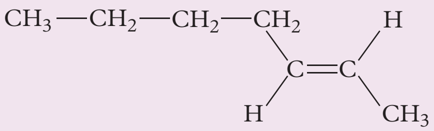
2 **Explain** the role that chirality has in stereoisomers.

Apply, analyse and interpret

3 **Deduce** the structural isomers of C_5H_{12}. **Sketch** and name each of them.

4 **Apply** IUPAC rules to name the following isomers.

a



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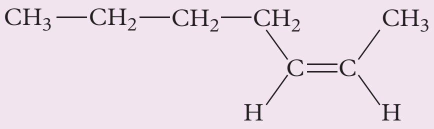


Investigate, evaluate and communicate

5 **Construct** the two geometrical isomers of pent-2-ene.

6 **Evaluate** whether the following pairs of molecules are isomers. If they are, identify the type of isomer by drawing the structures. (**Note:** A pair of molecules may be more than one type of isomer.)

- **a** Pentane and cyclopentane
- **b** 2-Methylbutane and pent-2-ene
- **c** 2-Fluorobutan-2-ol and 3-fluorobutan-2-ol

You can find the following resources for this section on your obook assess:

- » **Student book questions** 9.4 Check your learning
- » **Mandatory practical** 9.4 Modelling isomers of organic molecules
- » **Challenge** 9.4 Alkane structural isomers
- » **Weblink** Thalidomide

9.5 Physical properties of organic compounds

KEY IDEAS

In this section, you will learn about:

- trends in homologous series and the melting and boiling points of many classes of organic compounds
- how the structure of functional groups affects the properties of organic compounds, including melting and boiling points, and solubility in water and organic solvents.

Organic compounds have characteristic physical properties that depend on the atoms present and their arrangement within the compound. Such properties include melting point, boiling point, and solubility in water and organic solvents.

Homologous series

homologous series
a group of organic compounds with the same functional group but a different number of carbon atoms in the main chain

A **homologous series** is a group of organic compounds that have the same functional group, but increase by one carbon atom. The alkanes are an example of a homologous series and the first four members are methane, ethane, propane and butane.

With an increase by one carbon atom (and two hydrogen atoms), the molecular mass of the members of each homologous series increases by approximately 14 amu. As a result, there are more electrons available for intermolecular attraction within the molecule, and the increased attraction causes a slight increase in the melting and boiling points because the molecules are able to resist phase changes in higher temperatures. Table 1 lists the melting and boiling points of the first four members of the alkane homologous series.

TABLE 1 Physical properties of the alkane homologous series

Alkane	Melting point (°C)	Boiling point (°C)
Methane	–183	–161
Ethane	–172	–89
Propane	–188	–42
Butane	–135	–1

With the exception of propane, an increase in the number of carbon atoms causes an increase in the melting and boiling points, compared with other members of the same homologous series.

Hydrocarbons

Hydrocarbons have the lowest melting and boiling points of all organic compounds because they contain only carbon and hydrogen atoms joined by non-polar bonds. The attraction between non-polar molecules involves weak dispersion forces, so the molecules can separate easily and progress through phase changes.

Alkanes and alkenes are similar, but alkynes have a slightly higher boiling point (Table 2). Branched alkanes tend to have lower boiling points than their straight-chained equivalents.

This is because the reduced surface area of their molecular shape affects the dispersion forces and how close surrounding molecules can pack together. This is not always the case for melting point though.

TABLE 2 The boiling points of some hydrocarbons

Alkane	Boiling point (°C)	Alkene	Boiling point (°C)	Alkyne	Boiling point (°C)
Methane	–161				
Ethane	–89	Ethene	–104	Ethyne	–82
Propane	–42	Propene	–47	Propyne	–23
Butane	–1	But-1-ene	–6	But-1-yne	9
Pentane	36	Pent-1-ene	30	Pent-1-yne	40

These non-polar hydrocarbons are insoluble in water because of its polar nature, but they are soluble in non-polar organic solvents, such as benzene and dichloromethane.

CHALLENGE 9.5

Boiling points of hydrocarbons

Construct a graph of the boiling points of the first five alkanes, first four alkenes and first four alkynes. Identify the different trends in the data and discuss why the boiling points change between the different hydrocarbons.

Alcohols

Alcohols, containing a hydroxyl functional group, can take part in hydrogen bonding, both with other alcohol molecules and with water. The strongest of the intermolecular forces, hydrogen bonding is the result of the polar bonds between carbon and oxygen, and between oxygen and hydrogen (Figure 1).

The melting and boiling points of alcohols are significantly higher than those hydrocarbons, and somewhat higher than other organic compounds such as aldehydes, ketones, haloalkanes and amines. Some alcohols, such as methanol and ethanol, are relatively **volatile**, but volatility decreases as the alcohols increase in size through the homologous series.

volatile
evaporates easily at room temperature

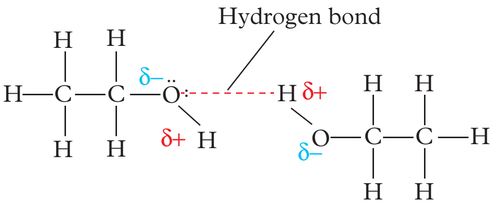


FIGURE 1 Hydrogen bonding between alcohol molecules

Table 3, on the next page, lists the boiling points of some alcohols. You can see that alcohols with two hydroxyl (diols) or three (triols) hydroxyl groups have higher boiling points than alcohols with a single hydroxyl group. This is because more hydrogen bonding takes place in diols and triols. For example, the boiling point of propan-1-ol is 97°C, whereas the boiling point of propane-1,2,3-triol is 290°C.

TABLE 3 The boiling points of some alcohols

Alcohol	Boiling point (°C)
Methanol	65
Ethan-1-ol	78
Propan-1-ol	97
Butan-1-ol	117
Pentan-1-ol	138
Ethane-1,2-diol	198
Propane-1,2,3-triol	290

Alcohols are soluble in organic solvents. As the number of carbon atoms in the alcohol increases, the polar end of the molecule becomes proportionally smaller and insignificant compared with the remaining non-polar part of the molecule. For this reason, the solubility in water decreases rapidly once alcohols have three or more carbons.

Aldehydes and ketones

Aldehydes and ketones contain a carbonyl functional group that can form hydrogen bonds with water (between the hydrogen of the water and the carbonyl oxygen atom) (Figure 2). Hydrogen bonds do not form between aldehyde molecules or between ketone molecules because there is no hydroxyl functional group. As with the alcohol homologous series, the first three members of the homologous series of ketones and aldehydes are **miscible** in water. Aldehydes and ketones are also soluble in non-polar organic solvents.

miscible
completely soluble

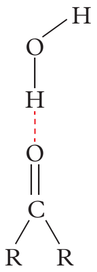


FIGURE 2 Hydrogen bonding between a ketone and water

Table 4 lists the boiling points of some aldehydes and ketones. The boiling and melting points of aldehydes and ketones are lower than those of the corresponding alcohols due to lack of hydroxyl functional group (which means they are more volatile than alcohols). The boiling and melting points are higher than for the corresponding hydrocarbons because the aldehydes and ketones can experience dipole–dipole interactions with other aldehydes and ketones. There is very little difference between the physical properties of aldehydes and ketones.

TABLE 4 Boiling points of some aldehydes and ketones

Aldehyde	Boiling point (°C)	Ketone	Boiling point (°C)
Methanal	–21		
Ethanal	20		
Propanal	49	Propanone	56
Butanal	76	Butan-2-one	80
Pentanal	103	Pentan-2-one	102
		Pentan-3-one	102

Carboxylic acids

The carbonyl and hydroxyl of the carboxyl functional group can both participate in hydrogen bonding (Figure 3). For this reason, carboxylic acids have higher boiling points (Table 5) and melting points than the corresponding alcohols (and most other organic compounds). However, the smaller carboxylic acids are volatile.

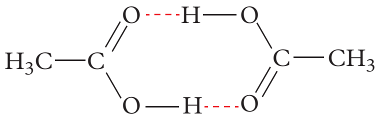


FIGURE 3 Hydrogen bonding between carboxylic acid molecules

The first four members of the carboxylic acid homologous series are polar, and so they are completely miscible in water, whereas the four-carbon alcohol is only partially soluble in water. Most carboxylic acids dissolve in organic solvents such as ethanol or acetone.

TABLE 5 The boiling points of some carboxylic acids

Carboxylic acid	Boiling point (°C)
Methanoic acid	101
Ethanoic acid	118
Propanoic acid	141
Butanoic acid	164
Pentanoic acid	186

Esters

The carbonyl and **alkoxy** functional group of esters have polar bonds between the carbon and oxygen atoms. Esters can form hydrogen bonds with water, and the first three members of the homologous series are soluble in water. Because esters do not have a hydroxyl group, many of their physical properties are similar to those of aldehydes and ketones, including the ability to dissolve in non-polar organic solvents. Table 6 lists some boiling points of esters.

alkoxy
a functional group containing an oxygen atom with a single bond to the main chain

TABLE 6 The boiling points of some esters

Ester	Boiling point (°C)
Methyl methanoate	32
Methyl ethanoate	57
Methyl propanoate	80
Ethyl methanoate	54
Ethyl ethanoate	77

FIGURE 4 Esters have a strong fruity fragrance.

Amines

The properties of an amine depend on the type of amine that it is. Primary and secondary amines have comparable boiling and melting points to those of aldehydes and ketones because the nitrogen and hydrogen atoms on the amine functional group can participate in hydrogen bonding. Primary amines can form more hydrogen bonds than secondary amines so they have slightly higher boiling and melting points. Tertiary amines have lower melting and boiling points, comparable with the hydrocarbons, because they contain only N–C bonds that contribute to dispersion forces.

All amines have comparable solubility in water to those of aldehydes and ketones, because of the possibility of hydrogen bonding between water and the amine functional group. However, beyond the fourth member of the homologous series, the miscibility of amines in water drops off significantly. Their solubility in organic solvents depends on the polarity of both the amine and the organic solvent.

Amides

Amides have the highest melting and boiling points of any organic compound because they can form both hydrogen bonds and participate in very strong dipole–dipole interactions characteristic of amides. The non-bonding pair of electrons on the nitrogen atom interacts with the oxygen atom to create positive and negative charges within the molecule, and a strong intermolecular attraction in addition to hydrogen bonding.

The properties of an amide depend on whether it is a primary, secondary or tertiary amide, in a similar way to amines. Tertiary amides do not have hydrogen bonding, just the strong dipole–dipole interaction. Primary and secondary amides have both. The solubility of amides in water is slightly higher than that of carboxylic acids in water.

Table 7 lists the boiling points of some amines and amides.

TABLE 7 The boiling points of some amines and amides

Amine	Boiling point (°C)	Amide	Boiling point (°C)
Trimethylamine	3	Ethanamide	221
N-Methylethylamine	36	*N*-Methylethanamide	204
Propylamine	47	*N*,*N*-Dimethylethanamide	165
Triethylamine	89		

Halogens

As the atomic mass of halogens increases (going down Group 7 in the periodic table) and their atomic radii get larger, their volatility decreases. This is because of the increasing number of electrons causing greater intermolecular attraction, which gives halogens a greater ability to resist phase changes.

Haloalkanes are generally liquids at room temperature, having higher boiling points than many of their individual alkane and halogen counterparts.

The volatility of haloalkanes follows the trend with atomic mass: R-I has a higher boiling point than that of R-Br, R-Cl and R-F. Also, as the size of the alkyl group increases, volatility decreases.

FIGURE 5 The halogen fluorine is a compound used to strengthen teeth

CHECK YOUR LEARNING 9.5

Describe and explain

1 **Describe** the term ‘homologous series’.

2 **Explain** the role of intermolecular forces in determining the physical properties of organic compounds.

3 **Describe** the term ‘volatile’.

4 **Describe** the term ‘non-polar solvent’. Explain why some organic compounds dissolve in non-polar solvent rather than in water.

5 **Describe** the term ‘miscible’.

Apply, analyse and interpret

6 **Analyse** the data from Table 8 from page 238 (repeated below) to **predict** the boiling point of pentane.

TABLE 8 Physical properties of the alkane homologous series

Alkane	Melting point (°C)	Boiling point (°C)
Methane	–183	–161
Ethane	–172	–89
Propane	–188	–42
Butane	–135	–1

7 **Analyse** the data in the graph in Figure 6, and **discuss** the significance of the trendlines with respect to the functional groups present in each of the organic compounds.

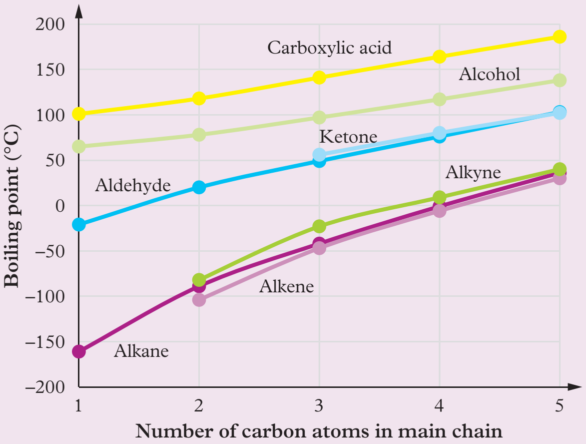


FIGURE 6 The boiling points of various organic compounds

Investigate, evaluate and communicate

8 **Investigate** the properties of ethylene glycol and its effects on the properties of water.

9 **Evaluate** the significance of hydrophobicity in members of a homologous series.

You can find the following resources for this section on your obook assess:

- » Student book questions
  9.5 Check your learning
- » Challenge
  9.5 Boiling points of hydrocarbons
- » Weblink
  Esters
- » Weblink
  Halides

SCIENCE AS A HUMAN ENDEAVOUR

9.6

Developments in biotechnology

KEY IDEAS

In this section, you will learn about:

- types of biological data available in protein data banks around the world
- the role of biological data in biotechnology
- recent developments in biotechnology.

Biotechnology is the use and manipulation of biological processes to develop new medicines, genetically modified plants, biofuels, textiles and sustainable food. An early form of biotechnology has been used in agriculture for at least 10 000 years. This involves selecting crops with the most desirable traits (such as taste, yield and resistance to disease and insects) and collecting the seeds to sow next season. Alternatively, a desirable species can be cross-pollinated with another species to produce a hybrid that has the best characteristics of each.

Bananas, strawberries and corn are crops that have been bred in his way. Selective breeding (or **artificial selection**) has also been used with animals. In this way, the many domestic dog breeds all originated from the wolf. Artificial selection has also increased the productivity of dairy cows and egg-laying hens, and increased the muscle mass of Belgium blue beef cattle (Figure 1).

artificial selection
the control of breeding of plants and animals to produce characteristics favourable to humans

Bioinformatics is a subcategory of modern biotechnology that focuses on analysing biological data using computational techniques. The result has been a rapid increase in the rate of progress made in the biotechnological field. The biological data can include sequences of **genes**, entire **genomes**, **amino acid** sequences in proteins, and three-dimensional structures of proteins by themselves or bonded in protein–**nucleic acid** complexes.

FIGURE 1 Belgian blue cattle have been selectively bred to produce desirable characteristics such as size.

gene
a segment of DNA on a chromosome

genome
all the DNA in a person's set of chromosomes

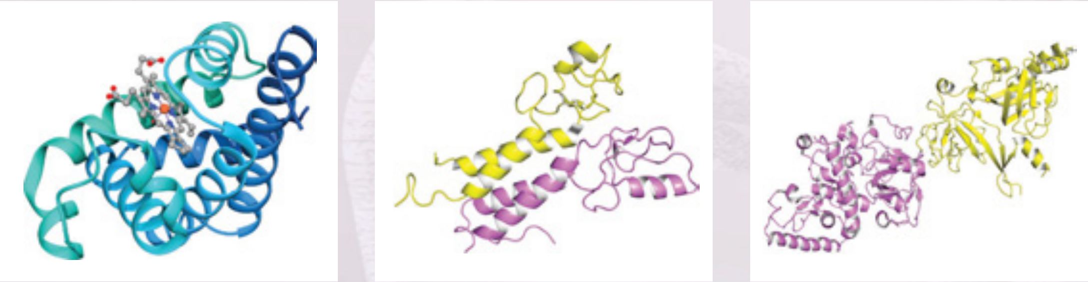
amino acid
an organic compound that contains an amino and a carboxyl functional group

nucleic acid
DNA or RNA

Data banks store the genetic sequences and three-dimensional structural data produced from scientific research and genome projects around the world. This data is available for public access. The world-wide Protein Data Bank (wwPDB) is a major database that you can search by using keywords, such as the name of a protein or a particular gene sequence. Scientists have developed algorithms to extrapolate the experimental data and predict the three-dimensional structure that a given amino acid sequence would generate.

Biological data such as genomic sequences are also used to link particular genes to particular diseases. The protein data bank includes the structures of the BRCA1 and BRCA2 genes that are associated with a high risk of breast and ovarian cancer (Figure 2). In the USA, scientists studied the Ashkenazi Jewish population in Washington DC because they had a high incidence of breast cancer. Volunteers had their genome sequenced, using blood from a finger-prick, and it was found that 5000 volunteers had alterations to their BRCA genes.

These gene alterations may cause a protein to be shortened, changing its three-dimensional structure and inhibiting its normal cell function. However, this is yet to be confirmed. People with a family history of breast cancer can be screened for these gene alterations, using a simple blood test to sequence their genome.



Chromosone 17 BRCA1 BRCA2

FIGURE 2 This three-dimensional structure of a protein complexed with a small molecule is available in the Protein Data Bank.

Pharmacogenomics is a relatively new field of biotechnology that analyses a person's genomic sequence to provide them with an individualised treatment, rather than the traditional 'one size fits all' approach. In the traditional approach, doctors use trial and error to prescribe different available medications until they find one that has suitable levels of **toxicity** and **efficacy** for the patient. The pharmacogenomics approach analyses the patient's genome to determine which medication would suit them best, and in what concentration. Pharmacogenomics is currently being used for some HIV, colon cancer, lymphoblastic leukemia and breast cancer patients, and is expected to expand to the treatment of heart disease, other cancers, asthma and depression in the near future.

toxicity
the degree to which a medicine causes adverse side effects

efficacy
the ability of a medication to produce the desired result

CHECK YOUR LEARNING 9.6

Describe and explain

1 **Describe** the term 'artificial selection'.

Investigate, evaluate and communicate

2 **Investigate** the role of biotechnology in the development of new and improved biofuels and textiles.

3 X-ray diffraction, nuclear magnetic resonance and electron microscopy are used to determine the three-dimensional structures of biological molecules. **Investigate** the usefulness of these methods in terms of quality of results, ease of use, and any limitations they encounter.

You can find the following resources for this section on your obook assess:

- » Student book questions
  9.6 Check your learning
- » Weblink
  Bioinformatics
- » Weblink
  Pharmacogenomics

CHAPTER 9

Review

Chapter summary

9.1
- Hydrocarbons are the simplest of the organic compounds, containing only carbon and hydrogen atoms. The nomenclature of hydrocarbons depends on the number of carbon atoms in the main chain, the presence of multiple bonds, whether the hydrocarbon is cyclic or non-cyclic, and what substituents are present. Locants identify where the multiple bonds and substituents are in the hydrocarbon.

9.2
- Organic compounds containing oxygen atoms include alcohols, aldehydes, ketones, carboxylic acids and esters. Alcohols can be classified as primary, secondary or tertiary depending on the number of adjacent carbon bonds.
- Organic compounds containing nitrogen atoms include amines, amides and nitriles. Amines are classified according to the number of carbon atoms directly bonded to the nitrogen.
- Organic compounds containing halogen atoms are haloalkanes. The halogen is always treated as a substituent, rather than the principal functional group.
- Organic compounds can contain more than one functional group.

9.3
- Structural formulas represent the atom arrangement and bonding of organic compounds. Extended structural formulas provide all of this information, but condensed structural formulas provide information about the atom arrangement only.
- Line structural formulas provide information about the bonding and limited information about the atom arrangement.

9.4
- Structural isomers have the same molecular formula but different atom arrangement and molecular names.
- Stereoisomers have the same structural formula but different atom spatial arrangement. Stereoisomers can be further classified into geometrical isomers and enantiomers.

9.5
- Members of a homologous series have the same functional group but vary in the size of the main chain. As the main chain increases in size, the melting and boiling points of organic compounds increases.

9.6
- Biological data includes DNA sequences of genes or entire genomes, amino acid sequences of proteins, and three-dimensional structures of proteins by themselves, or bonded in protein–nucleic acid complexes.
- The study of functional group interactions within biological molecules has been enabled from the breadth of biological data available to the public. Many developments are taking place in biotechnology, including the synthesis of new medications, identification of links between disease and a person's genome, and the personalisation of medical treatments.

Key terms

- alcohol
- aldehyde
- alkane
- alkene
- alkoxy
- alkyl group
- alkyne
- amide
- amine
- amino acid
- artificial selection
- carbonyl
- carboxyl
- carboxylic acid
- cyclic
- efficacy
- enantiomers
- ester
- functional group
- gene
- genome
- geometrical isomers
- haloalkane
- homologous series
- hydrocarbon
- hydroxyl
- ketone
- locant
- main chain
- miscible
- multiple bond
- multiplier
- nitrile
- nomenclature
- non-cyclic
- nucleic acid
- prefix
- primary alcohol
- secondary alcohol
- stereoisomers
- structural formula
- structural isomers
- substituent
- suffix
- tertiary alcohol
- toxicity
- volatile

Revision questions

The relative difficulty of these questions is indicated by the number of stars beside each question number: ★ = low; ★★ = medium; ★★★ = high.

Multiple choice

1 An alkene is best described as a hydrocarbon consisting of:

A only single carbon bonds
B only double carbon bonds
C one or more double carbon bonds
D one or more triple carbon bonds.

2 A functional group is best described as a group of atoms that:

A are easily recognisable in an organic compound
B is the location of reactivity in an organic compound
C contains only atoms other than carbon and hydrogen
D has names such as ester, amide and aldehyde.

3 A condensed structural formula provides information about:

A only the bonding between the atoms
B the bonding and atom arrangement
C only the atom arrangement
D only the number of atoms.

4 The physical properties of organic compounds include:

A how toxic an organic compound is to the environment
B the stability and reactivity of the organic compound
C which atoms and bonds are present in the molecule
D melting points, boiling points and solubility.

5 Biotechnology is best defined as the:

A use and manipulation of biological processes
B study of interactions between proteins and nucleic acids
C application of biological data using computational techniques
D sequencing of a person's genome to individualise their treatment.

6 An amine is best described as an organic compound containing a nitrogen atom:

A attached to alkyl groups and hydrogens
B attached to carbonyl groups and hydrogens

C triple bonded to a carbon
D triple bonded to an oxygen.

7 A six-carbon hydrocarbon is called:
A ethane
B butane
C hexane
D octane.

8 'Stereoisomers' is a general term used to describe:
A enantiomers and structural isomers
B enantiomers and geometric isomers
C enantiomers and chiral centre isomers
D structural and geometric isomers.

9 A compound containing a carbon with a double bond to an oxygen could be:
A an alcohol or an amine
B an alcohol or a ketone
C an amine or an ester
D a ketone or an ester.

10 The type of structural formula that shows the bonds between carbons (and their surrounding hydrogens) in a hydrocarbon is known as:
A extended
B condensed
C line
D basic.

Short answer

Describe and explain

★ 11 **Describe** the structure of the carboxyl functional group.

★ 12 **Define** the three types of alcohols, and explain the effect of the type of alcohol on its reactivity.

★ 13 **Describe** the term 'structural isomer'.

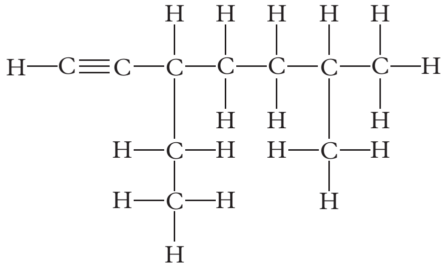
★ 14 **Explain** how geometrical isomers and enantiomers are both classified as stereoisomers.

★ 15 **Explain** the trends present within members of a homologous series.

★ 16 **Explain** why the term 'alk' is used in organic chemistry.

★★ 17 **Identify** the functional groups in the following organic compounds.

a



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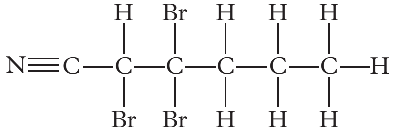

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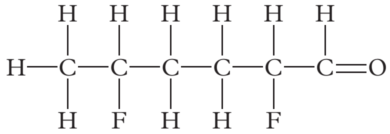
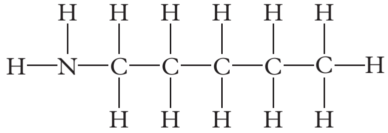
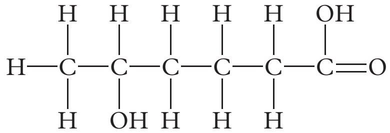


d



e



★★ 18 **Construct** the sixth alkane in the homologous series.

★★★ 19 **Construct** the two geometrical isomers of 2,3-dichlorobut-2-ene.

★★★ 20 **Construct** the following molecules as extended structural formula – cyclohexanone, 2,3,3-trichlorobutanoic acid, and *N*-pentylpropanamide.

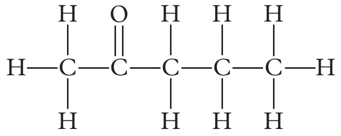
★★★ 21 **Calculate** the gradient and *y*-intercept for the mathematical relationship represented by the data in Table 1 on page 238.

★★★ 22 **Identify** the functional group in the following organic compounds and draw diagrams.
a 1-Ethyl-3,3-dimethylpropylcyclopentane
b 2,3,4-Trihydroxyoctanal

★★ **23** **Construct** diagrams of the molecules hexyl methanoate and *N*-ethyloctanamine.

Apply, analyse and interpret

★ **24** **Apply** IUPAC rules to name the organic compound.



$$\mathrm{H{-}\underset{H}{\overset{H}{C}}{-}\overset{O}{\overset{\|}{C}}{-}\underset{H}{\overset{H}{C}}{-}\underset{H}{\overset{H}{C}}{-}\underset{H}{\overset{H}{C}}{-}H}$$

★★ **25** **Deduce** the extended and condensed structural formulas of 3-methylbut-1-yne.

★★ **26** **Apply** IUPAC rules to name the hydrocarbons in question 19.

★★ **27** **Deduce** the structural isomers of C_6H_{14}. **Sketch** and name each of them.

★★★ **28** **Analyse** the diagram of two enantiomeric forms of a drug in Figure 1 by considering their ability to interact with the drug binding site. Components a and b of the drug binding site are hydrophobic and component c is hydrophilic.

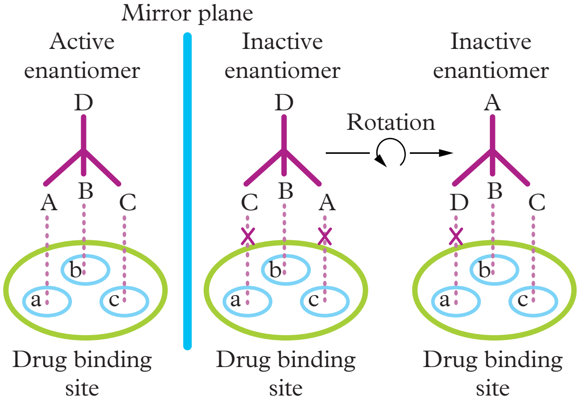


FIGURE 1 Two enantiomers of a drug

Investigate, evaluate and communicate

★★★ **29** The most volatile hydrohalide is HCl, followed by HBr, HI and finally HF. **Evaluate** the role that hydrogen bonding has in making HF the least volatile hydrohalide.

★★★ **30** **Evaluate** the name of 4-oxo-3,3-methylpentan-2-ol to discuss what errors have been made and suggest how they should be fixed.

★★★ **31** An algebraic expression of the alkane class of organic compounds is represented as C_nH_{2n+2}, where *n* is any number.

a **Investigate** the algebraic expressions used to represent the alkene, alkyne, alcohol and carboxyl classes of organic compounds.

b **Evaluate** the effectiveness of these algebraic expressions in terms of more complex organic compounds such as polysubstituted diols and biological molecules.

★★★ **32** **Evaluate** the names of the following organic compounds to **discuss** the errors made and suggest how they should be fixed:

a 3-methylbut-2-yne
b 2,3-dimethyl-4-ethylnonane
c butan-1-one
d 2-ethyl-2-methylhexane
e 2-oxobutane-1,3-diol
f 2-propyl-3-bromo-4-ethyl-5-fluoro-6-methyl-cyclohexan-1-ol.

You can find the following resources for this section on your obook assess:

- Student book questions
  Chapter 9 Revision questions
- Revision notes
  Chapter 9
- assess quiz
  Auto-correcting mutiple-choice quiz
- Flashcard glossary
  Chapter 9

CHAPTER 10

Organic reactions and reaction pathways

Organic reactions involve breaking strong covalent bonds. This often requires the input of energy, such as heat or UV radiation, or catalysis in the form of specific chemicals. Common reactions include addition, elimination, oxidation, reduction, condensation and substitution (of which there are many subcategories). Organic reactions are happening constantly and all around us, not just in the laboratory. They are involved with the production of cellulose in plants and DNA in cells and in the biochemical pathways that take place within our bodies.

OBJECTIVES

- → Appreciate that each class of organic compound displays characteristic chemical properties and undergoes specific reactions based on the functional group present; these reactions, including acid-base and oxidation reactions, can be used to identify the class of the organic compound.
- → Understand that saturated compounds contain single bonds only and undergo substitution reactions, and that unsaturated compounds contain double or triple bonds and undergo addition reactions.
- → Determine the primary, secondary and tertiary carbon atoms in halogenoalkanes and alcohols and apply IUPAC rules of nomenclature.
- → Describe, using equations: oxidation reactions of alcohols and the complete combustion of alkanes and alcohols substitution reactions of alkanes with halogens substitution reactions of haloalkanes with halogens, sodium hydroxide, ammonia and potassium cyanide addition reactions of alkenes with water, halogens and hydrogen halides addition reactions of alkenes to form poly(alkenes).
- → Recall the acid–base properties of carboxylic acids and explain, using equations, that esterification is a reversible reaction between an alcohol and a carboxylic acid.
- → Recognise the acid–base properties of amines and explain, using equations, the reaction with carboxylic acids to form amides.
- → Recognise reduction reactions and explain, using equations, the reaction of nitriles to form amines and alkenes to form alkanes.

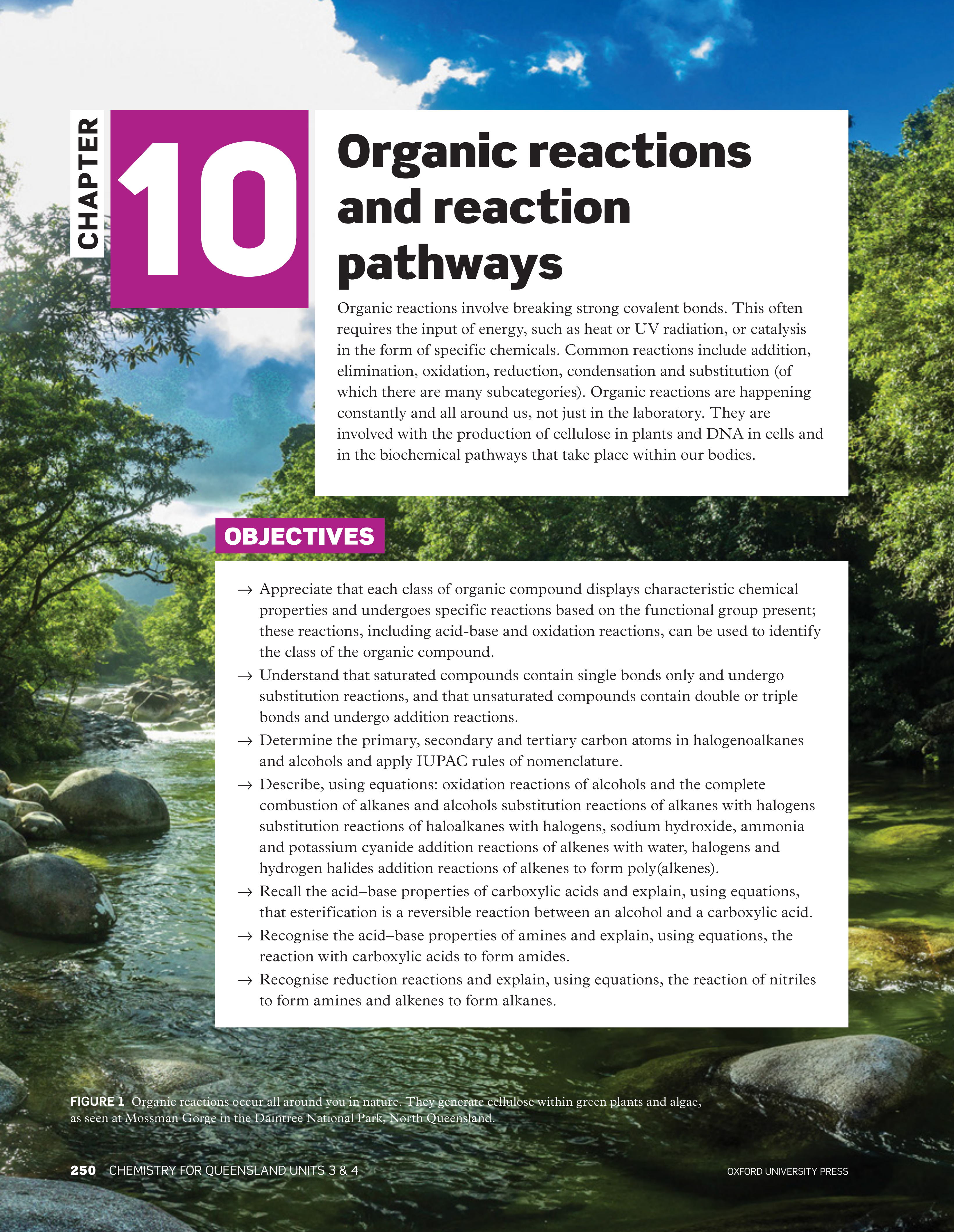


FIGURE 1 Organic reactions occur all around you in nature. They generate cellulose within green plants and algae, as seen at Mossman Gorge in the Daintree National Park, North Queensland.

- → Recognise and explain, using equations, that: esters and amides are formed by condensation reactions elimination reactions can produce unsaturated molecule and explain, using equations, the reaction of haloalkanes to form alkenes.
- → Understand that organic reactions can be identified using characteristic observations and recall tests to distinguish between: alkanes and alkenes using bromine water primary, secondary and tertiary alcohols using acidified potassium dichromate(VI) and potassium manganate(VII).
- → Understand that the synthesis of organic compounds often involves constructing reaction pathways that may include more than one chemical reaction.
- → Deduce reaction pathways, including reagents, condition and chemical equations, given the starting materials and the product.

Source: *Chemistry 2019 v 1.3 General Senior Syllabus* © Queensland Curriculum & Assessment Authority

PRACTICALS

SUGGESTED PRACTICAL	**10.1** Bromination of unsaturated hydrocarbons
SUGGESTED PRACTICAL	**10.2** Oxidation of alcohols

10.1 Addition and elimination reactions

KEY IDEAS

In this section, you will learn about:

- addition and elimination reactions, which use chemical reagents to change the level of saturation of an organic compound
- identifying alkanes and alkenes through the use of halogenation reactions as chemical tests
- Markovnikov's rule, which refers to the general trends seen by the hydrohalogenation or hydration of asymmetrical alkenes.

Addition reactions

addition the addition of substituents across a carbon–carbon multiple bond

Addition reactions occur when atoms add across a double or triple bond in an unsaturated hydrocarbon. A multiple bond breaks as two substituents are added from the chemical reagent used in the reaction.

Hydrogenation

hydrogenation the addition of hydrogen across a multiple bond

Hydrogenation is the addition of hydrogen (H_2) across a double or triple bond. Heat is not required, but a metal catalyst is. The catalyst can be in the form of finely divided platinum, palladium or nickel. A hydrogenation reaction adds one hydrogen atom onto each carbon atom of the multiple bond. When writing the chemical equation for the hydrogenation reaction, you must include the catalyst on top of the arrow (Figure 1).

Study tip

To refresh your understanding of saturated hydrocarbons, which have only single carbon–carbon bonds, see Section 9.1. Unsaturated hydrocarbons contain double or triple bonds between carbon atoms.

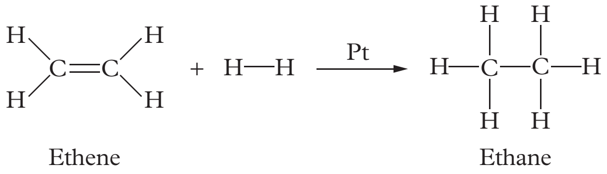


FIGURE 1 Hydrogenation of ethene with a platinum catalyst forms ethane.

Halogenation

halogenation the addition of a halogen across a multiple bond

Halogenation is the addition of a halogen (Br_2 or Cl_2) across a double or triple bond. This reaction does not require heat or catalysts (Figure 2).

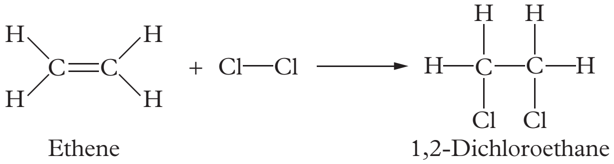


FIGURE 2 Halogenation (chlorination) of ethene to produce dichloroethane does not require a catalyst.

SUGGESTED PRACTICAL
10.1 Bromination of unsaturated hydrocarbons
Go to your obook assess »

Chemical tests to distinguish alkanes and alkenes

The addition of bromine (either dissolved in water or as a 1% solution in carbon tetrachloride (CCl_4)) is used as a chemical test to distinguish whether a hydrocarbon is saturated or unsaturated. The bromine reagent is a bright orange colour (Figure 3). This colour disappears as bromine reacts and adds across a multiple bond, indicating that the hydrocarbon is unsaturated (contains double or triple bonds). If the orange colour does not disappear, then this indicates that the hydrocarbon is saturated (it is an alkane) and will not undergo an addition reaction.

FIGURE 3 Bromine water is a bright orange colour. If bromine reacts with an unsaturated hydrocarbon, the colour disappears.

Hydrohalogenation

Hydrohalogenation is the addition of a hydrohalide (HBr or HCl) across a double bond. Similar to the halogenation reaction, the hydrohalogenation does not require heat or catalysts.

Hydrohalides (e.g. HCl, HBr) are asymmetrical. If the unsaturated hydrocarbon is also asymmetrical, then different products can be formed. Vladimir Markovnikov was a Russian chemist who studied this reaction and discovered a trend (Figure 5). He found that when a hydrohalide adds across a double bond, the hydrogen atom in the hydrohalide bonds with the carbon with the most hydrogen atoms (typically the carbon atom on the end of the chain). The halogen in the hydrohalide bonds with the carbon with the least number of hydrogen atoms (typically the second carbon in the chain) (Figure 4). This has become known as Markovnikov's rule.

hydro-halogenation
the addition of a hydrogen atom and a halogen atom across a double bond

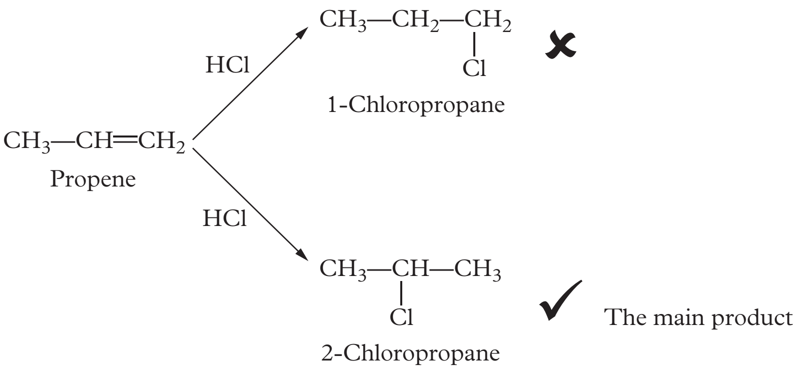


FIGURE 4 The hydrohalogenation of propene. According to Markovnikov's rule, when HCl adds across the double bond, hydrogen adds to the carbon with the most hydrogens and chlorine adds to the carbon with the least hydrogens.

FIGURE 5 Vladimir Markovnikov, the Russian chemist who devised Markovnikov's rule

Note that hydrohalogenations do not always follow Markovnikov's rule. Usually a reaction produces about 90% of the Markovnikov product and 10% of the anti-Markovnikov product. The products then need to be separated and the different compounds purified.

Hydration

Hydration is the addition of water across a double bond. The two substituents that add to the double bond are a hydrogen atom and a hydroxyl group. This reaction produces an alcohol.

hydration
the addition of water across a double bond

Hydration reactions require high temperatures (>100°C), high pressures and a catalyst in the form of trace amounts of a strong acid such as hydrochloric acid, sulfuric acid or phosphoric acid. The hydration of ethene to produce ethanol, using phosphoric acid as a catalyst at 300°C and 60 atm, is shown in Figure 6 on the next page.

Study tip

Use the analogy 'the rich get richer' to help remember that Markovnikov's rule states that the hydrogen atom will go to the carbon with the most hydrogen atoms.

polymerisation
the successive addition reactions of alkene monomers to form a polymer

monomer
a single unit within a polymer

polymer
a large molecule made of many monomers

Study tip

It is important to write the reaction conditions on the chemical equation arrow.

elimination reaction
the removal of substituents to form a multiple bond

reflux
heating a reaction vessel with a vertical condenser attached to capture escaping gases and return them to the reaction vessel

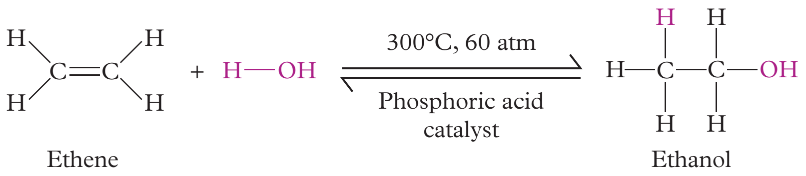


FIGURE 6 The hydration of ethene to produce ethanol requires high temperatures and pressures and a catalyst.

Polymerisation

Polymerisation is the successive addition reactions of alkene **monomers** to form a polymer. A catalyst is required to break the double bond and produce a long chain of carbon atoms. The initial hydrocarbon is the monomer. Hundreds of thousands of monomers link together to form the **polymer**. Polymers can be synthetic; for example, plastics, fibres and rubbers. Polymers are also found in nature; for example, carbohydrates, proteins and nucleic acids. Because polymers are so large, to draw them we use brackets and the symbol *n* to represent the number of repeating monomers (Figure 7).

Polymerisation is a self-addition reaction. This means that if other reagents were present, the polymerisation reaction would be prevented from taking place. The reactions require heat, high pressure and a catalyst that helps generate unpaired non-bonding electrons.

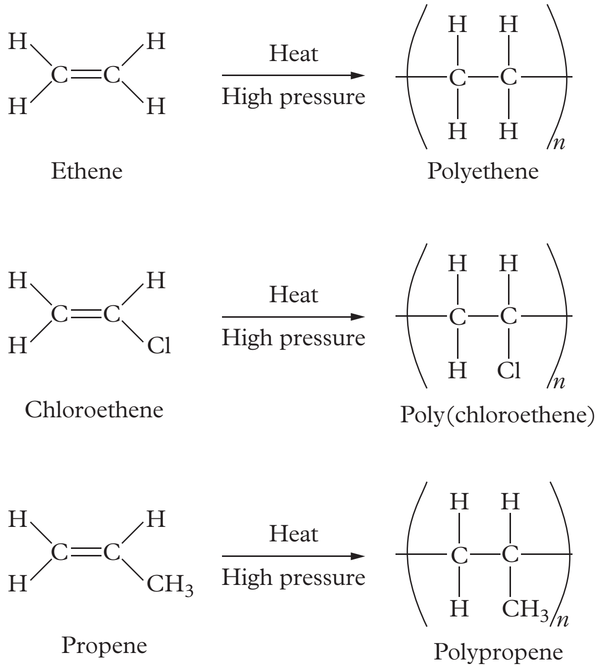


FIGURE 7 Polymerisation of several alkenes to form polyalkanes

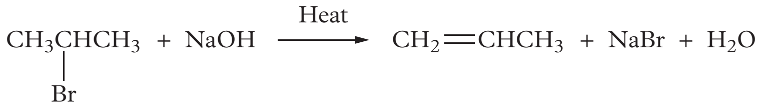
Elimination reactions

Elimination reactions involve the removal of substituents from two adjacent carbon atoms in a haloalkane to form a multiple bond. The reaction involves heating the haloalkane under **reflux** with a concentrated solution of either sodium hydroxide or potassium hydroxide in ethanol.

The type of haloalkane determines the type of reaction that takes place. Tertiary haloalkanes mostly undergo elimination reactions. However, secondary haloalkanes undergo a mixture of elimination reactions and substitution reactions. (Substitution reactions are discussed in section 10.4.) When using ethanol as a solvent, higher temperatures and higher concentrations of sodium hydroxide all favour the haloalkane undergoing an elimination reaction (Figure 8).

Study tip

To help remember the reactant and product characteristics, consider elimination reactions as being the opposite of addition reactions.



$$\mathrm{CH_3\underset{\underset{Br}{|}}{C}HCH_3 + NaOH \xrightarrow{Heat} CH_2{=}CHCH_3 + NaBr + H_2O}$$

2-Bromopropane Propene

FIGURE 8 The elimination of secondary haloalkane: 2-bromopropane reacts with sodium hydroxide to produce propene, sodium bromide and water.

CHECK YOUR LEARNING 10.1

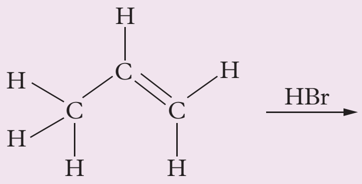
Describe and explain

1. **Explain** how the level of saturation of a hydrocarbon can be determined by chemical reactions.
2. **Describe** Markovnikov's rule and when it is applicable.
3. **Identify** the reagents and conditions required for:
   - **a** hydrogenation
   - **b** halogenation (for a bromo substituent)
   - **c** hydrohalogenation (for a chloro substituent)
   - **d** hydration.

Apply, analyse and interpret

4. **Determine** the balanced chemical equation for the addition reaction of oct-3-ene with:
   - **a** water
   - **b** fluorine gas
   - **c** hydrogen bromide.
5. **Determine** the balanced chemical equation for the:
   - **a** polymerisation of five monomers of ethene
   - **b** elimination reaction of 3-bromopentane.
6. **Interpret** the diagrams to **identify** the products formed.

a



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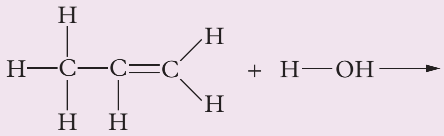
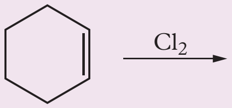


c



You can find the following resources for this section on your obook assess:

- Student book questions
  10.1 Check your learning
- Suggested practical
  10.1 Bromination of unsaturated hydrocarbons
- Weblink
  Markovnikov's rule

10.2

Oxidation and reduction reactions

KEY IDEAS

In this section, you will learn about:

- how organic compounds can participate in redox reactions, at the location of their functional group
- identifying primary, secondary and tertiary alcohols through the use of oxidation reactions as chemical tests.

Oxidation reactions

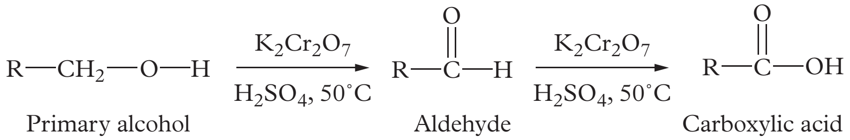
oxidation reaction
an organic reaction involving the gain of oxygen atoms and/or the loss of hydrogen atoms

reduction reaction
an organic reaction involving the loss of oxygen atoms and/or the gain of hydrogen atoms

Oxidation reactions can be defined as the loss of electrons, the loss of hydrogen atoms, or the gain of oxygen atoms. Oxidation reactions occur in conjunction with **reduction reactions**, which means that the reagent used is reduced during the reaction. Collectively, reduction and oxidation reactions are known as redox reactions.

Oxidation of primary alcohols

Primary alcohols are organic compounds that contain a hydroxyl functional group on the end of the carbon main chain. So, the molecule contains a $-CH_2OH$ group. Oxidation of a primary alcohol involves the loss of two hydrogen atoms to form an aldehyde. Further oxidation changes the aldehyde into a carboxylic acid, through the gain of an oxygen atom. Both stages of the oxidation reaction require a warm solution (50°C) with potassium dichromate ($K_2Cr_2O_7$) that has been acidified with sulfuric acid (H_2SO_4) (Figure 1).

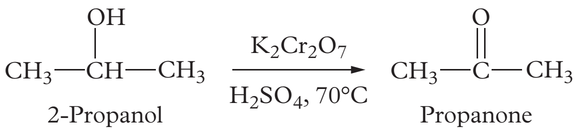


$$R-CH_2-O-H \xrightarrow[H_2SO_4,\ 50^\circ C]{K_2Cr_2O_7} R-\overset{\overset{\displaystyle O}{\|}}{C}-H \xrightarrow[H_2SO_4,\ 50^\circ C]{K_2Cr_2O_7} R-\overset{\overset{\displaystyle O}{\|}}{C}-OH$$

FIGURE 1 The oxidation of a primary alcohol to an aldehyde and then a carboxylic acid

Oxidation of secondary alcohols

Secondary alcohols contain a hydroxyl functional group in the middle of the carbon main chain. The molecule contains a $-CHROH$ group. Oxidation of a secondary alcohol involves the loss of two hydrogen atoms to form a ketone. The ketone cannot be further oxidised. The oxidation reaction requires a warm solution (70°C) with potassium dichromate ($K_2Cr_2O_7$) that has been acidified with sulfuric acid (H_2SO_4) (Figure 2).



$$CH_3-\overset{\overset{\displaystyle OH}{|}}{CH}-CH_3 \xrightarrow[H_2SO_4,\ 70^\circ C]{K_2Cr_2O_7} CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3$$

FIGURE 2 The oxidation of a secondary alcohol to a ketone: 2-propanol is oxidised to propanone

SUGGESTED PRACTICAL
10.2 Oxidation of alcohols
Go to your obook assess »

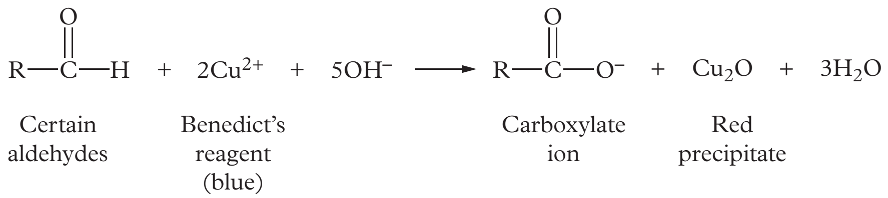
Chemical tests to distinguish primary, secondary and tertiary alcohols

Oxidation reactions that use colour-changing reagents can be followed by observing the change in colour. In this way, you can test whether an alcohol is a primary, secondary or tertiary alcohol. A tertiary alcohol (which contains a –CRR′OH group) cannot be oxidised because there are no hydrogen atoms available to lose. So, if there is no change in colour on adding an oxidising reagent, this indicates the presence of a tertiary alcohol.

Primary alcohols oxidise twice (to aldehydes and then carboxylic acids) and secondary alcohols oxidise once (to ketones). To distinguish between primary and secondary alcohols, you need to oxidise the alcohol to an aldehyde or ketone first. To decide if you have an aldehyde or a ketone, you need to test whether the compound can be further oxidised – an aldehyde will be oxidised to a carboxylic acid but a ketone will not be oxidised.

Oxidsing reagents that can be used to use to distinguish an aldehyde from a ketone include:

- potassium permanganate ($KMnO_4$) (a purple aqueous solution), which is reduced to manganese dioxide (MnO_2), a brown precipitate
- potassium dichromate ($K_2Cr_2O_7$) (an orange aqueous solution), which is reduced to Cr^{3+}, a green aqueous solution
- Benedict's solution – copper sulfate ($CuSO_4$) (blue), which is reduced to copper oxide (CuO), a bright red precipitate (Figure 3).



$$R{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}H + 2Cu^{2+} + 5OH^- \longrightarrow R{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}O^- + Cu_2O + 3H_2O$$

FIGURE 3 Using Benedict's solution to distinguish aldehydes from ketones. Aldehydes react to form carboxylic acids. Ketones do not react because they do not undergo further oxidation.

Oxidation of alkanes and alcohols by combustion

Alkanes and alcohols also undergo oxidation. **Complete combustion reactions** are oxidation reactions that involve the exothermic burning of a fuel in excess oxygen to produce carbon dioxide and water.

complete combustion reaction
the combustion reaction between a fuel and oxygen to produce carbon dioxide and water

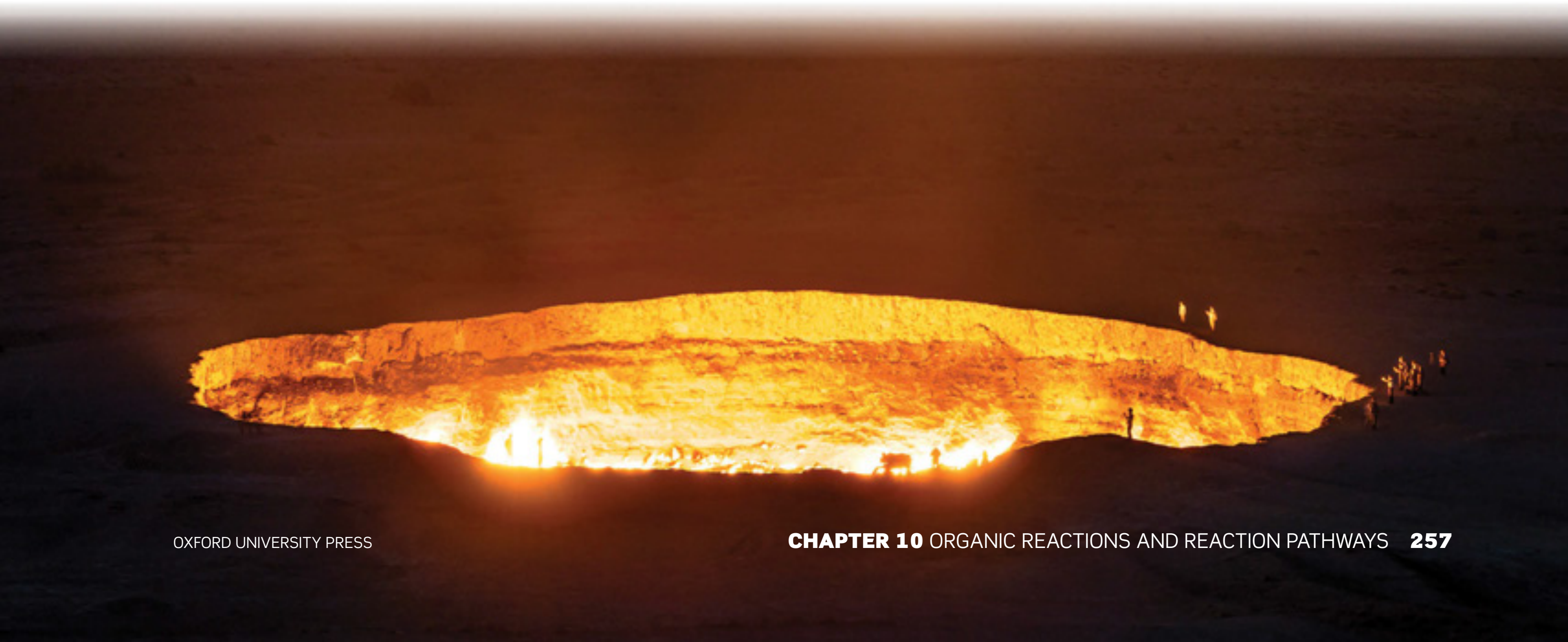


FIGURE 4 Methane burns in a complete combustion reaction at the Darvaza gas crater, also known as the Gates of Hell crater, in Turkmenistan. The gas was set on fire by scientists in 1971 to prevent the methane spreading.

Common fuels are alcohols and alkanes, such as ethanol, butane, propane (Figure 5) and methane.

$$\underset{\text{Propane}}{C_3H_8} + \underset{\text{Oxygen gas}}{5O_2} \longrightarrow \underset{\text{Carbon dioxide}}{3CO_2} + \underset{\text{Water}}{4H_2O} + \text{Heat and light}$$

FIGURE 5 The combustion of propane to produce carbon dioxide and water

CHALLENGE 10.2

Decay

Decay is a type of redox reaction, whereby dead plants and animals react with oxygen in the surrounding environment to break down the complex structures and recycle the atoms.

Research the chemical reactions involved in decay to determine whether they are oxidation or reduction, and what factors affect the rate of decomposition.

Reduction reactions

Reduction reactions can be defined as the gain of electrons, the gain of hydrogen atoms, or the loss of oxygen atoms. Reduction reactions occur in conjunction with oxidation reactions, which means that the reagent used is oxidised during the reaction. You should be familiar with redox reactions from Chapter 6.

Reduction of alkenes

Alkenes and alkynes are reduced when hydrogen is added across a double or triple bond, increasing the level of saturation of the hydrocarbon. These reactions require high temperatures (300°C), hydrogen gas and a metal catalyst (Pt, Pd or Ni). They are also known as catalytic hydrogenation.

Reduction of nitriles

Nitriles can be reduced to primary amines with lithium aluminium hydride ($LiAlH_4$) in the presence of water. The metal reagent helps break the triple bond in the nitrile group, and provides some of the hydrogen atoms required to form the primary amine (Figure 6).

$$\underset{\text{Nitrile}}{R{-}C{\equiv}N} \xrightarrow[H_2O]{LiAlH_3} \underset{\text{Primary amine}}{R{-}CH_2{-}NH_2}$$

FIGURE 6 The reduction of a nitrile to a primary amine by $LiAlH_4$ in the presence of water

You can also use hydrogen gas and a metal catalyst such as palladium, platinum or nickel to reduce nitriles – the same reagents used to reduce alkenes. This reaction also requires a high temperature and pressure.

CHECK YOUR LEARNING 10.2

Describe and explain

1 **Explain** how the type of alcohol can be identified by tests that use chemical reactions.

2 **Describe** combustion reactions.

3 **Identify** the reagents and conditions required for oxidation and reduction reactions.

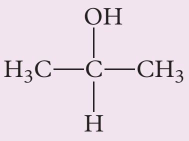
Apply, analyse and interpret

4 **Apply** IUPAC rules to name the product of the oxidation of 2-methylhexan-3-ol.

5 **Determine** the balanced chemical equation for the oxidation of propan-2-ol.

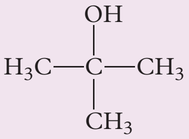
6 **Classify** the following alcohols as primary, secondary or tertiary, and name them according to IUPAC rules.

a



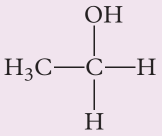
$$\begin{array}{c} OH \\ | \\ H_3C-C-CH_3 \\ | \\ H \end{array}$$

b



$$\begin{array}{c} OH \\ | \\ H_3C-C-CH_3 \\ | \\ CH_3 \end{array}$$

c

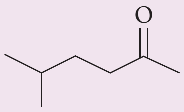


$$\begin{array}{c} OH \\ | \\ H_3C-C-H \\ | \\ H \end{array}$$

7 **Determine** the balanced chemical equation for the reduction of propanenitrile, using hydrogen gas and a nickel catalyst.

8 **Identify** the reactant used to produce:

a



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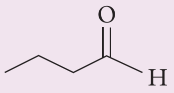


Investigate, evaluate and communicate

9 Oxidation reactions are the opposite of reduction reactions, so the same reaction pathways can be used for both. Using only redox reactions, **evaluate** the possibility of propanoic acid becoming propyne. **Discuss** whether it is possible at all and **explain** your reasoning.

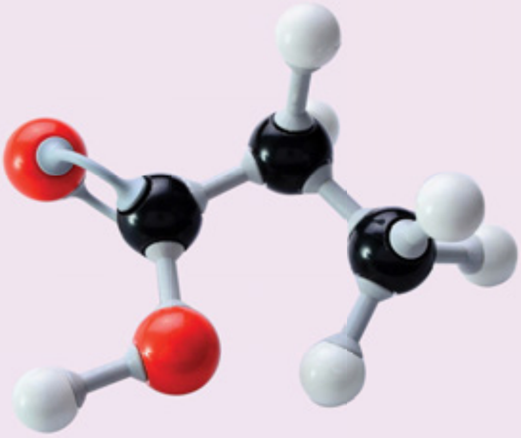


FIGURE 7 3D model of propanoic acid

You can find the following resources for this section on your obook assess:

- » Student book questions
  10.2 Check your learning
- » Suggested practical
  10.2 Oxidation of alcohols
- » Challenge
  10.2 Decay
- » Weblink
  Redox of organics

10.3

Condensation reactions

KEY IDEAS

In this section, you will learn about:

- condensation reactions, which combine two reactants to form a large organic product (an ester or amide) with water as a by-product
- esters are weak acids, turning blue litmus red
- how amines are weak bases, bonding with hydrogen ions about 7% of the time, and turning red litmus blue.

condensation reaction
a reaction in which two organic compounds are combined

by-product
a product of a chemical reaction that was not the intended product

esterification
a condensation reaction between a carboxylic acid and alcohol that generates an ester

A **condensation reaction** occurs when two molecules combine to form a larger molecule and a small **by-product** such as water. Amides and esters are synthesised by condensation reactions.

Esterification reactions

An ester functional group contains a carbonyl group attached to an oxygen linked to another carbon. The ester group is formed in an **esterification** reaction between a carboxyl group of a carboxylic acid and a hydroxy group of an alcohol. The reaction requires heat and trace amounts of a mineral acid catalyst such as sulfuric acid. It is a reversible reaction.

The main chain of the ester is derived from the main chain of the carboxylic acid (R in Figure 1). The alcohol main chain forms the ester substituent (R′ in Figure 1). This is reflected in the name of an ester. For example, the ester formed from ethanoic acid and methanol is called methyl ethanoate.

Esters are weak acids because they are in equilibrium with the parent carboxylic acids. As a result, an ester turns litmus paper from blue to red.

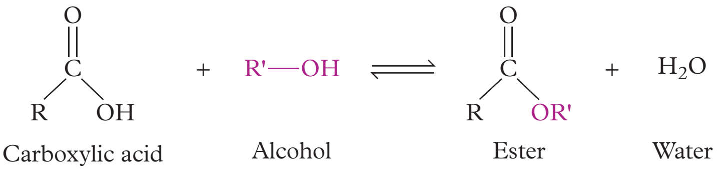


FIGURE 1 An esterification reaction

WORKED EXAMPLE 10.3

Identify the ester that is synthesised from propanoic acid and hexan-1-ol.

SOLUTION

The carbon main chain of the primary alcohol forms the ester substituent, and the carbon main chain of the carboxylic acid forms the ester main chain. Therefore, the name of the ester is hexyl propanoate.

CASE STUDY 10.3

Phosphate esters in nature

A phosphate ester is an ester derived from phosphoric acid ($O{=}P(OH)_3$) and an alcohol (ROH). Phosphate esters are found in important biological molecules, including adenosine triphosphate (ATP) and adenosine diphosphate (ADP).

ATP and ADP are responsible for providing the energy for cellular processes. ATP has three phosphate (PO_4^{3-}) groups and ADP has two phosphate groups.

ATP is hydrolysed to ADP by removal of a phosphate group. The phosphate group can take part in a phosphate ester synthesis by reacting with a hydroxyl functional group of a glucose molecule to produce glucose-6-phosphate (Figure 2). The phosphate esterification is aided by the biological catalyst hexokinase, and is the first step in the biochemical reaction called glycolysis. Several other phosphate esterifications are performed in this multistep biochemical reaction.

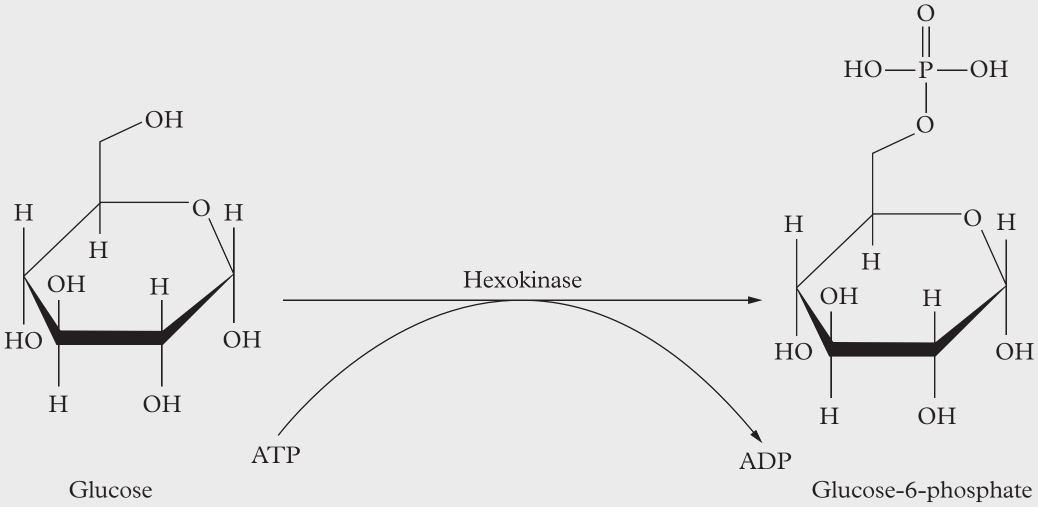


FIGURE 2 The phosphate ester synthesis of glucose-6-phosphate

Amide synthesis reactions

Amides are synthesised from carboxylic acids and amines. In the reaction, the hydroxyl functional group on the carboxylic acid is replaced by the amine functional group. The reaction requires heat (>100°C) and is reversible (similar to esterifications). The by-product, water, comes from the hydroxyl group and a hydrogen from the amine functional group (Figure 3).

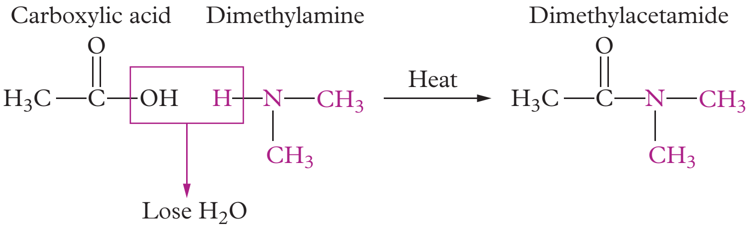


FIGURE 3 The synthesis of an amide from a carboxylic acid and an amine

The amine reactant is a weak base because it has a non-bonding pair of electrons, which can bond with hydrogen ions from water and acids about 7% of the time. Red litmus paper can be used to monitor the reaction progress because it will turn blue if there is still amine reactant present (Figure 4).

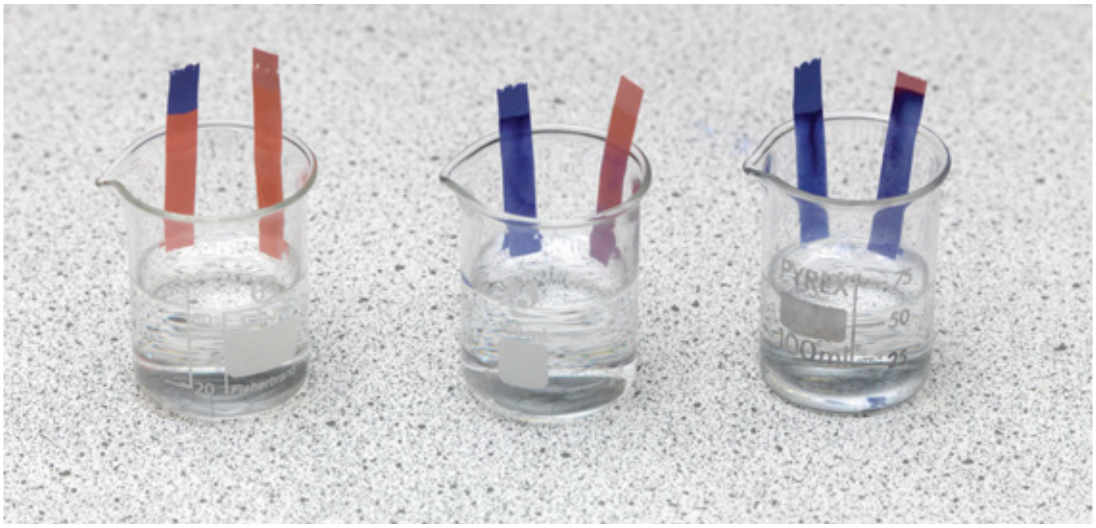


FIGURE 4 Red and blue litmus paper can be used to determine the progress of esterification and amide syntheses.

CHECK YOUR LEARNING 10.3

Describe and explain

1 **Describe** the term ‘condensation reaction’.

2 **Explain** the process of esterification, including how to **determine** when the reaction has gone to completion.

Apply, analyse and interpret

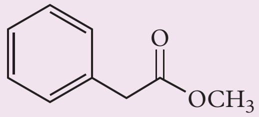
3 **Identify** the reagents and conditions required for the two types of condensation reactions.

4 **Determine** the balanced chemical equation for the condensation of pentanoic acid with:

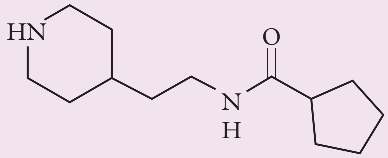
- **a** octan-2-ol
- **b** ethylamine.

5 **Interpret** the diagrams of condensation products to identify (and draw) the reactants that were involved in the condensation reactions.

a



b



You can find the following resources for this section on your obook assess:

- » Student book questions 10.3 Check your learning
- » Weblink Esterfication reactions
- » Weblink Phosphate esters

10.4

Substitution reactions

KEY IDEAS

In this section, you will learn about:

- substitution reactions, in which one substituent is replaced with another, on a saturated hydrocarbon
- how hydrogen atoms can be substituted by halogens
- how halogens can be substituted by nitriles, hydroxyls, other halogens and amines.

substitution
a reaction in which one substituent in a saturated organic compound is replaced by another

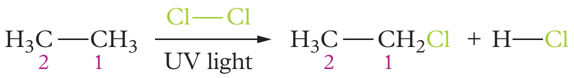
Substitution involves replacing one substituent on a saturated organic compound with another substituent. Unsaturated organic compounds tend to undergo addition reactions rather than substitution reactions.

Substitution of alkanes

Haloalkanes are formed by the substitution reactions of alkanes with halogens (Br_2 or Cl_2) in the presence of UV light (from sunlight or another source) or at temperatures of about 200°C. One of the hydrogen atoms of the alkane is replaced by one of the halogen atoms from the reagent. The leftover hydrogen and second halogen atom (from the reagent) form a hydrohalide by-product (Figure 1).

Study tip

Haloalkanes can also be called halogenoalkanes or alkyl halides.



$$\underset{2}{H_3C}-\underset{1}{CH_3} \xrightarrow[\text{UV light}]{Cl-Cl} \underset{2}{H_3C}-\underset{1}{CH_2Cl} + H-Cl$$

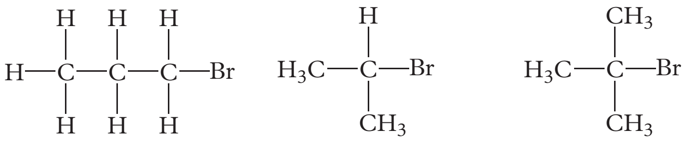
FIGURE 1 A substitution reaction of ethane with chlorine to form chloroethane

The reaction can be somewhat unpredictable, generating dihaloalkanes, trihaloalkanes and even tetrahaloalkanes as well as the expected haloalkanes. If you want to produce a dihaloalkane, then you can react the monoalkane under the same conditions to cause a second substitution of a hydrogen atom with a halogen:

$$CH_3Cl + Cl_2 \xrightarrow[\text{or heat}]{\text{UV light}} CH_2Cl_2 + HCl$$

Primary, secondary and tertiary haloalkanes

Haloalkanes can be classified as primary, secondary or tertiary (Figure 2) depending on number of hydrogens on carbon that the halogen is bonded to. The different haloalkanes have different reactivities. Primary and secondary haloalkanes are not as 'bulky' as tertiary haloalkanes, so their reactions happen more easily. A tertiary haloalkane contains a carbon atom surrounded by three carbon substituents – this tetrahedral bonding geometry affects how easily the molecule can react.



1-Bromopropane
Primary

2-Bromopropane
Secondary

2-Bromo-2-methylpropane
Tertiary

FIGURE 2 Primary, secondary and tertiary bromopropanes

Substitution of haloalkanes

The carbon–halogen bond in haloalkanes is polar. This polarity makes the carbon atom electron poor and susceptible to substitution reactions by reagents that have a non-bonding pair of electrons. Reagents that can substitute the halogen atom include cyanide (CN^-), iodide (I^-), hydroxide (OH^-), chloride (Cl^-), ammonia (NH_3), acetate ($CH_3CO_2^-$), hydride (H^-) and methanol (CH_3OH).

Using potassium cyanide

If you heat a haloalkane under reflux with a solution of potassium cyanide in ethanol, the halogen will be substituted by a nitrile functional group (Figure 3). If the solvent is water instead of ethanol, then the reaction will produce a hydroxyl group instead.

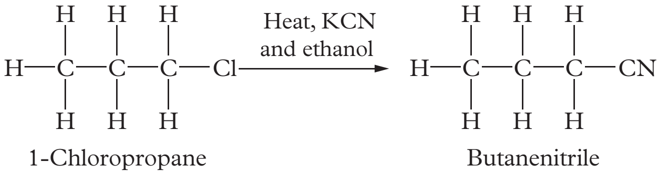


FIGURE 3 Substitution of a haloalkane to form a nitrile: 1-chloropropane reacts with KCN in ethanol to produce propanenitrile.

CHALLENGE 10.4

Steric effects of haloalkanes

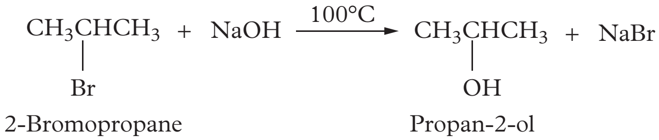
In most instances, when we are discussing the substitution of haloalkanes, we are referring to primary haloalkanes. In primary haloalkanes, the halogen is bonded to a carbon atom at the end of a chain. The substitution reactions of bulkier secondary and tertiary haloalkanes are hindered by steric crowding.

Conduct some research on steric effects in substitution and esterification reactions.

Using sodium hydroxide

If you heat a haloalkane with a solution of sodium or potassium hydroxide in 50:50 ethanol and water under reflux, the halogen substituent is replaced by a hydroxyl functional group (to product an alcohol).

These are very similar conditions for making a haloalkane undergo an elimination reaction, so it is important to note that the type of haloalkane determines which reactions will take place. Primary haloalkanes mostly undergo substitution reactions and secondary haloalkanes undergo a mixture of substitution and elimination reactions. If water is the solvent, lower temperatures and lower concentrations of sodium hydroxide favour the haloalkane undergoing a substitution reaction (Figure 4).



$$\mathrm{CH_3\underset{\underset{Br}{|}}{C}HCH_3} + \mathrm{NaOH} \xrightarrow{100°\mathrm{C}} \mathrm{CH_3\underset{\underset{OH}{|}}{C}HCH_3} + \mathrm{NaBr}$$

FIGURE 4 Substitution of a haloalkane to form an alcohol: 2-bromopropane reacts with sodium hydroxide to produce propan-2-ol.

Using halogens

If you add a haloalkane (RX) to a solution of sodium iodide in ethanol (or another organic solvent) and stir, the halogen will be substituted by iodine (Figure 5). Iodide is the most reactive of the halides for this type of substitution, followed by bromide and then chloride.

$$\text{R–X(aq)} + \text{NaI(aq)} \xrightarrow[\text{Stir}]{\text{Ethanol}} \text{R–I(aq)} + \text{NaX(s)}$$

FIGURE 5 The substitution of a haloalkane to form another haloalkane

Using ammonia

If you heat a haloalkane with a concentrated solution of ammonia in ethanol, within a sealed tube rather than a condenser (so the ammonia cannot escape), the halogen will be substituted by an amine functional group. The reaction involves many steps (some reversible) and can produce a mixture of primary, secondary and tertiary amines. Figure 6 is a simplified version of this, with the intended primary amine.

$$\underset{\text{Bromoethane}}{CH_3CH_2Br} + \underset{\text{Ammonia}}{2NH_3} \xrightarrow[\text{Heat}]{\text{Ethanol, sealed tube}} \underset{\text{Ethyl amine}}{CH_3CH_2NH_2} + \underset{\text{Ammonium bromide}}{NH_4Br}$$

FIGURE 6 The substitution of a haloalkane to form an amine

CHECK YOUR LEARNING 10.4

Describe and explain

1 **Describe** the term ‘substitution reaction’.

2 **Identify** the type of haloalkane that predominantly undergoes:
  - **a** a substitution reaction
  - **b** an elimination reaction.

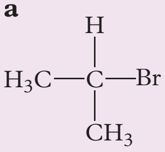
3 **Identify** the reagents and conditions required for substitution reactions that form:
  - **a** haloalkanes
  - **b** dihaloalkanes
  - **c** nitriles
  - **d** alcohols
  - **e** amines.

Apply, analyse and interpret

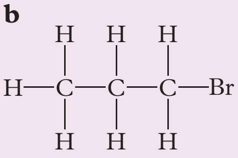
4 **Determine** the balanced chemical equation for the substitution of:
  - **a** ethane with chlorine gas
  - **b** fluoromethane with chlorine gas.

5 **Classify** the following haloalkanes as primary, secondary or tertiary, and name them using IUPAC rules.

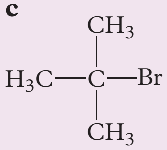
a



b



c



6 **Determine** the balanced chemical equation for the substitution of 4-bromononane with:
  - **a** sodium hydroxide
  - **b** ammonia
  - **c** potassium cyanide.

You can find the following resources for this section on your obook assess:

- » Student book questions
  10.4 Check your learning
- » Challenge
  10.4 Steric effects of haloalkanes
- » Weblink
  Substitution in organic equations

SCIENCE AS A HUMAN ENDEAVOUR

10.5

Organochlorine insecticides

KEY IDEAS

In this section, you will learn about:

- the use of insecticides to kill or harm insects in order to protect crops
- how insecticides can be broad spectrum or targeted, depending on their mechanism of action
- the damaging effect of organochlorine insecticides on the environment between 1940 and the 1950s.

Insecticides are chemicals designed to kill or harm insects, in an attempt to increase crop yields. Insecticides work by disrupting an insect's nervous system, damaging their **exoskeleton** or controlling their growth.

exoskeleton
the outer structure of an animal, e.g. a shell

FIGURE 1 In Queensland, the cane beetle is a pest to the sugar cane. Insecticides are one way to control their population.

There are two types of insecticides.

- Broad-spectrum insecticides affect most, if not all, of the insect species in the treated area through many mechanisms.
- Targeted insecticides are better for the environment because they don't harm **beneficial insect** species (e.g. bees, ladybugs and wasps) in the treated area.

beneficial insect
an insect that helps human enterprises such as farming, through pollination or by killing destructive insects

The concept of using a chemical to kill or harm insects is not new. Plants produce some insecticides themselves, such as nicotine and pyrethrum.

Insecticides can work in a variety of ways.

- Broad-spectrum insecticides are sprayed on stored products and start working when an insect inhales them. Hydrogen cyanide, naphthalene, nicotine and methyl bromide are broad-spectrum insecticides.
- Insecticide-covered leaves are consumed by insects with chewing parts. So this targets caterpillars, beetles and grasshoppers. Copper acetoarsenite, lead arsenate, calcium arsenate, sodium fluoride and cryolite are insecticides that are sprayed on leaves.
- Contact penetration is targeted at arthropods that pierce plants to suck out the juices. Insecticides that operate in this way include nicotine, pyrethrum, rotenone, organochlorines, organophosphates and carbamates.

Dichlorodiphenyltrichloroethane (DDT) (Figure 2) is an organochlorine insecticide spray that was introduced in the 1940s to replace dangerous lead- and arsenic-based insecticides. DDT works by opening the ion channels of nerve cells. This increases the active transport of sodium and potassium ions across the cell membranes to produce spontaneous nerve impulses. The spontaneous firing of nerve impulses results in muscle twitches in the insects, eventually leading to convulsions and death.

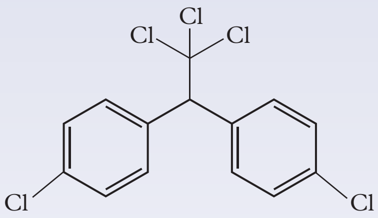


FIGURE 2 The structure of DDT

Lindane is another organochlorine insecticide used in the past. Lindane consists of a hexachlorocyclohexane structure (Figure 3). There are five hexachlorocyclohexane isomers but lindane is the only one with insecticidal properties. Lindane interferes with the transport of chloride ions in nerve cells, which increases the rate of respiration in the cells of insects. This leads to an increase in insect activity, followed by twitches and convulsions, and exhaustion. Lindane was used to treat food crops, as well as seeds, livestock and pets up until 2006 but it has since been banned and restricted.

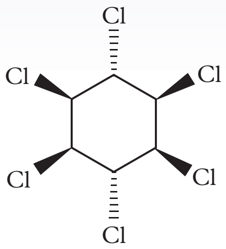


FIGURE 3 The structure of lindane ($C_6H_6Cl_6$)

Chlordane is an organochlorine insecticide (Figure 4). Chlordane is used on termites and soil-borne insects. It is not affected by the ultraviolet radiation of sunlight. Its mode of action is different from that of DDT and lindane because it inhibits rather than accelerates the transport of chloride ions into nerve cells. However, it has similar side effects – tremors, convulsions and exhaustion.

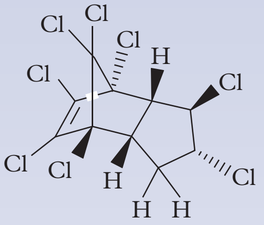


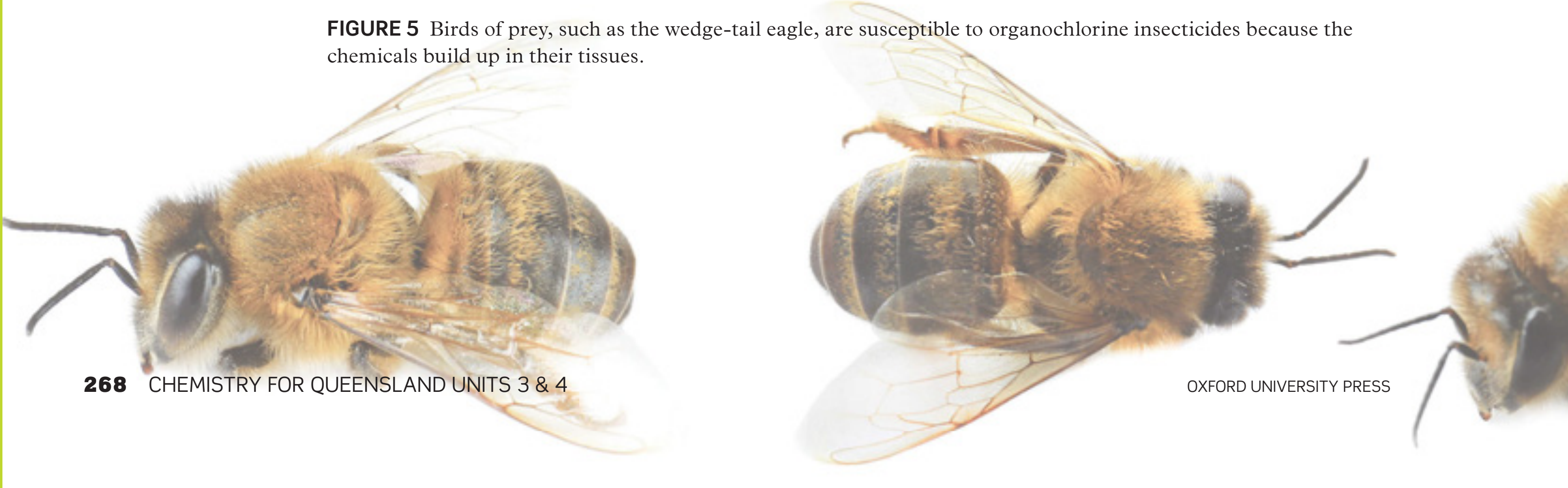
FIGURE 4 The structure of chlordane

The organochlorines are notorious because of their effects, which were not known about at the time. Organochlorines are not reactive and very hydrophobic, which means that they are long lasting. This makes them attractive to customers but significantly detrimental to the environment. In 1962, Rachel Carson's wrote the book *Silent Spring*, which noted the correlation between the introduction of DDT as a major insecticide spray and growing environmental concerns such as the prevalence of cancers and the declining population of birds. Carson suggested that humans should consider the interconnectedness of living things and systems, and use extreme caution to avoid more destruction.

When DDT and similar organochlorine compounds are used on insects, any animal consuming those insects becomes contaminated with a small dose of insecticide. At the top of the food web, birds of prey (such as falcons, hawks and eagles (Figure 5)) that consume large quantities of small animals were experiencing **bioaccumulation**. The dose of insecticide in their body was concentrated enough to affect their own physiology.

bioaccumulation
a build-up of stored substances in an organism

FIGURE 5 Birds of prey, such as the wedge-tail eagle, are susceptible to organochlorine insecticides because the chemicals build up in their tissues.



The **hydrophobic** insecticide collected in the fatty tissue of the birds. The shells of their eggs became thinner and so were less likely to result in successful offspring, so population numbers decline.

hydrophobic
unable to dissolve in water

As a result, the organochlorine insecticides were restricted and even banned in some cases. However, their long-lasting nature means they still persist in soil and waterways, disrupting ecosystems. The use of insecticides continues to be controversial and treated areas are heavily monitored.

CHECK YOUR LEARNING 10.5

Describe and explain

1 **Describe** the modes of action of insecticides that harm and kill their targets.

2 **Explain** the environmental impact of organochlorine insecticides.

Investigate, evaluate and communicate

3 **Research** and **compare** the effects of organochlorine and organophosphate insecticides.

4 **Research** and **compare** the use of transgenic insecticides and standard biological controls.

5 **Investigate** the use of biochemicals and plant-incorporated protectants as current biorational insecticides.

6 **Investigate** how insect pheromones are used to study insect locations and their population numbers.

You can find the following resources for this section on your obook assess:

» Student book questions
10.5 Check your learning

» Weblink
Insecticides

» Weblink
DDT

CHAPTER 10

Review

Chapter summary

10.1
- Addition reactions break a double or triple bond and replace it with two substituents. Addition reactions can be a hydrogenation, halogenation, hydrohalogenation or hydration reaction.
- Markovnikov's rule explains the general trend that a hydrogen from an asymmetrical reagent will bond to the carbon atom that is bonded to the most hydrogen atoms already.
- Addition reactions also create polymers. A polymerisation catalyst is used.
- Elimination reactions use a concentrated strong base under reflux conditions to remove substituents and replace with a double bond.

10.2
- Oxidation reactions are defined as the loss of hydrogen atoms or gain of oxygen atoms. These gains and losses take place at the functional group of the organic compound, and the products can be predetermined using the oxidation pathways:
  - primary alcohol → aldehyde → carboxylic acid
  - secondary alcohol → ketone
- Combustion reactions are also oxidation reactions, and use alkanes and alcohols as the fuel.
- Reduction reactions are the gain of hydrogen atoms or loss of oxygen atoms. The reduction pathways are:
  - alkyne → alkene → alkane
  - nitrile → amine

10.3
- Condensation reactions synthesise esters and amides.
- Esterification reactions combine an alcohol with a carboxylic acid to form an ester and water. They require sulfuric acid as a catalyst and are reversible.
- Amide condensation reactions combine an amine with a carboxylic acid to form an amide and water. They require a high temperature and are reversible.

10.4
- Substitution reactions require saturated organic reactants. Unsaturated reactants undergo addition reactions.
- Halogens easily substitute onto hydrocarbons, replacing a hydrogen atom.
- To replace a halogen in a substitution reaction, additional experimental conditions are required (such as heating under reflux and using an organic solvent). Halogens can be substituted for nitriles, hydroxyls, other halogens and amines.

10.5
- Insecticides act by disrupting the insect's nervous system, damaging their exoskeleton, or regulating their growth.
- Insecticides can be broad spectrum or targeted, depending on their mechanism of action (inhalation, ingestion or contact penetration).
- The organochlorines were examples of contact penetration insecticides that attacked the insect's nervous system by disrupting normal functioning of ion channels. Their longevity caused significant environmental damage and bioaccumulation within ecosystems.

Key terms

- addition
- beneficial insect
- bioaccumulation
- by-product
- complete combustion reaction
- condensation reaction
- elimination reaction
- esterification
- exoskeleton
- halogenation
- hydration
- hydrogenation
- hydrohalogenation
- hydrophobic
- monomer
- oxidation reaction
- polymer
- polymerisation
- reduction reaction
- reflux
- substitution

Revision questions

The relative difficulty of these questions is indicated by the number of stars beside each question number: ★ = low; ★★ = medium; ★★★ = high.

Multiple choice

1 You can identify an organic compound's class by studying its:

A chemical properties
B physical properties
C molar mass
D elements.

2 A combustion reaction is a type of:

A addition
B elimination
C oxidation
D reduction.

3 The most oxidised product of a primary alcohol is:

A an ester
B a ketone
C an aldehyde
D a carboxylic acid.

4 Markovnikov's rule states that the:

FIGURE 1 Vladimir Markovnikov, the Russian chemist who devised Markovnikov's rule

A hydrogen atom in the pure halogen reagent will bond to the carbon from the double bond that has the least hydrogen atoms attached

B hydrogen atom in the pure halogen reagent will bond to the carbon from the double bond that has the most hydrogen atoms attached

C hydrogen atom in the hydrohalide reagent will bond to the carbon from the double bond that has the least hydrogen atoms attached

D hydrogen atom in the hydrohalide reagent will bond to the carbon from the double bond that has the most hydrogen atoms attached.

5 An elimination reaction is defined as the breaking of:

A a double bond to replace with two substituents
B a double bond to replace with one substituent
C two substituents to replace with a double bond
D one substituent to replace with a double bond.

6 Amines can be formed by:

A addition or substitution
B addition or condensation
C substitution or reduction
D reduction or condensation.

7 The substitution of potassium cyanide with 1-chloroheptane produces:

★ **A** 1-chloroheptanenitrile

B 1-chlorooctanenitrile

C heptanenitrile

★★ **D** octanenitrile.

8 Examples of organochlorine insecticides are:

A hydrogen cyanide and methyl bromide

B sodium fluoride and naphthalene

C nicotine and lead arsenate

D DDT and lindane.

FIGURE 2 Farm machinery spraying insecticides

9 The addition of water to pent-2-ene results in:

A pentane

B pent-2-ane

C pentan-2-ol

D pent-2-en-2-ol.

10 When using sodium hydroxide, what are the experimental conditions required to favour an elimination reaction over a substitution reaction?

A Ethanol as a solvent and high temperatures

B Ethanol as a solvent and low temperatures

C Water as a solvent and high temperatures

D Water as a solvent and low temperatures

Short answer

Describe and explain

★ 11 **Describe** the terms ‘oxidation’ and ‘reduction’ in relation to organic chemistry.

★ 12 **Describe** the acidic and basic properties of functional groups in organic compounds.

★ 13 **Describe** how the synthesis of an organic compound often requires more than one chemical reaction.

★ 14 **Explain** what the term ‘reversible’ represents in reference to esterification reactions.

★★ 15 **Identify** the reagents and conditions required for an:

a elimination reaction of a haloalkane

b addition of water

c addition polymerisation.

★★ 16 **Explain**, using your understanding of electronegativity, why alcohols and carboxylic acids are soluble in water but most esters are not.

★★ 17 **Explain**, using equations, the reaction that forms amines (from nitriles) and alkanes (from alkenes).

★★★ 18 **Describe**, using equations:

a hydrogenation

b halogenation

c hydrohalogenation

d hydration

e polymerisation

f elimination

g oxidation

h reduction

i esterification

j amide synthesis

k substitution.

Apply, analyse and interpret

★ 19 **Determine** the balanced chemical equation for the combustion of butane gas.

★ 20 **Apply** IUPAC rules to name the product formed when cyclopentanol oxidises.

★ 21 **Contrast** the terms ‘class’ and ‘functional group’.

★ 22 **Interpret** the structure in Figure 3 to identify the reactants used to form this compound.

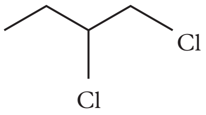


FIGURE 3 Organic structure of compound.

★ 23 **Determine** the balanced chemical equation for the polymerisation of five monomers of propene.

★ 24 **Apply** IUPAC rules to name the reactant that oxidises to form propanal.

★★ 25 **Compare** saturated and unsaturated compounds, in terms of their bonding and reactivity.

★★★ 26 **Identify** the products for the reaction of:

- **a** ethane and bromine
- **b** but-1-ene and iodine
- **c** propene and water
- **d** 3-bromoheptane and sodium hydroxide
- **e** 2-pent-2-yne and two equivalents of fluorine
- **f** heptan-4-ol and butanoic acid.

★★ 27 **Interpret** the following condensed structural formulas to **identify** the alcohols that were oxidised to produce them.

- **a** CH_3CH_2CHO
- **b** $CH_3(CH_2)_4CO_2H$
- **c** $CH_3CH_2CH(O)CH_2CH_3$

Investigate, evaluate and communicate

★★★ 28 **Research** how:

- **a** an alkane can become an amine
- **b** a haloalkane can become a carboxylic acid
- **c** an amide can be formed from an alkene.

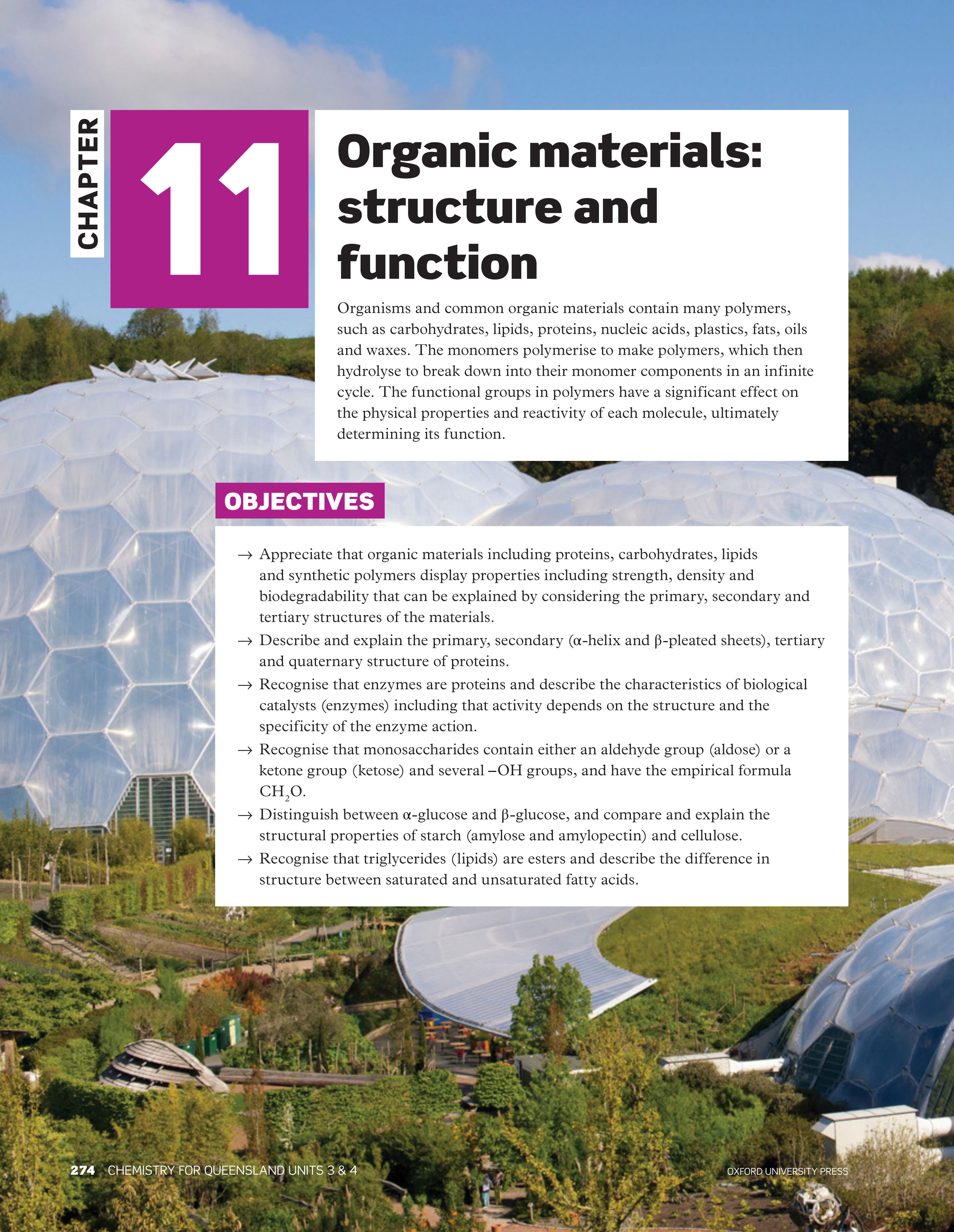
★★ 29 Aromatic compounds participate in substitution reactions rather than addition reactions. **Investigate** how this takes place, despite the fact they have numerous double bonds.

★★★ 30 Two unlabelled flasks contained organic compounds, both with the general formula $C_nH_{2n}O_2$ and the molar mass of 102 g mol^{-1}. The liquid in flask A turned blue litmus red, and the liquid in flask B had an apple/pear aroma. **Evaluate** the information provided to identify the structures and names of the two compounds. (Hint: There are four possible answers for liquid B. The correct answer has the longest main chain.)

FIGURE 4 Unlabelled flasks

You can find the following resources for this section on your obook assess:

- » Student book questions
  Chapter 10 Revision questions
- » Revision notes
  Chapter 10
- » assess quiz
  Auto-correcting mutiple-choice quiz
- » Flashcard glossary
  Chapter 10



CHAPTER 11

Organic materials: structure and function

Organisms and common organic materials contain many polymers, such as carbohydrates, lipids, proteins, nucleic acids, plastics, fats, oils and waxes. The monomers polymerise to make polymers, which then hydrolyse to break down into their monomer components in an infinite cycle. The functional groups in polymers have a significant effect on the physical properties and reactivity of each molecule, ultimately determining its function.

OBJECTIVES

- → Appreciate that organic materials including proteins, carbohydrates, lipids and synthetic polymers display properties including strength, density and biodegradability that can be explained by considering the primary, secondary and tertiary structures of the materials.
- → Describe and explain the primary, secondary (α-helix and β-pleated sheets), tertiary and quaternary structure of proteins.
- → Recognise that enzymes are proteins and describe the characteristics of biological catalysts (enzymes) including that activity depends on the structure and the specificity of the enzyme action.
- → Recognise that monosaccharides contain either an aldehyde group (aldose) or a ketone group (ketose) and several –OH groups, and have the empirical formula CH_2O.
- → Distinguish between α-glucose and β-glucose, and compare and explain the structural properties of starch (amylose and amylopectin) and cellulose.
- → Recognise that triglycerides (lipids) are esters and describe the difference in structure between saturated and unsaturated fatty acids.

→ Describe, using equations, the base hydrolysis (saponification) of fats (triglycerides) to produce glycerol and its long chain fatty acid salt (soap), and explain how their cleaning action and solubility in hard water is related to their chemical structure.

→ Explain how the properties of polymers depends on their structural features including; the degree of branching in polyethene (LDPE and HDPE), the position of the methyl group in polypropene (syntactic, isotactic and atactic) and polytetrafluorethylene.

Source: *Chemistry 2019 v1.3 General Senior Syllabus* © Queensland Curriculum & Assessment Authority

PRACTICALS

SUGGESTED PRACTICAL	**11.3** Catalysing decomposition reactions

FIGURE 1 The synthetic polymer ethylene tetrafluoroethylene (ETFE) is used in large construction projects as plastic roofing.

11.1 Carbohydrates

KEY IDEAS

In this section, you will learn about:

- monosaccharides, which are the monomers of sugar, such as glucose
- disaccharides and polysaccharides, which are polymers of monosaccharides that are joined by glycosidic linkages
- sucrose as an example of a disaccharide, and starch and cellulose as examples of polysaccharides.

Monosaccharides

monosaccharide a single sugar monomer

Study tip

The thicker lines in structural formulas represent bonds that are protruding out from the book's surface. You may see 3D molecules shown with or without this thick line.

Monosaccharides are sugar monomers and have the empirical formula CH_2O. They consist of a carbon chain with several hydroxyl groups attached, and either an aldehyde or a ketone functional group. In aqueous solution, monosaccharides exist as two forms in dynamic equilibrium – a straight chain and an α-ring. The three-dimensional structure of the α-ring can be drawn in either a Haworth projection or a chair conformation (Figure 1). The straight chain can be represented two-dimensionally in a Fischer projection (Figure 2).

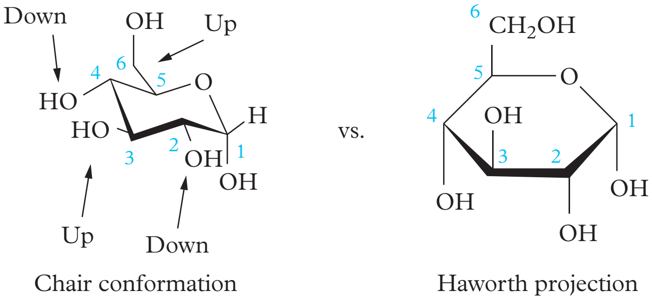


FIGURE 1 The chair conformation and Haworth projection of glucose

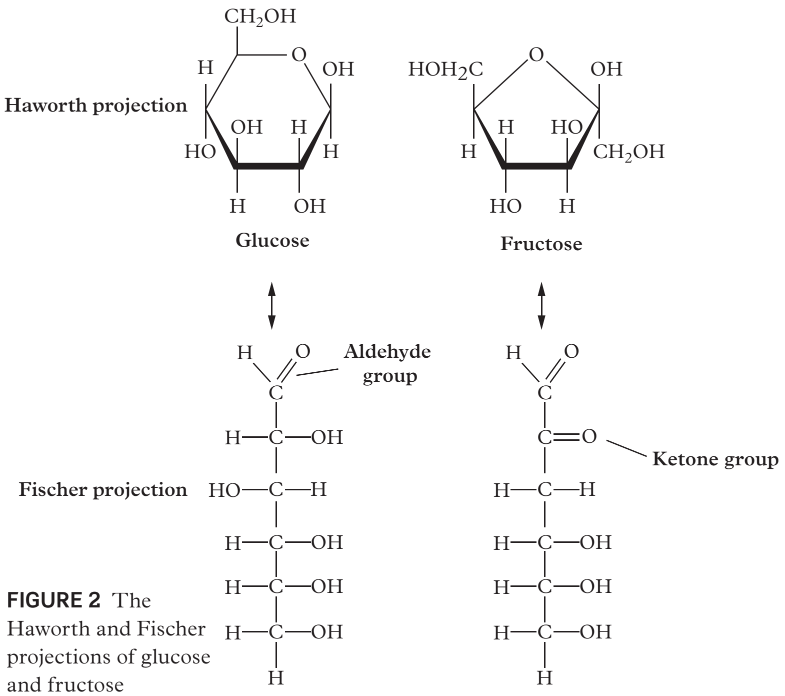


FIGURE 2 The Haworth and Fischer projections of glucose and fructose

Glucose and fructose are common monosaccharides. They are found in fruits and vegetables. Glucose contains an aldehyde so is classified as an aldose, and fructose contains a ketose functional group so is classified as a ketone.

Glucose

Glucose also exists in two ring configurations – α and β. The configurations differ in the position of the hydroxyl functional group of carbon 1, which is the carbon atom next to the oxygen in the ring (Figure 3).

α-Glucose has a vertical bond down to the hydroxyl (in the opposite direction of the carbon 6 hydroxyl), and β-glucose has an upward diagonal bond to the hydroxyl (in a similar direction to the carbon 6 hydroxyl).

This slight difference in geometry means β-glucose is more stable and less crowded than α-glucose and has a melting point approximately 5°C higher.

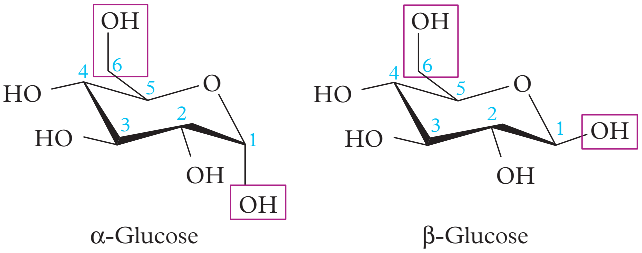


FIGURE 3 The structures of α-glucose and β-glucose in the chair conformation

Disaccharides

Disaccharides are simple sugars made from two monosaccharides in a condensation polymerisation reaction. Sucrose (table sugar) is a common disaccharide consisting of a glucose molecule bonded to a fructose molecule through an α-1,4-**glycosidic linkage** (Figure 4).

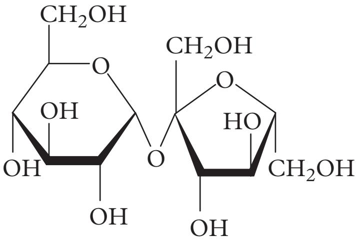


FIGURE 4 The structure of sucrose in the Haworth projection

disaccharide
two sugar monomers bonded together

glycosidic linkage
a bond that connects sugar monomers together

Study tip

More detail on carbohydrates and their formation can be found in Chapter 15.

Study tip

Words ending in -ase often signify enzymes.

CASE STUDY 11.1

Lactose intolerance

Lactose is an important disaccharide that makes up approximately 8% of mammalian milk. A lactose molecule is made up of two monosaccharides: glucose and galactose, which is an isomer of glucose.

FIGURE 5 These dairy products contain the disaccharide lactose. Some people cannot digest lactose because they are deficient in the enzyme lactase.

Normally, food containing lactose (Figure 5), is broken down in the small intestine to its monosaccarides by the enzyme lactase. Glucose and galactose then pass through the intestinal wall. Adult humans are often deficient in lactase because of a genetic condition, so 20–80% of adults cannot easily digest lactose. Without lactase, the lactose disaccharide accumulates in the small intestine because the molecule is too large to pass through the intestinal walls. Lactose-intolerant adults experience abdominal pain, nausea and diarrhoea after ingesting lactose products. Pressure in the small intestine builds, causing the body to dilute the lactose solution, and utilise the bacteria in the colon to ferment the lactose into carbon dioxide gas and acid by-products.

Polysaccharides

polysaccharide
a complex sugar consisting of multiple sugar monomers bonded together

Polysaccharides are complex sugars made up of many monosaccharides (sometimes hundreds). Common examples are starch, cellulose, glycogen (used for energy storage in animals, fungi and bacteria) and chitin (found in the exoskeletons of insects and crustaceans).

FIGURE 6 Potatoes contain a large amount of starch, a polymer of glucose.

Starch

Starch is a polymer of glucose units found in plants. It is partially soluble in water and is edible. Starch forms a major part of the modern diet in corn, rice, beans, peas, cereals, pasta, bread and potatoes (Figure 6). Amylose and amylopectin are two different types of polyglucose molecules in starch. Amylose is an unbranched glucose polymer with α-glycosidic linkages connecting carbons 1 and 4. Amylopectin is a branched glucose polymer with α-glycosidic linkages connecting carbons 1 and 4, as well as carbons 1 and 6.

Cellulose

Cellulose is another common polysaccharide, also made of glucose units. In cellulose, the glucose monomers are joined through β-1,4-glycosidic linkages. Adjacent unbranched cellulose molecules are linked by hydrogen bonding to form an extended three-dimensional conformation (Figure 8). The conformation forms strong, fibrous bundles with significantly different properties from those of starch. Cellulose is insoluble in water and indigestible to most animals (except cattle and termites who have specialised digestive tracts). Its rigid nature makes it suitable as a structural carbohydrate in trees, cotton clothing and the cell walls of plants.

FIGURE 7 Trees contain the rigid carbohydrate, cellulose.

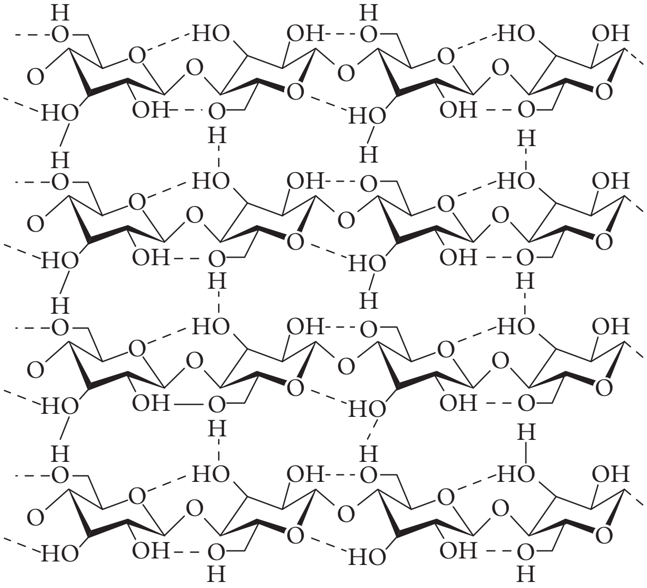


FIGURE 8 The hydrogen bonding of cellulose shown through the chair conformation

CHECK YOUR LEARNING 11.1

Describe and explain

1 **Describe** the term ‘glycosidic linkage’.

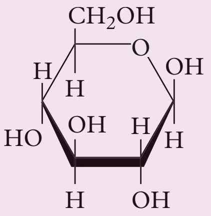
2 **Explain** how the bonding in disaccharides and polysaccharides affects their properties.

Apply, analyse and interpret

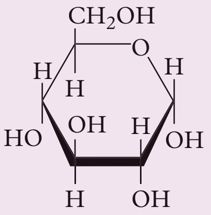
3 **Contrast** the straight chain and α-ring structures of glucose and fructose.

4 **Interpret** the following diagrams to classify each as α-glucose or β-glucose. **Determine** whether the structures are represented as chair confirmations or Haworth projections.

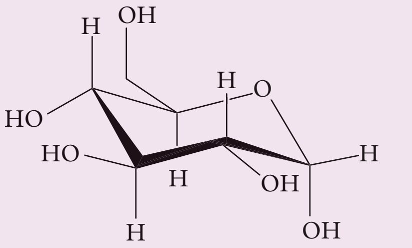
a



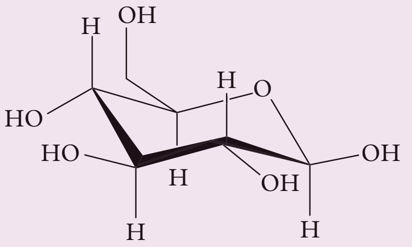
b



c



d



5 The positions of the hydroxyl groups on a carbohydrate play a significant role in its reactivity. **Investigate** the following common monosaccharides to compare their physical structure and its effect on their reactivity.

- Allose
- Altrose
- Galactose
- Glucose
- Gulose
- Idose
- Mannose
- Talose

6 **Evaluate** the significance of the effect of each hydroxyl change in question 5, in comparison to the other effects. Were some positions more significant than others? Why?

You can find the following resources for this section on your obook assess:

- » Student book questions
  11.1 Check your learning
- » Weblink
  Lactose intolerance
- » Weblink
  Cellulose

11.2

Lipids

KEY IDEAS

In this section, you will learn about:

- lipids, which are fats, oils and waxes
- triglycerides as common examples of lipids, and which are made of a glycerol with three ester linkages to fatty acids (large carbon chains with a carboxylic acid functional group)
- the saponification of triglycerides, which breaks the ester linkages and makes soap.

hydrophilic
having a strong affinity for water, e.g. polar organic compounds

fatty acid
a carboxylic acid that has a long hydrocarbon chain

Lipids are polymers with low melting points, and which are insoluble in water. Common lipids include triglycerides (animal fats and plant oils), waxes, glycerophospholipids (detergents), sphingolipids (nerve cell membranes), steroids and fat-soluble vitamins (A, D, E and K). Lipids generally contain both hydrophobic and **hydrophilic** components. Lipids contain mostly hydrophobic components and so are insoluble in water.

Fatty acids

Many lipids contain one or more **fatty acids** – carboxylic acids with long carbon chains – which can be categorised as either saturated or unsaturated. Unsaturated fatty acids include monounsaturated (one double bond) and polyunsaturated (several double bonds). There are only two essential fatty acids for animal diets – linoleic acid and linolenic acid. These essential fatty acids are both polyunsaturated and sourced from plants.

The melting points of lipids containing fatty acids increase as the length of the carbon chain increases and decrease as the level of unsaturation (double bonds) increases. Melting points of unsaturated fatty acids are also affected by geometric isomerism – *cis* conformations have lower melting points than *trans* conformations because they cannot pack closely together, which would increase intermolecular forces.

Triglycerides

Plants and animals use triglycerides to prevent water loss, store fat and provide a barrier against microorganisms. Triglycerides consist of three fatty acids and glycerol (propane-1,2,3-triol), and they are essentially very large esters. The carbon chains on each of the fatty acids are 10–30 carbon atoms long, and can be either saturated or unsaturated.

FIGURE 1 Whales store large amounts of fat for warmth and buoyancy. Triglycerides help them accomplish this.

Saponification of triglycerides

Saponification (otherwise known as base hydrolysis) of triglycerides involves boiling the animal fat or plant oil with excess aqueous sodium hydroxide, to break the three ester linkages. Saponification produces a glycerol molecule and three fatty acid salts (commonly called soap) (Figure 2).

saponification
the organic reaction between an acidic ester and a strong base to produce a fatty acid salt

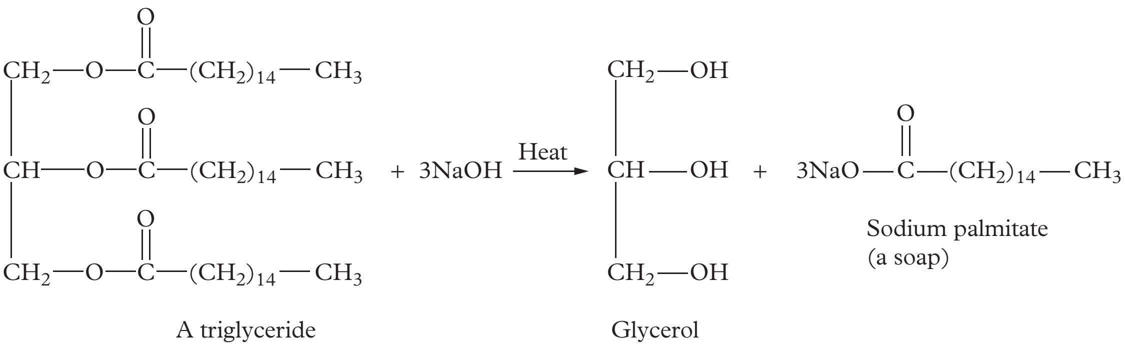


FIGURE 2 The saponification of a triglyceride

Study tip

'Like dissolves like' means that non-polar substances dissolve in other non-polar substances, and polar substances dissolve in other polar substances. Polar and non-polar substances do not have strong interactions; for example, oil and water.

Soap is **amphipathic** – it contains a small hydrophilic 'head' (the carboxyl functional group and metal cation) and a large hydrophobic 'tail' (the carbon chain). This is important for the cleansing action of soap (Figure 3). Dirt and grease are hydrophobic so they are attracted to the hydrophobic part of a soap molecule. At the same time, the hydrophilic head of the soap dissolves in water because it can generate polar interactions. The soap breaks the dirt or grease into smaller particles, surrounded by the hydrophobic tails of the soap molecules. Each dirt particle can then dissolve in water because the surface of each dirt particle contains only the hydrophilic heads of the soap molecules.

amphipathic
having both hydrophobic and hydrophilic parts

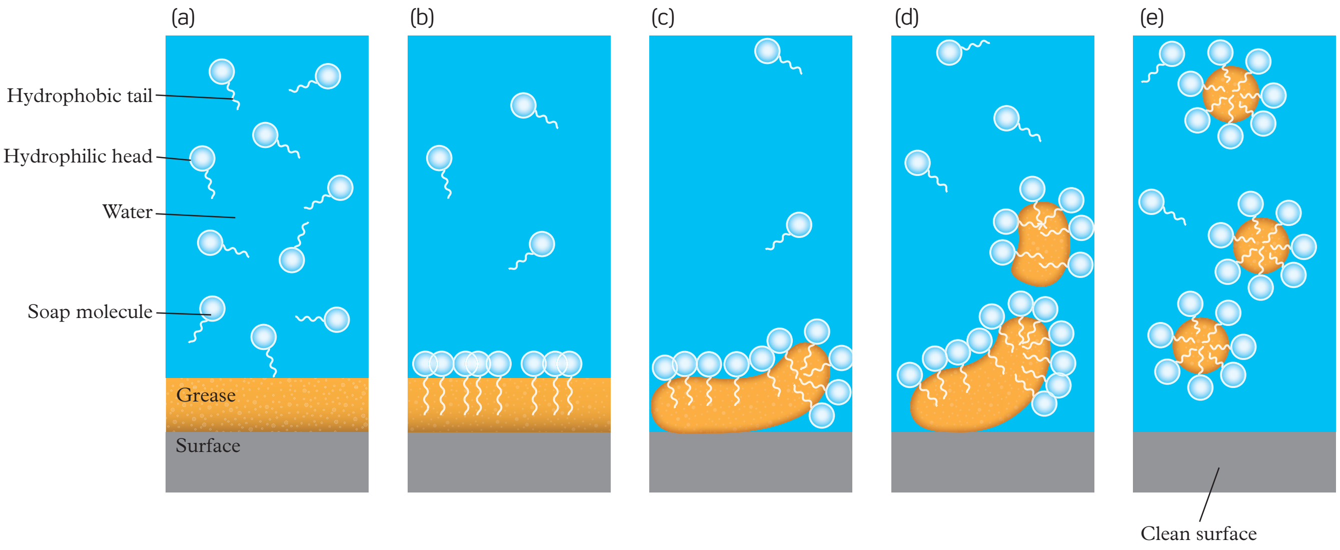


FIGURE 3 The cleansing action of soap. (a) Soap dissolves in water. (b) The hydrophobic tail is in the grease and the hydrophilic head is in the water. (c) Agitation lifts the grease from the surface. (d) The cleaning action continues until (e) it is complete.

hard water
water containing high concentrations of dissolved metal cations, such as Ca^{2+}, Mg^{2+}, Fe^{2+} and Fe^{3+}

The metal cation present in soap is either sodium or potassium. **Hard water** contains high levels of dissolved Ca^{2+}, Mg^{2+}, Fe^{2+} and Fe^{3+}. When soap is used in hard water, the metal cations in the water neutralise the charge on the hydrophilic end of the soap molecule and insoluble compounds are formed. Therefore, if you clean in hard water, you need to use more soap, so that some of the soap molecules still have sodium or potassium and can perform the cleaning action. Alternatively, you can use an ion-exchange device to soften the household water by replacing the Ca^{2+}, Mg^{2+}, Fe^{2+} and Fe^{3+} with Na^+.

FIGURE 4 Soap molecules form ionic bonds with carboxyl functional groups to make it insoluble in water.

CHECK YOUR LEARNING 11.2

Describe and explain

1 **Describe** the structure of triglycerides.
2 **Explain** why you need more soap to clean with hard water.
3 **Describe** the general properties of lipids.
4 **Identify** common examples of lipids in everyday life.
5 **Contrast** saturated and unsaturated fatty acids.

Investigate, evaluate and communicate

6 **Investigate** the sources and health effects of saturated and unsaturated fatty acids.
7 **Construct** the saponification of triglyceride in Figure 5 as an equation.

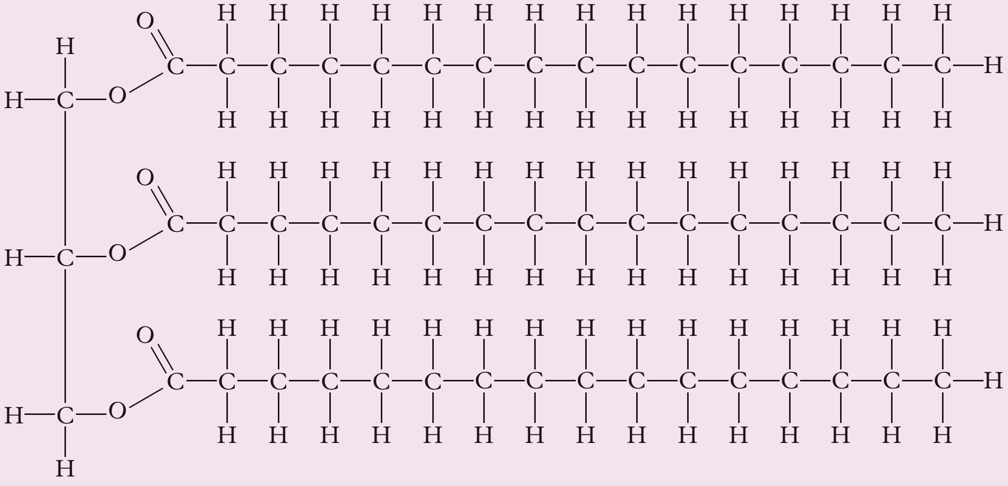


FIGURE 5 Triglycerides

You can find the following resources for this section on your obook assess:

- Student book questions
  11.2 Check your learning
- Weblink
  Triglycerides
- Weblink
  Soap

11.3 Proteins

KEY IDEAS

In this section, you will learn about:

- proteins, which are polymers of amino acids that are joined by peptide bonds
- the primary, secondary, tertiary and quaternary structures of a protein, which determine its function
- enzymes, which are proteins that catalyse biochemical reactions.

Proteins are essential biological molecules. There are more than 100 000 proteins and each has a unique biological function. Proteins can catalyse reactions, transport molecules and ions, regulate cellular activity, defend against pathogens, store nutrients, and more.

Study tip

The common names, symbols, structural formulas and pH of the isoelectric points of the 20 amino acids will be provided in the QCAA Chemistry formula and data book for the external assessment.

Amino acids

The monomer of a protein is an amino acid, which is an organic compound with both amino ($-NH_2$) and carboxyl ($-COOH$) functional groups. There are 20 amino acids that make up the proteins in the human body. They differ in their side chain (R group), which can be non-polar neutral, polar neutral, polar acidic or polar basic. Amino acids have common names but are also referred to by their three-letter and one-letter symbols (Table 1).

In solution, the hydrogen atom is released from the acidic carboxyl group and accepted by the basic amino group, so the amino acid is in the form $^+H_3N-CHR-COO^-$. This is called a **zwitterion** (Figure 1).

zwitterion
a molecule that has separate positively and negatively charged parts

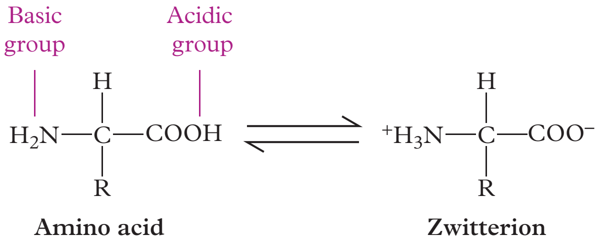
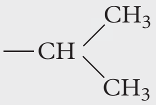
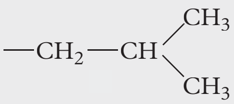
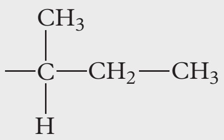
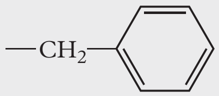
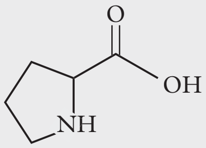
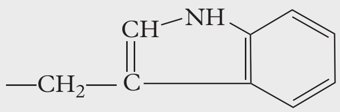
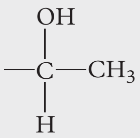
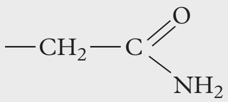
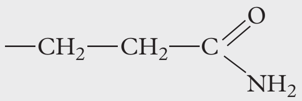
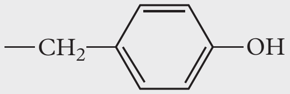
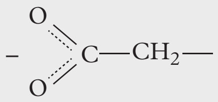
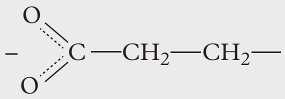
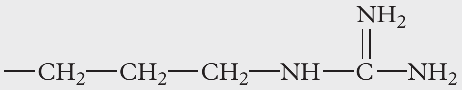
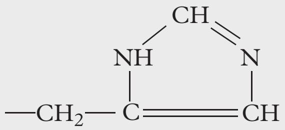


FIGURE 1 The general structure of an amino acid

TABLE 1 The 20 amino acids found in the human body

	Common name	Symbol		Side chain
Non-polar neutral	Glycine	Gly	G	$-H$
	Alanine	Ala	A	$-CH_3$
	Valine	Val	V	 $-CH(CH_3)_2$
	Leucine	Leu	L	 $-CH_2-CH(CH_3)_2$

	Common name	Symbol		Side chain
	Isoleucine	Ile	I	 $-\overset{CH_3}{\underset{H}{C}}-CH_2-CH_3$
	Phenylalanine	Phe	F	
	Methionine	Met	M	$-CH_2-CH_2-S-CH_3$
	Proline	Pro	P	
	Tryptophan	Trp	W	
Polar neutral	Cysteine	Cys	C	$-CH_2-SH$
	Serine	Ser	S	$-CH_2-OH$
	Threonine	Thr	T	 $-\overset{OH}{\underset{H}{C}}-CH_3$
	Aspargine	Asn	N	
	Glutamine	Gln	Q	
	Tyrosine	Try	Y	
Polar acidic	Aspartic acid	Asp	D	
	Glutamic acid	Glu	E	
Polar basic	Lysine	Lys	K	$-CH_2-CH_2-CH_2-CH_2-NH_3^+$
	Arginine	Arg	R	 $-CH_2-CH_2-CH_2-NH-\overset{NH_2}{C}-NH_2$
	Histidine	His	H	

Types of protein structures

The overall structure of a protein (and thus its function) depends on its primary, secondary, and tertiary structures. Some complex proteins also have quaternary structures.

peptide bond
the bond joining amino acid monomers together, between the carboxyl and amine groups of adjacent amino acids

peptide
a polymer of amino acid monomers

polypeptide
a large polymer of amino acid monomers

Primary structure

The primary structure of a protein is the sequence of amino acids. The amino acids are joined together by **peptide bonds** formed by the condensation reaction between the carboxyl end of one amino acid and the amino end of another (and producing water as a by-product) (Figure 2). A **peptide** is a polymer made of amino acid monomers, and a **polypeptide** is a large peptide containing many amino acids.

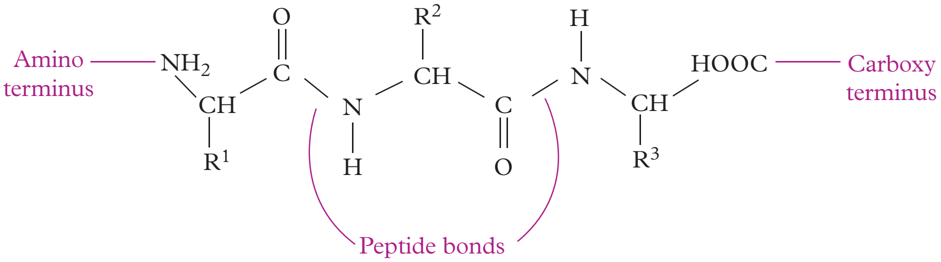


FIGURE 2 Peptide bonds between amino acids

The primary structure of a protein has a significant role in its biological function. For example, if a protein contains a large number of non-polar amino acids in a sequence, the protein adopts a particular shape in water so that the non-polar amino acids do not come into contact with water and other polar substances. The shape of the protein determines its function.

Secondary structure

The secondary structure of a protein is the localised folding of the polypeptide. The amino acids in the polypeptide must maintain their bond lengths and bond angles (particularly the rigid peptide bonds), which limits the options folding to an α-helix and a β-pleated sheet. Figure 3 on the next page shows the two types of secondary structures in proteins: α-helix coil and β-pleated sheet.

α-Helix

The α-helix (or α-helices (plural)) is a coiled spring structure in which the side chains of each amino acid extend beyond the helix itself. The coil is stabilised by hydrogen bonding between each peptide bond's carbonyl oxygen atom and the amino hydrogen atom of the peptide bond four amino acids along the polypeptide.

β-Pleated sheet

The β-pleated sheet is formed when adjacent polypeptides interact through hydrogen bonding between the peptide bonds, in a similar manner to the α-helix. The polypeptide sheets have a 'wavy' appearance due to the size of the amino acid side chains that protrude from the sheet, alternating between above and below.

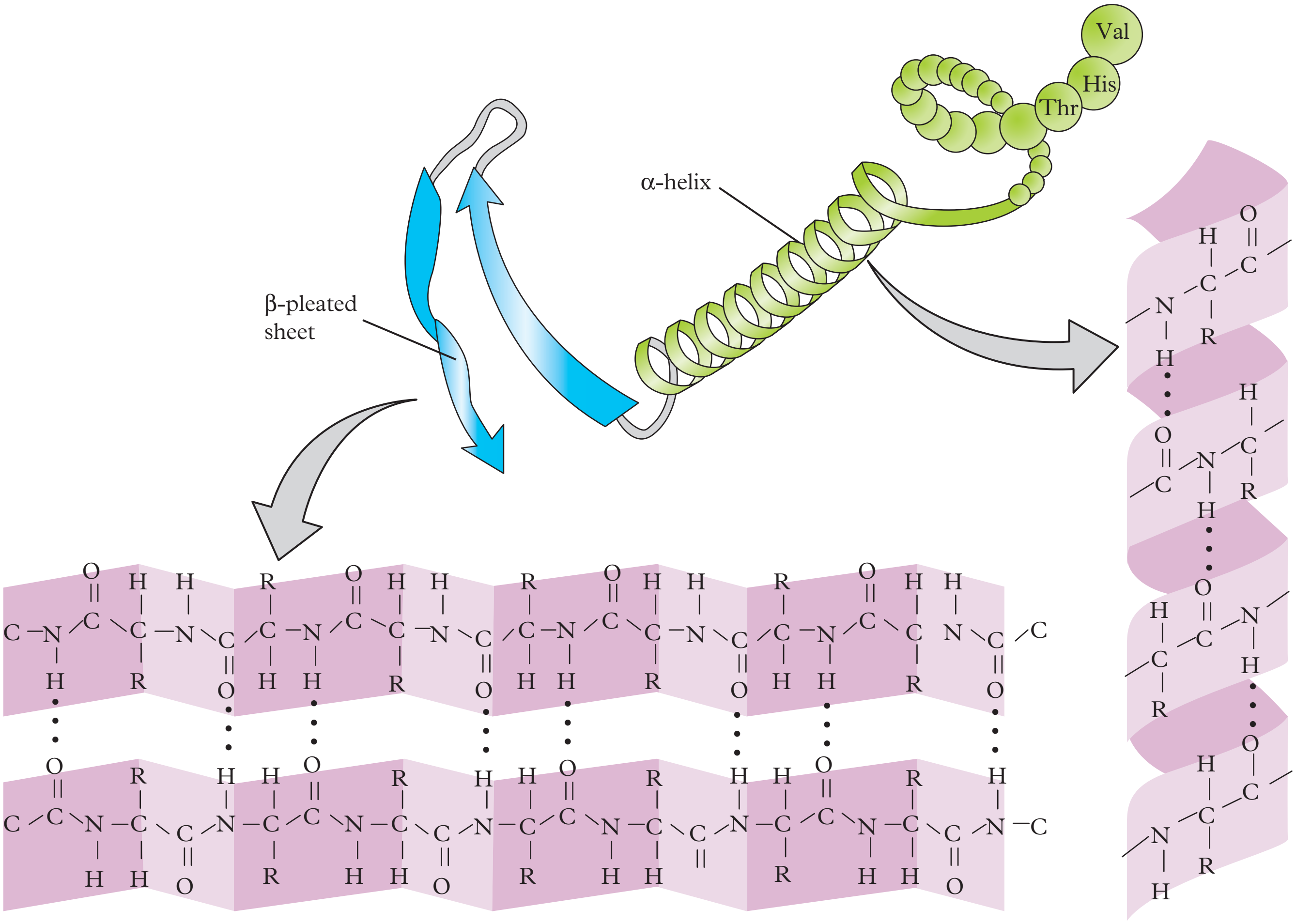


FIGURE 3 The types of secondary structures in proteins: an α-helix and a β-pleated sheet

Overall structures of proteins

Proteins fold into three-dimensional structures for two purposes – to minimise repulsion and maximise attraction between amino acids and with the surrounding environment.

- The hydrophobic effect refers to the folding of a protein to 'bury' non-polar amino acids within the interior of a protein's structure in order to shield them from water at the surface of the protein. Conversely, polar amino acids tend to exist on the surface of the protein so interactions with water takes place.
- Non-polar amino acids interact through hydrophobic interactions.
- Polar neutral amino acids interact through hydrogen bonding.
- Polar acidic and basic amino acids interact through ionic bonds, called a salt bridge.
- Cysteine amino acids interact through bonding of their sulfur atoms in a disulfide bridge.

Figure 4 illustrates the interactions that affect the overall structure of a protein.

α-Keratin is a protein found in hair, skin, nails and wool. α-Keratin contains disulfide bridges that bond many α-helices together, creating an insoluble, strong protein structure that is resistant to stretching. The number of disulfide bridges determines how hard the protein will be.

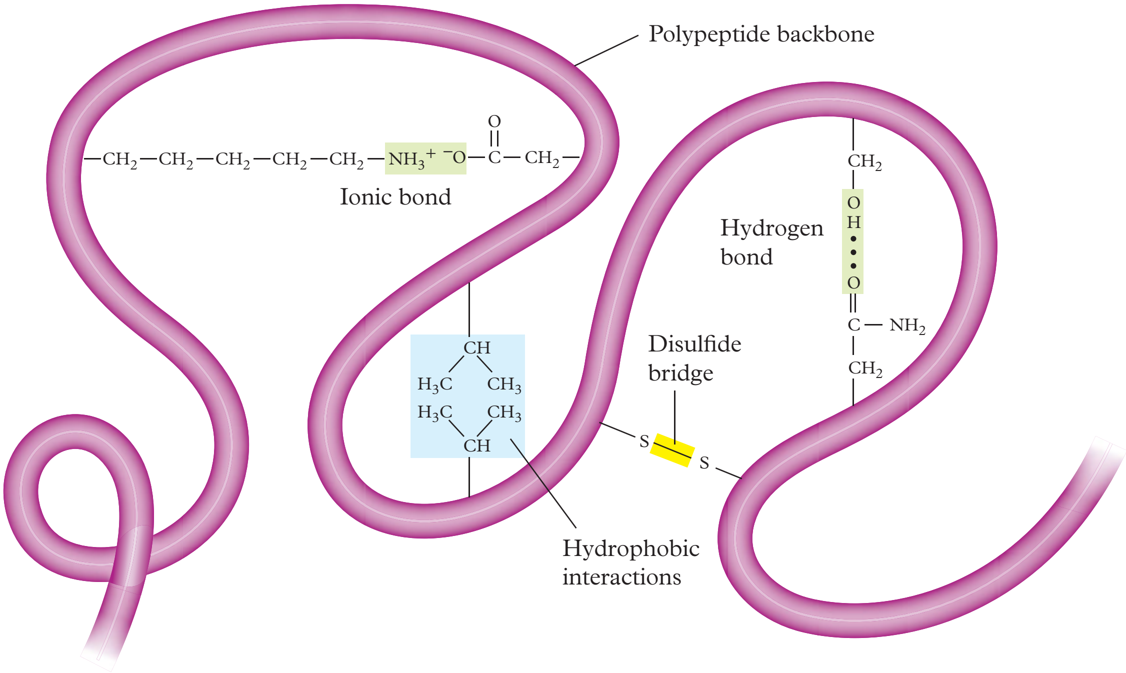


FIGURE 4 The types of amino acid interactions that contribute to the overall structure of a protein

Collagen is another insoluble protein, which is found in bone, cartilage, teeth and tendons. Collagen contains three α-helices bonded together. The difference between α-keratin and collagen is the type of amino acids present. Collagen does not have disulfide bridges because it does not contain cysteine. Instead, collagen's shape is determined by hydrogen bonding and cross-linking with amino acids such as lysine and histidine.

Tertiary structure

The tertiary structure of proteins is the three-dimensional interactions between the numerous secondary structures present in a polypeptide.

Myoglobin is the soluble protein in muscle tissue responsible for storing oxygen molecules to use when the muscle is working very hard. It is made of a single polypeptide chain of 153 amino acids with a combination of secondary structures. Myoglobin's tertiary structure results from non-polar amino acids participating in the hydrophobic effect. This leaves the polar amino acids on the surface of the protein, so that myoglobin is soluble in water, and has a hydrophobic cavity where the oxygen molecules are stored.

Quaternary structure

Polypeptides with 50 or more amino acids and their own biological function are referred to as simple proteins. Typical proteins are a combination of several polypeptides, and the interaction between these polypeptides forms the quaternary structure.

Haemoglobin is the soluble protein in red blood cells that transports oxygen molecules throughout the body. It has a similar structure to myoglobin. Haemoglobin consists of four polypeptides (instead of one as in myoglobin). It has more non-polar amino acids than myoglobin on the surface of the tertiary structures. Hydrophobic interactions between the polypeptides stabilise the protein's quaternary structure (and keep the non-polar amino acids away from the surrounding aqueous environment). Figure 5 on the next page shows the primary, secondary, tertiary and quaternary structures of a protein.

SUGGESTED PRACTICAL

11.3 Catalysing decomposition reactions
Go to your obook assess »

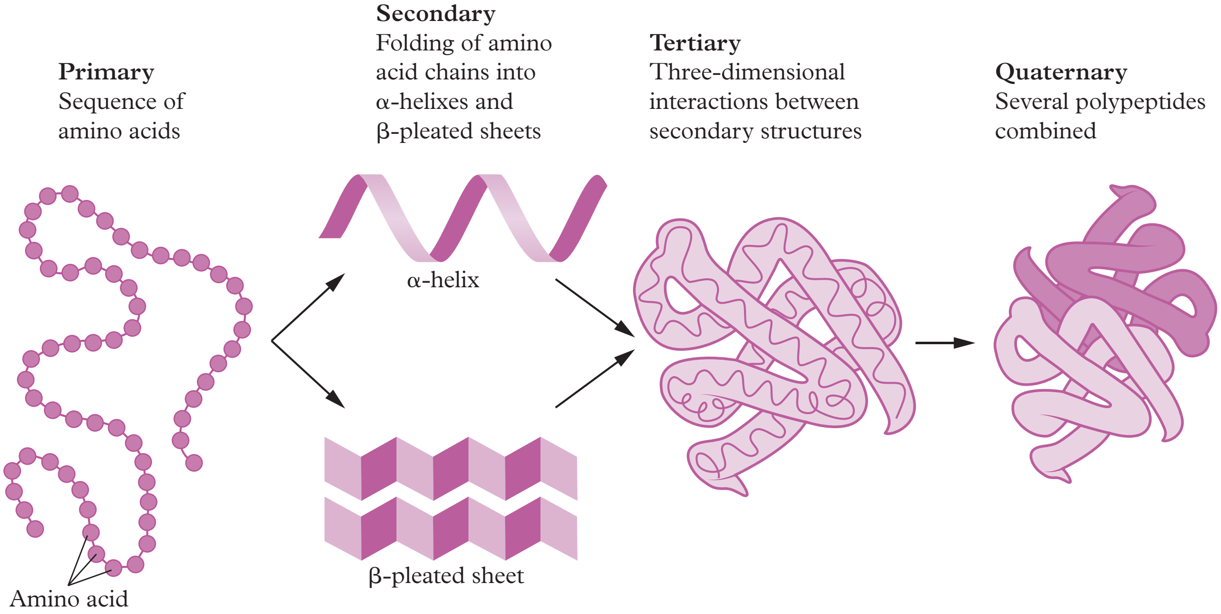


FIGURE 5 A summary of the four protein structures

Enzymes

enzyme
a biological catalyst

Study tip

Think of the interaction between an enzyme and its substrate as a lock and key. The substrate 'key' fits into the enzyme's active site to 'lock'.

Enzymes are proteins that catalyse chemical reactions in living organisms. Their structure is essential for their function as biological catalysts because many enzymes have an active site that is specific for one substrate. For example, the enzyme amylase catalyses the breakdown of starch into glucose molecules. Amylase will not break down any other polysaccharides such as cellulose.

The active site is an indentation in the protein structure that is big enough to fit the chemical reactants in the correct orientation for the reaction to take place. Interactions between the enzyme and its substrate involve the side chains on the amino acids to generate hydrophobic, hydrophilic, neutral and/or charged areas within the active site, with which the substrate interacts. Once the chemical reaction has taken place, the products leave the active site, and the enzyme is unchanged in structure and ready for the next chemical reaction (Figure 6). For example, carbonic anhydrase can catalyse 36 million chemical reactions in just 1 minute.

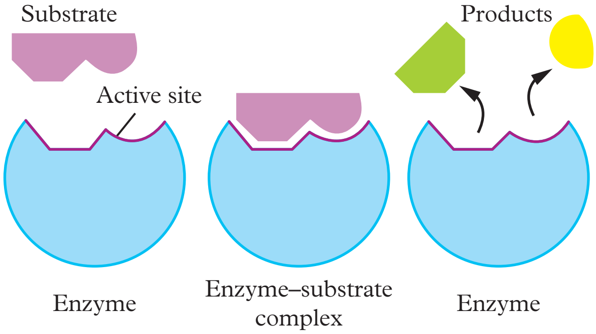


FIGURE 6 The interaction between an enzyme and a substrate

CHALLENGE 11.3

Nucleic acids

Nucleic acids are polymers in cell nuclei that store genetic information and synthesise proteins. They are known as deoxyribonucleic acid (DNA) and ribonucleic acid (RNA). The monomers of nucleic acid are called nucleotides – organic compounds made of a phosphate ion, a five-carbon sugar and a base (it contains amines).

Research the different types of bases in DNA and RNA, and how they interact with each other through hydrogen bonding.

CHECK YOUR LEARNING 11.3

Describe and explain

1 **Describe** the characteristics that enzymes require to be a catalyst.

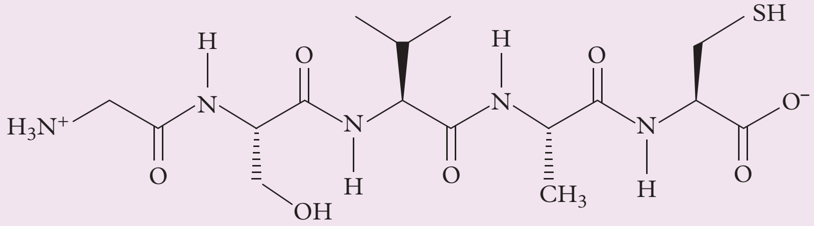
2 **Explain** how the primary, secondary and tertiary structures of proteins affect their properties.

Apply, analyse and interpret

3 **Compare** the α-helix and the β-pleated sheets of proteins.

4 **Interpret** the two polypeptides below to **identify** the location of the peptide bonds, and each of the amino acids in the sequence.

a



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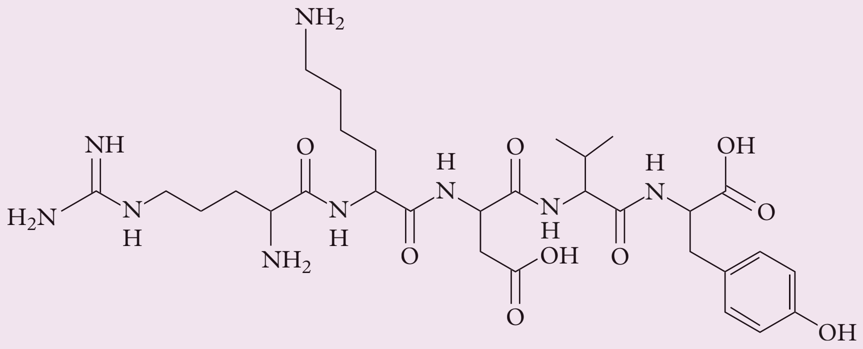


You can find the following resources for this section on your obook assess:

- » Student book questions
  11.3 Check your learning
- » Suggested practical
  11.3 Catalysing decomposition reactions
- » Challenge
  11.3 Nucleic acids

11.4 Synthetic polymers

KEY IDEAS

In this section, you will learn about:

- the formation of synthetic polymers by either condensation or addition reactions
- examples of synthetic polymers such as nylon, Teflon, polyethylene (PE), polyvinyl chloride (PVC), polytetrafluoroethylene (PTFE) and polypropylene.

macromolecule
a very large molecule

In 1920, German chemist Hermann Staudinger proposed synthetic polymers as molecules of high molecular mass (**macromolecules**) that were made of many small molecules. Although the study of polymers dates back thousands of years to pre-Columbian Mexico, Staudinger's ideas marked the beginning of our chemical understanding of polymers. Staudinger called the macromolecule synthesis reaction a polymerisation. The polymer industry took off from there, producing synthetic polymers such as nylon, synthetic rubber, Teflon and Kevlar (Figure 1).

FIGURE 1 The army uses the synthetic polymer Kevlar for helmets and other protective equipment such as bulletproof vests.

Polyethylene

Polyethylene (the polymer of ethene, also called polyethene) is the most common plastic to date (Figure 2). It is not hard or **rigid**, is chemically resistant (insoluble at room temperature) and easy to clean, and has a melting point of 80°C. These properties make it suitable for use as plastic milk bottles, laboratory wash bottles and plastic bags. When the polyethylene chain is approximately 200 carbons in length, it has the consistency of wax, but the larger the polymer the harder its consistency.

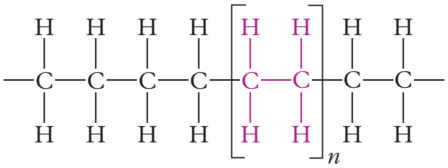


FIGURE 2 Polyethylene – a polymer of ethene

rigid
unable to change shape

Polymers experience significant dispersion forces, because of the number of electrons present in such a large molecule. However, dispersion forces are only effective when in close proximity. For this reason, high-density polyethylene (HDPE) is the strongest polymer because it has minimal branching. Low-density polyethylene (LDPE) has a higher degree of branching, so has less dispersion forces and is weaker (Figure 3).

FIGURE 3 Types of branching in polyethylene – high-density (HDPE) and low-density (LDPE) polyethylene

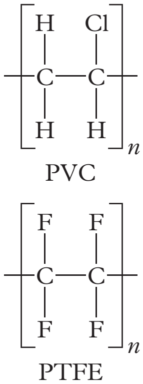
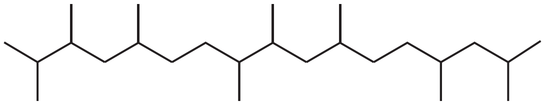


FIGURE 4 Substituted polymers – polyvinyl chloride (PVC) and polytetrafluoroethylene (PTFE)

Substituted polymers

Substituted polymers of ethene are very common and include polyvinyl chloride (PVC) and polytetrafluoroethylene (PTFE) as shown in Figure 4. Polytetrafluoroethylene has strong polar bonds between carbon and fluorine atoms, yet the molecule is non-polar because the polarity of each bond is counteracted by the polarity of the bonds on the opposing side of the polymer. As a result, PTFE is hydrophobic and unreactive. It is the major component of Teflon – the non–stick surface of frypans.

Polypropylene (the polymer of propene, also known as polypropene) is an asymmetrically substituted polymer containing many **chiral centres**, which result in three stereoisomers: isotactic, syntactic and atactic (Figure 5). The tacticity of a polymer determines the melting point, solubility and strength. The isotactic polymer has methyl groups on the same side along the length of the polymer. It has a melting point of 165°C and is strong, used effectively for carpeting. The syntactic polymer has alternating methyl groups on either side and a melting point of 125°C. It is used for glass microsphere insulation in deep water. The atactic polymer has randomly oriented methyl groups, making it rubbery and flexible, and effective for use as soft-drink bottles.


Atactic polyprophlene (aPP)


Isotactic polypropylene (iPP)

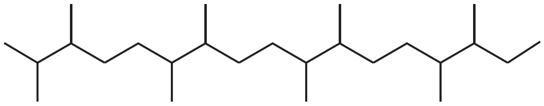

Syntactic polypropylene (sPP)

FIGURE 5 Types of polypropylene

Rubber is a natural polymer sourced from the rubber tree. It can also be synthesised by addition polymerisation reactions of 2-methylbut-1,3-diene (isoprene). Synthetic rubber is called poly-*cis*-isoprene. The elasticity of rubber is a result of its coiled bonding, which can stretch as the coils unwind and then recover when released.

chiral centre
a carbon atom bonded to four different substituents

CHECK YOUR LEARNING 11.4

Describe and explain

1 **Explain** how branching in polymers affect their properties.

2 **Explain** how bonding in synthetic polymers affects their properties.

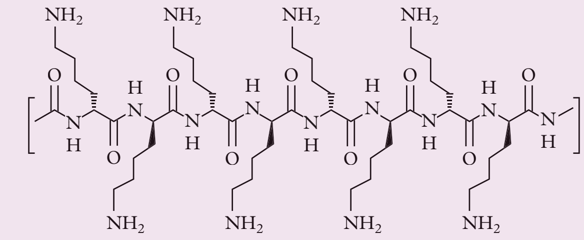
Apply, analyse and interpret

3 **Compare** the structure and properties of polyethylene with its substituted version polytetrafluoroethylene.

4 **Compare** the syntactic, isotactic and atactic versions of polypropene.

5 **Interpret** the two polymers to the right and identify the monomers used. Represent the monomers by using square brackets.

a



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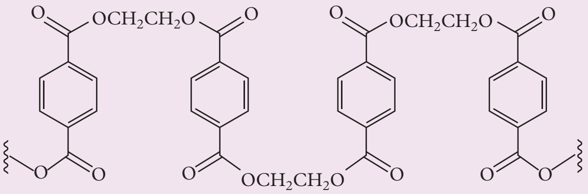


You can find the following resources for this section on your obook assess:

- » Student book questions 11.4 Check your learning
- » Weblink Kevlar
- » Weblink Rubber

SCIENCE AS A HUMAN ENDEAVOUR

11.5 Green polymer chemistry

KEY IDEAS

In this section, you will learn about:

- biodegradable polymers, which can break down into their monomer units
- bio-based polymers, which are sourced from renewable natural products, but are not necessarily biodegradable
- sustainable polymers, which are biodegradable bio-based polymers.

fossil fuel
a fuel sourced from the decomposition of dead organisms

durability
the ability to withstand damage

Synthetic fibres were first used by the textile industry in the 1930s when materials such as nylon (artificial silk) and polyester (stretchy and wrinkle-resistant) were introduced. Synthetic fibres are sourced from non-renewable **fossil fuels** and modified by scientists and engineers. Synthetic materials became popular because they are **durable**, stretchy, stain resistant and waterproof. For example, nylon is a popular choice of material for umbrellas (Figure 1) because it is waterproof. However, synthetic materials can be flammable, can generate static electricity, and do not ‘breathe’.


FIGURE 1 Nylon is used to make umbrellas because it is waterproof.

Many people are concerned about the risk posed by hazardous chemicals and environmental pollution by the textile industry. In 2011, the environmental organisation Greenpeace started the Detox campaign, which aims to reduce the use of hazardous chemicals by the textile industry and monitor contaminants in wastewater.

biodegradable
can be broken down by living organisms

Outside of the textile industry, there has been significant progress with **biodegradable** polymers. Reducing the time taken for rubbish to degrade is advantageous for landfill areas and waterways. Polyesters are polymers formed from a condensation reaction (esterification) of an organic compound with two carboxylic acid groups and another organic compound with two alcohol groups. Water is produced as a by-product. Polyesters are biodegradable because microorganisms can break the ester linkages with hydrolysis reactions. The internal sutures used in surgical procedures are biodegradable polyesters – the body can break them down within 90 days.

However, even though polyesters are biodegradable, they are not considered ‘green’ because of how they are synthesised. Polyesters are sourced from non-renewable fossil fuels and a significant amount of electricity and water is used in the production process. Green polymer chemistry focuses on producing polymers that are both biodegradable and sourced from renewable resources such as plants, waste products and waste gases.

There are three types of green (or sustainable) polymers: modified natural polymers, polymerised monomers from crops, and polymers synthesised by bacteria.

- Starch, cellulose and alginate are natural polymers that are modified to vary their properties and widen their applicability.
- Polylactic acid (PLA) is a polymer sourced from the fermentation of crops such as corn and potatoes into their monomer units and then polymerised. PLA is a transparent

and rigid polymer used in electronic, medical and automotive applications. It is the most popular material used in 3D printing (Figure 2). PLA is synthesised by a condensation reaction. However, the water by-product limits the number of monomer units that can be used in the process, so alternative reactions are used to compliment the polymerisation, to achieve the desired product.

- Polyhydroxyalkanoates (PHA) are a group of bio-based polymers that are produced naturally by bacterial fermentation. Examples include medium-chain-length PHA (mcl-PHA), polyhydroxybutyrate (PHB) and polyhydroxybutyrate-co-hydroxyvalerate (PHB-co-V). PHB is a mouldable plastic that has potential application for disposable nappies and packaging such as bottles, bags and wrapping. PHB is initially synthesised by the fermentation of glucose molecules by the bacteria *Alcaligenes eutrophus*, and degrades within 4 weeks in landfill by an ester hydrolysis and an elimination reaction.

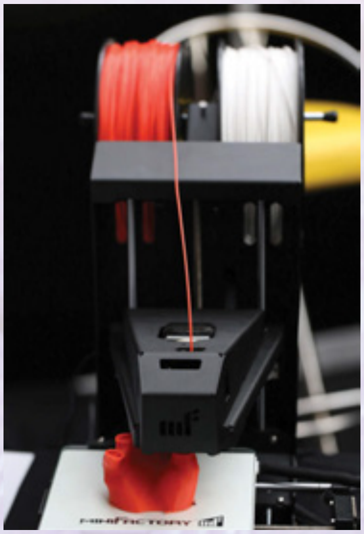


FIGURE 2 Polylactic acid is a polymer that is sourced from crops. It is used in 3D printing.

Although still at an early stage, biodegradable bio-based polymers offer a much-needed change in the polymer industry. They are already being used in plastic cutlery, food containers, clothing fibres, mobile phone cases, seating cushions and memory foam pillows. They are designed to last while the product is being used (rather than on the shelf waiting to be used). Scientists continue to research how to improve the applicability of sustainable polymers to simulate more of the physical properties of traditional synthetic polymers (such as melting point, elasticity and toughness).

CHECK YOUR LEARNING 11.5

Describe and explain

1 **Describe** the term ‘synthetic polymer’.

2 **Explain** how a biodegradable polymer may not be a sustainable polymer.

Apply, analyse and interpret

3 **Compare** the physical properties of common synthetic polymers to those of sustainable polymers.

Investigate, evaluate and communicate

4 **Investigate** the role of polyethylene as a sustainable polymer as well as a traditional synthetic polymer.

5 **Investigate** the polyhydroxyalkanoate group of bio-based polymers in terms of their synthetic and destructive chemical reactions.

You can find the following resources for this section on your obook assess:

» Student book questions
11.5 Check your learning

» Weblink
Nylon

» Weblink
PLA

CHAPTER **11**

Review

Chapter summary

11.1
- Monosaccharides are sugar monomers. They consist of a carbon chain with several hydroxyl groups, and either an aldehyde or a ketone, and in aqueous solution they exist as two forms in dynamic equilibrium – a straight chain and an α-ring.
- Polysaccharides are complex sugars containing many (sometimes hundreds) monosaccharides. Common examples are starch, cellulose, glycogen and chitin.

11.2
- Lipids are low-melting polymers. Lipids generally contain both hydrophobic and hydrophilic components. They are insoluble in water because they contain hydrophobic components, called fatty acids.
- Saponification of triglycerides involves boiling the lipid with an excess of aqueous sodium hydroxide, and breaking the three ester linkages to produce a glycerol molecule and three amphipathic fatty acid salts (commonly called soap).

11.3
- The monomer of a protein is called an amino acid. Amino acids have both amino and carboxyl functional groups.
- A protein's function depends on its primary, secondary, tertiary and quaternary structures.
- The primary structure of a protein is the sequence of amino acids that are joined together by peptide bonds.
- The secondary structure is the localised folding of a polypeptide, and can be categorised as α-helix or β-pleated sheet.
- The tertiary structure results from folding into three-dimensional structures for two purposes – to minimise repulsion and maximise attraction of the functional groups on their amino acids.
- The quaternaty structure results when many polypeptides interact as one protein.
- Enzymes are proteins that catalyse chemical reactions in living organisms.

11.4
- Synthetic polymers are formed by condensation or addition reactions of many monomer units.
- Polymers can contain elements other than carbon and hydrogen, as well as substituent branching that is consistent, alternating or randomly placed.
- The structure of a synthetic polymer determines its intermolecular forces, as well as its physical and chemical properties.

11.5
- Synthetic materials are made from non-renewable fossil fuel sources and modified by scientists and engineers.
- Significant progress has been made into biodegradable polymers in order to reduce the time taken for rubbish to degrade in landfill areas.
- Green polymer chemistry focuses on generating sustainable polymers that are both biodegradable and sourced from renewable resources such as plants, waste products and waste gases.

Key terms

- amphipathic
- biodegradable
- chiral centre
- disaccharide
- durability
- enzyme
- fatty acid
- fossil fuel
- glycosidic linkage
- hard water
- hydrophilic
- macromolecule
- monosaccharide
- peptide
- peptide bond
- polypeptide
- polysaccharide
- rigid
- saponification
- zwitterion

Revision questions

The relative difficulty of these questions is indicated by the number of stars beside each question number: ★ = low; ★★ = medium; ★★★ = high.

Multiple choice

1 Enzymes are proteins that:

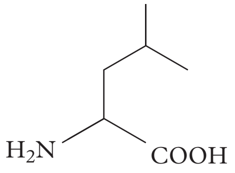
A transport molecules and ions
B defend against pathogens
C provide structural integrity
D catalyse reactions.

2 The empirical formula of monosaccharides is:

A CHO
B CH_2O
C CH_3O
D CH_4O.

3 Identify the structure of the amino acid tryptophan.

A



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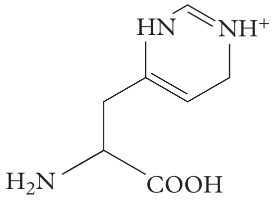

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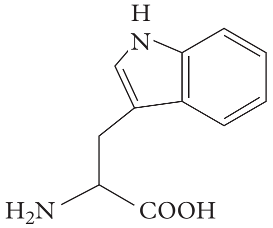

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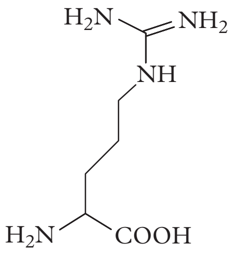
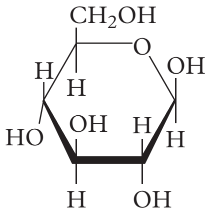


4 Hard water can be defined as water that contains:

A Al^{3+}
B Ca^{2+}
C Na^{+}
D Cl^{-}

5 The chair conformation of the β-glucose molecule is:

A



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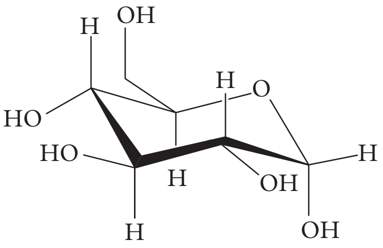

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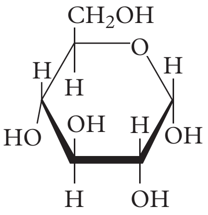

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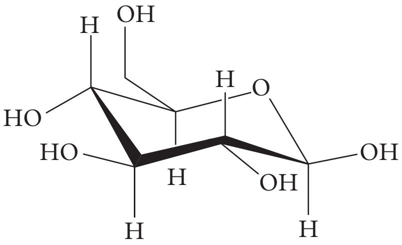


6 A zwitterion contains:

A NH_2 and CO_2^-

B NH_2 and CO_2H

C NH_3^+ and CO_2^-

D NH_3^+ and CO_2H.

Short answer

Describe and explain

★ **7** **Describe** the role of a protein's primary structure.

★ **8** **Define** a carbohydrate by its structural features.

★ **9** **Explain** how the bonding in lipids affects their properties.

★ **10** **Explain** how the structure of fatty acid salts makes them applicable as soaps.

Apply, analyse and interpret

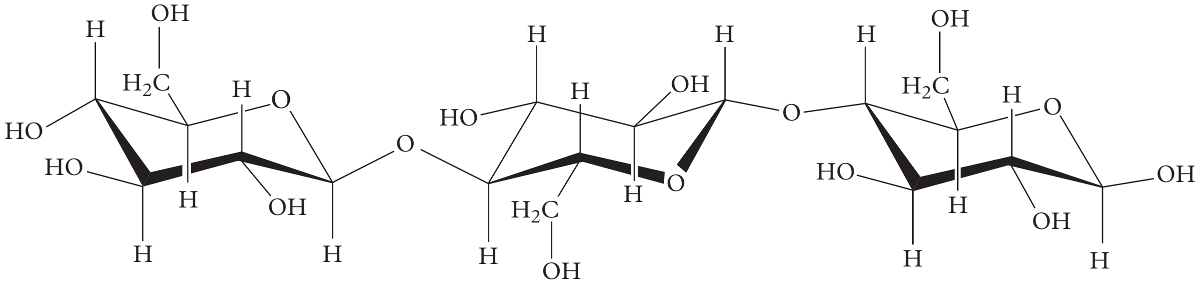
★ **11** **Compare** the structural properties of starch and cellulose.

★ **12** **Compare** the tertiary and quaternary structures of proteins.

★★ **13** Benedict's solution is often used to detect the presence of glucose. **Analyse** the structure of glucose to discuss how this is possible.

★★★ **14** **Interpret** the three polysaccharides below and on the next page, to **identify** and name each of the glycosidic bonds. Include whether they are α or β and **identify** the carbon atoms being bonded by their number.

a



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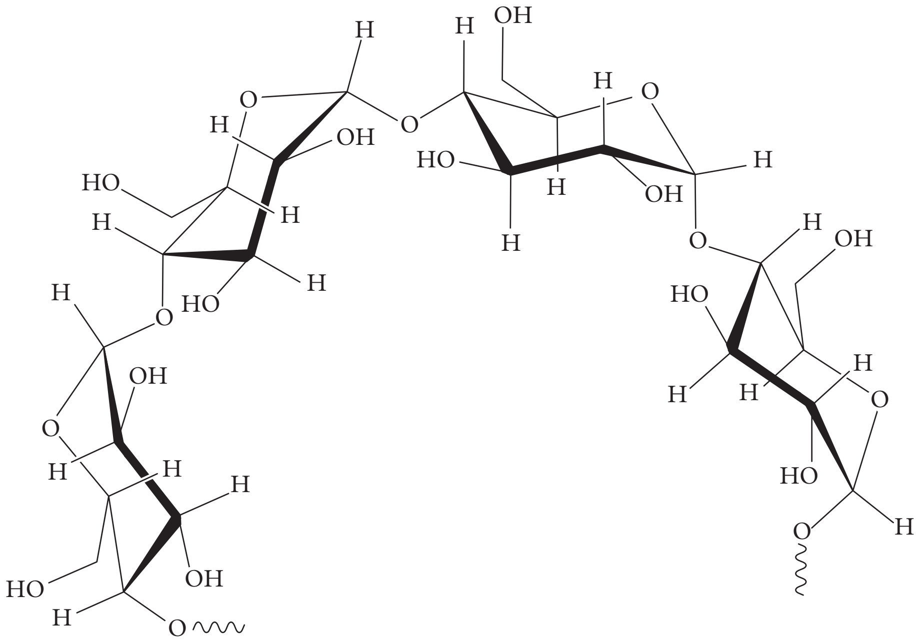

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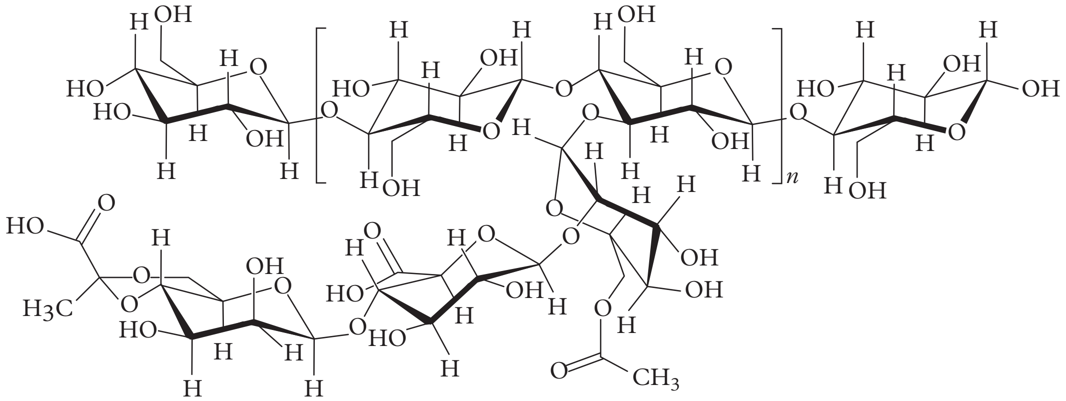

Investigate, evaluate and communicate

★★ **15** **Evaluate** how lipids can dissolve in acetone but not in water, even though acetone has an electronegative oxygen atom.

★★★ **16** **Investigate** the significance on the properties of soap caused by changing the fatty acids in the starting reagent of saponification reactions.

★★★ **17** **Investigate** artificial sweeteners in terms of their structure and properties, including their sweetness relative to standard sugars.

You can find the following resources for this section on your obook assess:

- » Student book questions
  Chapter 11 Revision questions
- » Revision notes
  Chapter 11
- » assess quiz
  Auto-correcting mutiple-choice quiz
- » Flashcard glossary
  Chapter 11

CHAPTER 12

Analytical techniques

When a new compound is isolated and purified from a natural source or is made in the laboratory, how does a chemist know what the structure of that compound is? If scientists know the structure, they can predict how a compound may react, how it can be synthesised and how it may work as a drug. There are several analytical techniques available to help chemists with this task. Each technique reveals different kinds of information about the compound. Larger molecules such as proteins can also be investigated by techniques such as protein gel electrophoresis (Figure 1).

OBJECTIVES

- → Select and use data from analytical techniques, including mass spectrometry, X-ray crystallography and infrared spectroscopy, to determine the structure of organic molecules.
- → Analyse data from spectra, including mass spectrometry and infrared spectroscopy, to communicate conceptual understanding, solve problems and make predictions.
- → Explain how proteins can be analysed by chromatography and electrophoresis.

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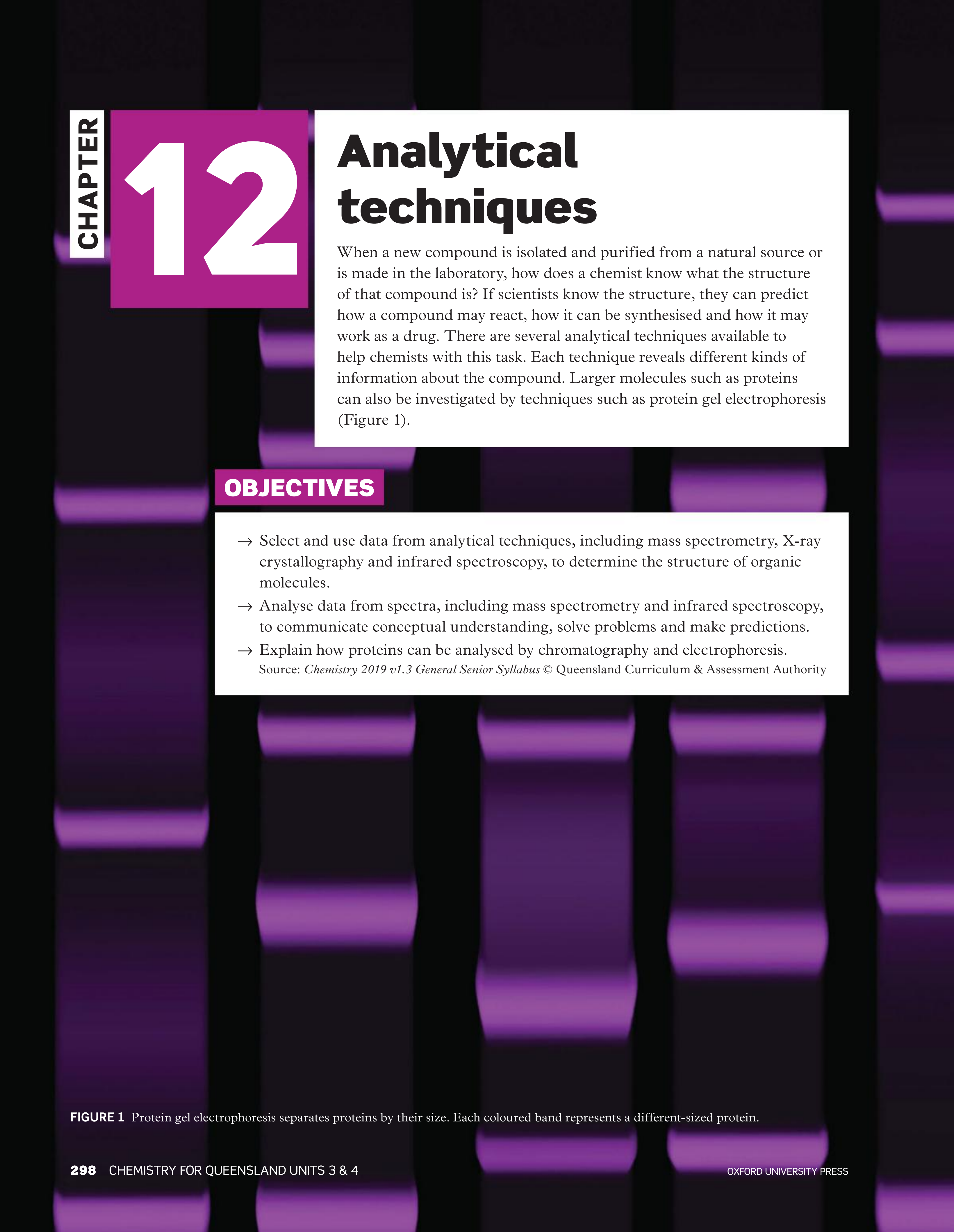
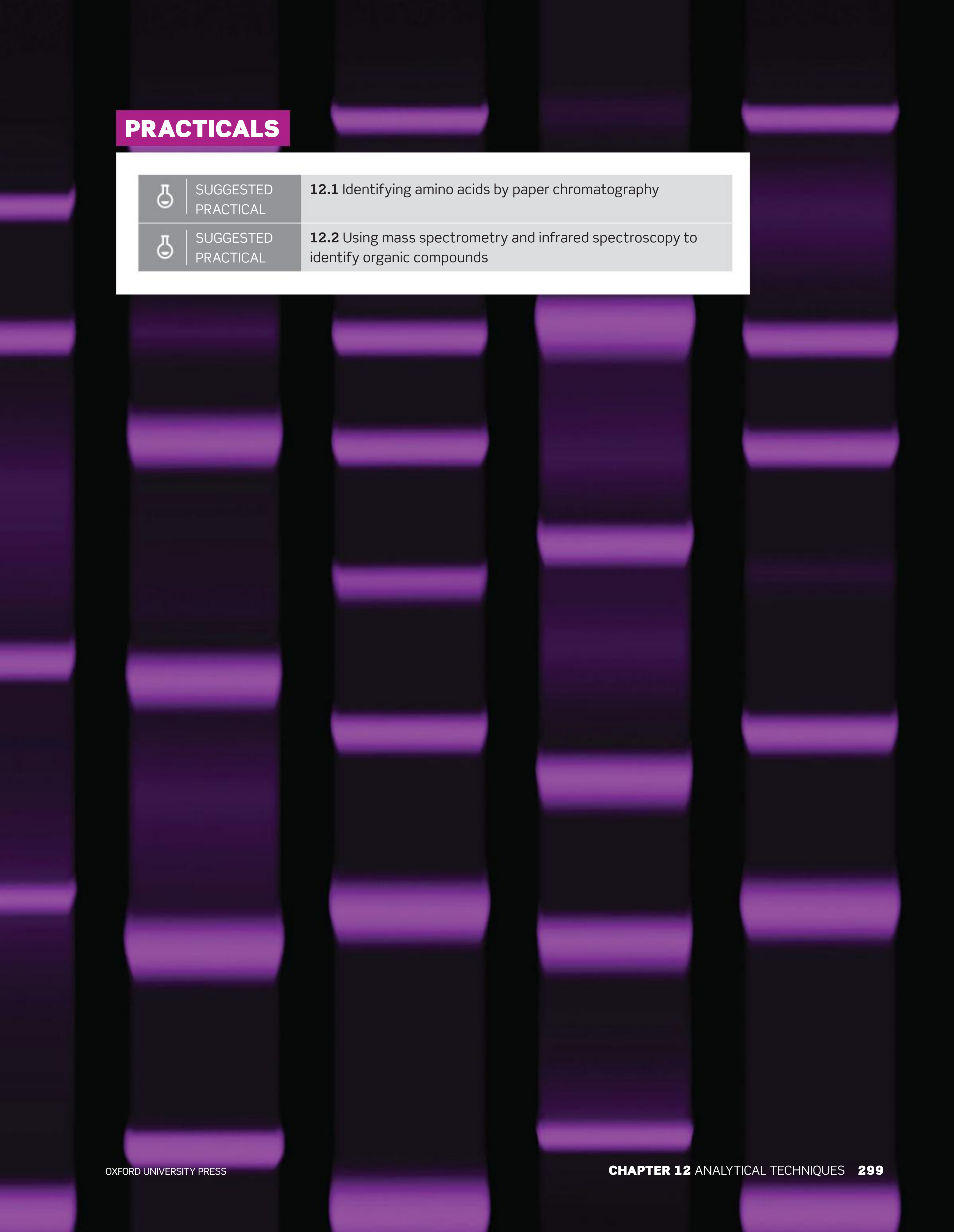


FIGURE 1 Protein gel electrophoresis separates proteins by their size. Each coloured band represents a different-sized protein.



PRACTICALS

SUGGESTED PRACTICAL	**12.1** Identifying amino acids by paper chromatography
SUGGESTED PRACTICAL	**12.2** Using mass spectrometry and infrared spectroscopy to identify organic compounds

12.1

Chromatography and electrophoresis of proteins

KEY IDEAS

In this section, you will learn about:

- how proteins can be separated and purified by size
- how the movement of proteins in an electrical field (electrophoresis) can give information about their overall charge and size.

Proteins are biological polymers – large molecules with repeating units of amino acid residues joined together by peptide bonds (Figure 1). An amino-acid residue is what remains when two or more amino acids combine to form a peptide and the elements of water are removed.

Proteins may naturally bind tightly but reversibly to certain small molecules such as sugars, biotin or metal ions. Binding regions can be added to proteins by genetic engineering techniques.

Proteins can be separated from each other on the basis of size, charge and binding affinity. Refer to the Increase your knowledge on your obook assess for more information on charge and binding affinity.

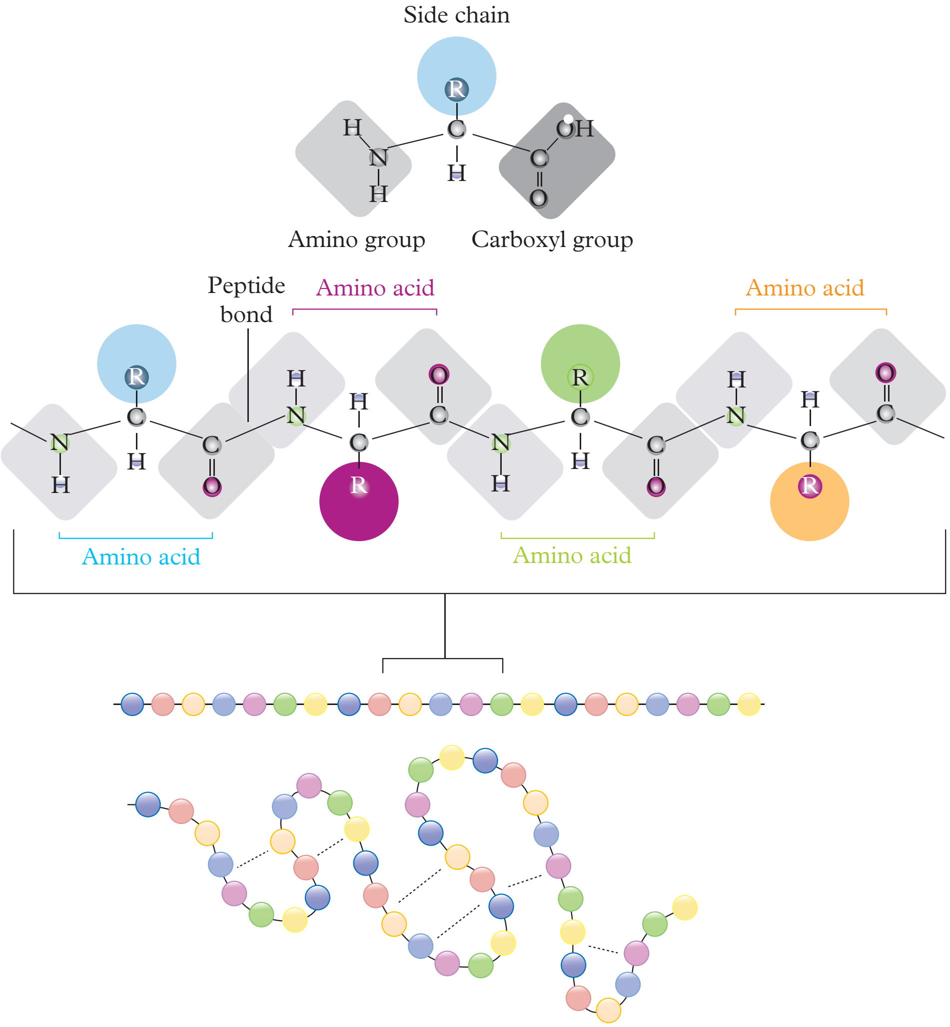


FIGURE 1 Proteins are long chain-like polymers made up of repeating amino acids, joined together by amide or peptide bonds. There are 20 common amino acids found in proteins.

SUGGESTED PRACTICAL

12.1 Identifying amino acids by paper chromatography
Go to your obook assess »

Size

The typical protein in organisms whose cells have a membrane-bound nucleus (eukaryotes) is about 400 amino acid residues long, although this can vary significantly. **Size exclusion chromatography** is a technique that separates proteins on the basis of size using an eluent (or buffer) solution.

size exclusion chromatography a type of chromatography that separates molecules on the basis of size, with the largest molecules eluting first

In size exclusion chromatography, a solution containing proteins is loaded onto the top of a column containing a resin or gel. A buffer solution is added and the proteins are washed through the column in different volumes of the eluting solution. The eluted solution is collected in small portions called fractions. The presence of a protein in a fraction can be detected by a UV–visible spectrometer because the amide groups and aromatic groups in the amino acid side chains absorb UV light.

The largest proteins elute first from the column because proteins that are too large to fit into the pores of the resin pass straight through the column – in the void volume – with no separation (Figure 2). The void volume (V_0) of the column can be measured by using a coloured dye of very high molecular mass.

Medium-sized proteins distribute between the mobile phase inside and outside of the gel. Smaller proteins spend more time inside the pores of the resin and take longer to elute. You can estimate the molecular mass and size of a protein by measuring how long it takes to elute from a column and comparing this to the times for proteins of known molecular mass and similar shape. Biochemists tend to use the unit of kilodalton (kDa) to measure molecular mass. An amino acid residue is around 135 Da, so a protein that contains 250 amino acids is 33.8 kDa in size, or 33 800 g mol^{-1}.

Study tip

One kilodalton is the same as a molar mass of 1 kg mol^{-1}.

You can use the following formula to determine the proportion of pores available for the molecule (K_{av}) for each protein eluting:

$$K_{av} = \frac{V_{eltn} - V_0}{V_c - V_0}$$

where V_0 is the void volume, V_c is the total volume of the column, and (V_{eltn}) is the volume at which the protein eluted. K_{av} is then graphed against $\log_{10}$(molecular mass kDa).

Proteins that are small enough to fit inside the pores completely take the longest time to leave the column (Figure 2). As with the large proteins that elute in the void volume, there is no separation of these small molecules. These proteins are said to be beneath the penetration limit for the column. Only the medium-sized proteins will be in the inclusion limits.

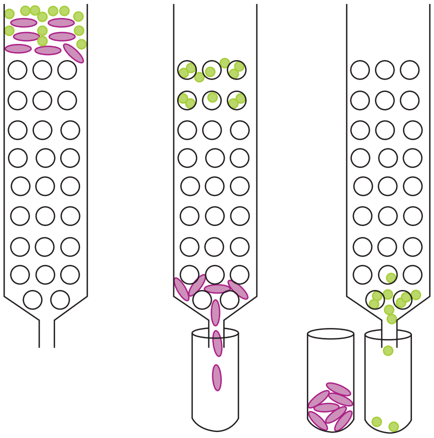


FIGURE 2 A size exclusion chromatography column. The purple proteins are too large to fit in the pores of the resin so elute first. The smaller green proteins elute last. There is no separation into different sizes for these two groups of proteins.

For adequate separation, choose the right type of resin, which will separate proteins in the desired size range.

WORKED EXAMPLE 12.1

A size exclusion chromatography experiment was run to estimate the size of a newly discovered protein, called Qld01. Proteins of known molecular mass were run as standards on a column with a total column volume of 150 mL. The experimental data is reported in Table 1.

Estimate the size of the Qld01 protein from the data given, if the elution volume of the fraction containing Qld01 protein was 118.0 mL.

TABLE 1 Protein size and elution volume for known proteins and elution volume for Qld01 protein

Protein molecular mass (kDa)	Elution volume (mL)
251.2	52
158.5	52
151.2	100
112.0	105
63.15	114
35.42	123
28.81	127
19.56	138
Qld01 (unknown)	118

SOLUTION

The first two entries in Table 1 for elution volume are identical. This suggests that both of those proteins have eluted in the void volume.

Therefore, the void volume (V_0) is 52 mL. The total volume of the column was given in the question and is 150 mL.

There is an inverse linear relationship between K_{av} and $\log_{10}$(molecular mass) for proteins that are in the inclusion limits. Construct a table (Table 2) of these values and then plot a graph (Figure 3).

TABLE 2 The relationship between K_{av} and $\log_{10}$ (molecular mass)

Protein molecular mass (kDa)	Log_{10} (molecular mass kDa)	Elution volume (mL)	$K_{av} = \frac{V_{eltn} - V_0}{V_c - V_0}$
251.2	-	52	-
158.5	-	52	-
151.2	2.1796	100	0.489
112.0	2.0492	105	0.541
63.15	1.8004	114	0.633
35.42	1.5492	123	0.724
28.81	1.4595	127	0.765
19.56	1.2914	138	0.878
Qld01	Unknown	118	0.673

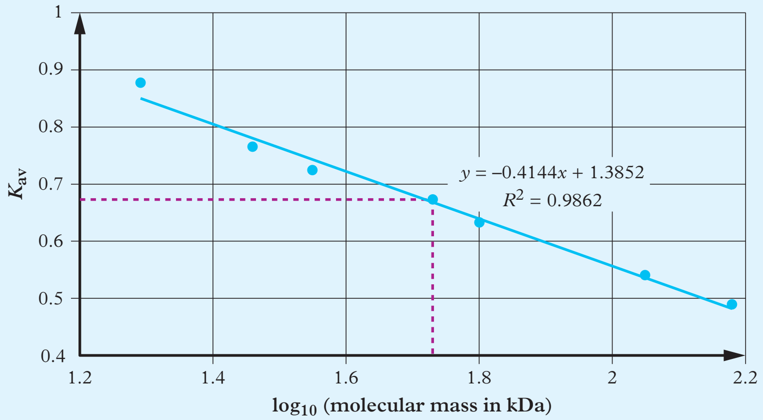


FIGURE 3 The graph of K_{av} vs $\log_{10}$(molecular mass in kDa)

You can calculate the value of K_{av} for the Qld01 protein as 0.673. From the graph, you can see that the value of $\log_{10}$(molecular mass in kDa) is a little more than 1.7. You can calculate a more precise value by using the equation for the line of best fit, of 1.72.

$$\begin{aligned}\text{Molecular mass (kDa)} &= 10^{1.72}\\ &= 52.5\,\text{kDa}\end{aligned}$$

An amino acid residue is 135 Da so this length is about 389 amino acid residues.

Does this answer make sense? The elution volume of 118 mL is between that of proteins with a molecular mass of 63 and 35 kDa, so the answer is in the right range.

Electrophoresis of proteins

In **electrophoresis**, proteins are separated on the basis of their net charge, size and shape, all of which affect how they will move through a gel in the presence of an electrical field. Proteins are attracted to the electrode with an opposite charge to their own. Proteins that are more highly charged move faster through the gel. This technique is known as native gel PAGE (polyacrylamide gel electrophoresis) because the protein is in its native state. The size of the protein and its shape also affect how it moves through the pores of the gel. Alkaline buffers are usually used for **native PAGE**, so most proteins will have a negative overall charge under these conditions.

electrophoresis
a separation technique that involves the movement of charged particles, such as proteins, along an electric field

native PAGE
polyacrylamide gel electrophoresis under conditions in which the protein retains its natural shape

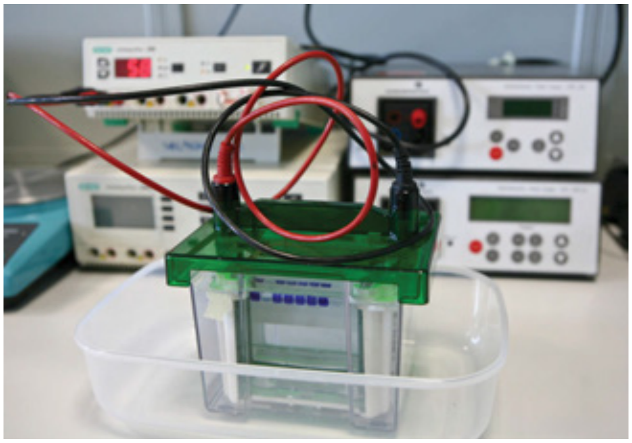


FIGURE 4 A gel electrophoresis tank. An electrical field is applied across a gel to separate charged biomolecules such as proteins or DNA.

SDS-PAGE
sodium dodecyl sulfate polyacrylamide gel electrophoresis; a purification technique that separates proteins on the basis of size when they pass through a gel under an applied electrical potential

A second type of gel electrophoresis, called **SDS-PAGE** (sodium dodecyl sulfate PAGE) is more common and can be used to calculate the molecular mass of proteins (Figure 5). An anionic detergent called sodium dodecyl sulfate (SDS) is added to the protein mixture. This detergent binds tightly (but non-covalently) to protein molecules and denatures or unwraps them, disrupting their native structure. These all have a very similar overall charge because the detergent is anionic, which cancels any positive charges on the protein. Proteins move through the gel depending on their size. The distance travelled by a protein band can then be related to bands from proteins of known molecular masses. The standards contain proteins of different sizes over a suitable range, and the standards are often known as molecular mass markers or protein ladders.

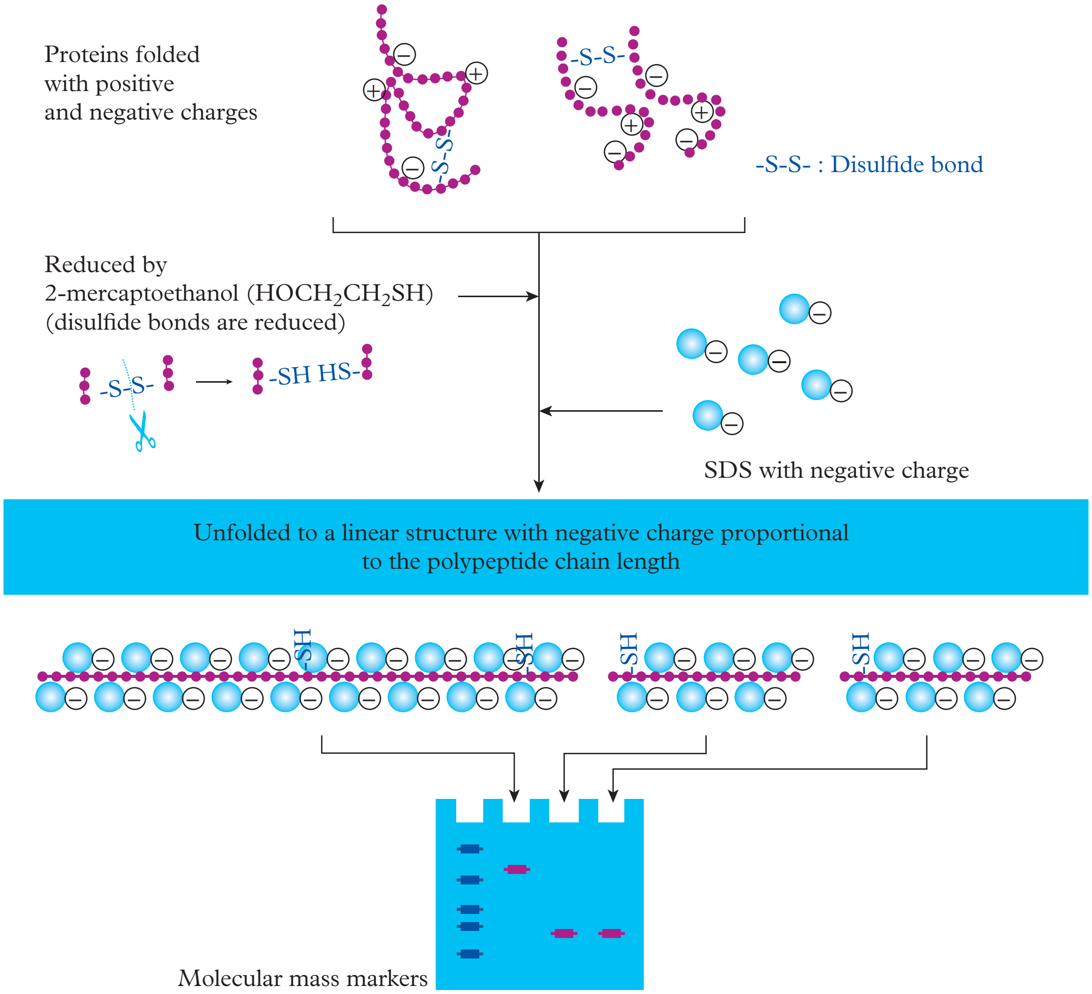


FIGURE 5 During SDS-PAGE, proteins are denatured and disulfide bonds are reduced. The presence of negatively charged detergent molecules associated with the proteins means that separation is purely on the basis of size of the protein.

After the gel is run, the proteins on the gel are made visible with a protein stain. The positions of the bands are measured and compared to proteins of known molecular mass. The density of the band is proportional to the amount of protein present and you can measure this quantitatively with UV light and image analysis software. If the gel has uniform cross-linking throughout, the R_f (retention factor) is inversely proportional to the log of the mass of the protein. If proteins of known mass are run simultaneously with the unknowns, you can plot the relationship between R_f and mass, and estimate the masses of the unknown proteins.

Gel electrophoresis can also be used to separate other charged biological macromolecules, such as DNA.

CHECK YOUR LEARNING 12.1

Describe and explain

1 **Describe** how size exclusion chromatography works to separate proteins.

Apply, analyse and interpret

2 A protein biochemist wishes to purify the protein insulin from a solution that contains several other proteins. The molecular masses of the proteins are shown in Table 3.

TABLE 3 Molecular masses of proteins in a solution

Protein	Molecular mass (kDa)
1	32
2	4.2
3	18
Human insulin	5.8

If the biochemist wants to separate insulin from the other proteins by size exclusion chromatography, which protein fraction would contain insulin (first fraction eluted, second, third etc.)? **Explain** your answer in terms of how size exclusion chromatography works.

Investigate, evaluate and communicate

3 Lactoferrin is a very common protein in milk. It is an iron-binding protein that has antimicrobial properties and is purified from milk and sold in tablet form or added to infant formula. **Investigate** how lactoferrin is purified from milk and present this information as a flow chart to show the process involved.

FIGURE 6 Lactoferrin is a protein that is purified from milk.

You can find the following resources for this section on your obook assess:

- Student book questions
  12.1 Check your learning
- Suggested practical
  12.1 Identifying amino acids by paper chromatography
- Increase your knowledge
  Charge and binding affinity

12.2 Data from analytical techniques

KEY IDEAS

In this section, you will learn about:

- mass spectrometry, a technique to determine the mass of organic molecules and give information about their composition
- using infrared spectroscopy to determine the presence of functional groups in an organic compound
- X-ray crystallography, which can be used to reveal the bond lengths and angles in a molecule.

Mass spectrometry

Mass spectrometry allows you to determine the molecular mass and the molecular formula of a compound. It can also give some information about the structure of a molecule and can be used as a 'molecular fingerprint'.

mass spectrometry a technique used to determine the molecular mass of a compound

Mass spectrometry only requires very small amounts of sample, which can be solid, liquid or gas. The sample is introduced into the mass spectrometer, where it is vaporised by heating or other techniques. There are many types of mass spectrometers, but all rely on creating charged particles. In the oldest type of mass spectrometer, a beam of high-energy electrons collides with the vaporised sample. The impact of the electrons causes an electron to be lost from the molecule, producing a **molecular ion**, which is a type of radical cation, having both a positive charge and one unpaired electron. Because of the large amount of energy transferred to the molecular ion, it can break apart into smaller fragments. Other ionisation methods, such as chemical ionisation, electrospray ionisation and matrix-assisted laser desorption/ionisation are often used, because these are gentler ionisation methods.

molecular ion the ion formed when an electron is lost from a neutral molecule; in a mass spectrum this ion has the highest *m/z* value

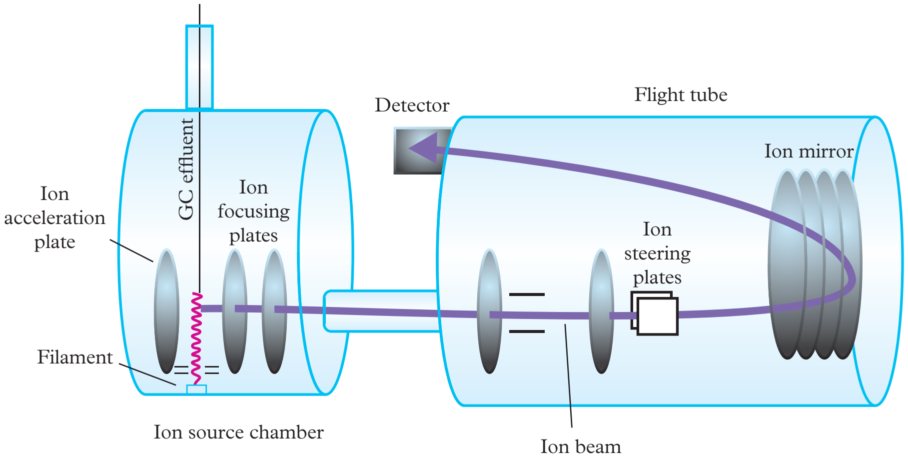


FIGURE 1 The components of a time-of-flight (TOF) mass spectrometer

A time-of-flight (TOF) mass spectrometer (Figure 1) works on the basic principle that ions that are given the same amount of **kinetic energy** will have velocities proportional to their respective mass-to-charge (*m*/*z*) ratio. In the ion source chamber, the filament is powered up for a very short period of time, which creates a pulse of ions, all of different *m*/*z* ratios.

kinetic energy the energy associated with moving particles

SUGGESTED PRACTICAL

12.2 Using mass spectrometry and infrared spectroscopy to identify organic compounds
Go to your obook assess »

The signals from the detector are plotted against time, which are then converted directly into *m*/*z* values. The spectrometer can measure differences in arrival time of as little as 1 nanosecond. The slowest moving ions take the longest time to arrive and thus have the highest *m*/*z* ratios. A TOF mass spectrometer is popular because it can measure a wide range of *m*/*z* values and is the fastest type of analyser.

If the molecular ion is stable enough, it will remain intact and reach the detector. This ion will have the highest *m*/*z* value. Because nearly all of the ions will have a +1 charge, the mass can easily be calculated from the *m*/*z* value. The high-energy electron beam causes some of the molecular ions to break apart into lower molecular mass fragments. These positively charged fragments reach the detector before the molecular ion, because of their lower *m*/*z* values.

Study tip

To understand how to calculate *m/z*, go to your obook assess for an Increase your knowledge worksheet.

Study tip

Remember spectra is plural for spectrum.

Figure 2 shows a typical mass spectrum.

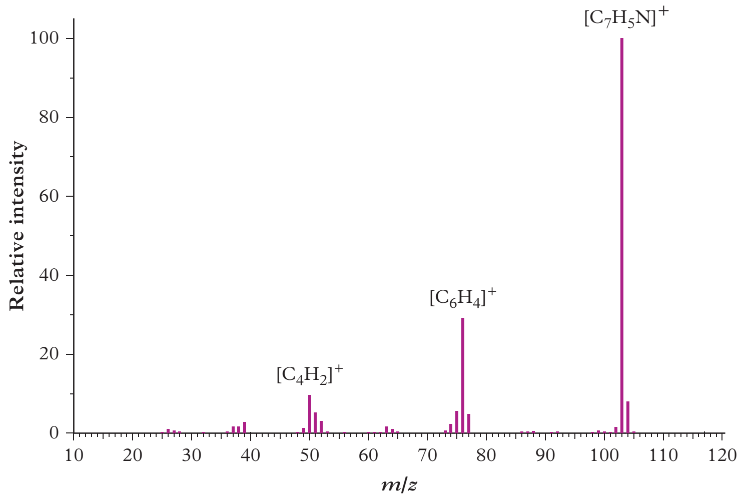


FIGURE 2 The mass spectrum of benzonitrile (C_7H_5N). The molecular ion is observed at *m*/*z* 103 and smaller fragment ions appear at around *m*/*z* 76, 50 and 39.

Infrared spectroscopy

Infrared radiation is the part of the electromagnetic spectrum between the visible and microwave regions. It is often measured in **wavenumbers** ($\bar{\nu}$) (the reciprocal of wavelength, λ) in units of reciprocal centimetres (cm^{-1}):

$$\bar{\nu}\,(\mathrm{cm^{-1}}) = \frac{1}{\lambda\,(\mathrm{cm})}$$

Recall that for the electromagnetic spectrum:

$$\lambda v = c$$

where λ is wavelength (m), v is frequency (Hz or s^{-1}) and *c* is the speed of light in a vacuum ($2.998 \times 10^8\,\mathrm{m\,s^{-1}}$), and:

$$E = hv = \frac{hc}{\lambda}$$

where *E* is energy (J) and *h* is Planck's constant ($6.626 \times 10^{-34}\,\mathrm{J\,s}$).

Atoms in molecules are constantly vibrating and bonds behave more like springs than rigid rods. The two most common types of vibrations are **stretching** and **bending vibrations**.

infrared radiation electromagnetic radiation in the region between visible light and microwave radiation

wavenumber the reciprocal of wavelength (where wavelength is measured in cm)

stretching vibration a vibration of a molecule or ion that involves a change in bond distances

bending vibration a vibration of a molecule or ion that involves a change in bond angle

bond length
the distance between the nuclei of two bonded atoms

infrared spectroscopy
a technique that looks at how molecules interact with infrared light

bond angle
the angle defined by three atoms, where the two outer atoms are both covalently bonded to the central atom

Stretching vibrations change the **bond length** and occur along the axis of a bond. In **infrared spectroscopy**, you can observe these stretching vibrations in organic molecules at wavenumbers from about 4000 to 1400 cm^{-1}.

Bending vibrations result in changes of **bond angles**; they do not occur along the axis of a bond. These occur at lower energy than stretching vibrations, from about 1400 to 600 cm^{-1}.

Each type of vibration occurs at a particular frequency. Different types of bonds have different characteristic vibrational frequencies, so if you measure the frequencies of light that are absorbed, you can work out what functional groups are present in a particular compound. For example, the C=O functional group absorbs in the region 1780–1650 cm^{-1}, which is in the infrared region of the electromagnetic spectrum (Figure 3). Stretching vibrations are the most useful for working out the functional groups in a compound.

Study tip

C–C stretches are often quite weak and are not generally useful for identifying functional groups or molecules because nearly every organic molecule has C–C bonds.

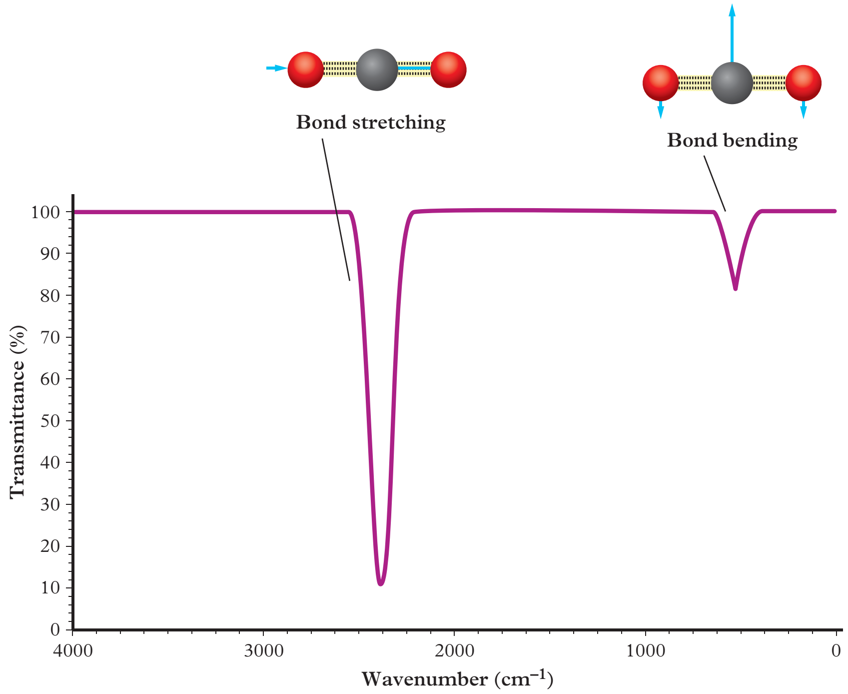


FIGURE 3 Vibrations of carbon dioxide and the accompanying infrared absorptions

The frequency of a vibration depends on the atoms in the bond and the type of bond between those atoms. Bond strength increases from single to double and then triple bonds. Subsequently, the wavenumber of associated stretching vibrations also increases.

Study tip

The QCAA Chemistry formula and data book show other characteristic infrared regions with different bond types.

TABLE 1 Characteristic infrared regions for different stretching vibrations

Type of bond	Wavenumber region for stretching vibrations (cm^{-1})
C–N	1230–1020
C=N	1650–1550
C≡N	2260–2220
C–O	1410–1050
C=O	1750–1700
C=C	1680–1620
C≡C	2260–2100

transmittance
the ratio of the intensity of transmitted light (light that has passed through the sample) to incident light (the light first put out by the light source).

An infrared spectrum is typically shown with **transmittance** as a percentage on the *y*-axis and wavenumber on the *x*-axis, starting from high wavenumbers on the left (Figure 4). More strongly absorbing bands will have lower transmittance (%) values.

The relationship between transmittance and absorbance is:

Absorbance = $2 - \log^{10}$(transmittance (%))

The intensity of an absorption band depends on the size of the change in the dipole moment with the stretching vibration. Larger changes in the dipole moment result in increased absorption. This explains why you can distinguish infrared absorptions due to C=O and C=C bands even though they occur in overlapping regions of the infrared spectrum. Because the C=O bond is more polar, its stretching vibrations result in a greater change in dipole moment, and greater absorbance. Figures 5 and 6 show the infrared spectra of propanone (which contains a C=O group) and 2-methyl-1-propene (which contains a C=C group). You can see that the band due to the C=C bond (about 1650 cm^{-1}) is much smaller that the band due to the C=O bond (1750 cm^{-1}).

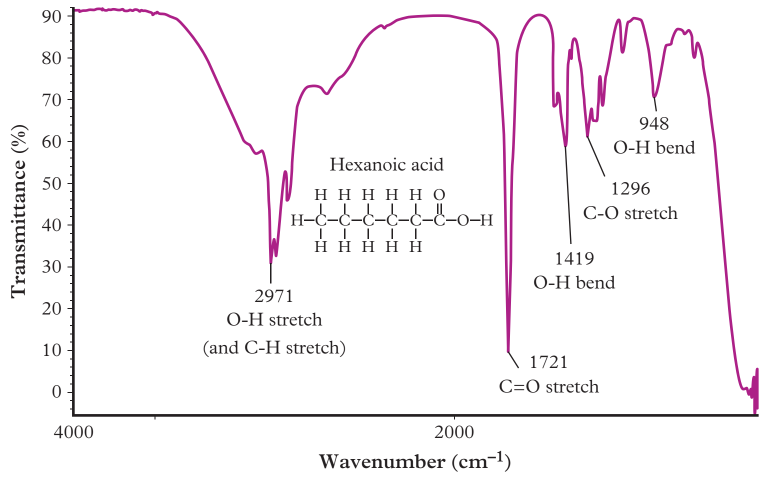


FIGURE 4 The infrared spectrum of hexanoic acid

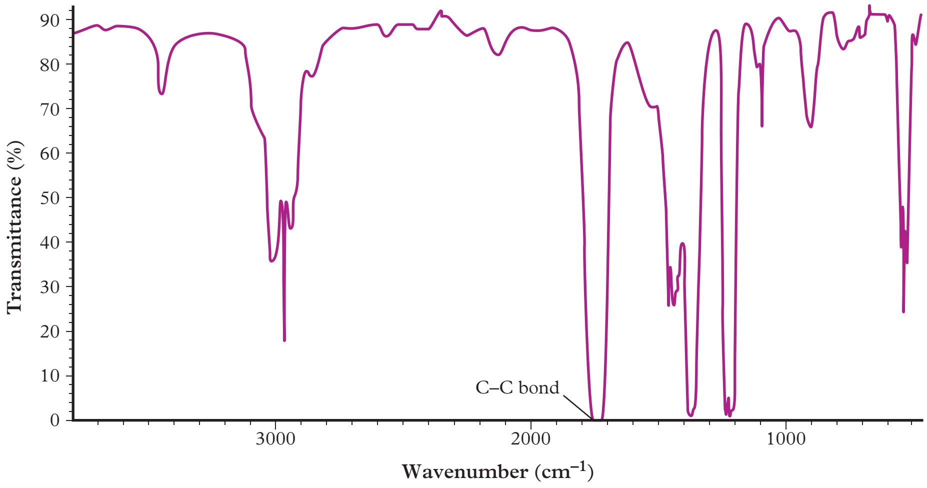


FIGURE 5 The infrared spectrum of propanone (acetone) ($(CH_3)_2C=O$)

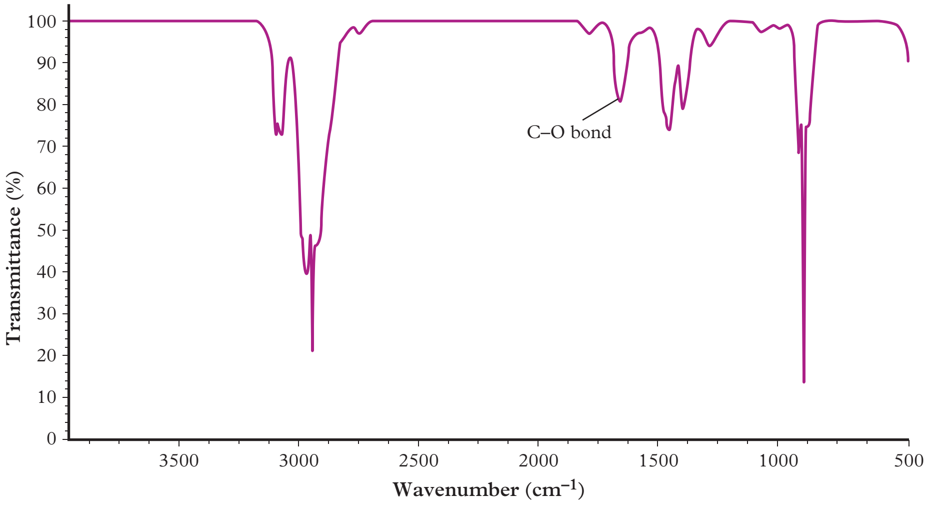


FIGURE 6 The infrared spectrum of 2-methyl-1-propene ($H_2C=C(CH_3)_2$)

Chemists use infrared correlation tables to match functional groups with characteristic infrared peaks. Both the presence and absence of characteristic peaks can be useful when deciding which functional groups are present. The correlation tables also show the expected intensity of peaks as strong (s), medium (m) or weak (w). The strongest peaks have the lowest percentage transmittance values.

X-ray crystallography

X-ray crystallography gives information about the relative positions of the atoms or ions in a compound. The substance must be a solid that forms crystals. The structure is described in terms of the bond lengths or distances between atoms as well as bond angles. Importantly, X-ray crystallography also provides information about intramolecular and intermolecular non-bonded interactions, including hydrogen bonding.

X-rays are used because their wavelengths are similar to the sizes of atoms. The X-rays are directed at the crystal, which causes them to scatter and create a **diffraction** pattern. The intensity of the scattering from an atom is proportional to its number of electrons.

It only takes a few hours for computer programs to collect the data and solve the structure for most organic and inorganic compounds. The most time-consuming step is growing crystals of sufficient quality.

X-ray crystallography
a technique that gives information about the positions of atoms within the repeating units that make up crystals

diffraction
the changes in the angle and intensity of X-rays due to interaction with a crystal

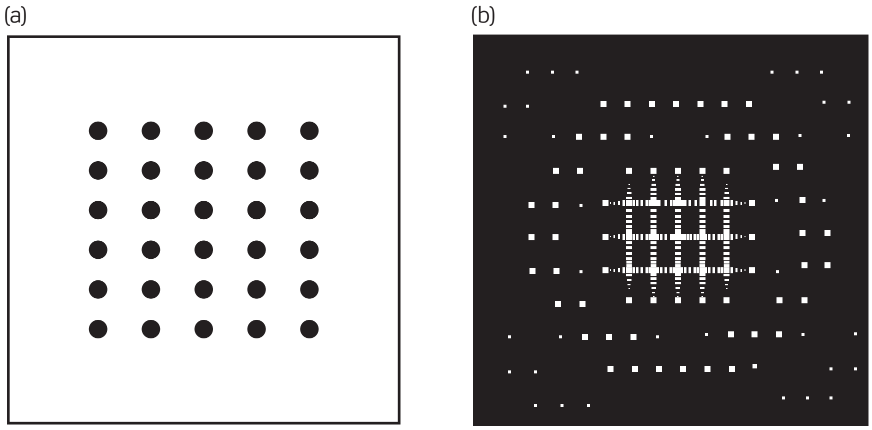


FIGURE 7 (a) Scientists use computers to reconstruct the arrangement of atoms in a crystal from (b) the observed diffraction pattern.

angstrom (Å)
a unit of distance equal to 1×10^{-10} m

Study tip

Now is a good time to revise your knowledge of VSEPR from *Chemistry for Queensland Units 1 & 2*, Chapter 12 because the terms for the geometrical shapes of molecules are useful for describing the results of X-ray crystallography.

Interpreting X-ray crystallography information

X-ray crystal structures can tell you the:

- identity of atoms, based on their number of electrons. Atoms with higher atomic masses and hence a greater number of electrons diffract X-rays more than lighter atoms
- distances between atoms. These distances are often given in units of nanometres (1 nm = 1×10^{-9} m), **angstroms** (1 Å = 1×10^{-10} m) or picometres (1 pm = 1×10^{-12} m). By consulting reference tables of typical bond distances (Table 2), you can determine the type of bond between two atoms. For example, in aromatic molecules, such as benzene, the C–C bond distances (1.40 Å) are intermediate between those of single and double bonds
- bond angles.

TABLE 2 Average bond lengths for selected bond types

Single bond	Average bond length (Å)	Double bond	Average bond length (Å)	Triple bond	Average bond length (Å)
C–H	1.08				
C–C	1.54	C=C	1.34	C≡C	1.20
C–N	1.47	C=N	1.30	C≡N	1.16
C–O	1.43	C=O	1.22	C≡O (carbon monoxide)	1.13

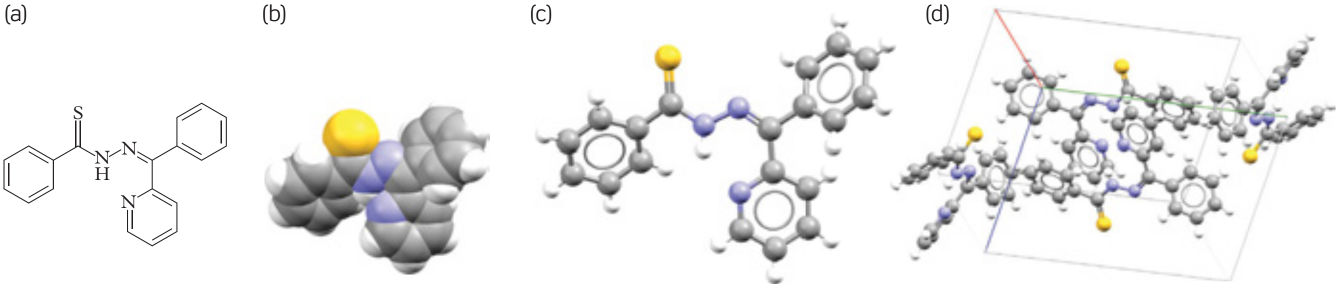


FIGURE 8 (a) A chemical structure of an organic molecule. (b) A space-filling model of the X-ray crystal structure. (c) A ball and stick model of the same molecule. (d) The arrangement of multiple molecules within the repeating three-dimensional unit that makes up the crystal structure.

CHECK YOUR LEARNING 12.2

Describe and explain

1 **Describe** the information that can be obtained about a compound from each of mass spectrometry, infrared spectroscopy and X-ray crystallography.

2 **Explain** why it can be difficult to distinguish between cobalt and nickel ions in a compound by X-ray crystallography, but easy to distinguish between cobalt and rhodium ions.

Apply, analyse and interpret

3 The spectroscopic techniques mentioned in this section are complementary because of their relative strengths and weaknesses. **Determine** two disadvantages of each technique.

4 **Identify** the most appropriate technique for each situation.

- **a** Identifying polymers in drink containers at a recycling station
- **b** Identifying traces of an accelerant fuel at a suspected arson site
- **c** Working out the shape of a newly synthesised drug

Investigate, evaluate and communicate

5 **Investigate** areas where mass spectrometry is used other than in a chemistry laboratory. Write a paragraph that explains how and why mass spectrometry is used in this area.

You can find the following resources for this section on your obook assess:

» Student book questions
12.2 Check your learning

» Suggested practical
12.2 Using mass spectrometry and infrared spectroscopy to identify organic compounds

» Increase your knowledge
IR correlation table

» Weblink
Spectra database for organic compounds

12.3 Analysing data from spectra

KEY IDEAS

In this section, you will learn about:

- using mass spectrometry information to determine the molar masses of compounds
- using infrared spectroscopy to determine the functional groups in molecules
- interpreting X-ray crystallography to understand the structure of compounds and the intermolecular interactions between molecules in the solid state.

Chemists use many different spectroscopic techniques to gather information about a compound. Each technique can provide different, complementary, information.

Interpreting a mass spectrum

A mass spectrum can give information about the molar mass of a compound and sometimes information about the structure of a compound.

The 'rule of 13' and base value

base value
in mass spectrometry, the hydrocarbon molecular formula (C_xH_y) that matches the mass of a molecular ion

The 'rule of 13' method uses the **base value** to find a starting point for the molecular formula from the *m*/*z* value of the molecular ion. The base value is the molecular formula the molecule would have it only contained carbon and hydrogen. The molar mass of CH is 13 amu, so it will be a multiple of 13, plus a remainder. The base value provides a starting point for the maximum possible number of carbon atoms in the molecule.

WORKED EXAMPLE 12.3A

Identify the linear (straight chain) hydrocarbon from the mass spectrum in Figure 1.

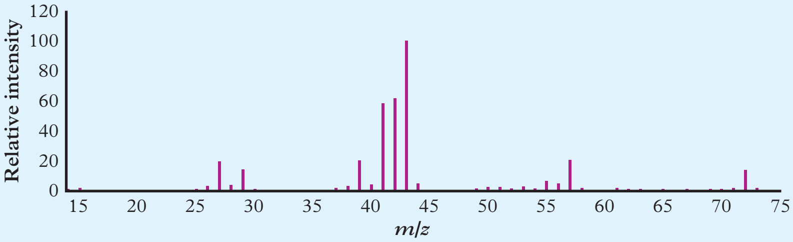


FIGURE 1 The mass spectrum of a hydrocarbon with a molecular ion of *m*/*z* 72

SOLUTION

1. The molecular ion is at *m*/*z* 72.
2. Find the base value by dividing the *m*/*z* value of the molecular ion by 13.

$$\frac{72}{13} = 5\text{, remainder } 7$$

The molecule contains a maximum of five carbons.

3. To work out the number of hydrogens, add the number of carbon atoms to the remainder.

$$5 + 7 = 12\text{, so there are 12 hydrogens}$$

The compound has a base value of C_5H_{12}.

4 Check that this is correct by calculating the mass of C_5H_{12}.

$$\text{Mass } C_5H_{12} = 5 \times 12\,\text{amu} + 12 \times 1\,\text{amu}$$
$$= 72\,\text{amu}$$

5 The linear hydrocarbon with 5 carbons and 12 hydrogens is pentane.

WORKED EXAMPLE 12.3B

Identify a possible structure of the ester whose mass spectrum is shown in Figure 2.

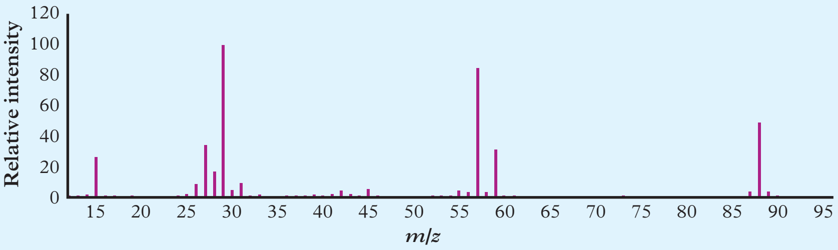


FIGURE 2 The mass spectrum of an unknown ester

SOLUTION

1 The molecular ion is at *m*/*z* 88.

2 Find the base value by dividing the *m*/*z* value of the molecular ion by 13.

$$\frac{88}{13} = 6\text{, remainder } 10$$

The molecule contains a maximum of six carbons and 16 hydrogens (6 + 10).

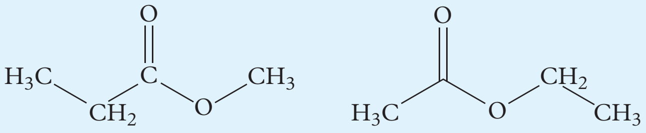
3 However, given that this is an ester, it must contain at least two oxygens. So adjust the base value to allow for two oxygens. Each oxygen atom has an amu of 16, which is equal to the mass of one carbon atom (12 amu) plus four hydrogen atoms (4 × 1 amu). So to add two oxygens, you need to subtract two carbon atoms and eight hydrogens.

$$\text{Molecular formula} = C_{(6-2)}H_{(16-8)}O_{(0+2)}$$
$$= C_4H_8O_2$$

Check that this molecular formula is correct:

$$6 \times 12\,\text{amu} + 8 \times 1\,\text{amu} + 2 \times 16\,\text{amu} = 88\,\text{amu}$$

There are three esters that have this molecular formula. They are constitutional isomers. Two of these esters are shown. Can you identify the third possibility?



Methyl propanoate

Ethyl ethanoate

FIGURE 3 The chemical structures of two isomeric esters with a molar mass of $88\,\text{g}\,\text{mol}^{-1}$

4 The mass spectrum shown is that of methyl propanoate. The fragmentation pattern can be used to distinguish between different isomeric possibilities. The peak at *m*/*z* 57 corresponds to the loss of OCH_3 (*m*/*z* 31) from the molecular ion, so the compound is the methyl ester. A peak due to a loss of 45 (OCH_2CH_3) would be observed for an ethyl ester, but there is no peak observed at *m*/*z* 43 (88 – 45 = 43).

'Nitrogen is odd'

Molecules that have an odd number of nitrogens have a molecular ion with an odd m/z value because nitrogen (atomic mass 14 amu) forms three bonds in neutral molecules. If you observe an odd m/z, you can assume that the molecule contains one nitrogen.

Isotope patterns in mass spectroscopy – M+1 and M+2 peaks

The mass spectra in Figures 1 and 2 on the previous pages include small peaks 1 m/z unit above the molecular ion peaks. These peaks are known as M+1 peaks. Mass spectra may also contain M+2 peaks. These peaks represent different isomers of the molecule that contain different isotopes of the same element. The heights of the peaks (relative abundance) depend on the amount of the different isotopes in the sample. The set of peaks related to the same ion is known as the **isotope pattern**.

isotope pattern
a set of peaks in a mass spectrum related to ions with the same chemical formula but containing different isotopes; the pattern reflects the relative abundance of the isotopes

Table 1 shows the natural abundance of selected isotopes found in organic compounds.

TABLE 1 Natural abundance of main elements with isotopes and pattern observed in mass spectra

Element	Isotopes and their natural abundance		Pattern for a single isotope substitution
Carbon	^{12}C (98.9%)	^{13}C (1.1%)	M : M+1 = 100:1.1
Sulfur*	^{32}S (95.0%)	^{34}S (4.2%)	M : M+2 = 24:1
Chlorine	^{35}Cl (75.8%)	^{37}Cl (24.2%)	M : M+2 = 3:1
Bromine	^{79}Br (50.7%)	^{81}Br (49.3%)	M : M+2 = 1:1

*Percentages for S do not quite add to 100% because samples would also contain ^{33}S (0.76%) and ^{36}S (0.02%).

The mass spectra of organic compounds often show a small M+1 peak, due to the presence of ^{13}C isotopes. (For example, the mass spectrum of methyl propanoate in Figure 2 has a very small peak at m/z 89.) These peaks are always smaller than the M peak, because there is only a small chance of any one particular ^{12}C atom being replaced by a ^{13}C atom. The relative intensities of the two peaks can be used as a guide to the number of C atoms in an ion.

base peak
the tallest peak in a mass spectrum; is usually assigned an abundance of 100% and other peak heights are given relative to it

The peak at 89 in Figure 2 has an intensity relative to the **base peak** of 2.45%, whereas the molecular ion peak has a relative intensity of 49.6%. These values were taken from a table of peak data, which usually accompanies a spectrum. To work out the number of C atoms in the compound, use this formula:

$$\text{Number of C atoms} = \frac{100}{1.1} \times \frac{\text{abundance M+1 ion}}{\text{abundance M}^+\text{ion}}$$

In the example,

$$\begin{aligned}\text{Number of C atoms} &= \frac{100}{1.1} \times \frac{2.45}{49.6} \\ &= 4.49\,\text{atoms}\end{aligned}$$

However, 4.49 atoms does not make sense as an answer because a molecule must have a whole number of atoms of a particular element. We would usually round to the nearest whole number. In this case, the best we can say is that the molecule contains either 4 or 5 carbon atoms.

The number is slightly higher than the 4 carbons that was calculated by using the rule of 13 in Worked example 12.3B because there are also small contributions to the M+1 peak from isotopomers that contain ^{17}O and ^{2}H.

From Table 1, you can see that some elements have a much higher proportion of greater mass isotopes. For example, chlorine is made up of ^{35}Cl and ^{37}Cl isotopes, in an almost 3:1 ratio. So it is easy to recognise compounds that contain Cl from their mass spectrum, due to the characteristic pattern of M:M+2 peaks in the relative ratio of 3:1.

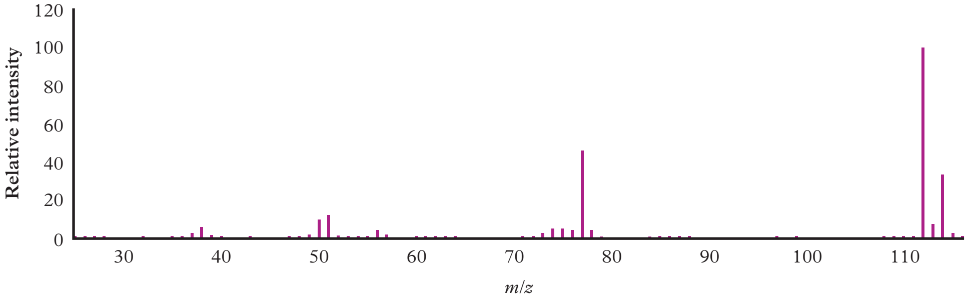


FIGURE 4 The mass spectrum of chlorobenzene (C_6H_5Cl)

Figure 4 shows the mass spectrum of chlorobenzene. The ratio of the peaks at 112 and 114 is 100:32.9 or roughly 3:1. This is evidence for the presence of Cl in the compound. Further evidence is the peak at *m*/*z* 77 because 112 – 77 = 35, which is the atomic mass of ^{35}Cl.

The peak at 77 results from the loss of Cl, but there is no peak at 79 with one-third of the intensity, because Cl is not present in that fragment. The fragment at *m*/*z* 77 is consistent with $[C_6H_5]^+$, which matches with the compound being chlorobenzene.

Interpreting an infrared spectrum

An infrared spectrum can tell you which functional groups are present, as well as which functional groups are absent. Infrared spectra can be quite complicated because they can include bending and stretching vibrations from all the bonds in a molecule. It is not useful (or even possible) to assign every band in the spectrum.

Where to start

The most important region to begin with is 4000–1300 cm^{-1}. This is where you will see characteristic bands for stretching vibrations of OH and NH, as well as the usually intense C=O stretch. The absence of bands in this region is also important. For example, if no band is observed at 1870–1540 cm^{-1}, then the compound does not contain a carbonyl group. Concentrate on assigning the strongest bands first (the ones with lowest values for percentage transmittance).

OH groups

Hydroxyl groups are often hydrogen-bonded to each other in both solid and liquid samples. A non-hydrogen-bonded OH group absorbs strongly at 3700–3580 cm^{-1}, as a narrow peak. Hydrogen bonding shifts this to 3550–3200 cm^{-1} and broadens the peak considerably. You can see this in the infrared spectrum of ethanol in Figure 5. O–H bending vibrations occur in the region 1420–1330 cm^{-1}. Figure 5 on the next page shows the infrared spectrum of liquid ethanol with a O–H stretching vibration around 3360 cm^{-1}.

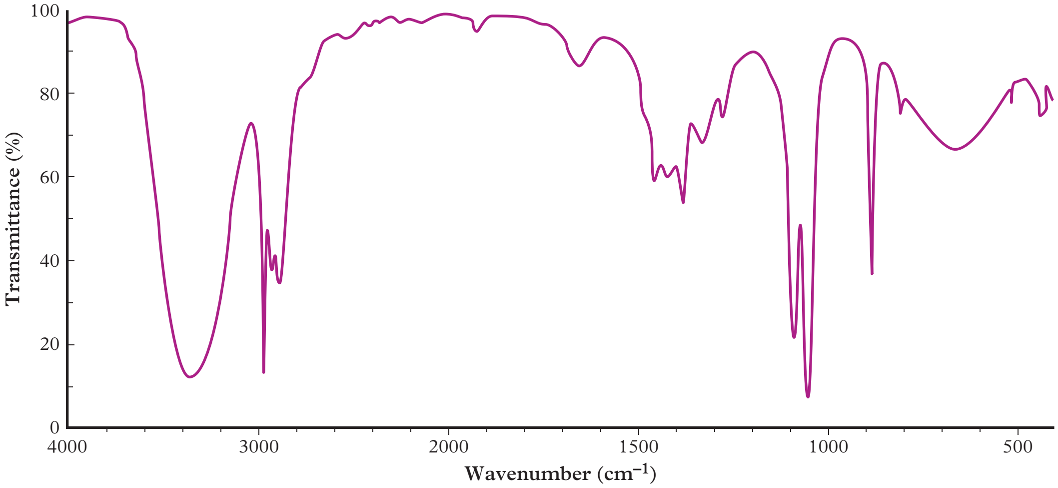


FIGURE 5 The infrared spectrum of liquid ethanol. There is a characteristic broad O–H stretching vibration around 3360 cm^{-1}. The C–O stretch is also strongly absorbing at 1050 cm^{-1}.

NH groups

aliphatic
an organic compound or group containing carbon and hydrogen joined together in straight chains, branched chains, or non-aromatic rings

N–H stretching vibrations are also affected by hydrogen bonding, which shifts their peaks to lower wavenumbers. **Aliphatic** primary amines give bands at 3400–3300 and 3330–3250 cm^{-1}. Aromatic primary amines give bands at slightly higher wavenumbers. N–H bending vibrations occur at 1650–1580 cm^{-1} as a medium-to-strong-intensity band.

Figure 6 shows the infrared spectrum of isopentylamine. You can see that the bands for N–H stretching at 3370 and 3290 cm^{-1} are much less intense and narrower than the O–H stretch in Figure 6.

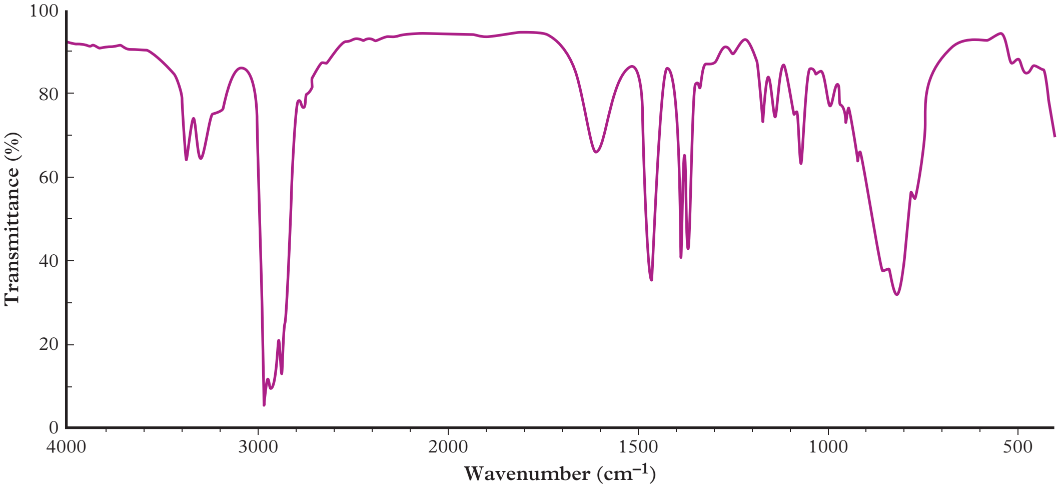


FIGURE 6 The infrared spectrum of isopentylamine. The N–H stretches show as a doublet at 3370 and 3290 cm^{-1}. The N-H bend gives the broad peak around 1600 cm^{-1}.

C=O stretching vibrations

The carbonyl group is one of the first groups to look for in an infrared spectrum. This is because it gives a very intense stretching band at 1870–1540 cm^{-1}. This region of the spectrum does not usually show bands for other functional groups, so the carbonyl group is relatively easy to identify.

The C=O group is found in aldehydes, ketones, carboxylic acids, esters, amides and other carboxylic acid derivatives. Table 2 outlines some indicators that will help you distinguish these different carbonyl-containing groups.

TABLE 2 Distinguishing carbonyl (C=O) groups

Functional group	Carbonyl stretching vibration	Other notable bands
Aldehyde	1740–1720 cm^{-1} aliphatic aldehydes	2830–2695 cm^{-1} C–H stretch, two moderately intense bands
Ketone	Around 1715 cm^{-1} saturated ketone 1685–1665 cm^{-1} neighbouring phenyl group (conjugation)	1300–1100 cm^{-1} bending vibration involving the carbonyl group may also be observed, moderate absorption 1230–1100 cm^{-1} aliphatic ketones, with aromatic ketones at higher wavenumbers
Carboxylic acid	More intense than ketones 1720–1706 cm^{-1} aliphatic carboxylic acids	3300–2500 cm^{-1}, usually centred on 3000 cm^{-1}, very broad intense OH stretch
Carboxylate salt	1650–1550 cm^{-1} strong stretching band around 1400 cm^{-1} weaker band	No OH band present
Ester	1750–1735 cm^{-1} aliphatic esters 1730–1715 cm^{-1} benzoate esters	1210–1160 cm^{-1} stretching vibration for saturated esters 1240 cm^{-1} ethanoate (acetate) esters for simple alcohols 1300–1250 cm^{-1} aromatic acid esters
Amide	Occurs at lower wavenumbers than most other carbonyl groups. Amide band – position depends on hydrogen bonding Around 1650 cm^{-1} primary amides as solid sample 1640 cm^{-1} secondary 1680–1630 cm^{-1} tertiary	1650–1515 cm^{-1} a second amide band for primary and secondary amides 3520 and 3400 cm^{-1} N–H stretches for primary amides

Alkanes, alkenes and alkynes

C–H stretching vibrations in alkanes are generally observed at 3000–2840 cm^{-1}. In alkanes, methyl groups often give rise to bands at 2962 and 2872 cm^{-1}, with bending vibrations for methyl groups seen at 1375 and 1450 cm^{-1}.

Methylene groups ($-CH_2-$) are seen at 2926 and 2853 cm^{-1}. A bending vibration is observed around 1465 cm^{-1}, which often overlaps with the bending vibration of methyl groups.

Alkenes give a moderate absorption around 1667–1642 cm^{-1} due to a C=C stretching vibration, with the more substituted alkenes absorbing near 1680 cm^{-1} for *trans*-substituted alkenes and 1650 cm^{-1} for *cis*-substituted alkenes. C–H stretching bands above 3000 cm^{-1} are evidence of unsaturation.

Alkynes give rise to a weak stretching band at 2260–2100 cm^{-1}. Nitriles (R–C≡N) also absorb in this region, but have stronger peaks because of the difference in electronegativities between C and N. You do not usually observe a C≡C band if the alkyne is symmetrical; for example, $H_3C{\equiv}CCH_3$. The H–C≡C– stretch of terminal alkynes is a strong and narrow band, seen between 3330 and 3270 cm^{-1}. It is narrower than OH or NH bands that could also occur in this region. A C–H bending vibration of terminal alkynes is also seen as a strong, broad absorption at 700–610 cm^{-1}.

WORKED EXAMPLE 12.3C

Consider the infrared spectrum in Figure 7. What can you conclude about the functional groups in the molecule?

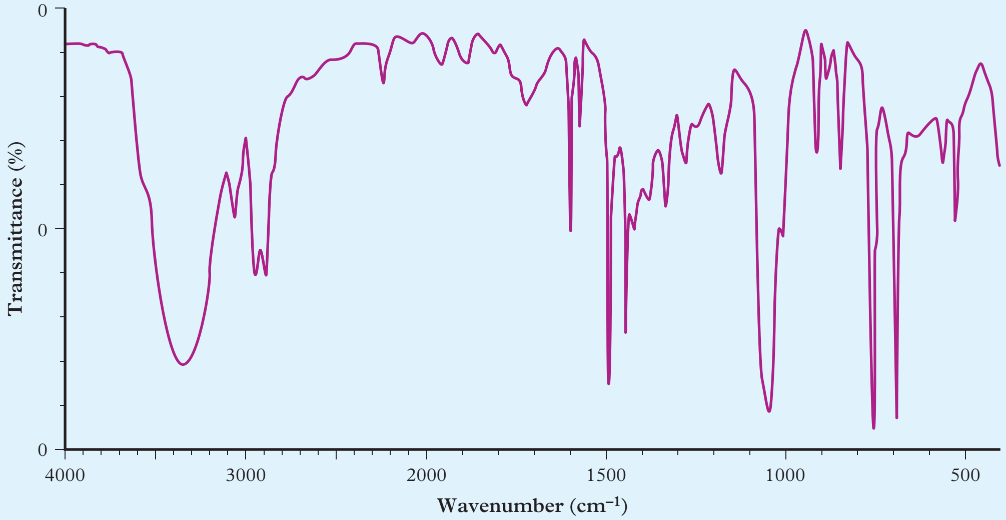


FIGURE 7 The infrared spectrum of an unknown compound

1 Look for peaks of OH, NH and C=O groups.

The broad, intense peak around 3330 cm^{-1} matches what would be expected for an OH group. It would be less intense if there an NH group was present instead. A carbonyl group would give an intense peak in the region 1870–1540 cm^{-1}. There is a strong peak at 1491 cm^{-1}, but this is outside the expected range.

Therefore, there is an OH group present, but no NH or C=O groups.

A C–O stretching vibration would appear as a strong peak in the region of about 1250–1050 cm^{-1} and of strong intensity. This is consistent with the peaks at about 1168 and 1045 cm^{-1}.

2 Look for peaks of other functional groups.

The strong peaks at 767 and 692 cm^{-1} indicate the presence of an aromatic group. The peaks observed at 1598 and 1442 cm^{-1} confirm this. The peaks to the left of 3000 cm^{-1} look like C–H stretches in aromatic molecules.

3 Look for other important peaks.

The peak at 2239 cm^{-1} could easily be overlooked, but this is in a region of the spectrum that is usually fairly empty, except for stretching vibrations of triple bonds. This is of weak intensity, which suggests a C≡C bond, rather than a C≡N bond, which would be of greater intensity.

There is no narrow peak due to a H–C≡C at 3330–3270 cm^{-1}. This suggests an internal alkyne, not a terminal alkyne.

4 How correct were those conclusions?

The spectrum is that of 4-phenyl-3-butyn-1-ol, with the structure shown in Figure 8. It has an alcohol (hydroxyl) functional group, an internal alkyne group and an aromatic phenyl group.

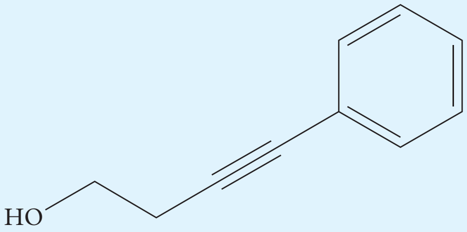


FIGURE 8 Structure of 4-phenyl-3-butyn-1-ol

CHECK YOUR LEARNING 12.3

Describe and explain

1 Copy and annotate the mass spectrum in Figure 9, showing clearly the position of the base peak and the molecular ion. **Explain** what information can be determined from particular parts of the spectrum.

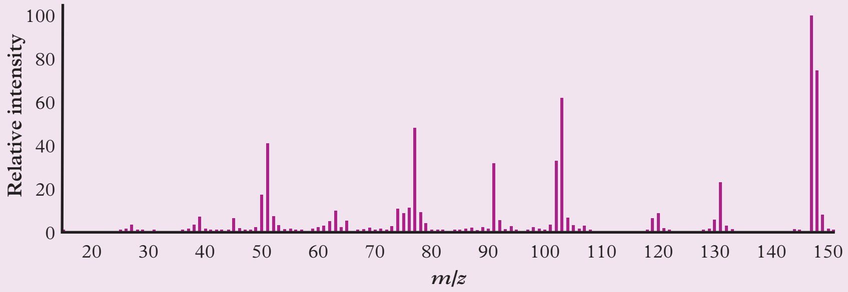
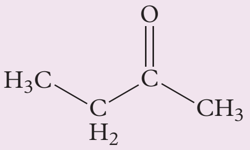


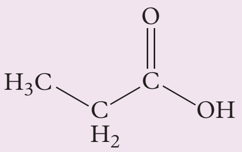
FIGURE 9 The mass spectrum of *trans*-cinnamic acid

Apply, analyse and interpret

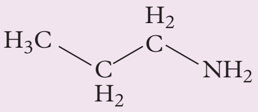
2 **Consider** the following three pairs of compounds. **Analyse** which absorption band in the infrared spectrum could be used to distinguish between them.

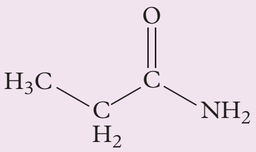
a



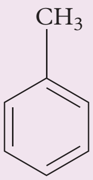


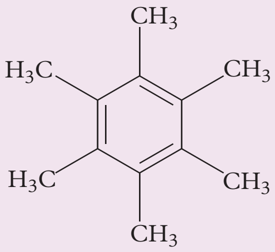
b





c





3 **Determine** the relative intensities of peaks related to the molecular ion for 1,2-dibromoethane. **Sketch** a diagram of the pattern that you would expect.

Investigate, evaluate and communicate

4 **Investigate** how infrared spectroscopy was used as a tool in the investigation of forgery of paintings claimed to be by Jackson Pollock. **Create** a short news article of no more than three paragraphs explaining how the forgery was detected.

5 **Create** a flow chart that summarises the main steps for interpreting a mass spectrum. **Compare** your flow chart with the flow charts of your classmates and make any improvements required to your own flow chart.

You can find the following resources for this section on your obook assess:

- Student book questions
  12.3 Check your learning
- Weblink
  Mass spectra
- Weblink
  Infrared spectra

CHAPTER 12

Review

Chapter summary

12.1
- Proteins can be separated by size, charge and binding affinity.
- In size exclusion chromatography, the largest proteins elute first.
- In electrophoresis, proteins are separated on the basis of the distance they move through a gel under the influence of an electrical field. Native gel electrophoresis depends on the charge, size and shape of the protein. SDS-PAGE involves the addition of a detergent, which denatures the proteins, and the protein–detergent assemblies all have similar negative charges.

12.2
- In mass spectrometry, compounds are converted to charged ions, which can be molecular ions or fragment ions. The ions are separated by their mass-to-charge ratio.
- In infrared spectroscopy, functional groups on molecules absorb infrared radiation corresponding to the energy of vibrations.
- X-ray crystallography gives information about the positions of atoms within the repeating units that make up crystals. Atoms are identified by their ability to diffract X-rays, with heavier atoms diffracting more.

12.3
- In mass spectrometry, useful information can be determined from the mass of the molecular ion, whether the m/z of the molecular ion is odd (contains an odd number of nitrogen atoms), the presence of isotope patterns (e.g. presence of Cl or Br) and the formation of fragment ions, representing the loss of particular groups of atoms.
- In infrared spectroscopy, you should first look for the presence or absence of OH, NH or C=O bands. The carbonyl band is very useful for identifying the particular functional group present. Alkynes and aromatic functional groups also have distinctive peaks.

Key terms

- aliphatic
- angstrom
- base peak
- base value
- bending vibration
- bond angle
- bond length
- diffraction
- electrophoresis
- infrared radiation
- infrared spectroscopy
- isotope pattern
- kinetic energy
- mass spectrometry
- molecular ion
- native PAGE
- SDS-PAGE
- size exclusion chromatography
- stretching vibration
- transmittance
- wavenumber
- X-ray crystallography

Key formulas

Number of C atoms	Numbers of C atoms $= \frac{100}{1.1} \times \frac{\text{abundance M+1 ion}}{\text{abundance M}^+\text{ ion}}$

Revision questions

The relative difficulty of these questions is indicated by the number of stars beside each question number: ★ = low; ★★ = medium; ★★★ = high.

Multiple choice

1 In size exclusion chromatography of proteins, the proteins eluted first are those with:
  - **A** the smallest molecular mass
  - **B** no net charge at the pH used
  - **C** the largest molecular mass
  - **D** the lowest mass-to-charge ratio at the pH used.

2 Time-of-flight (TOF) mass spectrometry separates ions on the basis of differences in:
  - **A** charge
  - **B** velocity
  - **C** kinetic energy
  - **D** ionic radius.

3 A halogen-containing compound gives the molecular ion pattern shown in Figure 1.

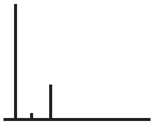


FIGURE 1 Molecular ion pattern of a halogen-containing compound

From the pattern, it can be concluded that the compound contains:
  - **A** fluorine
  - **B** chlorine
  - **C** bromine
  - **D** iodine.

4 Identify the bond that would show the strongest absorption in the infrared region.
  - **A** C=C
  - **B** H–C
  - **C** H–O
  - **D** H–N

5 Which of the following is *not* a limitation of X-ray crystallography?
  - **A** Both the direction and intensity of scattered X-rays must be recorded.
  - **B** Compounds to be investigated must form ordered solids.
  - **C** Hydrogen atoms are often not observable directly.
  - **D** It is only applicable to compounds with a molecular mass below approximately 1000 g mol^{-1}.

Short answer

Describe and explain

★ **6** **Explain** why when interpreting an infrared spectrum, you should first look for peaks attributable to O–H, N–H or C=O stretches.

★★ 7 **Explain** how a TOF mass spectrometer works.

Investigate, evaluate and communicate

★★ **8** **Investigate** how MALDI-TOF mass spectrometry is used to investigate proteins. Prepare a half-page summary of the process.

★★★ **9** Using an online scientific database such as ScienceDirect, compare the number of research papers published in the last 15 years referring to X-ray crystallography, mass spectroscopy and infrared spectroscopy. **Design** a graph that shows the trends in use of these three terms and use this to evaluate which technique is most often used by scientists.

You can find the following resources for this section on your obook assess:

- » Student book questions
  Chapter 12 Revision questions
- » Revision notes
  Chapter 12
- » assess quiz
  Auto-correcting mutiple-choice quiz
- » Flashcard glossary
  Chapter 12

CHAPTER 13

Chemical synthesis

A lot of progress has been made in science since the invention of the wheel. However, the discovery of chemical synthesis has probably had the biggest impact on our everyday life. For example, chemical synthesis enables us to drive cars, treat aches and pains with painkillers, and continually improve the resilience of smartphone screens.

OBJECTIVES

→ Appreciate that chemical synthesis involves the selection of particular reagents to form a product with specific properties.

→ Understand that reagents and reaction conditions are chosen to optimise the yield and rate for chemical synthesis processes, including the production of ammonia (Haber process), sulfuric acid (contact process) and biodiesel (base-catalysed and lipase-catalysed methods).

→ Understand that fuels, including biodiesel, ethanol and hydrogen, can be synthesised from a range of chemical reactions including addition, oxidation and esterification.

→ Understand that enzymes can be used on an industrial scale for chemical synthesis to achieve an economically viable rate, including fermentation to produce ethanol and lipase-catalysed transesterification to produce biodiesel.

→ Describe, using equations, the production of ethanol from fermentation and the hydration of ethane.

→ Describe, using equations, the transesterification of triglycerides to produce biodiesel.

→ Discuss, using diagrams and relevant half-equations, the operation of a hydrogen fuel cell under acidic and alkaline conditions.

→ Calculate the yield of chemical synthesis reactions by comparing stoichiometric quantities with actual quantities and by determining limiting reagents.

Source: *Chemistry 2019 v1.3 General Senior Syllabus* © Queensland Curriculum & Assessment Authority

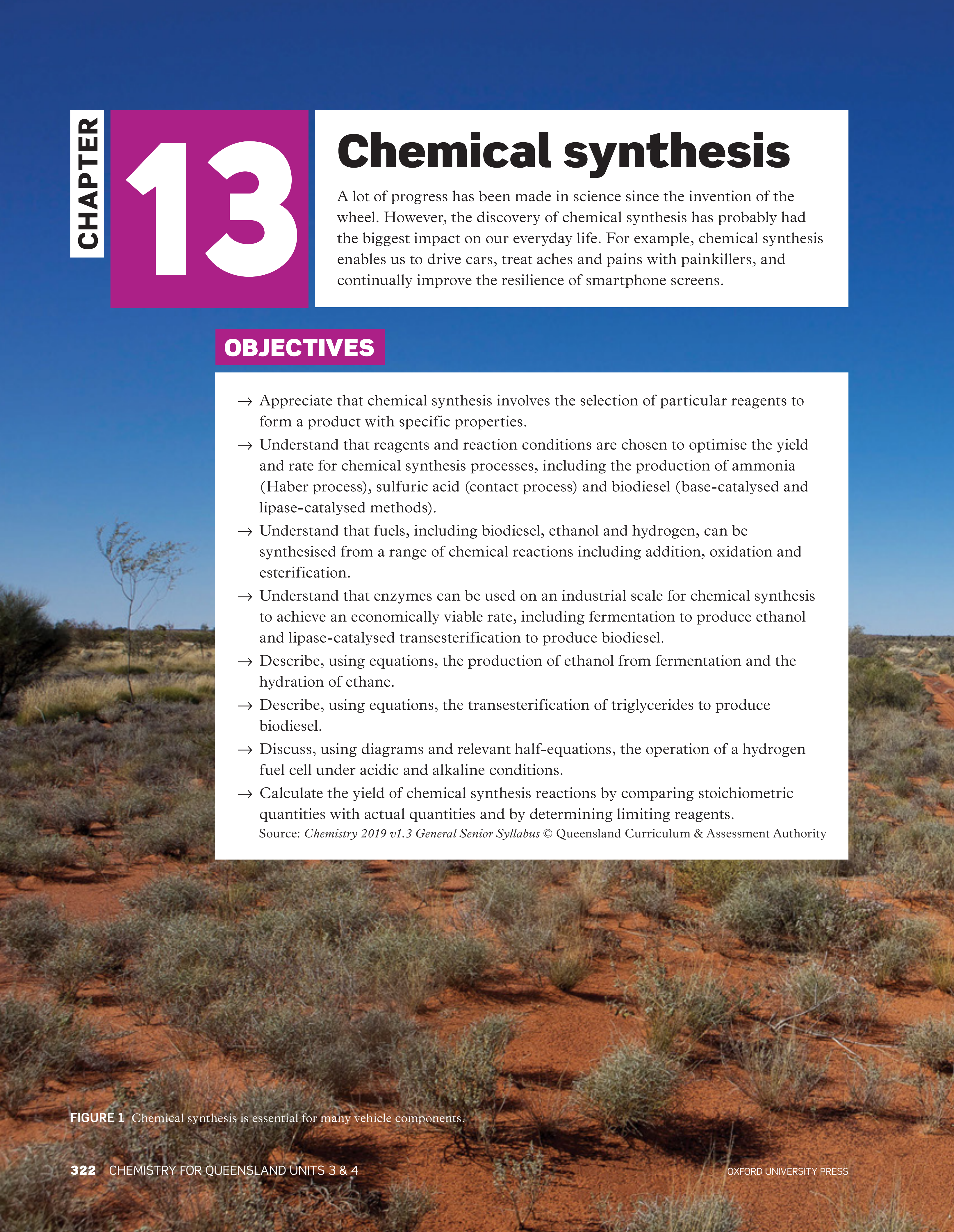


FIGURE 1 Chemical synthesis is essential for many vehicle components.

PRACTICALS

SUGGESTED PRACTICAL	**13.1A** Haber process simulation using Wolfram
SUGGESTED PRACTICAL	**13.1B** Video simulation of the contact process

13.1

Chemical synthesis

KEY IDEAS

In this section, you will learn about:

- chemical synthesis and selecting reagents to form a product with desirable properties
- selecting ideal reagents and reaction conditions for optimal outcomes
- the production of ammonia (Haber process)
- the production of sulfuric acid (contact process).

Have you ever dropped your phone and experienced that moment before you pick it up, when you don't know if it'll be cracked or not? The front of a smartphone (Figure 1) is not purely glass, which would make it extremely fragile. It is a synthetic glass-ceramic material, designed to endure stress. This material has properties of both glass and ceramics.

Glass is an amorphous solid. The atoms in glass cannot slip past each other, so there is no way to relieve stress and glass cracks easily. Ceramics are often crystalline with strong forces of attraction between ions of opposite charges across planes. This makes it difficult for one plane to slip past another. Therefore, ceramics are brittle, which means they can resist compression, but break when they are bent. Glass-ceramic is formed by overheating glass in a controlled way then crystallising to form a material that endures much more stress than its original components.

FIGURE 1 The front of a smartphone is typically a synthetic glass-ceramic material.

There are many applications of chemical synthesis to obtain a desired or purposeful product. The first step is to select **reagents** and the reaction conditions to optimise the **yield** and rate for the chemical synthesis processes.

reagent
a substance or compound used to initiate a chemical reaction

yield
the amount of product obtained from a chemical reaction

Haber process
the production of ammonia by a nitrogen-fixation process

contact process
the production of very concentrated sulfuric acid

Reagent and reaction conditions

A reagent is a substance or compound. When it is added to a system, it causes a chemical reaction. The term 'reagent' is often used interchangeably with 'reactant'.

Chemical synthesis processes involve selecting specific reagents and reaction conditions to optimise the rate and yield (see section 13.5) of the product. To form desired products by a chemical synthesis process, you may need reaction sequences involving more than one chemical reaction.

Two industrial chemical synthesis processes are the **Haber process**, which is the production of ammonia, and the **contact process**, which is the production of sulfuric acid.

SUGGESTED PRACTICAL

13.1A Haber process simulation using Wolfram
Go to your obook assess »

Haber process – the production of ammonia

Ammonia (NH_3) exists naturally in the environment and the human body, but is also manufactured for many industrial applications. Ammonia is used to produce fertilisers, refrigeration gases, explosives and many household and industrial cleaning products.

The Haber process (also known as the Haber–Bosch process) was invented by German chemist Fritz Haber (Figure 2) and his brother-in-law Karl Bosch. The process was designed to maximise the amount of ammonia produced and minimise unwanted pollutants.

The Haber process combines nitrogen from the air with hydrogen from natural gas in a 1:3 mole ratio:

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

As such, this is an artificial nitrogen-fixation process. (In biological nitrogen fixation, bacteria use an enzyme to convert nitrogen into ammonia.) The Haber process is typically conducted under high pressure (approximately 200 atm) and at high temperatures (400–500°C). Nitrogen and hydrogen are passed over catalysts (reagents), as shown in Figure 3, and any unreacted gases are recycled and passed through the process again until complete conversion is achieved. In the condenser, the ammonia vapour is cooled and condensed into liquid ammonia.

FIGURE 2 Fritz Haber (1868–1934), one of the inventors of the ammonia synthesis process, working in his laboratory in Karlsruhe

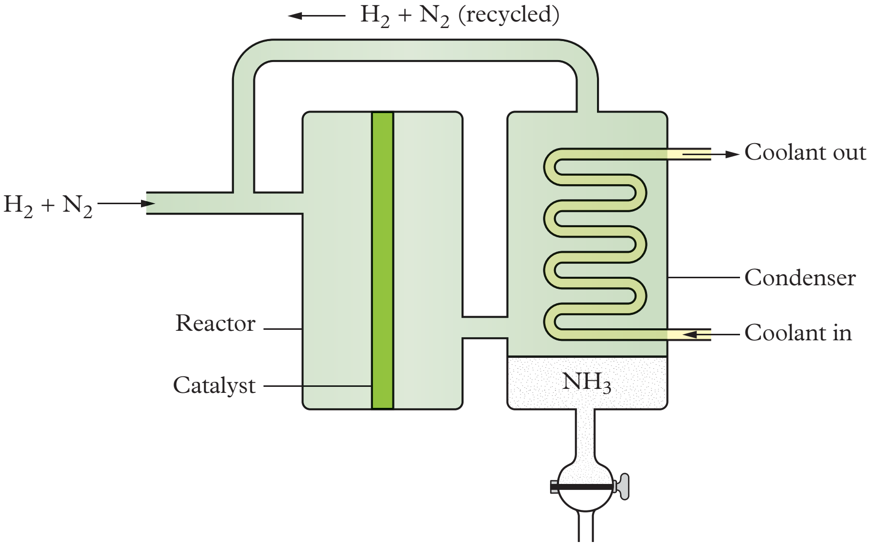


FIGURE 3 The Haber process for producing ammonia

Reaction conditions

The Haber process is affected by pressure and temperature. The higher the pressure, the more ammonia can be formed (Figure 4). The pressure is limited by the reaction vessel and its ability to withstand high pressures.

At higher temperatures, less ammonia is formed. This is because the chemical reaction between N_2 and H_2 is exothermic (releases heat) and the reverse reaction is endothermic (absorbs heat). As the temperature increases, the reverse reaction is favoured, and ammonia is converted into N_2 and H_2. At lower temperatures, the rate of reaction is very slow and the reaction is not efficient. Hence, the reaction

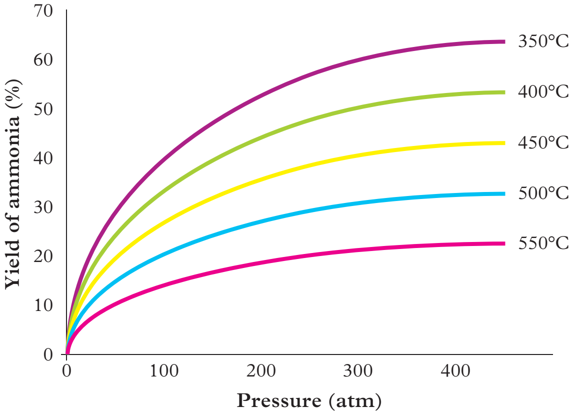


FIGURE 4 The yield of ammonia (%) (see section 13.5) at different pressures and temperatures

SUGGESTED PRACTICAL

13.1B Video simulation of the contact process
Go to your obook assess »

conditions of 200 atm and 400–500°C is a compromise. The yield of ammonia does not seem to be very high (around 35%), but the continuous removal of ammonia means equilibrium is never reached. This has the effect of favouring the forward reaction and the continuous production of ammonia.

Contact process – the production of sulfuric acid

Sulfuric acid (H_2SO_4) is formed naturally by the oxidation of sulfide (S^{2-}) minerals in rocks and the oxidation of sulfur dioxide (SO_2) in burning fuels, precipitating as acid rain in the presence of water.

Sulfuric acid has many industrial applications. It is used to produce fertilisers, explosives and pharmaceuticals. Highly concentrated sulfuric acid has been produced for a long time by the contact process. The process was developed by British vinegar merchant Peregrine Phillips and was patented in 1831 (Figure 5).

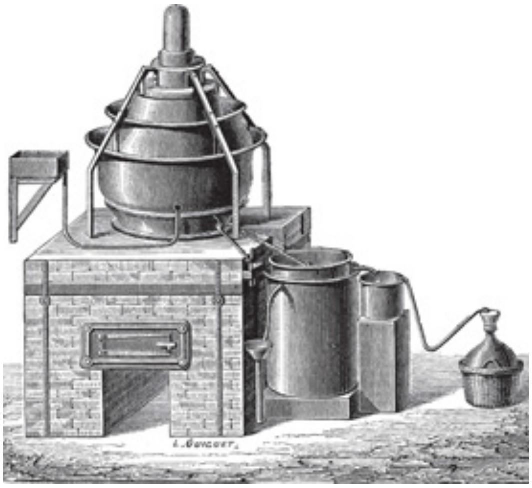


FIGURE 5 The equipment that was used in the early production of highly concentrated sulfuric acid

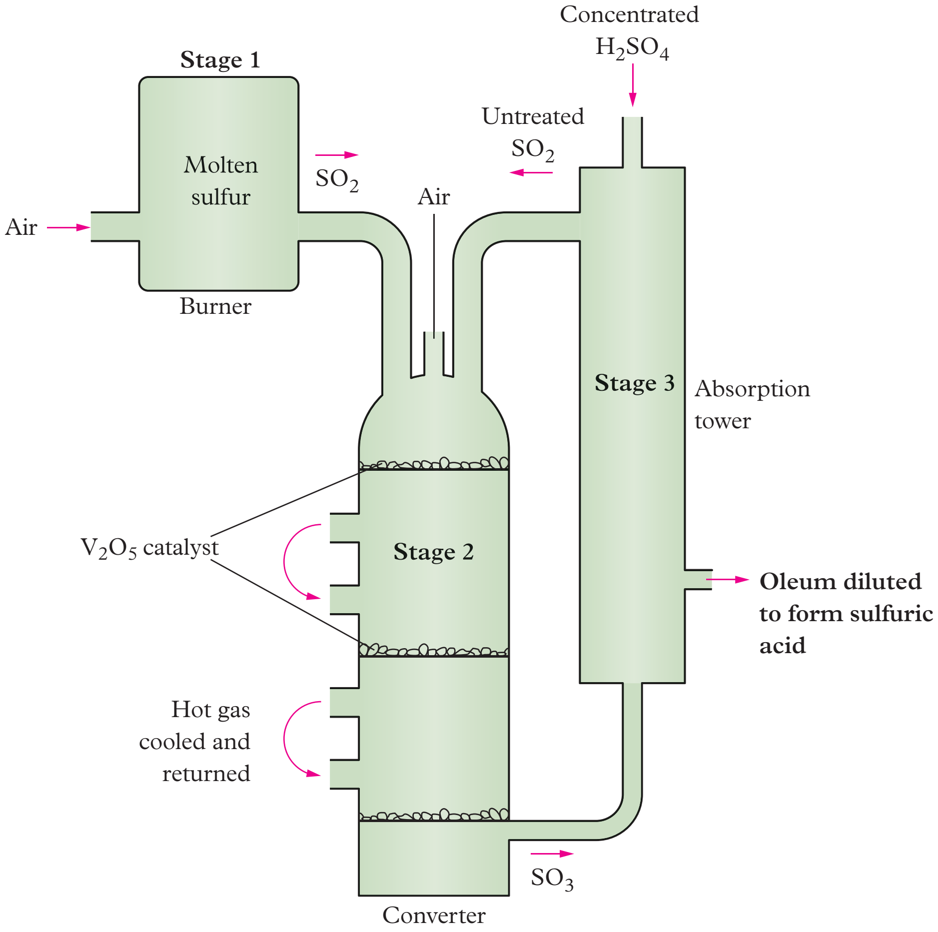


FIGURE 6 The contact process for producing sulfuric acid

There are three main stages in the contact process (Figure 6):

1 Sulfur or materials containing sulfur are burnt to produce sulfur dioxide:

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

2 Sulfur dioxide (SO_2) is reacted with O_2 in the presence of a vanadium oxide (V_2O_5) catalyst to produce sulfur trioxide (SO_3):

$$2SO_2(g) + O_2(g) \xrightarrow{V_2O_5} 2SO_3(g)$$

At low temperatures, the equilibrium lies far to the left so only a small amount of SO_3 is formed. To improve the yield, the reaction is conducted at 400–500°C and 1–2 atm.

3 Sulfur trioxide is converted into concentrated sulfuric acid.

The sulfur trioxide is first dissolved in concentrated sulfuric acid, which forms **oleum** ($H_2S_2O_7(l)$; fuming sulfuric acid):

$$SO_3(g) + H_2SO_4(l) \rightarrow H_2S_2O_7(l)$$

Oleum can then be safely reacted with water to form concentrated H_2SO_4:

$$H_2S_2O_7(l) + H_2O(l) \rightarrow 2H_2SO_4(l)$$

oleum
a solution of sulfur trioxide in sulfuric acid, also called fuming sulfuric acid

Reaction conditions

The second stage is crucial. This is where SO_2 reacts with O_2 to form SO_3. The forward reaction is exothermic, so at high temperatures the backward reaction is favoured, which reduces the yield of SO_3. However, at too low temperatures, SO_2 reacts with O_2 very slowly. At a temperature of about 450°C, the rate of SO_3 formation is high and the rate of decomposition is minimal.

When SO_3 is formed, the volume decreases because of a decrease in the number of moles of the gaseous components. This leads to an increase in pressure, which favours the forward reaction, and therefore an increase in the rate of SO_3 formation. At higher pressures, the yield does not continuously increase but the rate of corrosion of the vessels does. Hence, pressures around 1.5–1.7 atm are used.

CHECK YOUR LEARNING 13.1

Describe and explain

1 **Describe** the Haber process.

2 **Explain** the three stages in the contact process.

3 **Explain** the difference between a reagent and a reactant.

Apply, analyse and interpret

4 **Analyse** and **compare** the percentage yields for ammonia at 200 atm and 350°C and at 200 atm and 550°C. Which of the two conditions leads to a larger yield and why?

You can find the following resources for this section on your obook assess:

- Student book questions 13.1 Check your learning
- Suggested practical 13.1A Haber process simulation using Wolfram
- Suggested practical 13.1B Video simulation of the contact process

13.2 Fuels

KEY IDEAS

In this section, you will learn about:

- the production of biodiesel (base-catalysed and lipase-catalysed methods)
- how fuels can be synthesised from a range of chemical reactions such as addition, oxidation and esterification
- enzymes that can be used on an industrial scale for chemical synthesis (lipase-catalysed method)
- the production of ethanol (fermentation and hydration of ethane).

renewable
replaceable at a rate equal to or greater than the rate of use, over an indefinite period

biofuel
a fuel made from biological raw materials

synthesise
to combine compounds and form a more complex entity

biodiesel
fatty acid alkyl esters made from fats and oils

transesterification
a reaction between an ester and an alcohol that produces a new ester and a new alcohol

percentage yield
the percentage ratio of the actual yield to the theoretical yield

It is hard to imagine our modern world without fuels. We use fuels in power plants to generate electricity, for transport and to run barbecues. Although renewable fuels are becoming more popular, fossil fuels, with their finite availability and impact on climate change, are still widely used.

Renewable fuels, such as **biofuel**, ethanol and hydrogen, can be **synthesised** and are better for the environment because they contribute less to the carbon cycle and typically produce lower amounts of greenhouse gases. However, some people argue that biofuels are not a green alternative to fossil fuels because large areas of land are required to produce only a small amount of fuel.

Biofuels

Biofuels are liquid fuels that are obtained from materials such as plants and animal matter. Two biofuels are currently produced in Australia – **biodiesel** and ethanol, which are used as replacements for diesel and petrol. E10 is a type of fuel now available at petrol stations. E10 is a blend of unleaded petrol with 9–10% ethanol. Biofuels have been promoted as being able to reduce carbon emissions by up to 85%.

FIGURE 1 E10 is unleaded petrol blended with 9–10% ethanol.

Biodiesel

Biodiesel can be produced from waste vegetable oils, and animal fats and oils. The two most common ways of producing biofuels are by base catalysis and lipase catalysis.

Base-catalysed transesterification method

The process of **transesterification** exchanges an ester with an alcohol to form a new ester and a new alcohol. The base-catalysed transesterification method involves combining an organic oil (e.g. vegetable oil) with an alcohol, catalysed by a proton-accepting base. The process can be performed at relatively low temperatures and pressures, and has a **percentage yield** of approximately 98%. So base-catalysed transesterification is an efficient and inexpensive method of producing biodiesel.

Most commonly, triglycerides from vegetable oil are used as the ester, methanol (CH_3OH) is used as the alcohol, and either sodium hydroxide ($NaOH$) or potassium hydroxide (KOH) is used as the catalyst as a strong base. The chemical equation is shown in Figure 2.

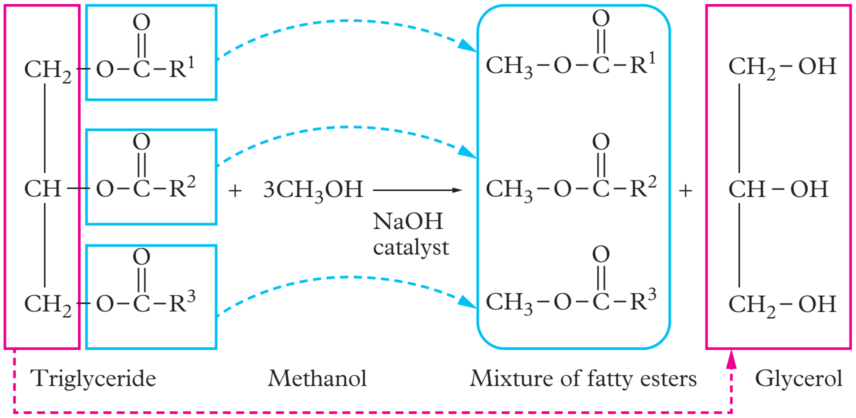


FIGURE 2 The transesterification reaction

The process takes place in two main steps.

1 Methanol is mixed with sodium hydroxide, which acts as the catalyst. Sodium hydroxide dissociates into Na^+ and OH^-. The sodium hydroxide needs to be very dry; otherwise, a saponification reaction occurs, which produces soap and alcohol. The OH^- removes a proton from methanol to form water and CH_3O^-.

2 The alcohol–catalyst mixture is added to the triglyceride at atmospheric pressure and 60–70°C, which results in the transesterification reaction. The triglyceride reacts with 3 moles of methanol. The three attached carbons and their hydrogens from the triglyceride molecule (highlighted red in Figure 2) react with OH^- and form propane-1,2,3-triol (also known as glycerol or glycerin). The CH_3 group reacts with the free fatty acid to form the fatty acid methyl ester that we use as biodiesel.

Lipase-catalysed method

A different method of producing biodiesel involves the use of an enzyme called **lipase**, which is a catalyst for fat (lipid) hydrolysis. This method is slower and more expensive than when using a chemical catalyst method, and has lower yields. However, it is environmentally friendlier, the product has higher purity, and the by-product – glycerol – is easily separated.

lipase
an enzyme that catalyses the hydrolysis of lipids, e.g. fats or oils

Ethanol

Ethanol (C_2H_6O) (Figure 3), one of the most common types of alcohol, is produced in Australia by **fermentation** of biomass. Raw materials used in the process include sugar cane and molasses (a by-product of the sugar industry), starch from corn, wheat or grains, or cellulose from wood. Alternatively, ethanol can be produced by the **catalytic hydration** of ethene.

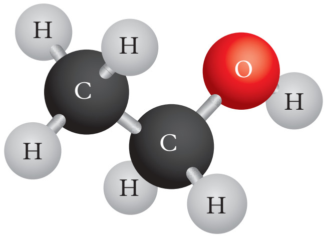


FIGURE 3 The structure of an ethanol molecule

fermentation
the chemical breakdown of a substance by bacteria, yeasts or other microorganisms

catalytic hydration
the reaction between water and an organic compound in the presence of a catalyst

Ethanol fermentation

Ethanol fermentation, also called alcoholic fermentation, is a reaction in which an organic compound is simultaneously oxidised and reduced. In Australia, waste products of sugar cane, starch production and red sorghum are used, so it does not interfere with the food production.

The sugar products are first ground, pulverised and mixed with water. Some of the insoluble sugars are mixed with enzymes and go through a process called saccharification. This is the hydrolysis of polysaccharides to turn them into soluble sugars such as glucose and sucrose. The sugars are then slowly decomposed by a yeast enzyme during the fermentation. For example, glucose reacts to form ethanol and carbon dioxide. The bubbles seen in Figure 4 are therefore CO_2 and the chemical reaction is:

$$C_6H_{12}O_6 \xrightarrow{\text{yeast enzyme}} 2C_2H_6O + 2CO_2$$

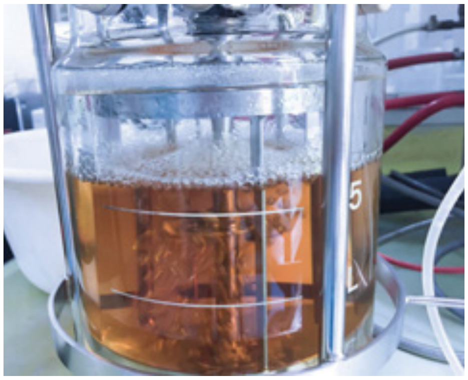


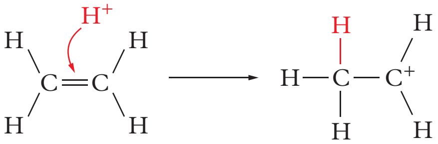
FIGURE 4 Fermentation of ethanol aided by yeast respiration

The reaction is anaerobic, which means no oxygen is involved. The process stops once the ethanol concentration reaches approximately 13% because yeast will not function at higher concentrations. To produce higher concentrations of ethanol, distillation is used.

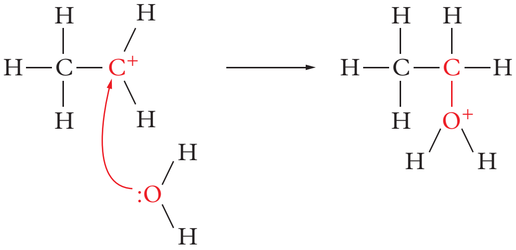
Hydration of ethene

protonate
adding a proton (hydrogen) to a molecule

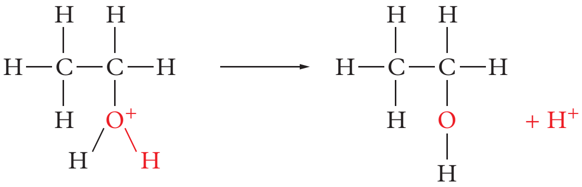
Most ethanol is produced by the direct hydration of ethene, under typical conditions of 300°C and 70 atm. A H^+ ion from phosphoric acid acts as the catalyst and **protonates** ethene:



Note that the carbon atom that does not bond to the hydrogen ion becomes positively charged. Consequently, a water molecule from steam reacts with the positively charged carbon:



Because the oxygen in the water molecule donates a lone pair to the positively charged carbon, it becomes positively charged itself. Finally, a hydrogen ion is lost, forming ethanol:



Note that the initial hydrogen, from phosphoric acid in the first reaction, is released again at the end. Therefore, phosphoric acid can be considered as the catalyst.

Hydrogen

Hydrogen is the most abundant element in the universe. It can be produced from many domestic resources including fossil fuels, biomass and water electrolysis with electricity. The environmental impact and energy efficiency of hydrogen depends on how it is produced.

More than 90% of hydrogen is produced by the **steam reforming** of methane and other components of natural gas. Steam at 700–1000°C reacts with methane in the presence of a metal-based catalyst (nickel) to produce hydrogen and carbon monoxide:

steam reforming a process that uses high-temperature steam (700–1000°C) to produce hydrogen from a methane source such as natural gas

$$CH_4 + H_2O \xrightarrow{\text{nickel catalyst}} CO + 3H_2$$

The carbon monoxide then reacts with water in the water-gas shift reaction:

$$CO + H_2O \rightarrow CO_2 + H_2$$

so, more hydrogen is formed.

Another method for producing hydrogen is by the electrolysis of water (Figure 5). However, electrolysis only accounts for about 4% of the world's hydrogen production.

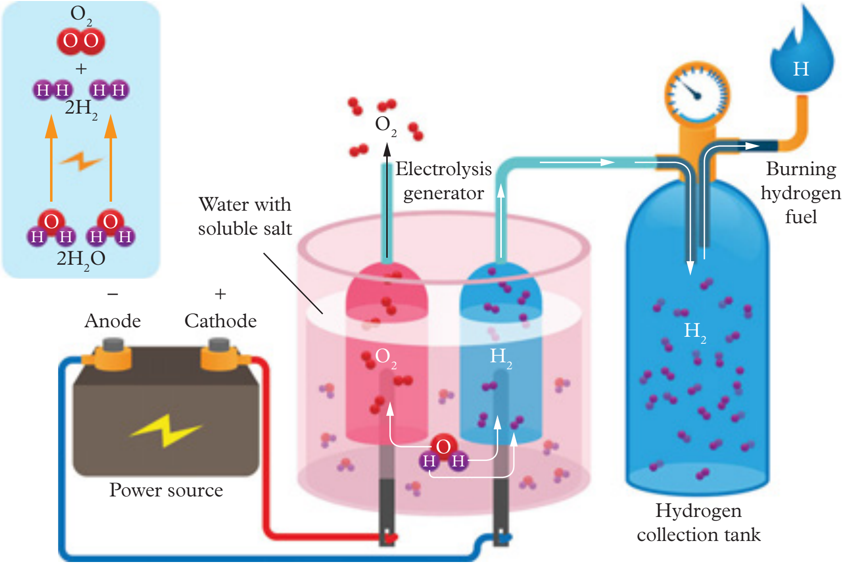


FIGURE 5 The production of hydrogen by electrolysis

CHECK YOUR LEARNING 13.2

Describe and explain

1 **Describe** what biofuels are.

2 **Explain** two ways of producing biodiesel.

3 **Describe** how ethanol can be produced.

4 **Describe** the three reactions in the hydration of ethene.

Investigate, evaluate and communicate

5 **Investigate** the advantages and disadvantages of biofuels.

You can find the following resources for this section on your obook assess:

» Student book questions
13.2 Check your learning

» Weblink
Biofuels

» Weblink
Hydrogen

SCIENCE AS A HUMAN ENDEAVOUR

13.3 Atom economy and green synthesis methods

KEY IDEAS

In this section, you will learn about:

- what green synthesis methods are
- atom economy.

Green chemistry aims to design products and processes that minimise the use and production of hazardous or environmentally unfriendly substances. Green chemistry involves designing high-performing and cost-effective technology that is environmentally friendly and safe for human health. It follows 12 principles. These principles are discussed further in Chapter 14.

1 Waste prevention
2 Atom economy
3 Less hazardous chemical synthesis
4 Designing safer chemicals
5 Safer solvents and auxiliaries
6 Design for energy efficiency
7 Use of renewable feedstocks
8 Reduce derivatives
9 Catalysis
10 Design for degradation
11 Real-time pollution prevention
12 Safer chemistry for accident prevention

Atom economy

Atom economy or atom efficiency describes the number of atoms involved in a chemical reaction that end up in the desired product. It can be expressed as the ratio of the molar mass of the desired product to the sum of the molar masses of all the reactants, adjusted for the respective stoichiometric coefficients.

Catalytic hydrogenation is one of the most efficient chemical reactions. Hydrogenation is a chemical reaction between molecular hydrogen (H_2) and another compound or element. In order to produce a usable reaction, a catalyst is required.

Green synthesis (less hazardous chemical synthesis)

Green synthesis describes the techniques to eliminate hazardous substances. Chemists only tend to use toxic substance because of their other, favourable properties. It is important to find alternatives through chemical synthesis.

green synthesis
a synthetic technique that aims to reduce or eliminate the use production of hazardous materials

FIGURE 1 The pharmaceutical industry is seeking ways of making medicines that produce less toxic waste.

One example in the field of medicine is the green synthesis of sitagliptin ($C_{16}H_{15}F_6N_5O$), the active ingredient in a diabetes medication. The production of sitagliptin involves an enzymatic process that reduces waste, improves yield and safety, and eliminates the need for a metal catalyst. New research into biocatalysts indicates they may also be useful in manufacturing other pharmaceuticals.

CHECK YOUR LEARNING 13.3

Describe and explain

1 **Define** 'atom economy'.

2 **Construct** a research question for green synthesis.

Investigate, evaluate and communicate

3 **Investigate** the other green chemistry principles and produce a poster explaining how each one works.

4 **Research** methods for producing safer solvents.

You can find the following resources for this section on your obook assess:

- Student book questions
  13.3 Check your learning
- Weblink
  Atomic economy
- Weblink
  Green synthesis

13.4 Hydrogen fuel cells

KEY IDEAS

In this section, you will learn about:

- how hydrogen fuel cells operate
- using diagrams and relevant half-equations.

hydrogen fuel cell an electrochemical cell that produces electricity and water

Humans have been exploring space for many decades. Rocket engines burn hydrogen gas to produce steam, this powers their engines. The same reaction is used in **hydrogen fuel cells** to produce electricity. Hydrogen fuel cells can achieve an efficiency of more than 75%, whereas petrol or diesel engines only have an efficiency of 25–30%. A fuel cell converts chemical potential energy, which is stored in molecular bonds, into electrical energy.

Some cars also use fuel cells instead of batteries. Fuel cells in cars generate electricity to power the motor, using oxygen from the air and compressed hydrogen from a tank (Figure 2). These cars are classified as zero-emission vehicles and only emit water and heat. However, pollutants are produced at the site of the hydrogen production, which is typically derived from reformed natural gas, and while transporting and storing hydrogen. But fuel cells are still considered to be environmentally friendlier than combustion engines.

FIGURE 1 Hydrogen is used to power space shuttles.

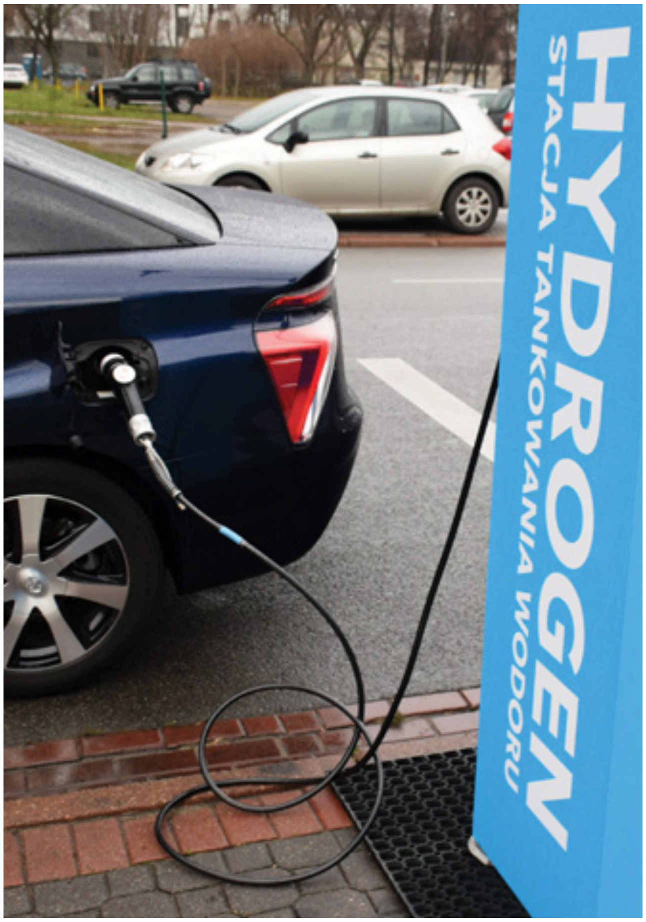


FIGURE 2 A hydrogen fuel cell car with zero emissions

Hydrogen fuel cell under acidic conditions

One example of a fuel cell based on acidic conditions is a **phosphoric acid fuel cell**, which uses liquid phosphoric acid (H_3PO_4). Its electrolyte is in the centre compartment (shaded green in Figure 3) at an operating range of 150–200°C. The electrolyte plays a key role in the process. It ideally only permits appropriate ions to pass between the anode and cathode. The anode and cathode are porous and usually coated with finely dispersed platinum as a catalyst to facilitate the reaction.

phosphoric acid fuel cell
a fuel cell that uses liquid phosphoric acid as an electrolyte, producing water, heat and electricity

The function of the fuel cell is as follows. Hydrogen molecules (H_2) enter at the anode, where they lose their electrons (purple in Figure 3) in a chemical reaction. So, the oxidation half-reaction is:

$$2H_2(g) \rightarrow 4H^+ + 4e^-$$

The ionised hydrogen travels through the electrolyte, while the electrons travel through a wire, providing electricity. Oxygen enters the fuel cell at the cathode and combines with the electrons and ionised hydrogen to form water. This is represented in the half-reaction:

$$O_2(g) + 4H^+ + 4e^- \rightarrow 2H_2O$$

The net chemical reaction is:

$$2H_2 + O_2 \rightarrow 2H_2O$$

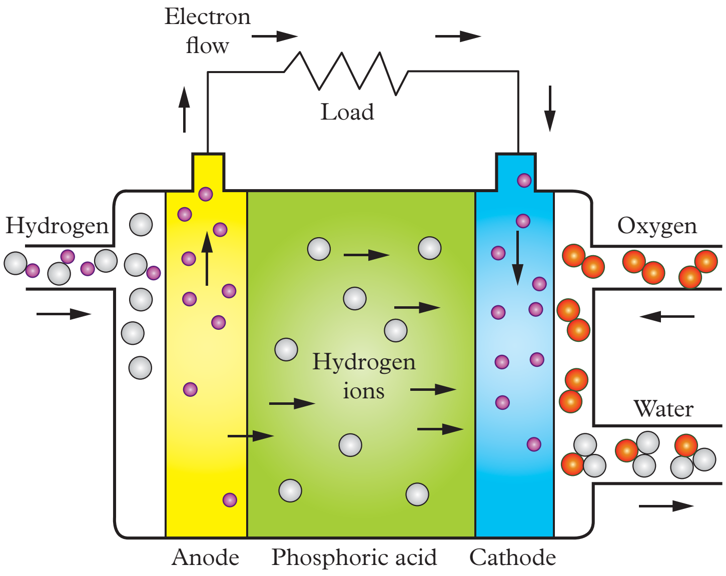


FIGURE 3 A phosphoric acid fuel cell

Hydrogen fuel cell under alkaline conditions

Alkaline fuel cells have been used by NASA since the mid-1960s in the Apollo missions. Power is produced through a redox reaction between hydrogen and oxygen. An alkaline solution such as NaOH or KOH is in the centre compartment (shaded green in Figure 4), which speeds up the reduction of oxygen. An alkaline fuel cell consumes hydrogen, which

alkaline fuel cell
a fuel cell that consumes hydrogen and oxygen, producing water, heat and electricity

is oxidised at the anode side (Figure 4), producing water and releasing electrons. This is represented in the half-reaction:

$$H_2 + 2OH^- \rightarrow 2H_2O + 2e^-$$

The electrons flow through an external circuit and return to the cathode where oxygen is reduced and hydroxide ions are produced:

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$$

The net chemical reaction produces water, electricity and heat. Alkaline fuel cells can include a catalyst, such as nickel or platinum metal, to speed up the reactions occurring at the anode and cathode.

$$2H_2 + O_2 \rightarrow 2H_2O + \text{heat energy}$$

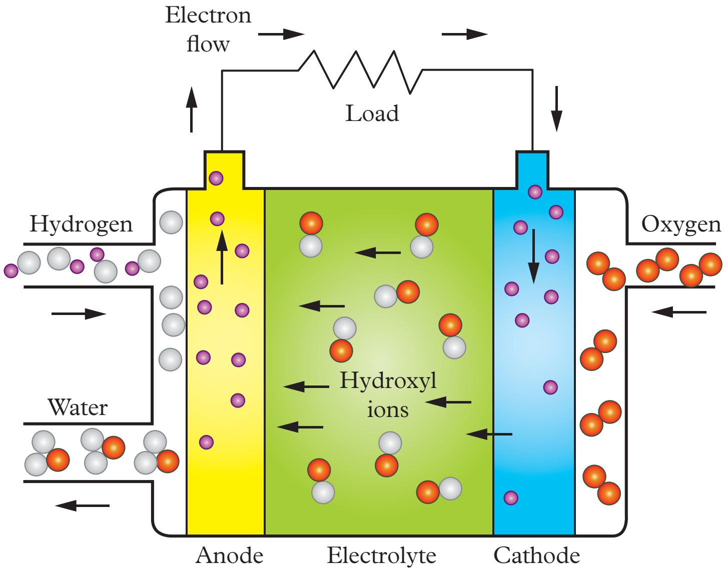


FIGURE 4 An alkaline fuel cell

CHECK YOUR LEARNING 13.4

Describe and explain

1 **Describe** the steps involved in a hydrogen fuel cell under:
  a acidic conditions
  b alkaline conditions.

Apply, analyse and interpret

2 **Derive** the chemical equations for a hydrogen fuel cell using aqueous potassium hydroxide (KOH) as the electrolyte.

3 **Discriminate** between a hydrogen fuel cell under acidic conditions and one alkaline conditions.

You can find the following resources for this section on your obook assess:

- Student book questions
  13.4 Check your learning
- Weblink
  Phosphoric acid fuel cells
- Weblink
  Alkaline fuel cells

13.5

Chemical synthesis reaction yields

KEY IDEAS

In this section, you will learn about:

- how to calculate the yield of chemical synthesis reactions
- comparing stoichiometric quantities with actual quantities
- determining the limiting reagents.

To understand the concept of limiting reagents and theoretical yield, you can use an analogy that involves ice creams. Imagine you have four ice-cream cones and a full tub of ice cream (Figure 1). One ice-cream cone combines with one scoop of ice cream, so the number of ice creams you can make is determined by the number of cones you have. In chemical terms, the cones are the **limiting reagent**. The ice creams that are ready to be consumed are the **theoretical yield** and the ice cream left in the tub is the **excess reagent**.

limiting reagent
the reactant in a chemical reaction that determines how much of the products are made

theoretical yield
the maximum amount of product expected by a chemical reaction

excess reagent
the reactant in a chemical reaction that is not completely used up

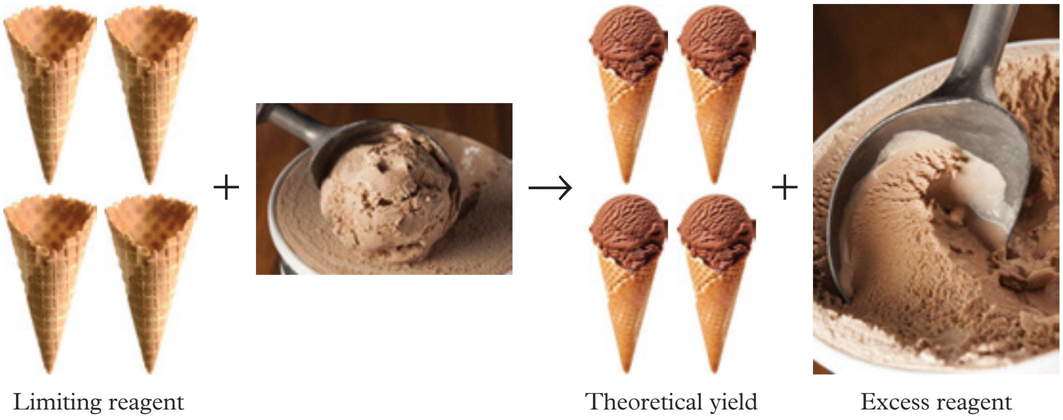


FIGURE 1 An analogy for understanding limiting reagents and theoretical yield

In chemistry, not every reaction goes to completion. But you can predict the quantity of the reactants (theoretical yield) by applying stoichiometry. In a chemical reaction, there is usually a limiting reagent that determines how much of the products are formed.

Theoretical yield

The theoretical yield is the predicted quantity of a product obtained from the complete conversion of the limiting reagent. Worked example 13.5A shows you how to calculate theoretical yield.

WORKED EXAMPLE 13.5A

Aspirin (acetylsalicylic acid, $C_9H_8O_4$) is a medicine widely used as a painkiller. Aspirin is produced by the reaction of salicylic acid ($C_7H_6O_3$) and acetic anhydride ($C_4H_6O_3$). Ethanoic acid is produced as a by-product.

Calculate the theoretical yield of aspirin if you have 5 g of each reactant.

SOLUTION

1 Write the balanced chemical equation.

$$C_7H_6O_3 + C_4H_6O_3 \rightarrow C_9H_8O_4 + C_2H_4O_2$$

Salicylic acid + acetic anhydride → acetylsalicylic acid + ethanoic acid

2 Find the limiting reagent. Because salicylic acid and acetic anhydride react in a 1:1 molar ratio, the reagent with the smallest number of moles is the limiting reagent.

a Determine the molar mass of both reactants.

$C_7H_6O_3$:

$7 \times 12\,\text{g mol}^{-1}(\text{C}) + 6 \times 1\,\text{g mol}^{-1}(\text{H}) + 3 \times 16\,\text{g mol}^{-1}(\text{O}) = 138\,\text{g mol}^{-1}$

$C_4H_6O_3$:

$4 \times 12\,\text{g mol}^{-1}(\text{C}) + 6 \times 1\,\text{g mol}^{-1}(\text{H}) + 3 \times 16\,\text{g mol}^{-1}(\text{O}) = 102\,\text{g mol}^{-1}$

b Convert the amount of each reactant from grams to moles.

$$\frac{5\,\text{g of } C_7H_6O_3}{138\,\text{g mol}^{-1}} = 0.036\,\text{mol of } C_7H_6O_3$$

$$\frac{5\,\text{g of } C_4H_6O_3}{102\,\text{g mol}^{-1}} = 0.049\,\text{mol of } C_4H_6O_3$$

c From the balanced chemical equation, you can see that 1 mol of $C_7H_6O_3$ reacts with 1 mol of $C_4H_6O_3$. So the amount of product will be determined by the limiting reagent, which is 0.036 mol of $C_7H_6O_3$.

$$C_7H_6O_3 + C_4H_6O_3 \rightarrow C_9H_8O_4 + C_2H_4O_2$$

Molecular weight of aspirin ($C_9H_8O_4$) = $162\,\text{g mol}^{-1}$

Therefore:

$$0.036\,\text{mol} \times 162\,\text{g mol}^{-1}\ (C_9H_8O_4) = 5.8\,\text{g}$$

The theoretical yield of aspirin is 5.8 g.

Percentage yield

experimental yield
the actual amount of the product

Another common measure is the percentage yield. The **experimental yield** of a product (measured on scales) is typically less than the theoretical expected yield for many reasons such as spills, incomplete reactions and undesirable side reactions. So chemists also calculate the percentage yield. The percentage yield serves as a measure of effectiveness of the synthesis.

$$\text{percentage yield} = \frac{\text{experimental yield}}{\text{theoretical yield}} \times 100\%$$

WORKED EXAMPLE 13.5B

When 39.75 g of magnesium carbonate decomposed in an experiment, 15 g of magnesium oxide was formed. Determine the percentage yield of magnesium oxide. The theoretical yield for MgO was calculated to be 19.00 g.

$$MgCO_3 \rightarrow MgO + CO_2$$

SOLUTION

1 Calculate the percentage yield.

$$\begin{aligned}\text{Percentage yield} &= \frac{\text{experimental yield}}{\text{theoretical yield}} \times 100\% \\ &= \frac{15}{19} \times 100\% \\ &= 78\%\end{aligned}$$

CHECK YOUR LEARNING 13.5

Describe and explain

1 **Explain** the terms:
  - **a** theoretical yield
  - **b** percentage yield
  - **c** excess reagent
  - **d** limiting reagent.

Apply, analyse and interpret

2 **Derive** an analogy, similar to the ice cream analogy in Figure 1, to describe theoretical yield, percentage yield, excess reagent and limiting reagent.

3 Consider the following synthesis reaction:

$$2K + Cl_2 \rightarrow 2KCl$$

1 g of each reagent is available.
  - **a** **Determine** the limiting reagent.
  - **b** **Calculate** the theoretical yield.

Investigate, evaluate and communicate

4 **Research** reasons why chemist would be interested in a percentage yield.

You can find the following resources for this section on your obook assess:

- » Student book questions
  13.5 Check your learning
- » Weblink
  Theoretical yield
- » Weblink
  Percentage yield

CHAPTER 13

Review

Chapter summary

13.1

- Chemical synthesis involves using simpler reactants to produce more complex products that are often important to daily life.
- The production of ammonia by the Haber process and the production of sulfuric acid by the contact process are two examples of chemical synthesis.

13.2

- There are many alternatives to fossil fuels. Some of the important ones are biofuels, which include biodiesel, ethanol and hydrogen.

13.3

- Green chemistry aims to exchange toxic and environmentally unfriendly products and processes with safer and environmentally friendly ones. The 12 principles of green chemistry outline how to achieve this goal.

13.4

- Hydrogen can be used to power engines. There are two different types of fuel cells – one runs under acidic conditions and the other one under alkaline conditions.

13.5

- The theoretical yield describes the predicted quantity of a product as determined by the limiting reagent.
- The actual yield is the quantity of product formed. The actual yield is typically lower than the theoretical yield because of spills or incomplete reactions.

Key terms

- alkaline fuel cell
- biodiesel
- biofuel
- catalytic hydration
- cathode
- contact process
- excess reagent
- experimental yield
- fermentation
- green synthesis
- Haber process
- hydrogen fuel cell
- limiting reagent
- lipase
- oleum
- percentage yield
- phosphoric acid fuel cell
- reagent
- renewable
- steam reforming
- stoichiometry
- synthesise
- theoretical yield
- transesterification
- yield

Key formulas

Percentage yield	$\text{percentage yield} = \frac{\text{experimental yield}}{\text{theoretical yield}} \times 100\%$

Revision questions

The relative difficulty of these questions is indicated by the number of stars beside each question number: ★ = low; ★★ = medium; ★★★ = high.

Multiple choice

1 Which of the following is **not** produced through chemical synthesis?
- **A** Phone screens
- **B** Car doors
- **C** Drink bottles
- **D** Sausages

2 Ethanol's structural formula is:
- **A** C_2H_5
- **B** C_3H_8O
- **C** C_2H_4O
- **D** C_2H_6O

3 Which one of the following is **not** involved in the process of converting an organic compound into ethanol?
- **A** Transesterification
- **B** Fermentation
- **C** Saccharification
- **D** Yeast

4 In a hydrogen fuel cell, power is generated by:
- **A** fission
- **B** fusion
- **C** redox reactions
- **D** combustion.

5 The limiting reagent can be identified by finding the reagent:
- **A** with the smallest number of moles
- **B** with the biggest number of moles
- **C** that is least reactive
- **D** that is most reactive.

6 A gas produced during fermentation is:
- **A** hydrogen
- **B** water vapour
- **C** methane
- **D** carbon dioxide.

Short answer

Describe and explain

★ 7 **Define** 'chemical synthesis'.

★★ 8 **Explain** the production of ethanol by the hydration of ethene. Include appropriate chemical equations.

★★ 9 **Explain** how a hydrogen fuel cell works under alkaline conditions. In your explanation, use the terms anode, cathode, electrolyte, electrons, oxygen and hydrogen.

Include all chemical equations involved.

Apply, analyse and interpret

★★★ 10 **Consider** the following synthesis reaction:

$$4Fe(s) + 3O_2(g) \rightarrow 2Fe_2O_3(s)$$

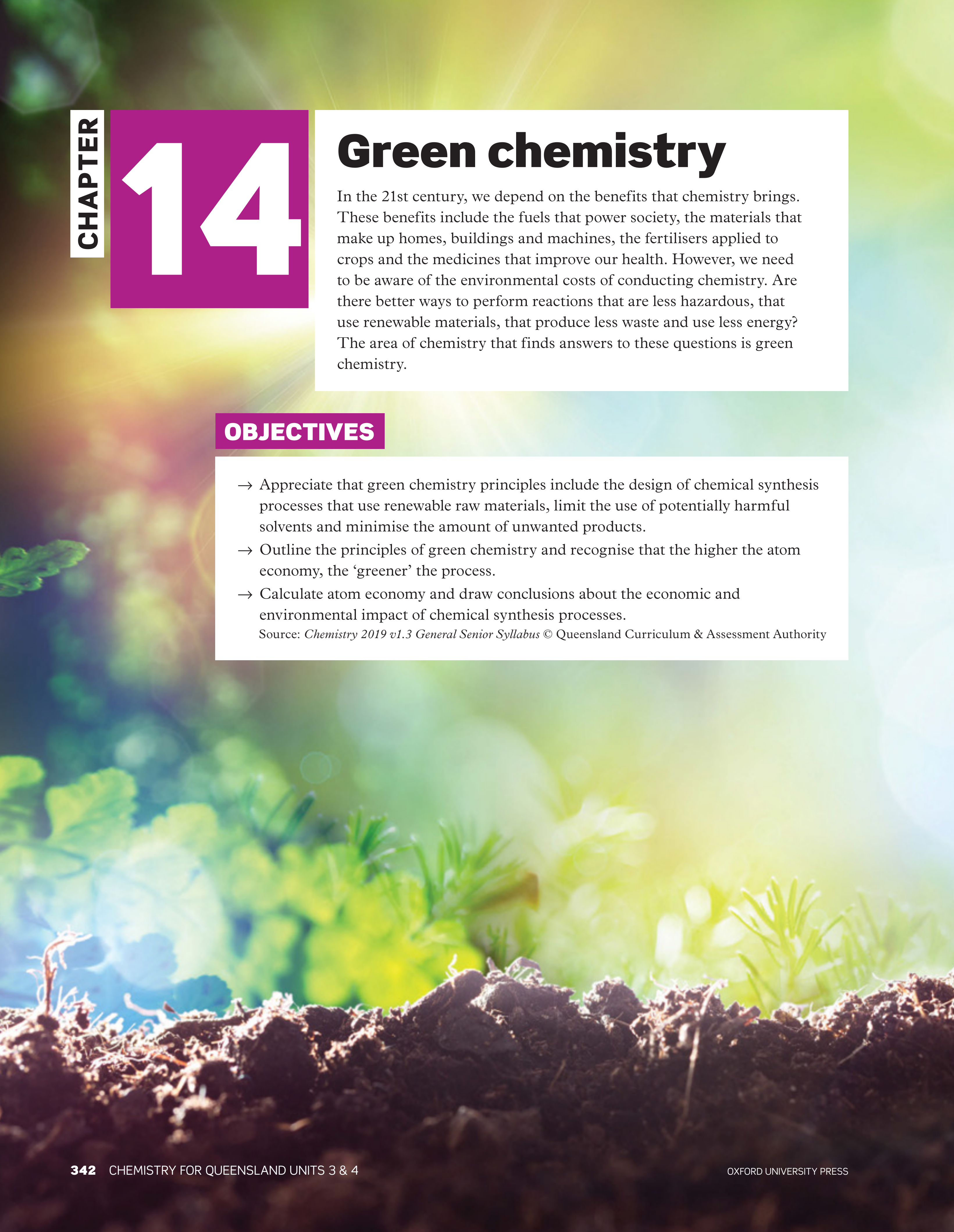
5 g of each reagent is available.
- **a** **Determine** the limiting reagent.
- **b** **Calculate** the theoretical yield.
- **c** If there is an excess reagent, **determine** what it would be and its amount (in grams).

Investigate, evaluate and communicate

★★ 11 **Investigate** the different chemical synthesis reactions involved in producing ibuprofen.

You can find the following resources for this section on your obook assess:

- » Student book questions
  Chapter 13 Revision questions
- » Revision notes
  Chapter 13
- » assess quiz
  Auto-correcting mutiple-choice quiz
- » Flashcard glossary
  Chapter 13



CHAPTER 14

Green chemistry

In the 21st century, we depend on the benefits that chemistry brings. These benefits include the fuels that power society, the materials that make up homes, buildings and machines, the fertilisers applied to crops and the medicines that improve our health. However, we need to be aware of the environmental costs of conducting chemistry. Are there better ways to perform reactions that are less hazardous, that use renewable materials, that produce less waste and use less energy? The area of chemistry that finds answers to these questions is green chemistry.

OBJECTIVES

→ Appreciate that green chemistry principles include the design of chemical synthesis processes that use renewable raw materials, limit the use of potentially harmful solvents and minimise the amount of unwanted products.

→ Outline the principles of green chemistry and recognise that the higher the atom economy, the ‘greener’ the process.

→ Calculate atom economy and draw conclusions about the economic and environmental impact of chemical synthesis processes.

Source: *Chemistry 2019 v1.3 General Senior Syllabus* © Queensland Curriculum & Assessment Authority

FIGURE 1 Green chemistry aims to reduce waste and energy use.

14.1

Making chemistry greener

KEY IDEAS

In this section, you will learn about:

- three of the principles of green chemistry
- reducing the environmental impact of chemistry by applying green chemistry principles.

green chemistry chemistry that designs products and processes that reduce the use or production of hazardous substances

Green chemistry, or sustainable chemistry, is the area of chemistry that aims to develop or design chemical products or processes that reduce or eliminate the use or generation of hazardous substances. By applying environmentally friendlier methods, chemists can reduce the negative impacts of chemistry and encourage a shift to sustainable development. Green chemistry uses insights and knowledge from across all areas of chemistry to accomplish these goals.

The principles of green chemistry

The ideas underlying green chemistry have been summarised in the phrase, 'benign by design'. By better planning of chemical processes, we can maximise the amount of raw materials that end up in the final product, both saving money and decreasing waste. We can improve the energy efficiency of processes and use more environmentally friendly solvents, or avoid using solvents altogether. Green chemistry considers the whole life cycle of a chemical product, from its manufacture and use to its recycling or disposal.

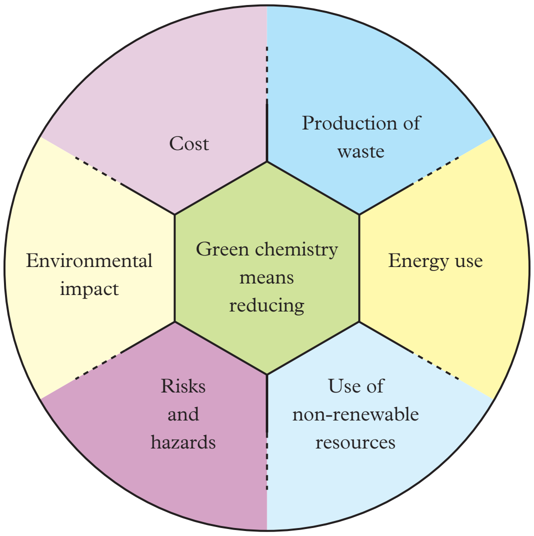


FIGURE 1 Green chemistry reduces the impact of chemistry on the environment.

In the 1990s, US chemists Paul Anastas and John Warner developed 12 principles of green chemistry (Table 1). It may not be possible to satisfy all the principles completely, so in practice chemists have to decide which aspects are more important in a particular situation.

TABLE 1 The 12 principles of green chemistry proposed by Anastas and Warner.

The 12 principles of green chemistry	
Green chemistry is an approach to chemistry that aims to maximise efficiency and minimise hazardous effects on human health and the environment. While no reaction can be perfectly 'green', the overall negative impact of chemistry research and the chemical industry can be reduced by implementing the 12 principles of green chemistry wherever possible.	
1 Waste prevention	• Prioritise the prevention of waste, rather than cleaning up and treating waste after it has been created. • Plan ahead to minimise waste at every step.
2 Atom economy	• Reduce waste at the molecular level by maximising the number of atoms from all reagents that are incorporated into the final product. • Use atom economy to evaulate reaction efficiency.
3 Less hazardous chemical synthesis	• Design chemical reactions and synthetic routes to be as safe as possible. • Consider the hazards of all substances handled during the reaction, including waste.
4 Designing safer chemicals	• Minimise toxicity directly by molecular design. • Predict and evaluate aspects such as physical properties, toxicity and environmental fate throughout the design process.
5 Safer solvents and auxiliaries	• Choose the safest solvent available for any given step. • Minimise the total amount of solvents and auxiliary substances used, as these make up a large percentage of the total waste created.
6 Design for energy efficiency	• Choose the least energy-intensive chemical route. • Avoid heating and cooling as well as pressurised and vacuum conditions (i.e. ambient temperature and pressure are optimal).
7 Use of renewable feedstocks	• Use chemicals which are made from renewable (i.e. plant-based) sources, rather than other, equivalent chemicals originating from petrochemical sources.
8 Reduce derivatives	• Minimise the use of temporary **derivatives** such as **protecting groups**. • Avoid derivatives to reduce reaction steps, resources required, and waste created.
9 Catalysis	• Use catalytic instead of stoichiometric reagents in reactions. • Choose catalysts to help increase selectivity, minimise waste, and reduce reaction times and energy demands.
10 Design for degradation	• Design chemicals that degrade and can be discarded easily. • Ensure that both chemicals and their degradation products are not toxic, **bioaccumulative** or environmentally persistent.
11 Real-time pollution prevention	• Monitor chemical reactions in real time as they occur to prevent the formation and release of any potentially hazardous and polluting substances.
12 Safer chemistry for accident prevention	• Choose and develop chemical procedures that are safer and inherently minimise the risk of accidents. • Know the possible risks and assess them beforehand.

derivative
a compound that can be synthesised easily from a parent compound by replacing an atom or group of atoms

protecting group
a temporary functional group added during a chemical synthesis to prevent that part of the molecule from reacting; it is later removed to regenerate the original functional group

bioaccumulative
a toxic compound that can build up in living organisms over time, and tends to be concentrated in organisms at the top of the food chain

Study tip

Consider how the 12 principles of green chemistry can be grouped according to reducing waste, making reactions safer, reducing the use of energy, and reducing environmental impact. This will make them easier to study.

CHALLENGE 14.1

Firefighting foams

Perfluorooctanesulfonic acid (PFOS) and a related chemical perfluorooctanoic acid (PFOA) were used in firefighting foams at a number of locations around Queensland. They are no longer used because they contaminated ground water and land around several airfields and ports.

Investigate why these products were used and which principles of green chemistry were not adequately considered. Evaluate the replacement products that have been proposed and how they are an improvement. Communicate your findings as a bullet-point summary.

CHECK YOUR LEARNING 14.1

Describe and explain

1 **Describe** the goals of green chemistry.

2 Using what you already know about catalysis, **explain** the advantages of catalysed reactions over non-catalysed reactions in terms of environmental concerns.

Apply, analyse and interpret

3 Consider the statement: 'Green chemistry principles are just as much about business common sense as environmental common sense'. **Interpret** this statement and **explain** how adopting green chemistry principles could reduce costs for a manufacturer of chemicals.

4 In 2000, a large number of countries agreed on the Millennium Development Goals. Goal 7 is to 'ensure environmental sustainability', with one specific target being to 'integrate the principles of sustainable development into country policies and programmes and reverse the loss of environmental resources'. **Apply** your understanding of green chemistry and indicate how any two of the green chemistry principles relate to this target.

Investigate, evaluate and communicate

5 The Bhopal disaster of December 1984 has been called the world's worst industrial disaster. More than 500 000 people in India were exposed to methyl isocyanate gas. **Investigate** what methyl isocyanate is used for and why it is so toxic. How can the risks of using methyl isocyanate be reduced?

You can find the following resources for this section on your obook assess:

- Student book questions
  14.1 Check your learning
- Challenge
  14.1 Firefighting foams
- Weblink
  Principles of green chemistry

14.2 Principles of green chemistry

KEY IDEAS

In this section, you will learn about:

- three of the 12 principles of green chemistry in greater detail
- how chemists and chemical engineers use these principles to develop new processes and materials that are environmentally more sustainable.

The 12 principles of green chemistry have been developed to help chemists, chemical engineers and manufacturers think about how to reduce the environmental impacts of their work. Some of these principles are explained in detail in this section.

Using safer solvents (principle 5)

Solvents are used in chemical processes to extract (transfer compounds from one phase to another) and recrystallise desired products. They are also used as reaction solvents to speed up reactions by increasing the likelihood of two reactants encountering each other. Solvents also absorb heat released by exothermic reactions.

Some reactions can be done without an added solvent. For example, in the laboratory a mortar and pestle are used to grind together *ortho*-vanillin (melting point 40–42°C) and *para*-toluidine (melting point 41–46°C). This is an example of a **solid-phase reaction**. The product that forms is a bright orange imine (Figure 1). Water is also produced, but the heat produced by the reaction helps to evaporate it.

solid-phase reaction
a reaction in which all the reactants are in the solid state

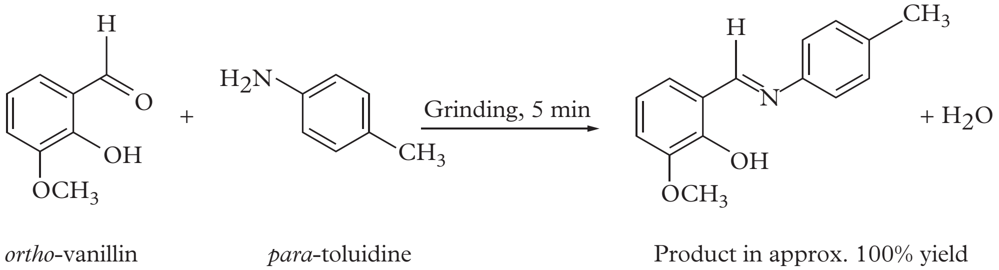


FIGURE 1 The reaction of *ortho*-vanillin and *para*-toluidine to make an imine product is an example of a solid-phase reaction that does not require a solvent.

Even if you cannot eliminate a solvent entirely from a reaction, it may be possible to replace a solvent with a less toxic or sustainably sourced one. Environmentally, the ideal solvent is water, but many substances are not soluble in water or the reactions needed are not compatible with water. One way around this is to add surfactant or detergent molecules to form a **micelle**. A micelle has a non-polar interior where the desired reaction can take place, often at faster rates, because the reactants are present in high concentrations within the micelles. Figure 2 on the next page shows the stucture of a micelle.

micelle
an aggregation of surfactant molecules

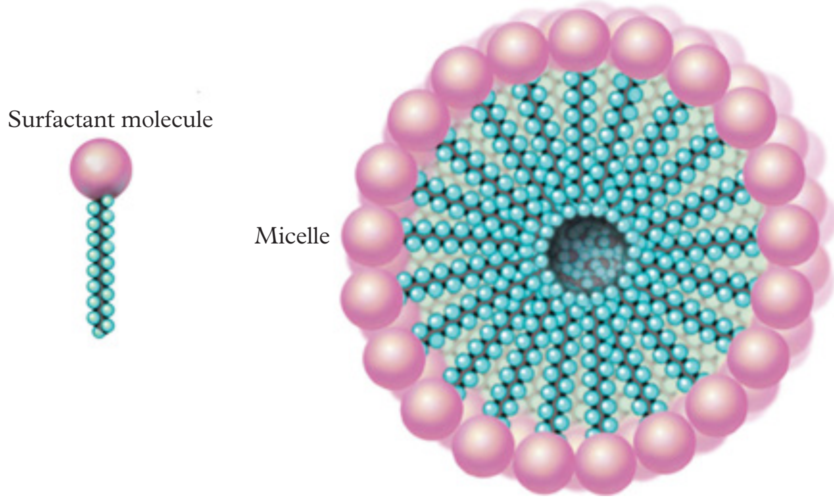


FIGURE 2 Micelles are an ordered assembly of surfactant molecules with a polar surface and a non-polar interior. They enable reactions to occur in water that otherwise would not proceed.

Another alternative to organic solvents is **supercritical fluids**. A supercritical fluid is a substance that has properties of both liquids and gases at certain temperatures and pressures. For example, when carbon dioxide is heated above its critical temperature and pressure, it is in the supercritical fluid phase and its properties are intermediate between a gas and a liquid (Figure 3). The properties can be changed by changing the temperature and pressure. Supercritical carbon dioxide ($scCO_2$) is a good solvent and can be easily removed from the reaction and recycled. Supercritical fluids are also non-toxic, non-flammable and readily available. When CO_2 is used as a supercritical fluid, it is often a by-product of other industrial processes, such as the manufacture of ammonia.

supercritical fluid
a substance at a temperature and pressure beyond its critical point, where the substance has properties of both a gas and liquid

$scCO_2$ is used to decaffeinate coffee. Before this, dichloromethane (CH_2Cl_2) was used. $scCO_2$ is preferred to CH_2Cl_2 (a chlorinated solvent) because CH_2Cl_2 is a potential cancer-causing agent (carcinogen), and residues of the solvent remained in the decaffeinated coffee.

To decaffeinate coffee, green (unroasted) coffee beans are fed into an extractor unit with $scCO_2$. The caffeine is extracted into the supercritical fluid. The CO_2 containing caffeine is then washed with water to make a dilute caffeine solution and the CO_2 is recycled back to the extractor. The aqueous solution of caffeine is concentrated by reverse osmosis (similar to the process in a desalination plant), and the caffeine is sold to soft-drink or pharmaceutical manufacturers.

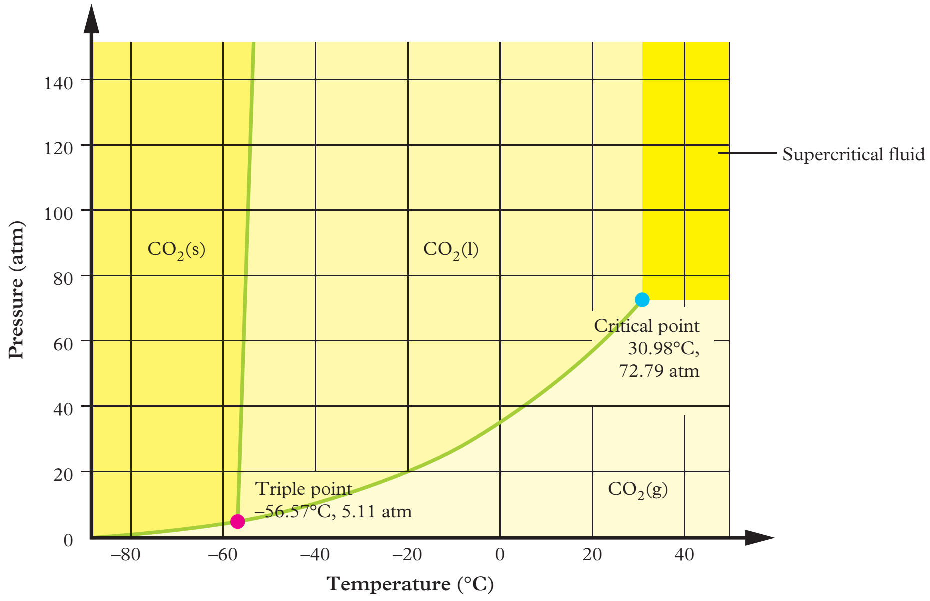


FIGURE 3 A phase diagram for CO_2. Above the critical point, CO_2 does not exist as either a gas or a liquid but as a supercritical fluid, and has properties between those of liquid CO_2 and gaseous CO_2.

Designing for energy efficiency (principle 6)

In Australia, chemical manufacturing uses about 18% of the total energy used by the manufacturing sector (Figure 4). Many chemical processes use energy from fossil fuels to produce thermal energy. However, this energy is not directly targeted at the molecules that are undergoing reaction. Energy is used in heating up reactors and solvents and some heat energy is simply lost to the environment. Energy savings can be made by using **catalysts** that allow reactions to run at lower temperatures. For example, the Haber process for producing ammonia from nitrogen gas uses 40% less energy than the original process did because it uses an iron–aluminium catalyst.

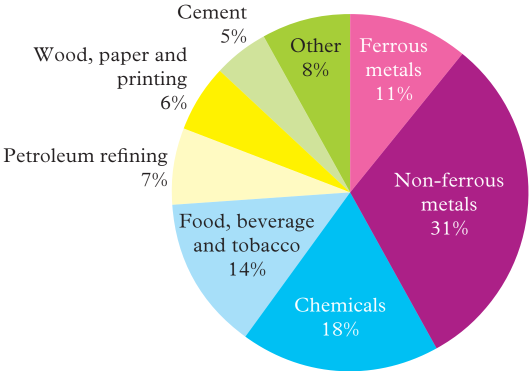


FIGURE 4 Relative consumption of energy in Australian manufacturing, 2015–16. Chemical production uses about 18% of the total energy. This corresponds to 203.8 petajoules, or 2.038×10^{17} joules.

catalyst
a substance that increases the rate of a reaction without itself being consumed in the reaction

Another way to save energy is to use technologies that specifically add energy to the reacting molecules. For example, microwave ovens heat some substances much more rapidly than others. Microwave heating is more efficient than conventional heating because energy is put directly into the reaction medium, rather than first being transferred through a reaction container. Any molecules in the reaction mixture that contain a dipole, a permanent separation of charge, such as water, tend to align themselves with the oscillating electric field of the microwave. Ions are dragged through the medium. The result is the generation of heat through collisions between molecules. In a sealed container, solvents can rapidly reach temperatures above their normal boiling points. These high temperatures rapidly accelerate reactions. Faster reaction times can result in greater yields of the desired product, because decomposition or side reactions have less time in which to occur.

An example of a reaction that can be accelerated by microwave heating is the hydrolysis of benzamide to benzoic acid in acidic solution (Figure 5).

Some reactions with microwave heating can be very rapid. For example, secondary alcohols can be oxidised to ketones in the presence of an oxidising agent in less than a minute.

Other potential techniques for reducing energy use are photochemistry and sonochemistry – using light and ultrasound to initiate reactions.

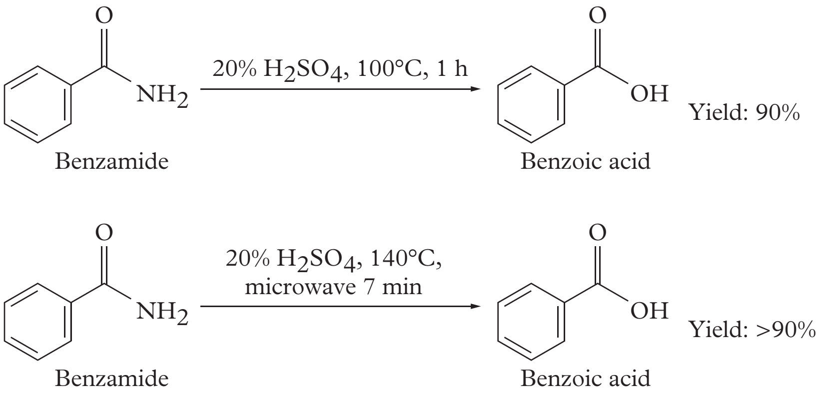


FIGURE 5 The hydrolysis of benzamide with microwave heating results in faster reaction times and higher yields than the same reaction without microwave heating.

Designing for degradation (principle 10)

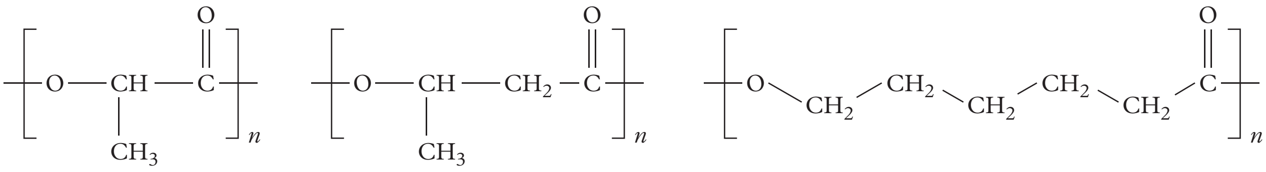
This principle is about designing chemicals that break down into harmless products that do not persist in the environment.

In the late Iron Age through to the Middle Ages, pollution from lead and silver mining spread from Europe and Northern Africa to Greenland and the North Pole, where it is now detected in ice cores. Today, many more chemicals, in greater concentrations, are dispersed around the world, far from their original site of release. These include **persistent organic pollutants (POPs)**, organic compounds that can accumulate and move up the food chain. POPs are broken down very slowly in the environment.

FIGURE 6 The very slow breakdown of plastics has caused substantial environmental problems.

Medicines can also cause problems. Medications that people take can end up in the sewerage system and then in the environment, if they are not removed by the sewage treatment process. Also, many plastics are very stable and can end up in landfill or as litter (Figure 6) or form microplastic particles, which are small pieces of plastic that pollute the environment. Examples of microplastic particles include microfibres from clothing, microbeads from cosmetics and plastic pellets (nurdles), used in the manufacture of plastic containers.

One answer to the growing problem of plastic pollution is to switch to newer types of plastics that can be degraded by microorganisms into harmless biological molecules. Another advantage of these plastics is that their starting materials are also often sourced from renewable materials. Attempts have been made to add segments of biodegradable polymers to existing polymer materials (Figure 7).



Polylactic acid (PLA) Poly-3-hydroxybutanoate (P3HB) Polycaprolactone (PCL)

FIGURE 7 Examples of biodegradable polymers

persistent organic pollutant (POP)
a toxic organic compound that is resistant to breakdown by organisms or other chemical processes

Another strategy is to enhance the rate of breakdown of polymers (either by light or by chemical treatment) by including other chemicals in the polymer structure.

One problem with the breakdown of polymers is that the end products (under favourable conditions) are CO_2 and water, which would contribute to rising levels of CO_2 in the atmosphere. Under low-oxygen conditions, the polymer breaks down to methane, which is a more potent greenhouse gas than CO_2.

There are some rules of thumb to guide the development of biodegradable polymers.

- Structures that more closely resemble natural molecules are more likely to be broken down more rapidly.
- Linear chains are broken down more rapidly than highly branched chains. If the polymer contains benzene groups, it will break down faster if the benzene groups have two adjacent unsubstituted carbons.
- Materials that contain chlorine or fluorine take longer to break down because of the strength of the carbon–halogen bonds.
- As the molecular weight of a polymer chain increases, the rate of degradation decreases.

CHECK YOUR LEARNING 14.2

Describe and explain

1 **Explain** how microwaves can be used to heat reactions and how this can be more energy efficient.

2 **Describe** the structure of the biodegradable polymer poly-3-hydroxybutanoate (P3HB).

Apply, analyse and interpret

3 Compare the phase diagrams for water and carbon dioxide (Figure 8).

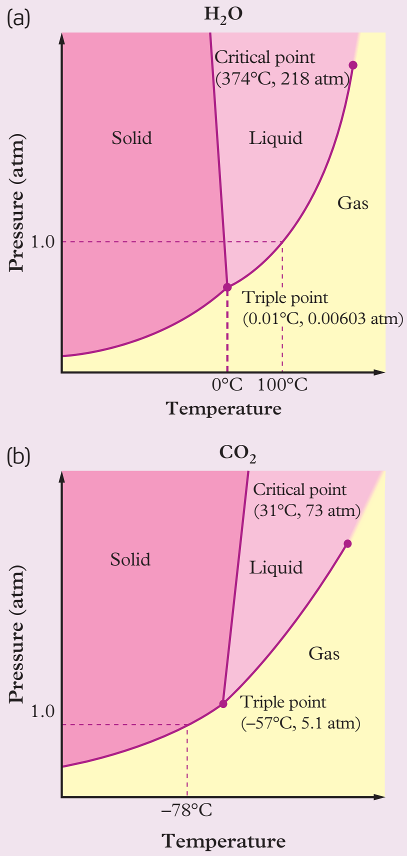


FIGURE 8 Phase diagrams of (a) H_2O and (b) CO_2

Interpret the diagrams to explain why there would be an advantage to using supercritical CO_2 rather than supercritical water in an extraction process.

Investigate, evaluate and communicate

4 Ball-milling can be used on an industrial scale for solid-phase reactions. **Investigate** how ball-milling works and produce a labelled diagram of a ball mill that communicates the main parts of the process.

5 A waste-to-energy plant has been proposed for Ipswich that will burn municipal waste to provide energy to generate electricity. **Investigate** the possible advantages and disadvantages of this proposal. **Evaluate** these and communicate your conclusions in the form of a half-page summary report for Ipswich City Council members.

6 The toy company LEGO has set itself the challenge of replacing the ABS polymer presently used for making LEGO bricks with a more sustainable polymer by the year 2030. **Investigate** the structure of the ABS polymer and the replacements that have been proposed. Communicate this in the form of an A4-sized advertisement that will inform consumers how LEGO is trying to adopt green chemistry principles.

FIGURE 9 LEGO (a predominately plastic corporation) is trying to adopt green principles for producing its products.

You can find the following resources for this section on your obook assess:

- Student book questions
  14.2 Check your learning
- Weblink
  Energy efficiency
- Weblink
  Biodegradation

SCIENCE AS A HUMAN ENDEAVOUR

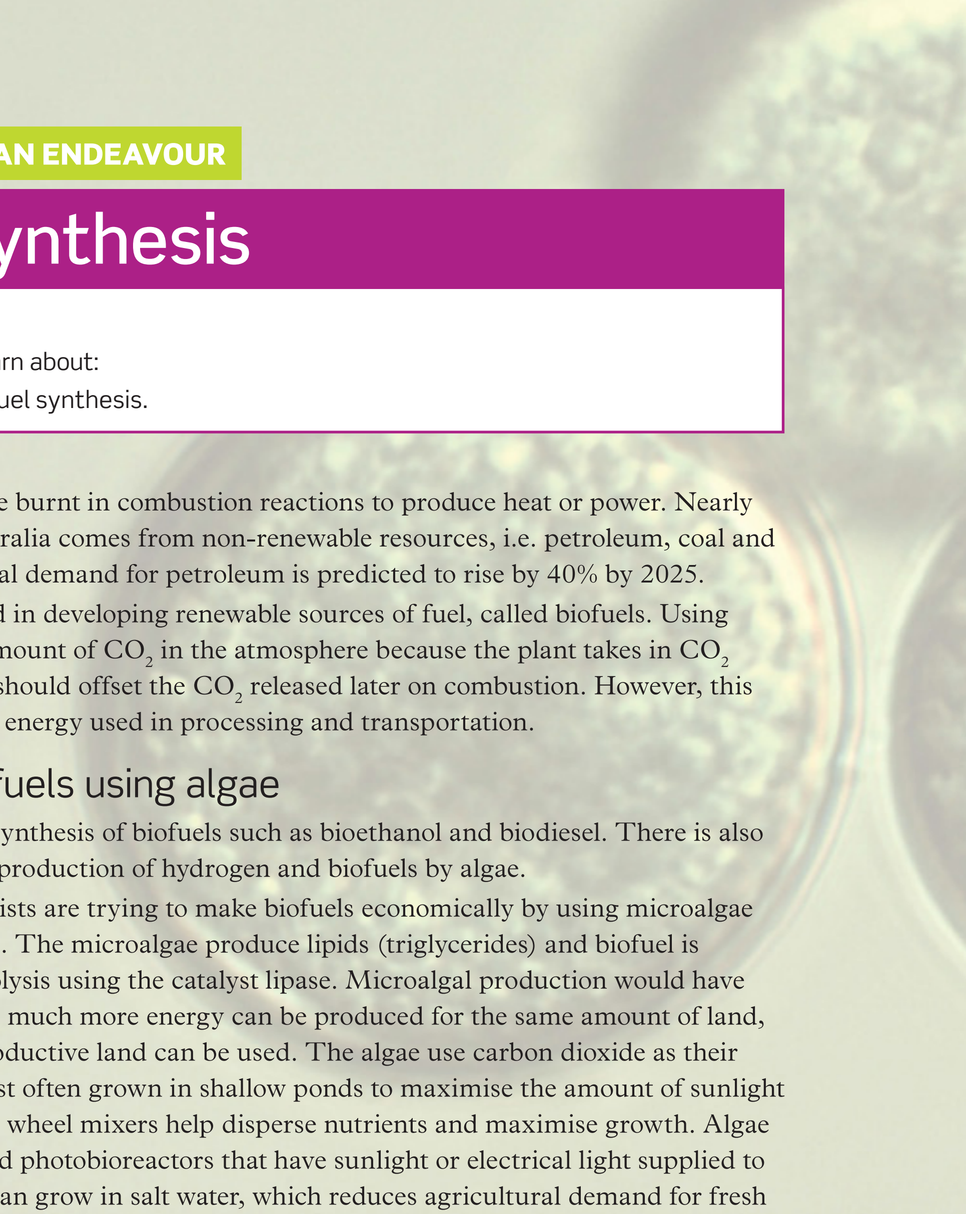
14.3

Biofuel synthesis

KEY IDEAS

In this section, you will learn about:

- the role of algae in biofuel synthesis.



Fuels are materials that are burnt in combustion reactions to produce heat or power. Nearly all of the fuel used in Australia comes from non-renewable resources, i.e. petroleum, coal and natural gas deposits. Global demand for petroleum is predicted to rise by 40% by 2025.

Scientists are interested in developing renewable sources of fuel, called biofuels. Using biofuels may reduce the amount of CO_2 in the atmosphere because the plant takes in CO_2 during its lifetime, which should offset the CO_2 released later on combustion. However, this does not take into account energy used in processing and transportation.

Production of biofuels using algae

Chapter 13 discusses the synthesis of biofuels such as bioethanol and biodiesel. There is also ongoing research into the production of hydrogen and biofuels by algae.

Currently, many scientists are trying to make biofuels economically by using microalgae (third-generation biofuels). The microalgae produce lipids (triglycerides) and biofuel is produced from lipid hydrolysis using the catalyst lipase. Microalgal production would have many advantages, because much more energy can be produced for the same amount of land, and non-agriculturally productive land can be used. The algae use carbon dioxide as their carbon source and are most often grown in shallow ponds to maximise the amount of sunlight for photosynthesis. Paddle wheel mixers help disperse nutrients and maximise growth. Algae can also be grown in closed photobioreactors that have sunlight or electrical light supplied to maximise growth. Algae can grow in salt water, which reduces agricultural demand for fresh water. Depending on the species and strain of microalgae, the lipid content can be as high as 40% of the dry mass of the algae. Other microalgae have a high starch content, making them suitable for ethanol production, and the algae *Botryococcus braunii* makes hydrocarbons, similar to those found in petroleum. The algal **biomass** can also be harvested, dried and used in a **gasification** process.

biomass
living or recently living matter that can be used as a fuel source

gasification
a high-temperature process under low oxygen concentrations that converts carbon-containing materials into a mixture of carbon monoxide, carbon dioxide, hydrogen and methane

However, biofuel production from algae is currently too expensive to compete with oil-based fuels, because of the cost of harvesting and processing. Problems that need to be overcome include that the highest lipid concentrations of algae tend to occur at low growth rates, although genetic engineering may overcome this. The triglycerides produced by algae also tend to have higher numbers of double bonds in the fatty acid side chains, which can cause problems with polymerisation in the biodiesel produced.

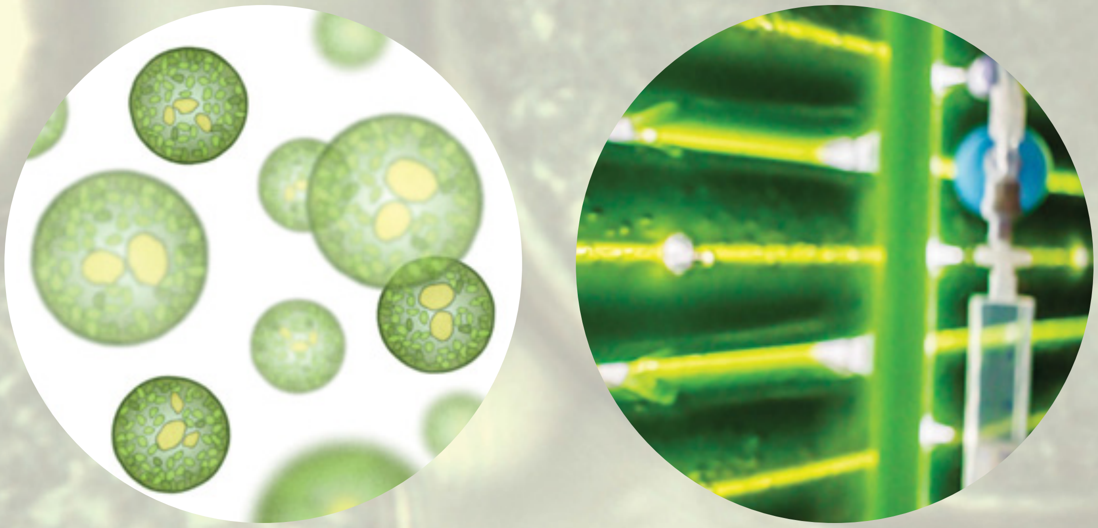


FIGURE 1 (a) Microscopic view of microalgae cells, containing yellow droplets of triglyceride oil. (b) A photobioreactor, in which microalgae can be grown at higher densities than open ponds.

Most companies that are investigating algal fuel production are hoping to combine fuel production with the synthesis of high-value chemicals, such as natural food colours, omega-3-fatty acids or other biochemicals, or to make bioplastics, to replace oil-based plastics, or use the algae as a source of protein-rich food.

Scientists are also researching the use of algae to make hydrogen as a fuel, a process that uses two enzymes called nitrogenase and hydrogenase. Only water and sunlight are required, but the system can only have a very low concentration of oxygen.

CHECK YOUR LEARNING 14.3

Describe and explain

1 **Describe** the term biofuel.

Apply, analyse and interpret

2 ‘One of the main advantages of biofuels is that they are necessarily carbon neutral.’ **Interpret** and **discuss** this statement.

Investigate, evaluate and communicate

3 **Investigate** the advantages and disadvantages of using algae to produce biofuels. **Discuss** how this is different from what you learnt in Chapter 13 on bioethanol and biodiesel.

You can find the following resources for this section on your obook assess:

- Student book questions
  14.3 Check your learning
- Weblink
  Renewables
- Weblink
  Algae and biofuels

14.4

Measuring 'greenness' with atom economy

KEY IDEAS

In this section, you will learn about:

- atom economy in reactions
- how to calculate atom economy.

Traditionally, when chemists have compared different methods for making a compound, they have concentrated on product yields, often expressed as a percentage. The closer the percentage yield is to 100%, the 'better' the reaction.

The percentage yield of a reaction does not take into account all of the materials that may be used in a reaction and everything that is produced as a result of the reaction. It was for this reason that the concept of **atom economy** was first developed by US chemist Barry Trost in 1991.

atom economy
the efficiency of a chemical reaction or process at converting the mass of reactants into desired products

Atom economy is a calculation of how much of the mass of the reactants remains in the final product.

For a reaction:

$$a\mathrm{A} + b\mathrm{B} \xrightarrow[\text{solvent catalysts}]{\text{reagents}} p\mathrm{P} + d\mathrm{D}$$

where A and B are reactants, P is the desired product and D is a side-product, and *a*, *b*, *p* and *d* are the stoichiometric coefficients for the respective reactants and products.

$$\%\ \text{atom economy} = \frac{(p \times \text{molar mass of P})\ \mathrm{g\,mol^{-1}}}{(a \times \text{molar mass A} + b \times \text{molar mass B})\ \mathrm{g\,mol^{-1}}} \times 100\%$$

This formula is for a reaction with two reactants, but can be extended to include the actual number of reactants involved.

Therefore, atom economy is the ratio of the molar mass of the desired product to the sum of the molar masses of all the reactants, adjusted for the respective stoichiometric coefficients. This means you need a balanced, stoichiometrically correct reaction, but it does not use actual experimental masses or volumes of materials.

A reactant in this context means anything that is incorporated into a reaction intermediate or product during the synthesis; for example, acids or bases that may be added to neutralise a reaction. Catalysts that are used in trace amounts are not included in the calculation because they do not contribute atoms to any reaction intermediates or the final product.

For example, Figure 1 shows two reactions for making maleic anhydride. Maleic anhydride can be made from a number of possible starting materials, in reactions that use oxygen and a vanadium-containing catalyst. Maleic anhydride is an important intermediate in coatings and polymers and it is estimated that more than 2 million tonnes will be made annually worldwide by the mid-2020s. So, the choice of which reaction to use has important real-world consequences.

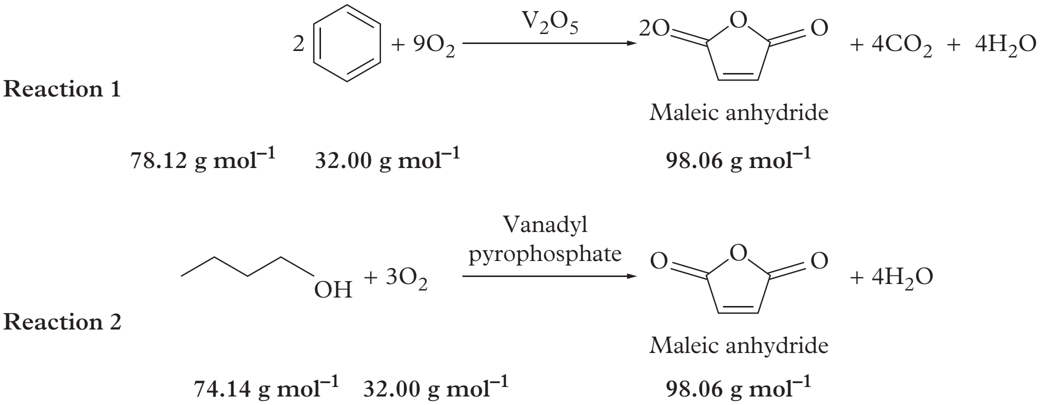


FIGURE 1 Two reactions for the synthesis of maleic anhydride, starting either from benzene (reaction 1) or 1-butanol (reaction 2)

WORKED EXAMPLE 14.4

Which reaction for the production of maleic anhydride in Figure 1 is the more atom efficient? First make a prediction, then check your prediction by performing the calculation for both reactions.

SOLUTION

Reaction 1 includes carbon dioxide and water as additional products. It also uses benzene, and not all the carbon atoms in the reactant end up in the product maleic anhydride. It is reasonable to predict that reaction 2 is more atom efficient.

The balanced stoichiometric equations are presented for both reactions and the molar masses of reactants and products are also given. The molar masses of the vanadium compounds are not included in the calculations because they are being used as catalysts. Carbon dioxide and water are not included because they are by-products.

For reaction 1:

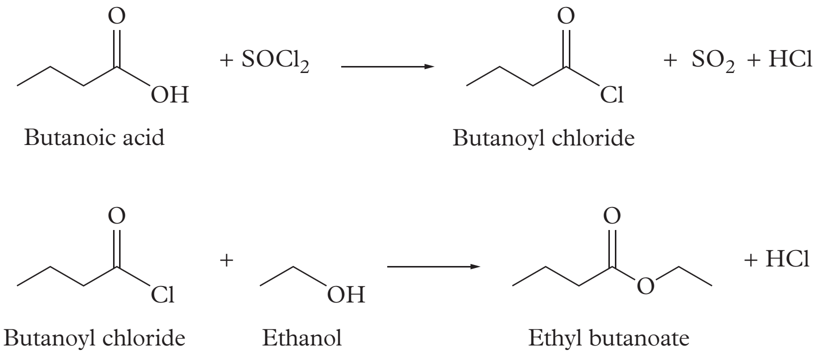
$$\begin{aligned}\%\text{ atom economy} &= \frac{(p \times \text{molar mass of P})\,\text{g mol}^{-1}}{(a \times \text{molar mass A} + b \times \text{molar mass B})\,\text{g mol}^{-1}} \times 100\% \\ &= \frac{2 \times \text{molar mass of maleic anhydride}\,\text{g mol}^{-1}}{(2 \times \text{molar mass of benzene} + 9 \times \text{molar mass oxygen, O}_2)\,\text{g mol}^{-1}} \times 100\% \\ &= \frac{2 \times 98.06\,\text{g mol}^{-1}}{(2 \times 78.12 + 9 \times 32.00)\,\text{g mol}^{-1}} \times 100\% \\ &= \frac{196.12\,\text{g mol}^{-1}}{444.24\,\text{g mol}^{-1}} \times 100\% \\ &= 44.15\%\end{aligned}$$

For reaction 2:

$$\begin{aligned}\%\text{ atom economy} &= \frac{(p \times \text{molar mass of P})\,\text{g mol}^{-1}}{(a \times \text{molar mass A} + b \times \text{molar mass B})\,\text{g mol}^{-1}} \times 100\% \\ &= \frac{\text{molar mass of maleic anhydride}\,\text{g mol}^{-1}}{(\text{molar mass of 1-butanol} + 3 \times \text{molar mass oxygen, O}_2)\,\text{g mol}^{-1}} \times 100\% \\ &= \frac{98.06\,\text{g mol}^{-1}}{(74.14 + 3 \times 32.00)\,\text{g mol}^{-1}} \times 100\% \\ &= \frac{98.06\,\text{g mol}^{-1}}{170.14\,\text{g mol}^{-1}} \times 100\% \\ &= 57.63\%\end{aligned}$$

The reaction that uses 1-butanol to produce maleic anhydride has the higher atomic efficiency, which matches the initial prediction.

When a reaction consists of multiple steps, you can combine the step-reactions to give one overall reaction and calculate the atom economy for that reaction. For example, the production of ethyl butanoate – an ester that is used as an artificial flavouring – can be accomplished in two steps from butanoic acid (Figure 2).



The overall reaction is:

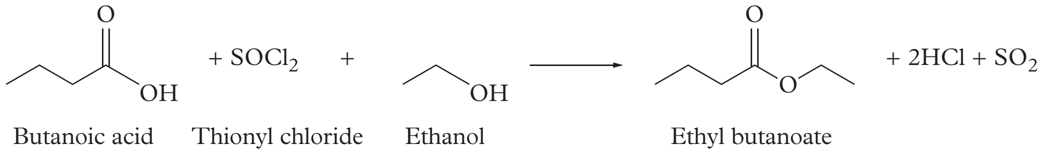


FIGURE 2 The reaction for the production of ethyl butanoate from butanoic acid has two steps.

$$\%\,\text{atom economy} = \frac{\text{molar mass ethyl butanoate}}{\text{molar mass butanoic acid} + \text{molar mass thionyl chloride} + \text{molar mass ethanol}} \times 100\%$$

$$= \frac{116.16\,\text{g mol}^{-1}}{(88.11 + 118.97 + 46.07)\,\text{g mol}^{-1}} \times 100\%$$

$$= 45.89\%$$

Some reactions are 100% atom efficient. These include addition reactions, in which two reagents are added together to make a single product; for example, hydrogenation reactions in which an alkene or alkyne is reduced to an alkane by the addition of hydrogen.

Some reactions are always less than 100% atom efficient. For example, the atom economies of substitution and elimination reactions are always less than 100% because not all atoms in the starting materials end up in the desired product.

atom efficiency
the efficiency of a chemical reaction or process at converting the mass of reactants into desired products

The **atom efficiency** is a starting point for assessing a reaction and its environmental impact, but it is a theoretical calculation. If you combine the atom economy with the percentage reaction yield, then you can calculate what percentage of the mass of the reactants ends up in the desired product. However, atom efficiency is not always the most important factor in determining the ‘greenness’ of a reaction process. For example, a reaction that has water as a by-product may be preferable to a reaction that has a higher atom economy but which uses more energy or a more hazardous process.

E-factor
the ratio of mass of waste produced in a reaction to the mass of desired product

Another way to measure the ‘greenness’ of a reaction is the **E-factor** (environmental factor). The E-factor compares the mass of waste generated to the amount of product made. The lower the E-factor of a reaction, the more environmentally friendly it is.

$$\text{E-factor} = \frac{\text{mass of waste generated}}{\text{mass of product synthesised}}$$

CHECK YOUR LEARNING 14.4

Describe and explain

1 **Explain** which types of reactions will have atom economies of 100%. **Identify** an example of each.

2 **Describe** the differences between atom economy and E-factor.

Apply, analyse and interpret

3 **Apply** your knowledge to **explain** why atom economy on its own is an insufficient measure of the 'greenness' of a chemical reaction.

4 Phenol is made industrially mainly by the cumene reaction pathway (Figure 3). This is a highly efficient reaction, with typical experimental yields of 90%, based on benzene. **Analyse** the reaction pathway in Figure 2 and report the percentage atom economy. Based on the yield given, what is the percentage of the mass of reactants that makes it into the phenol product?

Investigate, evaluate and communicate

5 **Evaluate** the two proposed routes to propenol ($CH_2{=}CHCH_2OH$) and **explain** which route would be preferred on the grounds of atom efficiency. Is the more atom-economic route also the greener route overall? What factors would you need to consider in deciding this?

Route 1:

$$CH_2{=}CHCH_2Cl + H_2O \rightarrow CH_2{=}CHCH_2OH + HCl$$

Route 2:

$$CH_2{=}CHCH_3 + CH_3COOH + \tfrac{1}{2}O_2 \rightarrow CH_2{=}CHCH_2O_2COCH_3 + H_2O$$

$$CH_2{=}CHCH_2O_2COCH_3 + H_2O \rightarrow CH_2{=}CHCH_2OH + CH_3CO_2H$$

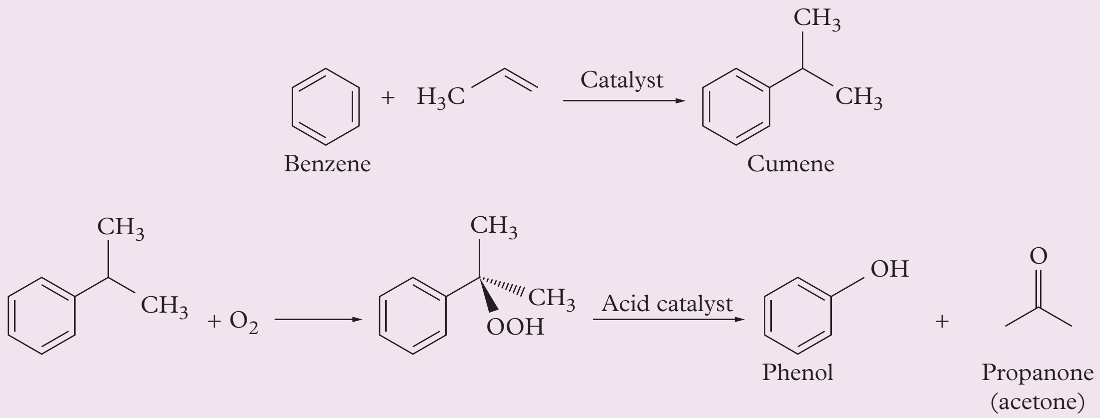


FIGURE 3 The reaction pathway for the production of phenol

You can find the following resources for this section on your obook assess:

- Student book questions
  14.4 Check your learning
- Weblink
  Atom efficiency
- Weblink
  E-factor

CHAPTER 14

Review

Chapter summary

14.1
- Green chemistry, or sustainable chemistry, is the area of chemistry that aims to develop or design chemical products or processes to reduce or eliminate the use or generation of hazardous substances.
- The 12 principles of green chemistry aim to reduce waste, energy use, environmental impacts, risks and hazards.

14.2
- Green chemistry principles include using less energy-intensive processes such as microwave heating.
- Designing products that degrade at the end of their life to environmentally non-hazardous materials includes the design of biodegradable polymers.
- An important factor in the design of greener chemistry processes is to consider the use of solvents.

14.3
- Biofuels are fuels made from renewable resources.
- Algae are being investigated as a source of third-generation biofuels, to produce ethanol, biodiesel or hydrocarbons, using sunlight and CO_2.

14.4
- Atom economy is a measure of how much of the mass of the reactants ends up in the desired product. Reactions with high atom economy may result in less waste than lower atom economy reactions, although reaction yield must also be considered.

Key terms

- atom economy
- atom efficiency
- bioaccumulative
- biomass
- catalyst
- E-factor
- gasification
- green chemistry
- micelle
- persistent organic pollutant (POP)
- solid-phase reaction
- supercritical fluid

Key formulas

Atom economy	$\% \text{ atom economy} = \frac{p \times \text{molar mass of P g mol}^{-1}}{(a \times \text{molar mass A} + b \times \text{molar mass B}) \text{ g mol}^{-1}} \times 100\%$
E-factor	$\text{E-factor} = \frac{\text{mass of waste generated}}{\text{mass of product synthesised}}$

Revision questions

The relative difficulty of these questions is indicated by the number of stars beside each question number: ★ = low; ★★ = medium; ★★★ = high.

Multiple choice

1 Soy–oil-based inks are used for colour printing in newspapers and magazines. In green chemistry, this is an example of:

A preventing waste
B using renewable feedstocks
C atom economy
D reducing the use of derivatives.

2 Identify which of the following reaction types is most likely to be 100% atom efficient.

A Substitution
B Hydrogenation
C Elimination
D Double displacement

3 Identify which of the following is *not* likely to result in increased biological degradation of a polymer.

A Replacing methyl groups in the polymer backbone with hydrogens
B Replacing fluoro groups with hydroxy (OH) groups
C Increasing the average length of the polymer chains
D Decreasing the amount of branching in the polymer chains

4 Identify the correct statement about microwave heating.

A Microwave heating results in faster reactions, because the microwave energy is sufficient to break covalent bonds to create highly reactive intermediates.
B Microwave heating requires a reaction solvent that is non-polar such as hexane.
C Microwave heating can be more efficient than conventional heating because only the reaction medium is being heated and not the reaction vessel.
D Microwave heating can result in purer products because microwave heating removes dissolved gases in the reaction solvent that could otherwise interfere with the reaction.

Short answer

Describe and explain

★★ 5 **Explain** why microwave heating can reduce energy use in chemical reactions, compared to conventional heating with a hot plate.

Apply, analyse and interpret

★ 6 ‘Reaction yield is more important than atom economy in determining the greenness of a reaction.’ **Interpret** this statement and justify whether you agree or disagree with it.

★★ 7 One of the principles of green chemistry is that catalysts are preferable to stoichiometric reagents. **Analyse** the chemical reasons for this preference.

★★ 8 The ester ethyl ethanoate (or ethyl acetate ($CH_3CH_2O_2CCH_3$)) is recommended for use as a green solvent. **Analyse** the structure of ethyl ethanoate and explain why it has this recommendation.

★★ 9 **Apply** your knowledge of chemistry to give one example of a chemical reaction with 100% atom efficiency and one example of a chemical reaction with less than 50% atom efficiency.

You can find the following resources for this section on your obook assess:

- Student book questions
  Chapter 14 Revision questions
- Revision notes
  Chapter 14
- assess quiz
  Auto-correcting mutiple-choice quiz
- Flashcard glossary
  Chapter 14

CHAPTER 15

Macromolecules: polymers, proteins and carbohydrates

Macromolecules are very large, complex molecules. They are all around us and you encounter them every day. Polymers include human-made materials, such as plastics, glass, papers and rubbers, as well as natural biopolymers such as silk and wool, which are part of many fabrics.

Macromolecules have many different shapes and forms. For example, DNA is made up of molecules such as proteins and carbohydrates. Proteins are long chains. The long chains can fold to form strong structures such as hair, fingernails and muscle tissue. Carbohydrates can be obtained from our food and are the main energy source for our body.

OBJECTIVES

→ Describe, using equations, how addition polymers can be produced from their monomers including polyethene (LDPE and HDPE), polypropene and polytetrafluorethene.

→ Describe, using equations, how condensation polymers, including polypeptides (proteins), polysaccharides (carbohydrates) and polyesters, can be produced from their monomers.

→ Discuss the advantages and disadvantages of polymer use, including strength, density, lack of reactivity, use of natural resources and biodegradability.

→ Describe the condensation reaction of 2-amino acids to form polypeptides (involving up to three amino acids), and understand that polypeptides (proteins) are formed when amino acid monomers are joined by peptide bonds.

→ Describe the condensation reaction of monosaccharides to form disaccharides (lactose, maltose and sucrose) and polysaccharides (starch, glycogen and cellulose), and understand that polysaccharides are formed when monosaccharides monomers are joined by glycosidic bonds.

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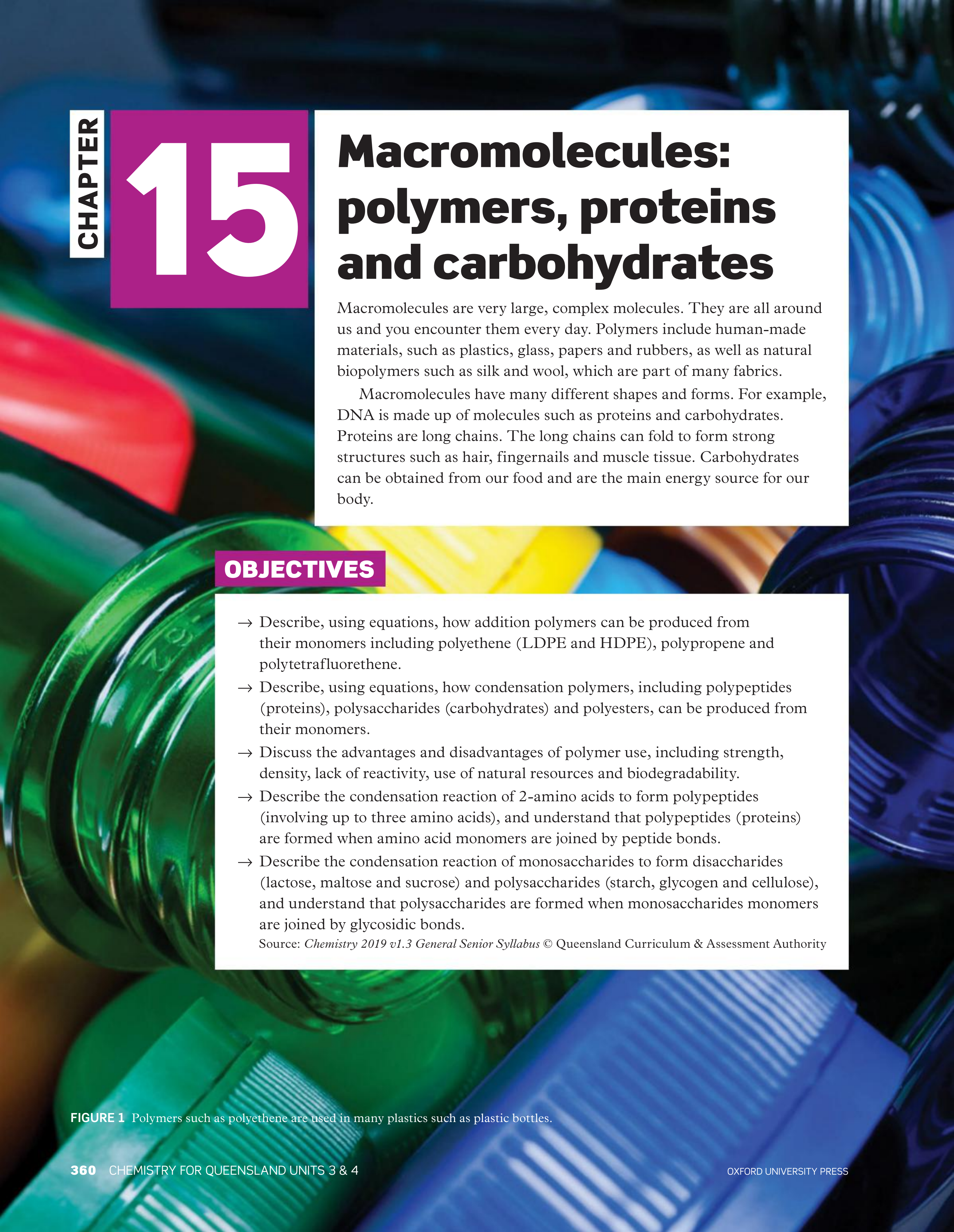


FIGURE 1 Polymers such as polyethene are used in many plastics such as plastic bottles.

15.1

Addition polymers

KEY IDEAS

In this topic, you will learn about:

- how addition polymers can be produced from their monomers
- polyethene (LDPE and HDPE), polypropene and polytetrafluoroethene.

addition polymer
a polymer formed by linking monomers

Polymers are long chains of monomers. **Addition polymers** are formed by addition polymerisation, which involves bonds rearranging within a monomer so that the monomers link with each other, as shown in Figure 1. Three common polymers are polyethene, polypropene and polytetrafluoroethene).

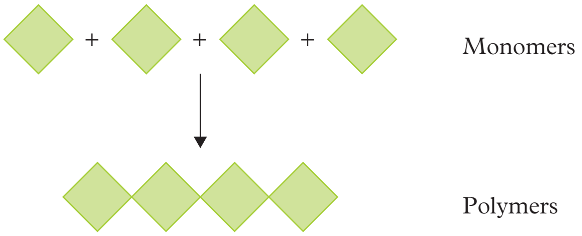


FIGURE 1 Addition polymerisation: monomers take part in an addition reaction and form polymers. No by-products are produced.

low-density polyethene (LDPE)
a polymer made from the monomer ethene, with a low strength-to-density ratio (also known as low-density polyethylene)

high-density polyethene (HDPE)
a polymer made from the monomer ethene, with a high strength-to-density ratio (also known as high-density polyethylene)

Polyethene (LDPE and HDPE)

Polyethene (also known as polyethylene) is the most common plastic and is used in packaging such as plastic bags and bottles. By changing catalysts and additives, you can control the polymerisation and therefore alter the density, degree of chain branching and crystallinity, and cross-linking. The average polymer molecule contains 4000–40 000 carbon atoms. The two types of plastics are **low-density polyethene (LDPE)** and **high-density polyethene (HDPE)**.

LDPE

LDPE is used for products such as trays, containers and playground slides like the one in Figure 2. LDPE is a thermoplastic, which means it becomes bendable or mouldable when heated to a specific temperature and solidifies when cooled down. LDPEs are recyclable and are often labelled with Code '4' for easy recognition, as shown in Figure 3.

LDPEs are produced under very high pressure (1000–3000 atm) at temperatures of about 300°C by passing ethene molecules onto a reactor with an initiator such as a small amount of oxygen and/or an organic peroxide (Figure 4).

The product, polyethene, is removed and cut into granules for further processing. The structure of the molecule has many branches, as shown in Figure 5.

The branches determine the degree of crystallinity of the polymer, which in turn determines the density of the polyethene. The branches prevent the molecules from coming close to each other and so LDPEs usually have low densities, as their name suggests. LDPEs are typically amorphous and transparent.

FIGURE 2 LDPEs have the recycling code '4'.

FIGURE 3 Water slides are made of LDPE.

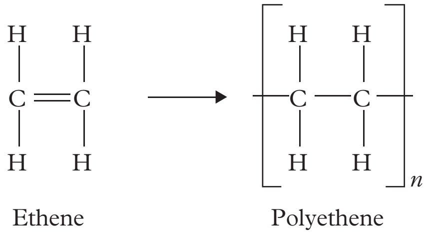


FIGURE 4 The production of polyethene from ethene monomers

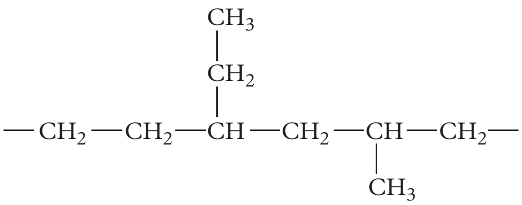


FIGURE 5 Part of a multi-branched molecule of LDPE

HDPE

HDPE is used to construct products such as outdoor furniture (Figure 6), bottles for household cleaners and household appliances. HDPE is a thermoplastic and has the recycling code ‘2’ (Figure 7).

FIGURE 7 HDPEs have the recycling code ‘2’.

HDPE is produced at low pressures and temperatures (a few atmospheres and about 60°). Catalysts such as the Ziegler–Natta and metallocene catalysts or activated chromium/silica enable the formation of free radicals (uncharged molecules with an unpaired valence electron) at the ends of the growing polyethene chains. There are no branches, so the polymer chains pack closely together, resulting in a very strong, dense, highly crystalline material. The melting point of HDPE is more than 120°C, which is higher than that of LDPE (in the range 105–115°C). HDPE can withstand temperatures above 120°C, which makes it durable enough that it can be sterilised.

FIGURE 6 Outdoor furniture is typically made of HDPE.

Polypropene (PP)

Polypropene (PP) (also known as polypropylene) is a thermoplastic that has a variety of applications where it is important that a structure resists fatigue. PP is used for plastic parts in products such as toys and automobile products. This plastic can withstand heat and so is also useful in medical and laboratory plastic products.

Polypropene is produced by an addition reaction of propene (Figure 9). Its recycling code is ‘5’ (Figure 8).

FIGURE 8 Polypropene has the recycling code ‘5’.

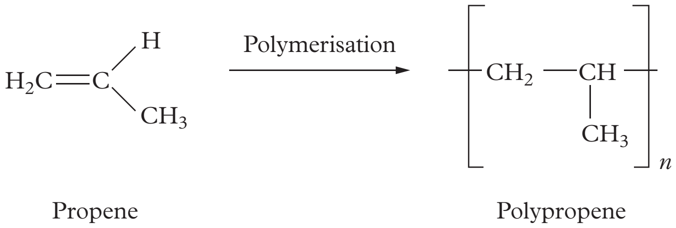


FIGURE 9 The production of polypropene from propene monomers

Study tip

Although ‘ethylene’ might be more commonly used, the IUPAC name is ‘ethene’.

Polytetrafluoroethene (PTFE)

Polytetrafluoroethene (PTFE) (also known as polytetrafluoroethylene) is a thermoplastic that has many applications because it is anticorrosive and non-reactive. For example, PTFE is used in non-stick frying pans (where it is known as Teflon) (Figure 10), medical implants, clothing, insulation in wire and cable wrap, and containers and pipes. PTFE does not have its own recycling code symbol.

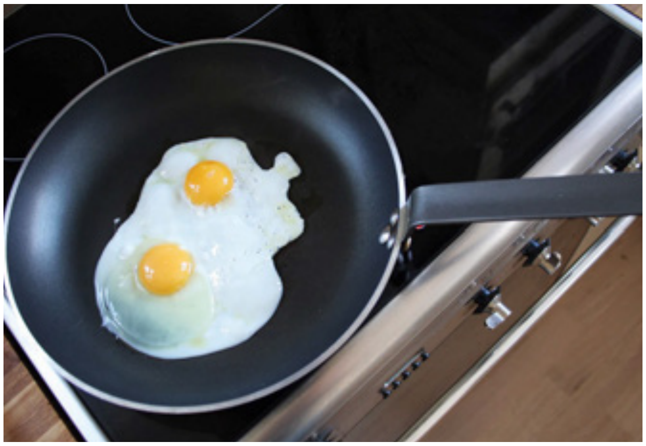


FIGURE 10 The surface of a non-stick frying pan is made of PTFE.

PTFE is a fluoropolymer or fluorocarbon that contains only carbon and fluorine. It is produced by free-radical polymerisation of tetrafluoroethene (Figure 11).Figure 10 The surface of a non-stick frying pan is made of PTFE.

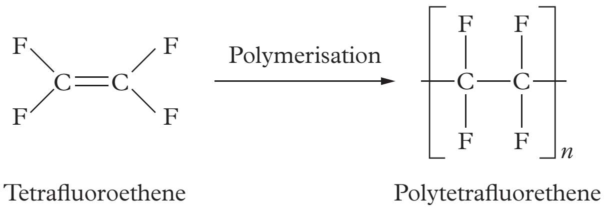


FIGURE 11 The production of polytetrafluoroethene from tetrafluoroethene

CASE STUDY 15.1

PTFE and geckos

FIGURE 12 Geckos cannot climb a smooth surface of dry polytetrafluoroethene.

PTFE has very useful properties that are different from those of polyethene. PTFE has electronegative fluorine atoms that reduce the strength of intermolecular bonds with other substances.

This property means that geckos and many insects cannot climb any smooth surface made of Teflon. Their toes have a series of ridges made of setae, a type of keratin. These ridges allow geckos to stick to most other surfaces through van der Waals forces, the attractive forces between molecules and atoms.

Interestingly, studies have shown that geckos can cling to wet Teflon. This discovery is controversial because wet surfaces usually disrupt the adhesive toe pads by decreasing the adhesive forces.

CHECK YOUR LEARNING 15.1

Describe and explain

1 **Describe** the difference between LDPE and HDPE.

2 **Explain** what an addition reaction is.

3 **Identify** which polyethene, LDPE or HDPE, requires:
  - **a** high temperatures and pressures for its formation
  - **b** Ziegler–Natta and metallocene catalysts.

4 **Construct** a section of the polymer made from an addition reaction of the monomer $CH_2=CHBr$.

Apply, analyse and interpret

5 **Determine** the molecular formula of a molecule made from an addition reaction of:
  - **a** three ethene monomers
  - **b** four tetrafluoroethene monomers
  - **c** three propene monomers.

6 **Determine** whether LDPE or HDPE would be best to use in:
  - **a** wrapping material for food
  - **b** drink bottles
  - **c** flexible plastic lids.

Investigate, evaluate and communicate

7 **Investigate** the difference in properties between LDPE and HDPE.

You can find the following resources for this section on your obook assess:

- » Student book questions
  15.1 Check your learning
- » Weblink
  Polyethene
- » Weblink
  Geckos

15.2 Condensation polymers

KEY IDEAS

In this topic, you will learn about:

- how to produce condensation polymers from monomers
- polypeptides, polysaccharides and polyesters.

A condensation reaction is an organic addition reaction in which two molecules combine and water or methanol is produced as a by-product (Figure 1). These kinds of reactions are essential for the formation of peptide bonds between amino acids (components of human muscles and other tissues) and the biosynthesis of fatty acids. Condensation polymerisation is a form of step-growth polymerisation and produces linear polymers from bifunctional monomers (monomers with two reactive end groups). Polypeptides (proteins), polysaccharides (carbohydrates) and polyesters are common condensation polymers.

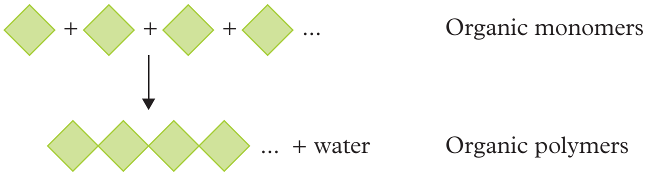


FIGURE 1 Condensation polymerisation: monomers take part in a condensation reaction and form polymers. Water is produced as a by-product.

Polypeptides (proteins)

Polypeptides are chains of amino acids. Amino acids contain an amino (NH_2) group and a carboxyl (COOH) group. Typically, there are 20 different amino acids found in proteins and usually at least 300 amino acids per protein molecule. Amino acids differ in their R groups and have different properties (Figure 2).

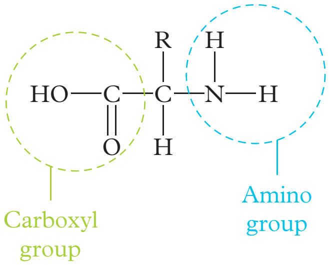


FIGURE 2 Amino acids have different R groups.

Polypeptides are formed when amino acids are joined together by peptide bonds in a condensation reaction in which the NH_2 of one amino acid bonds to a COOH group of another amino acid. Water is a by-product (Figure 3).

The sequence and number of amino acids in the polypeptide chain makes up the primary structure of a protein.

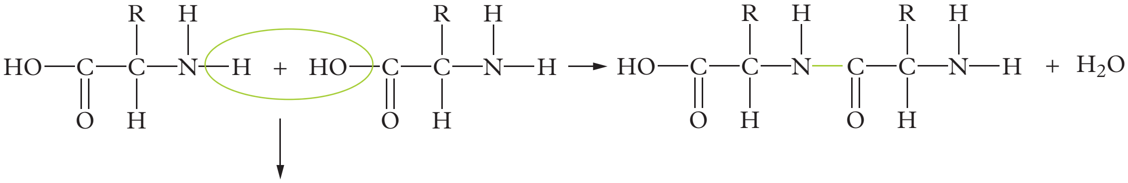


FIGURE 3 Polypeptides are formed in a condensation reaction between two amino acids.

Polysaccharides

Polysaccharides (carbohydrates) are long chains of smaller carbohydrates called monosaccharides. Carbohydrates are found in foods such as dairy products, fruit and grains. Polysaccharides provide us with energy when they are oxidised and form part of the structures of some cells and tissues. The monosaccharides are bonded together by glycosidic linkages – a type of covalent bond (see Chapter 11).

Glucose and fructose are two common monosaccharides. Figure 4 shows two glucose molecules undergoing a condensation reaction to form maltose (a disaccharide).

Polysaccharides can be linear or branched and are typically 200–2500 monosaccharides long.

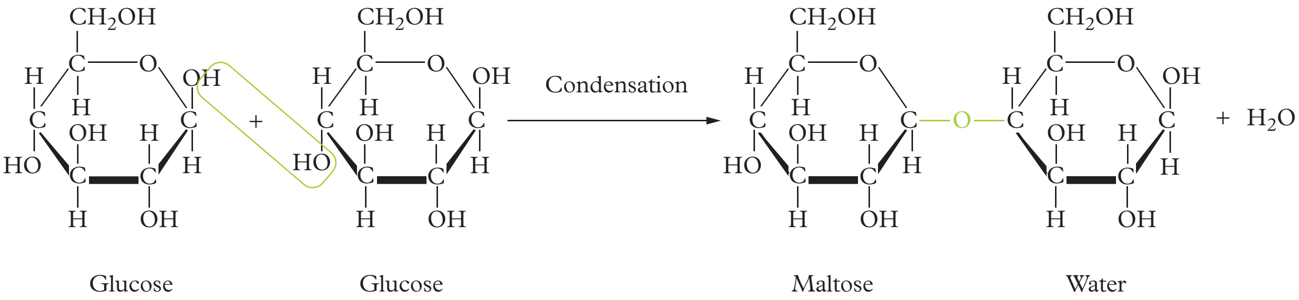


FIGURE 4 The condensation reaction of two glucose molecules to form maltose. Water is lost when a glycosidic bond is formed.

Polyesters

Polyesters are extremely important polymers that contain an ester functional group in their main chain. Polyesters are thermoplastics. Polyesters are extensively used for clothing and food packaging, and to make sky divers' suits and parachutes (Figure 5).

polyester
a type of polymer that contains an ester functional group in its main chain

FIGURE 5 Polyesters are typically used to make the suits and parachutes for sky divers.

The most common type of polyester is polyethylene terephthalate (PET, $(C_{10}H_8O_4)_n$), which is used in drink bottles. PET is made from an acid (benzene-1,4-dicarboxylic acid) and an alcohol (ethane-1,2-diol) (Figure 6).

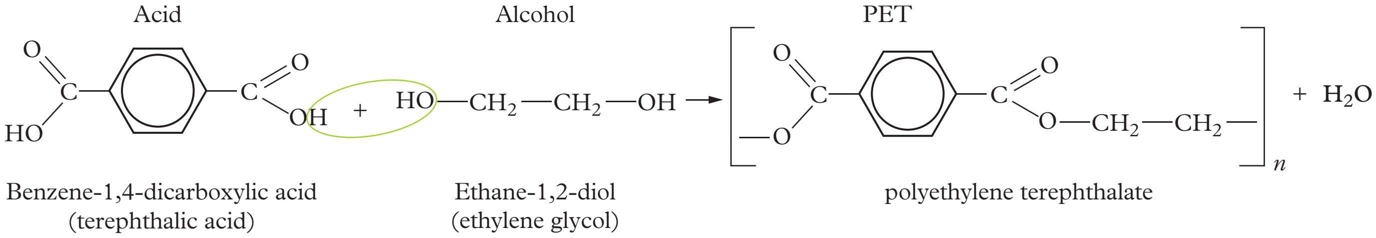


FIGURE 6 Formation of polyesters

CASE STUDY 15.2

Kevlar

Kevlar (polyparaphenylene terephthalamide) is a heat-resistant, synthetic polymer that has a very strong fibre. The fibre is strong because of the large number of bonds within the chains of the polymer.

Kevlar was developed by US chemist Stephanie Kwolek in 1965 and is a synthetic aromatic polyamide polymer. The aromatic polyamides are ring-like molecules connected in long chains. They act in a similar way to the steel rods within concrete, reinforcing the Kevlar fibres. These fibres are woven into a fabric that is widely used to produce bulletproof vests. Kevlar has five times the tensile strength of steel of the same mass.

FIGURE 7 A bulletproof vest made partly of Kevlar

CHECK YOUR LEARNING 15.2

Describe and explain

1 **Explain** what a condensation reaction is.

2 **Describe** what components are needed to produce:

  a a polypeptide

  b a polysaccharide

  c polyethylene terephthalate.

3 **Explain** what a glycosidic bond is.

Investigate, evaluate and communicate

4 **Investigate** how Kevlar gets its strength.

You can find the following resources for this section on your obook assess:

- Student book questions
  15.2 Check your learning
- Weblink
  Polyesters
- Weblink
  Polysaccharides

15.3 Polymer use

KEY IDEAS

In this topic, you will learn about:

- the advantages and disadvantages of using polymers
- the strength, density and lack of reactivity of polymers
- the use of natural resources and biodegradability.

Polymers are found in nearly all everyday materials. It would be hard to imagine life without them. Polymers are relatively cheap to produce and are very versatile. Polymers are in synthetic clothing fibres, polyethene cups, fibreglass, plastic bags, paints, foam cushions, silicone heart valves and Teflon-coated cookware.

Polymers can be synthetic or natural. Natural polymers include cellulose, starch and natural rubber.

Environmental effects of polymers

Although synthetic polymers enhance our lives in many ways, there are environmental problems associated with their use, which we need to solve. The oceans are polluted with polymers and this pollution is continuing to build up. There is an estimated 1.6 million square kilometres of garbage (mainly plastic) in the Great Pacific Garbage Patch alone. Many plastics break down to form microparticle polymers that enter the flesh of fish and which humans end up consuming. The consequences of wildlife and humans consuming plastics are not fully understood, but it is suggested that it would pose a health risk (Figure 1).

single-use plastic a plastic that is used once and then thrown away

Many organisations have reduced or stopped using **single-use plastics** in an effort to prevent the continual build-up of plastics on Earth. Single-use plastics include plastic bags, straws, plastic cutlery and plates, and takeaway coffee cups and containers. Plastics take many years to break down; for example, it is estimated that plastic bags would take anywhere between 20–1000 years to break down.

FIGURE 1 The mismanagement of polymer waste in the environment has had devastating effects on marine life.

Properties of polymers

Strength

In general, increasing the chain length of a polymer increases its strength and toughness. This is because van der Waals attractions and entanglements increase as chains get longer. These interactions reduce movement within and between individual chains, increasing resistance to deformation or breakage.

Many materials that were once commonly used have been replaced with polymers because they are stronger. For example, in aircraft and aquariums, glass has been replaced by polymethyl methacrylate (Figure 2), a transparent, shatter-resistant, strong polymer. Common names for this material are Perspex® and Plexiglas.

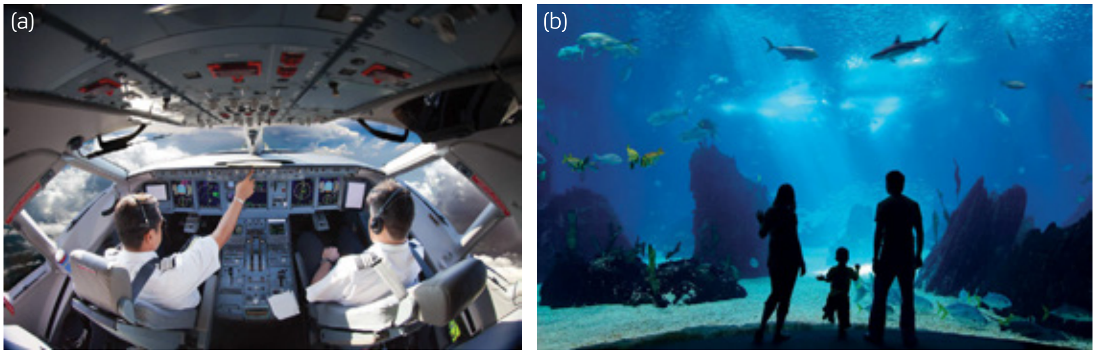


FIGURE 2 (a) Aircraft windscreens and (b) aquarium windows are commonly made of polymethyl methacrylate instead of glass.

Density

The densities of polymers vary greatly. A lot of sport equipment needs to be strong, flexible and light; for example, shin pads and kayaks (Figure 3).

FIGURE 3 (a) Shin pads and (b) kayaks need to be flexible, strong and light – properties of many polymers.

Low-density polymers are still relatively strong. In Figure 4, you can see that polymers (and composites) have very low density for their strength. For example, polymers have a similar strength to many metals and alloys, but they are less dense. They have a similar strength to wood, but are not susceptible to weather damage and do not decompose over time.

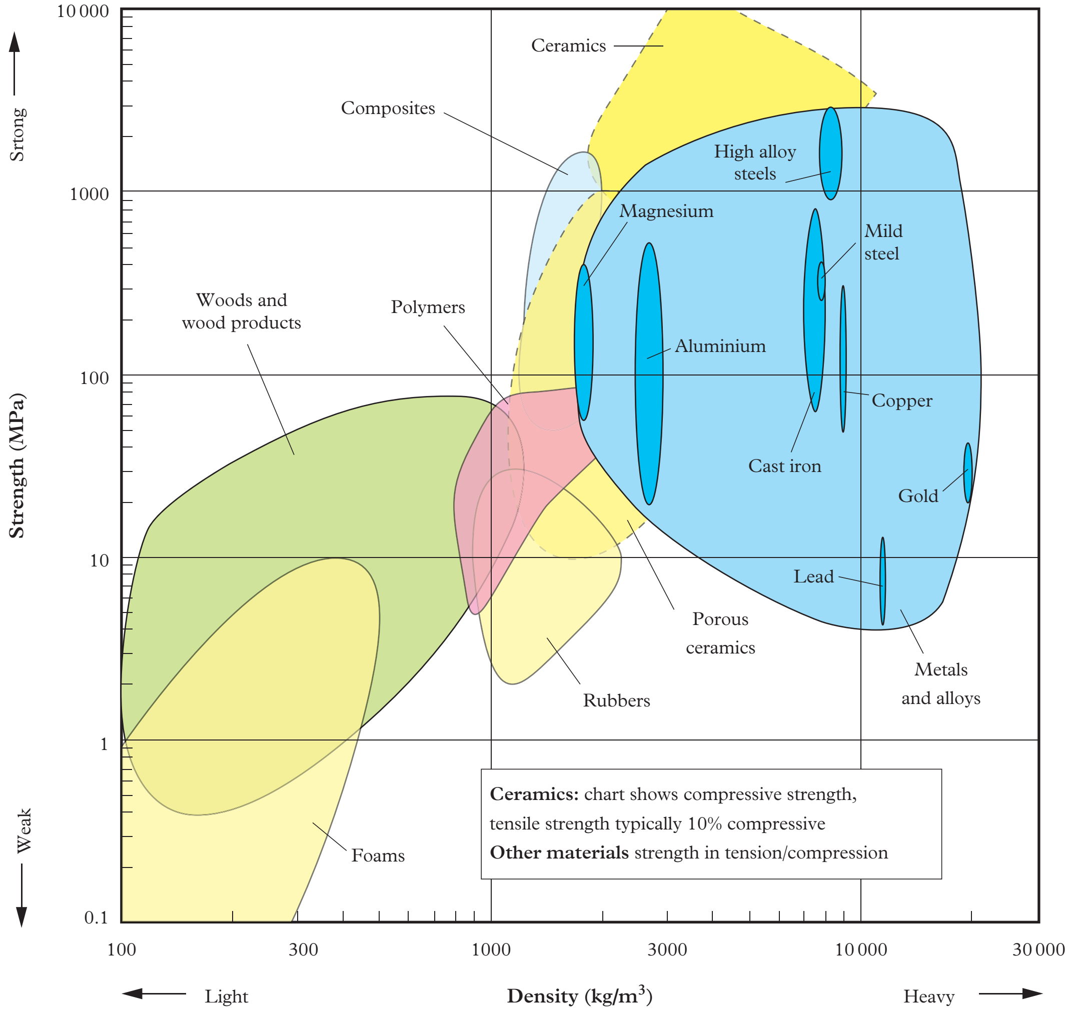


FIGURE 4 The density and strength of polymers compared with other materials

Lack of reactivity

Polymers are the preferred material for many applications because of their lack of reactivity. Unlike iron and its alloys, polymers do not rust, so are resistant to corrosion. This makes them useful in the aerospace, automotive, electronics and energy industries. In the field of electronics, polymers are used as insulators and semiconductors.

Use of natural resources and biodegradability

Most polymers are non-biodegradable. In the 1980s, the environmental challenges posed by polymers led to increased interest in biodegradable polymers. Most biodegradable polymers are condensation polymers from renewable sources such as plants; for example, corn starch. Biodegradable polymers have similar structures to biological macromolecules, such as carbohydrates or proteins. The similar structure enables them to break down much faster than synthetic polymers.

biodegradation the breakdown of a substance, such as plastic, by microorganisms

plastisphere an ecosystem that has adapted to live with plastic in the environment

One biodegradable polymer is polylactic acid, also known as polylactide (PLA). PLA is a bioactive thermoplastic made from renewable resources. It is used in biodegradable cups, medical applications and 3D printers (Figure 5). PLA is broken down into naturally occurring lactic acid monomers by microorganisms.

Scientists are very interested in the prospect of **biodegradation** of common polymers such as polyurethane. It has been found that *Pestalotiopsis microspore*, a fungus, breaks down and digests polyurethane. The fungus is found in fallen foliage of common ivy in Buenos Aires, Argentina. Other microorganisms, such as *Enterobacter asburiae* YT1 and *Bacillus* sp. YP1, can break down polyethene. Some scientists even suggest that microorganisms are now evolving to have genes capable of breaking down plastics, since the appearance and domination of the **plastisphere**.

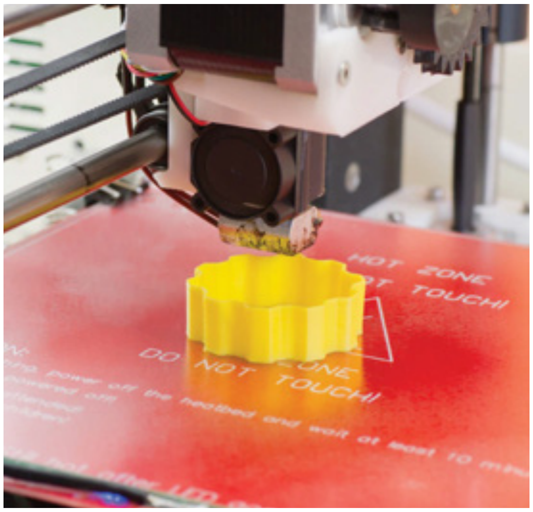


FIGURE 5 Biodegradable polylactic acid is used in 3D printers.

CHECK YOUR LEARNING 15.3

Describe and explain

1 **Describe** the relationship between the strength and density of polymers.

Investigate, evaluate and communicate

2 As a class, **decide** which items in the room are made of polymers.

3 **Research** more on the plastisphere and **identify** organisms that have adapted to this environment. **Consider** what would happen if these environments no longer existed. Would the organisms survive?

4 **Investigate** ways to decrease your personal use of plastics.

FIGURE 6 Humans need to consider alternatives to single-use plastics.

You can find the following resources for this section on your obook assess:

- » Student book questions
  15.3 Check your learning
- » Weblink
  One world one ocean campaign
- » Weblink
  Biodegradation of plastic

15.4

Amino acids and polypeptides

KEY IDEAS

In this topic, you will learn about:

- the structure and properties of amino acids
- amino acids as the building blocks of polypeptides and proteins
- how amino acids join together to form polymer polypeptide chains through condensation reactions.

Amino acids

Amino acids are vital for all life on Earth and are the building blocks of proteins. Twenty different amino acid monomers exist and can be joined together by ribosomes in cells in thousands of different combinations. The polypeptide chains then fold into proteins. Amino acids consist of an amino group (NH_2), a carboxyl group (COOH) and an organic R group or side chain, which gives each amino acid its unique properties (Figure 1).

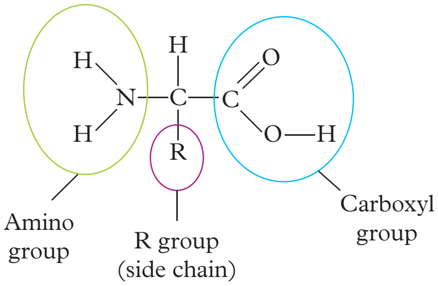


FIGURE 1 The general structure of an amino acid

Plants can produce all 20 amino acids, but animals cannot so they must obtain some through their diet. Humans can only synthesise 10 of the 20 amino acids. Of the remaining 10, nine are essential for vital functions such as tissue repair, protein synthesis, digestion and absorption of nutrients. They are arginine, histidine, isoleucine, leucine, lysine, methionine, phenylalanine, threonine and valine. These nine essential amino acids must be obtained through our diet in foods such as fish, chicken, eggs and soy (Figure 2). A poor diet can lead to an amino acid deficiency, which can result in hair loss, muscle tremors and impaired neurological activity. If pregnant women do not consume enough essential amino acids, their babies may be born underweight.

FIGURE 2 Fish, chicken, eggs and soy all provide the nine essential amino acids.

Polypeptides and proteins

Polypeptides

Polypeptide chains are made by joining amino acid monomers together through peptide bonds. Peptide bonds between amino acids are formed in a reaction between the carboxyl group of one amino acid and the amino group of another. This reaction is a dehydration synthesis or condensation reaction (see section 15.2) because it produces a molecule of water. Figure 3 shows the condensation reaction between two amino acids to form a peptide bond, creating a dipeptide molecule, and the beginning of a polypeptide chain.

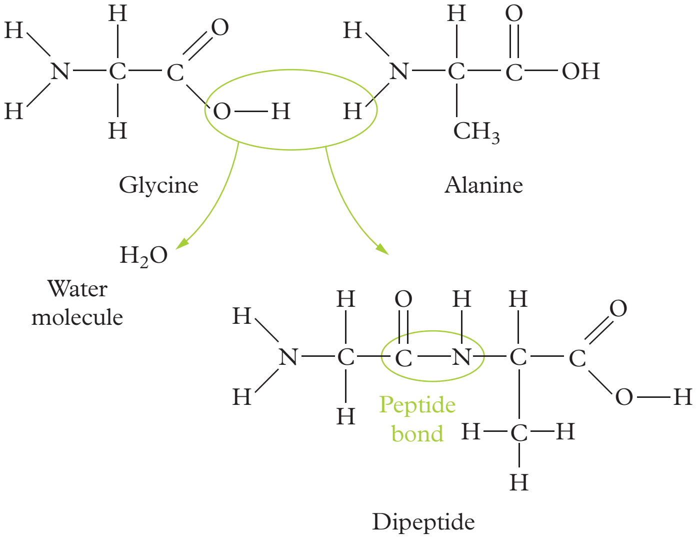


FIGURE 3 The condensation reaction of amino acid monomers glycine and alanine to produce a peptide bond and water as a by-product

Proteins

Proteins are three-dimensional molecules consisting of polypeptide chains, which are made from amino acid monomers. Proteins are produced in the cells of living organisms, exist in a wide variety of molecular structures and perform various roles. Proteins can be:

- antibodies, which identify pathogens and fight infection
- enzymes, which speed up reactions such as digestion of lactose in milk
- structural proteins, which produce parts of our body such as hair, skin, and fingernails (Figure 4).
- transport proteins such as haemoglobin (Figure 5), which transports oxygen in the blood

The polypeptide chain forms the primary structure of a protein. The secondary structure is formed when coiling or pleating occurs due to hydrogen bonds between different sections of the polypeptide chain (Figure 6).

Secondary structures then combine to form a three-dimensional tertiary structure, which provides a protein with its unique shape and allows it to perform its specific function within the organism.

For more information about the structure of proteins, refer back to Chapter 11.

FIGURE 4 Fingernails and skin are made from proteins.

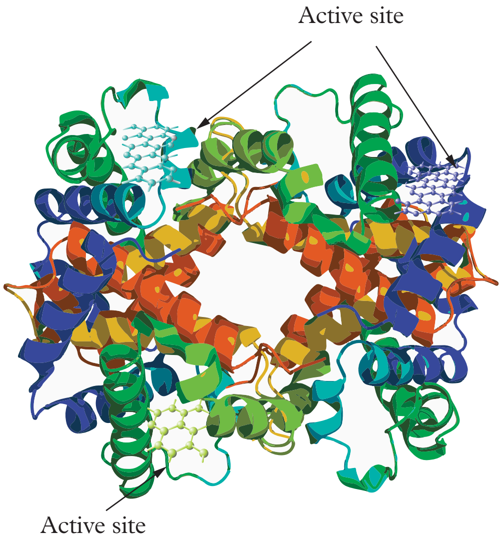


FIGURE 5 The tertiary structure of a haemoglobin molecule. Its three-dimensional shape allows the active site to reversibly bind with oxygen and transport it around the body.

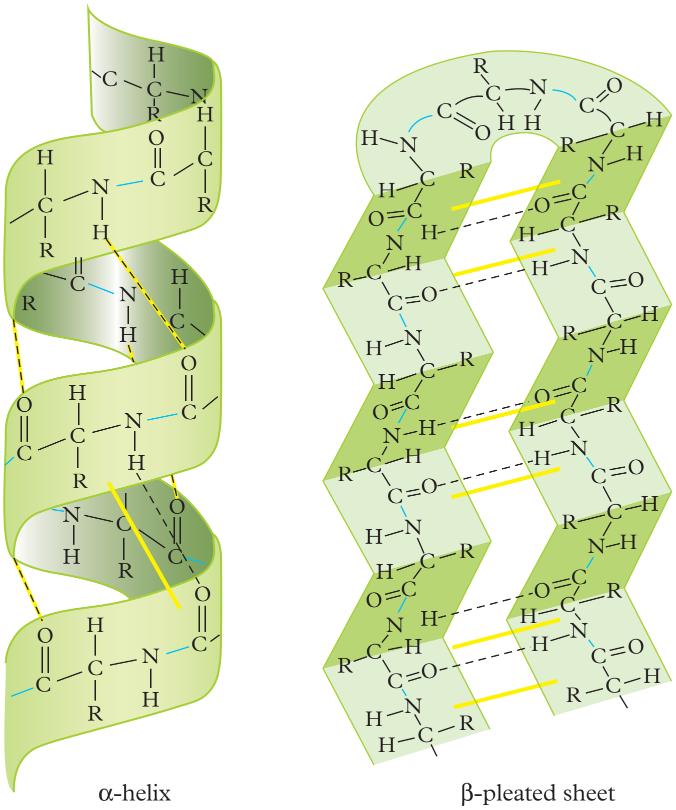


FIGURE 6 Secondary structures of proteins form a coiled α-helix or a β-pleated sheet due to hydrogen bonds between sections of the polypeptide primary structure

CHECK YOUR LEARNING 15.4

Describe and explain

1 **Describe** the structure of an amino acid.

Apply, analyse and interpret

2 If someone does not eat meat, fish or eggs, **determine** which essential nutrients could be missing from their diet. Which foods should this person eat to ensure they remain healthy?

Investigate, evaluate and communicate

3 Select two amino acids to **research**. **Construct** a diagram showing the structure of the amino acid molecules individually and the dipeptide formed from the two amino acids. Include any by-products produced in the reaction to form the dipeptide.

4 **Research** the nine essential amino acids that humans must obtain through their food. List each amino acid and provide one example of a food containing this amino acid.

5 **Design** a poster that shows the process of protein production from individual amino acids, through primary, secondary and tertiary structures, to a three-dimensional protein with active sites.

You can find the following resources for this section on your obook assess:

- Student book questions
  15.4 Check your learning
- Weblink
  Amino acids
- Weblink
  Polypeptides

15.5 Monosaccharides, disaccharides and polysaccharides

KEY IDEAS

In this topic, you will learn about:

- condensation reactions of monosaccharides to form disaccharides and polysaccharides.

The term 'carbohydrate' is based on its two components – carbon ('carbo') and water ('hydrate'). Carbohydrates can be classified into monosaccharides, disaccharides and polysaccharides (refer back to Chapter 11). Now we will learn how these carbohydrates are formed through condensation reactions. This section is good for revising your knowledge of organics structure and function.

Monosaccharides

Monosaccharides are simple sugars with typically 3–7 carbons. Table 1 lists the names of monosaccharides according to the number of carbons. An aldose is a monosaccharide that contains an aldehyde group (R–CHO). A ketose is a monosaccharide that contains a ketone group (RC(=O)R′).

Monosaccharides can be linear chains or ring-shaped molecules, but they all have the same chemical formula, $C_6H_{12}O_6$. You can see some examples in Figure 1.

- Glucose is a common monosaccharide and is the energy source for cellular respiration in our body. Plants synthesise glucose from carbon dioxide and water.
- Galactose is found in milk and differs slightly from glucose in the orientation of the functional groups. Therefore, galactose has different properties from glucose. There are different galactose molecules; D-galactose is shown in Figure 1.
- Fructose is found in fruit and is a simple ketose.

TABLE 1 Naming monosaccharides according to the number of carbons

Number of carbons	Name
3	Triose
4	Tetrose
5	Pentose
6	Hexose
7	Heptose

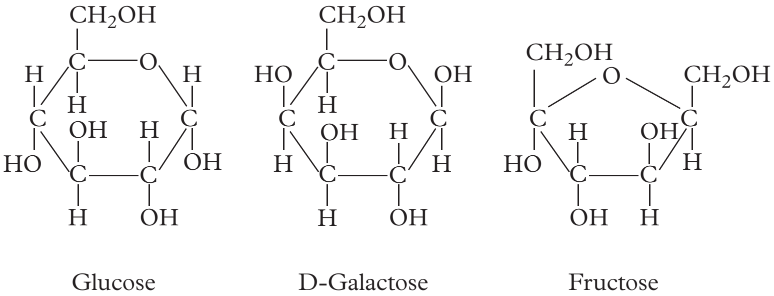


FIGURE 1 Glucose, D-galactose and fructose molecules

FIGURE 2 Fructose is found within every fruit and is a monosaccharide.

Disaccharides

Disaccharides are soluble sugars formed with two monosaccharides joined by glycosidic linkage in a condensation reaction. Three common disaccharides are lactose, maltose and sucrose, which all have the chemical formula $C_{12}H_{22}O_{11}$. When two monosaccharides react, the products are a disaccharide and a water molecule (H_2O).

Lactose

Lactose consists of the two monosaccharides – glucose and galactose – and is formed in a condensation reaction. Lactose is found in milk and is used in the food and pharmaceutical industries. Figure 3 shows the formation of lactose by a chemical reaction in which glucose and galactose are joined by a glycosidic bond.

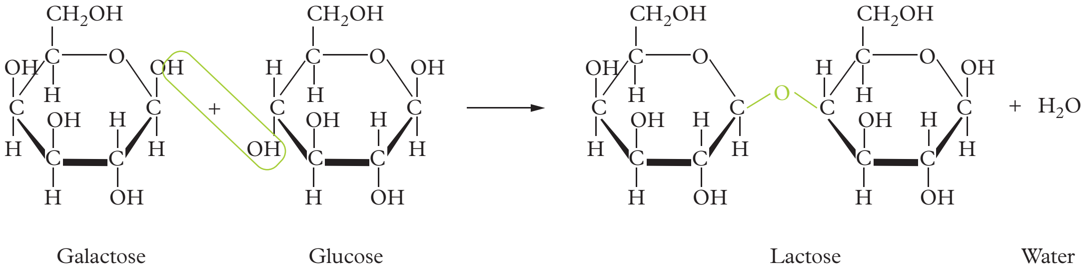


FIGURE 3 Lactose formation from glucose and galactose

Maltose

Maltose, also known as malt sugar, is formed by two units of glucose joined with a glycosidic bond. Specifically, maltose contains an α(1→4) bond between a hydroxyl oxygen atom on carbon-4 of one glucose and carbon-1 of another glucose (Figure 4).

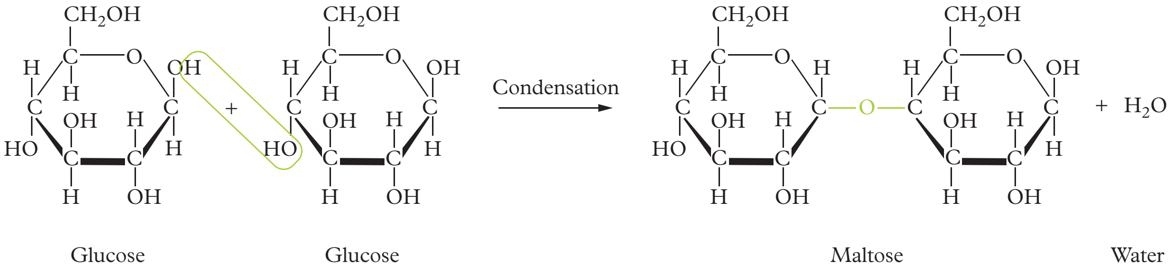


FIGURE 4 Maltose formation from two molecules of glucose

Sucrose

Sucrose is naturally produced by plants. We extract and refine this sugar from sugar cane and sugar beet. Sucrose is also known as table sugar and consists of two monosaccharides, glucose and fructose (Figure 5).

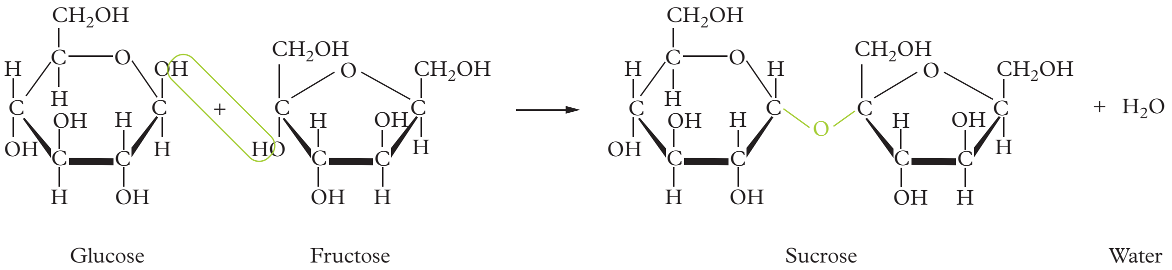


FIGURE 5 Sucrose formation from glucose and fructose

Polysaccharides

Polysaccharides consist of long chains of monosaccharides linked together through glycosidic bonds. The structure of polysaccharides varies from linear to highly branched. Three common polysaccharides are starch, glycogen and cellulose.

Starch

Starch is also known as amylum and consists of many (300–600) glucose molecules (Figure 6) with the chemical formula $(C_6H_{10}O_5)_n$. Most green plants produce starch to store energy and it can be found in our diet in foods such as potatoes, rice and wheat.

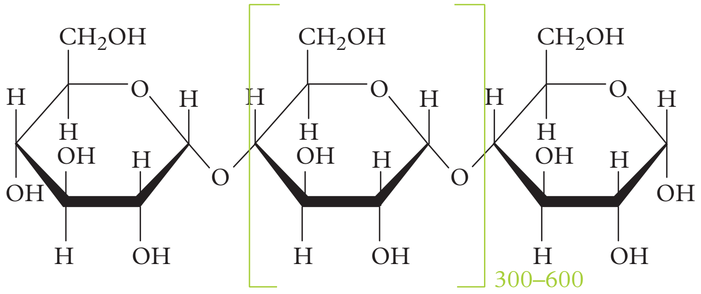


FIGURE 6 A starch molecule

Glycogen

Glycogen is a multi-branched polysaccharide made of glucose. It is used for energy storage in our body and is mainly in the cells of the liver and skeletal muscle. The molecule is a branched biopolymer made of linear chains of glucose residues. A glycogen molecule is built of approximately 8–12 glucose molecules. At its core is a glycogenin protein (Figure 8).

FIGURE 7 The human skeletal muscle is composed of glycogen - a multi-branched polysaccharide.

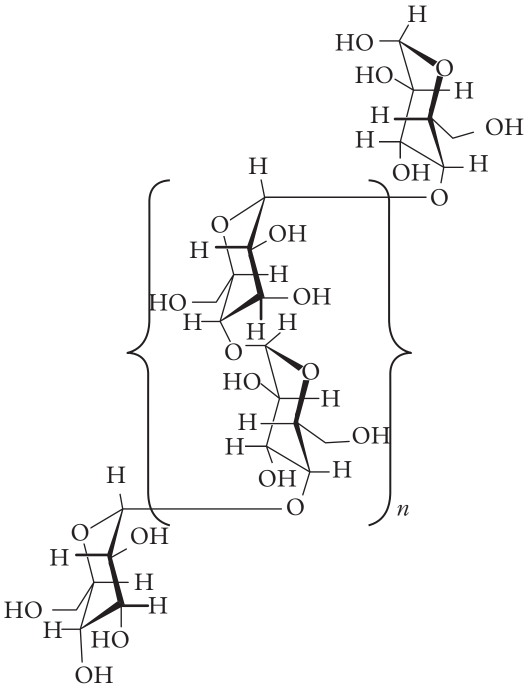


FIGURE 8 A glycogen molecule

Cellulose

Cellulose $(C_6H_{10}O_5)_n$ consists of a linear chain of glucose molecules and is the most abundant organic material. It is the major structural component of cell walls in green plants, and 90% of cotton fibre is cellulose (Figure 9). Cellulose is also used to produce products such as paper.

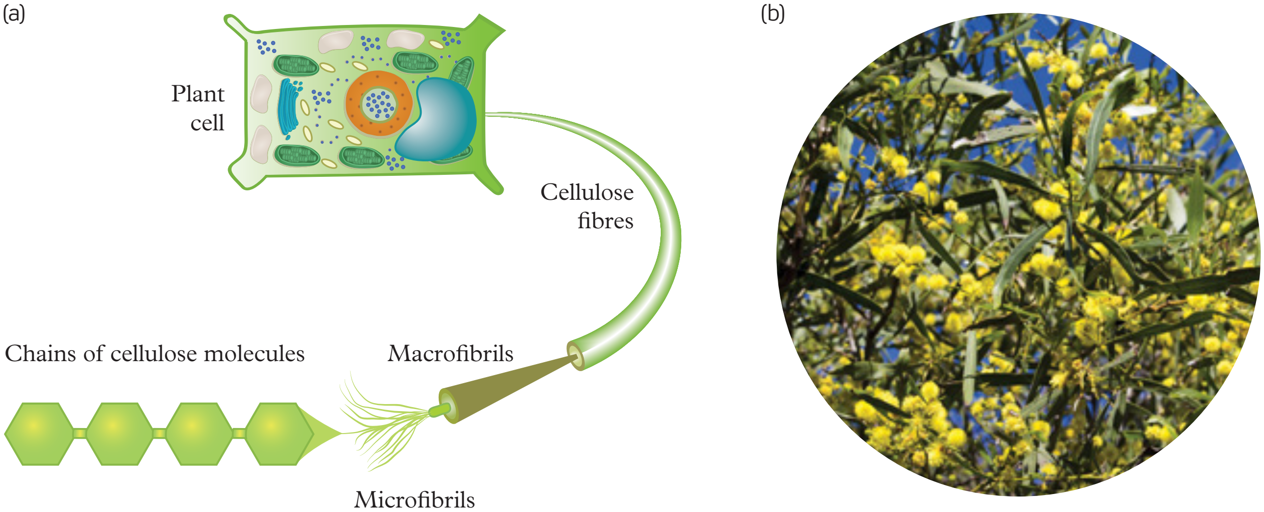


FIGURE 9 The primary cell wall of a plant is made of cellulose. (a) Plant cells combine together to form the (b) yellow West Australian wattle.

CHECK YOUR LEARNING 15.5

Describe and explain

1 **Identify** the chemical formula of:
  a fructose
  b maltose
  c starch.
2 **Describe** cellulose and its structure.
3 **Identify** the monosaccharides that have 3–7 carbons.
4 **Identify** the different disaccharides.

Apply, analyse and interpret

5 **Compare** cellulose, glycogen and starch.

You can find the following resources for this section on your obook assess:

- » **Student book questions** 15.5 Check your learning
- » **Weblink** Monosaccharides
- » **Weblink** Disaccharides

CHAPTER 15

Review

Chapter summary

15.1
- Addition polymerisation is the reaction that links monomers without generating other products such as water. Examples of addition polymers are polyethene, polypropene and polytetrafluoroethene.
- There are two types of polyethene – low-density polyethene (LDPE) and high-density polyethene (HDPE).

15.2
- Condensation polymers are polymers formed by condensation reactions, which are organic addition reactions producing water or methanol as a by-product. Condensation reactions produce linear polymers from bifunctional monomers.
- Polypeptides (proteins), polysaccharides (carbohydrates) and polyesters are condensation polymers.

15.3
- Polymers are used intensively in many areas of our lives. Polymers are relatively cheap to produce and very highly versatile.
- There are large-scale environmental concerns with the increasing production of plastics.

15.4
- Polypeptides and proteins, which are essential in our body, are formed through condensation reactions with amino acids as the building blocks.
- There are nine essential amino acids that must be part of the human diet. A deficiency can cause symptoms such as hair loss, muscle tremors and impaired neurological activity.

15.5
- Carbohydrates are an important part of our diet and are found in dairy products, fruit, grains and legumes.
- Carbohydrates are sugars and can be classified as monosaccharides, disaccharides and polysaccharides.

Key terms

- addition polymer
- biodegradation
- high-density polyethene (HDPE)
- low-density polyethene (LDPE)
- plastisphere
- polyester
- single-use plastic

Revision questions

The relative difficulty of these questions is indicated by the number of stars beside each question number: ★ = low; ★★ = medium; ★★★ = high.

Multiple choice

1 An addition reaction occurs when:
- **A** the products of different reactions are added together
- **B** two or more molecules combine to form a larger one
- **C** two substances are added together; therefore, all reactions are addition reactions
- **D** an additional substance is added after an initial reaction.

2 Starch is a:
- **A** polysaccharide
- **B** polyester
- **C** disaccharide
- **D** monosaccharide.

3 A monosaccharide is:
- **A** a simple sugar with 3–7 carbons
- **B** a building block of proteins
- **C** a polymer that contains the ester functional group in its main chain
- **D** naturally produced by plants from which we extract and refine sugar.

4 Plastics are harmful to the environment because:
- **A** they break down into microplastics and are eaten by organisms
- **B** they can take thousands of years to break down
- **C** they can wrap around animals and trap them
- **D** all of the above.

5 Kevlar is a type of:
- **A** protein
- **B** polytetrafluoroethene
- **C** synthetic polymer
- **D** polyester.

Short answer

Describe and explain

★ 6 **Describe** the difference between addition and condensation reactions.

★ 7 A polyethene has the chemical formula $CH_3(CH_2)_nCH_3$, where $n = 200$. **Calculate** its molecular mass.

★ 8 **Describe** the difference between a monosaccharide and polysaccharide.

★ 9 **Describe** the difference between Teflon and Kevlar.

Apply, analyse and interpret

★ 10 **Determine** the best material for the window of an aeroplane.

★★ 11 **Critique** the use of glass as opposed to the polymer polymethyl methacrylate in pressurised environments such as submarines.

Investigate, evaluate and communicate

★★★ 12 **Investigate** alternative materials for single-use plastics. **Create** a poster describing how to combat the over-production of these materials.

★★★ 13 **Research** how a vegan (who consumes no animal by-products) might receive all 20 essential amino acids.

You can find the following resources for this section on your obook assess:

- » Student book questions
  Chapter 15 Revision questions
- » Revision notes
  Chapter 15
- » assess quiz
  Auto-correcting mutiple-choice quiz
- » Flashcard glossary
  Chapter 15

CHAPTER 16

Molecular manufacturing

Molecular manufacturing is a technology proposed for building objects atom by atom, molecule by molecule. Robotic mechanisms would control the arrangement of atoms by positioning and reacting molecules. Such technology could produce stronger materials, new medical devices and smaller, faster computers. We could make products much cheaper and with much lower environmental impacts. However, scientists debate whether molecular manufacturing is economically feasible, let alone technically achievable within the next several decades. We need to consider the impact on society of such technology.

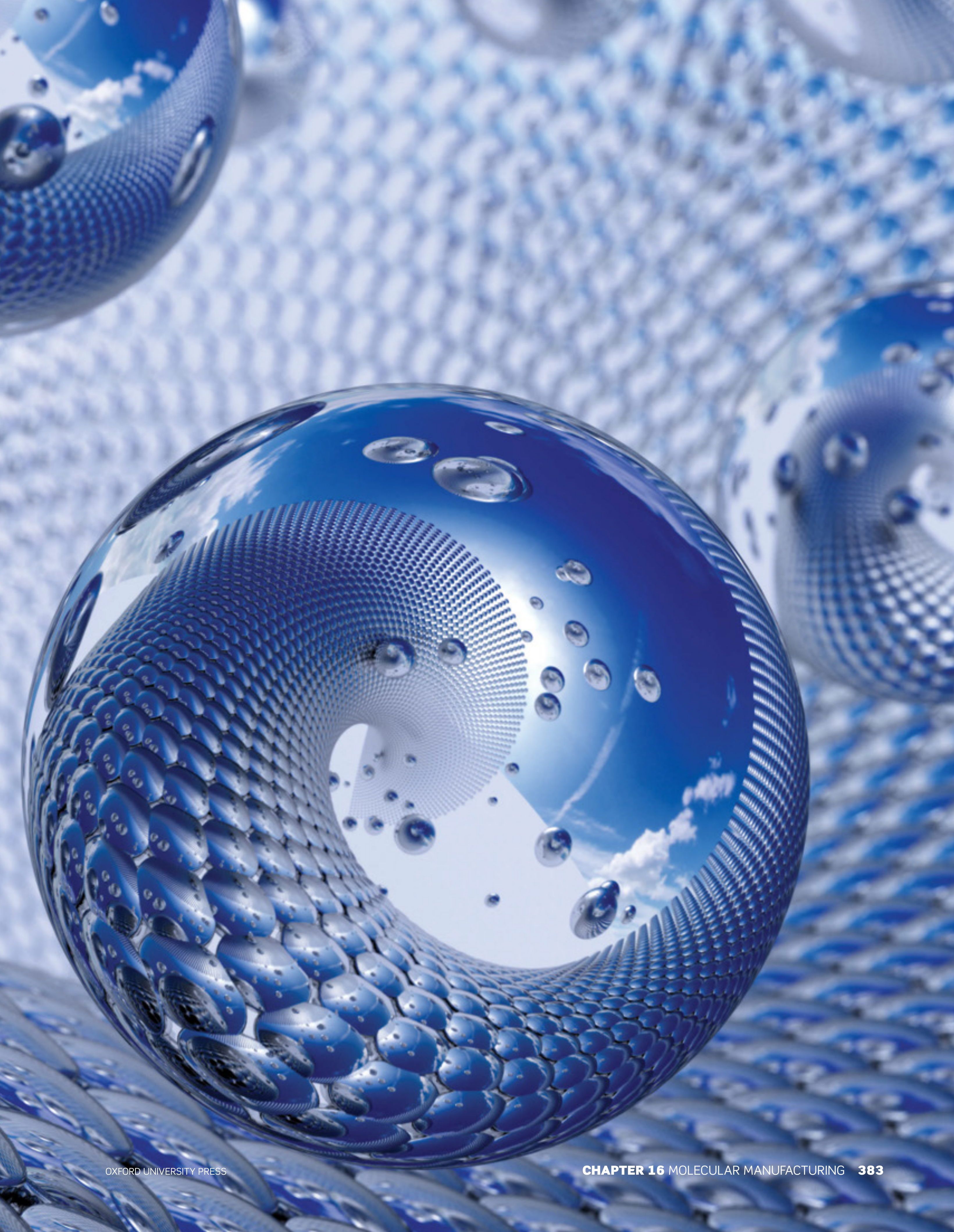
Chemists have already made molecular machines by standard chemical synthesis techniques. These molecular machines reproduce some of the characteristics of biological molecular machines found in nature.

OBJECTIVES

→ Appreciate that molecular manufacturing processes involve the positioning of molecules to facilitate a specific chemical reaction; such methods have the potential to synthesise specialised products, including proteins, carbon nanotubes, nanorobots and chemical sensors used in medicine.

Source: *Chemistry 2019 v1.3 General Senior Syllabus* © Queensland Curriculum & Assessment Authority

FIGURE 1 Molecular manufacturing is a type of nanotechnology that aims to make useful molecular machines by the precise placement of atoms and molecules.



16.1 Molecular manufacturing – fact, fiction or just far off?

KEY IDEAS

In this section, you will learn about:

- the inspirations for molecular manufacturing
- principles that underlie molecular manufacturing and make its development challenging.

molecular machine
a molecular system with defined energy input that can perform a useful function at the nanoscale

A **molecular machine** is a molecular system with defined energy input that can perform a useful function at the nanoscale which means having dimensions of less than 100 nanometres or 10^{-9} metre. The concept of molecular machines assembled from atoms or small molecules is a popular science fiction theme. The idea for molecular machines came from scientists observing biological molecular machines made from proteins and other biopolymers.

Proteins as atom assemblers and molecular recognition agents

One of the goals of molecular manufacturing is to make new products by the precise placement of atoms. Organisms have been using biological machines in the form of enzymes, or protein catalysts, to do just that. For example, the process of making vinegar relies on *Acetobacter* or *Gluconobacter* bacteria, which oxidise ethanol to acetic (ethanoic) acid, aerobically (Figure 1). The process depends on two enzymes, which oxidise ethanol to the aldehyde ethanal (acetaldehyde) and then to the carboxylic acid ethanoic acid. In the process, specific atoms are removed and added.

It is also possible to alter existing enzymes to carry out new types of chemical reactions. Part of the 2018 Nobel Prize in Chemistry was awarded to Frances Arnold (Figure 2). The award was for her work on directed evolution of enzymes, using multiple cycles of random mutation, artificial selection and screening to develop enzymes that could make new products or carry out new reactions. For example, over several rounds of directed evolution, Arnold improved an enzyme that could catalyse a reaction to form carbon–silicon bonds. The result was an enzyme that was 40 times better at the reaction than the starting enzyme and better than the best currently known molecular catalyst for the reaction.

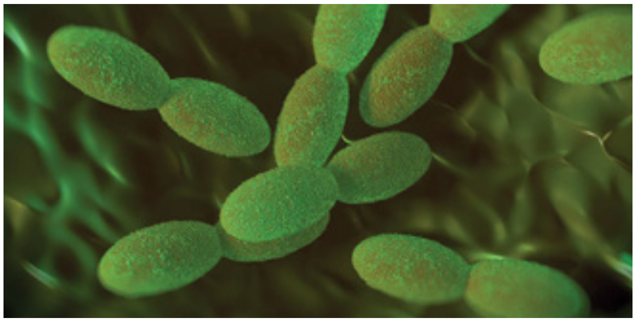


FIGURE 1 The bacteria *Acetobacter* uses enzymes to make vinegar from ethanol.

FIGURE 2 Frances Arnold shared the 2018 Nobel Prize in Chemistry for her work on directed enzyme evolution.

Artificial molecular machines

Producing an artificial molecular machine is not as simple as just shrinking an existing machine to the desired size. Machines need to be designed for the environment in which they will operate. At the micrometre scale, the effects of Brownian motion become important. You can observe the Brownian motion of dust particles lit up in a shaft of sunlight.

Albert Einstein said that Brownian motion was due to the continuous collision of molecules in the air with the larger, but still tiny, dust particles. For molecular machines, this effect is similar to you trying to walk during a cyclone. Because the collisions are random, they cannot be used to achieve controlled motion of a molecular machine. This means that an external input of energy must be provided instead.

The input of energy can be in the form of a chemical stimulus, such as a change in pH, the binding of metal ions, or the reduction or oxidation of a group within the molecular machine. Scientists have also used the absorption of light to drive changes in the conformation or shape of molecular machines, resulting in a change in function.

The advancement of molecular machines accelerated in the 1990s with the development of methods to make **mechanically interlocked molecular** systems, called catenanes and rotaxanes (Figure 3). The advantage of these systems was that the relative position of components could be controlled by outside stimuli such as changes in pH or reduction or oxidation. Chemists use them a bit like pieces of a toolkit, making larger molecular assemblies from these components.

mechanically interlocked molecules
assemblies of two or more separate molecular components that are not connected by chemical (i.e. covalent) bonds, but are held together physically, with components that can only be separated by breakage of covalent bonds

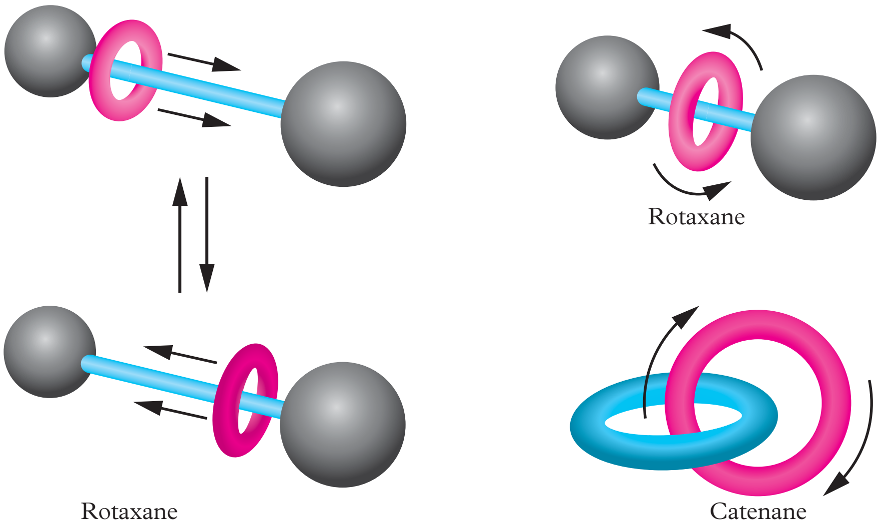


FIGURE 3 Rotaxanes and catenanes are mechanically interlocked molecules that can be used as molecular machines.

A **catenane** consists of two or more interlocked macrocycles. The interlocked rings cannot be separated without breaking covalent bonds.

A **rotaxane** consists of a dumbbell-shaped molecule that is threaded through a macrocycle. After the macrocycle has been threaded on, stoppers in the form of large, bulky groups are often added to the two ends to stop the macrocycle be coming unthreaded.

Chemists have also made rotaxanes in which the central axle is a single-walled carbon nanotube and the macrocycle is made around the nanotube (Figure 4). The macrocycle could only be removed by heating at 360°C for 30 minutes because of the dispersion forces between the macrocycle and the carbon nanotube.

catenane
an assembly of molecules containing two or more mechanically interlocked rings

rotaxane
an assembly of molecular components, including a dumbbell-shaped molecule that has one or more macrocyclic ring molecules threaded onto it

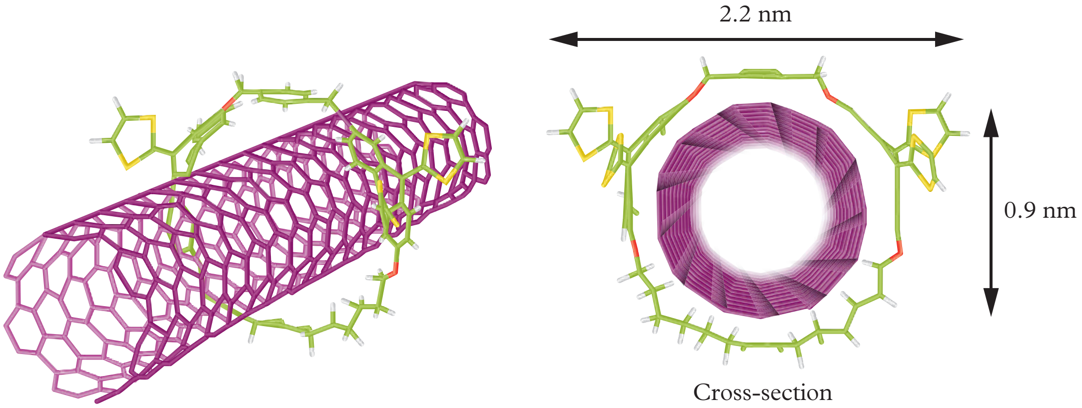


FIGURE 4 A nanomolecular machine made from a central carbon nanotube surrounded by a macrocycle. The single-walled carbon nanotube consists of carbon atoms (purple). The macrocycle is made of carbon (green), sulfur (yellow), oxygen (red) and hydrogen (white).

CASE STUDY 16.1

A molecular machine for assembling a peptide

British chemist David Leigh and his co-workers designed a molecular machine to mimic the function of a **ribosome**, a biological assembly of RNA and proteins that produces proteins.

ribosome
a protein and RNA-containing assembly inside cells that binds messenger RNA and transfer RNA in order to make proteins

The design of this molecular machine is based on a rotaxane, in which the macrocycle travels along a molecular chain that is preloaded with covalently bonded amino acid residues. The amino acids are represented by the coloured balls in Figure 5. A group attached to the rotaxane interacts with the bound amino acids. The design ensures that the macrocycle cannot slip off one end – the bulky group acts as a stopper on the end of the molecular rod.

There are some differences between how proteins are produced by molecular machines and ribosomes.

- Molecular machines are slower than ribosomes. The rotaxane assembly makes one peptide bond every 12 hours and operates in an organic solvent mixture. Ribosomes can make 10–20 peptide bonds every second in the aqueous environment of a cell, and the amino acids must be delivered to the ribosome as the protein is being made.
- Leigh's molecular machine synthesises the peptide from the C-terminus to the N-terminus of the peptide. Ribosomes synthesise the peptide in the opposite direction.
- The information encoding the peptide sequence is lost as the peptide is being made by the molecular machine. In ribosomal protein synthesis, the mRNA encoding the protein remains intact.
- Molecular machines can use amino acids that are not normally found in proteins.

Molecular machines have the potential to be useful, but currently they are not an effective way to make a protein or peptide.

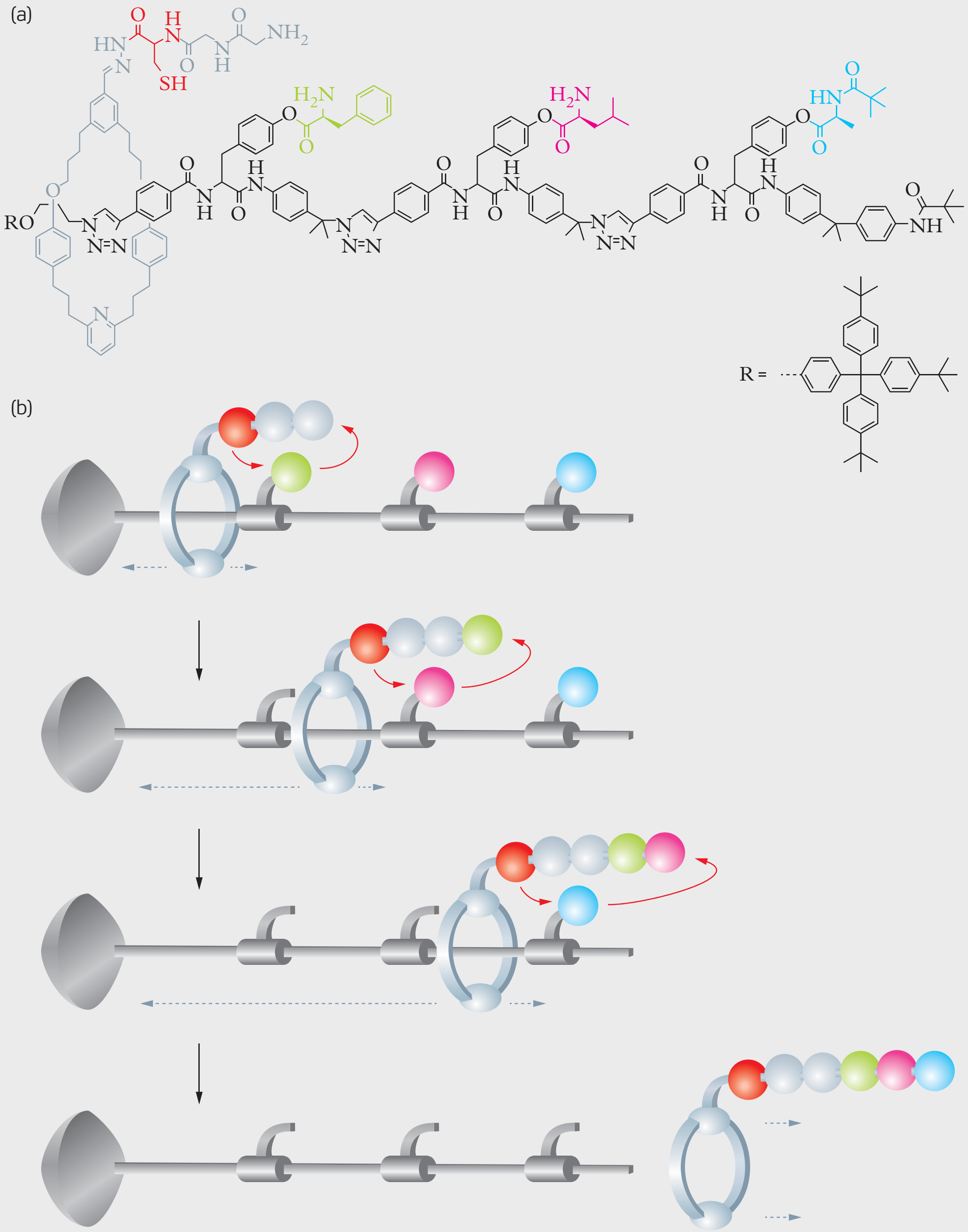


FIGURE 5 The (a) chemical structure and (b) model of the molecular machine made by David Leigh and members of his research group. The molecular machine can make a peptide by joining together amino acid ‘beads’ preloaded onto the rod portion of a rotaxane molecule.

Nanorobots

Although nanorobots are not currently used in medicine and other applications, nanotechnology researchers and futurists have imagined how they could be used in the future. Nanorobots would be extremely small (0.1–10 μm) so that they could perform specific tasks with a high degree of precision.

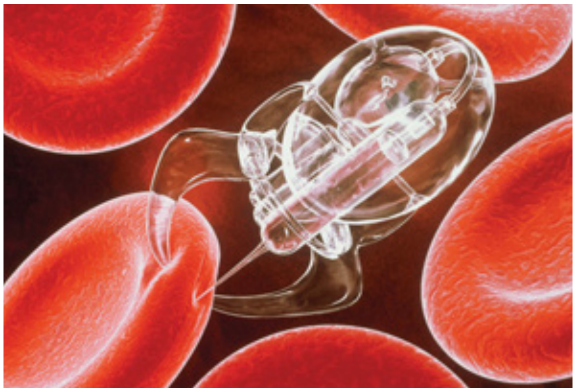


FIGURE 6 An artist's impression of a hypothetical nanorobot delivering a solution of a drug to a red blood cell

The inspiration for nanorobots is bacteria that can propel themselves around their environment, take in molecules to power themselves and even communicate with each other. Nanorobots would need components that can mimic these bacterial functions, such as:

- an onboard power supply or the ability to use fuel sources from the environment, such as glucose that is intended for use in the body or in solar cells
- sensors to guide their functions, such as moving towards the source of a chemical signal
- the ability to be directed or to communicate
- pumps to deliver precisely targeted amounts of chemicals, such as drugs (Figure 6)
- manipulators that could grab onto molecules or cells
- the ability to move around the environment.

Chemical sensors

Chemical sensors are used widely in medicine and have already improved the lives of many people. In the fields of medicine, pharmacy, forensics and toxicology, it is very important to be able to detect and measure important biological molecules in body fluids. Chemical sensors often rely on the very specific interactions between biological molecules and proteins.

FIGURE 7 A glucose blood sensor – a small amount of blood from a finger prick is drawn up into a glucose oxidase electrode.

Some of the best-known examples of sensors of this type measure glucose concentrations in blood. These chemical sensors are essential for people with diabetes who are insulin-dependent. This biosensor incorporates the enzyme glucose oxidase, which oxidises glucose to gluconic acid and hydrogen peroxide. The hydrogen peroxide is then detected electrochemically by oxidising the hydrogen peroxide to oxygen and water. This produces an electric current, which is proportional to the concentration of glucose.

Biosensors have become smaller and smaller and can now measure many more analytes. Since 2014, the companies Google and Novartis had been working on a 'smart' contact lens that could measure the amount of glucose in tears and report the information back to a smartphone (Figure 8). However, the research has been put on hold because it was discovered that tears are not a reliable way of measuring glucose levels in blood. This is a reminder that all inventions need to be scientifically feasible.

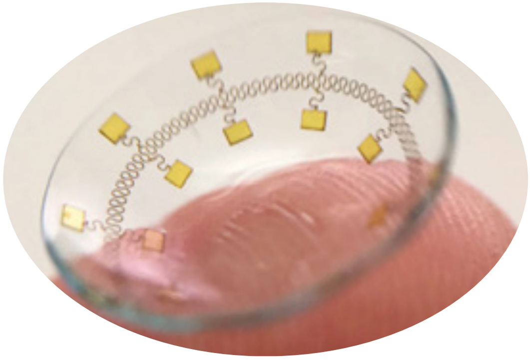


FIGURE 8 Experimental contact lens for measuring glucose levels

Building nanostructures

Top-down manufacturing

There are two approaches to building very small machines. In the **top-down approach**, scientists take a block of material and remove little bits of material one at a time until they have the desired object. This is similar to how a sculpture is made from a block of marble. The size limit of this approach is determined by the tools available.

Bottom-up manufacturing

In the **bottom-up approach** of **molecular manufacturing**, atoms or molecules would be placed precisely where they are needed. Molecular manufacturing is similar to 3D printing but would use atoms and molecules as the building blocks.

top-down approach
an approach to building nanostructures that involves removing material from larger structures

bottom-up approach
an approach to building nanostructures in which small building blocks such as atoms or molecules would be used to build larger assemblies

molecular manufacturing
the atomically precise placement of atoms or molecules in order to build larger molecular assemblies or molecular-based machines

CHECK YOUR LEARNING 16.1

Describe and explain

1 **Describe** the difference between rotaxanes and catenanes.

2 **Explain** how the molecular machine for making peptides works.

Apply, analyse and interpret

3 **Determine** what carbon nanotubes are.

You can find the following resources for this section on your obook assess:

- » Student book questions
  16.1 Check your learning
- » Weblink
  2018 Chemistry Nobel Prize winners
- » Weblink
  Carbon nanotubes

SCIENCE AS A HUMAN ENDEAVOUR

16.2 Development of molecular manufacturing processes

KEY IDEAS

In this section, you will learn about:

- the history of proposals for molecular manufacturing as well as some of the practical objections and safety concerns.

Molecular manufacturing (or molecular assembly) is a proposed method of using machines to precisely position and react molecules to build objects. Molecular manufacturing has the potential to quickly develop products such as stronger materials, and smaller, faster and more energy-efficient computers. It could also address a range of global issues by providing vital materials and products much cheaper and with less environmental impact than conventional methods.

History of molecular manufacturing

1959
Richard Feynman, USA
Gave a lecture 'There's plenty of room at the bottom: an invitation to enter a new field of physics', which outlined many of the possibilities and challenges for the development of what would be called molecular manufacturing.

1981
Invention of the scanning tunnelling microscope.

1986
K. Eric Drexler, USA
Wrote the book *Engines of Creation: The Coming Era of Nanotechnology*, which used the term 'nanotechnology' for the first time and considered the advantages and hazards of such a technology, including uncontrolled replication of nanomachines or 'grey goo'.

1989
Donald Eigler and Erhard Schweizer, USA
Used a scanning tunnelling microscope to position 35 xenon atoms on a nickel surface to spell out the corporate logo 'IBM'.

1999
Hyojune Lee and Wilson Ho, USA
Used a scanning probe tip to pick up and place one carbon monoxide molecule and covalently bond it to an iron atom adsorbed on a silver surface, using an electric pulse, then repeated with a second CO molecule at the same iron site, making a molecule of $Fe(CO)_2$.

2003
Noriaki Oyabu and colleagues, Japan
Lowered a silicon atomic force microscopy tip towards a cold silicon surface and pushed down on a single atom, mechanically breaking its bonds to neighbouring atoms, and allowing it to bind to the microscope tip.

2010
First patent granted on diamond mechanosynthesis (synthesis by mechanical atom placement) by Zyvex Labs, USA.
No practical demonstration announced yet.

2018
Kang-Kuen Ni and colleagues, USA
Carried out first two-atom reaction by using light tweezers. Two individual laser-cooled atoms (one sodium and one caesium) were held in separate optical tweezers and then merged together to form a NaCs molecule.

2018
Daniel Barredo and others, France
Arranged atoms into a three-dimensional array.

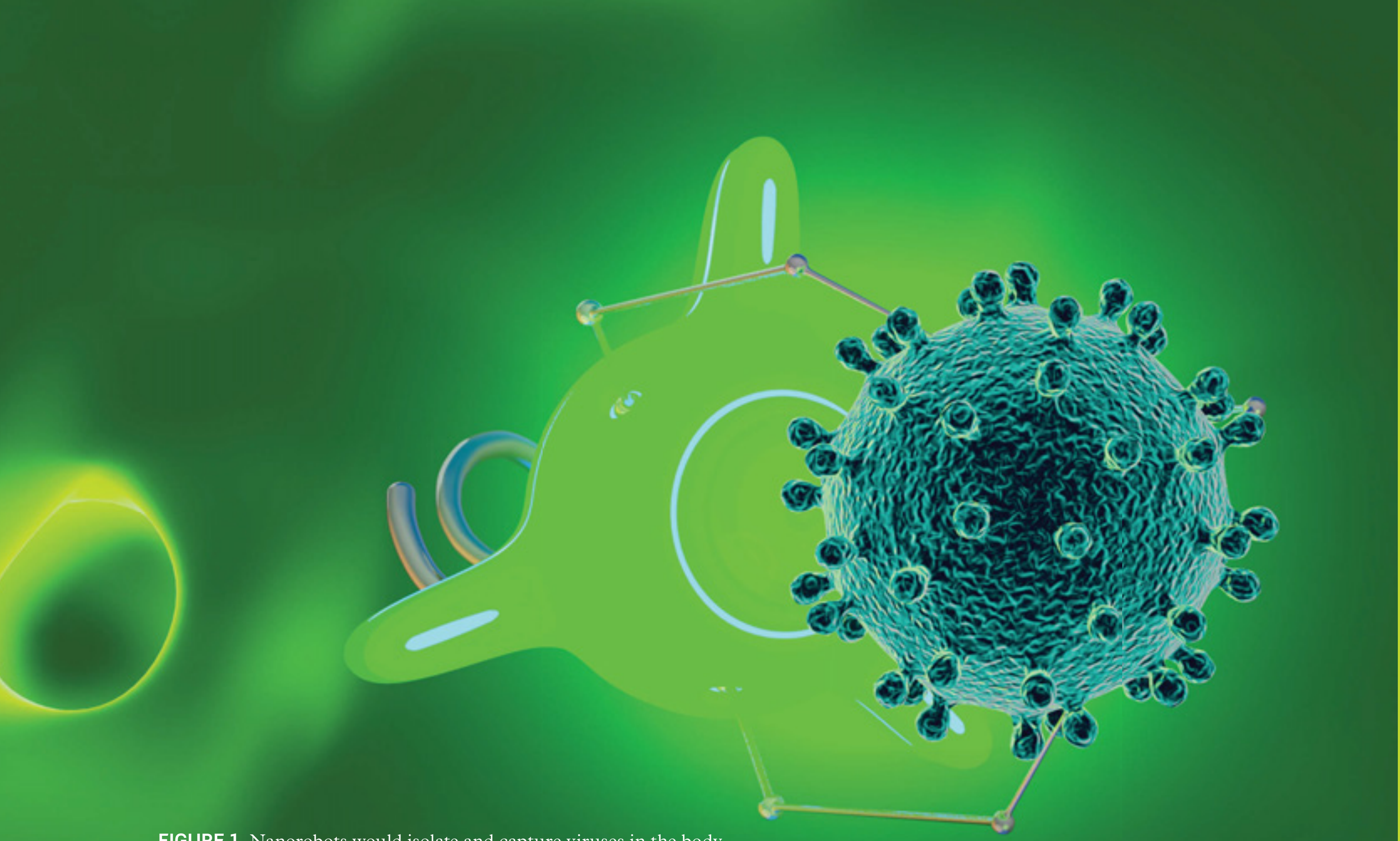


FIGURE 1 Nanorobots would isolate and capture viruses in the body.

Molecular manufacturing is the idea of assembling molecules or molecular systems by placing atoms and molecules with a high degree of precision in order to build up larger systems. Eric Drexler (see timeline) proposed three types of nanomachines:

- assemblers – molecular machines programmed to build molecular structures or devices from simpler building blocks
- disassemblers – molecular machines that could take apart an object a few atoms at a time, while recording its composition
- replicators – assemblers that could make copies of themselves.

Drexler outlined a vision of a world where large-scale use of such technology means there are abundant renewable resources, because it is possible to recycle all waste, to a point where producing goods becomes effectively free. We would be able to make highly complex materials.

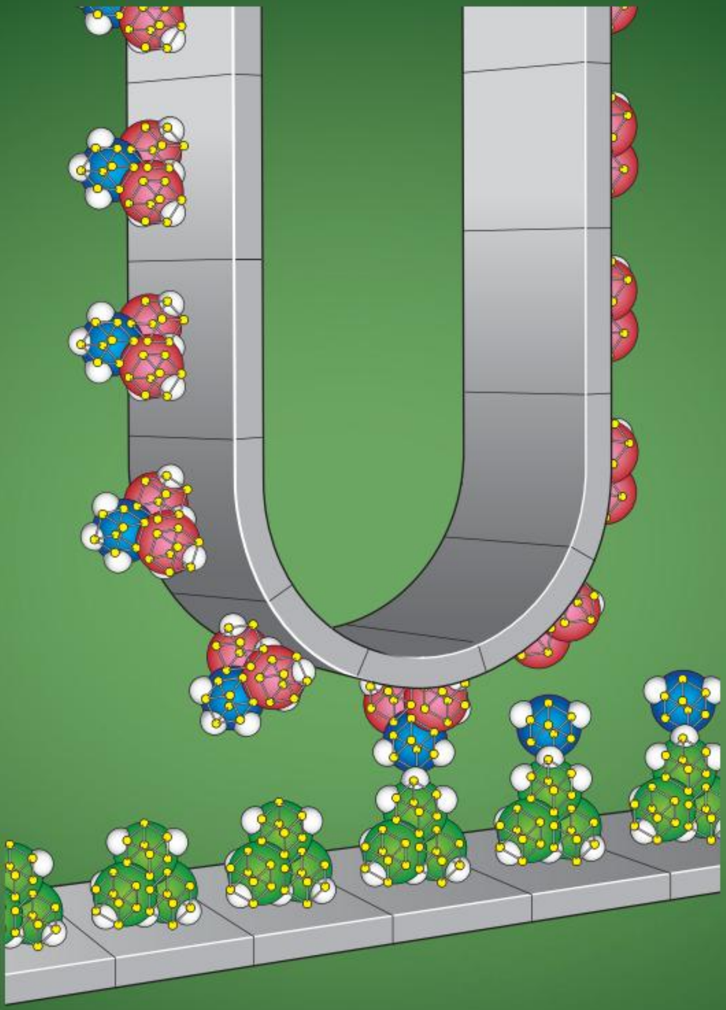


FIGURE 2 A molecular assembly line as proposed by Eric Drexler – different types of atoms would be added to a growing object.

mechanosynthesis the proposed synthesis of new chemical entities by controlling the physical placement or removal of chemical subunits

Drexler saw the goal of nanotechnology as making nanoscale factories or assembly lines, where objects could be constructed an atom at a time. This was based on the idea of **mechanosynthesis** – positioning individual molecules in close proximity to add or remove atoms in a controlled process. This was to be done in a nanoscale assembly line where different tool tips could be interchanged in order to add or remove different types of atoms to a growing structure (Figure 2).

Drexler predicted that eventually we would be able to make 1 kg objects in less than a few hours, with more than 10^6 steps per machine every second. He saw these nanofactories as using atoms of abundant elements, such as carbon, oxygen, nitrogen and silicon, as the building blocks and a series of nanoscale devices to guide the motion of reactive molecules to assemble objects, controlled by data files, much like 3D printers. The advantage of this approach is that we could control the synthesis process in a way that cannot be matched by traditional chemistry, which is based on molecules drifting through solution.

Critics of mechanosynthesis say that one of the problems is that every atom in a molecule would interact with other atoms nearby in a nano-assembler, including those in the tool tips and conveyor belt used to feed atoms into the process. To add a single atom would require all the atoms in the vicinity to be restrained, which would be impossible in practical terms. These problems have been termed ‘sticky fingers’ and ‘fat fingers’.

The time required for the nanomolecular assembly is also a problem. Scanning probe microscopes can take up to an hour to arrange a single atom or molecule. To make a 1 g diamond in this way would take around 6×10^{16} centuries!

An additional problem is how to deal with the heat generated by making so many bonds in such a confined area, because making chemical bonds is an exothermic (energy-releasing) process.

Some people have also expressed concerns about the dangers of widespread access to molecular manufacturing. One early concern was that self-replicating nanomachines could go out of control, consuming everything in their path while building more of themselves in an exponential process – the so-called ‘grey goo’. However, the growth of such replicating machines would be limited by access to resources, and there is no need to build self-replicating machines.

CHECK YOUR LEARNING 16.2

Describe and explain

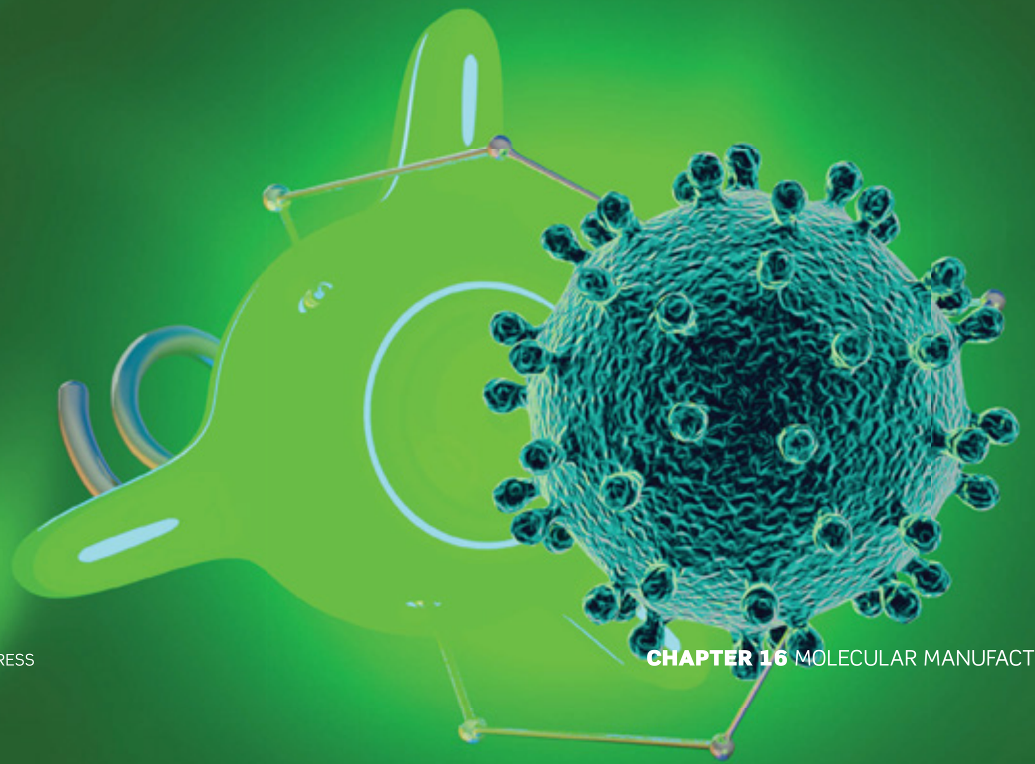
1 **Describe** a molecular assembly line.

Apply, analyse and interpret

2 **Apply** your knowledge of molecular manufacturing to **identify** other positive outcomes of the molecular assembly line.

You can find the following resources for this section on your obook assess:

- Student book questions
  16.2 Check your learning
- Weblink
  Foresight Institute, Freitas’ organisation
- Weblink
  Molecular manufacturing



CHAPTER 16

Review

Chapter summary

16.1

- Biological molecular machines such as enzymes and ribosomes can precisely control the structure of matter at the atomic level.
- Synthetic molecular assemblies can carry out useful functions, based on simple components such as rotaxanes and catenanes, and suggest ways to build more and more complicated molecular machines.
- The two approaches to making molecular machines are top-down and bottom-up.

16.2

- People such as Eric Drexler have argued that in the near future it will be possible to construct materials and nanomachines by the precise placement of molecular building blocks at an atomic level of accuracy. They envisage that this will affect all areas of society, greatly improving the quality of life and fixing many current environmental problems. Other scientists believe that these ideas are impractical, if not impossible.

Key terms

- bottom-up approach
- catenane
- mechanically interlocked molecules
- mechanosynthesis
- molecular machine
- molecular manufacturing
- ribosome
- rotaxane
- top-down approach

Revision questions

The relative difficulty of these questions is indicated by the number of stars beside each question number: ★ = low; ★★ = medium; ★★★ = high.

Short answer

Describe and explain

★ 1 **Explain** the difference between the top-down and bottom-up approach to making nanomachines.

★★ 2 **Describe** mechanosynthesis and the problems that critics have raised with this concept.

★★ 3 **Explain** the three types of nanomachines that were originally proposed by Eric Drexler.

Apply, analyse and interpret

★★ 4 **Compare** and **contrast** peptide synthesis as carried out by ribosomes and by the rotaxane molecular assembly created by David Leigh and his group.

★★★ 5 A commentator on Drexel's proposals has said:

‘Grounded in the theories and trends of the times, *Engines of Creation* is a depiction of how the world could be (better, cleaner, healthier, abundant …). However, it should be taken for what it really is: really good science fiction’.

Analyse this statement and **explain** whether or not you agree with the author.

Investigate, evaluate and communicate

★★★ 6 Imagine that you are on the committee for awarding the Nobel Prize in Chemistry for 2050. You must examine whether any of today's achievements should receive recognition. **Investigate** the most exciting advances for the current year in molecular manufacturing as reported in science news websites (e.g. ChemistryWorld, EurekAlert). In two paragraphs, **present** an argument about why the particular research you have chosen should be awarded the 2050 Nobel Prize in Chemistry. **Structure** the science clearly and **describe** why it is important.

★★★ 7 Chemistry allows society to change the world by forming new substances and materials. The question of how the discoveries of chemistry should be used affects everyone because it directly influences the world we live in. To be able to meaningfully contribute to resolving those questions, you need an understanding of chemistry. **Select** a story from a newspaper or news website and **communicate** how the story would be different if molecular manufacturing were at present, working, readily available technology.

You can find the following resources for this section on your obook assess:

- Student book questions
  Chapter 16 Revision questions
- Revision notes
  Chapter 16
- assess quiz
  Auto-correcting mutiple-choice quiz
- Flashcard glossary
  Chapter 16

UNIT 4

Practice exam-style questions

Structure, synthesis and design

Multiple choice

1 Functional groups that contain two oxygen atoms include:
   - **A** alkenes
   - **B** alcohols
   - **C** esters
   - **D** amides.

2 The physical properties affected by the functional groups in organic compounds are:
   - **A** melting point, boiling point, toxicity, flammability
   - **B** melting point, boiling point, solubility in water and organic solvents
   - **C** reactivity, boiling point, solubility in water and organic solvents
   - **D** reactivity, toxicity, flammability, electronegativity.

3 Unsaturated compounds contain:
   - **A** only single bonds
   - **B** only double bonds
   - **C** single or double bonds
   - **D** double or triple bonds.

4 What properties are determined by the primary, secondary and tertiary structures of organic macromolecules?
   - **A** Strength, density and biodegradability
   - **B** Strength, colour and transparency
   - **C** Colour, biodegradability and density
   - **D** Colour, strength and density

5 The generation of sulfuric acid occurs in three main stages. The second stage requires specific reaction conditions to optimise its yield. What are those reaction conditions?
   - **A** A low temperature (20°C) and low pressure (2 atm)
   - **B** A high temperature (400°C) and low pressure (2 atm)
   - **C** A low temperature (20°C) and high pressure (4 atm)
   - **D** A high temperature (400°C) and high pressure (4 atm)

6 Examples of reduction reactions include which two of the following?
   - **A** Ketone to secondary alcohol
   - **B** Aldehyde to carboxylic acid
   - **C** Alkene to polyalkane
   - **D** Nitrile to amine

7 Identify the type of glycosidic linkages present in the following amylose molecule.

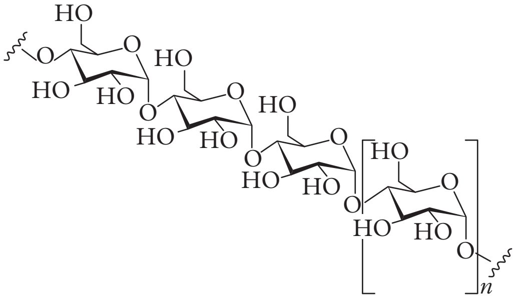


FIGURE 1 Amylose molecule.

   - **A** α-glycosidic linkages between carbon atoms 1 and 4
   - **B** α-glycosidic linkages between carbon atoms 1 and 6
   - **C** β-glycosidic linkages between carbon atoms 1 and 4
   - **D** β-glycosidic linkages between carbon atoms 1 and 6

8 Ammonia is produced in the:
   - **A** Bosch process
   - **B** contact process
   - **C** Haber process
   - **D** Phillips process.

9 The principles of green chemistry include which two of the following?

- **A** The deceleration of chemical reactions
- **B** The creation of longer-lasting products
- **C** The creation of shorter-lasting products
- **D** The prevention of waste and energy loss

10 Molecular manufacturing involves which two of the following?

- **A** The potential to make nanorobots and chemical sensors for medical use
- **B** An increase in reaction rate, to manufacture products quicker
- **C** The synthetic means of manufacturing products in the future
- **D** The positioning of molecules for specific chemical reactions

Short answer

11 **Describe** the primary and secondary structures of proteins.

12 **Describe** the structures of saturated and unsaturated fatty acids.

13 **Explain** the role of isomerism in organic compounds.

14 **Explain** how electrophoresis is a process used to analyse proteins.

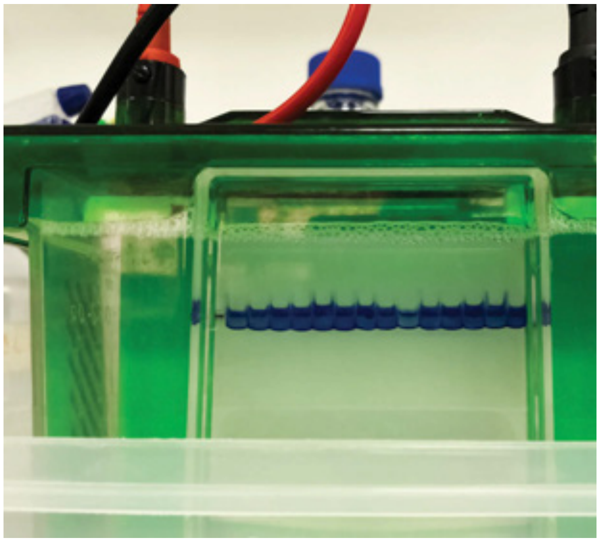


FIGURE 2 Gel electrophoresis box used to analyse proteins.

15 **Describe**, using equations, how the hydration of ethene forms ethanol.

16 **Deduce** the structural formula of 2-hydroxy-3-methylcyclohexanone.

17 **Calculate** the percentage yield of a double displacement reaction between 1 g of sodium carbonate and 1 g of calcium chloride that produces 0.75 g of insoluble calcium carbonate.

18 **Calculate** the atom economy for the condensation reaction between butanoic acid and ethanol.

19 **Deduce** the pros and cons of polymer use. **Consider** how polymer use affects the environment and what is currently being done to manage this issue.

FIGURE 3 Plastic polymers are both useful and cause consequences.

20 **Determine** the accuracy of infrared spectroscopy compared with other analytical techniques. **List** the other analytical techniques that are comparable to infrared spectroscopy.

CHAPTER 17

Practical manual

The QCAA Chemistry General Senior Syllabus outlines a number of mandatory and suggested practicals for completion in Units 3 & 4. Suggestions for methodology and materials have been supplied in this chapter and are outlined in the table on the next page. However, the following is not prescriptive; schools may complete the mandatory or suggested practicals in any other form suited to their resources.

The experiments in this chapter have been trialled, and obvious cautions of hazards are given; however, teachers are legally obliged to carry out their own risk assessment prior to undertaking any practical activity.

This chapter will highlight key safety concerns within each practical; however, there are some general safety concerns to be considered in all practicals.

- Tie back long hair.
- Do not eat or drink while in the lab.
- Always be aware of other students in the lab and act sensibly.
- Wear a lab coat, safety glasses and closed-toed shoes.
- Familiarise yourself with the school's safety procedures and the locations of eye wash, shower, spill kits and first aid kits.
- Handle all chemicals with care and consult your teacher and risk assessments for the hazards involved with each chemical.
- Check electrical equipment before use to ensure that there is no existing damage to cables.
- Keep open flames away from flammable materials.
- Use the appropriate equipment to handle hot materials (i.e. heat-resistant gloves or tongs).
- Complete fieldwork in groups and complete a full risk assessment.

If you are unsure of any procedures in the lab or need any clarification for a practical, consult your teacher and/or lab technician.

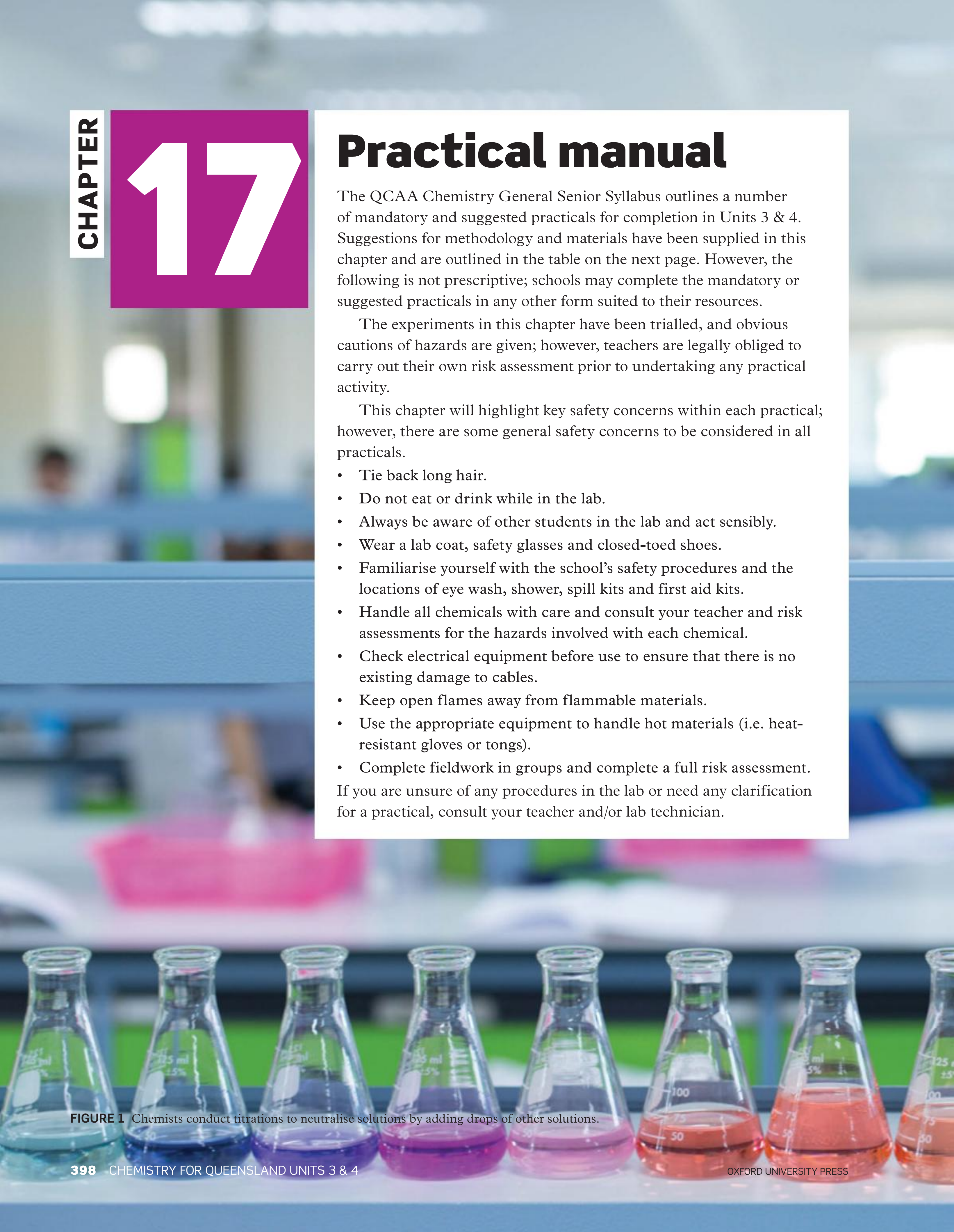


FIGURE 1 Chemists conduct titrations to neutralise solutions by adding drops of other solutions.

UNIT 3 PRACTICALS

⚗	SUGGESTED	**2.2A** Effect of concentration on equilibrium
⚗	SUGGESTED	**2.2B** Effect of volume and pressure on equilibrium (TEACHER-ONLY DEMONSTRATION)
⚗	SUGGESTED	**2.2C** Effect of temperature on equilibrium (TEACHER-ONLY DEMONSTRATION)
⚗	SUGGESTED	**3.7** Measuring pH
⚗	SUGGESTED	**4.1** Electrical conductivity of strong and weak acids and bases
⚗	MANDATORY (EITHER 5.1A OR 5.1B)	**5.1A** Titration of hydrochloric acid with a standard sodium carbonate solution
		5.1B Determining the concentration of ethanoic acid in white vinegar
⚗	MANDATORY	**6.1** Performing single displacement reactions
⚗	MANDATORY	**7.1** Constructing a galvanic cell
⚗	SUGGESTED	**8.1A** Electrolysis of water
⚗	SUGGESTED	**8.1B** Electroplating of copper

UNIT 4 PRACTICALS

⚗	SUGGESTED	**9.3** Interpreting 2D and 3D functional groups
⚗	MANDATORY	**9.4** Modelling isomers of organic molecules
⚗	SUGGESTED	**10.1** Bromination of unsaturated hydrocarbons (TEACHER-ONLY DEMONSTRATION)
⚗	SUGGESTED	**10.2** Oxidation of alcohols (TEACHER-ONLY DEMONSTRATION)
⚗	SUGGESTED	**11.3** Catalysing decomposition reactions
⚗	SUGGESTED	**12.1** Identifying amino acids by paper chromatography
⚗	SUGGESTED	**12.2** Using mass spectroscopy and infrared spectroscopy to identify organic compounds
⚗	SUGGESTED	**13.1A** Haber process simulation using Wolfram
⚗	SUGGESTED	**13.1B** Video simulation of the contact process

5.1A
MANDATORY PRACTICAL

Titration of hydrochloric acid with a standard sodium carbonate solution

CAUTION: ALL CHEMICALS ARE IRRITANTS. HCl IS CORROSIVE. WEAR PERSONAL PROTECTIVE EQUIPMENT AT ALL TIMES. IF THE CHEMICALS COME IN CONTACT WITH SKIN, FLUSH THE AFFECTED AREA FOR 15 MINUTES AND CONSULT A HEALTHCARE PROFESSIONAL.

Acid–base titration to calculate the concentration of a solution with reference to a standard solution.
Source: *Chemistry 2019 v1.3 General Senior Syllabus* © Queensland Curriculum & Assessment Authority

Note: Select Practical 5.1A or Practical 5.1B as the mandatory practical to cover this syllabus point.

Context

Sodium carbonate (Na_2CO_3) is a relatively strong base, which reacts with hydrochloric acid, a strong acid, according to the overall equation:

$$Na_2CO_3(aq) + 2HCl(aq) \rightarrow 2NaCl(aq) + H_2O(l) + CO_2(g)$$

This occurs in two steps.

Step 1:

$$Na_2CO_3(aq) + HCl(aq) \rightarrow NaHCO_3(aq) + NaCl(aq)$$

Step 2:

$$NaHCO_3(aq) + HCl(aq) \rightarrow NaCl(aq) + H_2O(l) + CO_2(g)$$

The overall equivalence point occurs at pH = 7 (neutral), but the first equivalence point occurs at about pH = 8.3 (basic) and the second equivalence point occurs at about pH = 3.7 (acidic).

In step 1, one of the sodium ions from Na_2CO_3 swaps places with the hydrogen ion in HCl. When the equivalence point is reached in Step 1, the product $NaHCO_3$ (sodium bicarbonate (baking soda)) makes the solution basic. Because the first equivalence point occurs in basic conditions, you could use a phenolphthalein indicator if measuring this step.

In Step 2, the bicarbonate reacts with more HCl to form a neutral solution of NaCl, H_2O and CO_2. Because the second equivalence point occurs at an acidic pH, you will use methyl orange as an indicator. Methyl orange changes colour from red at pH 3.7 to yellow at pH 4.4. This is in the equivalence point range of Step 2 of the reaction's titration curve.

Aim

To determine the concentration of a solution of hydrochloric acid by titration against a standard sodium carbonate solution, using a methyl orange indicator.

Materials

Part A

- 2.5 g pure sodium carbonate (Na_2CO_3)
- Deionised water
- 200 mL volumetric flask
- Electronic balance
- Weigh boat
- Spatula
- Funnel (Important: Ensure that the funnel has been washed with deionised water and allowed to completely air-dry before the experiment.)
- Pen for labelling glassware
- Plastic dropping pipette

Part B

- Standard solution of Na_2CO_3 from Part A
- Hydrochloric acid (HCl) solution (approximately 0.5 M)
- Methyl orange indicator
- 50 mL burette
- Retort stand and burette clamp (if there is no burette clamp, use a boss head and clamp)
- White tile
- 10.00 mL pipette
- Pipette bulb
- 3 × 100 mL beakers
- 250 mL beaker
- 3 × 100 mL conical flasks
- Wash bottle with deionised water
- Pen for labelling glassware

Method

Part A: Preparing a standard sodium carbonate solution

1 Place a weigh boat on the electronic balance and tare it to read zero.

2 Use a spatula to measure 2.5 g of sodium carbonate into the weigh boat and record its mass. This does not need to be exactly 2.5 g, but should be 2.5 ± 0.1 g.

3 Wash the volumetric flask with deionised water from the wash bottle. Add the lid, shake the flask and then tip the water down the sink. Repeat this two more times.

4 Add a small volume (approximately 20 mL) of deionised water to the volumetric flask. This will help to stop the Na_2CO_3 clumping together and solidifying at the bottom of the flask.

5 Put the prewashed and dried funnel in the mouth of the volumetric flask. Add the Na_2CO_3 to the volumetric flask by scraping it out of the weigh boat a small amount at a time. Ensure that the solid moves through the funnel and into the volumetric flask before adding more solid. Tap the funnel if the solid gets stuck. (Do not add water to wash it through – otherwise, the Na_2CO_3 will clump together and become very difficult to remove.) When nearly all of the solid is in the flask and only a small amount remains in the weigh boat and filter funnel, use the wash bottle to rinse the weigh boat into the funnel.

6 Fill the volumetric flask to one-quarter full and swirl it until all the Na_2CO_3 is dissolved. This may take extra time if the powder clumps together and solidifies but it will dissolve eventually.

7 Add deionised water until the bottom of the meniscus is on the mark (this should be on the neck of the flask).

8 Put the lid on the flask and tip the flask upside down and then upright again. Repeat this motion until the solution has an evenly distributed concentration.

9 Label the flask 'Na_2CO_3', add its concentration, the date it was prepared and your initials.

Part B: Determining the concentration of a hydrochloric acid solution

1 Label three 100 mL beakers 'Washing deionised water', 'HCl' and 'Na_2CO_3' and fill each beaker with its respective solution.

2 Wash three 100 mL conical flasks with deionised water and tip the waste down the sink.

3 Wash the 10 mL pipette with the HCl solution by drawing the solution up to the mark and then dispensing it down the sink. Repeat this step two more times.

4 Using the pipette, dispense 10 mL of the HCl solution into the conical flask. Repeat this step two more times so that all three conical flasks contain a 10 mL aliquot of HCl. Add three drops of methyl orange indicator to each conical flask.

5 Close the stopcock of the burette and wash it with deionised water from the wash bottle by adding some water and gently tipping the burette onto its side, then slowly spinning it to ensure the water has come in contact with the inside of the burette. Empty some of the water into the sink by tipping the burette upside down; pour the remaining water out the tip by opening the stopcock. Repeat this one more time.

6 Repeat Step 5, using no more than 10 mL of the standard Na_2CO_3 solution. Dispose of the solution in the waste beaker, not down the sink. This wash only needs to be performed once.

7 Set up the burette and clamp (see Figure 1).

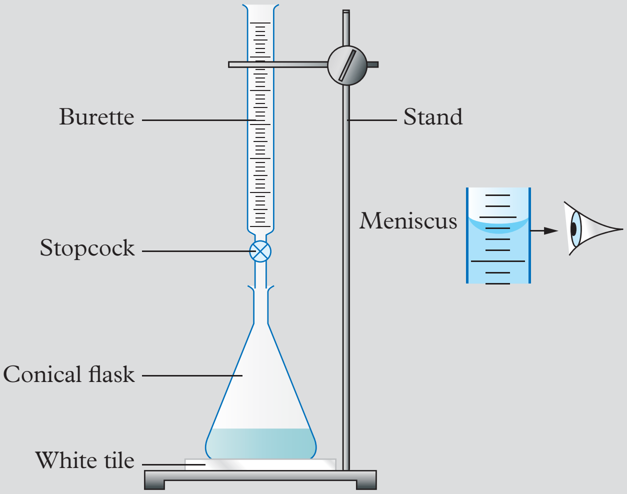


FIGURE 1 The apparatus for the titration

8 Place the 250 mL beaker under the burette (to collect the waste) and a funnel on the top. With the stopcock open, pour in the standard solution until no more than 1–2 mL has run through. Then close the stopcock and fill the burette to the top. (Note: You do not need to fill the burette to the 0.00 mL line. You will measure a final and initial volume, so it does not matter what value it starts on, as long as it is below 5 mL.) Remove the funnel from the top. Record the initial volume in the burette.

9 Place the first conical flask under the burette and carefully open the stopcock. As the Na_2CO_3 mixes with the HCl solution, constantly swirl the flask to turn the red to orange. If the solution turns yellow, the titration has gone too far (see Figure 2). This end point can be difficult to observe. Take your time, use the white tile and be careful. Turn the stopcock so that the Na_2CO_3 solution is dispensed at a slower rate. When reaching the end point (colour change from red to orange), the tap should be slowly dispensing one drop at a time. The white tile will help you to observe this colour change.

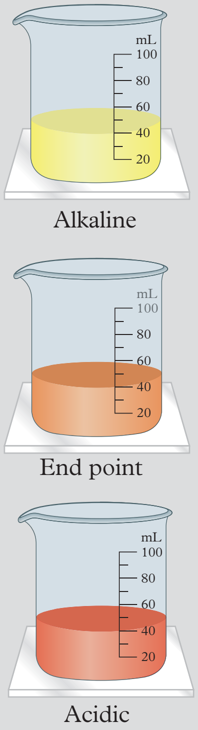


FIGURE 2 Methyl orange indicator in alkaline (left) and acidic (right) solutions. The middle solution demonstrates the end point.

10 Record the final volume in the burette. Subtract the initial volume from the final volume to calculate the titre volume.

11 Repeat Steps 9 and 10 until concordant titres (highest and lowest values within 0.1 mL) are obtained. Note: One drop is the equivalent of 0.05 mL, so it is important that your measuring is highly accurate throughout the experiment.

Results

Construct a results table that records the trial number, the initial volume of the burette, the final volume of the burette and the titre volume.

Trial number	Initial volume of burette (mL)	Final volume of burette (mL)	Titre volume (mL)

Discussion

1 Calculate the:
  a concentration of the standard Na_2CO_3 solution
  b average titre of Na_2CO_3
  c amount of Na_2CO_3 that reacted with the HCl
  d concentration (mol L^{-1}) of HCl in the aliquot
  e concentration (mol L^{-1}) of HCl in the original bottle.

2 What would happen to the concentrations that you calculated if there was water in the burette when it was filled with Na_2CO_3?

3 What would happen to the concentrations that you calculated if there was water in the pipette when it was filled with the HCl?

4 What would happen to the concentrations that you calculated if there was water in the conical flask when it was filled with the HCl?

Conclusion

Summarise the outcomes of this practical.

5.1B
MANDATORY PRACTICAL

Determining the concentration of ethanoic acid in white vinegar

CAUTION: ALL CHEMICALS ARE IRRITANTS. SOLID NaOH IS CORROSIVE. WEAR PERSONAL PROTECTIVE EQUIPMENT AT ALL TIMES. IF THE CHEMICALS COME IN CONTACT WITH SKIN, FLUSH THE AFFECTED AREA FOR 15 MINUTES AND CONSULT A HEALTHCARE PROFESSIONAL. IF SPILT, SWEEP INTO A WASTE BIN.

Acid–base titration to calculate the concentration of a solution with reference to a standard solution.

Source: *Chemistry 2019 v1.3 General Senior Syllabus* © Queensland Curriculum & Assessment Authority

Note: Select Practical 5.1A or Practical 5.1B as the mandatory practical to cover this syllabus point.

Context

White vinegar has an acetic acid (ethanoic acid) content of 4–8% v/v. This means that there is 4–8 mL of the acid per 100 mL of vinegar. Ethanoic acid is a weak acid, so it only partially ionises in water. The reaction of ethanoic acid with the strong base sodium hydroxide (NaOH) has an equivalence point at approximately pH 9. Phenolphthalein indicator is colourless in acidic conditions and turns pink between pH 8.3 and pH 10.0, making it an ideal indicator for this titration.

Ethanoic acid reacts with sodium hydroxide according to the following equation:

$$CH_3COOH(aq) + NaOH(aq) \rightleftharpoons CH_3COONa(aq) + H_2O(l)$$

Note: Over time, sodium hydroxide will absorb carbon dioxide from the atmosphere. Do not leave the solution for longer than a week and assume that it will have the same concentration. It should be used as soon as possible.

Aim

To determine the concentration of ethanoic acid in white vinegar by titration against a standard sodium hydroxide solution, using a phenolphthalein indicator.

Materials

Part A

- 0.8 g pure sodium hydroxide (NaOH) pellets
- 200 mL volumetric flask
- Electronic balance
- Weigh boat
- Spatula
- Wash bottle with deionised water
- Plastic dropping pipette
- Pen for labelling glassware

Part B

- Standard solution of NaOH from Part A
- 25 mL white vinegar
- Phenolphthalein indicator
- 250 mL volumetric flask
- 50 mL burette
- Retort stand and burette clamp (if there is no burette clamp, use a boss head and clamp)
- Funnel
- White tile
- 20.00 mL pipette
- 25.00 mL pipette
- Pipette bulb
- 100 mL beaker for water to wash pipette
- 3 × 100 mL beakers
- 250 mL beaker
- 3 × 100 mL conical flasks
- Wash bottle with deionised water
- Pen for labelling glassware

Method

Part A: Preparing a standard sodium hydroxide solution

1. Place a weigh boat on the electronic balance and tare it to read zero.
2. Use a spatula to measure 0.8 g of sodium hydroxide pellets into the weigh boat and record its mass. Note: This does not need to be exactly 0.8 g, but should be within 0.8 ± 0.1 g.

Never touch NaOH with your bare hands. If there is a spill, follow safety procedures.

3 Wash the volumetric flask with deionised water from the wash bottle. Add the lid, shake the flask and then tip the water down the sink. Repeat this two more times.

4 Add the NaOH pellets to the volumetric flask by scraping them out of the weigh boat with a spatula. There should be no residue to wash from the weigh boat into the flask because the NaOH is in pellet form.

5 Fill the volumetric flask to one-quarter full and swirl the flask until all the NaOH is dissolved. This may take some time because they are pellets and do not have a high surface area.

6 Add deionised water until the bottom of the meniscus is on the mark (this should be on the neck of the flask).

7 Put the lid on the flask and tip the flask upside down and then upright again. Repeat this motion until the solution has an evenly distributed concentration.

8 Label the flask ‘NaOH’, add its concentration, the date it was prepared and your initials.

Part B: Determining the concentration of a vinegar solution

1 Wash the 250 mL volumetric flask with deionised water from the wash bottle. Add the lid, shake the flask and then tip the water down the sink. Repeat this two more times.

2 Pour some deionised water into a 100 mL beaker and label the beaker ‘Washing water’. Wash the 25 mL pipette by drawing the washing water up to the mark and then dispensing it down the sink. Repeat this step two more times and then do a final wash with the vinegar solution.

3 Pour 55 mL of white vinegar into a 100 mL beaker and label the beaker ‘Undiluted vinegar’. Draw 25 mL of the vinegar into the pipette and dispense it into the 250 mL beaker, which should be labelled as ‘Waste’.

4 Use the 25 mL pipette to dispense 25 mL of the white vinegar into the washed 250 mL volumetric flask. Make the solution up to the mark with deionised water. Add the lid to the flask and tip the flask upside down and then upright again. Repeat this motion until the solution has an evenly distributed concentration.

5 Close the stopcock of the burette and wash it with deionised water from the wash bottle by adding some water and gently tipping the burette onto its side, then slowly spinning it to ensure the water has come in contact with the inside of the burette. Empty some of the water into the sink by tipping the burette upside down and pouring the remaining water out the tip by opening the stopcock. Repeat this one more time.

6 Pour some of the standard NaOH into a 100 mL beaker labelled ‘Standard NaOH’ and repeat Step 5. Only use 10 mL of the solution and do not put the solution down the sink. Dispose of it in the waste beaker. This wash only needs to be performed once.

7 Set up the burette and clamp (see Figure 1).

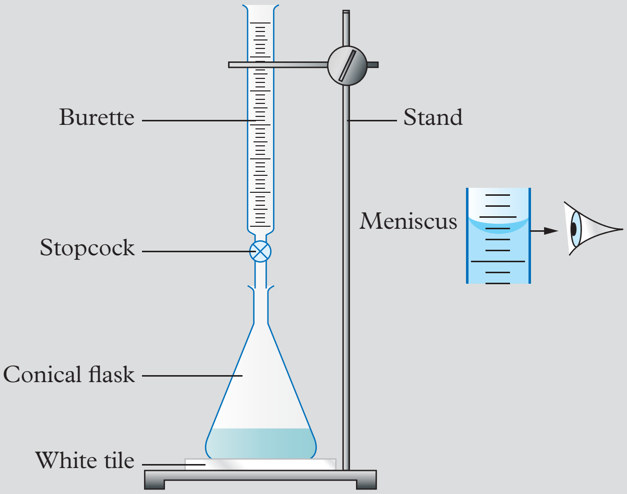


FIGURE 1 The apparatus for the titration

8 Place the waste beaker under the burette and a funnel on the top. With the stopcock open, pour in the standard solution until no more than 1–2 mL has run through. Then close the stopcock and fill the burette to the top. (Note: The burette does not need to be filled to the 0.00 mL line. A final and initial volume will be measured, so it does not matter what value it starts on, as long as it is below 5 mL.) Remove the funnel from the top. Record the initial volume in the burette.

9 Wash the 20 mL pipette as per Step 2 with deionised water. Pour some of the diluted vinegar solution into a 100 mL beaker and label it ‘Diluted vinegar’. Wash the pipette again with the diluted vinegar solution and dispense it into the waste beaker.

10 Wash the three conical flasks with deionised water and dispense 20 mL of diluted vinegar into each one by using the 20 mL pipette. Add three drops of phenolphthalein into each flask and swirl them. It should result in a colourless solution.

11 Place the first conical flask under the burette and carefully open the stopcock. As the NaOH mixes with the vinegar solution, a pink colour will be visible in the flask. Constantly swirl the flask to remove the pink. After a time, the pink colour will be harder to remove by swirling. Turn the stopcock so that the NaOH solution is dispensed more slowly. When approaching the end point (colour change from colourless to pink), the tap should be dispensing one drop at a time. It will only take one drop to cause the colour change and a pale pink will result. The white tile will aid in observing this colour change.

12 Record the final volume in the burette. Subtract the initial volume from the final volume to calculate the titre volume.

13 Repeat Steps 11 and 12 until concordant titres (highest and lowest values within 0.1 mL) are obtained. Note: One drop is the equivalent of 0.05 mL, so it is important your measuring is highly accurate throughout the experiment.

Results

Construct a results table that records the trial number, the initial volume of the burette, the final volume of the burette and the titre volume.

Trial number	Initial volume of burette (mL)	Final volume of burette (mL)	Titre volume (mL)

Trial number	Initial volume of burette (mL)	Final volume of burette (mL)	Titre volume (mL)

Discussion

1 Calculate the:
  - **a** concentration of the standard NaOH solution
  - **b** average titre of NaOH
  - **c** amount of NaOH that reacted with the ethanoic acid
  - **d** amount of ethanoic acid in the diluted aliquot
  - **e** concentration (mol L^{-1}) of ethanoic acid in the diluted aliquot
  - **f** concentration (mol L^{-1}) of ethanoic acid in the original undiluted 25 mL sample
  - **g** concentration (g L^{-1}) of ethanoic acid in the original undiluted 25 mL sample
  - **h** mass of ethanoic acid in 100 mL of white vinegar
  - **i** volume of ethanoic acid in the 100 mL of white vinegar (assume that the density of ethanoic acid is 1.05 g mL^{-1})
  - **j** %v/v (volume per 100 mL of vinegar) of ethanoic acid in the white vinegar.

2 What would happen to the concentrations that you calculated if there was water in the burette when it was filled with NaOH?

3 What would happen to the concentrations that you calculated if there was water in the pipette when it was filled with the diluted vinegar?

4 What would happen to the concentrations that you calculated if there was water in the conical flask when it was filled with the diluted vinegar?

5 Compare the result that you calculated with the theoretical concentration (on the bottle or in the introduction). Comment on the precision and accuracy of the results.

Conclusion

Summarise the outcomes of this practical.

6.1
MANDATORY PRACTICAL

Performing single displacement reactions

CAUTION: $CuSO_4$ IS TOXIC AND HARMFUL TO THE ENVIRONMENT. WEAR PERSONAL PROTECTIVE EQUIPMENT AT ALL TIMES. IF THE CHEMICAL COMES IN CONTACT WITH SKIN, FLUSH THE AFFECTED AREA FOR 15 MINUTES AND CONSULT A HEALTHCARE PROFESSIONAL. IF SWALLOWED, CONTACT THE POISON CENTRE. CONSULT YOUR LAB TECHNICIAN WHEN DISPOSING OF THE CHEMICAL. HYDROGEN GAS, WHICH IS HIGHLY FLAMMABLE, IS PRODUCED DURING THIS EXPERIMENT. KEEP AWAY FROM OPEN FLAMES UNTIL READY TO COMBUST.

Perform single displacement reactions in aqueous solutions.

Source: *Chemistry 2019 v1.3 General Senior Syllabus* © Queensland Curriculum & Assessment Authority

Context

Single displacement reactions occur when a stronger reducing agent replaces a weaker reducing agent.

Aim

To perform single displacement reactions and observe any changes.

Materials

- 1 M $CuSO_4$
- Zinc metal strip
- 1 M HCl
- Magnesium metal strip cut into 0.5 cm lengths
- 100 mL beaker
- 2 test tubes
- Test-tube rack
- Matches

Method

Part A

1 Pour 50 mL of 1 M $CuSO_4$ into a 100 mL beaker. Add the zinc metal strip.

2 Observe the changes every 2 minutes for 10 minutes. Record your observations about colour changes, bubbles, appearance of the metal and temperature.

Part B

1 Place five 0.5 cm lengths of magnesium metal strip into a test tube.

2 Add approximately 2–3 cm of 1 M HCl to the test tube and quickly place the second test tube on top (upside down or inverted) to trap any gases produced.

Note: Do not hold the test tube at the bottom; hold it at the top above the solution line.

3 Record your observations about colour changes, bubbles, appearance of the metal and temperature.

4 When the reaction stops producing bubbles, remove the top test tube and keep it inverted (upside down). Light a match and, when ready, hold it at the opening of the test tube.

5 Record any observations of the effects of holding the match under the test tube.

Results

Construct a results table.

Discussion

1 Explain what your observations indicate in terms of the reactants and products of both reactions.

2 Write balanced chemical equations for the three reactions.

3 Explain why the first reaction of each part is a displacement reaction.

4 Write half-equations for both reactions.

5 Identify the reduction and oxidation half-equations, as well as the oxidant and reductant in both reactions.

6 Write overall redox equations for both experiments.

Conclusion

Summarise the outcomes of this practical.

7.1
MANDATORY PRACTICAL

Constructing a galvanic cell

CAUTION: ALL CHEMICALS ARE IRRITANTS. $CuSO_4$ AND $FeCl_2$ ARE CORROSIVE. $Zn(NO_3)_2$ AND KNO_3 ARE FLAMMABLE; KEEP THEM AWAY FROM OPEN FLAMES. DO NOT DISPOSE OF ANY CHEMICALS DOWN THE SINK. WEAR PERSONAL PROTECTIVE EQUIPMENT AT ALL TIMES. IF CHEMICALS COME IN CONTACT WITH YOUR SKIN, FLUSH THE AFFECTED AREA FOR 15 MINUTES. CONSULT A HEALTHCARE PROFESSIONAL IF ANY CHEMICALS ARE INGESTED.

Construct a galvanic cell using two metal/metal-ion half-cells.

Source: *Chemistry 2019 v1.3 General Senior Syllabus* © Queensland Curriculum & Assessment Authority

Context

Galvanic cells are constructed from two half-cells, a salt bridge, connecting wires and a voltmeter. The reducing and oxidising ability of each half-cell determines the amount of energy produced by each cell, and can be measured with the voltmeter. The electrochemical series allows you to predict the outcome of a galvanic cell and the voltage that will result. These half-cells have been measured against the hydrogen half-cell (0.00 V) at 25°C, 1 M and 1 atm.

Aim

To determine the order of metals on the electrochemical series by constructing galvanic cells made from various metal/metal ion half-cells.

Materials

- 50 mL 1 M $CuSO_4$
- 50 mL 1 M $FeCl_2$
- 50 mL 1 M $Zn(NO_3)_2$
- 50 mL 1 M $Al(NO_3)_3$
- 200 mL 1 M KNO_3
- 4 × 100 mL beakers
- One 2 × 10 cm piece of each of copper, iron (or a nail), zinc and aluminium
- Pen for labelling glassware
- 6 strips of filter paper (approx. 3 × 15cm)
- 2 × alligator clips
- Plastic tweezers
- Voltmeter
- Emery paper
- Wash bottle with deionised water
- 200 mL waste beaker

Method

FIGURE 1 The experimental set-up of a galvanic cell

1. Construct four half-cells by placing 50 mL of the copper sulfate solution in a 100 mL beaker and adding the copper strip, which acts as the electrode. Repeat this for the iron, zinc and aluminium half-cells. Label each beaker as the respective solution. Remember to scour the metal strips with emery paper.
2. Immerse one piece of the filter paper in the potassium nitrate solution. Using the plastic tweezers, remove it from the solution and place it as a bridge between two of the half-cells (see Figure 1 on the previous page).
3. Connect an alligator clip to each of the metal electrodes.
4. Connect the other end of each electrode to the voltmeter. If the voltmeter has a negative reading, swap the wires that are connected to the terminals.

   Note: As soon as the electrodes are connected to the voltmeter, the electrochemical circuit is complete and the voltmeter will immediately measure the voltage of the cell. This must be recorded immediately because it will reduce over time.

   You must also record whether each electrode is positive or negative in the galvanic cell. This can be determined by looking at the voltmeter. The negative electrode connects to the negative terminal and the positive electrode connects to the positive terminal.
5. Deconstruct the galvanic cell, ensuring that the filter paper is disposed of in the waste beaker and that no solution in the half-cell contaminates another.
6. Reconstruct the galvanic cell until every pair of half-cells have been connected and the results have been recorded.

Results

Construct a table (such as the one below) that records the voltage produced by each of the six galvanic cells as well as the polarity of the electrodes.

Galvanic cell	Metal compound solution	Voltage (V)	Polarity of electrodes
1			
2			
3			
4			
5			
6			

Discussion

1. Which electrode is always negative, and which is always positive? Use this information to list the half-cells in order with the strongest oxidant first.
2. Does your half-cell order agree with the half-equations on the electrochemical series in the QCAA Chemistry formula and data book?
3. Use the electrochemical series to draw the six galvanic cells as they are explained in Worked example 7.1B (page 171). You must also add the $E°$ of each cell, as shown in Worked example 7.2 (page 176).
4. Do the theoretical and experimental $E°$ values match? Explain why this is.
5. What is the salt bridge in the experiment? Explain why this ionic solution was selected as the salt bridge.
6. On the electrochemical series, copper is the highest half-equation because copper ions are the strongest oxidant. What materials can be used to construct a copper half-cell if it is connected to a tin half-cell? Explain why you chose these materials.

Conclusion

Summarise the outcomes of this practical.

9.4
MANDATORY PRACTICAL

Modelling isomers of organic molecules

Construct 3D models of organic molecules.
Source: *Chemistry 2019 v1.3 General Senior Syllabus*
© Queensland Curriculum & Assessment Authority

Context

The covalent bonding between carbon and other elements involves sharing electrons. The spatial arrangement reflects the number of bonding and non-bonding electrons in the valence shell of each element. Although a two-dimensional representation of this is helpful, three-dimensional modelling provides much more information. In particular, isomers are best seen in three dimensions.

Aim

To construct 3D models of esters, amides, amines and isomers.

Materials

- 3D modelling kit for organic chemistry

Method

1. The 3D modelling kit has balls with different colours and number of holes. Identify the following:
   - Carbon atoms have four holes and are usually black.
   - Oxygen atoms have two holes and are usually red.
   - Hydrogen atoms have one hole and are usually white.
   - Nitrogen atoms have three holes and are usually blue.
   - Halogen atoms have one hole and are usually green.
2. Construct methyl propanoate from 4 black carbons, 2 red oxygens, 8 white hydrogens, 12 short bonds and 2 long bonds (for the double bond). Using the same atoms and bonds, construct two other structural isomers of methyl propanoate. Draw the condensed and line structural formulas, and name each structural isomer in your book.
3. Construct *N*-ethylethanamide from 4 black carbons, 1 red oxygen, 9 white hydrogens, 1 blue nitrogen, 13 short bonds and 2 long bonds. Using the same atoms and bonds, construct two other structural isomers of *N*-ethylethanamide. Draw the condensed and line structural formulas, and name each structural isomer in your book.
4. Construct as many viable organic molecules as possible from 3 black carbons, 9 white hydrogens, 1 blue nitrogen and 12 short bonds. Draw the condensed and line structural formulas, and name each structural isomer in your book.
5. Construct two enantiomers of 1-bromoethan-1-ol from 4 black carbons, 10 white hydrogens, 2 red oxygens, 2 green bromines and 16 short bonds. Rotate the two molecules and sit them close together to test whether they can be superimposed. Draw the enantiomers in your book, using dashed and solid wedged bonds.

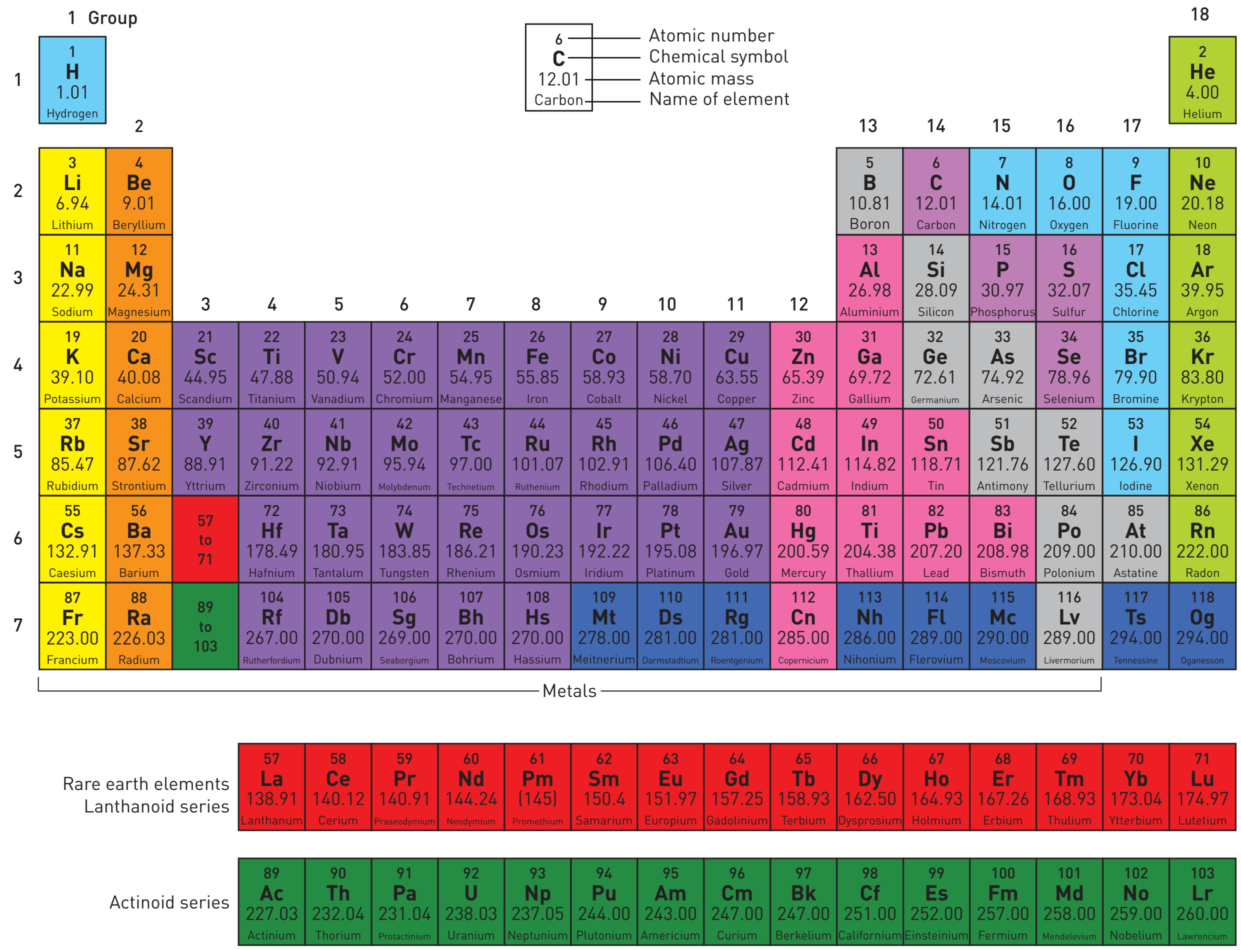
Discussion

1. Explain why the two holes in the oxygen atom were not directly opposite on the red ball.
2. Evaluate the significance of the types of isomerism, in terms of changing the properties of substances.
3. Explain why there are only ever two enantiomers of a compound with a single chiral atom.
4. The atoms, and groups of atoms, in the molecular models are able to rotate around and constantly shift the spatial arrangement of the molecule itself. Discuss how the lack of flexibility in a double bond leads to the possibility of geometrical isomerism.

Conclusion

Summarise the outcomes of this practical.

APPENDIX



6 — Atomic number
C — Chemical symbol
12.01 — Atomic mass
Carbon — Name of element

	1 Group	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1 **H** 1.01 Hydrogen																	2 **He** 4.00 Helium
2	3 **Li** 6.94 Lithium	4 **Be** 9.01 Beryllium											5 **B** 10.81 Boron	6 **C** 12.01 Carbon	7 **N** 14.01 Nitrogen	8 **O** 16.00 Oxygen	9 **F** 19.00 Fluorine	10 **Ne** 20.18 Neon
3	11 **Na** 22.99 Sodium	12 **Mg** 24.31 Magnesium											13 **Al** 26.98 Aluminium	14 **Si** 28.09 Silicon	15 **P** 30.97 Phosphorus	16 **S** 32.07 Sulfur	17 **Cl** 35.45 Chlorine	18 **Ar** 39.95 Argon
4	19 **K** 39.10 Potassium	20 **Ca** 40.08 Calcium	21 **Sc** 44.95 Scandium	22 **Ti** 47.88 Titanium	23 **V** 50.94 Vanadium	24 **Cr** 52.00 Chromium	25 **Mn** 54.95 Manganese	26 **Fe** 55.85 Iron	27 **Co** 58.93 Cobalt	28 **Ni** 58.70 Nickel	29 **Cu** 63.55 Copper	30 **Zn** 65.39 Zinc	31 **Ga** 69.72 Gallium	32 **Ge** 72.61 Germanium	33 **As** 74.92 Arsenic	34 **Se** 78.96 Selenium	35 **Br** 79.90 Bromine	36 **Kr** 83.80 Krypton
5	37 **Rb** 85.47 Rubidium	38 **Sr** 87.62 Strontium	39 **Y** 88.91 Yttrium	40 **Zr** 91.22 Zirconium	41 **Nb** 92.91 Niobium	42 **Mo** 95.94 Molybdenum	43 **Tc** 97.00 Technetium	44 **Ru** 101.07 Ruthenium	45 **Rh** 102.91 Rhodium	46 **Pd** 106.40 Palladium	47 **Ag** 107.87 Silver	48 **Cd** 112.41 Cadmium	49 **In** 114.82 Indium	50 **Sn** 118.71 Tin	51 **Sb** 121.76 Antimony	52 **Te** 127.60 Tellurium	53 **I** 126.90 Iodine	54 **Xe** 131.29 Xenon
6	55 **Cs** 132.91 Caesium	56 **Ba** 137.33 Barium	57 to 71	72 **Hf** 178.49 Hafnium	73 **Ta** 180.95 Tantalum	74 **W** 183.85 Tungsten	75 **Re** 186.21 Rhenium	76 **Os** 190.23 Osmium	77 **Ir** 192.22 Iridium	78 **Pt** 195.08 Platinum	79 **Au** 196.97 Gold	80 **Hg** 200.59 Mercury	81 **Ti** 204.38 Thallium	82 **Pb** 207.20 Lead	83 **Bi** 208.98 Bismuth	84 **Po** 209.00 Polonium	85 **At** 210.00 Astatine	86 **Rn** 222.00 Radon
7	87 **Fr** 223.00 Francium	88 **Ra** 226.03 Radium	89 to 103	104 **Rf** 267.00 Rutherfordium	105 **Db** 270.00 Dubnium	106 **Sg** 269.00 Seaborgium	107 **Bh** 270.00 Bohrium	108 **Hs** 270.00 Hassium	109 **Mt** 278.00 Meitnerium	110 **Ds** 281.00 Darmstadtium	111 **Rg** 281.00 Roentgenium	112 **Cn** 285.00 Copernicium	113 **Nh** 286.00 Nihonium	114 **Fl** 289.00 Flerovium	115 **Mc** 290.00 Moscovium	116 **Lv** 289.00 Livermorium	117 **Ts** 294.00 Tennessine	118 **Og** 294.00 Oganesson

Metals

Rare earth elements Lanthanoid series	57 **La** 138.91 Lanthanum	58 **Ce** 140.12 Cerium	59 **Pr** 140.91 Praseodymium	60 **Nd** 144.24 Neodymium	61 **Pm** (145) Promethium	62 **Sm** 150.4 Samarium	63 **Eu** 151.97 Europium	64 **Gd** 157.25 Gadolinium	65 **Tb** 158.93 Terbium	66 **Dy** 162.50 Dysprosium	67 **Ho** 164.93 Holmium	68 **Er** 167.26 Erbium	69 **Tm** 168.93 Thulium	70 **Yb** 173.04 Ytterbium	71 **Lu** 174.97 Lutetium
Actinoid series	89 **Ac** 227.03 Actinium	90 **Th** 232.04 Thorium	91 **Pa** 231.04 Protactinium	92 **U** 238.03 Uranium	93 **Np** 237.05 Neptunium	94 **Pu** 244.00 Plutonium	95 **Am** 243.00 Americium	96 **Cm** 247.00 Curium	97 **Bk** 247.00 Berkelium	98 **Cf** 251.00 Californium	99 **Es** 252.00 Einsteinium	100 **Fm** 257.00 Fermium	101 **Md** 258.00 Mendelevium	102 **No** 259.00 Nobelium	103 **Lr** 260.00 Lawrencium

METALS

- 🟨 alkali metal
- 🟧 alkaline earth metal
- 🟥 lanthanide
- 🟩 actinide
- 🟪 transition metals
- ■ post-transition metals

NON-METALS

- 🟦 diatomic non-metals
- ■ polyatomic non-metals
- ■ noble gases

OTHER

- ⬜ metalloids
- ■ unknown chemical properties

GLOSSARY

A

abstract
a summary of the most important findings of a research article

acid dissociation constant (K_a)
the equilibrium constant for the dissociation of an acid in aqueous solution

activation energy
the minimum amount of energy required in a collision for a reaction to occur

addition
the addition of substituents across a carbon–carbon multiple bond

addition polymer
a polymer formed by linking monomers

alcohol
a class of organic compound that contains a hydroxyl functional group (–OH)

aldehyde
a class of organic compound that has a carbonyl group on the end of the main chain

aliphatic
an organic compound or group containing carbon and hydrogen joined together in straight chains, branched chains, or non-aromatic rings

aliquot
a fixed volume of liquid measured by a pipette

alkaline
basic

alkaline fuel cell
a fuel cell that consumes hydrogen and oxygen, producing water, heat and electricity

alkane
a class of organic compound that contains single bonds between the carbon atoms

alkene
a class of organic compound that contains one or more double bonds between the carbon atoms

alkoxy
a functional group containing an oxygen atom with a single bond to the main chain

alkyl group
a group formed by removing a hydrogen from an alkane and can be present as a substituent in an organic compound

alkyne
a class of organic compound that contains one or more triple bonds between the carbon atoms

amide
a class of organic compound that contains amine and carbonyl functional groups adjacent to each other

amine
a class of organic compound that contains a nitrogen atom bonded to three other groups, either hydrogen atoms or alkyl groups

amino acid
an organic compound that contains an amino and a carboxyl functional group

amphipathic
having both hydrophobic and hydrophilic parts

amphiprotic
a molecule or ion that can either donate or accept a proton and so therefore can act as an acid or base

AN OX
a mnemonic to remember that oxidation occurs at the anode

analyte
a solution of unknown concentration

angstrom (Å)
a unit of distance equal to 1×10^{-10} m

anode
the electrode where oxidation occurs

artificial selection
the control of breeding of plants and animals to produce characteristics favourable to humans

atmosphere
the layers of gas that surround Earth

atom economy
the efficiency of a chemical reaction or process at converting the mass of reactants into desired products

atom efficiency
the efficiency of a chemical reaction or process at converting the mass of reactants into desired products

B

BAC
blood alcohol concentration

base dissociation constant (K_b)
the equilibrium constant for the dissociation of a base in aqueous solution

base peak
the tallest peak in a mass spectrum; is usually assigned an abundance of 100% and other peak heights are given relative to it

base value
in mass spectrometry, the hydrocarbon molecular formula (C_xH_y) that matches the mass of a molecular ion

bending vibration
a vibration of a molecule or ion that involves a change in bond angle

beneficial insect
an insect that helps human enterprises such as farming, through pollination or by killing destructive insects

bioaccumulation
a build-up of stored substances in an organism

bioaccumulative
a toxic compound that can build up in living organisms over time, and tends to be concentrated in organisms at the top of the food chain

biodegradable
can be broken down by living organisms

biodegradation
the breakdown of a substance, such as plastic, by microorganisms

biodiesel
fatty acid alkyl esters made from fats and oils

biofuel
a fuel made from biological raw materials

biomass
living or recently living matter used as a fuel source

bond angle
the angle defined by three atoms, where the two outer atoms are both covalently bonded to the central atom

bond length
the distance between the nuclei of two bonded atoms

bottom-up approach
an approach to building nanostructures in which small building blocks such as atoms or molecules would be used to build larger assemblies

breathalyser
a device for determining the blood alcohol concentration of a motorist

buffer region
the section of a titration curve that is relatively flat because adding more acid or base does not drastically affect the pH

buffer solution
a solution that resists changes in pH when small quantities of acids or alkalis are added

bulb
a piece of equipment responsible for drawing solutions into the pipette

burette
a graduated glass cylinder that dispenses highly accurate volumes of a standard solution

by-product
a product of a chemical reaction that was not the intended product

C

carbonyl
a functional group consisting of an oxygen atom double bonded to a carbon atom in the main chain (–CO–)

carboxyl
a functional group consisting of a hydroxyl group attached to the carbon of a carbonyl group (–COOH)

carboxylic acid
a class of organic compound that contains a carboxyl functional group

catalyst
a substance that increases the rate of a reaction without itself being consumed in the reaction

catalytic hydration
the reaction between water and an organic compound in the presence of a catalyst

catenane
an assembly of molecules containing two or more mechanically interlocked rings

cathode
the electrode where reduction occurs

cell diagram
a diagram of a galvanic cell that has all key components, reaction mechanisms and electron/ion movement labelled

cell potential difference
the electrical potential difference (V) between two electrodes, the voltage that the galvanic cell can generate under standard conditions

chiral centre
a carbon atom bonded to four different substituents

closed system
a reaction vessel that is closed off, or has a lid, meaning that no reactant or product particles can escape

combustion
a chemical reaction with oxygen to form a metal oxide, a covalent compound or carbon dioxide and water

complete combustion reaction
the combustion reaction between a fuel and oxygen to produce carbon dioxide and water

concentration
the amount of solute dissolved in a solution

concordant titres
volumes of standard solution dispensed from a burette that differ by only 0.1 mL from the highest and the lowest

condensation reaction
a reaction in which two organic compounds are combined

conjugate acid
an acid formed when a base accepts an H^+

conjugate base
a base formed by removing an H^+ from an acid

contact process
the production of very concentrated sulfuric acid

corrosion
the degradation of a metal to form a more stable metal oxide when exposed to gases and liquids

cyclic
an organic compound that consists of a ring of carbons

D

derivative
a compound that can be synthesised easily from a parent compound by replacing an atom or group of atoms

diffraction
the changes in the angle and intensity of X-rays due to interaction with a crystal

disaccharide
two sugar monomers bonded together

durability
the ability to withstand damage

dynamic equilibrium
the state a reaction reaches when the rates of the forward and reverse reactions are equal

E

E-factor
the ratio of mass of waste produced in a reaction to the mass of desired product

efficacy
the ability of a medication to produce the desired result

electrical conductivity
the degree to which a material conducts an electric current

electrochemical series
a table of the strongest oxidants and reductants written as reversible reduction half-equations; the strongest oxidant is at the top left of the table and the strongest reductant is at the bottom right

electrochlorination
the passage of electricity into salty water to generate hypochlorite, an antibacterial agent

electrode
a solid conductor of electricity either into or out of a half-cell

electrolysis
the process by which electrical energy is passed into a cell, using a power source, resulting in the reversal of spontaneous redox reactions

electrolyte
a substance that conducts electricity when melted or dissolved in a solution

electromotive force (EMF)
the difference in potential across a cell that generates electricity

electronegativity
the attraction between a positively charged nucleus and the negatively charged electrons of a neighbouring atom

electrophoresis
a separation technique that involves the movement of charged particles, such as proteins, along an electric field

elimination reaction
the removal of substituents to form a multiple bond

enantiomers
two organic compounds that have the same atoms and bonding but a different arrangement of four substituents around a chiral carbon atom

end point
the point in a titration when the indicator changes colour

enthalpy
the energy stored within chemical substances, referred to as its chemical energy or heat content

enzyme
a biological catalyst

equilibrium constant (K_c)
the ratio of reactants to products in a reaction when it is at equilibrium

equilibrium expression
the non-numerical representation of the equilibrium law, which states the chemicals to the power of their coefficients

equilibrium law
the concentration of products to the power of their coefficients, divided by the concentration of reactants to the power of their coefficients is equal to the equilibrium constant, $(K)_c$

equivalence point
the point in a titration when the reactants have reacted in the molar ratio of the balanced chemical equation

ester
a class of organic compound that contains a carbonyl attached to an oxygen, which is bonded to another carbon

esterification
a condensation reaction between a carboxylic acid and alcohol that generates an ester

excess reagent
the reactant in a chemical reaction that is not completely used up

exoskeleton
the outer structure of an animal, e.g. a shell

experimental yield
the actual amount of the product

external circuit
the electric circuit (wires) that allow for electron movement from anode to cathode

F

fatty acid
a carboxylic acid that has a long hydrocarbon chain

fermentation
the chemical breakdown of glucose, with a yeast catalyst, to form ethanol and carbon dioxide

forward reaction
the reaction between reactants to form products

fossil fuel
a fuel sourced from the decomposition of dead organisms

fuel cell
a galvanic cell that produces electricity by using a constant supply of reactants (often hydrogen and oxygen) and inert electrodes that do not break down

functional group
an atom or a group of atoms in an organic compound that determines the reactivity of that compound

G

galvanic cell
an electrochemical cell in which the reduction and oxidation half-equations are separated and connected through a circuit to generate electricity

gasification
a high-temperature process under low oxygen concentrations that converts carbon-containing materials into a mixture of carbon monoxide, carbon dioxide, hydrogen and methane

gene
a segment of DNA on a chromosome

genome
all the DNA in a person's set of chromosomes

geometrical isomers
two organic compounds that have *cis* or *trans* arrangements of atoms around a carbon–carbon double bond

glycosidic linkage
a bond that connects sugar monomers together

green chemistry
chemistry that designs products and processes that reduce the use or production of hazardous substances

green synthesis
a synthetic technique that aims to reduce or eliminate the use production of hazardous materials

H

Haber process
the production of ammonia by a nitrogen-fixation process

half-cell
half of an electrochemical cell, where either oxidation or reduction occurs

half-equation
an equation that represents either an oxidation or a reduction half of a chemical equation; it includes electrons to demonstrate electron transfer

half-equivalence point
a point in a titration curve where the concentration of the titre is equal to half the original concentration of the analyte; also called the midpoint

haloalkane
a class of organic compound that contains a halogen substituent

halogenation
the addition of a halogen across a multiple bond

hard water
water containing high concentrations of dissolved metal cations, such as Ca^{2+}, Mg^{2+}, Fe^{2+} and Fe^{3+}

high-density polyethene (HDPE)
a polymer made from the monomer ethene, with a high strength-to-density ratio (also known as high-density polyethylene)

homologous series
a group of organic compounds with the same functional group but a different number of carbon atoms in the main chain

hydration
the addition of water across a double bond

hydrocarbon
an organic compound consisting of only carbon and hydrogen atoms

hydrogen fuel cell
an electrochemical cell that produces electricity and water

hydrogenation
the addition of hydrogen across a multiple bond

hydrohalogenation
the addition of a hydrogen atom and a halogen atom across a double bond

hydrophilic
having a strong affinity for water, e.g. polar organic compounds

hydrophobic
unable to dissolve in water

hydrosphere
the bodies of water on Earth's surface, underground and in the atmosphere

hydroxyl
a functional group consisting of an –OH group, which is an oxygen atom and a hydrogen atom joined by a single bond

I

indicator
a chemical substance that changes colour at different pH values

inert electrode
an electrode that conducts electricity in the half-cell, but does not participate in the reaction, i.e. it is neither a reactant nor a product

infrared radiation
electromagnetic radiation in the region between visible light and microwave radiation

infrared spectroscopy
a technique that looks at how molecules interact with infrared light

internal circuit
the part of an electrochemical cell that allows for ion flow, e.g. the salt bridge

ionic product constant of water (K_w)
the equilibrium constant for the self-ionisation of water

ionisation energy
the energy (in $kJ\ mol^{-1}$) required by a gaseous atom to remove an electron from its valence shell

isotope pattern
a set of peaks in a mass spectrum related to ions with the same chemical formula but containing different isotopes; the pattern reflects the relative abundance of the isotopes

K

ketone
a class of organic compound that has a carbonyl group on a carbon within the main chain

kinetic energy
the energy associated with moving particles

L

Le Châtelier's principle
if an equilibrium system is subjected to a change, the system will adjust itself to partially oppose the effect of the change

limiting reagent
the reactant in a chemical reaction that determines how much of the products are made

lipase
an enzyme that catalyses the hydrolysis of lipids, e.g. fats or oils

lithosphere
the outermost layer of Earth

locant
a number or letter that indicates the position of a substituent or functional group within an organic compound

low-density polyethene (LDPE)
a polymer made from the monomer ethene, with a low strength-to-density ratio (also known as low-density polyethylene)

M

macromolecule
a very large molecule

main chain
the longest chain of carbon atoms in a hydrocarbon molecule

mass spectrometry
a technique used to determine the molecular mass of a compound

mechanically interlocked molecules
assemblies of two or more separate molecular components that are not connected by chemical (i.e. covalent) bonds, but are held together physically, with components that can only be separated by breakage of covalent bonds

mechanosynthesis
the proposed synthesis of new chemical entities by controlling the physical placement or removal of chemical subunits

meniscus
the curved upper surface of a liquid in a piece of measurement glassware

micelle
an aggregation of surfactant molecules

miscible
completely soluble

molecular ion
the ion formed when an electron is lost from a neutral molecule; in a mass spectrum this ion has the highest *m*/*z* value

molecular machine
a molecular system with defined energy input that can perform a useful function at the nanoscale

molecular manufacturing
the atomically precise placement of atoms or molecules in order to build larger molecular assemblies or molecular-based machines

molten
a substance that has been melted to form a liquid

monomer
a single unit within a polymer

monoprotic acid
an acid that can donate one hydrogen ion per molecule

monosaccharide
a single sugar monomer

multiple bond
a double or triple bond in an organic compound

multiplier
a term used to indicate the number of substituents of the same type

N

native PAGE
polyacrylamide gel electrophoresis under conditions in which the protein retains its natural shape

nitrile
a class of organic compound that contains a nitrogen atom with a triple bond to a carbon atom

nomenclature
a set of rules by IUPAC used to name organic compounds

non-cyclic
an organic compound that has a straight main chain with two ends

nucleic acid
DNA or RNA

O

oleum
a solution of sulfur trioxide in sulfuric acid, also called fuming sulfuric acid

open system
a reaction vessel that has no lid, meaning that reactants or products can be lost to the atmosphere

overall equation
a reaction that combines the two half-equations after electrons have been balanced and cancelled out

oxidation
a loss of electrons; also a reaction with oxygen

oxidation number
the number of electrons gained or lost by an atom

oxidation reaction
an organic reaction involving the gain of oxygen atoms and/or the loss of hydrogen atoms

oxidation state
oxidation number

oxidise
to lose electrons

oxidising agent
a reactant that causes another reactant to lose electrons and be oxidised and is itself reduced

P

peptide
a polymer of amino acid monomers

peptide bond
the bond joining amino acid monomers together, between the carboxyl and amine groups of adjacent amino acids

percentage yield
the percentage ratio of the actual yield to the theoretical yield

persistent organic pollutant (POP)
a toxic organic compound that is resistant to breakdown by organisms or other chemical processes

pH
a measure of hydrogen ion concentration in a solution and therefore a measure of the acidity or alkalinity of a solution

phosphoric acid fuel cell
a fuel cell that uses liquid phosphoric acid as an electrolyte, producing water, heat and electricity

pipette
a glass tube that dispenses highly accurate volumes of a solution of unknown concentration

pK_a
a measure of acid strength; the negative logarithm (to base 10) of the acid dissociation constant

pK_b
a measure of base strength; the negative logarithm (to base 10) of the base dissociation constant

plastiphere
an ecosystem that has adapted to live with plastic in the environment

pOH
a measure of hydroxide ion concentration in a solution and consequently a measure of basicity

polarity
the charge of an electrode, either positive or negative

polyester
a type of polymer that contains an ester functional group in its main chain

polymer
a large molecule made of many monomers

polymerisation
the successive addition reactions of alkene monomers to form a polymer

polypeptide
a large polymer of amino acid monomers

polyprotic acid
an acid that can donate more than one hydrogen ion per molecule

polysaccharide
a complex sugar consisting of multiple sugar monomers bonded together

precision
the consistency of a series of measurements

prefix
a group of letters added to the beginning of a word; the first part of an organic compound's name

pressure
the force exerted, per unit are, by one substance upon another substance

primary alcohol
an alcohol in which the carbon that is bonded to the OH group is bonded to one other carbon

primary cell
a non-rechargeable battery; a galvanic cell that produces an electrical current

primary standard
a substance that is dissolved in a solvent to create a standard solution

protecting group
a temporary functional group added during a chemical synthesis to prevent that part of the molecule from reacting; it is later removed to regenerate the original functional group

proton donor
a substance that can donate H^+ (hydrogen ions)

protonate
adding a proton (hydrogen ion) to a molecule

Q

qualitative
data that is descriptive and not numerical such as observations of chemical colours or the observable behaviour of gases

quantitative
data that is numerical and allows for mathematical analysis to identify trends, patterns, relationships, limitations and uncertainty

R

reaction quotient (Q_c)
the ratio of reactants to products in a reaction when it is not at equilibrium

reagent
a substance or compound used to initiate a chemical reaction

RED CAT
a mnemonic to remember that reduction occurs at the cathode

RED SOX
a method for determining whether two chemicals will react spontaneously in a redox reaction; it looks at the positions of the half-equations on the electrochemical series; 'RED' stands for reduction, the 'S' denotes the reactants and products and 'OX' stands for oxidation

redox
a chemical reaction involving the transfer of electrons from one reactant to another

redox reaction
a reaction involving oxidation of one reactant and reduction of the other reactant

reduce
to gain electrons

reducing agent
a reactant that causes another reactant to gain electrons and be reduced and is itself oxidised

reduction
a gain of electrons

reduction reaction
an organic reaction involving the loss of oxygen atoms and/or the gain of hydrogen atoms

reflux
heating a reaction vessel with a vertical condenser attached to capture escaping gases and return them to the reaction vessel

renewable
replaceable at a rate equal to or greater than the rate of use, over an indefinite period

research question
a clear question that gives the research an aim or focus

reverse reaction
the backwards reaction in which the products react to re-form the reactants

ribosome
a protein and RNA-containing assembly inside cells that binds messenger RNA and transfer RNA in order to make proteins

rigid
unable to change shape

risk assessment
a systematic evaluation of the potential risks and their likelihood when doing an experiment or activity

rotaxane
an assembly of molecular components, including a dumbbell-shaped molecule that has one or more macrocylic ring molecules threaded onto it

S

saccharification
the process of breaking down polysaccharides (starches) into simpler sugars

salt bridge
an electrical connection between the two half-cells of an electrochemical cell; it allows for the flow of charge by moving ions – cations to the cathode and anions to the anode

saponification
the organic reaction between an acidic ester and a strong base to produce a fatty acid salt

scientific method
the systematic exploration of a phenomenon or topic, using observation, measurement and experiment to support, disprove or modify hypotheses

SDS-PAGE
sodium dodecyl sulfate polyacrylamide gel electrophoresis; a purification technique that separates proteins on the basis of size when they pass through a gel under an applied electrical potential

secondary alcohol
an alcohol in which the carbon that is bonded to the OH group is bonded to two other carbons

secondary cell
a rechargeable battery; an electrochemical cell that operates as a galvanic cell, discharging energy, and an electrolytic cell, recharging to return chemicals to their original state in order to undergo a spontaneous reaction again

secondary evidence
evidence sourced from scientific works other than your own

self-ionisation of water
the reaction in which a water molecule loses a hydrogen ion to become a hydroxide ion (OH^-) and the hydrogen ion immediately reacts with another water molecule to form a hydronium (H_3O^+)

single displacement
a chemical reaction in which a more reactive metal ion replaces a less reactive metal ion in a molecule

single-use plastic
a plastic that is used once and then thrown away

size exclusion chromatography
a type of chromatography that separates molecules on the basis of size, with the largest molecules eluting first

solid-phase reaction
a reaction in which all the reactants are in the solid state

solute
the minor component of a solution; the substance dissolved in the solvent

solution
a mixture of a solute dissolved in a solvent

solvent
the major component of a solution; what the solute is dissolved in

spectator ion
an ion that exists in the same form on the reactant and product side of a redox reaction

standard conditions
the conditions under which all $E°$ values are measured: 25°C, 1 atm and 1 M

standard electrode potential ($E°$)
the electrical potential that an electrode generates under standard conditions

standard solution
a solution of accurately known concentration

steam reforming
a process that uses high-temperature steam (700–1000°C) to produce hydrogen from a methane source such as natural gas

stereoisomers
two or more organic compounds that have the same atoms and bonding but a different spatial arrangement

stoichiometric ratio
the coefficient ratio in a chemical equation

stoichiometry
the calculation of reactants and products in chemical reactions by using a balanced equation

stopcock
the tap attached to a burette

strength
the level of dissociation of an acid or a base

stretching vibration
a vibration of a molecule or ion that involves a change in bond distances

strong acid
an acid that completely ionises in water

strong base
a base that completely ionises in water

structural formula
a representation of an organic compound used to inform the arrangement and bonding of atoms

structural isomers
two or more organic compounds that have the same atoms but a different arrangement and bonding

substituent
an atom or group of atoms bonded to a carbon atom in the main chain

substitution
a reaction in which one substituent in a saturated organic compound is replaced by another

suffix
a group of letters added to the end of a word; the last part of an organic compound's name

sulfite
a group of organic compounds with an SO_3^{2-} anion, which can also contain SO(g)

supercritical fluid
a substance at a temperature and pressure beyond its critical point, where the substance has properties of both a gas and liquid

synthesise
to combine compounds and form a more complex entity

T

temperature
a measure of the average heat energy of the particles within a system

tertiary alcohol
an alcohol in which the carbon that is bonded to the OH group is bonded to three other carbons

theoretical yield
the maximum amount of product expected by a chemical reaction

titrand
a solution whose concentration is determined by titration

titrant
the standard solution in a burette that is added to a solution of unknown concentration

titration
the addition of a solution of known concentration to a known volume of a solution of unknown concentration until reaction reaches neutralisation

titration curve
a graph of pH against volume of reactant added

titre
the volume of standard solution dispensed from a burette

top-down approach
an approach to building nanostructures that involves removing material from larger structures

toxicity
the degree to which a medicine causes adverse side effects

transesterification
a reaction between an ester and an alcohol that produces a new ester and a new alcohol

transmittance
the ratio of the intensity of transmitted light (light that has passed through the sample) to incident light (the light first put out by the light source)

V

valence electron
an electron in the outermost shell of an atom, according to the Bohr model of electron configuration

volatile
evaporates easily at room temperature

volume
a measure of the space occupied by a substance

volumetric analysis
a quantitative analytical technique for determining the concentration of a solution by titrating it against a solution of known concentration

volumetric flask
a piece of laboratory glassware that can measure highly accurate volumes

W

wavenumber
the reciprocal of wavelength (where wavelength is measured in cm)

weak acid
an acid that does not completely ionise in water

weak base
a base that does not completely ionise in water

X

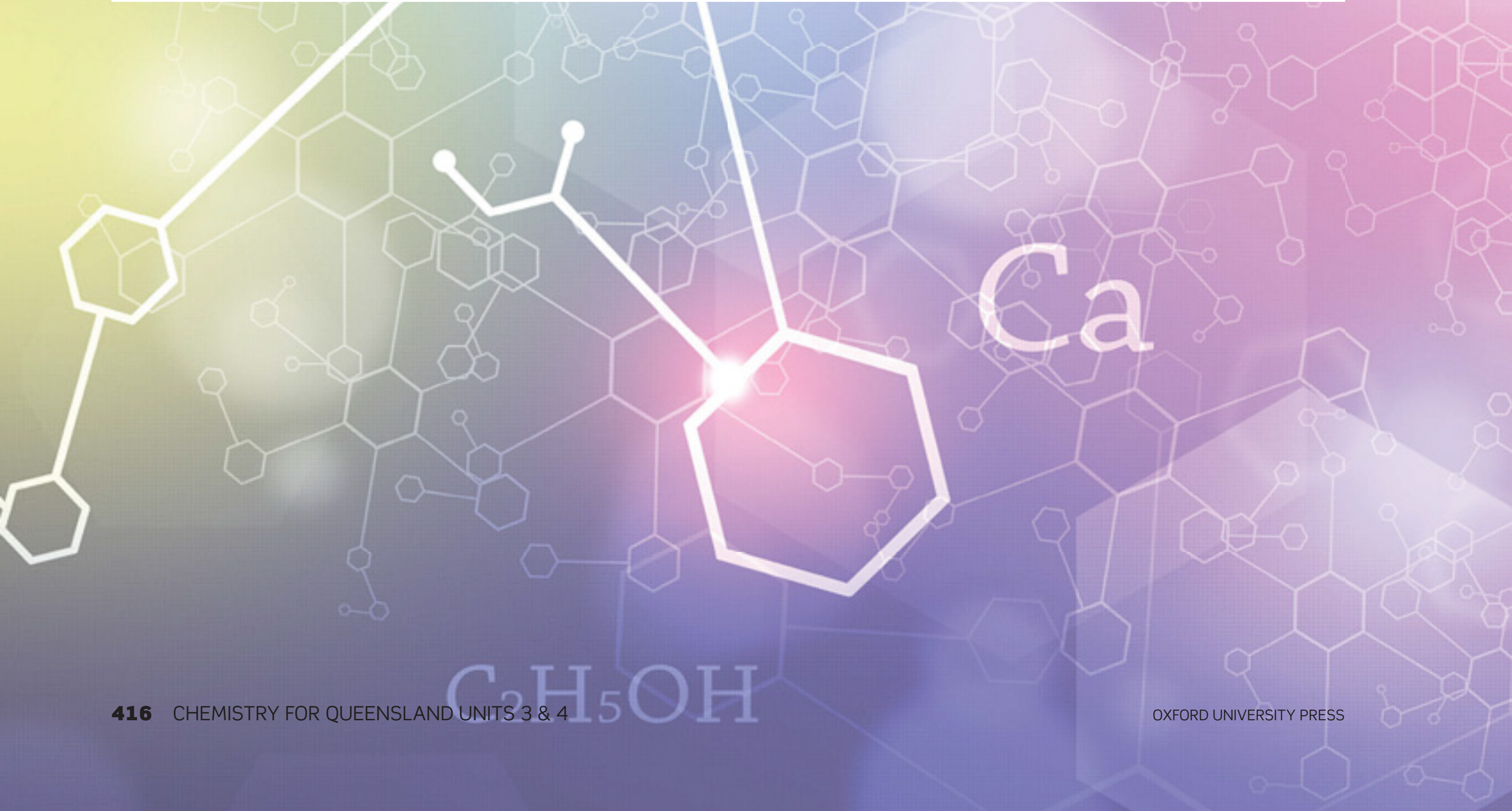
X-ray crystallography
a technique that gives information about the positions of atoms within the repeating units that make up crystals

Y

yield
the amount of product obtained from a chemical reaction

Z

zwitterion
a molecule that has separate positively and negatively charged parts



INDEX

The front cover shows a polarised light micrograph of a section through crystals of citric acid. Citric acid (a tricarboxylic acid) is a weak organic acid that can be obtained from natural products such as citrus fruits including lemons and limes.

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